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FAR-INFRARED STUDIES OF HIGH-\(T_c\) SUPERCONDUCTORS

by

Shu-heng Wang

B.Sc., Chinese University of Science and Technology, Hefei, China, 1982
M.Sc., Anhui Institute of Optics and Fine Mechanics, Hefei, China, 1985

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
Physics

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APPROVAL

Name: Shu-heng Wang

Degree: Doctor of Philosophy

Title of Thesis: Far-Infrared Studies of High-T_c Superconductors

Examining Committee:

Chairman: Dr. Crozier, E.D.

Dr. Clayman, B.P.
Senior Supervisor

Dr. Gygax, S.

Dr. Plischke, M.

Dr. Irwin, J.C.

Dr. Schlesinger, Z.
External Examiner
IBM T.J. Watson Research Center

Date Approved: Aug 29, 1991
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Far-Infrared Studies of High-Tc Superconductors

Author:

(Signature)

SHU-HENG WANG
(Name)

Sept 10, 1991
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ABSTRACT

This thesis presents infrared results measured on high-T\textsubscript{c} superconducting bulk ((Y,Eu)Ba\textsubscript{2}Cu\textsubscript{3}O<sub>7-x</sub> and n-type Nd\textsubscript{2-x}(Ce,Th)\textsubscript{x}CuO<sub>4-y</sub>) and film (Y-Ba-Cu-O and Bi(Pb)-Sr-Ca-Cu-O) samples. We attempt to find the superconducting energy gap(s) and any spectral features related to superconducting pairing.

Very strongly anisotropic properties are found to be common to both the superconducting and normal states. For the 1-2-3 materials, which have fewer sample preparation and characterization problems, our infrared reflectivity studies on both film and bulk samples revealed that the superconducting energy gap which corresponds to the ab plane is about 8 kT\textsubscript{c}, and is much greater than the ~3 kT\textsubscript{c} observed for the c-axis. Similar gap behavior is also found in the Bi(Pb)-Sr-Ca-Cu-O films. The gap sizes extracted from our experimental data are consistent with the infrared results on the single crystals measured by other groups. Beside the strong anisotropy, these gaps also have unusual temperature dependence: 2\Delta(T)/2\Delta(0) approaches zero more steeply at T=T\textsubscript{c} than for a conventional superconductor.

Our infrared reflectivity data of the n-type Nd\textsubscript{2-x}(Ce,Th)\textsubscript{x}CuO<sub>4-y</sub> polycrystalline samples show a ~3 kT\textsubscript{c} superconducting energy gap which we interpret as a c-axis gap. We also noted that there is some fine structure below this gap, which may imply that the actual c-axis gap is smaller.

Our far-infrared transmission spectra for Pb-doped Bi-Sr-Ca-Cu-O
sputtered films on MgO show low-frequency behavior expected for a conventional superconductor: low frequency ($\leq 110 \text{ cm}^{-1}$) transmission is lower in the superconducting state than in the normal state. This low-frequency behavior is consistent with the assumption that there is a superconducting energy gap above 110 cm$^{-1}$.

The behavior of infrared-active phonons in (Y,Eu)Ba$_2$Cu$_3$O$_{7-x}$ and n-type Nd$_{2-x}$(Ce,Th)$_x$CuO$_{4-y}$ polycrystalline samples is also studied.
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CHAPTER 1: FAR INFRARED SPECTROSCOPY IN CONVENTIONAL SUPERCONDUCTORS

1.1: INTRODUCTION

Historically, far-infrared technology is one of the best tools for us to investigate, understand, and interpret the phenomenon of superconductivity. Since 1911, when Kamerlingh Onnes\textsuperscript{(1)} discovered superconductivity, it has been known that for temperatures $T$ below the superconducting transition temperature $T_c$, a superconductor has no resistance to direct current. Subsequently it has been seen\textsuperscript{(2,3)} that for $T \ll T_c$, a superconductor is essentially a lossless conductor even for frequencies up into the centimeter microwave range. Yet it has also been found\textsuperscript{(4,5)} that there is no change in absorption between the superconducting and the normal states in the frequencies above the moderate-infrared region. This behavior suggested that there might be a minimum photon energy $\hbar \nu$ which could be absorbed by a superconductor at $T = 0$. This corresponds to an energy gap in the excitation spectrum of the superconducting metal, in contrast to the continuum of possible excited states in a normal metal.

In 1957, a theory of superconductivity developed by Bardeen, Cooper and Schrieffer\textsuperscript{(6)} (it hence is called BCS theory) showed that at $T = 0$ there should be a finite energy gap $\hbar \nu = 2\Delta (0) = 3.5 k_b T_c$, where $k_b$ is Boltzmann's constant, between the ground state of the superconductor and the lowest excited state, one in which a bound pair is broken and two Fermi excitations are created.
Experimental evidence for the existence of the energy gap can be obtained from specific heat, thermal conductivity, nuclear relaxation, ultrasonic attenuation, and electromagnetic absorption data.\(^{(7)}\) Unfortunately, most of those approaches require interpretation in terms of a detailed theory before a value of the energy gap can be deduced. In 1956, shortly before the appearance of the BCS-theory, Tinkham and his collaborators carried out the first experiment\(^{(8)}\) in which the energy gap of superconductors was measured directly by spectroscopic means\(^{(8-12)}\) using a grating monochromator with a mercury arc lamp as a radiation source. In these far-infrared experiments, the superconducting energy gap was measured in Pb, Sn, In, Hg, Ta, V, N, and La. Tinkham's experiments were paralleled and followed, particularly on Al and Zn, by millimeter microwave investigation of Biondi and Garfunkel\(^{(13,14)}\). These experiments showed that a gap existed, leading to an absence of absorption at \(T = 0\) for photon energies below \(2\Delta\). Further, they confirmed that \(2\Delta\) was typically in the range \(3.0\text{ to } 4.5\ \text{k}\text{T}_c\), near the prediction of the BCS theory, but showing characteristic differences from metal to metal. For example, the superconductors Pb and Hg were found to have unusually large gaps, \(4.2\ \text{k}\text{T}_c\) and \(4.6\ \text{k}\text{T}_c\), respectively; this was later explained theoretically by the more elaborate calculations\(^{(15)}\) using Green's function methods to treat the electron-phonon strong coupling interaction.

Since then, infrared technology is treated as a convenient and theory-independent method for the investigation of superconducting properties. It has played a very successful role for all of the conventional superconductors. When a revolution of discovery on new high-\(T_c\) oxides was first sparked by Bednorz and Müller\(^{(16)}\) in 1986, it was
very natural that one might expect to extract some useful information from these miraculous oxides by using the infrared technique.

This thesis presents infrared results measured on high-$T_c$ superconducting bulk and film samples. We attempt to find the superconducting energy gap and any spectral features responsible for the superconducting pairing, since we believe that knowledge of the symmetry, temperature dependence and magnitude of gap will generally explain the behavior of physical properties, and be very helpful for us to understand the mechanism of superconductivity in these oxides.

Section 1.1 of this chapter contains an introduction to the fundamental relationships between the optical constants of solids. This is followed by a brief review of the Kramers-Kronig relations and the determination of optical constants in section 1.2. The behavior of the ac conductivity in the BCS frame is shown in section 1.3. Some important historic works of infrared reflectivity and transmission measurements on the "old" superconductors are selected and introduced in section 1.4 and 1.5. Section 1.6 presents a "road map" to the rest of this thesis.
1.2: Fundamental Relationships Between the Optical Constants of Solids

Microscopic optical properties of a solid may be characterized quite generally by a frequency-dependent complex dielectric function \( \varepsilon(\omega) \) which can be written in terms of its real and imaginary parts as

\[
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)
\]  

(1-1)

as long as the material is uncharged, homogeneous, isotropic, linear and local in its response.

Other quantities, in addition to the real dielectric function \( \varepsilon_1(\omega) \) and the imaginary part \( \varepsilon_2 \), are often used to describe the optical properties of a material. They include the complex refractive index, \( n_c = n + ik \), and the complex conductivity, \( \sigma = \sigma_1 + i\sigma_2 \). However they are not independent quantities, being interrelated by

\[
\varepsilon(\omega) = 1 + i\sigma / \varepsilon_0 \omega
\]  

(1-2)

and

\[
\varepsilon(\omega) = n_c^2(\omega).
\]  

(1-3)

Eq.(1-2) is obtained from Maxwell's propagating equation

\[
\frac{\partial^2 E}{\partial x^2} = -\mu \frac{\varepsilon_0}{\mu_0} \frac{\partial E}{\partial t} - \mu \varepsilon \frac{\varepsilon_0}{\mu_0} \frac{\partial^2 E}{\partial t^2}
\]  

(1-4)

with a plane wave of frequency \( \omega \) propagating in the x-direction:
\begin{equation}
\hat{E} = E_0 \exp \left[ i \omega \left( \frac{n \cdot x}{c} - \tau \right) \right] \hat{e}_y
\end{equation}

Note that the magnetic permeability \( \mu_r \) usually equals unity for most nonmagnetic materials.

The simplest model for understanding metals was provided by Drude and Sommerfeld.\textsuperscript{(17)} In this model the behavior of electrons subjected to an external electric field in a metal is determined by a balance between two forces: (1) the \(-eE\) force exerted by the electric field and (2) a viscous damping force \( m \left( \frac{1}{\tau} \right) \frac{d\vec{r}}{dt} \) which provides for an energy loss mechanism raised from various scattering mechanisms in a solid.\textsuperscript{(18)} Here \( 1/\tau \) is the relaxation rate and equals \( V_F / \iota \), where \( V_F \) is the fermi velocity and \( \iota \) is the electronic mean free path.

The frequency-dependent (or ac) electric conductivity \( \sigma(\omega) \) in this model is given by\textsuperscript{(17)}

\begin{equation}
\sigma(\omega) = \frac{\sigma_0}{1 - i \omega \tau}
\end{equation}

where \( \sigma_0 \) is the dc electric conductivity and given by

\begin{equation}
\sigma_0 = \frac{n e^2 \tau}{m}
\end{equation}

Here \( n \) is the number of the electrons per unit volume, \( e \) is the electron charge and \( m \) is the electron mass. The ac conductivity falls steadily from this value with a characteristic width of \( 1/\tau \), a frequency typically in the microwave or far-infrared region of the spectrum. The mean collision time, namely, the relaxation time, for electrons in metals typically \( \ll \)
By substituting the Drude ac conductivity \( \sigma(\omega) \), i.e., eq.(1-6), into Eq.(1-2), the Drude complex dielectric function \( \varepsilon(\omega) \) can be written as

\[
\varepsilon(\omega) = 1 - \left( \frac{\sigma_0}{\varepsilon_0 \tau} \right) \left( \frac{1}{\omega^2 + i\omega/\tau} \right)
- 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau};
\tag{1-8}
\]

where \( \omega_p \) is the so-called plasma frequency, defined as

\[
\omega_p^2 = \frac{\sigma_0}{\varepsilon_0 \tau} = \frac{n e^2}{\varepsilon_0 \varepsilon_m}.
\tag{1-9}
\]

The plasma frequency of a metal is typically located in the visible or ultraviolet spectral region\(^{(20)}\) which corresponds to \( \omega > 3 \times 10^4 \text{ cm}^{-1} \).

The relationship between the optical constants and reflectivity of a solid at normal incidence is given by\(^{(21)}\)

\[
R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}.
\tag{1-10}
\]

When \( \omega \tau \ll 1 \), the reflectivity of a metal is given by the Hagen-Rubens relation:\(^{(22)}\)

\[
R \approx 1 - 2(2\omega/\sigma_0)^{1/2}.
\tag{1-11}
\]
1.3: Kramers-Kronig Relations and the Determination of Optical Constants.

The real and imaginary parts $\epsilon_1$ and $\epsilon_2$, respectively, are related to each other according to the Kramers-Kronig dispersion relations:\(^{(23)}\)

$$
\epsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} \, d\omega' 
$$

(1-12)

$$
\epsilon_2(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{\epsilon_1(\omega')}{\omega'^2 - \omega^2} \, d\omega' 
$$

(1-13)

Where $p$ is the Cauchy principal value of the integral:

$$
p \int_0^\infty = \lim_{a \to 0} \left( \int_0^{\omega-a} + \int_{\omega+a}^\infty \right)
$$

There are similar Kramers-Kronig relations between $\sigma_1$ and $\sigma_2$, $n$ and $k$.

There are a number of ways to determine experimentally the optical constants. A common way is to measure the reflectivity at normal incidence and use the above dispersion relation to determine the optical properties. The reflectivity for normal incidence is given\(^{(24)}\) by

$$
R(\omega) = \hat{r}(\omega) \hat{r}^*(\omega) = \rho^2(\omega) 
$$

(1-14)

where

$$
\hat{r}(\omega) = (n - 1 + ik) / (n + 1 + ik). 
$$

(1-15)
We can write the complex reflectivity amplitude as

\[ \hat{r}(\omega) = P(\omega) e^{i\theta(\omega)}. \]

According to the Kramers-Kronig relation\(^{24}\) relating the phase shift \( \theta \) to the reflectance \( R \),

\[
\theta(\omega) = -\frac{2\omega}{\pi} \int_{0}^{\infty} \frac{\ln \rho(\omega')}{\omega'^{2} - \omega^{2}} \, d\omega'.
\]

Then the optical constants \( n \) and \( k \) (then \( \epsilon_{1} \) and \( \epsilon_{2} \) or \( \sigma_{1} \) and \( \sigma_{2} \), etc.) can be determined by formula (1-15) after the phase shift \( \theta(\omega) \) is determined. The reflectivity \( R(\omega) \), or/and the reflectance wave amplitude \( \rho(\omega) \), is determined directly from experimental measurement; the integration of Eq. (1-16) must be done numerically.

Extrapolations of \( R(\omega) \) beyond the measured frequency interval are required. Typically, power laws are used at the end of high frequency,\(^{25}\) \( R \sim \omega^{-\alpha} \) with \( \alpha \leq \alpha \geq 4 \). At low frequency the reflectance is often assumed to follow the Hagen-Rubens relation, \( R = 1 - A\sqrt{\omega} \), for a metal sample.\(^{22,26}\)

The singularity of Eq. (1-16) at \( \omega' = \omega \) can be removed by adding a term:

\[
\frac{2\omega}{\pi} \int_{0}^{\infty} \frac{\ln \rho(\omega)}{\omega'^{2} - \omega^{2}} \, d\omega' (\omega = 0);
\]
then, the desired dispersion relation can be rewritten as

\[
\theta(\omega) = \frac{\omega}{\pi} p \int_0^\infty \frac{\ln R(\omega') - \ln R(\omega)}{\omega^2 - \omega'^2} \, d\omega'
\]  

(1-17)

From the above formula (Eq.1-17), we realize that, if the experimental reflectivity \( R(\omega) \) does not change in some frequency ranges, there will be no contribution to the phase shift \( \theta \), and thus no contribution to the other optical constants, from these frequency ranges. This property makes us feel easier in some cases about extrapolating reflectivity data in the frequency range beyond the measured interval.

A fundamentally important sum rule is related to the rate of energy absorption by transverse fields (photons):

\[
\int_0^\infty \omega \varepsilon_2(\omega) \, d\omega = \frac{1}{2} \pi \frac{\omega_p^2}{\varepsilon_0} 
\]

(1-18)

which can be rewritten as

\[
\int_0^\infty \sigma_1 \, d\omega = \frac{1}{2} \varepsilon_0 \pi \frac{\omega_p^2}{p} 
\]

(1-19)

An important consequence of the sum rule is that the area under the curve of \( \sigma_1(\omega) \) vs. \( \omega \) is a constant, whether it is in the superconducting or normal state.
1.4: The Frequency-Dependent Conductivity of Superconductors

By knowing the general complex conductivity expression, one can in principle solve any problem of electromagnetic response by using Maxwell's equation for the material in the normal state, or by using modified Maxwell's equations (such as London or Pippard's Eqs.) for the material in the superconducting state. This qualitative insight into the importance of the energy gap can be supported by detailed calculation. The convention is to use the complex optical conductivity \( \sigma(\omega) = \sigma_1 + i\sigma_2 \), rather than using the dielectric function \( \varepsilon(\omega) \) to describe the optical response. One can readily convert between conductivity and dielectric function by using Eq. (1-2).

Mattis and Bardeen \(^{(27)}\) (1958) calculated the real and imaginary parts of the frequency-dependent conductivity within the BCS framework. Their calculation is valid either in the extreme dirty limit, where the mean free path of the electron is much smaller than the Pippard coherence length \( \xi_0 \) \( (\xi_0 = V_F/\pi\Delta, \) here \( V_F \) is the Fermi velocity), or the extreme clean limit, where the opposite is true. The results are

\[
\frac{\sigma_{1s}}{\sigma_n} = \frac{2}{\hbar\omega} \int_{\Delta}^{\infty} \text{dE} \left[ f(E) - f(E + \hbar\omega) \right] \frac{E^2 + \Delta^2 + \hbar\omega E}{(E^2 - \Delta^2)^{1/2} [(E + \hbar\omega)^2 - \Delta^2]^{1/2}}
\]

\[
+ \frac{1}{\hbar\omega} \int_{\Delta - \hbar\omega}^{-\Delta} \text{dE} \left[ 1 - 2f(E + \hbar\omega) \right] \frac{E^2 + \Delta^2 + \hbar\omega E}{(E^2 - \Delta^2)^{1/2} [(E + \hbar\omega)^2 - \Delta^2]^{1/2}}
\]

\[(1-20a)\]
\[
\frac{\sigma_{2s}}{\sigma_n} = \frac{1}{\hbar \omega} \int_{\Delta-\hbar \omega}^{\Delta} dE \left[ 1 - 2f(E + \hbar \omega) \right] \frac{E^2 + \Delta^2 + \hbar \omega E}{(E^2 - \Delta^2)^{1/2} \left[ (E + \hbar \omega)^2 - \Delta^2 \right]^{1/2}}
\]

(1-20b)

The second term of (1-20a) does not appear for \( \hbar \omega \leq 2\Delta \); for \( \hbar \omega > 2\Delta \) the lower limit of the integral in (1-20b) is \(-\Delta\) rather than \(\Delta - \hbar \omega\). The Fermi function \( f \) given by

\[
f(E) = \frac{1}{1 + \exp \left( -\frac{E}{k_B T} \right)}.
\]

The results of a calculation of \( \sigma_{1s}/\sigma_n \) and \( \sigma_{2s}/\sigma_n \) at temperature of \( T = 0K \) are shown in Fig.1.1. It is clear that the superconducting energy gap, \( 2\Delta \), corresponds to a starting point above which the real part of conductivity in the superconducting state is no longer zero.

The physical interpretation of the above results is rather direct if we realize that the power absorbed in a unit volume of metal from a known electric field \( E \) is given by \( \sigma_1 E^2 \). Since photons below the superconducting gap cannot be absorbed to dissociate Cooper pairs, the real part of conductivity of material in the superconducting state, \( \sigma_{1s} \), must be zero in the frequency range below the gap to reflect this electrical response. When the frequencies of incident photons are greater than \( 2\Delta \), the absorption starts at \( \hbar \omega = 2\Delta \), and then the real part of conductivity in the superconducting state, \( \sigma_{1s} \), begins to approach smoothly that in the normal state.

Palmer and Tinkham\(^{(28)}\) carried out very precise measurements of both
Fig. 1.1: The calculated (from Eq. 1-20) real and imaginary parts of the frequency-dependent conductivity of a BCS-type superconductor.
transmission and reflection simultaneously on Pb films in order to avoid Kramers-Kronig transformations. Their experimental results, as shown in Fig. 4 of ref. 28, present a rather satisfactory agreement with the predictions of the BCS theory.

In many cases, the extreme dirty limit is unnecessarily confining, as it requires that $\omega \tau = 0$. In some superconductors, $\omega \tau$ may be of the order of unity in the far infrared. An extension of Mattis-Bardeen theory that does not assume either the extreme dirty or the extreme clean limit has been provided by Leplae, who wrote $\sigma_{1s}$ in a form that incorporates the normal-state conductivity. At $T = 0$, $\sigma_{1s} = 0$ for $\hbar \omega \leq 2\Delta$; whereas for $\hbar \omega > 2\Delta$,

$$
\sigma_{1s}(\omega) = \frac{1}{2\hbar \omega} \int_{\hbar \Delta}^{\hbar \omega-\Delta} \left\{ [g(E,E') - 1] \sigma_{1n}(|\epsilon'| - |\epsilon|) + 
\right.
\left. + [g(E,E') + 1] \sigma_{1n}(|\epsilon'| + |\epsilon|) \right\} dE
$$

where

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

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

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

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

Then $\sigma_{2s}$ can be obtained from $\sigma_{1}(\omega)$ by using the Kramers-Kronig relation

$$
\sigma_{2s} = \frac{2\omega}{\pi} \int_{0}^{\infty} \frac{\sigma_{1s}(\omega')}{\omega^2 - \omega'^2} d\omega' + \frac{2A}{\pi \omega}
$$

and $A$ is determined by the conductivity sum rule:
\[ A = \int_{0}^{\infty} d\omega \left[ \sigma_{1n}(\omega) - \sigma_{1s}(\omega) \right]. \]

In this development, if \( \sigma_n \) is inserted as the constant \( \sigma_0 \), the Mattis-Bardeen dirty limit is derived. For \( \sigma_n = \sigma_0/(1-i\omega r) \), the Drude form, a modified \( \sigma_{1s}(\omega) \) is obtained with relaxation time \( r \) as a new parameter.

The Mattis-Bardeen (MB) calculation is not adequate for describing the strong-coupling superconductors. Nam's theory\(^{(32)}\) provides very good results for members of this class of superconductor, though its application can be quite complex. Fortunately, the dominant effect of strong coupling is a uniform decrease in \( \sigma_{2s} \). This same behavior is found from the Leplae formulation for \( \omega r < 1 \). Therefore, reasonable fits to experimental results for strong-coupled materials can be obtained with its use, though its interpretation in this case is not so clear. Fig.1 of ref.23 and Fig.19 of ref.29 show the conductivity of a BCS fit and a Laplace fit to a film of homogeneous NbN. Both MB and Laplace theories fitted the experimental data of \( \sigma_1 \) very well, i.e., there were no difference between these two models for the real part of conductivity; but for the imaginary part, Laplace theory presented a better fit than MB theory, although the main feature of the curve of MB model for \( \sigma_2/\sigma_n \) was still similar to that of Laplace model.
1.5: Far-Infrared Reflectivity Measurement

By measuring the reflectivity and transmission of a specimen simultaneously and accurately, the conductivity ratio of $\frac{\sigma_s}{\sigma_n}$ can be obtained directly from the absorption. However in most cases, the conditions of either sample or experimental device do not meet the crucial requirement of these fine measurements.

When only the measurement of reflectivity (or transmission, as we discuss in section 1.6.) is carried out, one can still extract useful information about the optical properties in both superconducting- and normal-state from the measurement. The optical functions, such as optical conductivity $\sigma(\omega)$, and/or dielectric function $\epsilon(\omega)$, can be obtained from the reflectance spectrum by Kramers-Kronig transformation, as long as reflectivity data were collected in a wide enough frequency range.

Sometimes, we even do not need to measure the reflectivity data in a wide frequency range and carry out a complicated Kramers-Kronig analysis. We can still get some important information, such as the position of the superconducting energy gap, etc, by measuring the spectra around the gap. We explain it in the following.

Optical energy of a plane wave absorbed by the material in a unit of volume, as we know, is given by $\sigma E^2$. It is reasonable to expect an enhancement of superconducting reflectivity in the frequencies of $\omega<2\Delta$, because conductivity is zero ($\sigma_s=0$) at these low frequencies (as Fig.1.1 shows). Thus, a distinguishable edge may be found at the frequency location of the superconducting energy gap in the reflectivity ratio $\frac{R_s}{R_n}$.
A numerical analysis\textsuperscript{(34)} has given the details of this picture. Fig.1.2(a) presents the theoretical reflectivity curves of a metal with a Drude behavior in the normal state and MB dynamic response (i.e. its superconducting conductivity satisfies Eq.(1-20)) in the superconducting state. Fig.1.2(b) gives the reflectivity ratio $R_s/R_n$ of this material. In this case, we see that there is indeed an edge at the location of the gap frequency that corresponds to the onset of superconducting pair-breaking absorption.

In fact, as early as 1960, Richards and Tinkham\textsuperscript{(35)} measured far-infrared reflectivities on a series of metallic superconducting materials and obtained some useful results. Their samples were made as cavities with a bolometer located on the top. The shape of the cavity was adjusted so that photons entering at any angle made between 10 and 14 reflections before returning to the bolometer. The measurements were carried out on tantalum, tin, indium, vanadium, mercury, niobium, and lead by turning a magnetic field roughly double the critical field on and off (rather than changing the temperature) at the fixed low temperatures ($T<T_c$). Fig.4 of ref.35 shows the curve of $(P_s-P_n)/P_n$ plotted as a function of frequency for seven superconductors, and presents ratio spectra similar to those expected (see Fig.1.2(b)) from BCS theory. Here, $P_{n(s)}$ is the power that reached the bolometer when the sample was in the normal (superconducting)-state. Obviously $P_{n(s)}$ is proportional to the reflectance $R_{n(s)}$. The temperature dependence of the energy gaps of lead and vanadium showed that the experimental data agree very well with the prediction of BCS.
Fig.1.2: (a) Calculated reflectivities illustrating the ideal behavior of the far-infrared reflectivity in the normal and superconducting states of an ordinary metal. (b) The reflectivity in the superconducting state, $R_s$, divided by the reflectivity in the normal state, $R_n$. The peak in $R_s/R_n$ occurs at $2\Delta$. (From ref.34)
The potential advantages of using the infrared reflectivity spectrum to investigate the properties of a superconductor are obvious: the physical picture is very clear, the method is direct and effective. However the shortcoming of this method is also obvious: we cannot guarantee that all the edges appearing in the reflectivity ratio correspond to the superconducting energy gaps. It becomes even more serious for the investigation on the new high-$T_c$ materials, in which the critical field is usually too high for us to use an external magnetic field as a "switch" to turn off the superconducting-state. Instead, the temperature of the sample, now, must be changed to switch the states. Meanwhile, the superconducting energy gap of new high-$T_c$ materials is believed to appear at a higher frequency range, in which some other excitations (such as phonons) may also be present. These factors will certainly increase the difficulty of distinguishing the location of the superconducting gap from the complicated spectra. We will go into details in the following chapters.
1.6: Far-Infrared Transmission Measurement

A number of far-infrared transmission studies (for example, see ref. 36, 28, 37, 38) have been carried out with the thin superconducting films. Those, for mechanical strength, are usually mounted on substrates. With thin films, for which the thickness is comparable to the skin depth $\delta_c$, transmission measurements become possible.

Tinkham and Glover$^{36}$ presented an expression for $T_s / T_n$, the ratio of the power transmitted in the superconducting to that transmitted in the normal state, as

$$\frac{T_s}{T_n} = \left\{ \left[ T_n^{1/2} + (1 - T_n^{1/2}) \left( \frac{\sigma_1}{\sigma_n} \right) \right]^2 + \left[ (1 - T_n^{1/2}) \left( \frac{\sigma_2}{\sigma_n} \right) \right]^2 \right\}^{-1}$$

(1-23)

The experimentally measured quantity $T_s / T_n$ is described in terms of the ratio $\sigma_1 / \sigma_n$, $\sigma_2 / \sigma_n$, and $T_n$. Here $T_n$ is the ratio of the power transmitted with a film to that with no film and given by:

$$T_n = \frac{1}{\left| 1 + \sigma_n \frac{d}{r} \frac{Z_0}{n + 1} \right|^2}$$

(1-24)

where $d$ is the film thickness, $n$ is the index of refraction of the substrate, and $Z_0$ is the impedance of free space ($4\pi/c$, cgs; $\mu_0 c = 377$ ohms, mks). Since the conductivity of normal-state, $\sigma_n$, is a constant here, Eq.(1-24) predicts that $T_n$ should be a constant depending only on
This quantity is just the reciprocal of the dc resistance per square of the film, a quantity easily measured experimentally.

Hence, Eq. (1-23) can predict the transmission, given the correctness of the BCS model for $\sigma_s$ and the availability of other parameters. One striking feature in the ratio of $T_s$ to $T_n$ is an unmistakable peak that occurs near the gap frequency. Fig. 19 of ref. 25 shows $T_s/T_n$ for an amorphous film of NbN along with the theoretical fits using the conductivity ratios from the Mattis-Bardeen and Laplace calculations. All the curves confirm that a peak in the ratio of $T_s$ to $T_n$ occurs near the gap frequency.

However, the applicability of Eq (1-23) is limited by the following conditions:

1. **dc-limit**: all the terms varying with time disappear in the Maxwell's equations, and make the equations become electrostatics. The dc-limit may approached when the frequencies of the incident photons are in the low frequency range. All known experimental data measured for the conventional superconductors have shown that the formula of (1-23) is applicable when the frequency $\omega$ is less than 100 $\text{cm}^{-1}$. However for optical frequencies higher than 100 $\text{cm}^{-1}$ (in the cases of high-$T_c$ materials), we do not know the highest frequency at which use of the dc-limit is valid.

2. **substrate limit**: the optical parameters of the substrate must be unchanged when the other experimental conditions are changed (either the temperature of sample is changed or a external magnetic field is added to destroy the superconductivity of specimen). This is not usually a problem for the conventional
superconductors because their critical temperatures are much lower than those of the new materials. For the high-$T_c$ superconducting materials, there is no longer a simple formula as Eq (1-23) which can be used to describe the behavior of infrared transmission, simply due to the difficulty of finding a suitable substrate that will keep its optical parameters unchanged in a wide temperature range of $0<T<T_c$. We will discuss this effect later in the chapter 5.

Cook and Perkowitz\textsuperscript{(38)}, in 1986, published the first far-infrared transmission and reflection measurement results near the gap on thin Nb$_3$Sn films below and above $T_c (=23K)$. They found their data does not fit satisfactorily into either the MB (Mattis-Bardeen) or the Leplae model. These data could be fit by a model ("two-layer model") in which an additional layer of metal or superconductor (with a different $T_c$) was postulated.

In their experiment, superconducting and normal state data were collected over the frequency range 20 to 90 cm$^{-1}$ at 5.5 and 25 K respectively. The results were ratioed to obtain the normalized transmission $T_s/T_n$: in this case the ratio technique cancels most substrate effects. The calculated fits to the ratio $T_s/T_n$ are shown in Fig.1 and 2 of ref.52. The fit from Leplae theory is superior to that from the MB model in most cases.

Since the formula for the two-layer model is not published yet, according to first principles, we obtained it ourselves. It is shown as following:

\[
\frac{T_s}{T_n} = \left\{ \left[ T_n^{1/2} + (1 - T_n^{1/2}) \left( \frac{\sigma_s}{\sigma_n} + \frac{d_1}{d_2} \right) \frac{d_2}{d} \right] \right\}^2 + \]

21
Where $d_1$ is the thickness of the normal layer, $d$ is the thickness of the whole real film, and $\beta = d_1/d$, the definition of $T_n$ is still the same as before and given by Eq.(1-24). Above formula can be checked easily in the following two limiting cases:

(1) $\beta \to 1$: in this case, the thickness of top superconducting layer approaches zero. This means all the deposited film is not superconductor at all, so we should expect to get $T_s/T_n = T_0/T_n = 1$ from the above equation. This has proven to be the case.

(2) $\beta \to 0$: in this case, the thickness of the second layer, which is between the top superconducting layer and the the substrate, approaches zero. This means all the deposited film is superconductor and it corresponds to one layer model, so we should expect the Eq(1-25) will go back to the Eq(1-23).
has proven to be the case.

There are two interesting properties of the above two-layered model that is described by Eq(1-25).

(1) Symmetry property:

\[ T_n^{1/2}(\omega) \longleftrightarrow \beta(\omega) \]  \hspace{1cm} (1-24)

i.e., \( T_s/T_n \) would not change at all if the values of \( T_n^{1/2} \) and \( \beta \) are exchanged.

(2) Alternative property:

\[ T_n^{1/2}(2) - T_n^{1/2}(2)\beta + \beta \longleftrightarrow T_n^{1/2}(1) \]  \hspace{1cm} (1-25)

i.e., the term of \( (T_n^{1/2} - T_n^{1/2}\beta + \beta) \) in the two-layer model plays exactly the same role as \( T_n^{1/2} \) in the single-layer model.

Although above discussion of two-layer model is less important in the present studies on new high-\( T_c \) superconductors, it might be useful for the future infrared studies when more suitable (for transmission measurement) thin film samples of high-\( T_c \) materials become available.
1.7: The Road Map

Chapter 2 of this thesis describes the principle of the FTS 113v Bruker spectrometer used to carry out the work reported in this thesis. The sample and bolometer cryostats are also described in this chapter. Although the sputtering machine was only used to prepare the film samples, and hence should be presented only in chapter 4 and 5, in order to avoid an excessively long chapter we will introduce the sputtering system in chapter 2. Chapter 3 covers the results of our infrared reflectivity measurements on 1-2-3 ceramic samples which presented a strong anisotropy. The infrared reflectivity data on the high oriented films are discussed in chapter 4, while the transmission results on the film samples are presented in chapter 5. Chapter 6 details the results obtained from the infrared reflectivity measurement on n-type superconductors. The final chapter, chapter 7, presents the "big picture" of the optical properties of new high-$T_c$ superconductors based on our infrared results and a comparison with the work reported by other groups.

The results of our infrared reflectivity measurements on the polycrystalline samples, which will be introduced in chapter 3, was published in Phys. Rev. B 36 2368 (1987). The reflectivity and transmission infrared studies on sputtered thin films of Pb-doped Bi-Sr-Ca-Cu-O on MgO, which will be described in chapter 4 and 5, was published in Physica C 162-164 1077 (1989). The main results of our infrared reflectivity studies on n-type superconductors, which will be
presented in chapter 6, was published in Phys. Rev. Lett. 64 1067 (1990); it is the first paper that presented the very clear optical evidence of superconducting energy gap in these n-type materials.
CHAPTER 2: INSTRUMENTATION AND TERMINOLOGY

2.1: INTRODUCTION

All the infrared data we report in this thesis were measured with Bruker Fourier Transform Spectrometer, model IFS 113v. The technique of Fourier-transfer infrared spectroscopy allows all the frequencies of a broad region of infrared energy to be measured simultaneously. Because the record of such a measurement (known as an interferogram) is itself difficult to interpret, a mathematical operation called a Fourier transformation is used to convert the interferogram into a spectrum.

A computer system controls the operation of IFS 113v, transforms the interferograms and processes all the data. With this computerized instrument it is very easy to forget that one is doing anything so complicated as Fourier transformation spectroscopy.

However, considerable time and effort were expended in the manufacture of high-Tc bulk and film samples, as well as in the refinement of experimental detecting system. All the bulk samples, which were measured and their infrared data were reported in this thesis, were prepared by the author in physics laboratories of Simon Fraser University, with the exception of the n-type materials provided by Dr. Shelton’s group in University of California at Davis. All the superconducting film samples were also prepared by the author with the help and guidance of people in Dr. Parsons’s sputtering laboratory of University of British Columbia.
Brief reviews about the sample preparations are presented in the following chapters. In this Chapter, we will first present a brief review of the fundamentals of Fourier Transform Spectroscopy with using of IFS 113v Bruker, and then introduce the sample- and bolometer-cryostats. This is followed by a brief introduction to the sputtering system.
2.2: Fundamentals of Fourier Transform Spectroscopy and IFS 113v Bruker

Infrared interferometers do not differ in any fundamental way from equivalent systems, such as an Michelson interferometer, used in the visible and ultraviolet regions. Fig.2.1 is an optical schematic diagram of IFS 113v Bruker.

To understand the mechanics of the interferometer, one can start with the source, which is usually mated with a desired spectral region, such as mercury lamps for the far-infrared, Globar for the mid-infrared, and Tungsten-Halogen lamp for near-infrared. After the radiation beam is collimated by a mirror, it passes first to a modulator.

The beam is amplitude-divided at the beamsplitter. One part of the radiation beam goes from the fixed mirror 1, through the beamsplitter, to a fixed mirror 2, which reflects the beam to a "jittering" mirror. The returned beam then is reflected by the beamsplitter toward a focusing mirror 4. The other part of the radiation beam is reflected from the beamsplitter to the fixed mirror 3, then goes to and returns from the "jittering" mirror, is transmitted through the beamsplitter, and goes to the focusing mirror 4. The modulated (here, it is the so-called phase modulation) radiation then passes into the sample chamber, in which it interacts with the specimen in either reflection or transmission geometry.

The radiation leaves the sample area and is focused and received by the detector which produces, as its output, an ac signal whose amplitude is proportional to the incident intensity, and whose frequency is that of the modulation and whose envelope contains all the experimental
Fig. 2.1: Top view of the chamber of IFS 113v Bruker.
Phase modulation (PM), which is only available with two-beam interferometers, is achieved with the periodic motion of a mirror. A monochromatic source yields a cosine variation in the flux of the combined beams at the detector. The period of the cosine function is uniquely determined by the frequency of the radiation source and optical path difference for the radiation beams in the two arms. The recording of the detected signal versus the optical path difference is the interferogram. Fourier analysis enables one to convert the interferogram into a spectrum, i.e., signal versus frequency. An example of a phase modulation interferogram and the corresponding spectrum are shown in Fig. 4.5 of ref. 40.

For the reflectivity measurements, an additional mirror system must be installed in the experiment chamber of Bruker. This optical system, as Fig. 2.2 shows, is constituted of four ellipsoidal aluminum mirrors, and located on a movable bench.
Fig.2.2: Top view of the optical system for reflectivity measurement.

\( M_i (i=1,2,3,4) \) are ellipsoidal mirrors; \( S \) is the sample.
2.3: Sample- and Bolometer-Cryostats

In our infrared measurements, samples were held on the cold finger of a continuous He-flow cryostat, as Fig.2.3 shows. The cold finger is composed of a copper bar, heating coil, and a temperature sensor. A U-shape tube was sealed to the back of the copper bar to cool the cold finger. Several holes with -1 cm diameter in the cold finger make transmission measurements possible. The cryostat was pumped and kept at \( \sim 10^{-6} \) mbar before transferring any liquid of \( N_2 \) or \( He \). Temperatures of the cold finger, for our measurements, ranged from 7 K to room temperature. By careful adjustment of the Helium return valve, the sample temperature could be controlled to within \( \pm 0.2 \) K. A copper shield with a slot of 1.3 cm wide was used to cover the cold finger and screen the background radiation from outside. By adjusting the height of the benches, all the five sample positions could be reached, thus making it possible to move from sample to sample or to the reference (a mirror or an open hole).

Proper windows on the dewar were chosen to match the experimental frequency range. Normally mylar or polypropylene films were used as the window material, as they are transparent in the frequency range of our interest.\(^{(41)}\)

A He-cooled (2.5-4.5 K) germanium bolometer was used as a detector for low frequency and weak signal measurements, such as the transmission measurements on Bi-(Pb)-Sr-Ca-Cu-O film. It was also used for the reflectivity measurements on n-type superconductors in the frequency range of 20-700 cm\(^{-1}\).
Fig. 2.3: Cross-section view of the sample holder and cryostat.
A commercial bolometer cryostat (Infrared Laboratories Inc; model HD-3) was modified by us, as shown in Fig.2.4, to fit the IFS 113v Bruker. The optical beam passed through the bottom window of the bolometer, and was detected by the bolometer sensor which was cooled to temperature range of 2.5 to 4.5 K. A cooled-preamplifier which is a low-noise voltage amplifier is employed for the first-stage electronics. The electric signal is then transferred to the data input of Bruker. Helium consumption for twelve hours of experiment was about 4 liters.
Fig. 2.4: Cross section view of bolometer cryostat.
2.3: SPUTTERING AND THE SPUTTERING SYSTEM

"Sputtering" is a useful technique for the fabrication of thin solid films. In the process a glow discharge plasma (usually of Ar) is created in front of a cathode (the target material) by rf or dc excitation. Electrons flowing from the cathode cross the positive space charge, the sheath or dark space surrounding the cathode, and then ionize Ar atoms in the glow region by electron impact ionization. These Ar\(^+\) ions bombard the cathode, and by momentum transfer target atoms are sputtered from the surface and may subsequently be deposited on a substrate situated beyond the glow discharge plasma. The plasma is self-sustaining through the emission of secondary electrons from the target due to Ar\(^+\) ion bombardment.

The circular electromagnets behind the target generate a magnetic field above the target (hence 'magnetron') that constrains electrons to movement near the target surface, thus increasing the efficiency of Ar ionization and subsequently the ejection rate of target material. A further advantage of a magnetron source is that the substrate is not heated by stray electrons from the cathode. Dc sputtering is restricted to conducting targets, whereas rf sputtering must be used for nonconducting pressed Oxide targets.

Fig. 2.5 shows a cross section of the sputtering chamber used in our film sample preparation. It is a horizontally mounted cylindrical chamber evacuated through a port on its underside. The vacuum system consists of an oil diffusion pump used in conjunction with a cold trap. With this
Fig. 2.5: Schematic cross section of sputtering chamber.
system an ultimate chamber pressure of $10^{-5}$ Pa can be achieved.

Electrically the system is a diode.\(^{(42)}\) The cathode assembly, which consists of a water cooled plate, the sputtering target, and a circular electromagnet, is shown at the right of the diagram and the chamber itself acts as the anode. When the chamber is filled with gas (in this case a mixture of argon and oxygen) and an electric potential is applied to the cathode, any free electrons in the gas are accelerated by the electric field. These electrons undergo ionizing collisions with the neutral gas atoms and, under appropriate gas pressure conditions, a plasma forms. This plasma is a partially ionized gas in which the total charge equals zero. The plasma is sustained by constant ionization of neutrals by secondary electrons emitted during ion bombardment of the target. The ion bombardment gives the target atoms sufficient energy to escape the target and make their way to the substrate, where they are deposited, forming the sample film.
Chapter 3: Far-Infrared Studies of Reflectivity Spectrum of Polycrystalline YBa$_2$Cu$_3$O$_{7-x}$ and EuBa$_2$Cu$_3$O$_{7-x}$

3.1 Introduction

The discovery of superconductivity in La-Ba-Cu-O$^{(16)}$ compounds in 1986 has stimulated an enormous amount of interest and has led directly to the identification of a superconducting transition temperature of approximately 90 K in multiphase Y-Ba-Cu-O compounds.$^{(43-47)}$ The physical mechanism responsible for superconductivity in these elevated critical temperature layered materials is still controversial.$^{(48,49)}$ Several new models$^{(48-52)}$ involving interactions other than the usual electron-phonon coupling have been proposed in order to explain the high values of $T_c$. Experimental evidence is needed to decide among the various proposed mechanisms. Of prime importance for understanding the mechanism is the knowledge of the superconducting energy gap and its temperature-dependence.

As we mentioned in Chapter 1, historically far-infrared spectroscopy has been one of the most important tools for studying superconducting properties of the materials. At present, a large number of contributions report results of far-infrared (FIR) in the high-$T_c$ materials.$^{(53-62, for example)}$ The presence of a gap is deduced from a characteristic decrease of the FIR reflectance above a specific frequency below $T_c$.

We have realized that the exact determination of the gap position
from polycrystalline sample is difficult. In addition to the generally poor quality (such as non-superconducting components, oxygen defects, random orientation, etc.) of polycrystalline samples, the spectral range where the gap is expected to be found is covered by infrared-active phonons, which make unambiguous interpretation of features in the reflectance spectra difficult. Besides that, rough surfaces lead to Rayleigh scattering\(c_6\) which lowers the measured reflectivity at higher frequencies with a corresponding decrease in the sensitivity of the measurements. Finally, the anisotropic properties of these layered high-\(T_c\) superconductors make interpretation of the infrared spectra more complicated.

However, as the materials have become better understood and more work has been done in this area, especially the high degree of accuracy and reproducibility of infrared data measured on single crystals\(^{56,57,63,64,65}\) and oriented films\(^{66-69}\) of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) and other high-\(T_c\) materials\(^{54}\) are available (see the Chapter 4), we are in a better position to interpret and understand our experimental data measured on bulk samples, and a consistent picture is hence starting to emerge.

In this chapter, we will first introduce the crystal structure of 1-2-3 superconductors, discuss their optical anisotropy and related problems. Then we will present and discuss our infrared reflectivity data measured on polycrystalline samples of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) and \(\text{EuBa}_2\text{Cu}_3\text{O}_7\).

3.1.1: Crystal structure of \(\text{YBa}_2\text{Cu}_3\text{O}_7\)

The correct chemical formula for the superconducting phase with a ~90 K transition temperature in Y-Ba-Cu-O compounds is \(\text{YBa}_2\text{Cu}_3\text{O}_7\) (also called
"1-2-3 phase") that was first reported from a neutron powder diffraction study by Beno et al.\textsuperscript{(70)} The oxygen defect concentration, $x$, in YBa$_2$Cu$_{3-}$$_{7-x}$ varies between the lower limiting composition YBa$_2$Cu$_3$O$_6$ ($x=1$) and the upper limiting YBa$_2$Cu$_3$O$_7$ ($x=0$). For $0<x<0.5$ the compound is orthorhombic and superconducting, and for $0.5<x<1$ it is tetragonal and non-metallic. For the former at least two plateaus for $T_c$ are observed, one at $x<0.15$ ($T_c=90$ K), and the other at $0.25<x<0.45$ ($T_c=50-60$ K).\textsuperscript{(71)} Coexistence of two phases having different oxygen concentrations ($x=0$ and $x=0.3$) has been reported from x-ray diffraction of single crystals.\textsuperscript{(72)} The existence of at least five distinct phases in the compositional range $0<x<1$ has also been suggested by electron diffraction.\textsuperscript{(73)} As the oxygen content is reduced, the critical temperature decreases. With the disappearance of superconductivity the structural symmetry changes from orthorhombic to tetragonal.

The structure of YBa$_2$Cu$_3$O$_7$ can be derived from the perovskite structure ABO$_3$ by tripling one cell axis concurrent with the cation ordering -Y-Ba-Ba-Y-Ba-Ba- on the A site (hence the name "triple perovskite" structure), and by removing up to three (out of nine) oxygen atoms. The resulting metal-oxygen layers are stacked in the sequence -Y-CuO$_2$-BaO-CuO-BaO-CuO$_2$-Y etc, as Fig.3.1\textsuperscript{(74)} shows. The structure of YBa$_2$Cu$_{3-}$$_{7-x}$ ($0<x<0.5$) is orthorhombic, as we mentioned before, with the c-axis parallel to the long cell dimension, and b-axis parallel to the longer of the two (nearly equal) short cell dimensions ($a=3.8177$ Å, $b=3.8836$ Å, $c(=3a)=11.6827$ Å, at 320 K). The structure contains an yttrium site with its eight nearest oxygen neighbors in nearly cubic configuration, a barium site with the nearest oxygen neighbors in
Fig. 3.1: Unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$. 
truncated cube environment, two copper sites, i.e. a one-fold Cul site with square-planar, a two-fold Cu2 site with square-pyramidal oxygen coordination, and four oxygen sites. The planes of CuO2 are not strictly planar as the Cu2 site is shifted by 0.25 Å out of square-base towards the apical O1 site. The latter sites are linked by Cul. The pyramidal Cu2 site is often called "planar site" because the bond distances between it and the basal oxygen atoms, [Cu2-O2(03)] = 1.94 Å, are much shorter than those between it and the apical oxygen atom [Cu2-O1] = 2.30 Å. The square-planar Cul site is often called "linear chain site" because it is situated on linear (or nearly linear) O4-Cul-O4 chains that run along . The bond distances in these chains, [Cul-O4] = 1.94 Å, are longer than those perpendicular to the chains, [Cul-O1] = 1.86 Å. Due to defects on the O4 site the chains are usually interrupted. The crystal structure of YBa2BaCuO7-x has been confirmed by direct observation with a high-resolution electron micrograph.(75)

3.1.2: Infrared Conductivity of A Polycrystalline Sample

Original Kramers-Kronig analysis of infrared reflectivity data from polycrystalline samples of YBa2Cu3O7-x showed an extremely strong and broad feature in the real part of conductivity, \( \sigma_1(\omega) \), at 3000 cm\(^{-1}\) (0.37 ev).(76,77) This feature was interpreted as excitons. This can be seen in Fig.2 of ref.76, where for the case of x\(\leq0.1\), the electronic part of spectrum has a broad peak at 3000 cm\(^{-1}\), in contrast to the nonsuperconducting case (x=0.8) in which the peak is absent. This peak was then attributed to a charge-transfer band, or exciton, and as evidence of strong electron-electron Coulomb interactions(76) in these Cu-O layered
materials. Similar conclusions were reached from experiments on superconducting \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) polycrystalline samples. However, it has been subsequently argued that this charge transfer transition (excitons) band was an artifact associated with an incomplete treatment of anisotropy in the polycrystalline data analysis.\(^{79,80}\)

Orenstein and Rapkine, in ref. 79, modeled the high-\( T_c \) superconductors as optical uniaxial crystals with principle components of dielectric tensor \( \epsilon_\parallel \) and \( \epsilon_\perp \), for the c axis and a-b plane, respectively:

\[
\epsilon_\parallel = \epsilon_0
\]

and

\[
\epsilon_\perp = \epsilon_0 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}
\]

This reflects qualitatively the fact that the high-\( T_c \) superconductor is much like a quasi-2D metallic material. When the direction of propagation \( \hat{n} \) is not parallel to \( \hat{c} \), there are two distinct modes of propagation: the ordinary o mode for which the component of \( \hat{E} \) is perpendicular to the \( \hat{n}-\hat{c} \) plane, and the extraordinary e mode corresponding to the in-plane component of \( E \). The effective dielectric functions hence are

\[
\epsilon_o = \epsilon_\perp
\]

and

\[
\epsilon_e = \frac{\epsilon_\parallel \epsilon_\perp}{\epsilon_\parallel \cos^2 \theta + \epsilon_\perp \sin^2 \theta}
\]

Where \( \theta \) is the angle between \( \hat{n} \) and \( \hat{c} \). The conductivity \( \sigma^e_1(\omega) \) for these modes is calculated and plotted in Fig. 1 of ref. 79. \( \sigma^o_1(\omega) \) for the o mode
is the same as the o mode for $\theta = 0$, and has a peak at $\omega = 0$; but for nonzero $\theta$ the conductivity of the e mode develops a peak near $\omega = (\omega_p / \sqrt{\epsilon_0}) \sin \theta$.

The reflectivity $R$ is the sum of contributions from individual crystallites when $\lambda < \ell$, where $\lambda$ is the wavelength of light in the medium and $\ell$ is the typical crystalline dimension. For $\ell = 10 \, \mu m$ this range corresponds to $\hbar \omega > 0.05 \, ev$, which is the range in which the peak in $\sigma_1(\omega)$ has been observed. This effective ensemble-averaged reflectivity is calculated within this approach and expressed by (79)

$$<R> = \frac{1}{2} \left[ R_o + \int_0^{\pi/2} R_e(\theta) \sin \theta \, d\theta \right], \quad (3-5)$$

where $R_o$ and $R_e$ are the reflectivities of the o and e modes, respectively.

Finally, the effective ensemble-averaged conductivity, $<\sigma>$, is obtained from Kramers-Kronig transformation of $<R>$. A peak at about 0.5 ev was found in the spectrum of the conductivity $<\sigma>$.

On the basis of the striking similarity between the experimental results shown in Fig.2 in ref.76 and above calculated picture, we agree that the effects of optical anisotropy account for the pronounced peak in the optical conductivity of the polycrystalline samples of high-$T_c$ Cu-O layered superconductors.

This view is supported by the infrared measurements on $La_{2-x}Sr_xCuO_4$ (61), $YBa_2Cu_3O_7$ crystals, textured ceramics (65) and highly oriented thin films (67,68). The substantial conductivity extending into the mid-infrared range ($>0.5 \, ev$) does not reveal the sharp excitonic peak in $\sigma_1(\omega)$ reported earlier (76,77,78).
3.1.3: C-axis Reflectivity and Gap Anisotropy of Layered 1-2-3 Compounds

It has been recognized that anisotropy between the in-plane (a-b plane) and out-of-plane (c-axis) transport properties in the high-\(T_c\) Cu-\(O\) layered materials have made the interpretation of infrared measurements of polycrystalline samples very difficult. The platelike nature of the crystal structure and a much higher conductivity for the in-plane might be the reason for the scattered values of superconducting energy gaps reported in the early far-infrared measurements on polycrystalline samples. Improvements in the synthesis of superconducting materials, availability of single crystals and highly oriented thin films, in conjunction with a more complete picture of the infrared response along each of the principal crystal axes, have all contributed for a better understanding of the data on polycrystalline samples.

Infrared reflectivity measurements of crystalline \(\text{YBa}_2\text{Cu}_3\text{O}_{7}\) performed with the electric field both parallel and perpendicular to the Cu-\(O\) planes were first reported by Collins et al.\(^{(63)}\). The c-axis reflectivity and the real part of the conductivity, which was obtained from a Kramers-Kronig transformation of the reflectivity in the normal and superconducting states, are presented in Fig.3 of ref.63 and discussed as follows.

The c-axis reflectivity is very different from that of a-b plane (see Fig 1(a) of ref.63): the rich phonon structures in the c-axis reflectivity spectrum were replaced by a rather smooth curve in the ab-plane spectrum; and the low frequency reflectivity enhancement of the c-axis below \(T_c\) is almost twice as high as that of the ab plane. Both of these can reasonably be explained by a strong anisotropy of in-plane and out-of-plane...
conductivities. This anisotropy has been estimated, from the infrared data, to be at least of about 40:1 for the ab plane to c-axis, which is in the range of the lowest estimates from dc transport studies. As a consequence of this low c-axis conductivity, the c-axis phonons are not well screened, and the reflectivity enhancement in the low-frequency range below $T_c$ is bigger than that in the ab plane because the c-axis reflectivity in normal-state is rather low.

The rapid drop in the c-axis reflectivity ratio as the frequency increase through about 200 cm$^{-1}$, as shown in Fig.3(b) of ref.63, suggests the possibility of a c-axis energy gap in this vicinity. The calculated curve using a superconducting energy gap of 170 cm$^{-1}$ and phonons (Lorentz oscillators) at 155, 195, 220, 270, 310 and 570 cm$^{-1}$ is an approximate fit to the experimental data. The superconducting frequency scale for the c axis is thus about 170 cm$^{-1} \approx 3 K_T$, which is much lower than that obtained from the ab plane response (≈8K_T).
3.2: Sample Preparation and Characteristics

We synthesized $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ from appropriate amounts of $\text{Y(NO}_3)_3\text{H}_2\text{O}$, BaO, and CuO powders, usually mixed in a ball mill. The materials were preheated for 4 hours at 400°C in the air, ground and then fired at 960°C in oxygen flow for 10 hours. The samples usually contained, in addition to the 1-2-3 phase, the so-called green phase $\text{Y}_2\text{BaCuO}_5$ and several other phases. To obtain a single superconducting phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, we reground samples, homogenized them well, pressed them into pellets (1.27 cm diameter) and fired them again with oxygen flowing. A slow cooling process is required to get a full oxygen resorption to form $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with $x = 0$. This resorption of oxygen leads to the transition from the tetragonal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ ($x = 0.5$) to the orthorhombic superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($x = 0$) phase.

Resistance measurements on the same sintered material of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ gave a superconducting transition with a midpoint temperature of 91.5 K and a width (10% to 90%) of 1.8 K, as shown in Fig.3.2.

The sample of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ was prepared from appropriate amounts of EuO, BaO and CuO and followed by a cooking process similar to that for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The powders were fine-ground and mixed, then heated in an alumina crucible, with oxygen flowing, at 450°C for 2 hours, then at 940°C for 12 hours. The resultant sintered material was reground and pressed into 1.27 cm diameter pellets and sintered again for 12 hours at 940°C in oxygen. It was then allowed to cool slowly to room-temperature in flowing oxygen.
The resistance of the sample was measured by using a conventional four-point probe technique. The width (10% to 90%) of the resistive transition was about 2 K and the midpoint was 90.5 K, as shown in Fig 3.2.
Fig. 3.2: Resistance of YBa$_2$Cu$_{37-x}$ and EuBa$_2$Cu$_{37-x}$ polycrystalline samples. Both curves show a linear dependence on temperature before the onset of superconductivity.
3.3: Experimental Results and Discussion

The far-infrared reflectivity measurements near normal incidence were made using a Bruker 113v Fourier spectrophotometer. The samples were held in the helium cryostat described in Chapter 2. Reference spectra were taken using a stainless steel mirror and sample spectra were measured at a number of temperatures using a pyroelectric detector. The relative precision of the reflectance was estimated to be at least 0.1% for all temperatures; because of the possibility of systematic errors due to several effects related to the sample geometry, the relative accuracy of the measurements is no better than 1%. The spectra presented here were taken on several samples and were found to be unchanged in a number of remeasurements taken over a two month period.

3.3.1: Reflectivity Measurement on Polycrystalline YBa$_2$Cu$_{3-7-x}$O

Fig. 3.3 shows the reflectivity of YBa$_2$Cu$_{0.7}$O$_{7-x}$ at several temperatures over the spectral region in which the temperature-dependent features occur. At room temperature the reflectivity decreases gradually from ~ 0.7 at 50 cm$^{-1}$ to 0.15 at 700 cm$^{-1}$; at lower temperatures, while the general shape of the spectrum remains the same, the reflectivity increases slightly as temperature decreases until the critical temperature of the sample ($T_c - 91$ K) is approached. Comparing the reflectivity of YBa$_2$Cu$_{3-7-x}$O$_{7-x}$ in the superconducting state (i.e., 8 K) to the normal state (i.e., 100 K) shows an enhancement at the low frequency range of 50 - 200 cm$^{-1}$. These two reflectivities have a crossing point around ~ 200 cm$^{-1}$ which has been
Fig. 3.3: Infrared reflectivities of polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at several temperatures.
widely reported to be related to a frequency location of a c-axis superconducting energy gap.\(^{(63, 84, 85)}\) Above this frequency, the reflectivity of the superconducting-state is less than that of the normal-state. The behavior of reflectivity indicates that the superconductivity has a strong influence on the dynamic conductivity. There are some phonon-like features at about 106, 155, 194, 277, 311, and 570 cm\(^{-1}\) respectively.

Fig. 3.4 gives the ratio of reflectivity of YBa\(_2\)Cu\(_3\)O\(_{7-x}\) bulk sample in the superconducting state to that in normal state. Also included in this figure is the reflectivity ratio of a normal state (95 K) to that of another normal state (110K). It is obvious that there is a strong temperature dependence. The increased reflectivity in the superconducting state extends to ~ 200 cm\(^{-1}\); and several sharp line structures are presented more clearly at about 105, 155, 194, 277, 311 and 569 cm\(^{-1}\) in the ratio spectra. The temperature-dependence behaviors of the low frequency phonon-like features (105, 155 and 194 cm\(^{-1}\)) are very different from others, and will be discussed later.

Our infrared reflectivity data measured on bulk sample of YBa\(_2\)Cu\(_3\)O\(_{7-x}\) (Fig.3.3 and Fig.3.4) are in qualitative agreement with those reported by other groups.\(^{(85-89)}\) However, it should be noted that the values of our infrared reflectivity data for polycrystalline YBa\(_2\)Cu\(_3\)O\(_{7-x}\) are lower than those, so called "absolute reflectivity", of ref. 85, 89, and 61, especially in the high frequency range. These higher values were obtained by using the metal-coated bulk samples as the reference.\(^{(85, 88, 61)}\) The lower reflectivity values for our sample and other uncoated ceramics cannot be assigned to the random orientation of anisotropic crystal
Fig. 3.4: The ratios of reflectivity, $R_t/R_{110k}$, of polycrystalline $YBa_2Cu_3O_{7-x}$.
granules alone, because it ignores the fact that a high reflectivity value of 0.5 to 0.6, at about 700 cm\(^{-1}\) for the temperature between 10 to 100 K, has been observed in the measurement on the c-axis plane of single crystal of \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) with a polarized beam. A lower reflectivity is also observed for our polycrystalline \(\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}\), as will be shown in the following section.

The difference between our data and the "absolute" reflectivity found\(^{(61,85,89)}\) is mainly due to the roughness of our sample surface. Scattering may contribute to the lower reflectivity level at high frequencies for these bulk samples. The difference between the our crude data and theirs has been explained recently by Ose et al work.\(^{(61)}\) They found that the low reflectivity level at the high frequency for bulk samples maybe attributed to the effect of scattering which corresponds to the surface roughness of measured sample.

3.3.2: Reflectivity Measurement on Polycrystalline \(\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}\)

To better understand the electronic response and the behavior of low-energy excitation of layered 1-2-3 materials, we have also measured the far-infrared reflectivity response of the \(\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}\) polycrystalline superconductor whose transition temperature is 90.5 K. The data were taken in a frequency range of 30 - 700 cm\(^{-1}\) as a function of temperature over the full range of 10 K to room temperature. There is a remarkably rich spectrum with a dramatic temperature dependence similar to that of yttrium sample.

Fig.3.5 shows the reflectivity at four temperatures of 10, 100, 200 and 300 K. As in the case of \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\), the reflectivity of \(\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}\)
Fig. 3.5: Reflectivity spectra of polycrystalline EuBa$_2$Cu$_3$O$_{7-x}$. 
in the superconducting state is quite different from that in the normal state. Superconducting reflectivity is enhanced at low frequency range and four edges have appeared at about 70, 190, 320 and 430 cm$^{-1}$ respectively, although the last one is not as clear as the others.

The reflectivity ratio, $R_t/R_n$, of EuBa$_2$Cu$_{3}O_{7-x}$ is shown in Fig.3.6 for several temperatures. It is clear that there are four distinct regions of enhanced reflectivity in the 10 K spectrum: 0 - 120 cm$^{-1}$, 120 - 250 cm$^{-1}$, 250 - 400 cm$^{-1}$ and 400 - 600 cm$^{-1}$. Each region and each reflectivity ratio edge has its own dependence upon temperature, which is shown more clearly in Fig.3.6(b).

The superconducting reflectivities of EuBa$_2$Cu$_{3}O_{7-x}$ at 10 to 40 K are sharply decreased at 70 cm$^{-1}$, which can be seen in Fig.3.6(b), compared with other superconducting reflectivities, which measured at the higher temperatures around this frequency. It may indicate that there is another superconducting phase in which $T_c$ is about 40 to 60 K, and the gap is located at ~70 cm$^{-1}$. We will discuss this later. Beyond the frequency of 70 cm$^{-1}$, the superconducting reflectivities are almost the same for temperature range of 0 to 60 K. And nearly all the changes in the superconducting reflectivity happened primarily in temperature range of 60 K to $T_c$ (90.5 K).

Comparing our overall reflectivity spectra with those of other work$^{(60,90)}$ on this compound, we find a general similarity in most of the main features. The features appearing at about 115, 156, 180, 270 and 304 cm$^{-1}$ in our reflectivity spectra have been all attributed to phonons by Cardona et al.$^{(80)}$
Fig. 3.6: The ratios of reflectivity, \( R_t / R_{100k} \), of EuBa\(_2\)Cu\(_3\)O\(_{7-x}\).
Fig. 3.6(b): The reflectivity ratio, \( R_{\text{EuB}}/R_{\text{EuCuO}} \), of EuBa\(_2\)Cu\(_3\)O\(_{7-x}\) in the different frequency ranges.
3.3.3: Infrared - Active Phonons

The assignment of the TO-phonon modes of $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ (R is Y, Eu and/or other rare-earth ions) has been discussed by a number of groups. Here we will compare our measured model frequencies with lattice-dynamic calculations and the experimental results obtained by other groups. Since the most reliable experimental data were measured on yttrium sample, we will focus our attention mainly on this material. $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ has very similar phonon structures to that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Therefore the infrared data of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ will only be referred to occasionally.

It is usual to extract the physical information from the reflectivity data by using a Kramers-Kronig analysis. But in our case, uncertainty in the absolute values of the reflectivities, the strong anisotropy of layered Cu-O superconductors and random orientation of crystal granules in the polycrystalline samples, make the Kramers-Kronig results less useful. However, we can still use the K-K transformation here to extract some phonon information.

Using our low frequency infrared data of Fig.3.3 and Genzel's high frequency data, in a Kramers-Kronig calculation, we find the real part of frequency-dependent (AC) conductivity, $\sigma_1(\omega)$, of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, shown in Fig.3.7. The frequencies of the six phonons resulting from this analysis are summarized in Table 3.1. All those phonon modes are assigned as c-axis modes. It could be argued that, in a material which is orthorhombic with space group $P_{\text{mmn}}^{-1}$, there are over 11 (totally 21) symmetry-allowed infrared modes. However, the electron plasma is confined to the ab plane, and tends to screen the infrared phonon modes whose vibrations...
Fig. 3.7: Real part of conductivity, $\sigma_1$, obtained by K-K analysis of the data presented in Fig. 3.3 above and below $T_c$. 
TABLE 3.1. Lattice mode energies in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Y compound</th>
<th>Eu compound</th>
<th>Orientation(^{(a,b)})</th>
<th>Symmetry(^{(c)})</th>
<th>Type</th>
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<tbody>
<tr>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td></td>
<td>c</td>
<td>(B_{1u})</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>105</td>
<td>115</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td></td>
<td>(B_{1u})</td>
<td>Ba-mode</td>
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<tr>
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<td></td>
<td></td>
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<tr>
<td>(c)</td>
<td>154.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d)</td>
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</tr>
<tr>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>3.</td>
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<td></td>
<td>(B_{1u})</td>
<td>Y-mode</td>
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<td>(b)</td>
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<td></td>
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<tr>
<td>(c)</td>
<td>194.8</td>
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<td></td>
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<tr>
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</tr>
<tr>
<td>(a)</td>
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<td></td>
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<td>4.</td>
<td></td>
<td></td>
<td>(B_{1u})</td>
<td>Cu-O Plane Bending</td>
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<tr>
<td>(b)</td>
<td>319.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>275</td>
<td>270</td>
<td></td>
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</tr>
<tr>
<td>(d)</td>
<td>277</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
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<td>5.</td>
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<td></td>
<td>(B_{1u})</td>
<td>Cu-O Plane Bending</td>
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<tr>
<td>(b)</td>
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<td>(c)</td>
<td>311</td>
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<tr>
<td>(d)</td>
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<td></td>
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<td>(a)</td>
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<td>6.</td>
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<td></td>
<td>(B_{1u})</td>
<td>Cu-O Stretching</td>
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<td>(b)</td>
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<tr>
<td>(c)</td>
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</tr>
<tr>
<td>(d)</td>
<td>567</td>
<td>?</td>
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</table>

(a) from ref.85 (theoretic result).
(b) from ref.85.
(c) from ref.89.
(d) from our data.
are in this plane; thus, only modes in which the vibrational motion is perpendicular to this plane will be observed easily.\textsuperscript{(56,63)} Below we discuss our assignment of these modes.

It has been noted that the phonon mode at 94.5 cm\textsuperscript{-1} in both Y and Eu samples, which is a rather strong mode predicted by calculation\textsuperscript{(92)} and not observed in the infrared measurements by the other groups,\textsuperscript{(85,89)} can be distinguished clearly as the 105 (115) cm\textsuperscript{-1} mode for the Y (Eu) compound in our far-infrared data, though it is weak. Failure to observe this phonon mode by other group is probably due to the fact that the reflectivities measured by others\textsuperscript{(85,89)} are already so high that the low-frequency phonon structure is suppressed.

The very strong and sharp phonon found at 155 cm\textsuperscript{-1} in Y spectrum is assigned to the "barium" mode, due to its low frequency and the almost unchanged position when yttrium is substituted by the heavier rare earth metal of Eu. This mode has been thus assigned\textsuperscript{(85)} mainly due to the vibration of Ba against oxygen ions, although some other assignments have also been given.\textsuperscript{(88)} The observed phonon at 195 cm\textsuperscript{-1} in Y sample is clearly associated with the yttrium ion; it represents a largely localized vibration of the rare earth ion because it shifts dramatically to lower frequency (180 cm\textsuperscript{-1}) by replacing yttrium with the heavier Eu. Similar, consistent shifts connected with this mode also occur when Y is replaced by other heavier rare-earth ions.\textsuperscript{(60,84,90,91)} Since the frequency ratio of Y- to Eu-mode, which is 195 cm\textsuperscript{-1}/180 cm\textsuperscript{-1}=1.08, is less than what one may expect for a "pure" rare-earth mode, i.e., \((m_y/m_{\text{Eu}})^{1/2}=1.27\), above "yttrium" mode (195 cm\textsuperscript{-1}) must also include the other movements of the neighbor ions.
It has been pointed out\textsuperscript{(88,85,61)} that the vibrational features near 300 cm\textsuperscript{-1} may be associated with Cu-O plane bending modes. Our results do not contradict this assignment. The 560 cm\textsuperscript{-1} phonon can be assigned as a Cu-O stretching mode due to its high frequency. The only Cu-O stretch of $B_{1u}$ symmetry is the one involving the oxygen ions located between the Cu-O chains and the Cu-O planes\textsuperscript{(88)}: therefore, we assign the 560 cm\textsuperscript{-1} mode to this vibration.

Several papers\textsuperscript{(85,93,88,63,61)} show that some phonons become soft below $T_c$ and an attempt has been made to explain this effect within the framework of the strong-coupling theory.\textsuperscript{(94,95)} Based on this theory, the location of the phonon which is above the superconducting gap energy is predicted to shift to lower frequency (i.e., soften) when the sample is cooled through $T_c$. We are not going to present quantitative details of the temperature dependence of the phonon positions, since our resolution (2 cm\textsuperscript{-1}) is very close to the shifts (2 to 4 cm\textsuperscript{-1}) in the softening effect. However, by a rough determination of our infrared data of YBa$_2$Cu$_3$O$_{7-x}$, our results are very similar with that of ref.\textsuperscript{44}: The softening is apparent for the modes at 275 cm\textsuperscript{-1}, 311 cm\textsuperscript{-1}, and 569 cm\textsuperscript{-1}, while there is no clear effect seen for the 155 cm\textsuperscript{-1} mode. This may indicate that the 155 cm\textsuperscript{-1} phonon is at 10 K well below the essential gap region and suggests that the gap location is between 155 and 275 cm\textsuperscript{-1}.

3.3.4: Superconducting Energy Gap(s)

As we have discussed in section 3.1.2, it is of questionable to extract information about the electronic part of the conductivity from the experimental reflectivity data by the K-K transformation, due to the
strong anisotropy and the random orientation of grains in the bulk sample. However, by examining the ratio of the reflectivity in the superconducting state to that in the normal state, which predicted to be peaked at $2\Delta$ (as shown in Fig.1.2(b)), the superconducting energy gap $2\Delta$ and its temperature-dependence, might be obtained.

Recently some far infrared reflectivity experiments have been performed successfully on high-$T_c$ cubic oxides of $\text{BaPb}_{0.8}\text{Bi}_{0.2}O_3$ ($T_c \leq 12$ K) and $\text{Ba}_{0.6}\text{K}_{0.2}\text{BiO}_3$ ($T_c = 30$ K) which are isotropic. Like the infrared data from the conventional superconductors, these measurements show an enhancement of the low frequency reflectivity in the superconducting state, and hence a peak in the reflectivity ratio. An external magnetic field was also used to "switch" the sample from its superconducting to normal state at one fixed low temperature ($T \ll T_c$). A ratio of superconducting- to normal-state reflectivity obtained in this way also shows the same behavior as ratios in which the superconducting state was destroyed by increasing sample temperature. From the frequency of the peak in the ratio spectrum, $R_s/R_n$, an energy gap of $2\Delta \approx 3-4 K_T$, which is also consistent with a BCS-type mechanism, is inferred for both $\text{BaPb}_{0.8}\text{Bi}_{0.2}O_3$ and $\text{Ba}_{0.6}\text{K}_{0.2}\text{BiO}_3$.

From our reflectivity ratio, $R_s/R_n$, of Fig.3.4 and Fig.3.6, for polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$, it is evident that the situation in the high-$T_c$ Cu-O layered materials is not as simple as in the conventional superconductors, nor as simple as in the high-$T_c$ cubic bismuth oxides. The reflectivity spectrum of the layered high-$T_c$ material is no longer smooth below the possible superconducting energy gap. The rich phonon structure and strongly anisotropic optical properties of these
materials complicate the data analysis.

However a gap-like edge at about 200 cm\(^{-1}\) for both Y and Eu compound can still be identified easily from our reflectivity ratio of Fig.3.4 and Fig.3.6. Although the height of this edge decreases dramatically when temperature increases from 70 K to \(T_c\) (-91 K), its frequency location seems unchanged, even when the temperature approaches the transition point.

The behavior of phonon features in the far-infrared reflectivity spectrum at \(T < T_c\) can also used to identify the position of the superconducting energy gap.\(^{(84,85,56,63)}\) From our infrared data in Fig.3.3 on polycrystalline \(YBa_2Cu_3O_{7-x}\), it can be seen that at 10 K the low-frequency phonons, below 200 cm\(^{-1}\), correspond to dips in reflectance, while those above 250 cm\(^{-1}\) correspond to peaks. This is not the case for temperatures higher than \(T_c\) where all the phonons are peaks. Such behavior is more visible in the ratio spectra of Fig.3.4. It has been calculated and pointed out by Wittlin et al\(^{(84)}\), that the phonon behavior at the low frequency range (\(\nu<2\Delta\)) is a direct consequence of the presence of a superconducting gap. We could not find the same behavior in the reflectivity spectrum of our Eu sample, it may be related to the prediction that our Eu compound is likely not a single superconducting phase material. However its ratio spectrum (see Fig.3.6) still reveals a similar temperature-dependent phonon behavior as that in the Y sample.

In Fig.3.8, the temperature-dependence of this superconducting energy gap at 180 cm\(^{-1}\) for both Y and Eu compounds are shown. These findings are consistent with studies\(^{(84,87)}\) by other groups. Since the phonon lines make an unambiguous determination of the gap-related peak positions
difficult, Fig.3.8 is only a rough indication of the temperature dependence of the gap.

The behavior of this edge in the reflectivity ratio of 1-2-3 compounds can be interpreted as exhibiting a superconducting energy gap at $\sim 180 \text{ cm}^{-1}$. These findings are in a good agreement with other far-infrared studies, such as those of refs. 56, 84, 85, and 87.

In the conventional theory of superconductivity the magnitude of $2\Delta/KT_c$ is related to the coupling strength. By using $2\Delta \approx 180 \pm 20 \text{ cm}^{-1}$ with $T_c = 91 \text{ K}$, we estimate that $2\Delta/KT_c \approx 2.9 \pm 0.3$, a value consistent with BCS theory. But it is certainly not a pure BCS-type gap because there is no detectable shift toward lower frequency as the temperature approaches to $T_c$. This unusual temperature dependence of the superconducting energy gap for high-$T_c$ layered oxides has now been widely reported.

It has been suggested by infrared reflectivity measurements on polycrystalline $\text{RBa}_2\text{Cu}_3\text{O}_7$ (R can be Y, Gd, and Sm) that there is another superconducting energy gap at $\sim 580 \text{ cm}^{-1}$. It was found that the phonon at $\sim 570 \text{ cm}^{-1}$ appears as a shoulder on the ratio edge of Gd and Sm sample at temperatures $T < T_c$; i.e., the phonon feature at 570 cm$^{-1}$ can be separated from the possible superconducting gap peak at $\sim 580 \text{ cm}^{-1}$. This phonon mode was thus considered to be superimposed on the gap feature. From our infrared data of Figs.3.3, 3.4, 3.5, and 3.6, we cannot rule out this possibility. The strong and broad peak at $\sim 570 \text{ cm}^{-1}$ at 10 K in Fig.3.4 is consistent with the point of view in ref.87 (i.e., a gap at $\sim 580 \text{ cm}^{-1}$). Once again, the height of the ratio edge at $\sim 580 \text{ cm}^{-1}$ decreases with temperature and vanishes at $T_c$, but the position remains
Fig. 3.8: Gap frequency $\Delta(T)/\Delta(0)$ as a function of the reduced temperature $T/T_c$ for the 1-2-3 compounds. The solid line represents the BCS theory.
fixed. If it is considered to be a real gap, the size is ≈ 9.2 KTc, which is consistent with the result (~8 KTc) measured on ab plane of single crystals(58,57,63,64) and thus reflects a strong gap anisotropy.

The two (~3 KTc and 8 KTc) values of superconducting energy gap(s) measured on polycrystalline, oriented epitaxial films and single crystals of YBa2Cu3O7 and related compounds, were attributed to anisotropy of electronic property and different crystal orientations. These two gaps with different sizes were proposed(88,99) for directions in the ab plane (~8 KTc) and along the c-axis (~3 KTc), and confirmed by the recent polarized reflectivity measurement on the single crystal of YBa2Cu3O7.(63,64,66)

We also note that reflectivity and the reflectivity ratio of EuBa2Cu3O7-x in the low-frequency range are very different from those of YBa2Cu3O7-x. The enhancement of the reflectivity of Eu compound appears as a three step process at 10 K, as shown in Fig.3.5 and Fig.3.6. The first reflectivity edge at 60 cm⁻¹ has a dramatic change at 50 K, and almost disappears at 60 K. It may indicate that an additional superconducting phase, with a lower critical transition temperature, was included in our Eu sample. This point of view is confirmed by the observations of the iron-doped YBa2(Cu1-xFe)x3O7 compound with a sufficiently reduced oxygen content (x ≈ 0.21, Tc ≈ 68 K in this case)(88). Similar behavior in the reflectivity spectra was exhibited in above cases. By using 2Δ ~ 60 cm⁻¹ with Tc ~ 50 K, a value of ratio of energy gap, 2Δ/KTc ~ 1.7, for this lower Tc superconducting phase is estimated.
3.4: Conclusions

Our far-infrared reflectivity experiments on the polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and the related compound in which yttrium is substituted by the heavier rare earth metal Eu, revealed a superconducting energy gap $(2\Delta)$ at about $180 \text{ cm}^{-1}$, in which the ratio of $2\Delta/\text{KT}_c = 3.0 \pm 0.5$ close to that of a BCS weak-coupling superconductor. However, the temperature dependence of this gap indicates that it is not a truly BCS-type gap. Another possible superconducting energy gap at about $580 \text{ cm}^{-1}$ ($\sim 9.2 \text{ KT}_c$) was also discussed. The different values of superconducting energy gaps were related to the anisotropy of the crystal structure of these layered materials, and proposed for directions in the a-b-plane and along the c-axis.

We have also studied the infrared-active phonon modes in our far-infrared data. Six c-axis vibrational modes have been observed in which their shapes and frequency locations are consistent with the observations of other researchers. The strong and sharp phonon at $155 \text{ cm}^{-1}$ in Y spectrum is assigned to the "barium" mode, and the observed phonon at $195 \text{ cm}^{-1}$ in Y spectrum is clearly identified as the "yttrium" mode due to a analysis based on a observation of these phonon shifts when Y is replaced by Eu. The different temperature dependence of phonon modes in the superconducting state also indicated a superconducting energy gap at about $200 \text{ cm}^{-1}$.
Infrared measurements on the new high-$T_c$ superconducting oxides began with studies of ceramic samples, as we mentioned in Chapter 3, in which the presence of large, uncontrolled anisotropy was extremely problematic. These measurements were later essentially superseded by studies of epitaxial films grown on various substrates, and single crystalline specimens in which the response associated with the in-plane (a-b plane) and out-of-plane (the direction perpendicular to a-b plane) directions could be clearly identified.

Our discussion in this section is hence addressed primarily to the infrared properties of $\text{YBa}_2\text{Cu}_3\text{O}_7$. In addition to reasons mentioned above, there are other reasons: first of all, most reliable infrared data on the single crystal are taken from the 1-2-3 system; as the quality of the experimental results improved, our arguments can become more detailed and precise. Secondly, fully oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_7$ is the only known stoichiometric high-$T_c$ superconductor, and is the material from which the best crystals and films have been made: focusing our attention in this material can dramatically reduce the potential problems related to electronic inhomogeneity, structural disorder, and reproducibility.

As has been generally recognized, the high-$T_c$ layered superconductors have anomalous normal-state electronic properties. We will begin with a
discussion of the normal-state behavior of these Cu-O materials, in which the two approaches of "spin interaction"\cite{104,105} and "charge excitation"\cite{65} are concerned. Then a brief review follows, in which our attention is concentrated primarily on the reproducible infrared superconducting ab plane properties of the stoichiometric high-Tc single crystal YBa$_2$Cu$_3$O$_7$. We will also discuss the use of infrared measurements to address the nature of the superconducting energy gap in the layered cuprates. At the end of this section, a brief review of the studies of crystal structure and superconducting multiphase in the Bi(Pb)-Sr-Ca-Cu-O system is presented, as the crystal structure of YBa$_2$Cu$_3$O$_7$ was discussed in Chapter 3.

4.1.1: AB Plane Normal-State Conductivity of YBa$_2$Cu$_3$O$_7$

Early attempts to fit the room temperature a-b plane reflectivity of 1-2-3 material to a Drude model required a very large scattering rate.\cite{82,67,81} It was pointed out later by Kamaras et al.\cite{65,106} that would imply a very short mean-free path, and does not allow a reasonable interpretation of the temperature dependence of the dc conductivity. Recent infrared measurements\cite{56,65,104,105} have presented a strongly frequency- and temperature-dependent infrared conductivity. Extrapolations of the infrared conductivity to \( \omega = 0 \) give values in reasonable correspondence with dc measurement results.\cite{56}. At finite \( \omega \), the infrared conductivity falls much less rapidly with frequency than would be expected for an ordinary (Drude) metal.

Schlesinger and Collins et al. have measured the reflectivity on the
a-b plane of single crystal YBa$_2$Cu$_3$O$_7$ (T$_c$=92 K) up to 12000 cm$^{-1}$, as shown in Fig.1 in ref.105, or Fig.3 in ref.56. The reflectivity increases almost uniformly over a broad frequency range (100 - 8000 cm$^{-1}$) as T is reduced in the normal-state. The real part of the conductivity, $\sigma_1(\omega)$, at 250 and 100 K, is obtained by applying a Kramers-Kronig transformation. The normal-state conductivity $\sigma_{in}(\omega)$ exhibits a peak at the origin, which grows and sharpens as the temperature is lowered from 250 to 100 K. At T = 100 K the half-width of the extrapolated peak (at $\omega$=0) in $\sigma_{in}(\omega)$ is roughly 150 cm$^{-1}$. This is a crucial quantity when we try to determine whether our samples are "clean" or "dirty" superconductors. It will be discussed in more detail later.

Since the behavior of the dc conductivity and the far-infrared conductivity are fundamentally connected, by fitting a Hagen-Rubens form$^{(22)}$ to the lower end of reflectivity data, $\sigma_{in}(\omega)$ down to $\omega$=0 can be obtained by the K-K transformation. Extrapolated values of the dc conductivity as a function of temperature, obtained in this way, are reasonably consistent with typical measured dc resistivities both in terms of their approximately linear temperature dependence and their magnitude, as presented in Fig.4(b) of ref.56.

The real part of the dielectric function, $\epsilon_1(\omega)$, of YBa$_2$Cu$_3$O$_7$ is negative at low frequencies and crosses zero at about 8000 cm$^{-1}$ (see Fig.3(c) in ref.56). The frequency of this plasma edge is thus about a factor of 3-5 lower than that in a typical metal such as Ag.$^{(107)}$ It has been suggested that an a-b plane plasma edge is present in YBa$_2$Cu$_3$O$_7$ in a frequency range close to the superconducting energy gap, making it virtually impossible to determine an energy gap from infrared data.$^{(65)}$ As
shown in ref. 56, this is not the case; the a-b plane plasma edge lies well above the frequency range \((\lesssim 1000 \text{ cm}^{-1})\) in which the possible superconducting energy gap may appear.

The results of a polarization reflectivity measurement\(^{(64)}\) on single crystals of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) showed that the optical anisotropy even appears in the ab plane. The calculated difference of the real part of conductivity between \(\hat{a}\) and \(\hat{b}\) directions, i.e. \(\sigma_b(\omega) - \sigma_a(\omega)\), decreases gradually at 100 K from 1500 \((\Omega\text{-cm})^{-1}\) at 500 \(\text{cm}^{-1}\) to 500 \((\Omega\text{-cm})^{-1}\) at 8000 \(\text{cm}^{-1}\); it suggested that a background conductivity may associate with the Cu-O chains in the \(\hat{b}\) direction.

Attempts to understand the behavior of the conductivity of the \(\text{CuO}_2\) plane in the normal-state have been based on both "spin interaction"\(^{(104,105)}\) and "charge excitation" pictures.\(^{(65)}\) Both approaches are attempts to deal with the observation that the experimental results of infrared conductivity does not diminish with frequency as rapidly as one expects for a simple Drude picture (i.e., \(\sigma_1(\omega) \propto 1/\omega^2\)); instead, a broad background conductivity persists throughout the infrared.

In the spin-interaction model,\(^{(56,64,104,105)}\) all of the conductivity below about 8000 \(\text{cm}^{-1}\) (~1 eV) is accounted for within a single, strongly-coupled band. Interaction between the charge carriers and a spin-related excitation spectrum is believed to cause both the carrier mass and scattering rate to be strongly frequency and temperature dependent. It is suggested that mass enhancement at low frequency is associated with a "spin-excitation cloud" which is dragged along by the carrier, while at high frequency the carrier motion becomes too rapid for the spin excitations to follow, and thus the carriers shed their mass enhancement.
The scattering rate increases correspondingly from a relatively low value at low \( \omega \), to a much higher one at high \( \omega \) as the inelastic scattering processes become possible. In this picture, the conductivity can be written as

\[
\sigma(\omega) = \frac{n e^2 \tau^*(\omega)}{m^*(\omega) [1 - i\omega \tau^*(\omega)]},
\]

where \( m^*(\omega) = m_b [1 + \lambda(\omega)] \) is the renormalized mass and \( \tau^*(\omega) = \tau(\omega) [1 + \lambda(\omega)] \) is the renormalized scattering time, \( \lambda \) is the coupling strength.

This frequency-dependent scattering model has previously been used to treat electron-phonon interactions in ordinary metals\(^{108,109}\) and spin-related excitations in heavy-fermion system\(^{110,111}\). The detailed calculations for the function of frequency of \( r^{-1}(\omega) \), \( \lambda(\omega) \), and the plots of the conductivity fit, can be found from ref.105 and 56.

In the "charge excitation" approach\(^{65}\), a fit to the normal-state conductivity can be divided into three components:

1) a narrow Drude term caused by the free carriers, which peaks at low frequency;
2) a component which comes from phonon modes and could be insignificant for single crystals due to strong screening by the charge carriers.
3) a very strong and broad mid-infrared absorption band, which is identified as the difference between a calculated free carrier conductivity and the measured spectrum.

The above points are illustrated in Fig.1 of ref.65, in which a 110 K
conductivity spectrum, the individual contributions of the far-infrared Drude term, and the mid-infrared absorption of the textured ceramic $\text{YBa}_2\text{Cu}_3\text{O}_y$ are shown.

Both approaches explain the ab plane property in the normal-state equally well; at this moment it is still too early to say which approach, if either, is correct.

We must realize that both "spin-interaction" and "charge excitation" pictures implicitly assume that the background conductivity is associated with CuO$_2$ planes. However, there is another possibility that some of the background conductivity may partially come from the Cu-O chains. Recent polarized measurements on untwinned $\text{YBa}_2\text{Cu}_3\text{O}_y$ crystals$^{(64, 56)}$ suggested a large chain-related contribution to $\sigma_1(\omega)$, which could account for some of the broad background conductivity. We will discuss the results of this infrared measurement in some detail in next section.

4.1.2: a-b Plane Superconducting State of $\text{YBa}_2\text{Cu}_3\text{O}_y$

The ab plane reflectance $R$, real part of conductivity $\sigma_1(\omega)$ and dielectric function $\epsilon_1(\omega)$ of $\text{YBa}_2\text{Cu}_3\text{O}_y$ crystals with $T_c = 92$ K are shown in Fig. 5 of ref. 56 at temperature 150, 105 and 45 K respectively. Those quantities have little temperature dependence below about 55 K, thus the spectrum at 45 K is chosen to be representative of the superconducting state. Reflectivity in superconducting state is quite high at low frequency range, drops rapidly at about 500 cm$^{-1}$, and gradually approaches to that of normal state. There is a small "notch" in the vicinity of 800 cm$^{-1}$, in which the superconducting reflectivity lies below the
normal-state reflectivity. Correspondingly, the superconducting-state conductivity is depressed for $\omega \leq 500 \text{ cm}^{-1}$, and increases rapidly above this frequency. There is no fundamental difference between the corresponding dielectric functions, except $\epsilon_{\text{ls}}(\omega)$ crosses $\epsilon_{\text{ln}}(\omega)$ twice in the frequency range of 500 to 800 cm$^{-1}$.

In these data, the enhancement of the low-frequency reflectivity for $T < T_c$ leads to a reflectivity ratio, $R_s/R_n$, which is peaked at $\sim 500 \text{ cm}^{-1}$ as Fig.7 of ref.56 shows. From the reflectivity ratio spectra and the conductivity spectra in which there is a corresponding threshold at approximately 500 cm$^{-1}$, a characteristic energy gap of about 500 cm$^{-1}$ ($\sim 8kT_c$) has been identified. The detailed temperature dependence of the reflectivity also associates this energy scale with the superconducting state (see Fig.7 in ref.56).

Schlesinger et al. (56) have suggested that, if one considers the real part of the conductivity in the normal-state, $\sigma_{\text{ln}}(\omega)$, as consisting of a free-carrier component and a roughly constant background conductivity, a simple way to view $\sigma_{\text{ls}}(\omega)$ is as the superposition of a free-carrier conductivity spectrum with a gap at 500 cm$^{-1}$ and a roughly constant background conductivity. In this picture, the flat background conductivity does not change when the temperature is below $T_c$, but the free-carrier conductivity collapses its low frequency part into $\delta$ function at $\omega \sim 0$ and leaves the conductivity above 500 cm$^{-1}$ substantially unchanged. This is a signature of a superconducting energy gap at $\sim 500 \text{ cm}^{-1}$.

A fairly recent development is a polarized reflectivity measurement on an untwinned crystal of $\text{YBa}_2\text{Cu}_3\text{O}_7$, which revealed an intrinsic background conductivity in both normal- and superconducting-state probably
due to the Cu-0 chains along the b-axis.\(^{(64)}\) The infrared results of both reflectivity ratio and conductivity (see Fig.1,2, and 3 in ref.64) in normal and superconducting states for incident electric field \(\hat{E}\) parallel to the \(\hat{a}\) axis and the \(\hat{b}\) axis (i.e., \(\hat{E}\parallel \hat{a}\) and \(\hat{E}\parallel \hat{b}\)) indicated that the energy scale at 500 cm\(^{-1}\) is associated with the CuO\(_2\) planes, and present in both the \(\hat{a}\) and \(\hat{b}\) directions. However, both the detailed reflectivity and the corresponding conductivity spectra are not the same in the cases of \(\hat{E}\parallel \hat{a}\) and \(\hat{E}\parallel \hat{b}\). The superconducting reflectivity for \(\hat{E}\parallel \hat{a}\) is higher than that for \(\hat{E}\parallel \hat{b}\) over the whole frequency range, and approaches 100% in the low frequency range of \(\nu<500\) cm\(^{-1}\). Correspondingly, the conductivity (real part) of \(\hat{E}\parallel \hat{a}\) is lower than that of \(\hat{E}\parallel \hat{b}\). The excess conductivity in the \(\hat{b}\) direction, i.e. \(\sigma_b(\omega)-\sigma_a(\omega)\), presents an almost flat conductivity curve up to 3000 cm\(^{-1}\), and is assigned to that of the Cu-0 chains, since the chains along the \(\hat{b}\) direction is the only difference between \(\hat{a}\) and \(\hat{b}\) axis in 1-2-3 crystal structure. If this flat conductivity is confirmed to be associated with Cu-0 chains by future measurements on other high quality crystals, it will be great news for everyone who is working in this area, and both "spin-interaction" and "charge excitation" models introduced previously to address normal-state properties which put emphasis on different components, will have to be modified dramatically to become a "neutral-model".

It has been proposed\(^{(102)}\) that the 500 cm\(^{-1}\) absorption edge which is prominent in the superconducting state is actually a normal-state feature, which simply becomes exposed at low temperature in the superconducting state. Intrinsic to this suggestion is the belief that the conductivity is composed of a low-frequency Drude part, which fully collapses into a \(\delta\)
function at the superconducting transition, and a sequence of mid-infrared
modes that account for the remaining conductivity. This proposal has a
fundamental problem. Detailed calculation\textsuperscript{(112)} based on above assumption
has revealed that the non-Drude part of conductivity cannot exhibit the
500 cm\textsuperscript{-1} feature when collapsing the entire Drude part of the
conductivity, because the conductivity, in this way, returns to \(\sigma_{\text{in}}(\omega)\)
much more slowly than it should. In order to generate background
conductivity that returns to \(\sigma_{\text{in}}(\omega)\) appropriately, one would require a
Drude conductivity that vanishes abruptly between 500 cm\textsuperscript{-1} and 800 cm\textsuperscript{-1},
however, it has been shown that it is impossible using any choice of
parameters in the calculation.\textsuperscript{(112)}

Besides efforts in reflectivity ratio studies to extract information
about superconducting energy gap, an attempt\textsuperscript{(104)} was made to show
directly that the measured absorption below the gap vanishes in the
superconducting state as the temperature goes to zero. It was suggested
that the correct criterion for determining the energy of superconducting
gap from infrared data is to establish the frequency at which the
reflectivity first deviates from 100\%. By applying this 100\% criterion to
the oxygen-reduced YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-x} crystals, Thomas et al.\textsuperscript{(104)} have reported
evidence for a BCS-like gap (2\(\Delta \approx 3.5\) KT\(_c\)).

In the Cu-O layered superconductors the validity of the criterion of
100\% is still questionable. We realize that even if it is true, the
criterion is still not easy to apply in practice, because the
reflectivities in the low frequency range are already too high to
calibrate the absolute reflectivity accurately (i.e., establish the points
of 100\% reflectivity). The criterion of 100\% reflectivity is especially
difficult to apply to a "mosaic sample" which consists of pieces of several small crystal mounted together, because the reflected energy could be partially lost on the surface of nonsuperconducting material which is presented between these crystals at any temperature.

This uncertainty is not only due to external reasons, but also may be due to some intrinsic properties of the materials. As introduced above, the recent data concerning the polarized reflectivity of untwinned crystals of YBa$_2$Cu$_3$O$_7$ indicates that there is a conductivity related to Cu-O chains along the b direction. This might cause an absorption at a frequency even below the superconducting energy gap. On the other hand, we also noted that the superconducting reflectivities are \(~100\%\) up to 500 cm$^{-1}$ when $E \| a$ (i.e., no Cu-O chain absorption), and correspondingly the superconducting conductivity, $\sigma(\omega)$, is depressed to zero in the low frequency range of $\nu \leq 500$. It was thus indicated (see Fig.1,2,3 in ref.64) that the new high-T$_c$ layered materials in some cases may, and in some cases may not, satisfy this 100\% criterion.

4.1.3: Bi-Sr-Ca-Cu-O and Pb-Doped System

After the rush of activity on the 90K Y-Ba-Cu-O system, evidence of high-T$_c$ superconductivity was found near 85 and 110 K in the multiphase Bi-Sr-Ca-Cu-O system. Two superconducting phases in a Bi-Sr-Ca-Cu-O sample with T$_c$'s of 75 K and 105 K was first reported by Maedy et al.\(^{(113)}\) The determination of T$_c$ and the correct composition of compound was determined by Hazen et al.\(^{(114)}\) The nominal 85 K transition has been attributed\(^{(114-118)}\) to the phase $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{x}$ (2212-phase), which
contains a Bi$_2$O$_2$ double-layer and two consecutive CuO$_2$ layers that are separated by a Ca layer. The layer sequence Ca-CuO$_2$-SrO-(BiO)$_2$-SrO-CuO$_2$-Ca-etc., as Fig.4.1 shows, leads to translation periods perpendicular to the layers of about $c=30.9$ Å.$^{(117,118,119)}$ Here, we see again that the most obvious common structural feature of the presently known high-$T_c$ superconductors are the CuO$_2$ layers. CuO$_2$ layers occur in all high-$T_c$ superconducting oxide compounds, except (Ba$_{1-x}$K$_x$)BiO$_3$ ($T_c=30$ K).

In the 2212 phase, considerable disorder also occurs on the cation sites, such as on the calcium site that can be occupied by strontium,$^{(120,121,122)}$ or bismuth,$^{(123,124)}$ and the strontium site that can be occupied by calcium.$^{(121)}$ The Bi site may have vacancies,$^{(120)}$ and can be occupied by copper.$^{(121,125)}$ Due to quasi-periodic distortion along $a$ and/or $b$ and $c$ with approximate periodicities $a'=5a$,$^{(83)}$ $b'=19/4b$,$^{(126)}$ the atomic distribution in Bi$_2$O$_2$ layers, and in particular their oxygen content, is not well known.

The properties of the bismuth superconductor are less sensitive to the ambient atmosphere during the various heating cycles than those of the the 90 K rare earth superconductors, but the synthesis procedure is not entirely without subtleties. For example, the superconducting phase of composition 2212 is not readily formed when the metal ions in the starting mixture are in the same ratio as they are in the chemical formula.$^{(116)}$

Coexistence of the 110 K (2223) phase with the 85 K (2212) phase or the semiconducting (2201) phase has always been observed in this system. The orthorhombic unit-cell structures differ in the number (n) of CuO$_2$ planes in the Bi-Sr-Ca-Cu-O system. For n = 1, 2, and 3, the c-axis values are 24, 30.9, and 38 Å, respectively, and the corresponding $T_c$ values are...
Fig. 4.1: Basic building block of Bi$_2$Sr$_2$CaCu$_2$O$_8$ consists of two layers of CuO$_2$. 
20, 85, and 110 K, respectively.\textsuperscript{117,118} These structures have compositions of $\text{Bi}_2\text{SrCuO}_4$ (2101 phase, $n=1$, $T_c < 20$ K), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212 phase, $n=2$, $T_c = 85$ K), and $\text{Bi}_2\text{Sr}_2\text{Ca}_{2}\text{Cu}_3\text{O}_x$ (2223 phase, $n=3$, $T_c = 110$ K). The $\text{Bi}_2\text{Sr}_2\text{Ca}_{2}\text{Cu}_3\text{O}_x$ (2223) phase has been observed only in multiphase mixtures.\textsuperscript{114,119} The multiphase nature of the bismuth superconductor greatly complicates the structural determination and creates considerable difficulty for us when we try to isolate the superconducting phases in the Bi-Sr-Ca-Cu-O system.

It has been reported\textsuperscript{128} that both the initial composition of the starting materials and the heat treatment procedure are critical to obtain the 110 K (2223) phase. It was found that partial substitution of Pb for Bi is effective in increasing the ratio of the high-$T_c$ phase.\textsuperscript{128,130,131} The high-$T_c$ phase of Pb-doped Bi-Sr-Ca-Cu-O oxide superconductor was studied and the atomic positions of Pb in the crystal were determined directly by high-resolution analytical electron microscopy (HRAEM):\textsuperscript{132} this revealed that the Pb atoms were located in the Bi-O layers.
4.2 Sample Preparation and the Characteristics

All the film samples described here were deposited by dc or rf magnetron sputtering onto MgO substrates from the sintered targets. The substrates were single crystals with the c-axis normal to the surface, i.e., they are oriented with the (001) plane parallel to the surface. In all cases, precise control of the deposition conditions and postannealing treatment were critical in obtaining the correct composition, crystal structure, and high transition temperature. X-ray diffraction and the scanning electron microscope measurements were used to optimize the sample preparation process.

4.2.1: Y-Ba-Cu-O on MgO

Films of YBa$_2$Cu$_3$O$_x$ were prepared by dc magnetron sputtering from single sintered target. Sintered composite sputtering targets had been prepared by Mr. N.R. Osborne and the other members in Dr. Parsons' group as follows. A mixture of Y$_2$O$_3$, BaCO$_3$, and CuO in the stoichiometric ratio of Y:Ba:Cu = 1:2:3 was ground in an agate mortar and fired at 940 °C overnight in the air. The fired compound was reground, cold pressed into a disc, and then sintered for 16 hours at 960 °C in an oxygen-enriched atmosphere. The target was bonded to a copper backing plate using either silver epoxy or indium, and this assembly was inserted in a planar magnetron sputtering source which provided direct water cooling of the backing plate.
The base pressure of the vacuum system prior to deposition was $2 \times 10^{-6}$ Torr. During deposition, the diffusion pump was throttled and argon gas was introduced. The pressure of the argon gas was maintained at $8.6 \pm 0.4$ mtorr using gas flow control. A liquid nitrogen cold trap was used to prevent backstreaming of diffusion pump oil into the chamber and to minimize water vapor. The target current was kept constant at $440 \pm 10$ mA. The target voltage was about 160 V under these conditions. The target was sputter-cleaned for 5 min. before each deposition. Light was emitted from the plasma, seen parallel to the target surface. The substrate was stationary during film deposition and the substrate holder was floating with respect to the grounded chamber with a potential of $-19 \pm 1$ V.

Films were deposited for three hours. A profilometer was employed for the determination of the film thickness. Fig. 4.2 gives the thickness profiles for films deposited at distances of 4 and 8 cm from the target. The thickness of deposited film is a strong function of position on substrate, when the distance between target and substrate is 4 cm. However, when the distance becomes bigger (as 8 cm) the thickness of film is no longer sensitive to the position on substrate. Considerable inhomogeneity in the sputtered flux was observed in the case of stationary substrates, which leads to a radially symmetric composition. The center of the deposition area is yttrium rich while the fringe is barium rich.\(^\text{133}\) X-ray diffraction analysis\(^\text{133}\) of the films after annealing shows that the best composition is obtained, for a target-to-substrate distance of 4 cm, at a position 2.5 cm from the center of the deposit. At this radius the annealed films show only the peaks associated with the 1-2-3 phase, while at radii less than 3 cm or greater than 4 cm the films also show the
Fig. 4.2: Thickness profiles with target-to-substrate distance (A)=4 cm, and (B)=8 cm; measured from the center of the deposit.

Fig. 4.3: Annealing cycle: temperature of sample vs. time.
peaks associated with the semiconducting 2-1-1 phase.

Peaks are observed in the X-ray spectra\(^{(133)}\) only after a suitable annealing treatment in oxygen. Annealing was done in a quartz tube, temperature controlled to \(\pm 2^\circ\text{C}\), in 1 atm of oxygen with oxygen flow. Annealing temperature was in the range from 700 \(^\circ\text{C}\) to 950 \(^\circ\text{C}\), and annealing times from 30 min. to 18 h were investigated. The annealing cycle for our films is shown in Fig.4.3. The X-ray diffraction spectrum of the target, as shown in Fig.5(a) of ref.133, is characteristic of randomly oriented grains with 1-2-3 orthorhombic structure. As is evident from a comparison of curves in Fig.5(d) with (a) of ref.133, the film structure after annealing is that of the orthorhombic phase, and has a preferred ab plane orientation.

The temperature dependence of the resistance is shown in Fig.4.4 for our 1-2-3 films (A and B). The transition width (90%-10%) for sample A is about 10 K, with resistance equal to zero at about 79 K. In the case of sample B, the superconducting transition starts at about 91 K and is not complete until 83 K.

4.2.2: Bi-Sr-Ca-Cu-O film on MgO

Thin films of Bi-Sr-Ca-Cu-O were deposited by RF magnetron sputtering onto MgO substrates from a sintered Bi\(_{4}\)Sr\(_{3}\)Ca\(_{3}\)Cu\(_{4}\)O\(_{x}\) (4334) target, followed by a post-deposition anneal.

The (4334) target (provided by Dr. Parsons) had been prepared by initially mixing bismuth oxide, strontium carbonate, calcium carbonate and copper oxide. The mixture was then reacted and reground (after cooling)
Fig. 4.4: Resistivity of $YBa_2Cu_3O_{7-x}$ sputtered film on $MgO$. 

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three times at 800 °C, 830 °C, and 850 °C in air, with an average of six hours at each reaction temperature. The final mixture was a soft, black powder which was pressed into a 15 cm circular target and sintered at 860°C for three hours. In preparing our samples, the substrates MgO(001) were placed on a stationary substrate holder at a distance of 7.5 cm from the target. Since the composition of the Y-Ba-Cu-O thin film is known to vary radially with the distance from the center of the discharge of the target, the substrates were positioned at different locations to determine how the composition affected the nature of the superconducting transition.

The sputtering chamber was evacuated to a base pressure in the 10⁻⁶ Torr range before throttling the diffusion pump and introducing argon gas at a constant flow rate of 4 SCCM. During deposition the argon pressure was maintained at 1.4 Pa. After presputtering the target for 20 minutes, the films were deposited for three hours.

The thickness of the films varied from 4.5 μm to 2.5 μm for films deposited at a radius of 5 mm and 40 mm from the center of the discharge, respectively. In the case of our measured films, the thickness varied from 2.5 μm to 3.0 μm. The as-deposited films had a very high resistance and a post-deposition anneal was required to produce superconducting films. The films were annealed using a multi-step process; (1) a quick anneal in 100% oxygen gas, from 22 °C to 870 °C in 20 minutes and then immediate cooling to 200 °C over 30 minutes. This resulted in a sample whose resistivity is shown as curve A in Fig.4.5, which has a very broad transition range. Other films were annealed again in a third step, an anneal O₂ at 750 °C, cooling down with a rate of 0.1 °C/min to 200 °C. The final curve of resistance versus temperature is shown as curve B in Fig.4.5. It has a
Fig. 4.5: Resistance vs. temperature curve of sputtered Bi-Sr-Ca-Cu-O film on MgO.
steep slope, and there is an 8% drop in resistance around 110 K, which indicated that the sample has two phases with the transition temperature ~80 K and ~110 K respectively.

A scanning electron microscopic analysis was performed on the final sample whose resistance is shown as curve B in Fig.4.5, the result is shown in Fig.4.6. The scanning electron micro-picture shows the surface of sample is rough on the scale of the sample thickness. A number of 10 µ diameter leaf-shaped crystals lie on the MgO surface. This is consistent with the X-ray results given below which show that the film has its c-axis perpendicular to its surface.

An X-ray diffraction measurement confirms that the film is fairly highly oriented with its c-axis normal to the surface of sample, as Fig.4.7 shows. The only strong reflections are for (00l), where l=2, 6, 8, 10, 12, 16, and 20. X-ray spectrum of Fig.4.8 is identical with the results of other x-ray measurements\(^{134,135}\) for Bi-Sr-Ca-Cu-O films on MgO.

**4.2.3: Pb-doped Bi-Sr-Ca-Cu-O film on MgO**

Thin films of Pb-doped Bi-Sr-Ca-Cu-O were deposited by RF magnetron sputtering onto MgO crystal substrates from a sintered target whose composition was Pb\(\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x\). The substrates had the c-axis normal to their surface. The target was prepared by mixing and reacting lead oxide, bismuth oxide, strontium carbonate, calcium carbonate and copper oxide.

The 1 micron thick films were annealed by heating them in 100% oxygen
Fig. 4.6: A scanning electron micrograph of Bi-Sr-Ca-Cu-O sputtered film.
Fig. 4.7: X-ray diffraction pattern of Bi-Sr-Ca-Cu-O film deposited on MgO.
gas, from 22 °C to 870 °C over about 3 days. The final resistance versus temperature curve, as Fig.4.8 shows, has a fairly steep, linear slope just above $T_c$ and a transition width of 10 K with zero resistance at 53 K.

The scanning electron micrograph in Fig.4.9 shows that the surface of the substrate was uniformly covered by a layer of 1 μ diameter and 10 μ long needle-shaped crystals. Although the average thickness of the film is 1 μ, these needle-type crystals made the local thickness of the film unhomogeneous. Roughness on the film surface will result in scattering effects at high frequency which can not be ignored in the interpretation of the measured reflectivity. However, this local non-uniformity also provides the opportunity to make transmission measurements. In spite of the localized non-uniformity, Fig.4.9 does indicate that the film is pretty uniform in the larger space size, all the surface of MgO was well covered with sputtered material.

The X-ray diffraction spectrum in Fig.4.10 shows that the film is oriented, with the c-axis normal to the surface, consistent with other X-ray measurement,\textsuperscript{(134)} and predominantly has the (2212) structure.\textsuperscript{(128)}
Fig. 4.8: Resistance vs. temperature curve of Pb-doped Bi-Sr-Ca-Cu-O film deposited on MgO.
Fig. 4.9: Scanning electron micrograph of Pb-doped Bi-Sr-Ca-Cu-O film.
Fig. 4.10: X-ray diffraction spectrum of Pb-doped Bi-Sr-Ca-Cu-O film.
4.3: RESULTS AND DISCUSSION

Far-infrared reflectivity measurements were made near normal incidence. Sample temperatures were varied using a flow-type He cryostat as described in Chapter 2. All the spectra introduced here were taken with a 2 cm⁻¹ at various temperature from about 7 K to room temperature. Reference spectra were taken using a highly reflective stainless steel mirror at 77 K. All spectra of Y-Ba-Cu-O films were measured with a room temperature pyroelectric detector; however, a He-cooled detector system was used to collect the data of Pb-doped Bi-Sr-Ca-Cu-O films for improved signal-to-noise ratios.

4.3.1: Y-Ba-Cu-O films

Infrared reflectivity measurements were carried out on YBa₂Cu₃O₇₋ₓ film samples A and B; their superconducting transition temperatures were 78 K and 83 K, respectively. In Fig.4.11, the infrared reflectivity spectra of film A are presented up to 700 cm⁻¹ for various temperatures. Since the reflectivities are essentially independent of temperature below 50 K, which is consistent with the results of infrared measurements on YBa₂Cu₃O₇ single crystals, we only present a 50 K spectrum in Fig.4.11 as a representative of the superconducting states below 50 K. The reflectivity spectra of sample B are very similar to that in Fig.4.11 for film A, and hence not presented here. However, the temperature dependence of its reflectivity ratio spectra will be shown later, in Fig.4.13.
Fig. 4.11: Reflectivity spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sputtered film sample A for which $T_c=78$ K.
One of the first things one notices about the Fig.4.11 is that the reflectivity spectra at different temperatures can be easily recognized according to their different temperature dependent behaviors. One specific frequency, at $\sim 470$ cm$^{-1}$ for sample A and $\sim 530$ cm$^{-1}$ for sample B (which can be found from its ratio spectra in Fig.4.13), existed in the reflectivity spectra as a crossing point between the curves of superconducting and normal states. When the frequency is less than that of the crossing point, the reflectivity spectra are distributed into two separated groups according to their states. When the frequency is higher than the crossing point, the order of spectrum position is reversed and uniformly distributed with the temperature changing.

Since the thickness ($3\mu$) of films are much thicker than the infrared penetration depth ($\sim 1500$ Å)\(^{56}\), no feature in these spectra can be expected to be connected with any possible excitation from the MgO substrate. Compared to our reflectivity spectra measured on 1-2-3 bulk sample (see chapter 3), Fig.4.11 presents fairly high reflectivities in both superconducting and normal states, and shows the rather smooth curves in the whole measured frequency range. Such behavior is consistent with that of the films with a high degree of ab plane orientation on the sample surface. The differences of the reflectivity spectra between the epitaxial film and randomly oriented polycrystalline sample stem from the anisotropy in the electronic properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The layered nature of all known Cu-O high-$T_c$ superconductors is expected to give rise to a nearly two-dimensional band structure in which the conductivity along the c axis is small relative to that in the ab plane.\(^{136}\) The reflectivity which comes from the essentially metallic (ab) plane is hence certainly higher
than that from low conductivity (c) direction. The phonon features of ab plane are screened by the free carriers in the planes, so a smoother reflectivity spectrum is expected from the film sample. Infrared measurements have revealed a 40:1 anisotropy for conductivity in these two directions on single crystal of YBa$_2$Cu$_3$O$_7$.$^{(56)}$

Two peaks are seen in Fig.4.11 at ~310 and ~580 cm$^{-1}$, which were identified in chapter 3 as due to c-axis phonons, remind us that our sputtered YBa$_2$Cu$_3$O$_{7-x}$ films do not have a 100% ab plane orientation on the film surface, although the x-ray diffraction spectrum$^{(133)}$ measured on the film sample tell us it does. In another words, infrared spectroscopy is more sensitive than x-ray measurement to deviations from perfect ab plane alignment in these highly anisotropic materials. This was also confirmed in the case of an epitaxial bulk sample$^{(89)}$ in which strong c-axis phonons appeared in the reflectivity spectra measured on a mainly ab plane oriented (as indicated by the x-ray spectrum) bulk sample. Since the electronic screening of the phonons would be less effective along the lower conductivity c axis, the structures attributed to the phonon modes which are observed in our sputtered film samples could actually be due to the small regions partially oriented with the c-axis in the plane of the substrate surface.

The reflectivity ratios of films A and B are presented in Fig.4.12 and Fig.4.13 respectively. It is obvious that below ~500 cm$^{-1}$ the ratio spectra can be classified into two groups depending on whether they are taken above or below T$_c$. Above T$_c$, the sample is in the normal state and the reflectivity ratio spectrum is flat, and thus indicates no fundamental difference between two normal-state reflectivity spectra. However, when
Fig. 4.12: The reflectivity ratio spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sputtered film A on MgO. The $T_c$ of the film A is 78 K.
Fig. 4.13: The reflectivity ratio spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sputtered film B on MgO. The $T_c$ of the film B is 83 K.
sample temperature is decreased through $T_c$, the superconducting ratio spectrum is significantly different from that in normal state. In the low frequency range, i.e., $v<470\ \text{cm}^{-1}$ for sample A and $v<530\ \text{cm}^{-1}$ for sample B, the superconducting reflectivity is enhanced, and its ratio spectrum is thus higher than that of normal state, and both of them gradually increase with the decreasing frequency. When the frequency is greater than $470\ \text{cm}^{-1}$ for film A or $530\ \text{cm}^{-1}$ for sample B, the superconducting ratio spectrum becomes lower than that of normal state. Hence, a crossing point ($470\ \text{cm}^{-1}$ for sample A, and $530\ \text{cm}^{-1}$ for sample B) appears in these reflectivity ratio spectra as Fig.4.12 and Fig.4.13 shown.

We see from Fig.4.12 and 4.13 that the energy scales of $470\ \text{cm}^{-1}$ ($\sim 8.7\ kT_c$ for sample A with $T_c=78\ \text{K}$) and $530\ \text{cm}^{-1}$ ($\sim 9.1\ kT_c$ for sample B with $T_c=83\ \text{K}$) are clearly associated with the superconducting transition. These energy scales are slightly greater than that of $\sim 8\ kT_c$, a number which is found from infrared reflectivity measurements of Y-Ba-Cu-O single crystals.\(^{(56,64)}\) The apparent difference between these infrared results is probably due to the difference in the method of determining the critical temperature ($T_c$) from the resistivity curves. Single crystal samples show very narrow transition ($\Delta T \approx 1\text{K}$) whereas our film samples have $\Delta T \approx 10\text{K}$. The value of $T_c$ that has been chosen here (a zero-resistance point) maybe less than what should be used (like mid-point in resistivity curve, for example). If we chose the mid-point $85\ \text{K}$ for the sample A and $87\ \text{K}$ for the sample B, we find $2\Delta = 8.0\ kT_c$ and $8.7\ kT_c$ for sample A and B, respectively.

As noted in Chapter 1, a peak in the reflectivity ratio spectrum indicates the location of superconducting gap in most conventional superconductors; however, for our high-$T_c$ films, no peak is seen; instead,
a specific crossing point appeared. We must point out here, it is not a phenomenon unique to high-$T_c$ material; infrared reflectivity measurements on some practical and conventional superconductors, Nb$_3$Ge for example,$^{(38)}$ also presents a similar result, in which the values of the reflectivity ratio spectra are gradually decreased with the frequency increasing, and no significant peak seen. By comparing the reflectivity ratio data to the transmission data of Nb$_3$Ge film,$^{(38)}$ it is evident that the crossing point in the reflectivity ratio spectra occurred at the same energy as the superconducting gap. Thus we have some confidence in above discussion to treat the specific crossing point in our ratio spectra as a rough indication of superconducting energy gap.

One also can see from either the reflectivity (Fig.4.11) or the ratio spectra (Fig.4.12 & 13) that the temperature-dependence property of $ab$ plane superconducting gap ($8$~$9$ $KT_c$) is similar as that of $c$-axis ($3$ $KT_c$, in Fig.3.8). The energy of the superconducting gap seems to be independent of temperature, even near $T_c$. This is a common property to all known Cu-O layered new superconductors,$^{(56,84)}$ but is significantly different from that in BCS-like materials.

Our infrared reflectivity ratio spectra are similar to observations$^{(66)}$ on epitaxial sputtered YBa$_2$Cu$_3$O$_{7-x}$ film on a different substrate ($SrTiO_3$). The superconducting reflectivity enhancement in the low frequency range cited in the ref.25 leads to a similar crossing point at about $500$ cm$^{-1}$ in the ratio spectra. The superconducting critical transition temperature $T_c$~$90$ K (mid-point) and $2\Delta$~$8.0$ $kT_c$.

In 1989, Schüßmann et al.$^{(66)}$ investigated the laser-deposited epitaxial YBa$_2$Cu$_3$O$_{7-x}$ thin film ($T_c$ = $91$ K) on $SrTiO_3$ substrate. A laser
evaporation technique was employed to obtain a better quality film. The film is oriented with the ab plane in the film plane. Because of the high optical quality and high degree of orientation, the reflectivity spectra of this thin film are similar to those measured on 1-2-3 single crystals, in that, the reflectivity of laser-deposited film in the superconducting state is quite high in the low frequency range of \( \omega \leq 460 \) cm\(^{-1}\), and drops rapidly between 500 and 800 cm\(^{-1}\). With the analysis of both reflectivity and the conductivity spectra obtained through a Kramers-Kronig transformation of the reflectivity, a 400 cm\(^{-1}\) (\(\sim 6.2 \, K_{c}^{*}\)) energy was found to correspond to the ab plane superconducting energy gap. This smaller (\(\sim 6.2 \, K_{c}^{*}\)) energy scale we believe is due to the uncertainty of the determination of gap position that is associated with a broad drop in the reflectivity and the ratio spectra. We noted that the cross point in their reflectivity spectra is around 550 cm\(^{-1}\), and thus consistent with our infrared data.

The authors of ref.68 also claimed a smaller energy gap at about 130 cm\(^{-1}\), based on high reflectivity in the superconducting state and the depressed conductivity below 130 cm\(^{-1}\). Whether the 100\% reflectivity or the zero absorption in frequencies which are less than that of gap (2\(\Delta\)) indicates a real superconducting energy gap in a high-\(T_{c}\) superconductor is still an unsolved problem. But, one thing is sure: the Cu-O chain conductivity along b direction which is unchanged with temperature certainly makes the criterion unacceptable. It is simply because the superconducting reflectivity can never reach the 100\% value with a nonzero conductivity.

Comparing our infrared reflectivity on Y-Ba-Cu-O sputtering films
with the results taken from oriented bulk sample,\textsuperscript{(59)} sputtering films,\textsuperscript{(66)} laser deposited films,\textsuperscript{(68)} and the single crystals,\textsuperscript{(63,64)} we found our 1-2-3 film samples have a degree of orientation that is higher than that of oriented bulk sample, less than the laser-deposited films and the single crystal, and pretty close to other sputtered films.\textsuperscript{(66)} The anisotropies in the electronic and superconducting properties of 1-2-3 material and the imperfect orientation in our film sample should account for the some difference in the reflectivity spectrum of our Y-Ba-Cu-O films (A and B) and high oriented film\textsuperscript{(68)} and the single crystals.\textsuperscript{(63,64)} But one can see that the superconducting energy gaps extracted from our infrared measurements are still consistent with the results taken from laser deposited film samples or single crystals.

4.3.2: Pure and Pb-doped Bi-Sr-Ca-Cu-0 Films

Fig.4.14 shows the reflectivities of the Bi-Sr-Ca-Cu-O film at the different temperatures. The spectra at 7 K and 50 K are almost the same, so that either one can be the representative for all superconducting reflectivity spectra taken at temperatures in between. Data at 120 K and 160 K are representative of all data taken in the normal state. From Fig.4.14, it is clear that the spectra are separated into two typical groups, with higher and lower position in reflectance corresponding to superconducting and normal states, respectively. The only exception is the 90K spectrum which is in an intermediate position at frequencies below 300 cm\(^{-1}\). There are two main absorption edges located at \(-360\) and \(-590\) cm\(^{-1}\) which are presented in the spectra at all temperatures. In addition, there
Fig. 4.14: Reflectivity spectra of Bi-Sr-Cu-O film at five temperatures. The $T_c$ of film is $-80 \text{ K}$ but with a dip in resistivity at $-110 \text{ K}$, as shown in Fig. 4.5.
are a number of other features present with varying strengths.

Fig.4.15 shows the ratio, $R_t/R_n$, of the reflectance at four temperatures to one at 160 K. There is a distinct edge at 200 cm$^{-1}$ and less distinct edges around 290 and 550 cm$^{-1}$. The edges at about 200 and 290 cm$^{-1}$ do not correspond with any feature in the reflectance, and are not apparent until the ratio is calculated. The height of a step at ~200 cm$^{-1}$ is not small compared with a edge at ~550 cm$^{-1}$.

Fig.4.16 shows the reflectance of Pb-doped Bi-Sr-Ca-Cu-O thin film at 8 and 80 K. There are two main absorption edges located at 360 and 580 cm$^{-1}$ in both normal and superconducting states. In addition, there are a number of features presented with varying strengths at both temperatures.

Fig.4.17 is the reflectance ratio which shows more clearly the enhancement of reflectivity which occurs below ~600 cm$^{-1}$ in the superconducting state. There are distinct edges at 330 cm$^{-1}$ and 550 cm$^{-1}$ and a less distinct edge at about 200 cm$^{-1}$. The edge at 550 cm$^{-1}$ is not the same position as that (580 cm$^{-1}$) of the corresponding reflectivity edge.

From Fig.4.14 and Fig.4.16 we can find that the shape of reflectivity measured on Bi-Sr-Ca-Cu-O film is qualitatively the same as that of Pb-doped film; both of them have two abroad absorption edges in their reflectivity spectra at about 360 cm$^{-1}$ and about 590 cm$^{-1}$. However, some difference still exist. In Fig.4.14, reflectivity of superconducting state of the undoped film shows a fairly flat curve at low frequency up to 350 cm$^{-1}$; but the corresponding spectrum of Pb-doped film, in Fig.4.16, shows a flat and high reflectivity below 80 cm$^{-1}$, gradually decreasing as frequency increases, and the decrease stops at the vicinity of 300 cm$^{-1}$. 

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Fig. 4.15: Reflectivity ratio spectra of Bi-Sr-Ca-Cu-O film at four temperatures. The reference temperature of normal state is 160 K which is far away from $T_c$ of sample.
Fig. 4.16: The reflectivity spectra of Pb-doped Bi-Sr-Ca-Cu-O film in superconducting (8 K) and normal (80 K) states. Its resistance vs temperature was shown in Fig. 4.8.
Fig. 4.17: The ratio spectra of Pb-doped Bi-Sr-Ca-Cu-O film at the superconducting (8, 40, 50 K) and normal (66, 77 K) states.
There are two peaks (360 and 400 cm\textsuperscript{-1}) near the first sharp absorption edge in Fig.4.14; there are also two similar peaks in Fig.4.16, but located at 310 cm\textsuperscript{-1} and 360 cm\textsuperscript{-1}, i.e., with a 40-50 cm\textsuperscript{-1} shift to lower frequency. In the range of 500 cm\textsuperscript{-1} to 600 cm\textsuperscript{-1}, the difference between the reflectivity spectra of our Pb-doped and undoped Bi-Sr-Ca-Cu-O films becomes even more obvious. There are three peaks between 500 - 600 cm\textsuperscript{-1} in Fig.4.14, however only two peaks can be distinguished in this range for Pb-doped film. If there is only 2212 phase in these two films, as indicated in their X-ray spectra (Fig.4.7 & Fig.4.10), the fundamentally different reflectivity of these two materials between 500 to 600 cm\textsuperscript{-1} indicates that these features may be associated with Bi (Pb) atoms of crystal structure. But if there are more than two superconducting phases coexisting in these samples, as implicated in their resistance vs. temperature curves (Fig.4.5 & Fig.4.8), the above reflectivity difference may be due to the different concentration of the different superconducting phases in our pure and doped Bi-Sr-Ca-Cu-O films.

The positions of edges and peaks in these reflectivity and ratio spectra for our Bi-Sr-Ca-Cu-O and Pb-doped films are given in the Table 4-1.

In the low frequency range, the difference of reflectivity spectra is not only caused by doping effect, but also could be affected by the film thickness. As we mentioned before, the average thickness of Bi-Sr-Ca-Cu-O film is 2.5 \( \mu \) to 3.0 \( \mu \), and the Pb-doped film is less than 1\( \mu \), the substrate effect thus should be considered in the latter case. The successful transmission result (see next chapter) observed from the Pb-doped Bi-Sr-Ca-Cu-O film shows that part of light have passed through
Table 4-1 Frequencies (in cm\(^{-1}\)) of optical features of pure and Pb-doped Bi-Sr-Ca-Cu-O films

<table>
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<tr>
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<th>Bi-Sr-Ca-Cu-O Film ((T_c = 80 \text{ &amp; } 110\text{K}))</th>
<th>Pb-doped Bi-Sr-Ca-Cu-O Film ((T_c = 53\text{K}))</th>
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<tr>
<td>Edges in R</td>
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<td>Edges in Ratio</td>
<td>200, 290, 550</td>
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<tr>
<td>Peaks in R</td>
<td>360, 400, 500</td>
<td>310, 360, 500</td>
</tr>
<tr>
<td></td>
<td>550, 580, 640</td>
<td>580, 640</td>
</tr>
</tbody>
</table>

some areas of the film on the MgO substrate, which indicate that the incident radiation must be partially lost from the reflectance due to the transmission and MgO absorption. This may explain why the reflectivity measured on Pb-doped film is no longer flat in the low frequency range of 80 to 300 cm\(^{-1}\), if we compare Fig.4.16 with Fig.4.14.

Generally, the reflectivity spectra of both film samples, as Fig.4.14 and Fig.4.16 show, are similar to observations on ab plane of Bi\(_{2}\)Sr\(_2\)CaCu\(_2\)O\(_8\) (2212) single crystals which \(T_c\) is ~85 K\(^{103}\) except that the first reflectivity edge is shifted from 360 to ~310 cm\(^{-1}\). The shift
could be due to other superconducting phases (2223, for example) in our film samples.

One important experimental fact evident from Table 4-1 is that the positions of edges in both reflectivity and ratio spectra did not change significantly when some Bi atoms are replaced by Pb atoms, although the critical temperature $T_c$ of films are different. The distinct absorption edges in the reflectivity are enhanced at the superconducting transition; edges are also observed in the normal state reflectivity at the same or similar energies. The edges and features are thus intrinsic to the normal material, caused by either lattice vibrations or low-energy electronic processes. However, the three ratio edges located at 200 (200) cm$^{-1}$, 290 (330) cm$^{-1}$ and 550 (550) cm$^{-1}$ in Fig.4.15 and Fig.4.17 for Bi(Pb)-Sr-Ca-Cu-O films are not necessarily associated with the reflectivity edges. As we mentioned before, the reflectivity ratio edges at 200 and 290 cm$^{-1}$ in Bi-Sr-Ca-Cu-O film are not observed until a reflectivity ratio is performed; the position of the third edge in the ratio spectra of Pb-doped sample (at 550 cm$^{-1}$) also does not overlap the 580 cm$^{-1}$ edge in its reflectivity spectra. So, we cannot simply treat these reflectivity ratio edges as features which already exist in the normal state.

However, interpreting these edges is a difficult problem for us at this moment. Besides the very complicated spectrum of the high-$T_c$ layer materials due to their strong anisotropy, in the Bi(Pb)-Sr-Ca-Cu-O film, introduced before, there are two and possibly three superconducting phases coexisted in one sample, as partially indicated in the resistance versus temperature measurements (see Fig.4.6 and 4.9). The coexistence certainly
makes any interpretation for the spectra measured on such films defective or questionable. What follows are speculations on the edge determination based upon our data.

A simple way in which to view the ratio edge at about 200 cm\(^{-1}\) is as a superconducting energy gap associated with the out-of-plane (c-axis) property of 2212 phase in the Bi-Sr-Ca-Cu-O film. X-ray data in Fig.4.8 and Fig.4.11 show that the main component in our films is the 2212 compound with a ab-plane orientation in the film plane. However, as we discovered before, the sputtered films are not highly oriented, the superconducting features associated with the out-of-plane may still be observable because of the existing of partial c-axis components. It was demonstrated\(^{(80)}\) that a c-axis gap is easier to find than an ab plane gap due to the lower conductivity in that direction. This energy scale of \(2\Delta = 3.5 \, \text{K}_c\) (using \(T_c=80 \, \text{K}\) for the out-of-plane of Bi-Sr-Ca-Cu-O film is similar to that of \(\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\) sample \((2\Delta = 2-3 \, \text{K}_c\)) for Pb-doped film \((T_c=60 \, \text{K})\) the gap \(2\Delta = 4.7 \, \text{K}_c\) is outside of the values of conventional BCS-type superconductor. Since the resistance vs. temperature curve is a combinational result of different superconducting phases, and/or even non-supercor,ducting phases, in the measured sample, \(T_c=60 \, \text{K}\) maybe not a correct number for Pb-doped sample to obtain the right gap ratio result. We must note here: even for the single-phase superconductors with the different oxygen concentration (and thus with different \(T_c\)), \(\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\) in ref.16 for example, we still cannot get any meaningful gap ratio number as long as the oxygen is not uniformly taken from the sample.

It is shown in Fig.4.15 and 4.17 that the reflectivity ratio edges at 290 (330) cm\(^{-1}\) and 550 cm\(^{-1}\) are associated with the superconducting
transition temperature, and hence might be related with the other superconducting energy gaps. If the ~550 cm$^{-1}$ edge corresponds the ab-plane energy gap of 2212 (80 K) superconducting phase, a 9.8 KT$_c$ energy scale will be obtained; if 290 (330) cm$^{-1}$ edge corresponds the out-of-plane energy gap of another superconducting phase (2223 phase, T$_c$~110 K) in Bi(Pb)-Sr-Ca-Cu-O film, it will give a 3.7 (4.2) KT$_c$ energy scale. Further infrared studies on high quality Bi-Sr-Ca-Cu-O single crystals or thin films with high degree of orientation are required.

We noted recently-reported tunneling measurements$^{(137)}$ on Bi-Sr-Ca-Cu-O thin films for which T$_c$ ranged from 75 K to 84.5 K. The film samples have some properties similar to ours, which were polycrystalline and nominally 2212 phase, but also showed evidence of the 2223 phase in the resistance versus temperature profile. The experimental data explored the superconducting gaps for different junctions varied from 46(±4) to 64(±4) mev, i.e., from 330 to 545 cm$^{-1}$, which are consistent with the range of the ratio edges seen in our infrared observation.

The superconducting energy gap of the high-T$_c$ layered oxides has several very special properties; one of them is that the energy gap seems not to move with the variation of the superconducting critical temperature T$_c$. Such behavior was really not expected by us when we started these experiments. We were expecting to find some kind of shifts for these reflectivity ratio edges when T$_c$ of sample is dropped. This was one of the reasons that we made the Pb-doped sample with a lower superconducting transition temperature (T$_c$=60 K); however, as Fig.4.17 shows, we failed to observe any gap-shifts due to the change in T$_c$. This unusual behavior of superconducting energy gap in Bi-superconductor has also been observed.
in the 1-2-3 single crystals by Cooper et al.\(^{(57)}\) The reason is still unclear.

4.3.3: "Clean Limit"?

It has been suggested that the Cu-O layered superconductors are so clean that no one can find the superconducting energy gap from the infrared measurements.\(^{(65,102)}\) The clean limit is usually defined by the inequality \(\ell > \xi\), where \(\ell\) is the mean-free path and \(\xi\) is the superconducting coherence length. An equivalent definition, in terms of characteristic frequencies instead of lengths, is \((1/2\Delta \tau) < 1\), where \(2\Delta\) is the superconducting energy gap and \(1/\tau\) is the low-frequency scattering rate; \(1/\tau\) is the width of the (Drude) conductivity peak at low frequency. It is hence ultimately a quantitative rather than a qualitative question of how clean layered Cu-O materials are and whether or not one should be able to see the gap. The issue of the observability of a gap has been studied quantitatively by Timusk et al.\(^{(65,102)}\) and Schlesinger et al.\(^{(56,112)}\)

Timusk et al. have discussed the effect in the ratio, \(R_s/R_n\), in terms of the parameter \(\eta\) \((= (2\Delta \tau)^{-1})\); while Schlesinger et al. have discussed it in terms of the infrared conductivity. Both of their results, in fact, suggested, a superconducting energy gap should be seen for high-\(T_c\) superconductors under an appropriate condition.

In Fig. 5 of ref. 65, Timusk et al. show that a 400 cm\(^{-1}\) superconducting energy gap still can be identified from the reflectivity ratio when the superconductor is as clean as \(\eta=0.02\). In other words, for a gap at 400 cm\(^{-1}\) (7 kT\(_c\) for YBa\(_2\)Cu\(_3\)O\(_7\)) in the reflectivity spectrum to
appear, only a low-frequency scattering rate of $1/\tau \geq 10 \text{ cm}^{-1}$ is required. As discussed before, although the behavior of the normal state conductivity of the high-$T_c$ materials is, at present, still controversial, the low-frequency scattering rate $1/\tau$ (of YBa$_2$Cu$_3$O$_{7-\delta}$, for example, $1/\tau \approx 150 \text{ cm}^{-1}$, as we mentioned in section 4.1) was believed by all to be $\sim 15$ times greater than $10 \text{ cm}^{-1}$. So, we conclude that a $\sim 500 \text{ cm}^{-1}$ superconducting energy gap in 1-2-3 (or other similar) materials should be clearly identified by the infrared reflectivity measurements.

In Fig.16 of the ref.56, Schlesinger et al. calculated the conductivity of a model superconductor for several values of the scattering rate $\tau^{-1}$. For a superconductor in the extreme clean limit, the superconducting energy gap $2\Delta$ is much greater than $\tau^{-1}$, all of the area in $\sigma_1(\omega)$ goes to a $\delta$ function at $\omega=0$ when temperature goes to zero. The magnitude of $\sigma_1(\omega)$ at $\omega=2\Delta$ is so small that the gap may not be readily observable. In the moderately clean case, most of the area in $\sigma_1(\omega)$ still goes into the $\delta$ function, however, there is now sufficient conductivity at $\omega=2\Delta$ to make the gap observable. In the dirty limit, the normal state conductivity is essentially constant from dc up to $2\Delta$, and only a small fraction of the total area in $\sigma_1(\omega)$ goes into the $\delta$ function in the superconducting state. By the infrared reflectivity measurements (Fig.14 in ref.56, for example, where the real part of conductivity in the superconducting state approaches abruptly that in the normal state just after $\sim 500 \text{ cm}^{-1}$), we can see the layered high-$T_c$ superconductor (of YBa$_2$Cu$_3$O$_{7-\delta}$), at least, is moderately clean material, so the superconducting energy gap should be observable in the infrared reflectivity measurements.

In the classical theory of free-electron metals, $\tau$ is the mean free
time between collisions.\textsuperscript{(138)} Since the mean free time of film ($\tau_f$) is usually less than that of single crystal ($\tau_c$) due to the defects and boundary effects in the film sample, the film should be more "dirty" than single crystal. The superconducting gap in our film samples thus should be detectable.
4.4: Conclusions

We prepared YBa$_2$Cu$_3$O$_{7-x}$ sputtered films on MgO which $T_c$ (absolute zero resistance point) are 78 and 83 K for sample A and B, respectively. X-ray diffraction measurements show the film is 1-2-3 phase with its c-axis normal to the surface of sample. Our temperature-dependent infrared reflectivity data were interpreted to present the superconducting energy gap at ~470 cm$^{-1}$ (8.7 KT$_c$) for film A, and 530 cm$^{-1}$ (9.1 KT$_c$) for film B. Our results are consistent with those of 1-2-3 single crystals.$^{(56,64)}$

We also prepared pure and Pb-doped Bi-Sr-Ca-Cu-O films which $T_c$ (absolute zero resistance) are 76 K and 53 K respectively. The film's compositions were nominally 2212 phase, but the evidence of the 2223 phase were shown in the resistance versus temperature profile. Our infrared reflectivity data show that the positions of most of the edges in both reflectivity and ratio spectra did not change significantly when Bi atoms are partially replaced by Pb atoms. The three ratio edges located at 200(200) cm$^{-1}$, 290(330) cm$^{-1}$, and 550(550) cm$^{-1}$ on Bi(Pb)-Sr-Ca-Cu-O films are not associated with the reflectivity edges. However, any interpretation for such complicated spectra is questionable at this moment. Our speculations on these three ratio edges suggest the 200 cm$^{-1}$ and 550 cm$^{-1}$ correspond to out-of-plane and in-plane (ab plane) energy gaps, respectively, of 2212 superconducting phase, while the 290(330) cm$^{-1}$ may correspond to the out-of-plane (c-axis) energy gap of 2223 phase. Our infrared results are consistent with that of the recently reported tunneling measurements on the Bi-Sr-Ca-Cu-O films.
5.1 INTRODUCTION

As introduced in chapter one, far-infrared transmission experiments on thin films are a well-established and informative method of probing superconducting materials. The position of superconducting energy gap corresponds closely to the peak in the ratio of transmission in superconducting to normal state.

For conventional superconducting materials, both the experimental results and theoretical analysis show the infrared transmission measurement is a far more sensitive method than reflectivity measurement for exploring the possible superconducting energy gap presented in a superconducting material.\textsuperscript{(29)} In the reflectivity ratio spectrum the absorption edge, which corresponds to the superconducting energy gap of measured material, is usually 2-4% high, however, in the transmission ratio spectrum the peak that located at the position of the energy gap can be as high as 200-400%. For example, the infrared experiment measured on the thin Nb\textsubscript{3}Ge film\textsuperscript{(38)} shows that the superconducting energy gap at 55 cm\textsuperscript{-1} was indicated by a ~300% peak in the infrared superconducting-to-normal transmission ratio spectrum, however only a ~4% superconducting absorption edge appears at this frequency (i.e., 55 cm\textsuperscript{-1}) in the reflectivity ratio spectrum. Similar results were also observed from the
infrared measurements on other superconducting films, such as $V_3\text{Si}^{(139)}$ and NbN$^{(140)}$ et al..

Because of above reason, people used to measure infrared transmission data to extract information about superconducting properties of old superconductors. The optical work on the high-$T_c$ compounds, however, has been dominated by reflectance measurements, while transmission experiments have remained an essentially unexplored field due to the stringent restrictions imposed on the sample. The films have to be thin, of the order of a few hundred Å in thickness; the substrate must be transparent to infrared radiation, and, at the same time, must be suitable for epitaxial growth.

Up to now, very few papers$^{(141,142)}$ have been published in this area, and very limited data have been shown. Further studies of transmission measurements on the new high-$T_c$ superconducting thin film are therefore required to reveal the properties of these layered materials.

In this chapter our first experimental infrared transmission measurements for Pb-doped Bi-Sr-Ca-Cu-O thin film deposited on MgO are reported. The essential differences for the film transmission between the superconducting and normal state are studied. The possible absorption effect that may come from the substrate is also studied.
5.2 Sample Preparation and Characteristic

The Pb-doped Bi-Sr-Ca-Cu-O samples which were measured in the transmission experiments are the same as what we have discussed before (See section of 4.2.2 in chapter 4).
5.3 Experimental Results and Discussion

Attempts have been made\(^{143,144,133}\) to deposit the new high-\(T_c\) superconductors on the various substrates, such as MgO, SrTiO\(_3\), ZrO\(_2\), Al\(_2\)O\(_3\), and Si et al.. However only films based on MgO are suitable for infrared transmission studies in the frequency range less than 250 cm\(^{-1}\). All the other substrates have some essential problems with either the substrate opaqueness starting from a very low frequency or the poor superconductivity of film due to the uncontrolled reaction between the substrate and the composite chemical compounds in the depositing and annealing process.

In Fig.5.1, reflectivity and transmission of the pure single crystal substrate, MgO (001), are shown in (a) and (b) separately. Reflectivity of MgO is roughly constant at about 40\% up to about 300 cm\(^{-1}\); it rises rapidly beginning at a frequency of 300 cm\(^{-1}\) and stopping at about 400 cm\(^{-1}\), approaches a almost 100\% reflection in the frequency range of 400 to 550 cm\(^{-1}\), and finally drops down slowly after 550 cm\(^{-1}\). Corresponding to the behavior of reflectivity of MgO, the transmission spectra for both temperatures, as shown in Fig.5.1(b), have a higher degree of transparency in the low frequency range below about 250 cm\(^{-1}\), are dramatically reduced between 250 cm\(^{-1}\) and 350 cm\(^{-1}\), and are almost completely black for the frequencies higher than 350 cm\(^{-1}\).

No significant temperature dependence of reflectivity on MgO was found at 8 and 77 K, except a slight departure in the frequency range of 50-300 cm\(^{-1}\). However, transmission data show a great temperature
Fig. 5.1(a): Reflectivity spectra of single crystal MgO(001) at 8 and 80 K.
Fig. 5.1(b): Transmission spectra of single crystal MgO(001) at 8 and 80 K.
dependence from 8 to 80 K: low temperature (8 K) transmission is always higher than that of the high temperature (80 K) in overall frequency. There is a deep absorption located at about 100 cm$^{-1}$ in transmission spectrum at 80 K, which indicates the temperature effect on MgO must be considered in infrared data analysis of thin film sample. But the little peak at about 220 cm$^{-1}$ in 8K transmission spectrum is believed to be an artifact associated with the beam splitter change.

Obviously, the optical behavior of single crystal MgO (001) presents a stringent restriction imposed on the infrared transmission studies of high-$T_c$ layered superconducting thin films: no experimental transmission data can be taken at frequency over 300 cm$^{-1}$ for a film based on the MgO, no matter how thin and how good quality the superconducting film might be. On the other side, of course, we can still extract some very useful information from the transmission data and explore the optical behaviors of a new superconductor in the low frequencies ($\omega \leq 300$ cm$^{-1}$). Especially if the film is not perfectly ab plane oriented one might have an opportunity to study the possible superconducting energy gap in this low frequency range.

All the transmission measurements of Pb-doped superconducting film on MgO at normal incidence were made using a Bruker 113v spectrophotometer with a cryogenic bolometer at an operating temperature lower than 4.5 K when spectra were taken. The resolution of 2 cm$^{-1}$ was adopted for the data collected.

In Fig.5.2, transmission spectra of Pb-doped Bi-Sr-Ca-Cu-O film ($T_c = 60$ K) on MgO at 10 K and 80 K are shown. Features at about 125 cm$^{-1}$, 185 cm$^{-1}$ and 240 cm$^{-1}$ appear in the transmission spectra for both 10 K and
Fig. 5.2: Transmission spectra of Pb-doped Bi-Sr-Ca-Cu-O sputtered film on MgO at superconducting (8 K) and normal (80 K) states.
80 K. One very important result which we would like to point out is that the transmission of film in the superconducting state is less than that in the normal state at low frequency range ($\omega \leq 100 \text{ cm}^{-1}$). This low frequency behavior is similar to observations on a 200 Å thick $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ sputtering film by Hughes et al.\(^{(141)}\).

Although the average thickness of our Pb-doped film sample is about 1μ, and thus greater than the penetration depth (~2000 Å), the nonzero transmittance of this film is evidence that there are some areas where thickness is less than the penetration depth. The unusual lower superconducting transmission at low frequency ($\omega \leq 110 \text{ cm}^{-1}$), as Fig. 5.2 shows, must come from the film itself rather than the pure substrate MgO, as compared with the result of MgO transmission spectrum (see Fig. 5.1(b)). This is because the temperature dependence of transmission from a pure MgO suggested lower absorption or a higher transparency effect at a lower temperature for whole frequency range, especially in the vicinity of 100 cm\(^{-1}\). Hence, the lower superconducting transmission measured on film at a frequency less than 110 cm\(^{-1}\) (shown in Fig. 5.2) cannot be attributed to the effect of the temperature dependence of MgO.

The observed low-frequency transmission result on our thin films is consistent with the prediction of BCS theory. From chapter one, we know that superconducting transmission for the conventional superconductors is lower than those in normal state well below the gap. This was confirmed by all the infrared transmission experiments on a variety of old superconducting films.\(^{(29,139,140)}\) In our data, the lower transmission in superconducting states at frequencies less than 110 cm\(^{-1}\) may imply a superconducting gap located at frequency higher than 110 cm\(^{-1}\). However, we
are not able to indicate the exact position of the superconducting energy gap in the transmission spectrum due to the short transparency range and strong temperature dependence of MgO substrate.

The problem associated with temperature dependence of substrate can be ignored in the infrared transmission measurements for the old superconducting films, since their $T_c$ were very low (the maximum $T_c$ was about 23 K which was measured on Nb$_3$Sn) and optical properties of substrate did not change sufficiently in that frequency range to interfere with observation of the changes in transition due to the onset of superconductivity in the old superconducting films. We cannot expect such benefits in the present infrared studies on new high-$T_c$ superconducting thin films. The strong temperature dependence in MgO makes the transmission ratio spectrum of superconducting-to-normal state less useful. One cannot expect to observe a peak in the measured transmission ratio spectrum to correspond the position of superconducting energy gap. We have to include the substrate effect in our infrared transmission analysis.

How to get rid of the substrate effect is still an unresolved problem. We attempted to solve this problem by a purely mathematical calculation. As we discussed in Chapter one, transmission of "free standing" thin film is given by

$$\frac{T_s}{T_n} = \frac{(2 + Y_n)^2}{|2 + Y_s|^2}.$$  \hspace{1cm} (5-1)

where $T_s$ and $T_n$ are the transmissions of "free standing" film in
superconducting and normal states, respectively. This formula can be obtained from the equation of (1-21) by setting the index of refraction of substrate equals to 1. The definitions of functions of \( Y_n \) and \( Y_s \) are shown separately as following:

\[
Y_n = \sigma_n \cdot d \cdot Z_0 ,
\]

\[
Y_s = (\sigma_1 + i\sigma_2) \cdot d \cdot Z_0 .
\]

Here \( d \) is the thickness of the superconducting film, \( Z_0 \) is the impedance of free space and equals to 377 \( \Omega \), \( \sigma_n \) is dc conductivity of the film. If we can find the functions of \( Y_s \) and \( Y_n \) from our infrared transmission data, the substrate effect will be removed from the discussion.

\( Y_n(\omega) \) can be directly determined from the experimental transmission data by using the following formula:\((145)\)

\[
Y_n = (1 + n_n) [ ( T^n_{MgO} / T^n_n )^{1/2} - 1 ]
\]

(5-2)

\( T^n_n \) and \( T^n_{MgO} \) is the transmission spectrum measured on the film sample (i.e. light passed through both film and MgO) and pure MgO at temperature 80 K (i.e. \( T > T_c \)). Here \( n_n \) is the index of refraction of substrate at temperature of 80 K and can be obtained from the transmission data measured on pure MgO by

\[
n_n = a_x + (a_x^2 - 1)^{1/2},
\]
where

\[ a_x = 2 / T_{\text{MgO}}^{1/2} - 1. \]

If one gains the function of \( Y_s \) from the experimental infrared transmission data in a similar way as for \( Y_n \) above, then the transmission ratio of a "free standing" film can be obtained easily according to eq.5-1. Since the real part of conductivity is connected to its imaginary part though a Kramers-Kronig relationship, we should obtain, in principle, the complex function \( Y_s \) by the following formula:

\[
\frac{T_s}{T^n_{\text{MgO}}} = \frac{(1 + n_s)^2}{|1 + n_s + Y_s|^2}
\]

(5-3)

in which \( T_s/T^n_{\text{MgO}} \) is the ratio of transmission of the film (and MgO) to that of the pure substrate MgO at a temperature (10 K in our case) below \( T_c \), and \( n_s \) is the index of refraction of substrate at this temperature. However, the short range (\( \leq 350 \text{ cm}^{-1} \)) transparency of MgO make the K-K transformation less useful.

Although \( Y_s \) cannot be extracted directly from the experimental transmission data as we did for \( Y_n \), we can try another way. From the above eq.(5-3), we have

\[
4y_1 + y_2^2 + y_1^2 = (1+n_s)^2(T^n_{\text{MgO}}/T_s) - (n + 1)^2 - 2(n - 1)y_1
\]

(5-4)

where \( y_1 \) and \( y_2 \) are the real and imaginary parts of \( Y_s \), i.e., \( y_1 = \sigma_{1s} dZ_0 \), \( y_2 = \sigma_{2s} dZ_0 \). When the frequency is less than the gap frequency, i.e.,
\( \nu \leq 2\Delta, \ y_1 \) should be very small \( (y_1 \equiv 0 \) according to the BCS theory). When the frequency is higher than \( 2\Delta, \ y_1 \) should be smaller than \( Y_n \), i.e., \( y_1 < Y_n \), although the difference between \( y_1 \) and \( Y_n \) decreases with frequency increasing, according to the BCS theory. Because

\[
\frac{Y_n}{T_n} \leq (1+n) \left( \frac{T^s_{MgO}}{T^n_{MgO}} \right)^{1/2}
\]

according to eq.(5-2); and

\[
\frac{T^s_{MgO}}{T_s} \approx \frac{T^n_{MgO}}{T_n} \approx 100
\]

in our case, the third term in the right side of eq.(5-4) is then always at least one order smaller than the first term. So, we have

\[
4y_1^2 + y_2^2 + y_1^2 \approx (1+n)^2 \left( \frac{T^s_{MgO}}{T_s} \right) - (n+1)^2.
\]

The transmission ratio of eq.(5-1) can be rewritten as

\[
\frac{T^s_f}{T^n_f} = \frac{(2 + Y_n)^2}{4 + (1+n)^2 \left( \frac{T^s_{MgO}}{T_s} \right) - (1+n)^2} \quad (5-5)
\]

All the functions in the right side of above formula can be directly determined by transmission measurements on either film or pure MgO, thus the transmission ratio spectrum of "free standing" thin film is obtained in this way.

In Fig.5.3, the calculated (from Eq.5-5) transmission ratio of
superconducting (10 K)-to-normal state (80 K) on the "free standing" Pb-doped Bi-Sr-Ca-Cu-O film is shown. The calculated spectrum is rather smooth between 50 to 750 cm\(^{-1}\), no specific feature presented except a 25\% step at frequency around 200 cm\(^{-1}\). A rapid rise occurs beyond \(\sim 250 \text{ cm}^{-1}\), presenting a peak at \(\sim 300 \text{ cm}^{-1}\), and rises again.

The transmission data, as Fig.5.2 shows, presented a very weak signal beyond \(\sim 250 \text{ cm}^{-1}\). We interpret the rapid rise starting at \(\sim 250 \text{ cm}^{-1}\) in Fig.5.3 as a "fake" due to the bad ratio of signal-to-noise. However, for the 25\% step at \(\sim 200 \text{ cm}^{-1}\), we cannot simply identify it as a gap-like or noise feature. If the feature at \(\sim 200 \text{ cm}^{-1}\) is a real gap, we may expect it to correspond to a out-of-plane gap due to the small energy scale. Since our film sample is not completely oriented in its ab plane, as we discussed in the previous chapter, a c-axis gap might be measured through this infrared transmission measurement. This feature is also consistent with our result of the reflectivity observation, in which an absorption edge that has been related a possible c-axis energy gap was found in the reflectivity ratio at the same frequency.

As we mentioned before, in a conventional superconductor a division of the superconducting-transmission spectrum \(T_s\) by the normal-state spectrum \(T_n\) produces a peak around (usually higher than) the energy-gap frequency, thus making infrared transmission a straight-forward method for determining the superconducting energy gap. However, for Pb-doped Bi-Sr-Ca-Cu-O film, we cannot determine the gap location, which is believed to be at a higher frequency as been observed from the reflectivity measurements and implied from our transmission data in the low frequencies. The opaqueness of the substrate is the main shortcoming
Fig. 5.3: The transmission ratio (10K to 80K) of the "free standing" film calculated from the Eq. (5-5).
of the infrared transmission measurement in determining the energy gap of high-T\textsubscript{c} superconductor.

Recently, very important new developments in infrared transmission measurement have been achieved by a joint research group at the University of Florida, the state University of New York at Stony Brook, and Brookhaven National Laboratory\textsuperscript{(146)}. The transmission of a real free standing single crystal of Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8} (2212, T\textsubscript{c}=82 K) has been studied by using beamline U4-IR at the National Synchrotron Light Source and other sources over 100-3000 cm\textsuperscript{-1}. The crystals were approximately 0.3 mm\textsuperscript{2} in area and 130-200 nm thick, with the c-axis running along the short direction. The transmission spectra showed similar low frequency behavior as has been observed in 2212\textsuperscript{(141)} and in our Pb-doped Bi-Sr-Ca-Cu-O film samples. The low frequency transmission increases with temperature; at higher frequencies (above 500 cm\textsuperscript{-1}), however, the temperature dependence of the transmission is reversed, i.e, the transmission decreases with increasing temperature. It is shown by the transmission ratio spectra that a characteristic peak occurs at ω=700 cm\textsuperscript{-1} in the 2212 material below T\textsubscript{c}. No similar feature is found in the 2201 (non-superconducting but metallic) compound. A value of ħω=12 kT\textsubscript{c} (T\textsubscript{c}=82 K in this case) is therefore suggested to be associated with superconducting transition.
5.4 Conclusions

Our far-infrared transmission spectra for Pb-doped Bi-Sr-Ca-Cu-O sputtered film on MgO ($T_c=53$ K) shows a low-frequency behavior as what one could expect for a conventional superconductor, in which, the superconducting transmission $T_s$ is lower than $T_n$ in the low frequency range ($\leq 110 \text{ cm}^{-1}$). Above $110 \text{ cm}^{-1}$ the superconducting transmission intensity is higher than that in normal state. This was confirmed by a comparison with the transmission spectra on pure MgO in which the observed behavior belongs to the superconducting film rather than the substrate.

The low frequency behavior of our transmission data is consistent with the assumption that there is a superconducting energy gap above 110 cm$^{-1}$.

We also have tried to cancel, with limited success, the effect of temperature dependence of the MgO substrate: the calculated ratio $T_s/T_n$ on a hypothetical "free standing" film shows a smooth curve between 50 to 250 cm$^{-1}$ with a possible energy gap at 200 cm$^{-1}$ which may associated with an out-of-plane energy gap. This result is consistent with the observations in our reflectivity measurements.
CHAPTER 6: FIR STUDIES OF N-TYPE COPPER-OXIDE MATERIALS

6.1: INTRODUCTION

Prior to 1989, the prevailing view was that the charge carriers involved in high-\(T_c\) superconductivity were holes that move through conducting planes with the chemical composition \(\text{CuO}_2\). The \(\text{CuO}_2\) planes are the basic building blocks of the crystal structures of all of the presently known copper-oxide superconducting materials.

In January of 1989, Y. Tokura, H. Takagi and Shin-ichi Uchida published the first paper on n-type high-\(T_c\) superconductors.\(^{(147)}\) They reported observing superconductivity in \(\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4-y}\) with \(\text{Ln}\) denoting Pr, Nd, or Sm. Soon afterward, superconductivity in \((\text{Nd,Pr})_2\text{ThCuO}_{4-y}\) and in \(\text{Eu}_{2-x}\text{Ce}_x\text{CuO}_{4-y}\) was found.\(^{(148,149)}\) The Hall coefficient in the new superconductors is negative,\(^{(150)}\) unlike earlier cuprate superconductors, in which it is positive.\(^{(151,152)}\) Thus n-type high-\(T_c\) superconductors are obtained when a tetravalent lanthanide is partially substituted for the trivalent lanthanide in the parent compounds of the form \(\text{Ln}_2\text{CuO}_{4-y}\). These parent compounds are insulators. Increasing the concentration \(x\) of the tetravalent lanthanide, Ce or Th, apparently introduces more electrons into \(\text{CuO}_2\) planes, producing a continuous insulator-metal transition, yielding superconductivity with a maximum \(T_c = 25\) K and maximum flux expulsion at \(x=0.15\) and \(y=0.02\).\(^{(147,148)}\) A related compound with the
identical crystal structure, \( \text{Nd}_2\text{CuO}_{4-x-y} \), has also been found to display superconductivity with \( T_c = 25 \text{ K} \).\(^{153}\)

Chemically, the new electron materials are similar to the first family of cuprate superconductors discovered in January 1986 by George Bednorz and Alex Müller. The original hole-doped cuprate superconductors \( \text{La}_{2-x}(\text{Ba, Sr})_x\text{CuO}_4 \) were obtained by partially substituting divalent barium or strontium for the trivalent lanthanum in their parent compound \( \text{La}_2\text{CuO}_4 \) which is an insulator. As more holes are added in the \( \text{CuO}_2 \) planes by increasing the concentration \( x \), the material evolves continuously from an insulator to a metal, and the compound becomes superconducting with maximum transition temperature and flux expulsion (Meissner effect) at about \( x = 0.15 \) for different solutes.

These results suggest the existence of an electron-hole symmetry in the occurrence of the insulator-metal transition, magnetism, and superconductivity in copper oxides as a function of the concentration of charge carriers in the \( \text{CuO}_2 \) planes. These findings could have important implications regarding the theories of high \( T_c \) superconductivity\(^{154,155}\) as well as strategies for finding new high \( T_c \) superconductors.

The crystal structure of the electron superconductor is also similar to that of the hole-doped superconductor of \( \text{La}_{2-x}(\text{Ba, Sr})_x\text{CuO}_4 \); both of them are tetragonal in structure, and have the space group \( I4/mmm-D^{17}_{4h} \) with seven atoms per unit cell. The only difference between the two structures is that each copper atom is bound to four oxygen atoms in the electron superconductor, which is called \( T' \)-structure; whereas the copper is surrounded by an octahedron of oxygens in the hole superconductor\(^{156,157,158}\) which is \( T \)-structure, as shown in Fig. 6.1.
Fig. 6.1: Crystal structure of Nd$_2$CuO$_4$ (left), the parent material for electron superconductors. The tetragonal unit cell for Nd$_2$CuO$_4$ has, unlike in La$_2$CuO$_4$ — the parent material for hole superconductor (right), no apical oxygen atoms.
Several physical properties of the electron-doped superconductors are significantly different from those of their hole-doped counterparts. In n-type superconductor the critical temperature $T_c$ is increased with applied pressure $P$ (up to about 20 Kbar) at rates of about 0.1-0.25 K/Kbar; however, in the electron-doped superconductors the rate is smaller and becomes negative as the radius of the trivalent Ln ion decreases. Furthermore, measurements of the upper critical field $H_{c2}$ as a function of temperature on single-crystal specimens yield values of the superconducting coherence length of about 10 Å within the CuO$_2$ planes and few Å along the c axis for the hole-doped superconductors; the numbers for the n-type high-T$_c$ superconductors are 70 and 3.4 Å, respectively.\(^{(159)}\)

To get the information on both normal- and superconducting-state properties, it is better to study reflectivity from single crystals since the n-type superconductors are anisotropic like the other high-T$_c$ layered materials. But at the present time, high quality n-type superconducting crystals of a suitable size for infrared measurement are not available. This situation makes it necessary to study the reflectivity of polycrystalline samples. Although the random orientation of small crystal grains in the polycrystalline make it very difficult (if not impossible) to extract the frequency dependence of the optical conductivity $\sigma(\omega)$ from the reflectivity spectrum by Kramers-Kronig transformation, we can still extract some useful information from the reflectivity study of polycrystalline samples under the proper analysis. It is useful to compare the experimental spectrum of electron-doped superconductors with those of their hole-doped counterparts. The studies based on the new n-type superconducting materials will certainly enrich our understanding for the
high-$T_c$ copper oxide materials. In this chapter we will show and discuss our infrared reflectivity data on $\text{Nd}_{2-x}(\text{Ce, Th})_x\text{CuO}_{4-y}$ superconducting materials.
6.2: Sample Preparation and Characteristics

All of the electron-doped superconductors used have the same Nd$_2$CuO$_4$-type structure, with oxygen deficiency achieved by annealing in reduced atmosphere. The preparation of single phase materials for these compounds is very delicate as compared with hole-doped high-$T_c$ copper oxides. The n-type samples which were measured in our experiments were prepared and characterized by Dr. Peng in University of California at Davis, where results cited below were published in ref.160.

Samples of Nd$_{2-x}$(Ce, Th)$_x$CuO$_{4-y}$ were prepared by solid state reaction from high purity (99.999%) Nd$_2$O$_3$, (CeO$_2$,ThO$_2$), and CuO. Stoichiometric mixtures of the starting materials were ground thoroughly and heated in air using an Al$_2$O$_3$ crucible at 950 °C for 12 hours. The resulting powders were reground and pressed into pellets at 1 Kbar and fired in air at 1100 °C for 12 hours followed by quenching to room temperature. Both magnetization and resistivity measurements indicated that all of these samples quenched in air are not superconductors above 2 K. In order to obtain superconductivity, it was necessary to anneal the sintered pellets in a reducing atmosphere. The pellets, which were measured in our experiments, were placed in a furnace chamber with an Al$_2$O$_3$ boat filled with fresh titanium sponge next to the sample, and this sample chamber was pumped by a diffusion pump to a pressure near 10$^{-5}$ torr. The samples were then annealed under the vacuum at 875 °C for 6 hours with the pressure maintained at 10$^{-5}$ torr. Finally, the samples were furnace cooled to room temperature in 2 hours.
X-ray diffraction measurements on \( \text{Nd}_{1.85}^{\text{Ce,Th}}_{1.15}^{\text{CuO}} \) indicated that all samples were composed of single-phase, tetragonal material with lattice constants of \( a = 0.3959 \pm 0.0004 \text{ nm} \) and \( c = 1.211 \pm 0.002 \text{ nm} \) for the Ce compound and \( a = 0.3955 \pm 0.0004 \text{ nm} \) and \( c = 1.2116 \pm 0.0006 \text{ nm} \) for the Th compound.

The dc magnetic susceptibility measurements, which were made in a variety of fields using a Quantum Design SQUID magnetometer, are displayed in Fig. 6.2(a,b). The magnetic field used in the field-cooled magnetization (Meissner effect) versus temperature for the \( \text{Nd}_{1.85}^{\text{Ce}}_{1.15}^{\text{CuO}} \) is 5 Oe, for the \( \text{Nd}_{1.85}^{\text{Th}}_{1.15}^{\text{CuO}} \) is 10 Oe. Measurements of the dc magnetic susceptibility showed that the Meissner effect below 20 K (16 K in the Th sample) is approximately 20% that expected for full diamagnetism, indicating that superconductivity is a bulk property of the sample. Onset of the magnetic transition is at 26 K in the Ce compound and at 22 K in Th compound; the 10%-90% width is 4 K (Ce) and 5 K (Th).

The dc electric resistivity \( \rho(T) \) measurements were performed on rectangular specimens cut from sintered pellets employing the standard dc four-probe technique. To ensure good contacts between the electrical leads and the sample, four silver contacts were evaporated on to the sample surface, followed by annealing at 400 °C in a \( \text{N}_2 \) atmosphere for two hours to help the silver diffuse easily around the contacts on the sample surface. This process reduces the contact resistance dramatically. After this, platinum wires were attached to the silver contacts using silver paint. In zero field the midpoint of the resistive transition is \( 23 \pm 1 \text{ K} \) (Ce) and the 10%-90% width is about 5 K; for the Th sample, the corresponding values are \( 18.5 \pm 1 \text{ K} \) and 3 K. Zero resistance is reached at
Fig. 6.2(a): The dc magnetic susceptibility measurements on $\text{Nd}_{1.65}\text{Ce}_{0.15}\text{CuO}_{4-x}$. 
Fig. 6.2(b): The dc magnetic susceptibility measurements on Nd$_{1.85}$Th$_{0.15}$CuO$_{4-x}$. 
about 17.5 and 15 K, respectively. We take the midpoint of the resistive transition as \( T_c \). It is worth noting that if one were to consider lattice vibrations associated with only the Ce site as responsible for superconductivity in these materials and calculate the isotope shift of \( T_c \) due to the substitution of Ce by Th, one would obtain the ratio of 1.24 ± 0.09 for \( T_c \) compared with the BCS prediction of 1.25. This agreement may provide some insight as to the mechanism for superconductivity in these materials. Normal-state resistivity just above the transition (Ce) is 27 m\( \Omega \) cm and at room temperature 9 m\( \Omega \) cm; for the Th sample the corresponding values are 7.6 and 2 m\( \Omega \) cm.
6.3: Experimental Results and Discussion

Reflectivity measurements near normal incidence were made using a Bruker IFS-113V spectrophotometer in conjunction with a He-cooled bolometer in far infrared and a pyroelectric detector at higher energies; resolution was 2 cm⁻¹ from 20 to 10,000 cm⁻¹. Sample temperatures ranged from 7 to 77 K; room temperature reflectivity was also measured from 100 to 1000 cm⁻¹. Reference spectra were taken on a polished stainless steel mirror.

Figures 6.3(a,b) present the full spectra of both compounds, Nd₁.₈₅(Ce,Th)₀.₁₅CuO₄₋₇y, in both normal and superconducting states. The spectra show a number of prominent features. Those which show no significant temperature dependence over the temperature range of 7 to 77 K are assigned to lattice vibrations. The room temperature reflectivity of Ce compound from 100 to 1000 cm⁻¹ is very similar; the only differences are an overall reduction of about 10% in reflectivity and a significant increase in the strength of the feature at about 410 cm⁻¹.

Figures 6.4(a,b) show the low-frequency reflectivity ratios of Nd₁.₈₅(Ce,Th)₀.₁₅CuO₄₋₇y, including one additional intermediate temperature. Above about 100 cm⁻¹, there are no significant differences between reflectivities in the normal and superconducting states. A distinct enhancement of reflectivity occurs in the superconducting state with a plateau beginning at about 50 cm⁻¹. About 10 K, the plateau height decreases and the region of decreased reflectivity above 60 cm⁻¹ gradually disappears; the plateau loses its distinct edge, preventing precise
Fig. 6.3(a): The reflectance spectra of Nd$_{1.75}$Ce$_{0.15}$CuO$_{4-y}$ in normal (30 K) and superconducting (7 K) states. Insets show 30 K reflectivity and Drude-model fits (dots) using parameters given in text.
Fig. 6.3(b): The reflectance spectra of Nd$_{1.85}$Th$_{0.15}$CuO$_{4-y}$ in normal (30 K) and superconducting (7 K) states. Insets show 30 K reflectivity and Drude-model fits (dots) using parameters given in text.
Fig. 6.4(a): Ratio $R_2/R_1$ of the reflectance at three temperatures to that in the normal state for $\text{Nd}_{1.85} \text{Ce}_{0.15} \text{CuO}_{4-y}$. 

$\text{Nd}_{1.85} \text{Ce}_{0.15} \text{CuO}_{4-y}$
Fig. 6.4(b): Ratio $R'/R_n$ of the reflectance at three temperatures to that in the normal state for $\text{Nd}_{1.85}\text{Th}_{1.15}\text{CuO}_{4.7}$. 

$R(T)/R(30\text{K})$

- $7\text{ K} / 30\text{ K}$
- $10\text{ K} / 30\text{ K}$
- $25\text{ K} / 30\text{ K}$
determination of the temperature dependence of the edge (shown below to be associated with the gap energy).

6.3.1: Doping Effect and Anisotropy Model

To study Ce and Th doping effect, it is necessary to compare our infrared data with the spectrum\textsuperscript{(161,162)} taken from the so called "mother compound" Nd\textsubscript{2}CuO\textsubscript{4} of n-type superconducting materials. All the features in the spectrum of Nd\textsubscript{2}CuO\textsubscript{4} are still observable in Fig.6.3, but with dramatic changes in the strength for some of them. Two extra weaker phonon-like features at about 600 cm\textsuperscript{-1} and 670 cm\textsuperscript{-1} appear in the reflectivity spectra measured on n-type superconductors, and might be associated with the effect of Ce- or Th-doping, since they only occurred in the ion-doped cases. These two weak features seems to connect with the T (La\textsubscript{2}CuO\textsubscript{4})-structure rather than with the T' (Nd\textsubscript{2}CuO\textsubscript{4})-structure. Reasons for this will be discussed later.

A significant difference between Fig.6.3 and the reflectivity spectra\textsuperscript{(161,162)} taken from the ceramic samples of the mother compound, is that the reflectivity of Ce- or Th-doped material is higher than that of their mother compound in overall frequency range. Especially, when frequency is less than about 100 cm\textsuperscript{-1} the reflectance of n-type superconductor is almost double that of the mother compound. For materials which have the same crystal structure, a higher reflectivity spectrum implies higher optical conductivity near \(\omega\rightarrow0\); our infrared data on n-type superconductors are consistent with the well known fact that Ce or Th doping increases the dc conductivity.
We note that the reflectivity between 20 and 700 cm\(^{-1}\) is not sensitive to the temperature variation in the range of 6 - 77 K. Reflectivity between 700 and 10,000 cm\(^{-1}\) is totally temperature independent in the same temperature range. Similar results have been observed recently in mid-infrared measurements on the a-b plane of the n-type superconducting single crystal by a group at Princeton University.\(^{163}\) This temperature insensitivity in the reflectivity spectrum is similar to the results\(^{164}\) on the hole-doped superconductors \(\text{La}_{1.85} \text{Sr}_{0.15} \text{CuO}_4\)\(^{,165,166}\), but is significantly different from that of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) bulk\(^{85,89}\) and single crystal samples.\(^{105}\) As we discussed before, \(\text{YBa}_2\text{Cu}_3\text{O}_7\) mid-ir reflectivity and conductivity depend on temperature in the frequency range up to 1 ev.

By comparing our experimental reflectivity spectrum (see Fig.6.5) with that of \(\text{La}_{1.85} \text{Sr}_{0.15} \text{CuO}_4\),\(^{80,164,165}\) the hole-doped high-\(T_c\) compound which has a similar crystal structure and chemical composition, we find that the experimental data measured on \(\text{La}_{1.85} \text{Sr}_{0.15} \text{CuO}_4\) polycrystalline specimen (see Fig.2 in ref.80, as an example) shows a qualitatively similar result: the reflectivity spectrum approaches about 80% at low frequency, and 20% at frequency higher than 700 cm\(^{-1}\). This seems to be the common optical behavior of the ceramic sample materials.

One of the major problems in interpreting the optical data for high-\(T_c\) copper oxides has been taking into account the random orientations of the anisotropic material comprising the pressed powders. By analogy with the earlier work\(^{80,166}\) on \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\), we must consider our reflectivity as a composite spectrum consisting of contributions from a metallic ab plane and a nearly insulating c axis. Excitations in the a-b
plane will be highly screened; those along the c axis will not be. The actual superposition of the contributions from the two directions will depend on the size, shape and orientation of the crystallite and on the wavelength of the incident radiation. Where the incident wavelength $\lambda$ is much smaller than the characteristic dimensions of the crystallites $d$, a simple superposition of the reflectivities\(^{80}\)

$$R = (1 - f) R_{ab} + f R_c \quad (6-1)$$

may suffice. $R_{ab}$ is the reflectivity for incident optical-electric field $E$ directed along a-b plane, $R_c$ is the reflectivity for $E$ directed along c axis, and $f$ is the volume fraction of the $R_c$ component and usually be treated as $1/2$. These individual reflectivities $R_{ab}$ and $R_c$ can each be obtained by modeling the dielectric function written in form\(^{80}\)

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega \Gamma} + \sum \frac{\omega_n^2}{\omega_n^2 - \omega^2 - i\omega \Gamma_n} \quad (6-2)$$

where $\omega_p$ is the electronic plasma frequency, $\omega_n$, $\omega_p$, $\Gamma_n$ are the frequency, strength and damping of the phonon modes.

Doll et al.\(^{165}\) have also examined the effects of optical anisotropy within the limits of small crystalline dimensions relative to the wavelength of the incident light (i.e. $\lambda \gg d$) with the effective medium approximation (EMA)\(^{165}\). By modeling the experimental reflectance data of polycrystalline sample $\text{La}_{1.85} \text{Sr}_{0.15} \text{CuO}_4$ in above two limiting cases, Doll et al. claimed that "in the spectra region studied, both models describe the data well".
The anisotropy model described above gained some results in the analysis of ir reflectivity spectra of polycrystalline La$_{1.85}$Sr$_{0.15}$CuO$_{4-y}$ and its mother compound La$_2$CuO$_4$. Based on the single crystal reflectivity measurements on the isostructural compound La$_2$NiO$_4$, Schlesinger et al. identified the phonons at 240 and 500 cm$^{-1}$ with the lattice vibrations polarized along the c axis, and the phonons at 150, 350, and 680 cm$^{-1}$ with vibrations in the a-b plane. By comparing the calculated $R_{ab}$ and $R_{c}$ with Fig.1(b,a) in ref.167 which are polarized infrared reflectivity spectra in ab and c plane on single crystal of the mother material La$_2$CuO$_4$, they found that dopant only affects the electric property in CuO$_2$ (i.e., ab) plane, and does not affect the property of c-axis plane. Its usefulness was proven later by infrared polarized reflectivity experiments on the single crystal of La$_{2-x}$Sr$_x$CuO$_4$ in normal-state.

Because there are the similarities of stoichiometry, structure and infrared reflectivity spectra (as Fig.6.5 and Fig.2 in ref.80 show) between La$_{1.85}$Sr$_{0.15}$CuO$_4$ and Nd$_{1.85}$(Ce,Th)$_{0.15}$CuO$_{4-y}$, previous anisotropic studies on the polycrystalline sample La$_{2-x}$Sr$_x$CuO$_{4-y}$ put us in a better position to understand our spectra on n-type polycrystalline Nd$_{1.85}$(Ce,Th)$_{0.15}$CuO$_{4-y}$. We do not have to repeat above modeling work on our compounds. We can expect $R_{ab}$ and $R_{c}$ of n-type superconducting materials Nd$_{1.85}$(Ce,Th)$_{0.15}$CuO$_{4-y}$ have the similar spectra of Fig.2(a,b) in ref.167 which were obtained from measurements on the single crystal samples La$_{2-x}$Sr$_x$CuO$_4$. The dopant thus only affects the electric property in Cu$_2$O planes of n-type materials.

Based on this approach, we can explain some of the optical properties
in our n-type polycrystalline samples. Such as, we can find that the reason for the lower reflectivity of n-type polycrystalline than what one expects from a ideal superconductor or pure metal in the low frequency range is associated with anisotropic property of the Cu-O layered materials. What we obtained from the reflectance measurements on the polycrystalline specimens are composite spectra consisting two components, $R_{a-b}$ and $R_c$. A lower non-metallic reflectivity of out-of-plane in low frequencies ($\omega \leq 200$ cm$^{-1}$) certainly leads to a lower composite spectrum $R(\omega)$ in these frequencies.

6.3.2: Normal-State Properties and Phonons:

The spectrum of n-type materials are almost temperature independent in the range studied. It has three quite distinct aspects. Overall reflectivity decreases sharply between 100 and 2000 cm$^{-1}$, followed by a slight further overall decrease to 10,000 cm$^{-1}$. Superimposed on this are several sharp features in the 100-700 cm$^{-1}$ range and a broad, weak peak centered around 300 cm$^{-1}$. We will discuss each separately.

Since materials are anisotropic and polycrystalline, we have not attempted a detailed fit of the spectra by the usual superposition of a Drude term and Lorentz oscillator(s). It is interesting to fit the overall shape of the reflectivity spectrum by a Drude function: $\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau}$, where $\omega$ is the incident-photon frequency, $\omega_p$ and $\tau$ are the plasma frequency and the relaxation time of the free carriers, and $\varepsilon_\infty$ is the background dielectric constant. The fit parameters will not have
physical significance in themselves because they result from the complicated superposition of contributions from different crystalline directions. However, results can be compared with previous results on ceramic samples and with the results for the dc conductivity.

Drude fits are shown in the insets to Fig.6.5. Parameters of the fits are in terms of $\sigma_0 = \frac{\omega}{\rho} r \frac{\epsilon_0}{\epsilon} = 40 \text{ (}\Omega\text{cm})^{-1}$, $r=1\times10^{-15}$ sec and $\epsilon_\infty = 2.2$ (Ce) and 1.9 (Th). Our values of $r$ are in the same range as found for the Y-Ba-Cu-O ceramics;\(^{(65,63)}\) with values of the Fermi velocity in range $2 \times 10^8$ cm/sec, we find mean free paths of about 20 Å. The values of $\sigma_0$ are in rough agreement both with the values $1/\rho_{dc} = 37 \text{ (}\Omega\text{ cm})^{-1}$ (Ce) and 131 (\Omega cm)$^{-1}$ (Th) cited above and with the low-frequency values of $\sigma_\perp$ obtained by Kramers-Kronig analysis (not shown).

Low-frequency conductivity is that of a poor metal and is considerably lower than values observed in the Y-Ba-Cu-O system. The rapid decrease in reflectivity with increased frequency is characteristic of a poor conductor. The carrier density calculated from the Drude-fit parameters is $n = \sigma_0 m/\epsilon e^2 = 1.4\times10^{20}$ cm$^{-3}$, assuming free electron mass and charge; this should be compared with values of about $10^{21}$ cm$^{-3}$, found for Y-Ba-Cu-O polycrystalline samples\(^{(65,63)}\) through similar analysis. The plasma frequency found\(^{(169)}\) for the hole-type ceramic superconductor $\text{La}_{1.85} \text{Sr}_{0.15} \text{CuO}_4$ is similar to ours; their fit, however, included a Lorentz oscillator and found a high value of $\epsilon_\infty$, so the results are not strictly comparable.

Our results should also be compared with the near infrared reflectivity of Nd$_{1.4}$Ce$_{0.16}$CuO$_{1.4-y}$ thin films measured by Hirochi et al.\(^{(170)}\) Their films were highly oriented with the c axis normal to the
SrTiO$_3$ substrate. They found much higher reflectivities (e.g., about 0.35 at 4000 cm$^{-1}$). Their fit with the Drude model yielded longer relaxation times by a factor of about 4 and much higher carrier concentrations, in the range of $10^{22}$ cm$^{-3}$. The differences are clearly due to the differing orientations of the films; conductivity in the a-b plane will be much higher than along the c axis and will contribute heavily to the conductivity measured by Hirochi et al., but much less to our measurements on unoriented, polycrystalline samples.

The sharp features between 100 and 700 cm$^{-1}$ are clearly due to lattice vibrations. Because their contributions to the optical constants are additive to those of the charge carriers, it is difficult to perform precise determinations of the mode energies. As noted above, fitting the data with a superposition of a Drude model and Lorentz oscillators was not attempted. Instead, we use the energies of the peaks in $\sigma_1$, obtained through a Kramers-Kronig analysis, with constant extrapolation of reflectivity above 10 000 cm$^{-1}$ and below 20 cm$^{-1}$. Although the magnitudes of the calculated optical constants will not be meaningful due both to the extrapolations and to the polycrystalline of the samples, the locations of the peaks will nevertheless yield the mode energies. Mode energies, obtained in this manner, are given in Table I.

Assignment of the peaks makes use of recent work on the single crystals Pr$_2$CuO$_4$\textsuperscript{(171)} and Nd$_2$CuO$_4$\textsuperscript{(162)} which are the so called the mother compounds of the n-type superconductors, and the previous work on the very similar La-Sr-Cu-O (Refs.80, 165, 167, and 172) and La-Ni(Cu)-O (Refs.167, 172, and 168) systems. Since Nd$_2$CuO$_4$ has been observed to have a tetragonal structure with the space group $I4/mmm$,\textsuperscript{(173)} seven
TABLE 6-1. Lattice mode energies in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$A_{2u}$</th>
<th>$E_u$</th>
<th>other$^{(e)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$<em>{1.85}$Ce$</em>{0.15}$CuO$_{4-y}$ $^{(a)}$</td>
<td>139 275 518(?)</td>
<td>? 320 409 ?</td>
<td>594 670</td>
</tr>
<tr>
<td>Nd$<em>{1.85}$Th$</em>{0.15}$CuO$_{4-}$ $^{(a)}$</td>
<td>137 275 517</td>
<td>? 320 ? ?</td>
<td>593 670</td>
</tr>
<tr>
<td>Pr$_2$CuO$_4$ $^{(b)}$</td>
<td>135 271 505</td>
<td>124 300 336 486</td>
<td></td>
</tr>
<tr>
<td>Nd$_2$CuO$_4$ $^{(c)}$</td>
<td>134 269 505</td>
<td>129 300 350 509</td>
<td></td>
</tr>
<tr>
<td>La$_2$CuO$_4$ $^{(d)}$</td>
<td>242 342 501</td>
<td>132 358 ? 667</td>
<td></td>
</tr>
</tbody>
</table>

(a) Our infrared data
(b) Data taken from Ref.6-1
(c) Data taken from Ref.6-2
(d) Data taken from Ref.6-3
(e) Phonons in this column may correspond to the tetragonal T-structure.
infrared-active modes are expected: four $E_u$ modes with displacements in the a-b plane and three $A_{2u}$ modes parallel to the c axis. Assignments are shown in Table I. Assignments marked "?" are considered tentative or missing in the observation due to either the strong plasmon screen in the ab plane or the overlap with other $A_{2u}$ modes. For example, we cannot distinguish clearly the $E_u$ mode at $-500 \text{ cm}^{-1}$ from a $A_{2u}$ mode at $518 \text{ cm}^{-1}$.

Since the phonon-like feature at $670 \text{ cm}^{-1}$ in our spectra is far away from the modes of the mother compounds, and close to the highest one in the $\text{La}_2\text{CuO}_4$ crystal which is the mother compound of the corresponding hole-type superconductor, we interpret that the mode at $670 \text{ cm}^{-1}$ in n-type materials does not connect with the $T'$-structure, but with the $T$-structure. Dopant may slightly disorder the crystal structure of $\text{Nd}_2\text{CuO}_4$, i.e., the $T'$-structure, and form the crystal structure of $\text{La}_2\text{CuO}_4$, i.e., the $T$-structure. We also interpret the mode at $-590 \text{ cm}^{-1}$ in our data in this way, as corresponding to the $T$-structure.

We note that three of the modes shift to (very) slightly lower frequency upon replacement of Ce by the heavier Th, suggesting that these modes involve some motion of the Ce (or Th) ion. A simple isotopic substitution model (i.e., no change in interionic force constants) would predict a 29% shift in the frequency of a mode which involves only that ion. There is no explicit evidence of this in our results, suggesting that most of the observed infrared-active modes do not significantly involve Ce or Th. The only possible exception is the mode at $409 \text{ cm}^{-1}$ in the Ce compound which has no counterpart in the spectrum of the Th sample; it is possible that this mode does involve Ce significantly and its counterpart in the Th sample (if present) is obscured by another feature. The fact
that the feature strengthens with increased temperature suggests that it may, in fact, merely be defect induced and not an intrinsic mode of the system, although its presence (as an unresolved shoulder) in the parent compound argues against this.

We observe none of the Raman-active modes reported previously, although one might expect disorder caused by O vacancies which destroys translational symmetry to permit Raman-active modes to be observed.

6.3.3: Superconducting Energy Gap

The most striking features of our infrared data (see Fig. 6.5 and 6.6) on n-type superconducting polycrystalline are low-frequency \( \omega \leq 50 \text{ cm}^{-1} \) enhancements of the reflectivity in the superconducting state: above \(-100 \text{ cm}^{-1}\), spectra show no significant differences between normal and superconducting state.

As discussed in chapter 3 for 1-2-3 bulk samples, and following the method of analysis of ref. 80 for the La-Sr-Cu-O bulk sample, we realize that infrared gap measurement is selectively sensitive to the c-axis gap and almost completely insensitive to the gap in ab plane due to the strongly anisotropic conductivity. Thus, we interpret the edges of the plateau regions as c-axis gap energies and find gaps of \( 55\pm 5 \text{ cm}^{-1} \) \( (6.82\pm 0.62 \text{ mev}) \) for both compounds corresponding to \( 2A/k_{B}T_c \) of \( 3.5\pm 0.3 \) (Ce) and \( 4.3\pm 0.3 \) (Th). These values are within the range found for conventional metallic superconductors. They are consistent with the values of \( 2A=64 \text{ cm}^{-1} \) obtained from the tunneling measurements on
polycrystalline samples reported recently. Our infrared results were also confirmed with the value of $2\Delta=7.2$ meV (57.6 cm$^{-1}$) obtained$^{(176)}$ by another tunneling study done by a research group in the Argonne National Laboratory, in which the ceramic samples measured had the same preparation process as ours. As a reference we show in Fig. 6.5 the tunneling results measured on the Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$ ceramic sample.

Significantly different results have been presented$^{(177)}$ for Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$. 100% reflectivity was reported below 56 cm$^{-1}$ at 6 K. This surprising result is unique among studies on polycrystalline materials and is difficult to understand, in view of the characteristics of such materials as described above. Superconducting reflectivity rose above normal reflectivity at about 130 cm$^{-1}$, rather than at 60 cm$^{-1}$, as in the present work. Based on analysis of these results, the authors concluded that they could not determine the superconducting gap. It is possible that their sample surface contained crystallites preferentially aligned with the c axis perpendicular to the surface, yielding a much higher conductivity and reflectivity. Additional work is required to confirm the reason for these differences.

As we mentioned before, there is an argument, starting with the discovery of new high-T$_{c}$ oxide materials, whether or not the ir technology can be employed as a useful tool to study superconducting properties of these new high-T$_{c}$ materials. In opposition to the interpretation that associates the "edge" in the reflectance ratio spectra with a superconducting absorption, and hence with a superconducting energy gap, Bonn et al. proposed a plasmon model$^{(164)}$ to explain the ir behavior of La$_{1.85}$Sr$_{0.15}$CuO$_{4}$. Later this model was used to interpret the ir
Fig. 6.5: Tunneling measurements on $\text{Nb}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ show that the superconducting gap, $2\Delta$, located at 7.2 meV, i.e., $-57\text{ cm}^{-1}$, which is consistent with our infrared results (from ref. 176).
reflectance data on 1-2-3 sample (102) and other superconductors (103). They have assigned the edge in the reflectance ratio spectrum to a zero crossing of the real part of the dielectric function \( \varepsilon_1 \). For \( \text{La}_{1.85} \text{Sr}_{0.15} \text{CuO}_4 \), the zero crossing is caused by a strong resonance at 240 cm\(^{-1}\) and a weaker resonance at 500 cm\(^{-1}\) (164). Under this interpretation, neither the existence nor the value of the energy gap are obvious from far-infrared reflectance data. The intrinsic behavior of this plasmon model is based on the assumption that the new high-\( T_c \) superconductors are in the "extreme clean limit" \((1/\tau \ll 2\Delta)\) (62) which has been discussed in chapter 3 and 4 for other high-\( T_c \) Cu-O materials. In the clean limit all new high-\( T_c \) layered superconductors are assumed to be too clean to see the superconducting absorption edge from their ir reflectivity (or ratio) data. When the width of Drude peak of \( \sigma_1(\omega) \) is much smaller than the gap, the magnitude of normal-state conductivity at \( \omega = 2\Delta \) is too small to become a visible shoulder in superconducting edge. (58, 112) In addition, there remains a finite conductivity from the mid-infrared absorption to further diminish the importance of any contribution from the superconducting electrons at and above the gap. Thus no sharp feature can be found in the clean-limit reflectance at the gap frequency.

Since we have discussed applicability of "clean limit" for high-\( T_c \) Cu-O layered superconductors before, here we will repeat none of the questions but one: whether the superconducting gap seen in infrared data is a quantitative rather than qualitative problem. This can be calculated directly from infrared data. (56, 65, 112) Although unambiguous analysis yielding the optical constants of bulk samples are not available yet, the relaxation rate, \( 1/\tau \), of free carrier conductivity in \( \text{La}_{1.85} \text{Sr}_{0.15} \text{CuO}_{4-y} \)
(hence in our n-type materials due to the similar optical behavior) is believed in order of $3 \times 10^3$ cm$^{-1}$ \cite{62,80}. If we use $1/\tau = 33$ cm$^{-1}$, the minimum number which has been used to show how "clean" the sample is, the gap energy is still observable since the material parameter of $\eta = (2\tau \Delta)^{-1}$ equals $-0.6$ (a value of $2\Delta = 50$ cm$^{-1}$ has been used here) which is in a visible range. \cite{65} Finally we would like to mention that if the "clean limit" restricts IR gap measurement sensitively on the high-$T_c$ materials, it should also do the same on the conventional superconductors, since it based on BCS theory. The pure metals of Indium and Tin are conventional superconductors and "very clean", their parameters $\eta (=1/2\Delta\tau)$ are $1/300$ and $1/250$ \cite{12,19} respectively, but the superconducting energy gaps have been identified from the sharp feature in far-infrared reflectivity ratio spectra. \cite{12} This is a practical example which shows us how "clean" the material must be to hide its gap from infrared measurement. Up to now, there is no solid evidence to show any high-$T_c$ superconductor is such clean material.
6.4: Conclusions

Infrared reflectivity spectra have been measured for the n-type superconductors Nd$_{1.85}$(Ce, Th)$_{0.15}$CuO$_{4-y}$ up to 10,000 cm$^{-1}$ from 7 K to room temperature. The superconducting energy gaps at ~50 cm$^{-1}$ for both samples corresponding to $2\Delta/k_B T_c$ of 3.1 (Ce) and 3.9 (Th) are first found in our infrared reflectivity ratio spectra. These values are within the range of BCS values.

We find that the optical properties of the n-type superconductors, including evidence of a gap, are very similar to those of the hole-type La-Sr-Cu-O system, and thus that the mechanism for superconductivity is likely the same.

It is shown by our infrared data that the ion-doping n-type superconductors might not the pure tetragonal T' structure. Dopant makes the crystal structure partially form the T-structure.
CHAPTER 7: BIG PICTURE

In my thesis, infrared reflectivity and transmission studies on several different high-\(T_c\) superconductors are reported. The order of chapters in my thesis, in fact, basically reflected the order of discovery history of these high-\(T_c\) materials.

Reflectivity measurements on the polycrystalline samples of \(\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\) and \(\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}\) provided the information of phonon behavior and superconducting energy gap which may correspond to c-axis; the ab plane properties of 1-2-3 materials and the complicated Bi(Pb)-Sr-Ca-Cu-O system were also studied in the reflectivity measurements. Transmission measurements on Pb-doped Bi-Sr-Ca-Cu-O sputtered films on MgO revealed the optical behavior in the far infrared frequency range. Our studies on reflectivity spectra of n-type materials was the first to show a clear evidence for a superconducting energy gap located at \(\sim 60 \text{ cm}^{-1}\), which may correspond to c-axis. This measurement also provided a good opportunity for us to compare the optical behavior between the electron- and hole-doped superconductors.

At this moment, although the mechanism of high-\(T_c\) superconductors is still unknown, and some optical properties of these materials in both normal- and superconducting-state are still unclear, our infrared experimental data certainly provide some important information about these materials, our research results revealed and confirmed some unique properties of these materials.
All the discovered high-$T_c$ superconductors are oxides, and most of them are CuO$_2$ layered materials. Very strongly anisotropic properties were found to be common to both the superconducting and normal states. For the 1-2-3 materials, which have fewer problems of sample preparation and characterization and also have been well-studied, our infrared reflectivity studies on both film and bulk samples revealed that the superconducting energy gap(s) are strongly anisotropic. The gap which corresponds to the ab plane is about $8 \, kT_c$, and much greater than the $\sim 3 \, kT_c$ observed for the c-axis. The gap sizes extracted from our experimental data are consistent with the infrared results on the single crystals measured by other groups. The unusual large gap size on the ab plane has challenged all the theoretical work, especially those that include strong coupling between free carrier and phonon.

Besides the strong anisotropy, these gap(s) also presented the unusual temperature dependence. We have investigated the temperature dependent behavior about c-axis gap in 1-2-3 compounds. This gap behavior is very different from that of a BCS-type superconductor. $2\Delta(T)/2\Delta(0)$ approaches zero more steeply at $T-T_c$ than for a conventional superconductor. A similar temperature dependent behavior for the ab plane gap can be roughly found from our reflectivity ratio spectra, although we did not present them in the same detail.

Similar gap behaviors has been found in our Bi(Pb)-Sr-Ca-Cu-O system. Recent transmission measurements on the 2212 single crystal show$^{146}$ that a $-12 \, kT_c$ superconducting feature presents in the transmission ratio spectra. This discovery indicated that there may be a even larger ab plane
gap in this material.

For the n-type $\text{Nd}_{2-x}(\text{Ce, Th})_x\text{CuO}_{4-y}$ materials, our infrared reflectivity data show a $\sim 3\, kT_c$ superconducting energy gap which we interpret as a c-axis gap. We also noted that there are some fine structures below this gap, which may imply that the actual c-axis gap is smaller. To obtain more information about the gap anisotropic properties in these materials, reflectivity measurements on the high quality single crystals are required.

The behavior of infrared-active phonons in high-$T_c$ materials is studied in our data analysis. Most phonons presented in our spectra correspond to the vibrations along with the c-axis; this is due to metallic screening of phonon in the ab plane. We also observed the phenomenon of phonon softening in superconducting state around c-axis gap(s) for both 1-2-3 and n-type polycrystalline samples. This may imply that a strong free carrier-phonon coupling mechanism is responsible for superconductivity related to this gap.

For better understanding of these new materials, we still need to do more work on higher quality and suitable size single crystals for the future infrared reflectivity (and, even, for the transmission) measurements. Polarized optical measurements on these single crystal samples can provide more precise information about these strongly anisotropic materials. By comparing data of single crystals which usually provide the ab plane information and that of polycrystalline sample which usually provide out-of-plane (c-axis) information, we can obtain all the optical information about these materials. Up to now, Only $\text{YBa}_2\text{Cu}_3\text{O}_7$ has...
been studied in some detail, and most reliable infrared results are extracted from this material. We still need to obtain the high quality samples of other materials, because some important results which have been reported on 1-2-3 samples are still waiting for confirmation. For example, anisotropic conductivity has been found in 1-2-3 materials, even between the \( \hat{a} \) and \( \hat{b} \) directions; a background conductivity has been suggested to associated with Cu-O chains. Since the chains are only present in 1-2-3 materials, it is very important to carry out similar polarized infrared experiments on the single crystals of different materials, such as 2212 material. Meanwhile, some infrared measurements on single crystal of n-type materials are also required, as we mentioned before, to distinguish the positions of superconducting gaps of ab plane and c-axis. It is also very interesting to compare the behavior of gap-anisotropy in these lower-\( T_c \) (20-40 K) materials with that of high-\( T_c \) (over 77 K) materials. More information is also needed about temperature-dependent energy gap(s) in all the new superconductors.

Since transmission data, as we mentioned before, are easier to interpret than reflectivity data, it is thus very important for future infrared studies to obtain high quality thin superconducting films that deposited on suitable substrates which are less temperature dependent and more transparent in a wide temperature and frequency range.
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The tunneling data of ceramic Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$ was provided by Dr. J.L. Peng.