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Light scattering study of semiconductor heterostructures and high-temperature superconductor films

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The Ohio State University, 1991
LIGHT SCATTERING STUDY OF
SEMICONDUCTOR HETEROSTRUCTURES AND HIGH
TEMPERATURE SUPERCONDUCTOR FILMS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Yi Liu, B.S., M.S.

* * * * *

The Ohio State University
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TO MY FAMILY AND

MY FRIENDS IN TIAN AN MEN SQUARE
I would like to express my great appreciation to my adviser, Prof. R. Sooryakumar, for his guidance and insight throughout the research. He has introduced me into the field of optics in experimental condensed matter physics and his enthusiasm and thoroughness have always been inspiring. His earnest instruction and rigorous scholarship have been a key to my progress. My years in graduate school would have been a failure without his good nature, understanding and patience.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>VITA</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
</tbody>
</table>

## CHAPTERS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>EXPERIMENTAL SET-UP, THEORY OF RAMAN SCATTERING AND PROPERTIES OF GaAs QUANTUM WELLS</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Introduction</td>
<td>5</td>
</tr>
<tr>
<td>2.2</td>
<td>Instrumentation and Set-up</td>
<td>6</td>
</tr>
<tr>
<td>2.3</td>
<td>Raman Scattering Theory</td>
<td>10</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Interaction of an electromagnetic field with a solid</td>
<td>10</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Raman scattering by phonons</td>
<td>12</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Resonant light scattering</td>
<td>15</td>
</tr>
<tr>
<td>2.3.4</td>
<td>Conservation laws and selection rules</td>
<td>18</td>
</tr>
<tr>
<td>2.4</td>
<td>Properties of GaAs/Ga_{1-x}Al_xAs Quantum Wells</td>
<td>20</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Electronic states and excitonic effect in quantum wells</td>
<td>21</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Confined optical phonons in quantum wells</td>
<td>25</td>
</tr>
<tr>
<td>III</td>
<td>DIFFERENCE PHONON SCATTERING IN GaAs/GaAlAs SINGLE QUANTUM WELLS</td>
<td>29</td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>29</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1. Periodic parts of Block functions at the $\Gamma_6$, $\Gamma_7$, $\Gamma_8$ edges of GaAs bulk crystals</td>
<td>23</td>
</tr>
<tr>
<td>Table 4.1. Atom positions of $Y_1Ba_2Cu_3O_7$ and $Y_1Ba_2Cu_3O_6$ and their site symmetries</td>
<td>74</td>
</tr>
<tr>
<td>Table 4.2. Atom positions of $Y_1Ba_2Cu_3O_6$ and their site symmetries</td>
<td>78</td>
</tr>
<tr>
<td>Table 4.3. Fano asymmetry factor of 337 cm$^{-1}$ mode at different temperatures</td>
<td>116</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 2.1. Typical Raman set-up</td>
<td>7</td>
</tr>
<tr>
<td>Fig. 2.2. Band structure of bulk GaAs</td>
<td>22</td>
</tr>
<tr>
<td>Fig. 2.3. Resonant Raman spectra from QW3</td>
<td>28</td>
</tr>
<tr>
<td>Fig. 3.1. Sketch of a GaAs/AlGaAs quantum well</td>
<td>32</td>
</tr>
<tr>
<td>Fig. 3.2. Photoluminescence (PL) spectra from wafer II-61 and II-62</td>
<td>35</td>
</tr>
<tr>
<td>Fig. 3.3. Photoluminescence excitation (PLE) spectra from QW3 and QW4</td>
<td>37</td>
</tr>
<tr>
<td>Fig. 3.4. Triply resonant effect</td>
<td>38</td>
</tr>
<tr>
<td>Fig. 3.5. Peak R measured under different scattering geometries</td>
<td>40</td>
</tr>
<tr>
<td>Fig. 3.6. Typical processes involved in second-order Raman scattering by phonons</td>
<td>43</td>
</tr>
<tr>
<td>Fig. 3.7. Sketch of band dispersion in quantum well and TRRS condition</td>
<td>45</td>
</tr>
<tr>
<td>Fig. 3.8. Resonant profile of peak R in QW3</td>
<td>54</td>
</tr>
<tr>
<td>Fig. 3.9. Raman spectra of QW4 and QW2 under uniaxial stress</td>
<td>58</td>
</tr>
<tr>
<td>Fig. 3.10. 5K PL and PLE spectra of QW4</td>
<td>61</td>
</tr>
<tr>
<td>Fig. 3.11. PLE spectra of QW4 under different uniaxial stress along [110]</td>
<td>62</td>
</tr>
<tr>
<td>Fig. 3.12. The intensities of peak R under different uniaxial stress along [110] from QW4</td>
<td>64</td>
</tr>
<tr>
<td>Fig. 3.13. Power dependence of peak R from QW3</td>
<td>68</td>
</tr>
</tbody>
</table>
Fig. 4.1. Structures of superconductor $Y_{1.8}Ba_2Cu_3O_8(1:2:3)$, semiconductor $Y_{1.9}Ba_2Cu_3O_8$ and superconductor $Y_{1.8}Ba_2Cu_4O_8(1:2:4)$ ...... 73

Fig. 4.2. Atomic displacements of optic phonon modes in $Y_{1.8}Ba_2Cu_3O_{7-x}$ ...................... 76

Fig. 4.3. Schematic diagram of the co-evaporation system ................................................. 80

Fig. 4.4. Temperature dependence of the resistance of several $Y_{1.8}Ba_2Cu_3O_{7-x}$ films ............ 82

Fig. 4.5. X-ray diffraction from $1:2:3C//_1$ and $1:2:3C//_2$ films ................................. 83

Fig. 4.6. Scanning Electron Microscope pictures of $1:2:3$ and $1:2:4$ films .......................... 84

Fig. 4.7. Temperature dependence of the ac susceptibility of $1:2:4C//_1$ and $1:2:4C//_2$ films .......... 86

Fig. 4.8. X-ray diffraction pattern of $1:2:4$ and $1:2:3$ films grown on (100) and (110) surfaces of SrTiO$_3$ substrate ........................................... 87

Fig. 4.9. Raman spectra at 10 K of $1:2:4$ and $1:2:3$ oxygen rich films .................................. 90

Fig. 4.10. Temperature dependence of the frequencies of six phonon modes associated with CuO chains and CuO$_2$ planes in $1:2:4//_2$ .............. 95

Fig. 4.11. Raman spectra of $1:2:3C//_1$ after a sequence of annealing in argon and oxygen ......................... 100

Fig. 4.12. Raman spectra of $1:2:4C//_1$ film after a sequence of annealing in argon and oxygen ......................... 104

Fig. 4.13. Raman spectra of $1:2:4C//_3$ film after a sequence of annealing in argon and oxygen ......................... 105

Fig. 4.14. System with an electronic state at $E = 2\Delta$ and two phonon states $|P_1\rangle$, $|P_2\rangle$ coupled by matrix elements $V_1$, $V_2$ .................... 112

Fig. 4.15. Numerical results of ZZ theory .......... 120
Fig. 4.16. Impurity scattering rate effect on phonon self-energy ........................................ 123

Fig. 4.17. Linewidth of 337 cm\(^{-1}\) and 435 cm\(^{-1}\) phonons as a function of temperature ............. 125

Fig. 4.18. Theoretical fit of 337 cm\(^{-1}\) peak by equation 4.5 in the text ....................... 128
The coupling between electrons and lattice vibrations (phonons) is one of the most fundamental interactions in solids. The major consequences of this interaction include:

a.) To scatter conduction electrons from a state $K$ to another $K'$, leading to electrical resistivity.

b.) To cause electronic band transitions associated with the absorption (or creation) of phonons: the electron-phonon interaction is an important source of attenuation of ultrasonic and electronic waves in solids. It is also a crucial interaction in light scattering processes.

c.) To cause an attractive interaction between two electrons giving rise to conventional superconductivity with "low" transition temperatures.

d.) The electron will carry with it a lattice polarization field. The composite particle of an electron plus phonon field is called a polaron and has played an important role in ionic crystals.

These aspects of the electron-phonon interaction have
been studied since the early 1950's [1.1]. The emergence of semiconductor quantum hetero-structures in 1970 [1.2] and the discovery of high temperature superconductors in 1986 [1.3] have brought new challenges to understanding the consequences of the coupling between electrons and phonons in these systems.

In semiconductor quantum wells, the electronic states are quantized in a direction normal to the interface. However their motion parallel to the interface are not restricted. The resulting multitude of electronic subbands describe their behavior under reduced dimensions. Moreover, optical phonons are constrained by the barriers yielding the so-called confined phonons that are different from phonon behavior in the bulk. Therefore the electron-phonon interaction in the laminar geometry of a quantum well is different from that in three dimensions. In high temperature superconductors, although the mechanism which leads to the high transition temperature is still uncertain, the electron-phonon interaction has led to the renormalization of the vibrational modes associated with the planar oxygen atoms in the superconducting phase.

The primary goal of this thesis is to investigate, mainly through inelastic light (Raman) scattering, the electron-phonon interaction in GaAs/GaAlAs single quantum wells and the behavior of lattice vibrations in the normal
and superconducting states in high temperature superconducting films. Our study has resulted in the first observation of difference phonon scattering of optical phonons in quantum wells. We propose, and experimentally confirm a microscopic mechanism leading to a triply resonant scattering process to account for our observations in GaAs/GaAlAs single quantum wells.

In the high $T_c$ compounds, we study the Raman active optical phonons at zone center. The dependence of these phonons on oxygen content and temperature are investigated. From the temperature dependent Raman measurements, superconductivity-induced self-energy effects on the phonons in YBaCuO compounds are observed. We interpret our results based on the Zeyher and Zwicknagl (ZZ) strong-coupling theory. In particular the concurrent occurrence of softening and hardening of two phonons below $T_c$ allow us, based on the ZZ theory, to identify the superconducting energy gap. We obtain a value of $2\Delta/KT_c = 5$ for $Y_2Ba_2Cu_3O_{6.5}$ films. This value is in agreement with that deduced from Raman measurements on $Y_2Ba_2Cu_3O_{7-d}$.

The next chapter will briefly outline the experimental technique as well as provide a microscopic theory of Raman scattering. Chapter three describes results of the triply resonant Raman scattering process from GaAs/GaAlAs single quantum wells giving rise to the (LO-TO) difference phonon
modes. We use fourth-order perturbation theory to calculate the Raman scattering efficiency and discuss the electron-phonon interaction and its effect on selection rules. The consequence of tuning the energy separation between electronic subbands on the difference phonon excitation is also presented. Chapter IV presents results and conclusions of our Raman study on Yba$_2$Cu$_3$O$_{7-x}$ and Yba$_2$Cu$_4$O$_{8-x}$ films. We measured the Raman spectra under different oxygen contents by appropriate annealing conditions. These results and the temperature dependence of the Raman spectra associated with the vibrational modes are presented. The highlights of the ZZ strong-coupling theory are briefly discussed and its relation to our experimental results are also discussed in this chapter. The last chapter of this thesis summarizes the results and discussions and offers suggestions for further and continued study.
CHAPTER II
EXPERIMENTAL SET-UP, THEORY OF RAMAN SCATTERING AND PROPERTIES OF GaAs QUANTUM WELLS

2.1 Introduction

Raman scattering refers to inelastic scattering of light from diverse materials as for example, molecules, liquids, membranes, or solids. A typical scattering experiment involves a monochromatic beam of photons of frequency $\omega_L$ interacting with elementary excitations within the sample. The resulting scattered radiation thus has a distribution of frequencies $\omega_s$.

The frequency shift $|\omega_L - \omega_s|$, also called the Raman shift, is characteristic of the excitations that occur in the sample. This thesis mainly considers optical vibrational excitations that normally lie in the range of 10 to 1000 cm$^{-1}$. These inelastic contributions are further subdivided depending on whether $\omega_s < \omega_L$ giving rise to Stokes scattering or $\omega_s > \omega_L$ called anti-Stokes scattering. In general, Stokes and anti-Stokes scattering yield equivalent
information, and since Stokes scattered phonon intensities are normally stronger, Stokes spectra are sufficient and preferred.

The theory of the Raman effect can be treated classically by introducing the susceptibility $\chi(r)$. In this approach, the scattering cross section depends on the derivative of susceptibility with respect to the normal modes of vibrations [2.1]. We however treat the phenomenon of Raman scattering from a quantum mechanical point of view.

To understand the resonant Raman scattering process discussed in chapter III, a brief introduction to the electronic properties, excitonic effects and confined optical phonons in GaAs/GaAlAs quantum wells is provided in section 2.4.

2.2 Instrumentation and set-up

Figure 2.1 is a schematic representation of the set-up utilized for our Raman measurements. The radiation source is either a Kr$^+$-ion (Spectra Physics Model 171) laser [2.2], or a LD-700 dye laser (Spectra Physics Model 375B) pumped by all-lines from the Kr$^+$-ion laser. A single lasing mode with 0.23 cm$^{-1}$ half width can be selected from the dye laser by use of a three plate birefringent filter tuning element [2.3]. To reduce unwanted plasma emissions, a laser line interference filter with pass bandwidth of 40 cm$^{-1}$ is used.
Fig. 2.1. Typical Raman set-up.
For polarization analysis, the incident beam is sent through a polarization rotator, while an analyzer was placed in the path of the scattered beam.

The samples are typically mounted on a copper holder that is placed in an optical cryostat, capable of maintaining the sample temperature between 300 K and 1.8K. A Janis Research cryostat (Model 10DT) allows for cold, pumped He gas to pass over the sample from the bottom of the sample chamber. The temperature cited in the measurements is that recorded by a silicon diode mounted on the copper holder located close to the sample. Heaters are located in two positions. The first heats the He gas that passes over the sample. This procedure is followed when the desired temperature is above 40 K. The second heater is mounted on the copper holder, and is used to maintain the temperature steady below ~ 40 K. The temperature sensors and heaters are controlled by a Lake Shore DRC 82C temperature controller. For room temperature measurements, the sample chamber is evacuated to avoid Raman scattering from O₂ or N₂ rotational modes. The cryostat has five optical windows to allow for different scattering geometries. The sample holder can also be rotated about the vertical axis and be translated vertically so that several samples can be mounted.

The laser light is normally focused to about a 50
micron diameter spot on the sample using a lens with focal length \(\approx 10 \text{ cm}\) or spread to 1 cm long 50 micron wide line using a cylindrical lens with focal length \(\approx 8 \text{ cm}\). Typically 1 mW - 200 mW of radiation is incident on the samples. The scattered radiation is collected by a Canon Lens FD 85mm f/1.8 camera lens that matches the acceptance angle of the double grating spectrometer.

The light is dispersed by a double grating 3/4 meter SPEX model 1403 spectrometer with spectral coverage from 11000 cm\(^{-1}\) to 31000 cm\(^{-1}\). The dispersing elements are two holographic gratings with 110 x 110 mm area and 1800 grooves/mm density. The resolution in the green spectral region (2.5 ev) for 100 micron entrance and exit slit widths is \(\sim 1.2 \text{ cm}^{-1}\), and reduces to \(\sim 0.8 \text{ cm}^{-1}\) in the red [2.4]. For slit widths less than 400 microns, the resolution reduces almost linearly with increasing slit width. The light passing through the exit slit is focused onto a RCA photomultiplier (C31034) tube.

The grating drive of the spectrometer and the voltage to the photomultiplier tube are controlled by a DM1B SPEX computer [2.5]. The energy range to be scanned, the scanning rate, and the dwell time are selected prior to each scan. The data accumulated are stored in floppy disks, and printed through a Houston Instrument Plotter model DMB-40. The data files can also be transformed to the VAX
minicomputer for data analysis.

2.3 Raman Scattering Theory

2.3.1 Interaction of an electromagnetic field with a solid

The Hamiltonian describing interaction with light can be written as

\[
H = H_e + H_i + H_{e\mathbb{1}} + H_p + H_{er} + H_{ir} + H_{ep} \quad \text{(2.1)}
\]

where \( H_e, H_i \) and \( H_p \) are the Hamiltonian of the electrons, the ions, and photons respectively. \( H_{e\mathbb{1}} \) represents the electron-ion interaction while \( H_{er}, H_{ir} \) that of the electron-radiation and ion-radiation interaction. \( H_{ep} \) is the electron-phonon interaction. By using the adiabatic approximation, \( H_e + H_i + H_{e\mathbb{1}} \) can be solved and the electron and phonon eigenstates and eigenvectors calculated.

In order to simultaneously describe spontaneous and stimulated light scattering, it is convenient to treat photons in the second-quantized notation. Photons are bosons with creation and annihilation operators \( a_k^\dagger \) and \( a_k \), respectively. Their Hamiltonian \( H_p \) becomes [2.1]

\[
H_p = \sum_K \frac{1}{2} \omega(K) (a_k^\dagger a_k + a_k a_k^\dagger) \quad \text{(2.2)}
\]

By taking the thermodynamic expectation value of (2.2), we find
\[ <H_p>_k = \omega(k)(n_k + 1/2) = Ve_0<E^2>_k \]
\[ = V\omega^2/c^2<A^2>_k \]

where \( n_k \) is the thermal equilibrium statistical factor which can be represented as

\[ n_k = \frac{1}{\exp(h\omega(k)/kT)-1} \]

and \( V \) is the volume under consideration.

The electric field operator at \( r \), \( E(r) \) and corresponding vector potential \( A(r) \), can be obtained by inspection of (2.3, 2.4) and using Maxwell’s equations: [2.6]

\[ A(r) = \sum_k \frac{1}{2\varepsilon_0 V\omega(k)} \left( a_k e^{ik\cdot r} + a^*_k e^{-ik\cdot r} \right) e_k \]  
\[ E(r) = i\sum_k \frac{\omega(k)}{2\varepsilon_0 V} \left( a_k e^{ik\cdot r} - a^*_k e^{-ik\cdot r} \right) e_k \]

where \( e_k \) represents the polarization vector of the electric field and the equations apply to photons propagating in free space. The term \( H_{er} \) in (2.1) is easily obtained from the kinetic energy contribution to \( H_s \):

\[ 1/2\sum_j [(p_j + A(r_j))^2 = 1/2\sum_j (p_j)^2 + 1/2\sum_j [A(r_j)]^2 \]
\[ 1/2\sum_j (p_j \cdot A(r_j) + A(r_j) \cdot p_j) \]
Hence,

$$H_{ex} = H_{ex}' + H_{ex}''$$  \hspace{1cm} (2.8)

where

$$H_{ex}' = \frac{1}{2}\sum_{j} (p_j \cdot \Lambda(r_j) + \Lambda(r_j) \cdot p_j)$$  \hspace{1cm} (2.9)

$$H_{ex}'' = \frac{1}{2}\sum_{j} [\Lambda(p_j)]^2$$  \hspace{1cm} (2.10)

In the above equations, the summation index runs over all electrons. The electron-photon Hamiltonian $H_{ex}$ has two terms: $H_{ex}'$, linear in the electromagnetic field, and a quadratic term $H_{ex}''$. Expressions for $H_{ex}$ in terms of $a_k$ and $a_k^+$ are easily obtained by placing (2.5) into (2.9, 2.10). We find for Stokes scattering

$$H_{ex}' = \sum_j \left[ \frac{1}{2V\varepsilon_0} \right]^{1/2} \left[ \omega_{k_L}^{-1/2} a_{k_L} e^{i(k_L \cdot r_j)} e_j \cdot (p_j + 1/2k_L) ight]$$  \hspace{1cm} (2.11)

$$+ \omega_{k_n}^{-1/2} a_{k_n}^+ e^{-i(k_n \cdot r_j)} e_n \cdot (p_j - 1/2k_n) \right]$$

$$H_{ex}'' = \sum_j \frac{1}{2V\varepsilon_0 \omega_n^{1/2} \omega_L^{1/2}} e_n \cdot e_L e^{i(k_L - k_n) \cdot r_j}$$  \hspace{1cm} (2.12)

2.3.2 Raman Scattering by Phonons

Let us consider light scattering raising a solid from a ground state $\Psi_0$ to an excited state $\Psi_x$ and we treat these states in the adiabatic approximation, i.e., $\Psi$ is written as a product of an electronic wave function $\psi(r, R)$ and a
vibrational function $\varphi_v(R)$:

$$\Phi(r, R) = \psi(r, R)\varphi_v(R) \quad (2.13)$$

$v$ denotes the vibrational state under consideration. We treat scattering by phonons from a specific vibrational state $n_o$ to a state $n_r$. In this case, the electronic wave functions of the initial and final state are the same and the Hamiltonian $H''_{er}$ does not contribute to the scattering. The corresponding matrix element of $H''_{er}$ is zero because of the orthogonality of $\varphi_o$ and $\varphi_e$. Hence, the sole contribution to phonon scattering arises from $H'_{er}$. The $H'_{er}$ is linear in the photon creation and destruction operators, and its contribution to the scattering is in second order. Using Fermi's golden rule within second order perturbation theory, the Stokes cross section becomes [2.1]

$$\frac{\partial^2 \sigma}{\partial \omega_n \partial \Omega} = \frac{\omega_n^2}{\omega_c^2} \sum_{0, n_r} \langle i, n_i | e^{-i k_{sn} \cdot r_e} (p - 1/2 k_e) | 0, n_o \rangle \cdot \langle i, n_i | e^{i k_{1n} \cdot r_e} (p + 1/2 k_e) | 0, n_o \rangle \frac{1}{\omega_{1,n} - \omega_{o,n} - \omega_c} \quad (2.14)$$

$$+ \text{nonresonant term} \left( \frac{2}{\delta(\omega_{n_r} - \omega_{o,n} - \omega_c)} \right)_{n_o, n_r}$$

where the angular brackets represent the thermodynamic average over $n_o$ and $n_r$. In (2.14) we have written only the
so-called resonant terms explicitly. The nonresonant terms (NRT) are obtained from the resonant terms by permuting $e_L$, $k_L$ with $e_a$, $k_a$ and changing $-\omega_L$ into $+\omega_a$.

If we define the transition susceptibility of the solid as

$$\chi_a = \frac{4\pi V}{\omega_a \omega_L} \sum_{i,n_i} \langle 0,n_0+1| p|i,n_i \rangle \times \langle i,n_i| p|0,n_0 \rangle$$

$$\frac{1}{\omega_{i,n_i} - \omega_{0,n_0} - \omega_L} + \text{NRT}$$

(2.15)

and invoke the dipole approximation to equation 2.14, the first order Stokes cross section can then be represented as

$$\frac{\partial^2 \sigma_a}{\partial \omega_s \partial \Omega} = \frac{\omega_s^4 V}{(4\pi)^2 c^4} |e_a \cdot \chi_a \cdot e_L|^2$$

(2.16)

With comparison to classical scattering theory, we find the relation [2.1]

$$\chi_a = \frac{\partial \chi}{\partial \xi} <\xi^a>^{1/2}$$

(2.17)

$\xi$ is the normal mode coordinate, the susceptibility $\chi_a(r)$ is defined as the dipole moment per unit volume induced by a unit field
\[ \epsilon_0 \chi_\text{s}(r) = \sum_{R_i}^{N} \alpha(R_i) \delta(r - R_i) \]  

(2.18)

\( \alpha(R_i) \) is the polarizability of atom at position \( R_i \). The above discussion is suitable for most nonresonant (\( \omega_L \neq (\omega_i - \omega_0) \) in equation 2.14) Raman scattering processes in solids. However, we will see in the next section where resonant scattering is considered that the cross section will be strongly modified from the nonresonant situation.

### 2.3.3 Resonant light scattering

In the previous section, we have discussed the quantum theory of light scattering by phonons and defined the transition susceptibility \( \chi_\text{s} \). Let us consider the expression for \( \chi_\text{s} \) in equation 2.15 and use the Born-Oppenheimer wavefunction approximation (equation 2.13) for the eigenstates. We define a normal coordinate dependent electronic polarizability \( P_{10}(\xi) \) which only depends on electronic states \(|0>\) and \(|i>\) as

\[ P_{10}(\xi) = <i|p|0> \]  

(2.19)

By expanding \( P_{10}(\xi) \) in a power series of \( \xi \), we find

\[ P_{10}(\xi) = P_{10}(0) + \left( \frac{\partial P_{10}}{\partial \xi} \right)_0 \xi + \ldots \]  

(2.20)
Substituting eqn. 2.20 into eqn. 2.15, we find \[2.7,2.8\]

\[
P = \langle A \rangle + \langle B \rangle + NRT \tag{2.21}
\]

\[
A = \sum_{\substack{n_1 \leftrightarrow n_2}} \langle n_f^i| P_{10}(0)| n_i \rangle \langle n_i| P_{10}(0)| n_o \rangle \frac{1}{\omega_{1,n_1} - \omega_{0,n_0} - \omega_L} \tag{2.22}
\]

\[
B = \sum_{i,n_1} \left[ \langle n_f^i| \left( -\frac{\partial P_{10}}{\partial \xi} \right)_o \xi | n_o \rangle \frac{\langle n_f^i| P_{10}(0)| n_i \rangle}{\omega_{1,n_1} - \omega_{0,n_0} - \omega_L} \right] + \langle n_f^i| \left( -\frac{\partial P_{10}}{\partial \xi} \right)_o \xi | n_i \rangle \frac{\langle n_f^i| P_{10}(0)| n_o \rangle}{\omega_{1,n_1} - \omega_{0,n_0} - \omega_L} \tag{2.23}
\]

Term A is called the Frank-Condon Raman polarizability and it usually contributes to elastic scattering in solids except in the case of strongly localized vibrations like defect induced phonon modes \[2.8\].

In order to evaluate the term B (the Herzberg-Teller term), we must examine \((\partial P_{10}/\partial \xi)_o\). This derivative arises through a mixture of intermediate state \(i\) with other states \(j\) via the potential change induced by the phonon displacement, i.e. by the first order electron-phonon interaction Hamiltonian \(H_{op}\). Using first-order perturbation theory, we write

\[
\left( \frac{\partial P_{10}}{\partial \xi} \right)_o = \sum_j \frac{\langle i| H_{op} | j \rangle}{\omega_i - \omega_j} \tag{2.24}
\]

The matrix element \(\langle n_f^i| \xi | n_o \rangle = \delta_{n_0,n_{f1}}\) then appears in term B.
and yields the standard one-phonon Stokes ($n_r = n_0 + 1$) and anti-Stokes ($n_r = n_0 - 1$) scattering. By using the static approximation [2.9], we can further simplify $B$ as

$$B = \sum_{i,j} \langle n_r | P_i (0) | n_i \rangle \langle i | H_{sp} | j \rangle \langle n_j | P_j (0) | n_0 \rangle \langle \omega_{i,n_0} - \omega_{o,n_0} - \omega_L \rangle (\omega_{i,n_0} - \omega_{o,n_0} - \omega_s)$$

(2.25)

From this equation, it follows that a first order resonance can be achieved by changing the incident photon energy to equal to the energy difference between the ground state and the intermediate state. Two separate resonances are possible. For one $\omega_L = \omega_j - \omega_o$ (incoming resonance, with the incident radiation energy equal to an electronic transition) and the other occurring for $\omega_s = \omega_i - \omega_o$ (outgoing resonance, with the scattered radiation having an energy equal to an electronic transition) [2.10]

In first order phonon scattering the energy difference between the initial state $\omega_o$ and final state $\omega_s$ is a phonon energy. Thus incoming and outgoing resonances can be simultaneous achieved if the energy difference between the two intermediate states equals a phonon energy ($\omega_i - \omega_j = \omega_{ph}$).

In such doubly resonant Raman scattering (DRRS) processes both denominators in equation 2.25 resonate simultaneously. In quantum well structures, the DRRS condition has been achieved through choice of the quantum well dimensions [2.11] or by applying an electric field perpendicular to the
quantum well layers [2.12]. In bulk materials similar DRRS conditions are satisfied by use of uniaxial stress to tune the valence-band states [2.13], or applying a magnetic filed to adjust the Landau-level energies [2.14].

Second order phonon scattering involves two phonons. It is therefore possible to achieve a triply resonant Raman scattering process by carefully adjusting the energy differences between intermediate states to match the energies of both phonons. A general discussion of second order phonon scattering is a wide subject and is therefore not presented here. However, we will discuss second order phonon scattering processes and triply resonant conditions in a quantum well system in section 3.4.

2.3.4 Conservation laws and selection rules

The kinematics of Raman scattering processes are governed by energy conservation

\[ \omega_n = \omega_L \pm \omega_R \]  \hspace{1cm} (2.26)

and momentum conservation

\[ k_n = k_L \pm q_R \]  \hspace{1cm} (2.27)

Equation 2.26 reiterates that in a Raman experiment, the
energy of the excitation corresponds to a shift in energy from the laser frequency.

For typical visible photon wavevector, momentum conservation law for the phonons can be re-expressed as:

\[ q_R \approx 0 \]  

(2.28)

Raman scattering is thus often described as a probe of zone center \( q_n = 0 \) phonons.

The dependence of the Raman scattering cross section on a tensor \( \chi_a \) in equation (2.16) has led to the definition of a "Raman tensor" \( R \) as

\[ \frac{\partial^2 \sigma}{\partial \omega \partial \sigma} \sim |e_a \cdot R \cdot e_L|^2 \]  

(2.29)

The spatial properties of the scattering medium represented by \( R \) can then be described by the irreducible representations of its symmetry group. Let \( \Gamma_R \) be the irreducible representation appropriate to the excitation, and \( \Gamma_{vs} \) and \( \Gamma_{vl} \) the irreducible representations for the polar vectors \( e_a \) and \( e_L \) in the point group of the crystal. For the scattering cross section (equation 2.29) to be invariant, \( \Gamma_R \) must contain components which vary like the irreducible representations
\[ \Gamma_R = \Gamma_{vR} \times \Gamma_{vL} = \Gamma_{R1} + \Gamma_{R2} + \ldots \ldots \] (2.30)

Poulet and Matthew [2.15] provide a full account of the selection rules and symmetry properties of the Raman tensor and are tabulated in several references [2.1,2.15]. \( R \) is also discussed specifically for the tetragonal point groups \( D_{2d}, D_{2h} \) and \( D_{4h} \) in the appendices of this thesis since they relate to the GaAs/AlGaAs quantum wells and YBaCuO high temperature superconductors.

From equation 2.30 it is seen that the symmetry properties of the scattering cross section are determined by the symmetry properties of the Raman tensor. The spatial symmetry properties of the scattering medium hence yields different cross sections for different light scattering geometries from the same sample. In particular the cross sections for specific polarizations of incident and scattered radiation may vanish.

### 2.4 Properties of GaAs/Ga_{1-x}Al_{x}As quantum wells

There are several reviews on the electronic and phononic properties of semiconductor quantum wells [2.16,2.17]. We hence present only a brief introduction to these features of GaAs/Ga_{1-x}Al_{x}As quantum wells and discuss the electron-phonon interaction that is central to the triply resonant Raman process presented later.
2.4.1 Electronic states and excitonic effect in quantum wells

In bulk GaAs, like many III-V semiconductors, the electronic band edges relevant to optical and transport properties have $\Gamma_6, \Gamma_7$, and $\Gamma_8$ symmetries (figure 2.2). The $\Gamma_6$ symmetry identifies with the bottom of the conduction band and $\Gamma_8$ with the top of the valence band. In the valence band, light and heavy hole bands are degenerate at zone center. The $\Gamma_7$ valence band is spin-orbit split from the $\Gamma_8$ edge ($\Delta = \epsilon_{r_8} - \epsilon_{r_7} = 0.341$ ev [2.18]). The periodic parts of the Bloch functions at the $\Gamma_6, \Gamma_7, \Gamma_8$ edges are listed in table 2.1. Here $|s>, |x>, |y> \text{ and } |z> \text{ denote periodic functions which transform like atomic S, P}_x, \text{ P}_y \text{ and } \text{ P}_z \text{ functions transforming as } x, y, z \text{ under the T}_d \text{ point-group operators to map the local tetrahedron onto itself. } |\uparrow> \text{ and } |\downarrow> \text{ are the spin eigenfunctions. The energy gap } \epsilon_0 \text{ is } 1.48 \text{ ev [2.19] at room temperature and increases with decreasing temperature [2.20].} \text{ }

On neglecting barrier penetration in a semiconductor quantum well, the motion of electrons and holes is confined in a direction normal to the layers. The wave function for conduction-band electrons in a single quantum well can be represented as [2.21]

$$|E^{\uparrow}(\downarrow)> = A^{-1/2}e^{i\mathbf{k} \cdot \mathbf{r}}f(z)U_1 , \quad (i=1,2) \quad (2.31)$$
Fig. 2.2. Band structure of bulk GaAs showing the main interband critical points.
Table 2.1. Periodic parts of Block functions at the \( \Gamma_6, \Gamma_7, \Gamma_8 \) edges of GaAs bulk crystals. \( j \) denotes total angular momentum of the carrier \( (j = 1/2 \text{ or } j = 3/2) \) and \( m_j \) its quantum projection along z-axis.

<table>
<thead>
<tr>
<th>( u_i )</th>
<th>( \mid j, m_j \rangle )</th>
<th>( \Psi_{j m_j} )</th>
<th>( E(k=0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u_1 )</td>
<td>( \mid 11/2, 1/2 \rangle )</td>
<td>( \mid S \uparrow \rangle )</td>
<td>0</td>
</tr>
<tr>
<td>( u_3 )</td>
<td>( \mid 13/2, 1/2 \rangle )</td>
<td>(-\sqrt{2/3} \mid Z \uparrow \rangle + \sqrt{1/6} \mid (X+Y) \downarrow \rangle )</td>
<td>(-\varepsilon_0 )</td>
</tr>
<tr>
<td>( u_5 )</td>
<td>( \mid 13/2, 3/2 \rangle )</td>
<td>( \sqrt{2/3} \mid (X+iY) \uparrow \rangle )</td>
<td>(-\varepsilon_0 )</td>
</tr>
<tr>
<td>( u_7 )</td>
<td>( \mid 11/2, 1/2 \rangle )</td>
<td>( \sqrt{3} \mid (X+Y) \downarrow \rangle + \sqrt{1/3} \mid Z \uparrow \rangle )</td>
<td>(-\varepsilon_0 - \Delta )</td>
</tr>
<tr>
<td>( u_2 )</td>
<td>( \mid 11/2, -1/2 \rangle )</td>
<td>( \mid S \downarrow \rangle )</td>
<td>0</td>
</tr>
<tr>
<td>( u_4 )</td>
<td>( \mid 13/2, -1/2 \rangle )</td>
<td>(-\sqrt{1/6} \mid (X-Y) \downarrow \rangle - \sqrt{2/3} \mid Z \downarrow \rangle )</td>
<td>(-\varepsilon_0 )</td>
</tr>
<tr>
<td>( u_6 )</td>
<td>( \mid 13/2, -3/2 \rangle )</td>
<td>( \sqrt{2/3} \mid (X-iY) \downarrow \rangle )</td>
<td>(-\varepsilon_0 )</td>
</tr>
<tr>
<td>( u_8 )</td>
<td>( \mid 11/2, -1/2 \rangle )</td>
<td>(-\sqrt{3} \mid (X-iY) \uparrow \rangle + \sqrt{1/3} \mid Z \downarrow \rangle )</td>
<td>(-\varepsilon_0 - \Delta )</td>
</tr>
</tbody>
</table>
where \( \mathbf{U}_i \) are the band edge functions listed in table 2.1. \( \mathbf{U}_1 \) and \( \mathbf{U}_2 \) correspond to spin parallel and anti parallel to the \( z \)-axis. \( \mathbf{k} \) is the wave vector in the \( xy \) plane and \( A=(N\alpha_0)^2 \) is the cross-sectional area. In the infinite barrier approximation, the \( n \)th electron subband is characterized by the envelop function \( f(z) \), which is a sinusoidal function with a \( z \)-axis wave vector \( q = n\pi/d \), \( (n=0,1,2...) \), where \( d \) is the well thickness. The first two electronic subbands \( C_0 \) and \( C_1 \) are shown schematically in figure 3.1(a).

Due to the fourfold degeneracy of the valence-band in bulk GaAs, their effective-mass wave functions are more complex than the conduction band. For \( \mathbf{k} \approx 0 \), the hole states in the quantum well at \( \Gamma \) can be divided into heavy and light hole states that are represented by the valence-band-edge functions

\[
|H>_i = A^{-1/2}e^{ik\cdot r}g(z)\mathbf{U}_i, \quad (i=3,4,5,6)
\]

\( \mathbf{U}_i \) are the band edge functions shown in table 2.1. \( \mathbf{U}_5 \) and \( \mathbf{U}_6 \) identify with the heavy hole and have values of \( 3/2 \) and \(-3/2 \) for the \( z \) component of angular momentum. \( \mathbf{U}_3 \) and \( \mathbf{U}_4 \) are corresponding functions for the light hole. \( g(z) \) is the envelope functions which have similar characteristics as \( f(z) \) in equation 2.31. The first heavy-and light-hole
levels $\text{HH}_0$, $\text{LH}_0$ are illustrated in figure 3.1(a).

The electron and hole states are coupled by their Coulomb interaction leading to excitonic states. A two-subband exciton state $|\text{CHH}_0\rangle$ derived from the first electron subband ($\text{C}_0$) and the first heavy-hole (light hole) $\text{HH}(\text{LH})$ subband ($\text{HH}_0$ or $\text{LH}_0$) can be described as [2.22]

$$
|\text{CHH}_0(\text{CLH}_0)\rangle = S^{1/2} \sum_k G(k)f_0(z)U_1g_0^*(z)U_4^*
$$

(2.33)

where $i=1,2$, $j=3,4,5,6$ and $G(k)$ is the exciton correlation function in $k$ space. In the Wannier-Mott bulk exciton model we have [2.23]

$$
E_{\lambda,k} = E_g + \hbar^2 |k|^2 / 2m_r + \Delta E_{\lambda}
$$

(2.34)

where $\Delta E_{\lambda} = -R/p^2$ is the exciton binding energy, $p = 1,2,\ldots$, for the discrete spectrum, and $m_r = m_e + m_h$. $m_e (m_h)$ is the electron (hole) effective mass. $R$ is the exciton Rydberg and $E_g$ the energy gap between the bulk GaAs valence and conduction bands. Figure 3.7 shows schematically, the band structure of two exciton bands, $\text{CHH}_0$ and $\text{CLH}_0$. The dotted lines identifies the lifetime broadened exciton band.

2.4.2 Confined Optical Phonons in Quantum Wells

Optical phonons within a quantum well have been shown
[2.24] to be confined in the z direction with unrestricted in-plane wave vectors \( k_{r//} \). By using the dielectric continuum model, the LO and TO confined phonon mode frequencies in a quantum well can be derived. Similar to the case of the electronic wave functions, we introduce the wave vector \( k_z \) along z. Here, \( k_z = n\pi/w, n=1,2,... \) where \( w = d + a \), d is the well thickness and a is the lattice constant [2.25]. If we take the y-axis to lie along \( k_{r//} \), there are two types of TO phonons; one polarized parallel (referred to as TO\(_p\)) and the other perpendicular to the yz plane (referred to as TO\(_n\)). Their displacements can be represented as [2.26]

\[
\begin{align*}
\mathbf{u}_{\text{TOP}} &\propto \begin{pmatrix} 0 \\ i\frac{\partial \phi_n(z)}{\partial z} \\ k_{r//}\phi_n(z) \end{pmatrix} \\
\mathbf{u}_{\text{TON}} &\propto \begin{pmatrix} \psi_n(z) \\ 0 \\ 0 \end{pmatrix}
\end{align*}
\]

The displacements of the LO phonon can be described similarly

\[
\begin{align*}
\mathbf{u}_{\text{LO}} &\propto \begin{pmatrix} 0 \\ ik_{r//}\phi_n(z) \\ -\frac{\partial \phi_n(z)}{\partial z} \end{pmatrix} \\
\end{align*}
\]

The various order confined \( \phi_n(z) \), \( \psi_n(z) \) functions are given by
\[ \varphi_n(z) = \cos(n\pi z/w) - (-1)^{n/2} \quad n = 2, 4, 6, \ldots \]
\[ \varphi_n(z) \sim \sin(n\pi z/w) \pm 2(z/w) \quad n = 3, 5, 7, \ldots \] (2.38)

and

\[ \psi_n(z) = \cos(n\pi z/w) \quad n = 1, 3, 5, \ldots \]
\[ \psi_n(z) = \sin(n\pi z/w) \quad n = 2, 4, 6, \ldots \] (2.39)

We see that if \( k_y = 0 \), the LO modes are polarized along \( z \), the TO\(_{p}\) modes polarized along \( y \) and TO\(_{s}\) modes are polarized along \( x \). Since the quantum well structure belongs to the point group \( D_{2h} \) (Appendix B), phonons which correspond to \( n=\text{odd} \) have \( B_z \) symmetry because they have symmetric displacement amplitudes (relative to midlayer plane) while \( n=\text{even} \) phonons have \( A_1 \) symmetry which have antisymmetric displacement amplitudes.

Raman scattering measurements have been used extensively to study confined optical phonons in single quantum wells [2.27] and superlattices [2.28,2.29]. We present in figure 2.3 the Raman spectrum revealing confined LO phonons in a quantum well (QW3, see chapter III). The spectrum was recorded with the incident light energy equal to the energy of CHHO exciton. We observe a strong peak LO\(_2\) (292 cm\(^{-1}\)) and a few weaker peaks LO\(_m\) (\( m = 4, 6 \)). These results are comparable to those reported in Ref. 2.30.
Fig. 2.3. Resonant Raman spectra from a quantum well (QW3, see chapter III) with incident radiation energy close to the first heavy-hole exciton energy showing confined phonons $LO_2$, $LO_4$, and $LO_6$. The measurement was done at 8K and using 20 mW, 1688.7 meV incident radiation.
3.1 Introduction

Remarkable advances in semiconductor technology have made possible the fabrication of artificial microstructure with dimensions comparable to interatomic distance [3.1]. The availability of this class of semiconductor structures creates new avenues for the investigation of the physics of condensed matter under conditions of greatly reduced dimensionality where "quantum size" phenomena become apparent. In the case of electrons, quantum size effects occur when the physical dimensions are comparable to the characteristic lengths that determine electron behavior: the wave packet de Broglie wavelength, the Bohr radii, and the mean free path. These characteristic lengths range between 10 Å and 100 Å in the most common semiconductors. On the other hand, the propagation of atomic vibrations (acoustic and optic phonons) can be also effected by the reduced dimension which become comparable to the unit cell size
which varies between about 1 Å and 10 Å.

Semiconductor microstructure have also found many applications. Among the many semiconductor devices which utilize the concept of quantum confinement [3.2] are the semiconductor diode laser and charge coupled device detector.

Molecular beam epitaxy (MBE) [3.3] and metalorganic chemical vapor deposition (MOCVD) techniques are two methods routinely used to fabricate such heterostructures. The closely lattice-matched GaAs/GaAlAs heterostructure is the most widely used system and has now been perfected to a high degree.

Consequences of the "unique axis" normal to the layers in these artificial structures has revealed a wealth of novel physical phenomena. The unique axis represents the direction in which electron motion is strongly altered by ultrathin layering [3.4]. On the other hand, the carrier motion parallel to the layers is not substantially modified. On atomic vibrations, the propagation of optical phonons is confined along this special axis [3.5,3.6], while the interface between the two materials results in vibrations that have finite amplitudes localized near the interface [3.7].

Resonant Raman scattering has proven to be very effective in probing the vibrational, electronic and
electron-phonon interactions in semiconductors [3.8 - 3.10]. This chapter describes a resonant Raman scattering study of GaAs/GaAlAs quantum wells (QW). Our measurements have revealed the existence of a new Raman excitation associated with difference phonon scattering in quantum wells.

The next section describes the samples used and details of the experiment. The results revealing the (LO-TO) difference phonon mode will be presented in section 3.3. We discuss the well thicknesses and incident laser frequency dependence of this excitation. In section 3.4, a triply resonant process is established to describe this Raman mode.

We discuss the selection rules and demonstrate that the deformation potential mediated electron-phonon interaction is especially important to this process. To confirm our triply resonant model, in section 3.5 we present the results of measurements under uniaxial stress that was used to tune the subband energy spacings. Finally, we discuss the role of photo-induced phonons in the Raman scattering process.

3.2 Samples and experimental details

A typical GaAs/Ga$_{1-x}$Al$_x$As quantum well is shown in figure 3.1. The samples studied were grown by MBE at GTE laboratory. The wells were grown along the [001] direction on the (100) surface of a GaAs substrate. One wafer (called II-61) had five quantum wells with well thickness ($d_1$) of 5
Fig. 3.1. Sketch of a GaAs/AlGaAs quantum well. (a) Energy level structure of a GaAs/AlGaAs quantum well. The conduction electron subbands \( C_0 \), \( C_1 \) and heavy-hole subband \( HH_0 \), light-hole subband \( LH_0 \) are shown within the quantum well. (b) A quantum well with two \( 10^{-6} \) cm thick AlGaAs layers sandwiching a \( 2 \times 10^{-7} \) cm GaAs layer.
monolayer (ML) (1 ML ~ 2.56 Å), 9 ML, 14 ML, 25 ML and 46 ML and 58 ML respectively. The second wafer (II-62) had six quantum wells with $d_1$ of 7 ML, 11 ML, 18 ML, 28 ML, 39 ML and 80 ML. In order to avoid reabsorption effects, the wells in each wafer were grown such that the thickest quantum layer was furthest from the substrate. The growth rates and layer thicknesses $d_1$ were monitored through reflection high-energy electron diffraction (RHEED) oscillations. Since the substrate was not rotated during growth some fluctuations in $d_1$ were found across the sample. These fluctuations were more pronounced near the edges of the wafer. In order to minimize errors arising from such inhomogeneity, the peak of the luminescence was monitored prior to each Raman measurement. The barriers sandwiching the wells are 300 Å $\text{Ga}_0.68\text{Al}_{0.32}\text{As}$ layers. There is a half micron undoped GaAs layer between substrate and the quantum wells and a 200 Å GaAs cap layer on both wafers.

To confirm our results, two similar samples were grown at the University of California at Santa Barbara. One of these samples had wells of widths of 5, 7, 8, and 10 ML while the other had quantum wells of widths 6 and 9 ML. The barriers in these samples were the same as those in the wafers grown at GTE.

The Raman measurements were carried out in back-scattering along $z//[001]$ at 10 K. The spectra were excited
with less than 1 mW power from a cw LD-700 dye laser which was pumped by all red lines of the Kr+ laser. The intensity of the laser beam for measurements from different wells was calibrated via luminescence from a bulk GaAs sample. As a measure of the scattered intensity, we have taken the area of the observed peaks. We will present most of our spectra from four quantum wells in wafers II-61 and II-62 named as QW1, QW2, QW3 and QW4 with well thickness of 7 monolayer(ML), 9 ML 11 ML and 14 ML respectively. Quantum wells grown at UC Santa Barbara having well widths of 7 ML and 9 ML are named QW1' and QW2' respectively.

The discrete exciton states of quantum wells can be studied by absorption [3.4] or photoluminescence (PL) [3.11] techniques. We present in figure 3.2 the PL spectra from wafers II-61 and II-62 that contains the QW's studied.

The peaks in the PL spectra arise from the annihilation of excitons and the peak energy corresponds to that of free excitons or impurity bound excitons [3.12]. In the infinite well barrier approximation, the energy separation between the $C_0$ electron subband and HH0 heavy hole subband is approximately $E_0 + \pi^2\hbar^2/(2\mu d^2)$, where $\mu$ is the reduced mass of the electron and hole effective masses. As expected, figure 3.2 shows the thicker quantum wells having PL peaks at lower energies. The spectrum with the solid line corresponds to wafer II-61 while the dotted line refers to
Fig. 3.2. Photoluminescence (PL) spectra from wafers II-61 and II-62 that contain the quantum wells. Well widths are marked on top of each well. The four quantum wells identified as QW1, QW2, QW3 and QW4 have well thickness of 7 ML, 9 ML, 11 ML and 14 ML.
To observe the difference between the heavy hole exciton (CHHO) (electron in C and hole in HH0) and light hole exciton (LHH0) (electron in C and hole in LH0), photo excitation luminescence (PLE) spectra were measured. Two spectra from quantum wells (QW3 and QW4) are shown in 3.3.

3.3 Results of LO-TO difference phonon mode.

Figure 3.4(a) shows the resonant Raman spectra between -30 cm⁻¹ and +40 cm⁻¹ from the five quantum wells QW1, QW2, QW2', QW3 and QW4. The spectra show a broad background luminescence and the emergence and subsequent disappearance of the Stokes (R) and anti-Stokes (R') Raman peak at an energy of about 23 cm⁻¹. R is strong in QW2, QW2' and QW3 while R' is clearly evident in QW2 and QW3; thus excitations R and R' are observed in quantum wells nominally between 9 and 11 monolayer wide and absent from wells 7 (QW1) and 14 (QW4) monolayer thick. The peak is asymmetric, with the low energy tail evident to about 10 cm⁻¹. We will establish in this chapter that the excitation R arises from the difference scattering (LOₙ - TOₙ) of optical phonons confined to the quantum well.

Fig. 3.4(b) shows Raman spectra from QW3 recorded at five different incident radiation frequencies. The top
Fig. 3.3. Photoluminescence excitation (PLE) spectra from QW3 and QW4 showing the separation between HH$_0$ and LH$_0$. Measurements were at 10 K.
Fig. 3.4. Triply resonant effect observed by (1) choosing quantum wells with different well widths $d_i$ and (2) choosing different incident laser frequencies $\omega_L$. (a) Raman spectra from wells QW1 $\rightarrow$ QW4 and QW2'. The anti-Stokes peak R' is evident in QW2 and QW3. (b) Raman spectra from QW3 using different $\omega_L$. 
spectrum of Fig. 3.4(b) shows a weak R riding on a luminescence background. The intensity of peak R reaches a maximum at $\hbar \omega_L \sim 1691.21$ meV and diminishes to be immersed by the luminescence background when $\hbar \omega_L$ decreases below 1688.73 meV. It thus follows that mode R can be observed only within a narrow, 5 meV, range of exciting laser energies.

The spectral strength of R was largest when $\hbar \omega_L$ was tuned about 2.5 meV (20 cm$^{-1}$) above the corresponding photoluminescence (PL) peak. There are two possible reasons for this "blue shift" and are discussed in section 3.4.5. All Raman spectra in figure 3.4(a) were hence recorded with $\hbar \omega_L$ lying 2.5 meV (20 cm$^{-1}$) higher than the maximum of the corresponding PL emission.

In recording spectra of figure 3.4, the scattered radiation was not analyzed. In figure 3.5, we show that the scattering geometries $z(x',x')\bar{z}$ and $z(x',y')\bar{z}$ yield no difference to the peak intensities. This feature is consistent with selection rules described on page 50.

The most striking feature of Fig. 3.4(a) is the dramatic effect a few monolayer change in well width has on peak R. Since these structural modifications strongly perturb electron eigenstates, R must be closely associated with such states as confirmed below by the stress measurements. Moreover, since the experiments are resonant with spatially
Fig. 3.5. Peak R measured under different scattering geometries. Top spectrum was measured in \( z(x', x') \) and bottom in \( z(x', y') \) geometries at 10K.
confined, rather than extended, excitons our spectra are most sensitive to vibrational modes localized within the GaAs layer.

To determine the origin of mode R and to explain the resonance and polarization features, requires an understanding of the electronic and phononic properties of GaAs/Ga$_{1-x}$Al$_x$As quantum wells. An introduction to these properties was provided in chapter II.

3.4 (LO-TO) difference phonon mode and triply resonant Raman process

In this section we discuss the cross section for second order phonon scattering. We present the theory describing the (LO -TO) difference process that gives rise to the excitation R. This process involves a triply resonant Raman effect. Finally, a theoretical fit to the resonant profile is provided.

3.4.1. Triply resonant Raman process

In general triply resonant Raman processes results from scattering which involve two phonons. These events can be divided into combination processes (emitting two phonons) and difference (absorbing one phonon and emitting another) [3.13]. The microscopic theory of second-order scattering is described in a paper by Ganguly and Birman [3.14].
Feynman diagrams of three possible second order Stokes phonon scattering processes are shown in figure 3.6 with the intermediate state assumed to be excitons.

Since we are interested in resonant scattering mediated by difference phonon processes, the events in figure 3.6(a) will, as discussed below, dominate. This dominance arises because the energy difference between excitonic states $i_1$ and $i_2$ are close to phonon energies. We therefore only discuss this process which has two interaction vertices and three intermediate states. Each interaction is caused by a first order electron-phonon hamiltonian. We can extend equation 2.20 to second-order perturbation theory yielding

$$\left( \frac{\partial P_{10}}{\partial \xi} \right)_o = \sum_{i,j} P_{10}(0) \frac{\langle i \mid H_{ep} \mid j \rangle \langle j \mid H_{ep} \mid l \rangle}{(\omega_i - \omega_j)(\omega_j - \omega_l)}$$  \hspace{1cm} (3.1)

Introducing equation 3.1 to the Raman scattering efficiency discussed in chapter 2, we obtain the following term that is similar to $B$ in equation 2.21,

$$B = \sum_{i,j,l} \frac{\langle n_f \mid P_1(0) \mid n_i \rangle \langle i \mid H_{ep} \mid j \rangle \langle j \mid H_{ep} \mid l \rangle}{(\omega_j - \omega_o - \omega_l - \omega_n)(\omega_l - \omega_o - \omega_n - \omega_f)}$$ \hspace{1cm} (3.2)

$$\times \frac{\langle n_i \mid P_1(0) \mid n_o \rangle}{(\omega_i - \omega_o - \omega_n - \omega_f)}$$

Among the three denominators, the intermediate term can simultaneously resonate with the first(incoming) and the last(outgoing) denominators for appropriate wave vectors of
Fig. 3.6. Typical processes involved in second-order Raman scattering by phonons.
the scattering phonons. This condition provides a triply resonant condition for Raman scattering (TRRS).

Alexandrou et al. achieved conditions for triple resonance by tuning the valence subband separation to equal the energy sum of two optical phonons. This was realized by applying uniaxial stress on bulk GaAs [3.15], GaP [3.16] or choosing the thickness of GaAs/AlAs superlattice [3.17]. This triply resonant Raman scattering involves an iterated second-order phonon scattering (combination) which gives rise to a fourth-order process in perturbation theory.

The process giving rise to peak R in Fig. 3.4 is associated with a similar TRRS process which is schematically represented in figure 3.7. It shows the band structure of two exciton bands, CHHO and CLHO. The dotted lines sketch the lifetime broadened exciton band. As illustrated, the proposed scattering involves absorbing a TO phonon and emitting a LO phonon giving rise to an overall phonon difference scattering when the hole subband separation is close to the energies of TO and LO phonons. We will discuss this process by first introducing its Raman scattering efficiency.

3.4.2 Raman scattering efficiency

Using results of section 3.4.1, the Raman cross section can be written explicitly. Near the ground exciton the most
Fig. 3.7. Sketch of band dispersion of heavy-hole (CHH₀) and light-hole exciton (CLH₀) and the Raman scattering process under the triply resonant condition giving rise to peak R.
resonant contribution to the differential cross-section $d\sigma/d\Omega$ per unit volume for the scattering events of figure 3.7 is expressed as

$$d\sigma/d\Omega = \frac{[\omega_0 \omega_t^2 \eta_0 \eta_t]\left[(2\pi)^2 c^4(\hbar, \omega_t)^2\right]}{[(2\pi)^2 c^4(\hbar, \omega_t)^2]} |f_1 + f_2 + f_3 + f_4|^2$$  \hspace{1cm} (3.3)

where

$$f_1 = (m_0)^{-1} \sum_{K', K', K''} \frac{<0 | a_{k_0} H_H b_{k_0}^\dagger H_{HHK}|0> <0 | c_{\text{LO}, K', K''} b_{HH, K''} H_{EP} b_{HH, K'}^\dagger |0>}{[\omega + i\Gamma_3 - \epsilon_{\text{HHO}}(K'') + \Lambda_{\text{TO}}(k_0) - \Lambda_{\text{LOO}}(k_0)]}$$

$$\times \frac{<0 | b_{HH, K'} c_{\text{TO}, K_0}^\dagger H_{EP} b_{HH, K}^\dagger |0> <0 | b_{HH, K} a_{k_0} H_{EP} |0>}{[\omega + i\Gamma_3 - \epsilon_{\text{HHO}}(K') + \Lambda_{\text{TO}}(k_0)] [\omega + i\Gamma_3 - \epsilon_{\text{HHO}}(K)]}$$  \hspace{1cm} (3.4)

The state $|0\rangle$ represents the ground state of the system that has $m$ photons (emitted by laser), $n$ TO phonons (induced by incident radiation) and no excitons. The operators $a^\dagger(a)$, $b_{hh}^\dagger(b_{hh})$, $b_{hh}^\dagger(b_{hh})$, $C_{\text{TO}}^\dagger(C_{\text{TO}})$ and $C_{\text{LO}}^\dagger(C_{\text{LO}})$ are creation (annihilation) operators for a photon, a heavy- and light-hole exciton, and TO and LO phonons respectively. $H_H$, $H_{EP}$ describe the exciton-radiation and exciton-phonon interaction Hamiltonian respectively. $\Gamma_i$ ($i=1,2,3$) are the exciton lifetime broadenings at wave vector $K$, $K'$ and $K''$. $E_{\text{HHO}}(K)$ and $E_{\text{HHO}}(K)$ are respectively the ground heavy- and light-hole exciton energies. The factors $n^{-1}$, $m^{-1}$ arise from normalization factors of the intermediate states within the third and fourth matrix elements in the numerator.

$f_1$ describes the following process shown in figure 3.7.

(1) The incident photon in resonance with the fundamental gap is absorbed, creating a CHH, heavy hole exciton with the
hole in the ground heavy hole subband HH\( _0 \) and electron in
the lowest conduction subband C\( _0 \). (2) A confined optical
phonon of wavevector \((k_{//}, q)\) \((k_{//} \) along the plane and \(q\) along
\(z\)-axis) is absorbed and the exciton is scattered interband
into a CLH\( _0 \) exciton with the hole in the ground light hole
subband LH\( _0 \) and the electron remaining in C\( _0 \). (3) A second
confined phonon of wavevector \(-q\) is emitted and the exciton
is scattered, again interband, back to CHH\( _0 \). (4) Finally,
the exciton recombines and the scattered photon is emitted.
If a confined transverse optical phonon TO\( _n \) is involved in
step (2) while a longitudinal vibration LO\( _n \) mediates step
(3) (figure 3.7), the scattering gives rise to a Stokes
shifted peak corresponding to the energy difference \((E_{LO} -
E_{TO})\) of the two phonons. Anti-Stokes scattering will occur
if LO\( _n \) intervenes step (2) while TO\( _n \) takes part in (3) and
is described by amplitude \(f_2\). If the same type of phonon
(TO\( _n \) or LO\( _n \)) is involved in both step (2) and (3), no Raman
shift will be produced. These elastic scattering processes
are described by \(f_3\) and \(f_4\). Note that life time broadening
for each exciton band is shown in figure 3.7 and that the
energy difference \(\approx 3\) meV) between confined LO and TO
phonons involved in the scattering is less than the life
time deduced below for the CHH\( _0 \), CLH\( _0 \) bands.

Despite the exciton scattering twice from phonons, and
thus the higher order of perturbation theory, peak R is
observed because of the three strongly resonant denominators of equation 3.4. By tuning \( \omega_L \) to the heavy exciton, \((\hbar\omega_L - E_{\text{cmho}})\) tends to zero. Through judicious choice of structural dimensions for QW3 and QW2 (or via the tunability of hole states by uniaxial stress in other wells), the \( \Delta E = (E_{\text{clho}} - E_{\text{cmho}}) \) subband separation has been nearly matched to the confined optical phonon energies. This is evident in figure 3.3(a) where \( \Delta E \) from QW3 is 32.2 meV which is very close to the first confined TO phonon energy of 33.2 meV. The condition \( (\Delta E \sim \hbar\omega_{\text{TO}}) \) ensures the remaining two denominators of equation 3.4 are also near resonance. It is this unusual triple resonance that leads to the observation of an intrinsic fourth order Raman process from single wells only a few monolayer wide.

The absence of peak R from QW's 1 and 4 reflects the importance of the resonant denominators \((\hbar\omega_L - E_{\text{clho}} + \hbar\omega_{\text{pon}})\), \((\hbar\omega_L - E_{\text{cmho}} + \hbar\omega_{\text{TO}} - \hbar\omega_{\text{LO}})\). In these wells \( \Delta E \) differs from the optical phonon energies by several meV, and thus do not support a strong resonance (for example, \( \Delta E \) is 28 meV in QW4 as measured from PLE spectrum in figure 3.3(a)).

3.4.3. Exciton-photon interaction

We now discuss the selection rules for the triply resonant process and thus focus the next two subsections on the numerators in equation 3.4. The excitonic optical
transition matrix element $<0 | b_{\mu n, \kappa} H_{\text{er}} a_{\nu \lambda}^\dagger | 0>$ has been explicitly calculated in reference 3.18 and is applicable to the GaAs quantum well used in the present study. Here $b_{\mu n, \kappa}^\dagger | 0>$ refers to the exciton state CHH0 as described by step 1 of figure 3.7. In addition to depending on the electron and hole envelope functions $f(z)$, $g(z)$ and the exciton correlation $G(k)$ term, the exciton-photon matrix amplitude is proportional to $<U_i | p \cdot \epsilon | U_j>$. $p$ is the electron momentum and $U_i$, $U_j$ refer to the band edge conduction and four valence edge functions (table 2.1). This integral of $p$ can be readily expressed in terms of the following matrices [3.18]

$$
\begin{pmatrix}
P/\sqrt{2} & 0 & P/\sqrt{6} & 0 \\
-iP/\sqrt{2} & 0 & -iP/\sqrt{6} & 0 \\
0 & -P/\sqrt{6}/3 & 0 & 0
\end{pmatrix}
$$

for electron spin up

and

$$
\begin{pmatrix}
0 & -iP/\sqrt{6} & 0 & iP/\sqrt{2} \\
0 & -P & 0 & P/\sqrt{2} \\
0 & 0 & P/\sqrt{6}/3 & 0
\end{pmatrix}
$$

for electron spin down

(3.5)

The parameter $P$ is given by

$$
P = V_0^{-1} \int dr SP_x X = V_0^{-1} \int dr SP_y Y = V_0^{-1} \int dr SP_z Z
$$

(3.6)

In equation 3.5 the three rows identify with the $x$, $y$ and $z$ components of momentum while the four columns relate
respectively to the angular momentum components \( j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2} \) and \(-\frac{3}{2}\) band edge valence states described in section 2.4. A similar expression holds for the term 

\[ <0| a_{k\beta} b^{\dagger}_{+,\vec{m},\vec{k}'}|0> \]

that describes step 4 of figure 3.7, the final annihilation of the heavy hole-exciton CHH_0.

Following equation 3.5 we note that, in order to distinguish between \( j = \frac{3}{2} \) and \(-\frac{3}{2}\) CHH_0 excitons mediating the amplitudes \( f_1 \) and \( f_2 \), circularly polarized radiation must be utilized to excite the Raman process and circular components of the scattered photons must be analyzed. In our study however, only linear polarized radiation was measured and thus the heavy-hole excitons were not distinguished. This results in realizing the same intensity for peak R for the two scattering geometries utilized in figure 3.5.

3.4.4. Exciton-phonon coupling

The matrix element 

\[ <0| b_{\text{LH},k} b^{\dagger}_{\text{EP},\vec{k}} c^{\dagger}_{\vec{R},k'} b^{\dagger}_{\text{HH},\vec{k}'}|0> \]

relates to step 2, the interband exciton scattering of CHH_0 to CLH_0, of figure 3.7. The amplitude \( f_1 \) requires a TO phonon mediating this event and we hence only consider the deformation potential mechanism. In step 3 of figure 3.7, the CLH_0 exciton is returned to CHH_0 by a LO phonon. Hence this interband scattering described by 

\[ <0| c_{\text{LO},k'} b_{\text{HH},k'} b^{\dagger}_{\text{EP},\vec{k}} b^{\dagger}_{\text{LH},\vec{k}}|0> \]

in equation 3.4, can involve both
the deformation $H_{dp}$ and Fröhlich $H_{fr}$ electron-phonon coupling mechanisms [3.13]. Corresponding statements can be made for amplitude $f_z$.

The deformation potential interaction $H_{dp}$ arises from the perturbation of the periodic lattice potential by optic phonons and, in the linear approximation, can be represented as $H_{dp} = u \cdot U$ [3.19]. The vector $U$ is determined by energy band properties of GaAs and is independent of the mode displacement $u$. The integral of the $U$ functions between conduction-band-edge functions vanish due to symmetry. However several elements of the corresponding inter valence subband coupling matrix $D_{mn}$ are finite. This confirms that $H_{dp}$ does couple heavy- and light-hole subbands via transverse phonons $TO_p$ and $TO_o$.

There are special features of the interaction matrix $<0| b_{lr,k} H_{dp} C_{TO,k,q}^{*} b_{mn,k}^{*}|0>$ that provides insight into the symmetry of the TO phonons part taking in the interband scattering. In evaluating $<0| b_{lr,k} H_{dp} C_{TO,k,q}^{*} b_{mn,k}^{*}|0>$, integration along $z$ includes envelope functions $g_{oh}$, $g_{ol}$ associated with the ground heavy- and light-hole subbands. Thus only certain TO phonons with appropriate $z$ displacement vectors $u(z)$ would yield a non-zero interaction. Specifically since $g_{oh}$ and $g_{ol}$ are proportional to $\cos(\pi z/d_o)$, the deformation interaction can couple $CHH_0$ and $CLH_0$ exciton bands through transverse phonons whose displacements are represented by
even functions. From equations 2.35, 2.36, 2.38 and 2.39, it follows that this step can be mediated by $T_{O_p}$ and $T_{O_s}$ phonons of $B_2$ symmetry regardless of their in-plane wavevector. Moreover for $k_\perp \neq 0$ $T_{O_p}$ phonons of $A_1$ symmetry can scatter.

The deformation potential mediated scattering of LO phonons can be analyzed in a similar manner. In this case it follows from equations 2.37 and 2.38 that the two exciton bands $CHH_0$ and $CLH_0$ can be coupled through LO phonons of $A_1$ symmetry which have nonzero in-plane wavevector $k_\perp$. $B_2$ LO phonons can also mediate this same step regardless of their in-plane wavevector.

We note that the wave vectors of the first heavy- and light-hole state envelope functions are $\pi/d_0$ ($n=1$) while the displacement vector $u$ has a component of $m\pi/(d_0 + a_0)$. Thus it is the $B_2$ and $A_1$ phonons corresponding to $m = 1$ and $m=2$ that will provide the dominant contribution to interband scattering. Lower order confined optical phonons should hence yield the largest Raman intensity associated with amplitude $f_1$ and $f_2$. $(LO_1 - TO_1)$ and $(LO_2 - TO_2)$ difference modes have an energy of about 23 cm$^{-1}$. The $(LO_1 - TO_2)$ and $(LO_2 - TO_1)$ modes occur at 25 and 21 cm$^{-1}$ and cannot be resolved from the peak associated with $(LO_1 - TO_1)$.

We now turn to the Fröhlich interaction that may also mediate, via LO phonons, the scattering of $CLH_0$ exciton to
CHHₖ. The inter-band Fröhlich coupling between states |λ₁>, |λ₂> is described by <λ₁|q·p/q|λ₂> (1-δ₁₂) [3.8]. Scattering between the lowest heavy and light subbands |λ₁>, |λ₂> mediated by the q·p/q hamiltonian is hence forbidden because their band edge functions transform as x,y,z (table 2.1). On the other hand, intra-band scattering processes are described by the hamiltonian δ₁₂/q. In the presence of band-mixing between heavy and light hole states for kₓ ≠ 0, this Hamiltonian can couple LO phonons in scattering a ground (band mixed) light exciton to (or from) a ground (band mixed) heavy exciton state. Based on discussions in reference 3.18, only LO phonons of A₁ symmetry can mediate step 3 in figure 3.7 by the Fröhlich interaction. A (LO₂ - TO₁) difference mode may hence have higher intensity than a (LO₁ - TO₂) excitation due to the additional Fröhlich interaction mediating the LO₂ phonon. This could give rise to the asymmetrical shape of peak R.

3.4.5 Resonance Profile

To further explore the TRRS process we have proposed, the resonance profile of peak R as a function of ℏω₂ was studied. The results from QW3 are presented in figure 3.8. In order to normalize the peak intensities, each data point was calibrated with respect to the exciton photoluminescence peak of a bulk GaAs sample. Note that we only show the
Fig. 3.8. Resonant profile of peak R in QW3. Arrow identifies position of free exciton energy $E_x$ in equation 3.7.
profile for the \( z(x',x')z \) geometry. However, consistent with our discussion in section 3.4.3, the \( z(x',y')z \) scattering showed no difference in intensity. In figure 3.8 we have fitted the measured (*'s) resonant intensity profile of \( R \) to equation 3.3. In doing so, we have rewritten that part of equation 3.4 associated with Stokes scattering in the form

\[
A/[(\hbar \omega_l + i\Gamma_1 - E_1)(\hbar \omega_l + i\Gamma_2 - E_2)(\hbar \omega_l + i\Gamma_3 - E_3)]
\]  

(3.7)

Here \( A \) incorporates all prefactors of equation 3.3 and the numerator of equation 3.4. These prefactors are all taken to be independent of \( \hbar \omega_l \) over the limited energy range in which \( R \) and \( R' \) are observed. \( E_1, E_2 \) and \( E_3 \) are respectively the energy of the free heavy-hole exciton \( E_{\text{cH}0} \), the energy \( (E_{\text{cH}0} - \hbar \Omega_{ro}) \) and \( (E_{\text{cH}0} - \hbar \Omega_{ro} + \hbar \Omega_{lo}) \) and are hence all parameters that can be deduced from our measurements. To determine \( E_1 \), we utilize the PL peak from QW3. We observed that the highest intensity of \( R \) in QW3 was recorded when \( \hbar \omega_l \) was about 2.5 meV (20 cm\(^{-1}\)) above the PL peak of 1691.1 meV. Based on the discussion in the next paragraph that this maximum intensity occurs when \( \hbar \omega_l \) is 1 meV (8 cm\(^{-1}\)) above the free heavy hole-exciton, we place \( E_1 \) at 1692.6 meV. This energy \( E_1 \) is indicated by an arrow in figure 3.8. The difference between the free exciton energy and the PL peak
energy suggests that the major contribution to the PL spectra arises from trapped or bound excitons. $E_2 (1691.2$ meV) and $E_3 (1695.4$ meV) are directly derived from $E_1$ and the measured separation of 32.2 meV between the HH0 and LH0 peaks in the PLE spectrum (figure 3.3) and the optical phonon energies. $\Gamma_1 (= \Gamma_3 = 4.4$ meV) the lifetime broadening of the heavy-hole exciton, and $\Gamma_2 (= 6.8$ meV) the light-hole exciton lifetime are given by the width of HH0 and LH0 peaks in the same PLE spectrum (Fig. 3.3).

It follows that in fitting the data of figure 3.8, the only adjustable parameter in equation 3.7 is the constant $A$ that merely calibrates the y-axis. The result of our fitting is shown by the solid line in figure 3.8. The maximum of the profile is about 1 meV above the energy $E_1$ and results from an interference between the three resonant denominators of equation 3.4. This shift is not sensitive to within 10% of the chosen value of $E_1$ and thus is not affected by fluctuations in well width. The good agreement of the fit to the resonant profile, provides support for the proposed triply resonant Raman process.

We note that the first and third denominators of equation 3.4, $(\hbar \omega_L - E^{\text{cmo}})$ and $(\hbar \omega_L - E^{\text{cmo}} + \hbar \Omega_{\text{to}} - \hbar \Omega_L)$, have an energy difference of about 2.8 meV. However, the exciton lifetime broadenings ($\Gamma_1$) are larger than this energy difference and therefore the resonant conditions are
satisfied simultaneously; these conditions are illustrated in figure 3.7.

3.5. The effect of uniaxial stress on the triply resonant process

While the effect of selecting $\omega_\ell$ has been discussed in section 3.4.5, the role of the hole subband energy spacings $\Delta E$ in controlling the Raman activity of $R$ can be monitored through changes in the hole eigenstates. We have shown that the occurrence of $R$ and $R'$ in $QW2$, $QW2'$ and $QW3$ required the separation $\Delta E$ between $CHH_0$ and $CLH_0$ to be close to $TO$ and $LO$ phonon energies. Unfavorable subband spacings suppresses the scattering efficiency and thus the excitation is not observed from $QW1$ and $QW2$. Compressive uniaxial stress applied to the quantum well will allow $\Delta E$ to be continuously changed. We therefore investigated the TRRS process under the influence of uniaxial stress to confirm the importance of $\Delta E$ in the higher order Raman process.

Figure 3.9 presents Raman spectra recorded with the quantum wells under uniaxial stress. The stress was applied separately along both the [110] and [001] directions. Compressive uniaxial stress applied normal to the epitaxial layers decreases $\Delta E$ [3.20]. Fig. 3.9(b) shows that a moderate stress of about 0.4 kbar "tunes in" the resonance for $QW1$ when the subband spacing approaches the LO
Fig. 3.9. Raman spectra of QW4, QW2, under uniaxial stress $X$ applied along [110] showing the emergence of peak $R$ in (a) and its weakening in (c) respectively. (b) and (d) show the spectra from QW1 and QW3 under compression along [001]. The magnitude of $X$ was deduced from the shift of the luminescence. Some uncertainty in $\Delta E$ may arise from fluctuations (see text) in well width across the sample.
frequency from above. In contrast, the resonance is substantially weakened when QW3 is subject to a similar stress and Fig. 3.9(d) shows a significant reduction in the intensity of R when $\Delta E$ is estimated to be lowered by about 3 meV. Similarly, since in-plane compression along [110] moves the CHH0, CLH0 subbands apart [3.20], $\Delta E$ in QW4 was tuned into phonon resonance - Fig. 3.9(a). The small decreasing oscillator strength of R in QW2 (Fig. 3.9(c)) occurs when $\Delta E$ was increased moderately beyond the LO vibrational energy. In view of the discussion in the previous section, all Raman measurements were done with the incident light energy 2.5 meV above the corresponding PL peak position.

As stated in section 3.2, during growth of the wafers the substrates were not rotated and thus fluctuations in the well thickness of each quantum well are to be expected. This fluctuation is characterized by the presence of some regions of the well having widths of $(n+1)(a/2)$ in a nominally n monolayer quantum well [3.21], where $a/2$ is the thickness of a monolayer of GaAs. In order to have better control on the consequences of this nonuniformity in layer thickness, the above uniaxial stress measurements were reconfirmed by measuring the intensity of peak R and the hole subband spacing ($\Delta E$) simultaneously. This was achieved through PLE measurements.
Due to thermal population effects, the low temperature PL spectrum is dominated by the electron-hole recombination from layers of width \((n+1)(a/2)\). The dotted line in Fig. 3.10 is the PL spectrum of QW 4 at 5K. We note that the free exciton energy \(E'_{\text{CHHO}}\) should be about 1.5 meV higher than the PL peak which is dominated by bound excitons (see discussion on page 56). Therefore, the value of \(E'_{\text{CHHO}}\) is determined by adding 1.5 meV to the PL peak position. On the other hand, the PLE spectrum (solid line) reveals the exciton transitions in layers \(n(a/2)\) wide since detection was set on the high energy side of PL peak [3.21]. \(E_{\text{CHHO}}\) and \(E_{\text{CLHO}}\) identify the heavy- and light-hole excitons from layers \(n(a/2)\) wide. The energy difference between \(E'_{\text{CHHO}}\) and \(E_{\text{CHHO}}\) is about 6 meV. This difference is consistent with measurement by Weisbuch et al. [3.22] as being caused by monolayer well width fluctuation.

Figure 3.11 shows how \(E_{\text{CHHO}}, E_{\text{CLHO}}\) from QW 4 a well nominally \(n(a/2)\) wide, changes with increasing stress along [110]. Peak R is also evident in these PLE spectra. In order to reduce errors in evaluating the spectral strength \((I_R)\) of peak R under stress, care was taken in the selection of the PLE detection energy. In particular several PLE spectra were recorded for each stress, with detection set at different locations with respect to the CHH\(_0\) peak. The variation of \(I_R\) as a function of the energy separation \(E_{XR}\)
Fig. 3.10. 5K PL (dashed line) and PLE (continuous line) spectra of QW4 from the same spot. $E'_\text{CHHO}$ is the energy of heavy-hole exciton from $(n+1)(a/2)$ wide layer and lies about 1 meV above the maximum of the dashed line. $E_{\text{CHHO}}$ and $E_{\text{CLHO}}$ are the energies of heavy- and light-hole exciton from $n(a/2)$ wide layer.
Fig. 3.11. PLE spectra at 5K of QW4 under different uniaxial stress along [110]. The two broad peaks in each spectrum are from excitons CHH₀ and CLH₀ respectively. The peak R is the (LO-TO) difference phonon mode.
between R and the CHH₀ exciton peak was recorded at each stress condition. These experimental values (Iᵣ vs Eₓₓ) were then fitted to a parabola, which provided the maximum Raman peak intensity and its position with respect to the CHH₀ exciton energies for the given stress. The PLE spectra presented in figure 3.11 are those closest to the case when Iᵣ corresponds to the maximum given by the parabolic fit.

The observation of peak R in the top spectrum of figure 3.11 (1 bar) is surprising because ΔE is only 26.5 meV, which is well separated from the TO phonon energy. We suspect that the presence of R in this case is caused by scattering of phonons between Eₐ'chho band (from layers (n+1)(a/2) wide) and Eₐchho (from layer n(a/2) wide). The energy separation between these two bands is close to a TO phonon energy [(Eₐchho - Eₐ'chho) = (Eₐchho - Eₐchho) + (Eₐchho - Eₐ'chho) ≈ 32 meV]. We believe that R is not observed in a direct Raman measurement from QW4 under zero stress (figure 3.4) because the sample utilized for the Raman study was from the center of the wafer where width fluctuations are small while the PLE spectra (figure 3.11) were measured from the edge of wafer where large thickness fluctuations are more likely.

The maximum intensities Iᵣ as deduced from the parabolic fit described above are plotted (*) against ΔE in figure 3.12. Data for 1 bar stress are not included for reasons outlined in the previous paragraph. We again utilize
Fig. 3.12. The intensities of peak R under different uniaxial stress along [110] from QW4. The ΔE are measured directly from the PLE spectra.
equation 3.7 to describe the scattering cross-section of R under compressive stress along [110]. The solid line in figure 3.12 is a fit based on equation 3.7 for QW4 as a function of the subband spacing $\Delta E$. To obtain this fit, we took $(\hbar \omega_L - E_1 = 1 \text{ meV})$. At this condition $I_r$ is at a maximum, as evident from figure 3.8. Again, $\Gamma_1 (= \Gamma_3 = 4.25 \text{ meV})$ and $\Gamma_3 (= 5.85 \text{ meV})$ are measured from the PLE spectrum of QW4 in figure 3.3(a). Similar to the fit in figure 3.8, only the amplitude $A$ remains an adjustable parameter. The good agreement to the data thus further supports the claim that equation 3.4 correctly describes the excitation $R$. We note that $\Delta E$ measured from figure 3.11 is associated with layers $n(a/2)$ wide. However the peak $R$ arises from layers of thickness $(n+1)(a/2)$ because $\hbar \omega_L$ is in resonance with the free exciton in the wider $(n+1)(a/2)$ layers. Therefore $\Delta E$ (*'s in figure 3.12) should in fact be lowered by about 1 meV which is energy difference of $\Delta E$ between layers $(n+1)(a/2)$ and $n(a/2)$ wide [3.23]. This shift would not alter the quality of the fitting shown in Fig. 3.12.

3.6 Photo-induced phonons in triply resonant process

Since step 2 (figure 3.7) in the TRRS process involves absorption of a TO phonon, an occupation factor $n(\omega)$ must be included in the scattering cross section. On evaluating the operators in equation 3.4, a factor of $(m \cdot n)^{1/2}$ occurs in the
amplitude \( f_1 \) [3.24], where \( m \) and \( n \) are the number of photons and TO phonons in the ground state. At low temperature (< 10K), the equilibrium optical phonon population obeys the Bose distribution and is very small. It therefore follows that equilibrium phonons cannot mediate step 2 of figure 3.7. We hence consider the role of nonequilibrium phonons in the TRRS produced by the light scattering process itself.

The nonequilibrium phonons considered are photon generated and are evident in first order Raman scattering - figure 2.3. The factor that will allow such phonons to participate in the TRRS process is that they should live long enough to be scattered by excitons. Their lifetime has been measured and is about 5 ps [3.25] and was also found not to depend significantly on well thickness. On the other hand the electron-phonon scattering time, as measured by the interband coupling constant, is found to be at least two orders smaller than the phonon lifetime [3.25]. (Note although Ref. 3.25 calculated the scattering rate based solely on the Fröhlich interaction, scattering via the deformation potential yields a similar rate [3.26].) Photo-induced phonons can thus mediate the TRRS process.

The participation of photo-induced phonons can be verified by the power dependence of the Raman scattering intensity. As noted on previous page, the right hand side of equation 3.4 is proportional to \((m\cdot n)^{1/2}\). Photo-induced
phonons are created by first order Raman scattering and therefore their population \( n \) is proportional to \( m \), the number of incident photons. The Raman intensity of the TRRS is thus proportional to \( m^2 \). In the absence of absorption effects, \( m \) is determined by the power (\( P \)) of the incident beam. The Raman intensity of peak \( R \) should thus be proportional to \( P^2 \) if absorption effects are unimportant.

The results of the power dependence of the \( R \) in QW3 is shown in figure 3.13. Below a power density of 10W/cm\(^2\), the \( I_s \) was found to vary as \( P^{1.2 \pm 0.2} \) and saturates at higher power densities. A \( P^2 \) variation as discussed above was not found and reabsorption effects are believed to account for the decrease. This was confirmed by the power dependence of the confined LO phonons measured from the same sample. In the inset to Fig. 3.13, a nonlinear variation proportional to \( P^{0.6 \pm 0.2} \) was found for the intensity of the confined LO phonons where as a linear power dependence was expected. This behavior, namely a \( P^{0.6} \) dependence for one phonon and \( P^{1.2} \) dependence for peak \( R \), thus reveals the participation of photon-induced phonons in the proposed TRRS process.

In summary, we have observed a Raman excitation associated with the difference scattering of optical phonons in single GaAs quantum wells. These quantum wells are characterized by the \((E_{CLHO} - E_{CHHO})\) subband spacing being equal to an optical phonon energy and support a triply
Fig. 3.13. Power dependence of peak $R$ from QW3. The inset shows the power dependence of confined $LO_2$ phonon from QW3.
resonant Raman process. The Raman scattering efficiency is discussed in terms of the exciton-photon and exciton-phonon interaction. Both deformation potential and Fröhlich mediated interactions are discussed for coupling between excitons and confined LO, TO phonons. The resonance profile of peak R was measured and agreed well with the theory of the TRRS process. Uniaxial stress provides a convenient means to modify the electronic energy levels, thus allowing the resonant interaction to be tuned into wells whose structural parameters are not favorable for bearing the triple resonance. The power dependence of the Raman intensity was measured and utilized to reveal the participation of photo-induced phonons.
4.1 Introduction

The discovery [4.1,4.2] of high temperature superconductivity has been a major recent development in the physics community. While the BCS theory had successfully explained conventional (low $T_c$) superconductivity [4.3,4.4], the fundamental mechanism of high temperature superconductivity effect remains unclear. Central to the BCS theory is the interaction between phonons and electrons to create an effective attraction between electrons in the vicinity of the Fermi surface. As a result, it is advantageous for such electrons to condense into bound pairs with zero total momentum and spin and form the ground state - the so called Cooper pairs. This interaction leads to the well known isotope effect [4.5,4.6] which was convincing evidence of the phononic origin of the pairing mechanism.

In 1987, experiments performed on the high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ with oxygen isotopically substituted revealed no isotope effect [4.7], while a subsequent study showed a small isotopic shift of $\Delta T_c \sim 0.4$
K ± 0.1 K [4.8]. This suppression in $T_c$ was too small for the conventional BCS theory to explain the origin of high $T_c$ superconductivity. Since then, several mechanisms have been proposed. These theories include purely electronic pairing mechanisms that are of magnetic [4.9,4.10,4.11] and of charge fluctuation character [4.12,4.13]. Several observations however suggested the possibility of strong electron-phonon interaction existing in these materials that has several consequences upon superconductivity. Among these effects are the following: (1) The phonon density of states as measured by neutron time-of-flight spectroscopy shows pronounced softening as the high temperature materials are changed from insulating parent compounds to conductors and superconductors [4.14]. (2) The peak and notchlike structures of electron-phonon scattering rate determined from the mid-infrared conductivity [4.15]. (3) There are other experimental indications that the electron-phonon interaction is strong (e.g. tunneling spectroscopy [4.16], specific heat [4.17], thermal conductivity [4.18]). (4) There is recent evidence for a large isotope shift of $T_c$ for particular dopant concentrations in $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ [4.19].

We dedicate this chapter to the Raman study of $YBa_2Cu_3O_{7-\delta}(1:2:3)$ and $YBa_2Cu_3O_{8-\delta}(1:2:4)$ films to provide further experimental insight into the role of phonons and their
effect on superconductivity.

We first provide a brief introduction to the crystal structure of YBa$_2$Cu$_3$O$_{7-\delta}$ and YBa$_2$Cu$_4$O$_{8-\delta}$. Based on group theory analysis, the Raman activity of the materials are discussed. We then discuss the quality of the films used in our study and identify the correlation between these Raman modes and the vibration of atoms. Our results and the dependence of the Raman phonon frequencies on temperature, oxygen content are then presented. Finally in section 4.4, we will discuss the theory of the phonon self-energy modifications with temperature as presented by R. Zeyher and G. Zwicknagl (ZZ theory) [4.20]. Their theory is based on the Eliasberg strong coupling theory and attempts, among other results, to explain the temperature dependence of two Raman phonon modes associated with the CuO$_2$ planes.

4.2 Phonon symmetry analysis of Y$_1$Ba$_2$Cu$_3$O$_7$, Y$_1$Ba$_2$Cu$_3$O$_6$ and Y$_1$Ba$_2$Cu$_4$O$_8$

YBa$_2$Cu$_3$O$_{7-\delta}$ ($\delta<0.5$), consists of a pair of CuO$_2$ planes separated by a layer of CuO chains. The structure is shown in figure 4.1(a). Table 4.1 (a) gives positions of all atoms in the unit cell and their site symmetry. The YBa$_2$Cu$_3$O$_{7-\delta}$ (1:2:3) unit cell belongs to the D$_{2h}$(P$_{mm}$) space group which supports 36 optic phonon modes with representations (see Appendix C)
Fig. 4.1. Structures of the superconductor Y$_1$Ba$_2$Cu$_3$O$_y$ (1:2:3), semiconductor Y$_1$Ba$_2$Cu$_3$O$_6$ and superconductor Y$_1$Ba$_2$Cu$_4$O$_8$ (1:2:4). (a) Orthorhombic unit cell of 1:2:3. (b) Tetragonal unit cell of Y$_1$Ba$_2$Cu$_3$O$_6$. (c) Orthorhombic unit cell of 1:2:4. The unit cells of 1:2:3 and Y$_1$Ba$_2$Cu$_3$O$_6$ are their primitive cells. The 1:2:4 primitive cell is discussed in the text.
Table 4.1. Atom positions of Y$_i$Ba$_2$Cu$_3$O$_7$ and Y$_i$Ba$_2$Cu$_3$O$_6$ and their site symmetries.

(a) Orthorhombic Pmmm ($D^{12h}_2$)

\( a = b = 3.9 \text{ Å} \quad c = 11.8 \text{ Å} \)

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† occupancies O1A >> O1B << 1.0

(b) Tetragonal P4/mmm ($D^{7h}_4$)

\( a = b = 3.9 \text{ Å} \quad c = 11.8 \text{ Å} \)

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<tr>
<td>Ba</td>
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<td>mmm</td>
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<td>1/2</td>
<td>0.38</td>
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</table>

*occupancy O1 << 1.0
\[ \Gamma = 5A_g + 5B_{2g} + 5B_{3g} + 7B_{1u} + 7B_{2u} + 7B_{3u} \] (4.1)

The Raman active vibrations are symmetric (g) while the odd (u) modes are mutually exclusive ir phonons. \( A_g \) represents atomic vibration along the c-axis while \( B_{2g} \) and \( B_{3g} \) represent atomic vibrations along a- and b- axes.

In figure 4.2, we show the atomic displacement of optic phonon modes in the upper half of the unit cell. The motion of the atoms in the lower half may be easily obtained by extending the displacements of atoms symmetrically through the inversion center (Y-atom) to yield even parity for the Raman modes and odd parity for ir modes. Fig. 4.2 only shows \( B_{3g} \) and \( B_{2u} \) modes with atoms move along b-axis. The corresponding \( B_{2g} \) and \( B_{3u} \) may be obtained by changing the motion of atoms along a-axis.

The semiconductor phase \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) (\( x<0.5 \)) is tetragonal and has lost all or part of the oxygen in the chain (figure 4.1(b)) compared to the superconducting phase \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \). Table 4.1(b) gives the corresponding atomic positions in the unit cell and their site symmetry. This unit cell belongs to the \( D_{4h}^7(P4/mmm) \) space group supporting 33 optic phonon modes with representations (see Appendix C)

\[ \Gamma = 4A_{1g} + 1B_{1g} + 5E_g + 5A_{2u} + 1B_{2u} + 6E_u \] (4.2)
Fig. 4.2. Atomic displacements of optic phonon modes in Y$_2$Ba$_2$Cu$_3$O$_{7-δ}$. The atoms shown from the upper half of the unit cell in Fig. 4.1(a). The displacements can be extended easily to the lower half according to the symmetry (even or odd with respect to the center of inversion). [This figure is from Ref. 4.24].
Compared with modes in superconducting \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \), \( B_{2g} \) and \( B_{3g} \) vibrations merge into doubly degenerate \( E_g \) modes, since now the \( a- \) and \( b- \) axes are indistinguishable when the oxygen \( O(1) \) atom is removed. The single \( B_{1u} \) mode represents the out-of-phase \( O(2)-O(3) \) planar oxygen vibration along the \( c- \)axis.

The ordered defect structure, \( \text{YBa}_2\text{Cu}_4\text{O}_{8-x} \) (1:2:4) has a \( c- \)axis lattice parameter of about 27.2 Å, which is just larger than twice that in the 1:2:3 phase. The expansion in this parameter results from the insertion of an additional Cu-O chain to the 1:2:3 lattice, as shown in figure 4.1(c). This 1:2:4 unit cell thus consists of two unit cells of 1:2:3, shifted relative to each other by half of the \( a- \)axis lattice parameter. Table 4.2 shows positions of all atoms in the unit cell and their site symmetry. As shown in figure 4.1(c), the central section of the 1:2:4 unit cell is identical to the 1:2:3 unit cell. The 1:2:4 unit cell contains two primitive cells which is characterized by the same \( a \) and \( b \) vectors as the unit cell while the primitive \( c \) vector connects the central \( Y \) atom of figure 4.1(c) to one of the other \( Y \) atoms. The 15-atom 1:2:4 primitive cell has 42 optic phonon modes with representations (see Appendix C)

\[
\Gamma = 7A_g + 7B_{2g} + 7B_{3g} + 7B_{1u} + 7B_{2u} + 7B_{3u}
\] (4.3)
Table 4.2  Atom positions of Y$_2$Ba$_2$Cu$_4$O$_8$ and their site symmetries.

Orthorhombic Ammm ($D_{19h}$)

\[ a = b = 3.9 \, \text{Å} \quad c = 27.2 \]

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<td>O$_1$</td>
<td>4i</td>
<td>mm</td>
<td>0</td>
<td>1/2</td>
<td>0.22</td>
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</table>
Compared to the 1:2:3 superconducting phase, the double CuO chains introduce two A_g Raman active modes associated with chain atoms Cu(1) and O(1) moving along c-axis. There are also two chain modes associated with each of the symmetries B_2g and B_3g, representing the Cu(1) and O(1) moving along a- and b- axes.

4.3 Y_{1}Ba_{2}Cu_{3}O_{7-δ} and Y_{1}Ba_{2}Cu_{4}O_{6-δ} films

The high temperature superconducting films utilized in this thesis were grown in Professor T. Lemberger's group. They were produced by codeposition of Y from an e-gun, and Cu and BaF_2 through resistively heated sources onto a Y-stabilized ZrO_2 or SrTiO_3 substrate at ambient temperature in a vacuum system (P<10^{-6} Torr). The deposition rate from each source was monitored and controlled by a quartz crystal controller. Figure 4.3 shows a sketch of the deposition system. After deposition the film was slowly introduced into a tube furnace at 900 C that had had oxygen flowing in it for several hours. The oxygen was bubbled through distilled water at room temperature before flowing through the furnace to reduce the annealing time [4.21]. By control of the deposition rates, films on differently oriented SrTiO_3 substrates were also produced. Through different Cu deposition rates, 1:2:3 and 1:2:4 films were grown.

The films are characterized by resistivity,
Fig. 4.3. Schematic diagram of the co-evaporation system.
susceptibility, x-ray and Scanning Electron Microscopy (SEM) measurements. The properties of five films used in this thesis are summarized below.

(1) **Film 1:2:3C///:** 1:2:3 phase grown on (100) surface of ZrO$_2$ with film thickness about 5000 Å; $T_c = 89$ K (mid point between 10% and 90% of resistivity data, (curve (a), figure 4.4). The x-ray diffraction pattern of this film (curve 3, figure 4.5), with coincident (110) and (103) peaks that dominate the spectrum, shows that this film is oriented with the $c$ axis lying parallel to the substrate surface over most of the film. This is confirmed by SEM results (figure 4.6(a)) that reveal in addition that the surface has a smooth structure on the scale of microns.

(2) **Film 1:2:3C:** 1:2:3 phase grown on (100) surface of SrTiO$_3$ with a film thickness of about 5000 Å; $T_c = 91$ K (curve (f), figure 4.4). The strong x-ray diffraction peaks (curve 2 figure 4.5) from (002), (003), (005) and (006) planes, prove that the $c$ axis is predominantly oriented normal to the substrate surface. SEM studies from this film (figure 4.6(b)) shows that the surface is also largely smooth but supports a few random thin rod-shaped features, that may be misoriented growth with $c$ axis along the surface.

(3) **Film 1:2:4C///:** 1:2:4 phase deposited on (100) surface of SrTiO$_3$ with film thickness of about 5000 Å; $T_c = 78$K (mid
Fig. 4.4. Temperature dependence of the resistance of several $Y_{1.15}Ba_{2.2}Cu_{3}O_{7-\delta}$ films. The curves a and e are measured from as grown 1:2:3C, and 1:2:3C, films respectively. The other curves are measured from the 1:2:3C, film for various oxygen deficiency. These curves are labeled chronologically according to oxygen removal (b,c) and reintroduction (d,e). $T_c$ is measured by the midpoint between 10% and 90% of resistivity data from each curve.
Fig. 4.5. X-ray diffraction from 1:2:3C₉, and 1:2:3C₁ films. The diffraction from a sintered powder (curve 1) of the material is provided for comparison.
Fig. 4.6. Scanning Electron Microscope pictures of 1:2:3 and 1:2:4 films. (a) 1:2:3C, (b) 1:2:3C, (c) 1:2:4C, (d) 1:2:4C.
point between 10% and 90% of susceptibility data (curve (l), figure 4.7(a)) and a transition width $\Delta T_c$ of 2.5 K. Because the $a$ and $b$ lattice constants of 1:2:4 are very close to that of cubic SrTiO$_3$, x-ray diffraction peaks from a 1:2:4 film oriented with the $a$- or $b$- axes lying normal to the surface almost coincide with peaks from the substrate. Figure 4.8(a) shows the x-ray diffraction spectrum from a film grown similar to 1:2:4C//1. Higher resolution scans at angles in the vicinity of the substrate peaks and SEM image (figure 4.6(c)) reveals that about 70% of the 1:2:4 material has the $a$- or $b$- axes normal to the film. The remaining 30% has the $c$ axis normal to the film, which is evident from the (00l) peaks up to $l=16$ in figure 4.8(a). Figure 4.8(a) also shows the x-ray diffraction from a 1:2:3 film on the (100) face of SrTiO$_3$, in which nearly 100% of the $c$-axis is normal to the film. Comparison with the 1:2:3 phase thus confirms the larger $c$ lattice constant in the 1:2:4 phase.

(4) Film 1:2:4C//2: Similar to 1:2:4C//1 except the thickness is 2000 Å and the film has almost 100% $a$ or $b$ axis oriented normal to the film and the $c$-axis lying in the plane of the film. Figure 4.6(d) shows a SEM image having the smoothest surface among all the samples discussed in this thesis.

(5) Film 1:2:4C//3: 1:2:4 phase grown on (110) oriented
Fig. 4.7. Temperature dependence of the ac susceptibility of 1:2:4C/\textsubscript{111} and 1:2:4C/\textsubscript{113} films. The two curves on the top are measured from as grown 1:2:4C/\textsubscript{111} and 1:2:4C/\textsubscript{113} films. The other curves are measured from these two films after different annealing processes. T\textsubscript{Ar}, T\textsubscript{Oxy} stand for the annealing temperature in Argon and Oxygen gas respectively. Arrows point to the transition temperature of oxygen rich 1:2:3 phase converted by annealing the 1:2:4 films in Argon above 700 C and reannealing in Oxygen at 550 C.
Fig. 4.8. X-ray diffraction pattern of 1:2:4 and 1:2:3 films grown on (100) and (110) surfaces of SrTiO$_3$ substrate. Because the a and b lattice constants of substrate and films are very close, some peaks originating from these components of the structure coincide.
SrTiO₃; film thickness of about 5000 Å; $T_c = 80$ K and $\Delta T_c = 2.5$ K. X-ray diffraction peaks in figure 4.8(b) confirm that the c-axis lies in the film plane while, in contrast to all previous samples, the a- and b- axes are oriented at 45° to the substrate surface.

4.4 Raman Spectra and Effect of Temperature and Oxygen Content

Raman spectra of high temperature superconducting films reveal information on the phonon energies and their symmetries, the energy gap $2\Delta$, electron-phonon interactions and structural phase transitions due to different oxygen concentrations [4.22,4.23,4.24]. We thus divide this section into three parts: In the first, we discuss the Raman spectra from oxygen-rich films and compare them to predictions of group theory. We then present the temperature dependence of the Raman frequencies in 1:2:4 films. This will include the unusual behavior below $T_c$ of the modes associated with O(2)-O(3) atoms below $T_c$. Since light scattering has proven to be a good probe of the microscopic effects of oxygen depletion in superconducting films, we will discuss how the Raman spectra are modified with oxygen stoichiometry and correlate these changes to the superconducting properties.
4.4.1 Raman spectra of oxygen-rich films

Figure 4.9 shows Raman spectra of five fully oxygenated samples. These Raman peaks observed from both 1:2:3 and 1:2:4 films can be grouped into two categories: five modes (identified by arrows) seen both in 1:2:3 and 1:2:4 films; and four new modes (marked by *'s) which observed only in 1:2:4 which we associate with the CuO chains.

We now discuss our assignments of the Raman modes. We base our conclusions on group theory analysis, other Raman reports on 1:2:3 single crystals [4.25,4.26,4.27] as well as lattice dynamical calculations [4.25,4.28,4.29,4.30,4.31]. We first focus on the five modes seen in both 1:2:3 and 1:2:4 (arrows in figure 4.9). Several groups have assigned the peak at 337 cm$^{-1}$ (435 cm$^{-1}$) in oxygen-rich materials (films a to e) to modes involving the out-of-phase (in-phase) vibrations of the planar O(2)-O(3) atoms along the c axis. Recent [4.25] results from 1:2:3 single crystals have shown that the $\alpha_{zz}$ component of the diagonal Raman tensor of the 337 cm$^{-1}$ vibration is virtually zero. Here x, y and z correspond respectively to a, b, and c axes. Thus for an oriented 1:2:3 film this phonon should be absent from spectra recorded with light polarized along the c axis. The observation of this mode in film 1:2:3C$_{ab}$ from back scattering normal to the surface confirms the non-uniform orientation of the c axis. The non-uniformity is also
Fig. 4.9. Raman spectra at 10 K of 1:2:4 and 1:2:3 oxygen rich films. Arrows identify peaks observed in both 1:2:3 and 1:2:4, while asterisks indicate modes from the CuO chains. The dashed lines represent the background and hence the zero for inelastic scattering.
suggested by the SEM result in figure 4.6(a). Further confirmation of this assignment is evident in figure 4.9 spectrum (b) (film 1:2:3C), where the back scattered photon wave vectors are along the c axis. The strong 337 cm\(^{-1}\) peak observed is a direct result of the finite \(\alpha_{xx}, \alpha_{yy}\) Raman tensor components.

The peak at about 500 cm\(^{-1}\), the strongest feature in films 1:2:3C\(_{1/2}\), 1:2:4C\(_{1/4}\) and 1:2:4C\(_{1/2}\), results from the bridging oxygen O(4) vibrating along c [4.25-27]. The absence of the 500 cm\(^{-1}\) peak in figure 4.9(b) supports this assignment as the polarizability components \(\alpha_{xx}, \alpha_{yy}\) for this vibration are very small compared to \(\alpha_{zz}\) in 1:2:3 [4.25]. The features at 114 and 150 cm\(^{-1}\) are \(\Lambda_g\) optic modes of the Ba and Cu(2) atoms moving along the c axis.

There are four Raman modes which we observe in fully oxygenated 1:2:4 films that are not detected in fully oxygenated 1:2:3 films. These modes, marked with asterisks in figure 4.9, occur at 257, 301, 312, and 600 cm\(^{-1}\) at 10K. We tentatively identify these as modes to be associated with the CuO chains. The highest frequency mode at 600 cm\(^{-1}\) is most likely the Cu-O axial stretching \(\Lambda_g\) mode, [Cu(3)-O(1) and Cu(1)-O(5)], because eigenfrequency calculations [4.25,4.28-31] place asymmetric O-Cu-O stretches in the range 550 - 650 cm\(^{-1}\) where both oxygens are moving out-of-phase with each other. For similar reasons, the 257 cm\(^{-1}\)
mode is most likely the $A_g$ mode associated with Cu(1) and Cu(3) atoms in the primitive cell moving out-of-phase. The increased frequency compared to the 150 cm$^{-1}$ Cu(2) mode is consistent with the smaller separation [4.24] between Cu(1) and O(4) than between Cu(2) and O(4). This assignment of the 600 cm$^{-1}$ and 257 cm$^{-1}$ modes as $A_g$ vibrations is also consistent, as discussed in the next paragraphs, with their manifestation as relatively strong peaks in figure 4.9(c) and 4.9(d).

In addition to the seven strong features just discussed, there are weak peaks at 301 and 312 cm$^{-1}$ that appear clearly in spectra from samples 1:2:4C$_{1/2}$ and 1:2:4C$_{1/3}$ [figures 4.9(d) and (e)]. Based on their behavior in the oxygen depletion study to be discussed below, their frequencies vis-à-vis lattice dynamical calculations, and their weakness in the Raman spectrum, we assign them to $B_2g$ and $B_3g$ modes associated with the CuO chains.

Raman tensor analysis of the differences in Raman peak intensities among film 1:2:4C$_{1/3}$, the other 1:2:4 films, and 1:2:3C$_{1/2}$ reveals interesting information about the Raman tensor for several modes. Note that the Raman tensor of $A_g$ modes is diagonal in orthorhombic lattices [4.32]. The key difference between spectra from 1:2:4C$_{1/3}$ and the other films is that in 1:2:4C$_{1/3}$, the a and b axes are oriented at 45° to the film surface so projections of the electric field of the
incident light onto the a and b axes is the same. The main differences between the 1:2:4C$_{\ell}$/3 spectrum and the other 1:2:4 films are that all of the A$_g$ modes are weaker. Indeed, only the 337 cm$^{-1}$ [O(2)-O(3) out-of-phase] and 500 cm$^{-1}$ [O(4)] modes are clearly visible; the modes at 150 cm$^{-1}$ [Cu(2)], 257 cm$^{-1}$ [Cu-O chains], 435 cm$^{-1}$ [O(2)-O(3) in-phase], and 600 cm$^{-1}$ [Cu-O chains] are very weak. The Raman tensor for these latter four modes must have the form $\alpha_{xx}=-\alpha_{yy}$, $|\alpha_{zz}| << |\alpha_{xx}|$ so that the electric field in the a-b plane scatters weakly because the xx and yy signals cancel, and the electric field along the c axis scatters weakly because $\alpha_{zz}$ is small.

These results are surprising in light of the known Raman tensor for 1:2:3 [4.25]. In 1:2:3, the 150 cm$^{-1}$ mode has $\alpha_{xx} = \alpha_{yy}$ and $|\alpha_{zz}| \approx 1.2|\alpha_{xx}|$, so in 1:2:4 either $\alpha_{xx}$ or $\alpha_{yy}$ changes sign and $\alpha_{zz}$ is greatly reduced. In 1:2:3, the 337 cm$^{-1}$ has just the form above, namely $\alpha_{xx} \approx -\alpha_{yy}$, $|\alpha_{zz}| << |\alpha_{xx}|$, so its presence in the 1:2:4C$_{\ell}$/3 spectrum means that its symmetry is different in 1:2:4. In 1:2:3, the 435 cm$^{-1}$ and 500 cm$^{-1}$ modes have only $\alpha_{zz}$ non zero which would create no difference between 1:2:4C$_{\ell}$/3 and 1:2:4C$_{\ell}$/2 if the Raman tensor were the same in 1:2:4.

There has been a recent report [4.33] on the Raman activity of single crystals of 1:2:4. The Raman spectra are similar to those discussed in this thesis and there is
general agreement between results observed from 1:2:4 films and single crystals. The mode at \( \sim 230 \text{ cm}^{-1} \), however, has been assigned in this thesis to a "forbidden" Raman mode while it is identified in Ref. 4.33 as a \( B_{2g} \) vibration associated with the chain oxygen atoms. The results from single crystals also show that the Raman tensor of 150 cm\(^{-1}\), 337 cm\(^{-1}\) and 440 cm\(^{-1}\) appear to be consistent with those of the 1:2:3 phase. The Raman tensor of the 257 cm\(^{-1}\), 500 cm\(^{-1}\) and 600 cm\(^{-1}\) modes have a large \( xx \) component.

The reasons for these disagreements between films and single crystals are not clear at present, although the effect of a lack of perfect 1:2:4 film orientation may influence the results. It also remains for lattice-dynamical calculations to understand the significance, if any, of these differences.

4.4.2 Temperature Dependence of Raman Frequencies

Most of our studies on the temperature dependence of the Raman spectra were done on 1:2:4 films since both the 337 cm\(^{-1}\) and 435 cm\(^{-1}\) modes appear as strong features. Figure 4.10 shows the temperature dependence of the frequencies of several Raman lines observed in fully oxygenated 1:2:4C\(_{1/2}\). The solid lines are guides to the eye. The four lines we have associated with CuO chains are labeled as such, and they show no anomalous behavior at temperatures below \( \sim 80 \text{K} \),
Fig. 4.10. Temperature dependence of the frequencies of six phonon modes associated with CuO chains and CuO$_2$ planes in 1:2:4C$_{1/2}$. 
i.e. near Tc. This result is consistent with our expectations based on the Bi-related superconductors that have no "chains", thus showing that these linear elements are not as important to superconductivity as the CuO	extsubscript{2} planes. The modes at 150 cm\(^{-1}\) \([\text{Cu}(2)]\) and 500 cm\(^{-1}\) \([\text{O}(4)]\) also harden smoothly between 300K and 10K and hence are unaffected by the superconducting transition at the percent level.

As in 1:2:3 superconductors reported by several other groups \([4.25,4.34,4.35]\), the 337 cm\(^{-1}\) mode in the 1:2:4 films hardens as T decreases to T\(_{c}\) and then softens below T\(_{c}\). The anomaly is ~ 8 cm\(^{-1}\) in 1:2:3 single crystals \([4.26]\) while we observed a much reduced softening (3 cm\(^{-1}\)) in 1:2:3 films (not shown in this thesis). The overall softening of 337 cm\(^{-1}\) mode in film 1:2:4\(_{C/2}\) is only 2 cm\(^{-1}\), as shown in figure 4.10. The 337 cm\(^{-1}\) peak shows a weak asymmetry due to the interaction of this phonon with an electronic continuum \([4.26]\). Therefore we fit this mode to a Fano line shape \([4.36]\) to get the renormalized phonon energies. However, we find the asymmetry, as measured by the Fano q parameter, is much smaller than that found for the same mode in 1:2:3 single crystals \([4.24]\). The statistical uncertainty in the phonon frequencies from these fits were much smaller than the instrumental uncertainty of ± 0.5 cm\(^{-1}\).

Further, the 435 cm\(^{-1}\) \([\text{O}(2)-\text{O}(3), \text{in-phase}]\) mode in
1:2:4C\textsubscript{1/1} displays an enhanced frequency increase below \( T_c \) (figure 4.10). We observe similar enhancements in 1:2:4C\textsubscript{1/1} while in film 1:2:4C\textsubscript{3/3} the mode is too weak (figure 4.9(c)) to be studied accurately. To determine center frequencies, we fit this mode to a Lorentzian superposed on a weak linearly increasing background that is evident is figure 4.9(b). The larger error bars at the higher temperatures mainly reflect uncertainty in the fits and a larger scatter in the data above 200K. At lower temperatures, the instrumental uncertainty dominates the error bars. This hardening has also been recently reported in 1:2:3 superconductors [4.37]. However, it is observed more easily in 1:2:4 because the Raman intensity of this mode is higher [compare figures 4.9(a) and (b) to (d)].

We note that the 150 cm\(^{-1}\) mode [Cu(2)], which is the only other Raman active mode involving the CuO\(_2\) plane, gives rise to a strong Raman peak and is narrow enough to be studied with precision. However, no anomalous behavior was detected below \( T_c \) at a level of 0.5 cm\(^{-1}\). Since the 337 and 435 cm\(^{-1}\) phonons show opposite behaviors below \( T_c \), i.e., one softens while other hardens, while all other Raman modes including the 150 cm\(^{-1}\) Cu vibration behave normally, it seems unlikely that structural modifications are the cause of this unusual temperature dependence. A microscopic interpretation of the hardening and softening of the O(2)–O(3) vibration is
discussed in section 4.5.

4.4.3 Oxygen Depletion Study

There are several reasons to investigate the Raman activity in oxygen depleted superconducting films. The removal of oxygen from the superconductor can yield structural changes as well as changes in the carrier concentration and Raman scattering is sensitive to both these features. In addition, since films are generally too small for use in thermogravimetric analysis, there is a need for a secondary probe of their oxygen concentration. In the 1:2:4 phase, the oxygen resists removal at lower annealing temperature while it undergoes a phase transition to the 1:2:3 at higher annealing temperature [4.38]. Raman scattering can therefore be used to study structural changes on the atomic scale during this phase transition in 1:2:4 films.

a.) 1:2:3 films

We measured the Raman spectrum for the film 1:2:3C/, which, by repeated annealing in Ar or oxygen, was cycled reversibly through the orthorhombic → tetragonal → orthorhombic phase. Thus five different oxygen concentrations in the film 1:2:3C/, were studied, with each film labeled chronologically from a to e in figure 4.11.
Based on resistivity measurements, (figure 4.4 (a)-(e) corresponding respectively to films (a)-(e)) films a and e had the highest oxygen concentrations, near $\delta = 0$; b and d had low oxygen concentrations but were still in the orthorhombic phase and superconducting; film c had the lowest oxygen concentration, was tetragonal and not superconducting. Figure 4.11 shows the Raman spectra of the five different oxygen concentrations in the sample 1:2:3C, (a-e). Films a and e have the best resistive transitions for growth on ZrO$_2$ (see the temperature dependence of the resistance in figure 4.4, curve a and e) and very similar Raman spectra, showing the reversibility of the oxygen variation.

Let us first examine how the allowed modes are affected by oxygen depletion in 1:2:3 films, i.e., spectra (a)-(e) of figure 4.11. Of these only five $A_g$ modes are expected for $\delta = 0$ since depolarized scattering from single crystals have confirmed that the $B_{2g}$ and $B_{3g}$ vibrations are absent. The allowed phonons are apparent in all spectra from oxygen rich samples at approximately 114, 150, 337, 435 and 500 cm$^{-1}$. The phonon at 337 cm$^{-1}$ increases by a few wave numbers in the oxygen-depleted orthorhombic films b and d. There is no evidence for an increase in the Raman intensity associated with this mode in the orthorhombic phase, in contrast to some reports from sintered pellets [4.39]. In the
Fig. 4.11. Raman spectra of $1:2:3C_{\parallel}$ at 5 K after a sequence of annealing in argon and oxygen. The curves are labeled chronologically according to the curves in figure 4.3.
tetragonal phase (figure 4.11(c)), film c, this peak has stiffened to 342 cm$^{-1}$, and is clearly narrower and more intense than in the other spectra of figure 4.11. The mode at 150 cm$^{-1}$ softens to 141 cm$^{-1}$ in the tetragonal phase. Their softening in the semiconducting phase is consistent with the accompanying expansion of the unit cell along c axis. The peak around 504 cm$^{-1}$ softens to 478 cm$^{-1}$ in the non-superconducting state due to modifications of the c-axis lattice parameter upon oxygen depletion. We attribute the increasing width of the peak related to O(4) to a distribution of oxygen concentrations 6 and the proximity of O(4) to the chain oxygen O(1) from which oxygen is preferentially depleted. The latter could allow phonons associated with O(4), and having wave vectors away from the center of the Brillouin zone, to yield Raman scattering that would be forbidden in a perfect lattice.

When some oxygen is removed, but the lattice is still orthorhombic and superconducting (spectra (b) and (d), figure 4.11), the weak feature at about 570 cm$^{-1}$ seen in other films becomes a strong band containing several sharp modes. Additional modes appear at 232, 265 and 290 cm$^{-1}$ in this state. To assign the weak broad feature at 580 cm$^{-1}$, we note that lattice dynamical calculations have placed infrared active B$_{1u}$ phonons at 502 and 555 cm$^{-1}$. The observed enhancement of this structure with a decreased
oxygen concentration (spectra (b) and (d), figure 4.11) is consistent with it being assigned to these IR phonons associated with the chain and bridge oxygens rendered Raman active by the loss of translational symmetry. Indeed, peaks at 580 cm\(^{-1}\) have been observed in IR data from 1:2:3 ceramic material.

The structures at 232 and 630 cm\(^{-1}\), identified by arrows in curves (b) and (d) of Fig. 4.11, are assigned to the chain O(1) and Cu(1) atoms moving out-of-phase along the a and b axes, respectively. The highest frequency optic phonon has been estimated to be an IR active vibration at 576 cm\(^{-1}\) (except for a B\(_{2g}\) mode calculated at 586 cm\(^{-1}\) whose Raman polarizability is negligible). This mode supports the oscillations of the chain Cu(1) and O(1) atoms that we identify with forbidden scattering at 630 cm\(^{-1}\). Note that in the tetragonal structure, these forbidden peaks are absent/weak. The above assignments are hence consistent with oxygen being preferentially depleted from the chains, with the Cu-O planes sandwiching the Y being least susceptible to disruption.

Identification of the remaining weak oxygen-defect-induced structures at 264 and 290 cm\(^{-1}\) is more difficult with several likely candidates available. Based on the lattice dynamic calculations, these would include B\(_{3u}\) and B\(_{2u}\) in-plane vibrations and the B\(_{1u}\) O(2), O(3) vibrations along the
More data is required for any definitive conclusions.

b.) 1:2:4 films

Figures 4.12 and 4.13 show the Raman spectra of 1:2:4C/\(\alpha\) and 1:2:4C/\(\beta\) when fully oxygenated and after annealing for 90 minutes in flowing Ar at 500C, 600C, 700C, and finally for 60 minutes in flowing oxygen at 550C. Figure 4.7 shows the susceptibility of the 1:2:4 films subsequent to each of these annealing. In brief, the data from figures 4.7, 4.12 and 4.13 can be summarized as follows. Annealing in argon at 500C and 600C reduces \(T_c\), presumably by removing oxygen, and increases the width \(\Delta T_c\) of the transition. The modest decrease in \(T_c\) (only 10K in 1:2:4C/\(\beta\)) is consistent with the weak softening (~6 cm\(^{-1}\)) of the 500 cm\(^{-1}\) mode associated with O(4). In comparison, 1:2:3 films transform completely to the insulating state under identical annealing conditions and at the same time the O(4) Raman mode softens by 25 cm\(^{-1}\). This behavior of films 1:2:4C/\(\alpha\) and 1:2:4C/\(\beta\) hence reflects a greater stability of chain oxygen O(5) and O(1) in the 1:2:4 lattice due to bonding with Cu(3) and Cu(1).

A conjecture, which we have not verified directly, is that some oxygen diffuses into films from the SrTiO\(_3\) substrate at these annealing temperatures. The different response of 1:2:4C/\(\alpha\) and 1:2:4C/\(\beta\) to the 500C anneal may
Fig. 4.12. Raman spectra at 10 K of 1:2:4C/m film after a sequence of annealing in argon and oxygen. (a) Spectrum from as-grown film. (b), (c), (d) are spectra recorded after annealing for 90 minutes in argon at temperatures (T_Ar) of 500 C, 600 C and 700 C respectively. (e) spectrum subsequent to annealing in oxygen at 550 C for 60 minutes. The arrows and *'s identify features as in figure 4.11. ▽ (232 cm⁻¹) identifies a "forbidden" mode.
Fig. 4.13. Raman spectra at 10 K of 1:2:4C$_{113}$ film after a sequence of annealing in argon and oxygen. Annealing conditions similar to those of figure 4.12.
then arise from different rates of oxygen leaving the free surface of the film and being replaced by oxygen from the substrate. Diffusion rates have been measured [4.40] on SrTiO₃ and we estimate that during the 500C anneal, oxygen atoms within the substrate diffuse over a micron. Thus they could replenish some oxygen removed from the films during annealing with a steady-state oxygen concentration determined by the balance between these rates of oxygen intake and removal. A larger rate of oxygen loss from the (110) film surface than the (100) surface would account for the slightly stronger modifications to Tₒ and ΔTₒ of 1:2:4C₁/₃ following the 500C anneal.

Subsequent annealing at 600C has a negligible additional effect on Tₒ and ΔTₒ of both films. This suggests that the 90 minute 500C anneal was long enough to reach steady-state. Annealing at 700C for 90 minutes converts some 1:2:4 into 1:2:3 as well as further depleting oxygen from the 1:2:4 lattice, as indicated in figure 4.7 by the onset of the superconducting transition above 80K and its completion at about 40K. The occurrence of the kink in the inductive response above 80K indicates that the final 1:2:3 material has much more oxygen than is obtained when the 1:2:3 phase is annealed in Ar at 700C. The recent study by T. Wada, et. al. [4.38], using thermogravimetry and differential thermal analysis methods, has shown that the reciprocal of the 1:2:4
phase decomposition temperature $1/T_d$, is linearly proportional to the logarithm of oxygen partial pressure $P(O_2)$. Estimating $P(O_2) \sim 0.1$ Torr in our annealing process, we find the decomposition temperature is about 675°C, which is consistent with our results. Film 1:2:4C$_{1/3}$ correspondingly shows lower onset and finish temperatures than 1:2:4C$_{1/2}$, again consistent with the idea that the overall oxygen concentration is lower in 1:2:4C$_{1/3}$. The continued presence of chain modes (*'s figures 4.13, 14) subsequent to the 700°C anneal means that the conversion of 1:2:4 material into the 1:2:3 phase is incomplete. This inhomogeneity also explains the broadening of the O(4) line at 500 cm$^{-1}$ and its slightly increased central frequency relative to the spectra taken after the 600°C anneal.

Based on the disappearance of the chain modes from the Raman spectra of figures 4.12(e), 4.13(e), the similarity of these two spectra to the spectrum of 1:2:3C$_{1/2}$ [figure 4.9(e)], and the sharp transitions above 80K in the susceptibility measurement (figure 4.7), we conclude that the final oxygen anneal converts the remaining 1:2:4 material into the 1:2:3 phase. The 1:2:3 phase was also reconfirmed through x-ray diffraction. This final oxygen anneal was however not long enough to fully oxygenate the films and raise $T_c$ above 90K. The similarity of the Raman spectra of figures 4.12(e), 4.13(e) from 1:2:4C$_{1/3}$ and
1:2:4C\textsubscript{1/3}, suggests that the conversion to 1:2:3 results in films with similar distributions of crystalline orientations, regardless of the initial orientation.

There is one mode at 232 cm\textsuperscript{-1} that appears consistently only when oxygen is partially depleted from each film. The mode disappears after reannealing in oxygen and hence is most likely a forbidden mode. This mode, identified by V in figures 4.12 and 4.13, also occurs at the same frequency in partially oxygenated 1:2:3 films (figure 4.11). We suspect this to be a defect induced ir mode associated with the chain copper atoms.

4.5 Superconductivity-induced phonon self energies and their temperature dependence

In section 4.4.2, we have described the experimental results which showed the softening of the 337 cm\textsuperscript{-1} Raman mode and the non-thermal hardening of 435 cm\textsuperscript{-1} Raman mode below T\textsubscript{c}. As previously identified, these two modes are associated with the O(2)-O(3) atoms moving in- and out-of-phase. What does this temperature dependence imply and what is the physical origin of such behavior? We will address these questions in this section.

We first provide a very simple phenomenological model to explain how coupling between a single electronic state and the phonon modes can modify the phonon energies. In this
picture, depending on the relative energy of the phonons to that of the electronic state and the strength of the electron-phonon coupling, the phonon frequencies can renormalize to larger (harden) or smaller (soften) values in comparison to the uncoupled case. However, to obtain quantitative descriptions of (a) the temperature dependence of the phonon self-energy, (b) the magnitude of the phonon renormalization and (c) to deduce the value of the superconducting energy gap \(2\Delta\), we will discuss our results in terms of the recent theory by R. Zeyher and G. Zwicknagl (ZZ) [4.20]. Their theory provides a detailed description of the phonon self-energy and its dependence on the electron-phonon coupling constant, impurity scattering rate \(\tau\) and temperature. We will briefly discuss the main steps of the theory and present the major conclusions of their work. The greater focus in this thesis will be on the dependence of the phonon self-energy on temperature and the magnitude of superconducting energy gap.

Although the ZZ theory is based on the strong electron-phonon coupling mechanism and requires a large coupling constant \(\lambda = 2.9\) to explain the 93 K transition temperature, we note that measurements of \(\lambda\) in the high temperature superconductors are far from complete with the primary measurements being done on YBCO [4.41,4.42], NdCuO [4.43] and TlBaCaCuO [4.44]. In fact, there is a recent ab
initio frozen-phonon calculation by C. O. Rodriguez, et. al. [4.45] which has a calculated \( \lambda \) that is three times smaller than that predicted from the ZZ theory. Therefore, any agreement between our results and the ZZ theory only indicates the existence of strong electron-phonon interaction in our high \( T_c \) samples and shows the importance of this coupling to the phonon renormalization below \( T_c \). We do not, however, conclude the phononic origin of high temperature superconductivity.

4.5.1. Simple model of phonon renormalization due to the superconducting gap

The most important feature of the BCS theory is the occurrence of a superconducting energy gap \( 2\Delta \) below \( T_c \). It is generally agreed that there is (are) a superconducting energy gap (gaps) in the high \( T_c \) materials, although values of \( 2\Delta/kT_c \) varying from 3 [4.46] to as large as 13 [4.47] have been reported. These values are based on results from different techniques such as tunneling [4.47,4.48], infrared [4.46,4.49] and Raman [4.50,4.51] measurements on a variety of samples.

In the BCS theory, all superconducing electrons below the Fermi surface are paired to form the ground state of the system. Due to this pairing, the top of the ground state is an energy \( \Delta \) below the Fermi surface. In the excited state,
the density of electronic states has a maximum at an energy $2\Delta$ above the ground state [4.52] with states between the ground state and $2\Delta$ being suppressed. Assuming the high $T_c$ superconductors have a similar density of states which we describe, for simplicity, by a peak $\delta(E-2\Delta)$ at $2\Delta$. This is represented by $|e>$ in figure 4.14. In the normal state, the density of states in the vicinity of $2\Delta$ has little or no structure and hence we neglect its effect on phonons above $T_c$ within the simplified model. We further assume that, in the normal state there are two unperturbed phonon states ($|p_1>$, $|p_2>$ in figure 4.14) with energies $E_1$ and $E_2$ lying close to $2\Delta$, such that $E_2 > 2\Delta$ and $E_1 < 2\Delta$. In the superconducting state, the electron-phonon coupling is described by the matrix element $V_1$, $V_2$ between $|e>$ and states $|p_1>$, $|p_2>$. This produces a mutual repulsion between $|e>$ and $|p_1>$, $|p_2>$ which will move the two phonon states to new position $P_-, P_+$. Their energies ($E_1'$ and $E_2'$) are the roots of the secular equations (for simplicity $V_1$ are assumed to be real)

$$(E_i-E)(2\Delta-E)-V_i^2 = 0, \text{ where } i=1,2$$ (4.4)

This simple picture provides some insight into the phonon renormalization in the superconducting state. Namely, phonon modes with energies in the vicinity of $2\Delta$
Fig. 4.14. System with an electronic state at $E = 2\Delta$ and two phonon states $|P_1>$, $|P_2>$ coupled by matrix elements $V_1$, $V_2$. 
will respectively harden or soften with temperature below $T_c$ when their energies are larger or smaller than $2\Delta$. The magnitude of the renormalization will depend on the coupling constants $V_i$. We further see that for those phonons well separated from $2\Delta$ where the coupling is expected to be weak, the phonon self energies will be hardly influenced by the onset of superconductivity. Given the experimental results of section 4.4.2 showing that the $337$ cm$^{-1}$ mode softens while the $435$ cm$^{-1}$ hardens, $2\Delta$ can be approximately placed to lie between these frequencies.

The phonon lifetime, which is measured by the half width of the phonon peaks in Raman scattering, is described by the imaginary part of the phonon self energy and depends on the number of phonon decay channels. Due to the electron-phonon interaction, a phonon with energy higher than $2\Delta$ can decay by breaking a Cooper pair and reduce its lifetime. Therefore, its half width is expected to increase in the superconducting state. However, phonons which have energies less than $2\Delta$ are expected to sharpen because its energy is not sufficient to break a Cooper pair.

The lineshape of a phonon peak in a Raman spectrum is sometimes also determined by an interference interaction with the electrons. This gives rise to the so called Fano asymmetry. This effect has been observed in systems such as heavily doped semiconductors [4.53,4.54] and conventional
superconductors [4.55]. The asymmetry results from a
discrete phonon state interacting strongly with a broad
continuum of excitations. Light scattering studies of high
T_c compounds have provided evidence for such continuous
electronic features in both the superconducting and normal
states [4.56]. The presence of this continuum has led to a
characteristic Fano lineshape for some of the phonons in the
1:2:3 and 1:2:4 YBCO superconductors. These include the 337
cm⁻¹ 0(2)-0(3) vibration and the 116 cm⁻¹ Ba mode.

In describing the Fano asymmetry, let us consider the
Raman matrix elements T_e, T_p connecting respectively the
electronic ground state |g> to the electronic continuum (we
use ρ(E) to represent the state density of this continuum)
and to the phonon state |p> having a bare energy E_0. The
lineshape of the renormalized phonon as a function of energy
E is described by [4.57]

\[ I(ω) = \pi ρ(E)T_e^2 \frac{(q+\varepsilon)^2}{1+\varepsilon^2} \]  \hspace{1cm} (4.5)

where

\[ \varepsilon = \frac{E-E_0-V^2R(E)}{\pi V^2ρ(E)} \]  \hspace{1cm} (4.6)

\[ q = \frac{VT_p/T_e+V^2R(E)}{\pi V^2ρ(E)} \]  \hspace{1cm} (4.7)
R(E) is the Hilbert transform of the electronic state density ρ(E) and q is referred to as the asymmetry factor (or Fano q parameter). To fit our Raman data for the 337 cm⁻¹ mode, we modify [4.26, 4.58] equations 4.5 - 4.7 as

\[ I(\omega) = I_0 \frac{(q+\epsilon)^2}{1+\epsilon^2} + C \quad (4.8) \]

where

\[ \epsilon = \frac{E-E_0-\Delta E}{\Gamma} \quad (4.9) \]

\[ q = \frac{VT_p/T_c+\Delta E}{\Gamma} \quad (4.10) \]

where ΔE and Γ are the change in the phonon frequency and linewidth respectively. I₀ is a scaling factor and C is a constant that accounts for any frequency independent background. The phonon frequencies of this renormalized mode therefore occur at the energy \( E_0 + \Delta E \). It is this renormalized frequency that is plotted in figure 4.10. of section 4.4.2.

Table 4.3 lists the Fano asymmetry factor q for the 337 cm⁻¹ mode at different temperatures. The data do not reveal a clear systematic behavior. However, the smaller absolute values of q at temperatures just below \( T_c \) indicate a stronger electron-phonon interaction at those temperatures.

To quantitatively compare our results to the ZZ theory,
Table 4.3. Fano asymmetry factor $q$ of $337 \text{ cm}^{-1}$ mode at different temperatures. $\delta q$ is the uncertainty in $q$ and was evaluated in the routine in appendix D.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
<th>110</th>
<th>150</th>
<th>200</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta q$</td>
<td>0.3</td>
<td>0.4</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>
we now provide the main points of the theory and its major conclusions.

4.5.2 Highlights of Zeyher and Zwicknagl (ZZ) theory

While the BCS theory only considers the non-retarded interaction between electrons and phonons, the ZZ strong coupling theory includes the interaction between electrons and the effect of retardation. To simulate the real system, the theory considers the effect of impurities as well.

By introducing two-component Green's function and expanding it to lowest-order, ZZ calculated the change of the self-energy for optical zone-center phonons, $\Delta \Sigma_v = \Delta \omega_v - i \Delta \gamma_v$, of the $v'$th phonon mode due to scattering of pairs across the gap. They obtained the result that the relative change in the self-energy can be expressed as:

$$\frac{\Delta \Sigma_v}{\omega_v} = \lambda_v f(\omega_v/2\Delta)$$

(4.11)

where $f$ is an universal function of $\Omega = \omega_v/(2\Delta)$. The electron-phonon coupling constant $\lambda_v$ for the $v'$th mode is defined as

$$\lambda_v = 2N(0)<|g_{v}(k,k')|^2>_{RS}/\omega_v$$

(4.12)

in terms of the density of states per spin ($N(0)$) in the
normal state) and the average over the (normal state) Fermi surface (FS) of the square of the electron-phonon matrix element $g_v(k,k)$.

To obtain some insight into the form of the universal function $f$, we present the corresponding results in the weak-coupling (BCS) limit [4.37].

$$f(\Omega) = \begin{cases} 
-2x/\sin(2x) & \text{for } \sin(x) = \Omega < 1 \\
(2y-i\pi)/\sinh(2y) & \text{for } \cosh(y) = \Omega > 1 
\end{cases} \quad (4.13)$$

Since scattering only occurs when the phonon-energy $\omega$ exceeds the gap $2\Delta$, the self-energy is real for $\Omega < 1$ i.e. no lifetime broadening occurs because there are no electronic excitations below $2\Delta$ to support phonon damping. Moreover, since the interaction between the phonon and the gap-excitation result in their mutual repulsion, phonons with $\omega < 2\Delta$ soften ($f < 0$) while vibrations with energy $\omega > 2\Delta$ harden ($\text{Re } f > 0$). From equation 4.13, it is seen that $f \to -1$ for $\Omega \to 1$ while $f \to -\infty$ for $\Omega \to 1$; $f \to +1 - i\infty$ for $\Omega \to 1$, and $f \to 0$, for $\Omega \to \infty$. This means, that a low-frequency phonon softens by the relative amount $\lambda_v$ and that a phonon with frequency just above the gap hardens by the same relative amount $\lambda_v$.

However in the strong-coupling limit, an analytic expression of $f(\Omega)$ is not realized. The ZZ theory is based on a numerical calculation of the self-energy $\Sigma$ and their
results are shown in figure 4.15. Since they only present results for $\hbar/(2\Delta \tau) = 0$ and $\hbar/(2\Delta \tau) = 3$, we present results of the latter even though we estimate that $\tau$ in the 1:2:3 and 1:2:4 films we studied is about 6 times smaller. Nevertheless, there are several important results that can be derived from the ZZ calculation.

1.) The phonon self-energy is affected by their interaction with electrons. The real and imaginary parts of self-energy are proportional to the phonon energy and linewidth respectively. Phonons with energies lying near $2\Delta$ have the largest effect.

2.) Phonons with energies at about and below $2\Delta$ soften while phonons above $2\Delta$ harden.

3.) For $\hbar\omega_{\text{ph}} < 2\Delta$, the effective half width of phonons increases with temperature below $T_c$, then reaches a maximum when the gap passes through the phonon frequency, and finally decreases because the phonon enters the gap. For $\hbar\omega_{\text{ph}} > 2\Delta$, their effective half widths increase for temperature decreasing below $T_c$ (see Figure 4.15(b)).

4.) The strength of the electron-phonon interaction and the impurity scattering rate will determine the magnitude of the phonon frequency softening and hardening. Namely, the stronger the electron-phonon interaction, the bigger the changes to the phonon self-energies. The higher the impurity scattering rate, the smaller the degree of
Fig. 4.15. Numerical results of ZZ theory. (a) Relative phonon shifts $\delta\omega_0/\omega_0$ for 5 phonon frequencies as function of $T/T_c$ for $1/(2\Delta)=3$ using $\lambda=2.9$ and $\mu^*=0.25$. (b) Relative phonon widths $\gamma/\omega_0$ for 5 phonon frequencies as function of $T/T_c$ for $1/\tau=1$ using $\lambda=2.9$ and $\mu^*=0.25$. [From Ref. 4.20]
softening or hardening with superconductivity-induced phonon self-energy vanishing in the extreme dirty limit. Physically, this represents the fact that the adiabatic approximation used in the ZZ theory can only hold when the period of a phonon is shorter than the lifetime of an electron before it is scattered by impurities [4.59].

As described in section 4.4.2, the 337 cm\(^{-1}\) mode softens by about 0.6\% and the 435 cm\(^{-1}\) mode hardens by about 0.7\%. Based on Zeyher and Zwicknagl’s calculation, the crossover from softening to hardening occurs just above 2\(\Delta\). Although a relatively small percentage renormalization is observed, the observation of both softening and hardening from two phonons which have a small energy difference allow us to quantitatively interpret our data. We find that, for 1:2:4 films where \(T_c = 80\) K, 337 cm\(^{-1}\) \(\approx 1.2 \times 2\Delta(0)\) and 435 cm\(^{-1}\) \(\approx 1.6 \times 2\Delta(0)\) and thus 2\(\Delta(0)\) \(\approx 280\) cm\(^{-1}\) \(\approx 5K_Tc\). We estimate a 10\% uncertainty in this determination of 2\(\Delta(0)\).

We note that, in this interpretation the 150 cm\(^{-1}\) phonon should soften by about 1.5 cm\(^{-1}\) if the coupling to electrons is the same as for the planar oxygen phonons. So the lack of softening in our study indicates that the coupling is weaker.

Of course, the ZZ calculations were done with parameters specifically chosen for 1:2:3 but it seems reasonable to use the same parameters for 1:2:4. Moreover, the key point here
is that hardening of the 435 cm\(^{-1}\) phonon in addition to the softening of the nearby 337 cm\(^{-1}\) requires that \(2\Delta(0)\) is very close to the frequency of the lower-frequency phonon, relatively independently of the precise parameters of the calculation. In fact, our estimation of the energy gap is consistent with predications based on similar measurements performed on polycrystalline YBa\(_2\)Cu\(_3\)O\(_{7-x}\) samples \([4.37]\). However, there are three major differences between our data and those in reference 4.37 and results from single crystals \([4.56]\). They are

1. In our 1:2:4 films, the magnitude of the overall softening of the 337 cm\(^{-1}\) mode is about three times smaller than that observed in bulk YBa\(_2\)Cu\(_3\)O\(_{7-x}\) single crystal or powder samples. A similar reduced softening was also reported by Feile \([4.60]\) from 1:2:3 films. The Zeyher and Zwicknagl’s calculation points to two possible variables that could effect the degree of phonon softening. One is the electron-impurity scattering rate while the other is electron-phonon coupling constant \(\lambda\). Figure 4.16(a) shows the influence, as calculated by ZZ, of different scattering rates on \(\text{Re} \Sigma^{\parallel}(\omega) / |q_v|^2\) for \(T/T_c = 0.16\). We see that the largest effect of the scattering rate is on phonons having energies at about \(2\Delta\). It is seen from Fig. 4.16(a) that an enhancement of 10 in the scattering rate, results in a reduction by a factor of 2 in the degree of softening.
Fig. 4.16. Impurity scattering rate effect on phonon self-energy. (a) Real part of $\Sigma/N(0)$ and (b) imaginary part of $\Sigma/N(0)$ for $T/T_c=0.16$ and 4 different impurity scattering rates $1/(2\Delta\tau)$. [From Ref. 4.20]
Given the resistivity of the 1:2:4 films (~50-200 \times 10^{-6} \Omega\text{cm} at T_c) and other data such as magnetic penetration depth and coherence length (which are two important parameters related to the electron-impurity scattering time), we estimate that the 1:2:4 films used in our study have a scattering rate about twice as large as that estimated in 1:2:3 single crystals. Therefore, the large reduction in softening cannot entirely be due to a change in scattering rate in the films. The suppressed softening may result from weaker coupling between the phonon and the electronic continuum in the films in comparison to that in single crystal. This aspect is addressed further in the following paragraphs.

(2) The second difference is related to the phonon linewidth. As discussed earlier, the temperature dependence of the phonon linewidth should be sensitive to the interaction between phonons and electrons (figure 4.15 (b)). Figure 4.17 (a) presents the full width at half maximum of the 337 cm\(^{-1}\) measured from 1:2:4C\(_{1/2}\) film at different temperatures. In contrast to measurements from single crystals [4.26,4.46], the line width of the 337 cm\(^{-1}\) phonon in the film displays only a slight increase below T_c. Similar to the phonon energy, the scattering rate and the electron-phonon coupling strength are two factors having influence on the linewidth. Fig. 4.16(b) shows this influence, as calculated by ZZ, of different scattering
Fig. 4.17. Linewidth of 337 cm$^{-1}$ and 435 cm$^{-1}$ phonons as function of temperature. Linewidth was determined by a fit to a Fano lineshape. (a) 337 cm$^{-1}$ mode; (b) 435 cm$^{-1}$ mode.
rates on $\text{Im} \Pi(\omega) = \Delta \Sigma_v(\omega)/|g_v|^2$ for $T/T_c = 0.16$. From this figure, we again conclude that the scattering rate increase as estimated from resistivity measurements in 1:2:4 films alone cannot account for the linewidth change below $T_c$ in the film. It may also partially arise from a weaker coupling between the phonon and the electronic continuum.

Figure 4.17(b) shows the full width at half maximum of the 435 cm$^{-1}$ mode measured from film 1:2:4C$_{1/2}$ at different temperatures. This data does not in general reveal any clear systematic behavior over the full range of temperature studied. Below $T_c$ however the linewidth increases and saturates at about 20 cm$^{-1}$. The ZZ theory does provide a modest increase in linewidth below $T_c$ for this mode. Although their corresponding frequencies show variations that are consistent with the ZZ theory, the linewidth are not satisfactory explained, especially for $T \gtrsim T_c$. It is noted however that in similar measurements on single crystals both the frequency and linewidth behavior were well described by the ZZ theory [4.37,4.51]. Reasons for the discrepancy between films and single crystals are not clear at present.

(3) The third difference observed between 1:2:4 films and single crystal is that the absolute value of the asymmetry factor $q$ (equation 4.10) is six times bigger than that reported in bulk 1:2:3 single crystal [4.60] at $T = 10$ K.
Figure 4.18 shows experimental data for the 337 cm\(^{-1}\) phonon in film 1:2:4C\(_{1/2}\) with the solid line representing a fit based on equation 4.8. The program utilized to obtain the fit is presented in appendix D. The parameters we deduce from the fit are: \(\Gamma = 6\ \text{cm}^{-1}\) and \(q = -40\). As evident from equation 4.10, this large absolute value for the asymmetry parameter \(q\) may also reflect a weaker coupling of that phonon to the electronic continuum in the films than in single crystals [4.60].

In order to find possible explanations for the above differences between the results from films and single crystals we now consider the influence of the substrate and impurities.

It is known that there is a lattice mismatch between bulk \(\text{Y}_1\text{Ba}_2\text{Cu}_4\text{O}_{8-x}\) (a \(\approx 3.845\ \text{Å}\)) and the substrate SrTiO\(_3\) (a \(\approx 3.905\ \text{Å}\)). If the film grows commensurately with the substrate, this mismatch will lead to an additional stress in the film which may result in the elastic constants of the film being modified. Such modification in turn may effect the deformation potential mediated electron-phonon interaction to induce a weaker coupling between the phonon and electronic continuum. However, we have not confirmed by direct measurements if commensurate growth indeed occur throughout the 1:2:4 films which were about 2000 Å thick. A weaker electron-phonon interaction will account for
Fig. 4.18. Theoretical fit of 337 cm$^{-1}$ peak by equation 4.5 in the text. The *’s are data points and the solid line is the fit.
smaller softening and weaker asymmetry shape (larger absolute value of q factor in equation 4.10) observed for the 337 cm⁻¹ phonon the in 1:2:4 films. In fact, calculations in reference 4.37 that utilize $\lambda \sim 0.02$ (150 times less than that used by ZZ) has revealed a factor of three reduction in the degree of softening. As the ZZ theory does not provide numerical results for the role of $\lambda$, we are unable to estimate how much weaker the coupling constant need be to account for the reduced softening, broadening and asymmetry in films. We emphasize that the above argument on a reduced electron-phonon coupling in films due to changes in the elastic constants should be examined further by additional experiments and remains speculative at this time.

There is a recent report by McCarty, et al. [4.61] on the self-energy of phonons in twin free 1:2:3 single crystals. Although these crystals reveal a sharp resistive transition at $T_c (= 93K)$, they contain about 2% gold as impurity that was introduced during growth. It was found that in such impure samples the overall softening of the 337 cm⁻¹ phonon is only about 3.5 cm⁻¹. In addition its line width decreases below $T_c$ and displays a very weak asymmetry. These results are different from data measured from other "pure" single crystals and not unlike the results we have measured from 1:2:4 films. The origin of this effect
remains unknown at present. This confirms that small quantities of impurities in single crystalline $Y_1Ba_2Cu_3O_{7-\delta}$, while not affecting the transition temperature, does have a significant effect on the phonon self-energy behavior below $T_c$. It remains to be confirmed if a similar effect is indeed occurring in the 1:2:4 films utilized in our study. For example, "impurity" atoms could diffuse from the substrate to the film and modify the behavior of the $337 \text{ cm}^{-1}$ phonon below $T_c$.

Finally, we briefly comment on the electronic continuum that has been observed by some groups [4.62] in high temperature superconducting single crystals. In these studies, it was found that below $T_c$ a broad structure of $A_{1g}$ symmetry peaked around $350 \text{ cm}^{-1}$ and another structure peaked at $500 \text{ cm}^{-1}$ with $B_{1g}$ symmetry. The linear rise at small energy for temperatures below $T_c$ has been discussed in terms of a gapless electronic band structure [4.63]. The Raman spectra of the 1:2:4 and 1:2:3 films we measured has a strong elastic component extending to about $150-200 \text{ cm}^{-1}$ that has prevented us from observing clear evidence of electronic scattering at low energies. However, at higher energies beyond about $200 \text{ cm}^{-1}$, the background underlying the Raman spectra suggests the presence of an electronic contribution. This is evident in figure 4.9 where a background continuum of real inelastic scattering is evident above the zero
intensity level that is identified by the dash line in each spectrum. We note that the relative height of this background to the 337 cm\(^{-1}\) phonon peak intensity is comparable to others measured from single crystals [4.64]. However, the lack of single crystalline films prevent us from analyzing the symmetry dependence of this broad electronic continuum.

4.6 Summary

In summary, we have carried out Raman measurements on high quality \(Y_1Ba_2Cu_3O_{7-x}\) and \(Y_1Ba_2Cu_4O_{8-x}\) films with different orientations. We observed 5 \(A_g\) phonon modes in 1:2:3 films and 7 \(A_g\) phonon modes in 1:2:4 films which agree with the group theory analysis. In 1:2:3 films, as oxygen was removed, the resistance of the film increased, the transition moved to low temperatures and broadened, and finally disappeared altogether. By assigning the peaks in the corresponding Raman spectra to specific phonons, we demonstrated that the oxygen was removed primarily from Cu-O chains. In 1:2:4 films, the annealing study has also provided insight into the stability of the 1:2:4 lattice. We find that, in sharp contrast to the 1:2:3 phase, Raman frequencies in the 1:2:4 films are virtually insensitive to annealing in argon to temperatures of 700 C, which is in agreement with only relatively modest reduction in \(T_c\).
These features are consistent with the bonding of adjoining Cu-O chains that inhibits oxygen depletion.

In the 1:2:4 films, the 337 cm\(^{-1}\) Raman mode \((O(2)-O(3)\) out of phase) softens anomalously below \(T_c\) while the 440 cm\(^{-1}\) \((O(2)-O(3)\) in phase) hardens. This combination leads to the conclusion that \(2\Delta(0)/kT_c \approx 5 \pm 0.5\) when interpreted in the ZZ theory. The lack of softening of the 150 cm\(^{-1}\) \((Cu(2))\) mode indicates that electrons couple more strongly to the oxygen modes than to it. The modes involving Cu-O chain atoms behave normally below \(T_c\), confirming the accepted view that the chains play a less important role in superconductivity than do the CuO\(_2\) planes. Raman spectra taken on crystals and on oriented films of 1:2:3 and 1:2:4 differ with regard to the magnitude of asymmetries, phonon linewidth broadening and shifts induced in the phonon energies from their coupling to electronic states. Some possible reasons of this difference have been discussed.
CHAPTER V

SUMMARY AND PROJECTIONS

A: GaAs/Al$_x$Ga$_{1-x}$As quantum wells:

We have observed and studied the (LO-TO) difference phonon modes via a triply resonant Raman scattering process (TRRS) in GaAs quantum wells. The triple resonance was achieved when the incident and scattered radiation energies matched electronic transitions while the mediating phonons had energies equal to the subband spacing ($\Delta E = E_{\text{CLHO}} - E_{\text{CHHO}}$). In such triply resonant situations, contributions to the Raman intensity from lower order resonances can be neglected, and thus the large associated cross-sections allow electron-phonon coupling between specific energy bands to be investigated. Moreover, we have discussed the exciton-photon interaction and the selection rules of the TRRS based upon the symmetry of the subbands and the special format of the electron wavefunctions. We have also discussed different electron-phonon interactions, namely Fröhlich and deformation potential interaction. It was shown that both interactions can couple the ground light- and heavy-hole exciton states which gives rise to the TRRS.
Uniaxial stress has provided a method to tune ΔE and Raman measurements under the uniaxial compression has confirmed the triply resonant nature of the process. Moreover, power dependence measurements at low temperatures have suggested the involvement of photo-induced phonons in this Raman event.

B. High temperature superconducting films:

Several Raman active optical phonon modes are observed from $Y_1Ba_2Cu_3O_{7-δ}$, $Y_1Ba_2Cu_3O_{6.5}$ and $Y_1Ba_2Cu_4O_{8-δ}$ films. Their dependence on temperature and oxygen content are discussed. The phonon self-energies calculated on the basis of the ZZ strong coupling theory were used to interpret our results. This comparison enabled us to predict $2\Delta/kT_c$ to be equal to 5 for $Y_1Ba_2Cu_4O_{8-δ}$ films. We also discussed some differences in the self-energy of phonons in $Y_1Ba_2Cu_4O_{8-δ}$ films and single crystal.

To further extend our study, the effect of dopants substituted for the Cu sites would be valuable. Such doping that replaces Cu in the Cu-O planes will effect the electron-impurity scattering time and also reduces $T_c$. By lowering the $T_c$ of the sample, $2\Delta$ is altered and thus the relative energy positions between $2\Delta$ and phonons are modified. The softening and hardening of specific phonons in these doped films can provide a critical test of the ZZ
theory. As mentioned in chapter IV, it would be valuable to confirm if the electron-phonon interaction is weaker in films. A measure of the stiffness constants from YBCO films and single crystals will be valuable and may be measured by measuring the acoustic phonon velocity by Brillouin scattering.
The purpose of this appendix is to introduce the methods to derive the phonon modes in solids. There are different algorithms by which irreducible representations corresponding to the phonons of a crystal can be determined. Given the precise atomic locations in a crystal, its space group is defined [A.1]. To this space group belongs all the crystal transformations that map the primitive cell to itself: all rotations, reflections, and basis operations of a screw axis, or a glide plane. The point group is defined as the group obtained by removing all translations from the space group. A site group for each the atoms is defined as a subgroup of the point group. It contains all operations in the point group that keeps the specific atom on this site fixed.

For a primitive cell which contains N atoms, 3N phonon modes corresponding to the transnational degrees of freedom exist. For each operation \( P_r \) in the point group, one contains a reducible representation \( D(P_r) \) (a 3N by 3N matrix). The reduction of each \( D(P_r) \) into the irreducible components is then performed in the standard way by
calculating the traces $\chi^n$ of $D(P_r)$ and projecting them with those $\chi_1(P)$ of the irreducible representations of the point group with the use of standard character tables [A.2]

$$\sum_P \chi_1^*(P) \chi^n(P_r) = g s_1^n$$  \hspace{1cm} (A.1)

where

$g$ = number of elements in the point group

$s_1^n$ = number of times $\chi_1$ is contained in $\chi^n$

$\chi(P)$ = trace of the irreducible representation for the operation $P$ in the point group

$\chi^n(P_r)$ = trace of the reducible representation for the operation $P$ in the point group.

$\chi(P)$ can be found from the standard character tables [A.2]. $\chi^n(P_r)$ can be calculated by

$$\chi^n(P_r) = (\pm 1 + 2\cos\theta) U^n(P_r)$$  \hspace{1cm} (A.2)

where

$U^n(P_r)$ = number of atoms in the primitive cell which transforms back to itself after the operation $P_r$

$(\pm 1 + 2\cos\theta) = \text{trace of a unit displacement under the operation } P$

where $\theta$ is the angle of rotation for the operation; $+$ is used for a simple rotation, while $-$ is used for an operation which involves a reflection.

The above algorithm becomes tedious when the number of atoms in the primitive cell is large. Fateley [A.3] has
discussed an algorithm for crystals with a large number of atoms in the primitive cell. It involves use of standard correlation tables [A.2,A.4], that relates site groups of constituent atoms to the factor group of the crystal. All the atoms in the crystal are subdivided into subgroups of equivalent atoms i.e. atoms which transform onto each other under all the operations of the space group. These are conveniently located in the International tables [A.1]. The irreducible representations of the site group which transform like unit translations are then correlated with the elements of the factor group using correlation tables. Each correlation to a factor group's irreducible representation contribution of this site group to the phonon modes of the crystal. This procedure is completed for all the subgroups to exhaust the contributions of all the atoms in the primitive cell and give a total number of 3N phonons. Three of these phonons correspond to translations of the whole crystal along the x, y and z directions, and are the acoustic phonons. The 3N - 3 remaining optic phonons have higher energies and are the lattice vibrations probed in Raman scattering. We will use both algorithms to derive the phonon modes of the quantum wells and superconducting films in the following appendices.
Appendix B

The purpose of this appendix is to derive the phonon modes of the GaAs single quantum wells. The unit cell of zinc-blende GaAs is shown in figure B.1. It belongs to $T_d^2$ space group. For the simplicity, let us consider the GaAs quantum well which only contains two monolayers. It loses all the symmetry operations which depend on the periodicity along z-axis. The primitive cell of this two monolayer GaAs quantum well contains two Ga and two As atoms. It is difficult to determine its space group, however, it belongs to $D_{2d}$ point group. We can apply both algorithms discussed in appendix A to derive the phonon modes in terms of irreducible representations.

*Operation* ($P_2$): atomic transformations

\[ E : U(E) = 4; \text{ all atoms in the primitive cell transform back to themselves under the identity operation.} \]

\[ S_4 : U(S_4) = 0; \]

\[ C_2 : U(C_2) = 4; \text{ All atoms in the primitive cell transform back to themselves after an } 180^\circ \text{ rotation along } z\text{-axis.} \]
\( C_2' : \quad U(C_2') = 0 \)

\( \sigma_d : \quad U(\sigma_d) = 4; \) all atoms in the primitive cell transform back to themselves after the reflection by \([110]\) plane.

The character table can now be completed as:

<table>
<thead>
<tr>
<th></th>
<th>( D_{2d} )</th>
<th>E</th>
<th>( 2S_4 )</th>
<th>( C_2 )</th>
<th>( 2C_2' )</th>
<th>( 2\sigma_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>( B_1 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

\( U(P_f) \) 4 0 4 0 0

\( \pm 1 + 2 \cos \theta \) 3 -1 -1 -1 1

\( \chi(P_f) \) 12 0 -4 0 4

With \( g = 8 \), the order of the point group \( D_{2d} \), equation A.1 can now be used to count the number modes for each of the irreducible representations:

\( S_{A_1} = \frac{1}{8}(12-4+8) = 2 \)
\( S_{A_2} = \frac{1}{8}(12-4-8) = 0 \)
\( S_{B_1} = \frac{1}{8}(12-4-8) = 0 \)
\( S_{B_2} = \frac{1}{8}(12-4+8) = 2 \)
\( S_{E} = \frac{1}{8}(24+8) = 4 \)
The zone center phonons of the GaAs quantum well with $D_{2d}$ point group can now be written in terms of the irreducible representations of the $D_{2d}$ point group as, with subtracting the acoustic phonons ($A_1 + E$):

$$\Gamma = 1A_1 + 2B_2 + 3E \quad (B.1)$$

We can double check the results by using other algorithm based on correlation table. Following the standard notation [A.6], the 4 atoms in the primitive cell of two-monolayer GaAs quantum well can be classified as $C_{2v}$ (all four atoms) site groups. The following correlation table gives the zone center phonon modes in terms of the irreducible representations of the point group $D_{2n}$ as:

<table>
<thead>
<tr>
<th>site group</th>
<th>factor group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2v}$</td>
<td>$D_{2d}$</td>
</tr>
<tr>
<td>$A_1 (T_z)$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>$B_1 (T_x)$</td>
<td>$B_2 (T_z)$</td>
</tr>
<tr>
<td>$B_2 (T_y)$</td>
<td>$E (T_x, T_y)$</td>
</tr>
</tbody>
</table>

Therefore, each group of Ga and As atoms will support $A_1 + B_2 + E$ modes. Subtracting three acoustic phonon modes, the primitive cell of two monolayer GaAs quantum well yields:

$$\Gamma = 1A_1 + 2B_2 + 3E \quad (B.1)$$
Appendix C

The purpose of this appendix is to derive the phonon modes of the 1:2:3 and 1:2:4 YBCO compounds.

(1) \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7 \):

The \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7 \) primitive cell is same as its unit cell which belong to the \( D_{2h} \) (see figure 4.1(a)). The origin of this unit cell is chosen to coincide with \( \text{Y} \) atom. \( U(P_f) \) is calculated by counting the number of atoms that transform back to themselves under the various operations of the point group \( D_{2h} \):

**Operation \( (P_f) \): atomic transformations**

\( \text{E} \) : \( U(\text{E}) = 13; \) all atoms in the primitive cell transform back to themselves under the identity operation.

\( \text{C}_{2x} \) : \( U(\text{C}_{2x}) = 3; \) \( \text{Y} \), \( \text{Cu}(1) \) and \( \text{O}(1) \) transform back to themselves after an 180° rotation along \( x \)-axis.

\( \text{C}_{2y} \) : \( U(\text{C}_{2y}) = 3; \) \( \text{Y} \), \( \text{Cu}(1) \) and \( \text{O}(1) \) transform back to themselves after an 180° rotation along \( y \)-axis.
$C_2'$ : $U(C_2') = 13$; all atoms in the primitive cell transform back to themselves after an 180° rotation along z-axis.

$i$ : $U(i) = 3$; Y, Cu(1) and O(1) transform back to themselves after the inversion.

$\sigma_z$ : $U(\sigma_z) = 3$; Y, Cu(1) and O(1) transform back to themselves after the reflection by [001] plane.

$\sigma_y$ : $U(\sigma_y) = 13$; all atoms in the primitive cell transform back to themselves after the reflection by [010] plane.

$\sigma_x$ : $U(\sigma_x) = 13$; all atoms in the primitive cell transform back to themselves after the reflection by [100] plane.

The character table can now be completed as:

<table>
<thead>
<tr>
<th></th>
<th>$D_{2h}$</th>
<th>E</th>
<th>$C_2'$</th>
<th>$C_2^y$</th>
<th>$C_2^x$</th>
<th>i</th>
<th>$\sigma_z$</th>
<th>$\sigma_y$</th>
<th>$\sigma_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>
\[\begin{array}{cccccccccc}
U(P_\Gamma) & 13 & 13 & 3 & 3 & 3 & 3 & 13 & 13 \\
\pm 1 + 2 \cos \theta & 3 & -1 & -1 & -1 & -3 & 1 & 1 & 1 \\
\chi(P_\Gamma) & 39 & -13 & -3 & -3 & -9 & 3 & 13 & 13
\end{array}\]

With \( g = 8 \), the order of the point group \( D_{2h} \), equation A.1 can now be used to count the number modes for each of the irreducible representations:

- \( S_{A g} = \frac{1}{8}(39-13-3-3-9+3+13+13) = 5 \)
- \( S_{B_{1g}} = \frac{1}{8}(39-13+3-9+3-13-13) = 0 \)
- \( S_{B_{2g}} = \frac{1}{8}(39+13-3-9-3+13-13) = 5 \)
- \( S_{B_{3g}} = \frac{1}{8}(39+13+3-9-3+13+13) = 5 \)
- \( S_{A u} = \frac{1}{8}(39-13-3-9-3-13-13) = 0 \)
- \( S_{B_{1u}} = \frac{1}{8}(39-13+3+9-3+13+13) = 8 \)
- \( S_{B_{2u}} = \frac{1}{8}(39+13-3+9+3-13+13) = 8 \)
- \( S_{B_{3u}} = \frac{1}{8}(39+13+3+9+3+13-13) = 8 \)

The zone center phonons of \( Y_{1}Ba_{2}Cu_{3}O_{7} \) with \( D_{2h} \) space group can now be written in terms of the irreducible representations of the \( D_{2h} \) point group as, (subtracting the acoustic phonons \( B_{1u} + B_{2u} + B_{3u} \)):

\[ \Gamma = 5A_g + 5B_{2g} + 5B_{3g} + 7B_{1u} + 7B_{2u} + 7B_{3u} \] (C.1)

We can double check the results by using the algorithm based on correlation table. Following the standard notation [A.6], , the 13 atoms in the primitive cell of \( Y_{1}Ba_{2}Cu_{3}O_{7} \), can be classified as having \( D_{2h} \) \((Y, Cu(1) \text{ and } O(1))\) and \( C_{2v} \) \((Cu(2), Ba, O(2), O(3) \text{ and } O(4))\) site groups. The following
correlation table gives the zone center phonon modes in terms of the irreducible representations of the point group $D_{2h}$:

<table>
<thead>
<tr>
<th>site group</th>
<th>factor group</th>
<th></th>
<th>site group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2v}$</td>
<td>$D_{2h}$</td>
<td>$D_{2h}$</td>
<td></td>
</tr>
<tr>
<td>$A_1 \ (T_1)$</td>
<td>$A_g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{1u} \ (T_1)$</td>
<td>$B_u \ (T_1)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{1} \ (T_x)$</td>
<td>$B_{2g}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{3u} \ (T_x)$</td>
<td>$B_{3u} \ (T_x)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{2} \ (T_y)$</td>
<td>$B_{3g}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{2u} \ (T_y)$</td>
<td>$B_{2u} \ (T_y)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Therefore, $Y$, Cu(1) and O(1) will support $B_{1u} + B_{2u} + B_{3u}$ modes each; Ba, Cu(2), O(2), O(3) and O(4) will support $A_g$ + $B_{2g}$ + $B_{3g}$ + $B_{1u}$ + $B_{2u}$ + $B_{3u}$ modes each. Subtracting three acoustic phonon modes, the primitive cell of $Y_{1}Ba_{2}Cu_{2}O_{6}$ yields:

$$\Gamma = 5A_g + 5B_{2g} + 5B_{3g} + 7B_{1u} + 7B_{2u} + 7B_{3u} \quad (C.1)$$

(2) $Y_{1}Ba_{2}Cu_{2}O_{6}$:

The $Y_{1}Ba_{2}Cu_{2}O_{6}$ primitive cell is same as its unit cell which belong to the $D_{4h}$ (see figure 4.1(b)). The origin of this unit cell is chosen to coincide with Y atom. $U(P_z)$ is calculated by counting the number of atoms that transform
back to themselves under the various operations of the point group $D_{4h}$:

*Operation $(P_2)$*: atomic transformations

$E$ : $U(E) = 12$; all atoms in the primitive cell transform back to themselves under the identity operation.

$C_4$ : $U(C_4) = 8$; $Y$, two Ba, Cu(1), two Cu(2) and two O(4) transform back to themselves after a 90° rotation along z-axis.

$C_2$ : $U(C_2) = 12$; all atoms in the primitive cell transform back to themselves after a 180° rotation along z-axis.

$C_2'$ : $U(C_2') = 2$; $Y$ and Cu(1) transform back to themselves after an 180° rotation along x- or y-axis.

$C_2''$: $U(C_2'') = 2$; $Y$ and Cu(1) transform back to themselves after an 180° rotation along $[110]$ direction.

$i$ : $U(i) = 2$; $Y$ and Cu(1) transform back to themselves after the inversion.

$S_4$ : $U(S_4) = 2$; $Y$ and Cu(2) transform back to themselves after the a 90° rotation and a mirror reflection by [001] plane.
\[ \sigma_h : \ U(\sigma_h) = 2; \ Y \text{ and } Cu(1) \text{ transform back to themselves after a mirror reflection by } [001] \text{ plane.} \]

\[ \sigma_v : \ U(\sigma_v) = 12; \text{ all atoms in the primitive cell transform back to themselves after a mirror reflection by } [100] \text{ or } [010] \text{ plane.} \]

\[ \sigma_d : \ U(\sigma_d) = 8; \ Y, \text{ Two Ba, Cu}(1), \text{ Two Cu}(2), \text{ and two O}(4) \text{ transform back to themselves after a mirror reflection by } [110] \text{ plane.} \]

The character table can now be completed as:

<table>
<thead>
<tr>
<th></th>
<th>D(_{4h})</th>
<th>E</th>
<th>2C(_4)</th>
<th>C(_2)</th>
<th>2C(_{2'})</th>
<th>2C(_{2''})</th>
<th>i</th>
<th>2S(_4)</th>
<th>(\sigma_h)</th>
<th>2(\sigma_v)</th>
<th>2(\sigma_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(_{1g})</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A(_{2g})</td>
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<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>B(_{1g})</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B(_{2g})</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>E(_g)</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A(_{1u})</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>A(_{2u})</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>B(_{1u})</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>B(_{2u})</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>E(_u)</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
With \( g = 16 \), the order of the point group \( D_{2h} \), equation A.1 can now be used to count the number modes for each of the irreducible representations:

\[
\begin{align*}
S_{\text{A}_{1g}} &= 1/16(36+16-12-4-6-4+2+24+16) = 4 \\
S_{\text{A}_{2g}} &= 1/16(36+16-12+4+4-6-4+2-24-16) = 0 \\
S_{\text{B}_{1g}} &= 1/16(36-16-12+4+4-6+4+2+24-16) = 1 \\
S_{\text{B}_{2g}} &= 1/16(36-16-12+4-4+6-4+2-24-16) = 0 \\
S_{\text{E}_{g}} &= 1/16(72+24-12-4) = 5 \\
S_{\text{A}_{1u}} &= 1/16(36+16-12-4+6+4-2-24-16) = 0 \\
S_{\text{A}_{2u}} &= 1/16(36+16-12+4+4+6-4-2+24+16) = 6 \\
S_{\text{B}_{1u}} &= 1/16(36-16-12-4+4+6-4-2-24+16) = 0 \\
S_{\text{B}_{2u}} &= 1/16(36-16-12+4-4+6-4+2+24-16) = 1 \\
S_{\text{E}_{u}} &= 1/16(72+24+12+4) = 7
\end{align*}
\]

The zone center phonons of \( Y_{1}Ba_{2}Cu_{3}O_{6} \) with \( D_{4h} \) space group can now be written in terms of the irreducible representations of the \( D_{4h} \) point group as, (subtracting the acoustic phonons \( (A_{2u} + E_{u}) \)):

\[
\Gamma = 4A_{1g} + 1B_{1g} + 5E_{g} + 5A_{2u} + 1B_{2u} + 6E_{u} \quad (C.2)
\]

We can confirm the results by using the algorithm based on correlation table. The 12 atoms in the primitive cell of \( Y_{1}Ba_{2}Cu_{3}O_{6} \) can be classified as having \( D_{4h} \) (Y and Cu(1)) and
C\textsubscript{2v} (O(2) and O(3)) and C\textsubscript{4v} (Ba, Cu(2) and O(4)) site groups. The following correlation table gives the zone center phonon modes in terms of the irreducible representations of the point group D\textsubscript{4h} as:

<table>
<thead>
<tr>
<th>site group</th>
<th>factor group</th>
<th>site group</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{2v}</td>
<td>D\textsubscript{2h}</td>
<td>C\textsubscript{4v}</td>
</tr>
<tr>
<td>A\textsubscript{1g}</td>
<td>B\textsubscript{1g}</td>
<td>A\textsubscript{1g}</td>
</tr>
<tr>
<td>A\textsubscript{2u} (T\textsubscript{1})</td>
<td></td>
<td>A\textsubscript{1} (T\textsubscript{1})</td>
</tr>
<tr>
<td>B\textsubscript{2u}</td>
<td>E\textsubscript{g}</td>
<td>E (T\textsubscript{x}, T\textsubscript{y})</td>
</tr>
<tr>
<td>B\textsubscript{1} (T\textsubscript{x})</td>
<td>E\textsubscript{u} (T\textsubscript{y}, T\textsubscript{x})</td>
<td></td>
</tr>
</tbody>
</table>

Therefore, Y and Cu(1) will support A\textsubscript{2u} + E\textsubscript{u} modes each; Ba, Cu(2), and O(4) will support A\textsubscript{1g} + E\textsubscript{g} + A\textsubscript{2u} + E\textsubscript{u} modes each; O(2) and O(3) will support A\textsubscript{1g} + B\textsubscript{1g} + 2E\textsubscript{g} + A\textsubscript{2u} + B\textsubscript{2u} + 2E\textsubscript{u}. Subtracting three acoustic phonon modes, the primitive cell of Y\textsubscript{1}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6} yields:

\[ \Gamma = 4A\textsubscript{1g} + 1B\textsubscript{1g} + 5E\textsubscript{g} + 5A\textsubscript{2u} + 1B\textsubscript{2u} + 6E\textsubscript{u} \quad \text{(C.2)} \]

(3) Y\textsubscript{1}Ba\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8}:

The Y\textsubscript{1}Ba\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} primitive cell is not as obvious as 1:2:3. The unit cell of 1:2:4 in figure 4.1(c) contains two primitive cells. The 1:2:4 primitive cell can be
constructed by choosing the primitive \( c \) connecting the central \( \text{Y} \) atom of figure 4.1(c) to one of the other \( \text{Y} \) atoms. The primitive \( a \) and \( b \) vectors are chosen as same as 1:2:3. The 15-atom 1:2:4 primitive cell belongs to the \( D_{2h} \). The origin of this unit cell is chosen to coincide with \( \text{Y} \) atom. \( U(P) \) is calculated by counting the number of atoms that transform back to themselves under the various operations of the point group \( D_{2h} \):

\textbf{Operation (}P_x\textbf{): atomic transformations}

\textbf{E} : \( U(E) = 15 \); all atoms in the primitive cell transform back to themselves under the identity operation.

\textbf{C}_z^x : \( U(C_z^x) = 1 \); only \( \text{Y} \) transforms back to itself after an 180° rotation along \( x \)-axis.

\textbf{C}_z^y : \( U(C_z^y) = 1 \); only \( \text{Y} \) transform back to itself after an 180° rotation along \( y \)-axis.

\textbf{C}_z^z : \( U(C_z^z) = 15 \); all atoms in the primitive cell transform back to themselves after an 180° rotation along \( z \)-axis.

\textbf{i} : \( U(i) = 1 \); only \( \text{Y} \) transform back to itself under inversion.
\( \sigma_z : \ U(\sigma_z) = 1; \) only \( \gamma \) transform back to itself by a mirror reflection by \([001]\) plane.

\( \sigma_y : \ U(\sigma_y) = 15; \) all atoms in the primitive cell transform back to themselves under a mirror reflection by \([010]\) plane.

\( \sigma_x : \ U(\sigma_x) = 15; \) all atoms in the primitive cell transform back to themselves under a mirror reflection by \([100]\) plane.

The character table can now be completed as:

<table>
<thead>
<tr>
<th></th>
<th>D(_{2h})</th>
<th>E</th>
<th>C(_{2z})</th>
<th>C(_{2y})</th>
<th>C(_{2x})</th>
<th>i</th>
<th>( \sigma_z )</th>
<th>( \sigma_y )</th>
<th>( \sigma_x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( B_{1g} )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>( B_{3g} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>( A_u )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>( B_{1u} )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{2u} )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{3u} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ U(P_f) \] 15 15 1 1 1 1 15 15

\[ \pm 1 + 2 \cos \theta \] 3 -1 -1 -1 -3 1 1 1

\[ \chi(P_f) \] 45 -15 -1 -1 -3 1 15 15
With \( g = 8 \), the order of the point group \( D_{2h} \), equation A.1 can now be used to count the number modes for each of the irreducible representations:

\[
\begin{align*}
S_{\text{Ag}} &= \frac{1}{8}(45-15-1-1-3+1+15+15) = 7 \\
S_{\text{B1g}} &= \frac{1}{8}(45-15+1+1-3+1-15-15) = 0 \\
S_{\text{B2g}} &= \frac{1}{8}(45+15-1+1-3-1+15-15) = 7 \\
S_{\text{B3g}} &= \frac{1}{8}(45+15+1-1-3-1-15+15) = 7 \\
S_{\text{Au}} &= \frac{1}{8}(45-15-1-1+3-1-15-15) = 0 \\
S_{\text{B1u}} &= \frac{1}{8}(45-15+1+1+3-1+15+15) = 8 \\
S_{\text{B2u}} &= \frac{1}{8}(45+15-1+1+3+1-15+15) = 8 \\
S_{\text{B3u}} &= \frac{1}{8}(45+15+1-1+3+1+15-15) = 8
\end{align*}
\]

The zone center phonons of \( Y_1\text{Ba}_2\text{Cu}_4\text{O}_8 \) with \( D_{2h} \) space group can now be written in terms of the irreducible representations of the \( D_{2h} \) point group as, (subtracting the acoustic phonons \( (B_{1u} + B_{2u} + B_{3u}) \)):

\[
\Gamma = 7\text{Ag} + 7\text{B2g} + 7\text{B3g} + 7\text{B1u} + 7\text{B2u} + 7\text{B3u} \quad (C.3)
\]

The results can be confirmed by using the algorithm based on correlation table. Following the standard notation \([A.6]\), , the 15 atoms in the primitive cell of \( Y_1\text{Ba}_2\text{Cu}_4\text{O}_8 \) can be classified as having \( D_{2h} \) (Y only) and \( C_{2v} \) (all other atoms in 1:2:4 primitive cell) site groups. The following correlation table gives the zone center phonon modes in terms of the irreducible representations of the point group \( D_{2h} \) as:
<table>
<thead>
<tr>
<th>site group</th>
<th>factor group</th>
<th>site group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2v}$</td>
<td>$D_{2h}$</td>
<td>$D_{2h}$</td>
</tr>
<tr>
<td>$A_1 (T_z)$</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$B_{1u} (T_z)$</td>
<td>$B_{1u} (T_z)$</td>
</tr>
<tr>
<td>$B_1 (T_x)$</td>
<td>$B_{2g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$B_{3u} (T_x)$</td>
<td>$B_{3u} (T_x)$</td>
</tr>
<tr>
<td>$B_2 (T_y)$</td>
<td>$B_{3g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$B_{2u} (T_y)$</td>
<td>$B_{2u} (T_y)$</td>
</tr>
</tbody>
</table>

Therefore, $Y$ will support $B_{1u} + B_{2u} + B_{3u}$ modes; $Ba$, $Cu(1)$, $Cu(2)$, $O(1)$, $O(2)$, $O(3)$ and $O(4)$ will support $A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$ modes each. Subtracting three acoustic phonon modes, the primitive cell of $Y_{1}Ba_{2}Cu_{4}O_{8}$ yields:

$$\Gamma = 7A_g + 7B_{2g} + 7B_{3g} + 7B_{1u} + 7B_{2u} + 7B_{3u} \quad (C.3)$$
Appendix D

This program is using the least square method to fit a phonon peak by a Fano type curve. The formula used is
\[ I = B \cdot A \cdot \frac{(q \cdot \text{GARMA} + X - \text{OMEGA})^2}{(\text{GARMA} + (X - \text{OMEGA})^2)} \]
where B is the background, A is the amplitude, Q is the asymmetry factor, \( \text{GARMA} \) is the central frequency.

The use this program, the experimental data must be stored in a data file which has two columns as x and y. This file will then be read by this program. After getting the all five parameters based on best fit, the relative results are written in a new file. And the program will calculate the theoretical data points and stored them in an another new file.

The standard division of central frequency is also calculated and stored in the result file.

Here comes the program!!
Define all the parameters

\[
\text{INTEGER NOBS, NPARA, NTRY, NPOINT}
\]
\[
\text{REAL A, AI, OMEGA, OMEGAI, GARMA, GARMAI, Q, QT, XDATA(150), SD, YDATA(150), NEWY(150), BOX, BGY, BSLP, MIN, XP, XI, B, BI, DELTA}
\]
\[
\text{CHARACTER FILE1*30, FILE2*30, FILE3*30}
\]

The following is the main program.

Define the files.

\[
\text{WRITE(0,*) 'INPUT FILE NAME OF YOUR EXPERIMENTAL DATA'}
\text{READ(5,'(A)') FILE1}
\text{WRITE(0,*) 'INPUT FILE NAME OF THE RESULT'}
\text{READ(5,'(A)') FILE2}
\text{WRITE(5,*) 'INPUT FILE NAME OF YOUR THEORITICAL FIT'}
\text{READ(5,'(A)') FILE3}
\text{OPEN(1,FILE=FILE1,STATUS='OLD')}\]
\[
\text{OPEN(2,FILE=FILE2,STATUS='NEW')}
\text{OPEN(3,FILE=FILE3,STATUS='NEW')}
\]

Input the estimated the parameters.

\[
\text{WRITE(6,*) 'PLEASE ENTER THE BACKGROUND, THE BACKGROUND'}
\text{WRITE(6,*) 'INCREMENT, THE HEIGHT, THE HEIGHT INCREMENT,'}
\text{WRITE(6,*) 'THE PEAK, THE PEAK INCREMENT, THE WIDTH, THE'}
\text{WRITE(6,*) 'WIDTH INCREMENT, AND THE ASYMMETRY FACTOR, THE'}
\text{WRITE(6,*) 'INCREMENT OF THE ASYMMETRY FACTOR. ALSO ENTER'}
\text{WRITE(6,*) 'THE STANDARD DIVISION ESTIMATED.'}
\text{READ(5,*) B, BI, A, AI, OMEGA, OMEGAI, GARMA, GARMAI, Q, QT, SD}
\]

Initialize the parameters.

\[
\text{NPARA=0}
\text{NTRY=0}
\text{MIN=10ES}
\]

Reads in data.

\[
\text{DD 100 I=1,150}
\text{READ(1,*,END=101) XDATA(I), YDATA(I)}
\]
continued
101 NOBS=I-1
Use grid method to approaching the minimum point in the
Fano function.
10 NPOINT=0
IF (NPRAA=1) 11,12,40
11 NPOINT=NPOINT+1
Q=Q+Q
TEM=MIN
CALL SQRR(B,A,OMEGA,GAMMA,Q.XDATA,YDATA,NOBS,MIN)
IF (MIN.LT.TEW) GOTO 11
MIN=TEM
Q=Q+Q
IF (NPOINT.GT.1) GOTO 31
NPOINT=0
21 NPOINT=NPOINT+1
Q=Q+Q
TEM=MIN
CALL SQRR(B,A,OMEGA,GAMMA,Q.XDATA,YDATA,NOBS,MIN)
IF (MIN.LT.TEW) GOTO 21
MIN=TEM
Q=Q+Q
IF (NPOINT.GT.1) GOTO 31
NTRY=NTRY+1
NPRAA=1
IF (NTRY.GT.5) 10,20,20
31 NTRY=0
NPRAA=1
GOTO 10
12 NPOINT=NPOINT+1
GAMMA=GAMMA-GAMMAI
TEM=MIN
CALL SQRR(B,A,OMEGA,GAMMA,Q.XDATA,YDATA,NOBS,MIN)
IF (MIN.LT.TEW) GOTO 12
MIN=TEM
GAMMA=GAMMA+GAMMAI
IF (NPOINT.GT.1) GOTO 32
NPRAA=0
22 NPOINT=NPOINT+1
GAMMA=GAMMA+GAMMAI
TEM=MIN
CALL SQRR(B,A,OMEGA,GAMMA,Q.XDATA,YDATA,NOBS,MIN)
IF (MIN.LT.TEW) GOTO 22
MIN=TEM
GAMMA=GAMMA-GAMMAI
IF (NPOINT.GT.1) GOTO 32
NTRY=NTRY+1
NPRAA=2
IF (NTRY.GT.5) 10,20,20
32 NTRY=0
NPRAA=2
GOTO 10
40 IF (NPRAA=3) 13,14,15
13 NPOINT=NPOINT+1
OMEGA=OMEGA-OMEGAI
TEM=MIN
CALL SQRR(B,A,OMEGA,GAMMA,Q.XDATA,YDATA,NOBS,MIN)
IF (MIN.LT.TEW) GOTO 13
MIN=TEM
OMEGA=OMEGA+OMECAI
IF (NPOINT .GT. 1) GOTO 33
NPOINT=0
23 NPOINT=NPOINT+1
OMEGA=OMEGA+OMECAI
TEM=MIN
CALL SQER(B,A,OMEGA,GARMA, q, XDATA,YDATA, NOBS,MIN)
IF (MIN .LT. TEM) GOTO 23
MIN=TEM
OMEGA=OMEGA-OMECAI
IF (NPOINT .GT. 1) GOTO 33
NTRY=NTRY+1
NPARA=3
IF (NTRY=5) 10,20,20
33 NTRY=0
NPARA=3
GOTO 10
14 NPOINT=NPOINT+1
A=A-AI
TEM=MIN
CALL SQER(B,A,OMEGA,GARMA, q, XDATA,YDATA, NOBS,MIN)
IF (MIN .LT. TEM) GOTO 14
MIN=TEM
A=A+AI
IF (NPOINT .GT. 1) GOTO 34
NPPOINT=0
24 NPOINT=NPOINT+1
A=A+AI
TEM=MIN
CALL SQER(B,A,OMEGA,GARMA, q, XDATA,YDATA, NOBS,MIN)
IF (MIN .LT. TEM) GOTO 24
MIN=TEM
A=A-AI
IF (NPOINT .GT. 1) GOTO 34
NTRY=NTRY+1
NPARA=4
IF (NTRY=5) 10,20,20
34 NTRY=0
NPARA=4
GOTO 10
15 NPOINT=NPOINT+1
B=B-BI
TEM=MIN
CALL SQER(B,A,OMEGA,GARMA, q, XDATA,YDATA, NOBS,MIN)
IF (MIN .LT. TEM) GOTO 15
MIN=TEM
B=B+BI
IF (NPOINT .GT. 1) GOTO 35
NPPOINT=0
25 NPOINT=NPOINT+1
B=B+BI
TEM=MIN
CALL SQER(B,A,OMEGA,GARMA, q, XDATA,YDATA, NOBS,MIN)
IF (MIN .LT. TEM) GOTO 25
MIN=TEM
B=B-BI
IF (NPOINT .GT. 1) GOTO 35
NTRY=NTRY+1
NPARA=0
NPARA=0
IF (NTRY-5) 10,20,20
NTRY=0
NOFA=0
GOTO 10

C Calculate the standard division for centry frequency and store all the relative results to the new result file.

DEM=OMEGA+2*OMEGAI
CALL SQR2(B,A,OMEGA,GARMA,OMEGA,XDATA,YDATA,NOBS,MIN)
NORTH=SD/SQRT(2*OMEGA+OMEGAI/(MIN+MIN-TEMP+TEMP))
WORST=GARMA+2*GARMAI
CALL SQR2(B,A,OMEGA,GARMA,OMEGA,XDATA,YDATA,NOBS,MIN)
Q=Q+2*QI
CALL SQR2(B,A,OMEGA,GARMA,OMEGA,XDATA,YDATA,NOBS,MIN)
DELTA=OMEGA+SQRT(2*GARMAI/GARMAI/(MIN+MIN-TEMP+TEMP))
DELTA=DELTA-GARMA/GARMAI
WRITE(2,102)B,A,OMEGA,GARMA,OMEGA
102 FORMAT('B=',F10.2,'A=',F10.2,'OMEGA=',F10.3,'GARMA=',F10.3)

C Calculate the new points and store them in the new theoretical fit file.

DO 50 I=1,NOBS
NEWY(I)=A*(Q*GARMA+XDATA(I)-OMEGA)**2/(GARMA+GARMA+XDATA(I)-OMEGA)**2+B
WRITE(3,EB)XDATA(I),NEWY(I)
50 CONTINUE
CLOSE(3)
CLOSE(2)
CLOSE(1)
STOP
END

The following is the subroutine to calculate the square root of the sumation of each error square.

SUBROUTINE SQR2(B,A,OMEGA,GARMA,OMEGA,XDATA,YDATA,NOBS,MIN)
REAL SUM, LIMIT, XDATA(150), YDATA(150), MIN, OMEGA, GARMA
A, Q, B
SUM=0
LIMIT=MIN+MIN
DO 1 I=1,NOBS
IP (SUM>LIMIT) GOTO 2
SUM=SUM+(YDATA(I)-B-A*(Q*GARMA+XDATA(I)-OMEGA)**2)/
(GARMA+GARMA+XDATA(I)-OMEGA)**2
1 CONTINUE
MIN=SQRT(SUM)
2 CONTINUE
RETURN
END

The following is the subroutine to calculate the square root of the sumation of each error square.
SUBROUTINE SQER2(B, A, OMEGA, GAMMA, Q, XDATA, YDATA, NOBS, &        UIN)
REAL SUM, LIMIT, XDATA(ISO), YDATA(ISO), MIN, OMEGA, GAMMA &
&        A, Q, B
SUM=0
DO 1 I=1, NOBS
SUM=SUM+(YDATA(I)-B-A*(Q+GAMMA-XDATA(I)-OMEGA)**2/ &
& (GAMMA+GAMMA+(XDATA(I)-OMEGA)**2))**2
1 CONTINUE
MIN=SQRT(SUM)
2 CONTINUE
RETURN
END
LIST OF REFERENCES


2.20. ibid, p.233.


