Chapter 5

Phonon Anomaly in Raman
Active Phonons in Cuprates in
Normal State

5.1 Introduction

We consider the effect of electron-phonon coupling on the optical phonons of high temperature superconductors. It is well known that for superconductors, as for metals or heavily doped semiconductors, electron-phonon coupling contributes to the re-normalization of the electron spectrum. Similarly, any modification of the electron spectrum should influence the long wave length optical phonons because of electron-phonon coupling [1, 2]. In general however, the opening of a superconducting gap is expected to modify the phonons only slightly because the redistribution of electronic states occurs within a narrow range of energies $\Delta E$ close to Fermi surface ($\Delta E \approx 2\Delta$), where $2\Delta$ is the magnitude of the superconducting gap, (typically tens of mev for high temperature superconductors). The range of the energy $\Delta E$ is orders of magnitude smaller than the widths of the valance and conduction bands (typically a few ev). Though their strength is small, superconductivity related phonon
self-energy effects in high temperature superconductors were found experimentally soon after their discovery. Similarly, anti-ferromagnetism related phonon self-energy effects were also studied. The changes of frequency and damping of a given phonon mode upon entering the superconducting state is called phonon anomaly [3, 4]. The phonon anomaly in co-existence phase of superconductivity and anti-ferromagnetism needs rigorous study both experimentally and theoretically. So far, it has been extremely difficult to discern anomalies in the phonon dispersion curves for cuprates. An independent and often more direct way to search for the electron-phonon coupling effects is to look for a line broadening. The most direct indication of electron-phonon coupling effect are changes occurring close to superconducting transition temperature $T_c$ and Neel temperature $T_N$. A broadening of the phonon is expected below $T_c$ if its frequency is larger than the superconducting gap. This can be understood as a consequence of creating an additional decay channel for the phonon the energy corresponding to breaking a cooper pair. At the same time, one expects either a softening or hardening of the phonon frequency depending on the relative position of the phonon with respect to the gap. The anomalies occurring at $T_C$ have been analyzed in terms of the opening of the superconducting gap. It may be caused by the superconducting fluctuations above $T_c$.

Generally speaking, one can also expect an influence on the phonon self energy by other types of excitations which modify the Fermi surface, if the phonon couples to that particular part of it. Such an excitation could be spin excitation etc. Qualitative estimates of the electron-phonon interaction constant can be obtained in course of studies on the effect of superconducting transition in optical phonons. At superconducting phase transition, a gap $\Delta$ appears in the spectrum of quasi particles which essentially alters the form of the phonon self energy. For phonons of frequency $\omega > 2 \Delta$, the renormalization $\Delta \omega$ due to electron-phonon interaction leads to an increase in their frequency (hardening). For phonons with frequency $\omega < 2\Delta$, the renormalization leads to reduction in frequency (softening). An increase in the density of states at the superconducting transition in the energy range $\omega \geq 2\Delta$ also leads to an increase in the relaxation rate
Anomaly in Raman active phonons.

and line width. These effects are investigated theoretically in Raman scattering of the anti-ferromagnetic normal state of cuprates in chapter-4. The temperature dependence of phonon frequency and line width for different Raman modes change by varying the composition $R = La, Nd, Pr, Eu, \ldots$ and different impurity atoms.

5.1.1 Temperature dependence of phonon frequency

We present a comprehensive analysis of Raman spectra in $R_{2-x}Ce_xCuO_4$ as a function of temperature. Temperature dependence of phonon frequencies of $Nd = 2 : 1 : 4$, is displayed in Fig.5.a [5]. It was shown in [6] that the lattice parameters $a$ and $c$ of the tetragonal unit cell shrink by $0.25\%$ and $0.24\%$, respectively, when sample is cooled from room temperature to $10K$.

![Temperature dependence of observed phonon in Nd$_{1.85}$Ce$_0.15$CuO$_4$](image1)

![Temperature dependence of $B_{1g}$ phonon in $R_{2-x}Ce_xCuO_4$](image2)

Fig. 5.a,5.b Temperature dependence of the observed phonon in Nd$_{1.85}$Ce$_0.15$CuO$_4$

Temperature dependence of the $B_{1g}$ phonon in $R_{2-x}Ce_xCuO_4$
The corresponding contribution to the temperature dependence of phonon frequencies should be $\approx 0.8\%$ (thermal expansion effect) when going from $Gd - 2:1:4$ to $Pr - 2:1:4$. It is seen in Fig.5.a, that the $A_{1g}$, $E_g$ and $A_{ig}$ modes harden in agreement with this, where as the $B_{1g}$ mode hardens by as much as $11cm^{-1}$, i.e. $3.4\%$.

The high temperature superconducting materials $YBa_2Cu_3O_7-\delta$ show a regular hardening when the sample is cooled as in the case of $Nd - 2:1:4$. In all cases only the $B_{1g}$ mode and not the other phonon show an anomalous behaviour. This effect becomes even more dramatic if the temperature dependence of $B_{1g}$ phonon in the other $R - 2:1:4$ compounds are considered in Fig.5.b. It is noticed in the third and fourth panel in the Fig.5.b that the anomalous temperature behaviour does not depend on the $Ce$ concentration (carrier density) in the $Nd$ system. As the rare earth radius increases in the order $Gd, Sm, Nd, Pr$, the slope $\frac{d\omega}{dT}$ becomes more negative. In $Pr - 2:1:4$, the slope becomes positive yielding rarely obtained large slope. In other words, the phonon frequencies as well as their temperature dependence behave anomalously. For $R = Pr$ the $B_{1g}$ phonon shows softening effect while $R = Nd$ shows hardening effect. This is an indication of a highly an-harmonic ionic field in which the $O_2$ atoms for $Nd - 2:1:4$ and $Pr - 2:1:4$ are placed. No anomaly in Raman spectra is observed at the critical temperature. Since $T_c$ is only 25 percent of that in $YBa_2Cu_3O_7$, one expects a super-conducting gap near $2\Delta \leq 70cm^{-1}$, i.e. in a frequency region that is difficult to measure with the spectrometer used. Phonon shifts can only occur when the phonon frequency is close to $2\Delta$. Since there are no Raman active phonons at such low energy, no phonon anomalies are expected in superconducting R-2:1:4 cuprate compounds.

5.1.2 plan of this chapter

In our present work, we report anomaly in Raman active phonons to study the normal state behaviour of the doped system. For this purpose we describe a model electronic Hamiltonian for the anti-ferromagnetic ground state of the
system and introduce an electron-phonon interaction in section - 5.2. We express the renormalized phonon energy in section - 5.3. The results are reported graphically and studied by varying different model parameters in section - 5.4.

5.2 Formalism

The strongly correlated ground state of the cuprate systems can be described by the electronic Hamiltonian

\[ H_0 = H_d + H_s + H_v + H_f \]  

(5.1)

where \( H_d \) is the hopping Hamiltonian. \( H_s \) is the Hamiltonian describing the staggered magnetic field in the copper oxide plane. \( H_v \) represents the hybridization interaction between the conduction and the f- electrons. \( H_f \) is the On-site f-electron energy level. The total Hamiltonian \( H_0 \) is discussed in detail in section-2.2 of chapter-2. The total electronic Hamiltonian involves the energy parameters like : the kinetic energy of the conduction band (\( \epsilon_k \)), the staggered magnetic field (\( h \)), the hybridization matrix element (\( V \)), and the renormalized f-level position (\( \epsilon_f \)).

In addition to the electronic Hamiltonian \( H_0 \), the electron-phonon interaction plays a role in describing the elastic properties of the cuprates. For simplicity of calculation, we consider here coupling of phonons to the hybridization of f- and d- electrons. This interaction indirectly involves coupling of phonons to d-bands, f-electron states and anti-ferromagnetism. Electron-phonon interaction results from the volume dependence of the bare hybridization parameter \( V \). The electron-phonon interaction Hamiltonian is

\[ H_{e-p} = \Sigma_{k,q,\sigma} f(q) \left[ (a_{k+q,\sigma}^\dagger f_{1,k,\sigma} + b_{k+q,\sigma}^\dagger f_{1,k,\sigma}) + h.c. \right] A_q \]  

(5.2)

with \( A_q = b_q + b_q^\dagger \) where \( b_q \) (\( b_q^\dagger \)) are annihilation (creation) operators for phonons with wave vector \( q \) and \( f(q) \) is the electron-phonon coupling constant. The derivation of this interaction is already given in section-2.2 of
chapter-2. The free phonon Hamiltonian with phonon energy \( \omega_q \) is written as
\[
H_p = \sum_q \omega_q b_q^\dagger b_q.
\]
The total Hamiltonian of the system is
\[
H = H_0 + H_{e-p} + H_p
\]  \hspace{1cm} (5.3)

This model can be applied to both Nd- and La- systems as well as \( R_{2-x} M_x CuO_4 \).

5.3 Mathematical Expression for Renormalized Phonon Frequency

The renormalized phonon frequency is calculated by setting the denominator of the eq. (2.160) to zero. Then
\[
\left[ \omega^2 - \omega_0^2 - \Sigma_{q=0}^{\omega}(\omega) \right] = 0
\]  \hspace{1cm} (5.4)
or
\[
(\omega/\omega_0)^2 = 1 + \left\{4\pi f^2(0)\chi_{00}(\omega)/\omega_0\right\}
\]  \hspace{1cm} (5.5)

Replacing the \( \Sigma_k \) by \( \int N(0)\epsilon_0(k) \) over the conduction band width \( W \) from \((-W/2)\) to \((+W/2)\), we can express the phonon response function given in eq. (2.163,5.4) as
\[
\chi_{00}(\omega) = 2 N(0) \int_{-W/2}^{W/2} \epsilon_0(k) \Omega
\]  \hspace{1cm} (5.6)

where \( N(0) \) is the density of states of conduction electrons at the Fermi level \( (\epsilon_F) \) and \( \Omega \) is defined in eq. (2.158,2.159). The phonon self energy is influenced by the position of f- level \( (\epsilon_f) \) with respect to the Fermi level, the hybridization parameter \( (V) \), the staggered magnetic field \( (h) \), the phonon coupling constant \( (f(0)) \), the hoping integral \( (t) \), and temperature \( (T) \). To understand the behaviour of the systems, we have investigated the influence of these parameters on different physical properties of the strongly correlated cuprates in normal state i.e. velocity of sound in chapter - 3, Raman spectra and its peaks in chapter - 4 and Raman phonon frequencies in dynamic limit in chapter - 5. To achieve this we parametrized.
different quantities by dividing them by a suitable energy parameter. Different quantities involved in eq. (5.6) are made dimensionless by dividing them by 2t.

\[ g = f^2(0) N(0)/\omega_0; \quad d = \epsilon_f/2t; \quad c = \omega/2t; \quad V = V/2t \]

\[ x_0 = \epsilon_0(k)/2t; \quad h = h/2t; \quad x = \epsilon_k/2t; \quad b = 2t/2kT \quad (5.7) \]

and

\[ x = \{ x_0^2 + (h^2/4)\}^{1/2}; \quad \Delta = \Delta/2t = [(x - d)^2 + 8V^2]^{1/2} \]

\[ y_{1,2} = (x + d \pm \Delta)/2 \]

\[ \beta \Delta/2 = \beta b; \quad \beta \epsilon_0(k) = 2b x_0; \quad \beta (\epsilon_k + \epsilon_f) = 2b(x + d). \quad (5.8) \]

Using these dimensionless parameters mentioned above, phonon self energy given in eqs. (5.4-5.6) reduces to

\[ 4\pi f^2(0)\chi_{00}(\omega)/\omega_0 = 4g \int_{-W/2}^{W/2} dx_0 \tilde{\Omega} \quad (5.9) \]

where

\[ \tilde{\Omega} = \left[ \frac{P \exp(2b x_0) - \{Q \sinh(b \Delta) + P \cosh(b \Delta)\} \exp(-b x_0 + d)}{|D|\{y_1 + x_0\} \{y_2 + x_0\}} \right] \]

where P and Q are expressed in terms of the model parameters (g, V, h, d, b) and are given in eq.(2.171 of chapter - 2. Using the eqs. (5.4-5.9), the temperature dependence of phonon can be studied by varying the dimensionless physical parameters defined in eq. (5.7).

5.4 Result and Discussion

5.4.1 Different Raman Active Phonon Modes

We have investigated Raman spectra exclusively with the aid of a number of plots and discussed elaborately the parametric dependence of the Raman...
phonon modes illustrating their physical implications. Here we present the Raman spectra for a set of standard dimensionless parameters.

The Fig. 5.1 shows the variation of spectral density function $S(0, \omega)$ with reduced frequency $\tilde{\omega} = (\omega/\omega_0)$ for fixed values of $d$, $h$, $V$, $g$ and $b$. In this plot we observe five peaks. The first peak ($p_1$) centered at $\tilde{\omega} \approx 0.195$ appears due to the rare-earth atom $R$. The second peak ($p_2$) centered at $\tilde{\omega} \approx 0.585$ appears due to anti-ferromagnetic transition. The third peak ($p_0$) at $\tilde{\omega} \approx 1$ corresponding to the renormalized phonon frequency. The peak ($p_3$) at $\tilde{\omega} \approx 1.125$ and the peak ($p_4$) at $\tilde{\omega} \approx 2.295$ are due to the vibration of the out of plane and in-plane oxygen atoms. These two are termed as cooperative modes.

Fig. 5.1 The plot shows the variation of phonon spectral density with reduced frequency $(\omega/\omega_0)$ for $d = -1.1, h = 0.8, V = 0.06, g = 6 \times 10^{-9}$

We have defined earlier the dimensionless quantities: $c = \omega/2t$ and $z = \omega_0/2t$

We have used $c=0$ and studied the phonon energy in the static limit in chapter 2. Here we calculate different Raman active phonon frequencies from the reduced frequencies ($\tilde{\omega}$) obtained from Raman spectra. Different $c$ values can be
Anomaly in Raman active phonons

calculated by using the relation $c = \tilde{\omega} \times z$, where $z$ is fixed at 1.4 in the calculation. In addition to other fixed parameters, the different $c$ values corresponding to the peaks P1 to P4 are used to investigate the phonon anomalies in Raman spectra.

Fig. 5.2. show the variation of $(\omega/\omega_0)^2$ with $b$ for the four Raman active phonon peaks. The peaks P1 and P2 appear at lower frequencies below the anti-ferromagnetic (AFM) gap exhibit softening. The peaks P3 and P4 appear at the higher frequencies above the $AFM$ gap and exhibit the hardening in frequencies. The parameter dependence of the individual peaks will be investigated elaborately in subsequent subsections.

![Graph showing $(\omega/\omega_0)^2$ vs. $b$](image)

**Fig. 5.2** The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of different Raman active Phonons of frequency $c=0.2730$, $c=0.8190$, $c=1.5750$, $c=3.2130$ and for other fixed values of $d = -1.15$, $h = 0.8$, $V = 0.06$, $g = 6 \times 10^{-9}$. 

5.4.2 Temperature Dependence of Peak P1

Fig. 5.3 shows the influence of the position of the renormalized f-level (d) on phonon frequency. It is observed that phonon frequency remains unaffected up to a temperature of \( b \approx 1.5 \) i.e. in the high temperature region. When f-level remains below the Fermi level \( (\epsilon_f = 0) \), its position is taken as -ve. The phonon frequency initially shows slow softening and then softens very quickly and freezes at a lower temperature (i.e. \( b \approx 5.7 \)). As f-level moves down the Fermi level from \( d=-1 \) to \(-1.15\), the hybridization between f-electrons and the conduction electrons becomes stronger. This gives rise to stronger coupling of the phonons to the hybridization and hence quicker is the softening.

![Graph showing the variation of \( (\omega/\omega_0)^2 \) with \( b \) (inverse of temperature) of peak P1 for different values of the position of f-level.](image)

The Fig. 5.4 shows the influence of the staggered magnetic field \( (h) \) on frequency. It is observed that the phonon frequency remains unaffected at \( \tilde{\omega} = 1 \) up to a temperature \( b \approx 4 \). Towards low temperature \( (b > 4) \), phonon frequency softens. As staggered magnetic field \( h \) increases from 0.7 to 0.8, the phonon
frequency decreases and freezes at temperatures $\approx 5.70$ and $5.55$ respectively. This softening in frequency is expected for peaks with mode frequency lying in the lower side of the anti-ferromagnetic gap.

Fig. 5.4 The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of peak $p_1$ for different values staggered magnetic field $h=0.7$, $h=0.75$ and $h=0.8$ for other fixed values of $d=-1.15$, $V=0.06$, $g = 6 \times 10^{-9}$.

Fig.5.5 shows the influence of the hybridization strength ($V$) between f-level and conduction band on the phonon frequency of the peak $P_1$. For the set of fixed parameters shown in the Fig.5.5, the hybridization has not any effect on the phonon frequency. The hybridization is varied from $V=0.03$ to 0.08, but the frequency does not show any change for the temperature range up to $b \approx 5.55$. 
Anomaly in Raman active phonons.

Fig. 5.5 The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of peak p1 for different values of the hybridization $v=0.03, 0.06$ and $V=0.08$ as a function of $b$ (inverse of temperature) for other fixed values of $d=-1.15$, $h=0.8$, $g=6 \times 10^{-9}$.

Fig. 5.6 shows the influence of electron-phonon coupling strength $g$ on phonon frequency. It is observed that the phonon frequency remains constant at $\bar{\omega} = 1$ up to the high temperature $b \simeq 4.0$. This means that the phonon coupling to the hybridization is poor at high temperatures. For low temperatures with $b \simeq 4.0$, phonon softening starts as temperature decreases. In this temperature range, the phonon softening is highly enhanced as phonon coupling parameter increases from $g = 2 \times 10^{-9}$ to $6 \times 10^{-9}$. This is the region where phonons are strongly coupled to the hybridization. As a result, phonon self energy increases and hence phonon softens. The phonon softens quickly leading to the destabilization of the lattice and freezing of phonon energy.
Anomaly in Raman active phonons.

5.4.3 Temperature Dependence of Peak P2

Fig. 5.6 The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of peak P1 for different values of $g=2E-9$, $4E-9$ and $6E-9$ as a function of $b$ (inverse of temperature) for other fixed values of $d=-1.15$, $h=0.8$, $V=0.06$.

Fig. 5.7 shows the influence of electron-phonon interaction parameter $(g)$ on the frequency of the peak P2. It is observed that phonon softens as temperature decreases. As electron-phonon interaction increases from $g = 0.5 \times 10^{-9}$ to $6 \times 10^{-9}$ the phonon softens at higher temperatures and freezes at temperatures $b = 5.7$ and $5.1$ respectively.
Anomaly in Raman active phonons.

Fig. 5.7 The plot shows the variation of $\left(\frac{\omega}{\omega_0}\right)^2$ with $b$ (inverse of temperature) of peak p2 for different values of $g=2E-9, 4E-9$ and $g=6E-9$ for fixed values of $d=-1.15, V=0.06, h=0.8$.

Fig. 5.8 shows the influence of the position of the renormalized f-level on the phonon energy. It is observed that the phonon frequency remains unaffected at higher temperatures for different values of the f-level position. However, the phonon frequency softens at lower temperatures and then softens very quickly, as the f-level moves down and away from the Fermi level. As the f-level moves down from $d=-1.1$ to $d=-1.2$ the phonon frequency softens and freezes at temperatures $b=5.35$ and $5.1$ respectively.
Fig. 5.8 The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of peak p2 for different values $d = -1.1, -1.15, -1.2$ for fixed values of $g = 6E - 9, V = 0.06, h = 0.8$.

Fig. 5.9 shows the influence of the hybridization between the f-level and the conduction band on the phonon frequency. The phonon frequency remains unaffected at higher temperature for all values of hybridization. It is due to the fact that phonon coupling to electron distribution is very poor at higher temperatures. However, as hybridization increases from $V=0.03$ to $0.08$, the phonon frequency increases indicating the hardening of this mode. This mode appears near the anti-ferromagnetic gap. Perhaps, anti-ferromagnetism is induced in f-electron from conduction electrons. As a result, this mode exhibits hardening effect as the hybridization increases.
Anomaly in Raman active phonons.

Fig. 5.9 The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of peak p2 for different values $V = 0.03, 0.06, 0.08$ for fixed values of $d = -1.15, h = 0.8, g = 6E - 9$

5.4.4 Temperature Dependence of Peak P3

The phonon mode of peak P3 lies on the higher side of the anti-ferromagnetic (AFM) gap and exhibits a complex anomaly. It changes its character depending on the value of the model parameters of the cuprate system. The hardening and softening behaviour is expected due to the interplay between anti-ferromagnetism and electron-phonon interaction.
Fig. 5.10 shows the effect of electron-phonon interaction strength on phonon frequency. As $g$ increases from $2 \times 10^{-9}$ to $6 \times 10^{-9}$, the phonon frequency softens very quickly at a temperature $b_N \sim 7.3$ (at Neel temperature) separating the ordered (AFM) phase and disordered magnetic phase at high temperatures. The electron-phonon interaction increases the Neel temperature. It is observed that the phonon frequency remains unaffected at $\tilde{\omega} = 1$ up to a temperature $b \simeq 5.0$ for any value of electron-phonon interaction. For $b \geq 5.0$, the phonon frequency softens very quickly near the Neel temperature. Below the Neel temperature, the phonon frequency hardens sharply as temperature decreases. The phonon frequency as well as velocity of sound is zero in (AFM) phase at low temperatures.

Fig. 5.10 The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of peak p3 for different values of the electron-phonon coupling constant $g=2E-9$, $g=4E-9$, $g=6E-9$ as a function of $b$ (inverse of temperature) for other fixed values of $d=-1.15$, $h =0.8$, $V=0.06$.

Fig.5.11 shows the effect of hybridization ($V$) between f- and conduction electrons on the phonon frequency. As hybridization strength increases from $V =$
0.04 to 0.06, the Neel temperature decreases from $b_N = 6.2$ to 7.3. It is now obvious that the hybridization decreases the Neel temperature, but electron-phonon interaction decreases the Neel temperature associated with the phonon frequency of the peak. Hence this phonon mode show strong anomaly. An (AFM) gap appears at Neel temperature $b_N = 7.3$ separating low temperature AFM phase from high temperature disordered magnetic phase. It happens due to the fact that the hybridization destroys the AFM of copper lattice due to the exchange of $f$- and conduction electrons. Furthermore, hybridization does not effect the phonon energy at high temperatures. However phonon frequency shows sharp softening at low temperatures (for say $V=0.06$) and freezes at $b = 7.1$ and creates a AFM gap near this Neel temperature. Then, phonon frequency very sharply hardens just below the Neel temperature.

**Fig. 5.11** The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of peak p3 for different values of the electron-phonon coupling constant $V = 0.04, 0.05, 0.06$ as a function of $b$ (inverse of temperature) for other fixed values of $d = 1.15$, $h = 0.8$, $g = 6E-9$.

Fig. 5.12 shows the influence of staggered ($h$) on phonon frequency. As staggered
magnetic field increases from $h=0.78$ to 0.82, the phonon frequency increases in magnitude exhibiting the hardening behaviour. As staggered field increases from $h=0.78$ to 0.82 the Neel temperature decreases and attains a lower critical value of $b_N$ (critical) $\approx 7.3$ corresponding to a critical staggered field $h_c$. When staggered field becomes greater than $h_c$, the phonon frequency hardens permanently even if the temperature is lowered. In strong anti-ferromagnetic phase, anti-ferromagnetic dominate over the electron-phonon interaction. Under this condition, electron fluctuation becomes smaller and hence phonon coupling to hybridization reduces further and further. This causes hardening of anomalous phonon mode of peak P3.

**Fig. 5.12** The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of peak p3 for different values of the staggered magnetic field $h = 0.78, 0.8, 0.82$ for other fixed values of $d=-1.15, V=0.06, g=6E-9$

Fig.5.13 shows the influence of the renormalized f-level($d$) on phonon frequency, when f-level remains below the Fermi level ($\epsilon_F = 0$), its position is taken as -ve. It is observed that the phonon frequency remains unaffected up to a temperature of $b \approx 4.0$ for all positions of f-level. For lower temperatures with $b \geq 4.0$
Anomaly in Raman active phonons, the phonon frequency softens and exhibits anomaly near Neel temperature \( b_N \sim 7.3 \), when \( f \)-level moves down from \( d = -1.1 \) to \(-1.2\) below the Fermi-level. For \( d = -1.1 \), the phonon frequency starts hardening towards low temperatures for \( b > 6.0 \). For \( d = -1.15 \), the frequency softens quickly and freezes at \( b \approx 7.1 \). At still lower temperature, an anti-ferromagnetic (AFM) gap appears and then phonon frequency hardens sharply just before the on-set of AFM order at low temperatures. For \( d = -1.2 \), the frequency softens continuously and freezes at \( b \approx 6.0 \).

\[ \frac{(\omega/\omega_0)^2}{b} \]

Fig. 5.13 The plot shows the variation of \( (\omega/\omega_0)^2 \) with \( b \) (inverse of temperature) of peak p3 for different values of the position of \( f \)-level \( d = -1.1, -1.15, -1.2 \) for other fixed values of \( V = 0.06, \hbar = 0.8, g = 6E - 9 \).

5.4.5 Temperature dependence of the Peak P4

The peak P4 in Raman spectra appears at \( \bar{\omega} = 2.295 \). This is the highest frequency mode of the Raman active phonon modes. It appears due to in-plane oxygen vibration cooperative mode. Its vibration is governed mainly under the influence of anti-ferromagnetism (AFM) present in the \( Cu - O_2 \) plane. Hence
Anomaly in Raman active phonons.......

this phonon mode is expected to exhibit hardening behaviour. The degree of
hardening depends on the model parameters of the individual cuprate systems
of the type $R_{2-x}M_xCuO_4$. This behaviour is presented in Figs. 5.14-5.16.

Fig. 5.14 presents the influence of electron-phonon interaction $g$ on the phonon
frequency of the peak P4. It is observed that the phonon frequency remains
unchanged at $\tilde{\omega} = 1$ up to a temperature $b \simeq 3.7$. This indicates that the
phonon coupling to the hybridization is poor (i.e. $g \sim 10^{-9}$).

![Plot](image)

**Fig. 5.14** The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature)
of peak P4 for different values of the electron-phonon coupling constant $g = 0.5E - 9, 2E - 9, 6E - 9$ for other fixed values of $d = -1.15, h = 0.8, V = 0.06$

At still low temperatures (i.e. $b > 3.7$), the phonon frequency hardens very
quickly, when the phonon coupling increases from $g = 0.5 \times 10^{-9}$ to $6 \times 10^{-9}$. The
interesting anomaly in this phonon mode is that the phonon frequency increases
in magnitude instead of decreasing for a particular value of the electron-phonon
coupling parameter ($g$). Then the renormalized phonon frequency becomes
$\tilde{\omega} \gg 1$. This situation can be visualized physically. When electron-phonon
interaction increases, it enhances hybridization between f-electron and conduction electron. It induces AFM in f-electrons from Cu-electrons due to exchange. The induced AFM of f-electron in addition to AFM order of Cu-sites enhance the hardening of the phonon mode of the peak P4.

Fig. 5.15 shows the effect of the position of the renormalized f-level (d) on the phonon frequency of the peak P4. It is observed that the phonon frequency remains unaffected up to a temperature of $b \approx 3.5$ for the change of f-level (d). At still lower temperatures (i.e. $b > 3.5$), the phonon frequency hardens very quickly, when the f-level below Fermi-level moves down from $d = -1.1$ to $d = -1.2$. This hardening in frequency at low temperatures is an anomaly to be explained physically. When f-level moves down, it hybridizes more strongly with the electron of the Cu atom and induces anti-ferromagnetism to the f-electron due to exchange. The induced AFM order enhances the hardening of the phonon mode of the peak P4.

Fig. 5.15 The plot shows the variation of $(\omega/\omega_0)^2$ with $b$ (inverse of temperature) of peak p4 for different values of the position of f-level $d = -1.1, 1.15, 1.2$ for other fixed values of $V = 0.06, h = 0.08, g = 6E - 9$. 

Anomaly in Raman active phonons.....

Fig. 5.16 The plot shows the variation of \((\omega/\omega_0)^2\) with \(b\) (inverse of temperature) of peak p4 for different values of the staggered magnetic field \(h = 0.7, 0.75, 0.8\) as for other fixed values of \(d = -1.15, V = 0.06, g = 6E - 9\).

Fig. 5.16 presents the influence of staggered magnetic field \(h\) on the phonon frequency of the peak P4. It is observed that the phonon frequency remains unaffected up to a temperature of \(b \approx 3.7\) for the change of magnetic field \(h\). It is due to the fact that the staggered field \(h\) counteract the softening effect of electron-phonon interaction \(g\) in this high temperature range. At still lower temperatures (i.e. \(b > 3.7\)), the phonon frequency hardens very quickly, when the staggered field increases from \(h=0.7\) to 0.8. The hardening of phonon frequency at low temperatures, arises due to the anti-ferromagnetic (AFM) order. The AFM order dominates over the softening effect due to the electron-phonon interaction and hence enhances the hardening effect of the phonon mode of peak P4.
Bibliography