Ordering and low energy excitations in strongly correlated bronzes

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Chapter 2

Coherent excitations in K_{0.3}MoO_3: Pump-probe spectroscopy

A study of ultrafast dynamics of coherent and incoherent excitations in the charge-density-wave system K_{0.3}MoO_3 is presented in this chapter. The physics of generation of coherent excitations through two main mechanisms, viz, the Displacive mechanism (DECP) and Transient Stimulated Raman scattering (TSRS) are discussed with examples from the literature. The role of photoexcitation in the generation and the dephasing of the coherent amplitudons in K_{0.3}MoO_3 is discussed. The fast and ultra-fast physical processes observed in the transient reflectivity and their response to the variation of the wavelength and fluence of the pump pulse are presented. The data unravel the mechanism of creation and decay of coherent amplitudons in K_{0.3}MoO_3. Dephasing of the coherent amplitudon mode (AM) with the increased life-time of the quasi-particles indicates a strong coupling of the AM to the photo-excited quasi-particles.

2.1 Introduction

The study of ultrafast processes in solids has been gaining significance due to the advent of the state of the art techniques like time-resolved optical spectroscopy, and together with a rich variety of information it provides about the nonequilibrium and nonlinear properties of solid systems. One can address excitation and energy-relaxation of the photoexcited carriers, quasi-particles, energy-gap recov-
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Energy dynamics in superconductors, and charge-density waves and so on. For example, recent femtosecond time-resolved experiments on MgB$_2$ [1], a recently discovered superconductor [2], have revealed the Cooper pair-breaking dynamics. The interplay of the energy-relaxation among electron-electron and electron-phonon subsystems are addressed. These experiments are capable of addressing "how exactly the energy-relaxation takes place and what are the constituent physical processes which govern the relaxation processes?". The energy-relaxation of photoexcited quasi-particles mainly depend on the available density of states and consequently this also provides information about the density of states. The availability or the unavailability of the decay channels to the photoexcited carriers may provide indirect information about the density of states and their possible origin [3]. For instance, in this study the temperature dependence of the relaxation of the photoexcited carriers revealed the presence of intragap states. The energy-gap structures in materials with ground states like superconducting and charge-density wave may also be studied using femtosecond time resolved pump-probe technique. In a recent study the nature of the Fermi-surface has been revealed by measuring the relaxation-time of the quasi-2D dichalcogenides, 1T-TaS$_2$ and 2H-TaS$_2$, [4]. In this study the validity of the Fermi-liquid theory in the quasi-2D materials were addressed.

Ultrafast spectroscopic studies on metals were able to address the real-time electron-phonon interactions and thereby determining the electron-phonon interaction parameter (generally called $\lambda$) which is obtained by the measured electron-phonon relaxation-time.

These experiments exemplify how in time domain the various excitations interact with each other in solid systems, and they are important to understand the physics governing the ground state and low-energy excited states of materials. Understanding of the fast dynamics of photoexcited carriers is also important for technological applications of these materials, for instance, in the design of very fast switching devices.

A coherent excitation of phonons in solids is another vast field which is triggered by the femtosecond time-resolved pump-probe techniques [5]. The origin and decay/dephasing of the coherent phonons can also be addressed. Our aim in the present work is to understand the ultra-fast dynamics of the charge-density-wave (CDW) material $K_{0.3}MoO_3$.

2.1.1 Coherent phonons: As seen in literature

Since about two decades, many researchers have been studying the response of materials to optical pulses on a femtosecond time scale using optical pump-probe
techniques [6–9]. Two topics have attracted particular interest. First, the study of time resolved dynamics of various coherent and incoherent excitations, and second, there is an increasing interest towards optically induced phase transitions [10]. Femtosecond pump-probe techniques have been applied in the past to study ultra-fast physical processes in semiconductors and nowadays this has expanded to a large variety of materials including metals, magnetic materials and superconductors [11–13]. Coherent modes manifest themselves in transient measurements as a temporal modulation of the reflectivity or transmission with the frequency of the coherent mode. To excite such modes, laser pulses with a duration shorter than the inverse of the fundamental vibration frequency are a prerequisite. The coherently excited modes are associated with a coherent macroscopic occupation of the excited state. First time-resolved observations of non-equilibrium phonon dynamics were performed by means of time-resolved Raman scattering techniques [14]. Extensive investigations of the phonon dynamics in InP and GaAs have been performed by this technique by Vallée et al. [15–17]. The thirst for understanding the generation mechanism of coherent excitations mainly in semiconductors, drove the origin of two theories. A mechanism called displacive excitation of coherent phonons (DECP) was proposed to explain the generation of coherent phonons in absorbing condensed matter [18], whereas in the non-absorbing materials the transient stimulated Raman scattering mechanism [19] is more relevant. We briefly sketch the main essence of both the theories below.

### 2.1.2 Displacive Excitation of Coherent Phonons

The DECP mechanism was proposed by Zeiger et al., [18]. The main prerequisite of this mechanism is the existence of an \( A_1 \) mode which performs fully symmetric oscillations. When a laser pulse (‘pump’-pulse) of sufficient energy is incident on a solid surface it may create interband electronic excitations. At sufficiently short times followed by the photoexcitation one may find a finite electronic density \( n(t) \) in the higher bands. This also increases the electronic temperature at the Fermi level. The electronic excitation across the band destroys the thermodynamics equilibrium between the electronic and the lattice subsystems. Thus the new state created by the nonequilibrium electronic distribution creates a displacive potential to which the lattice subsystem responds to it by performing oscillatory motion. One can write the rate of change of the electrons in the excited bands as, \( n(t) = \rho P(t) - \beta n(t) \). Where, \( \rho \) is the constant of proportion which is determined by the absorption coefficient, and \( P(t) \) is the power density of the pump-pulse, and \( \beta \) is the decay rate of the excited electrons back to the ground state. The source of excitation of the \( A_1 \) mode is due to the dependence of the equilibrium nuclear
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coordinate $Q_0(t)$ on $n(t)$. In the first approximation this dependence is taken to be linear. If $Q(t)$ is the displaced equilibrium coordinate of the nuclii one can write the equation of motion as, $\ddot{Q}(t) = -\omega_0^2[Q(t) - Q_0(t)] - 2\gamma \dot{Q}(t)$. Where $\omega_0$ is the frequency and $\gamma$ is the damping constant of the mode, respectively. The density of the photoexcited carriers in the higher bands is determined by the energy of the pump-pulse and the absorption coefficient of the material. Thus the dependence of the photoexcited electronic density on the displaced nuclear coordinates is made clear [For a detailed derivation of the expressions refer [18]]. Since in the experiments one observes the reflectivity oscillations, one has to consider the various contributions to the change in the reflectivity. There can be three contributions, 1. due to the excited electrons in the higher bands, 2. due to the change in the electronic temperature, and 3. due to the change in the nuclear coordinates. Thus one can write the change in the reflectivity due to all the above factors as,

$$\frac{\Delta R(t)}{R} = A\cdot C + B\cdot \text{damp.} \int G(t-\tau)[e^{-\beta \tau} - e^{-\beta \tau}(\cos(\Omega \tau) - (\beta / \Omega)\sin(\Omega \tau))]d\tau,$$

Where

$A = \frac{1}{\rho_{\varepsilon \text{pump}}} \left[ \left( \frac{\partial R}{\partial \epsilon_1} \right) \left( \frac{\partial \epsilon_1}{\partial n} \right) + \left( \frac{\partial R}{\partial \epsilon_2} \right) \left( \frac{\partial \epsilon_2}{\partial n} \right) \right]$ which represents the change in the reflectivity due to the presence of the electrons in the excited band. As it can be seen from the expression it does not contain any oscillatory part and hence this appears as an exponential decay term in the transient reflectivity experiments.

$B = \frac{1}{\rho_{\varepsilon \text{pump}}} \left[ \left( \frac{\partial R}{\partial \epsilon_1} \right) \left( \frac{\partial \epsilon_1}{\partial Q} \right) + \left( \frac{\partial R}{\partial \epsilon_2} \right) \left( \frac{\partial \epsilon_2}{\partial Q} \right) \right]$ which represents the change in the reflectivity due to the nuclear coordinates and there is no oscillatory part in it.

The third term (the terms in the integral) contains both sign and cosine contributions which essentially involves the oscillations in the transient reflectivity.

When $\beta$ is large, which means a rapid decay of the excited electrons back to the ground state, the oscillations are suppressed. This indicates that the coherent phonons are generated due to the presence of the photoexcited electrons in the higher bands, which hints the significance of the absorption of the pump-pulse into the sample. Semimetals and semiconductors were observed to follow the DECP behavior. Typical examples are Sb, Bi, Te [18].

Although, absorbing materials are considered to show DECP behavior, recent experiments on Sb [19] shows that another, competing mechanism, called Transient Stimulated Raman Scattering (TSRS) is also present.

Another way that the sub-picosecond laser pulses generate the driving force is
by inducing a change in the polarizability of the second order Raman tensor \( \frac{\partial N}{\partial Q} \). This process is often called Stimulated Raman Scattering (SRS), and in the case of time-resolved measurements its often called Transient Stimulated Raman Scattering. TSRS is basically ultrafast conventional Stimulated Raman scattering which does not require an absorption of the pump pulse in the sample. TSRS is a coherent two photon process in which a photon from the pump-pulse makes a transition to an electronically excited state (possibly a virtual state) and a second photon from the same pump-pulse stimulates a transition to a final state. If the energy difference between the two photons matches with an excited state it can excite the mode. To observe excitations in a coherent way the width of the probe pulse must be less than the inverse of the frequency of the mode. While DECP deals with inter-band excitations that couple to real electronic states, Transient Stimulated Raman Scattering (SRS) deals with the coherent modes excited by laser pulses whose energies are typically below the band-gap and is more relevant in the case of transparent materials. A detailed discussion of both the mechanisms is beyond the scope of this work, however, one can refer [18, 19] for more details. Thus femtosecond time resolved pump-probe spectroscopy gives an excellent possibility to observe and study the ultra-fast processes in solid systems. The photoexcitation of quasi-particles, coherent phonons, phonons, and other fundamental excitations and their subsequent decay can be monitored in real-time. In the following section we briefly sketch the essence of the experimental technique.

2.2 Experimental set-up

2.2.1 Principle of the pump-probe measurement

In general, sub-picosecond laser pulses are a prerequisite for exciting and observing coherent excitations in solids. In the experiment a sub-picosecond pulse is split in to two pulses of unequal intensities. The more intense pulse (often called pump-pulse) is used to induce transient changes in the sample. The weak pulse is again split in to a reference pulse and a probe pulse. The probe pulse that is delayed with respect to the pump pulse measures the the photo-induced changes induced by the pump pulse in the solid system. Intensity of the probe pulse is at least two orders of magnitude lesser than the pump pulse which is essential in order not to perturb the sample. The reference pulse is reflected off the sample surface before the arrival of the pump pulse. The differential reflectivity of the reference and the probe pulses constitute the signal. The photoinduced effect appears as a transient change in the reflectivity/transmission of the sample.
2.2.2 The Experimental set-up

This section describes the experimental set-up of the standard femtosecond pump-probe spectroscopy along with the collection of signals using box-car detection techniques. A schematic optical plan of the experimental set-up is shown in the figure 2.1. The optical delay between the reference-pulse, pump-pulse and the probe-pulse are designed such that the reference-pulse reaches the sample surface before the pump-pulse and the probe-pulse after the pump-pulse. At the surface of the sample the pump and the probe pulses are focused to a spot of 150 microns and 50 microns respectively. The larger spot size of the pump pulse ensures a better spatial overlap with the probe pulse and a more homogeneous probe region. The lenses used in the experiment are not shown in the diagram. The sample is glued to a sample holder using silver paste and is placed in a He-flow cryostat which has quartz windows and allows to vary the temperature between 4.2 K and 300 K. The polarization of the pump beam is always kept parallel to the b-axis.

Figure 2.1: The Experimental set-up.
of $K_{0.3}MoO_3$ along which the CDW ordering develops. After reflecting from the sample the differential output between the probe pulse and the reference pulse constitutes the signal which is detected by a detector which is a photodiode difference detector. The output of the detector is fed in to either a lock-in amplifier or a Boxcar integrator. We briefly describe the operation of it. The Boxcar integrator used is a SR250 model gated versatile high speed module designed to recover fast analog signals from noisy backgrounds. The SR250 consists of a gate generator that provides an adjustable delay from a few nanoseconds to 100 milliseconds. The input signal will be sampled when the gate is on. The fast gated integrator integrates the input signal when the gate voltage is on. The output from the integrator is normalized by the gate width to provide a voltage that is proportional to the average of the input signal during the sampling gate. The signal is further amplified using an amplifier. The last sample output allows to do a shot-by-shot analysis of the signal. Finally, the output of the Boxcar is fed in to the computer through a suitable interface. Experiments are performed typically using polarized light in a reflection geometry with the angle of the pump and the probe pulses close to normal incidence with respect to the sample surface with a typical pump fluence (expressed as energy per $cm^2$) of 1-10 mJ/cm$^2$.

Thus, the requirements of the experiment are primarily a laser pulse with a width of about 120 fs and wavelength that can be tunable over a wide range. A Hurricane laser system can provide a laser pulse of 800 nm and 120 fs. To get wavelength tunable pulses we used a light conversion system called Travelling wave Optical Parametric Amplifier of Superfluorescence (TOPAS). Both these laser sources are coupled optically to meet the requirements of the experiment. The following paragraphs give a brief description of the femtosecond laser system used in the present study.

### 2.2.3 Description of the Hurricane

A schematic diagram of the laser system is shown in the figure 2.2. The laser system Hurricane consists of four main components, 1) A seeding laser called Mai-Tai 2) Evolution laser 3) Stretcher, compressor and 4. Regenerative amplifier. The Mai-Tai consists of two lasers, a cw (continuous-wave) diode-pumped laser and a mode locked Ti:Saphire pulsed laser, together with the other necessary elements like power supply unit, chiller etc. The cw diode-pumped laser emits 532 nm light with an output power of about 5 W. Since Ti:Saphire has a broad absorption band in the blue and green region the output of the 532 nm cw-laser acts as an ideal pump for the Ti:Saphire cavity. The second part of the Mai-Tai consists of mode-locked Ti:Saphire cavity which consists of Ti:Saphire rod, focusing mir-
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![Diagram of the Hurricane laser system]

Figure 2.2: The schematic diagram of the Hurricane laser system.

rors and other optical elements. The Mai-Tai thus delivers continuously tunable pulsed output at 80 MHz repetition rate over a range of near infrared wavelengths from 750 to 850 or 790 - 810 nm with a pulse width of about 100 fs. The Evolution laser is a diode-pumped, intracavity doubled Nd:YLF laser which is capable of producing Q-switched pulses with an average power of about 6 W at 523.5 nm at a repetition rate of 1 kHz. The main elements of the Evolution laser are a Diode-pumped Nd:YLF laser head, Optical resonator, Acousto-optical Q-switch and a LBO (Lithium triborate) frequency doubling crystal. In this laser the lasing material used is Nd:YLF (Nd:LiYF$_4$) which has two laser transitions at 1053 nm and 1047 nm with different polarizations. Among these two lines, the Evolution laser system utilizes 1047 nm due to a higher gain cross section. The Q-switching is achieved when the light beam is diffracted on an optical phase grating which is generated by launching an ultrasonic wave on a transparent material. The laser comes to the high-Q state by controlling the voltage supply to the piezo-electric transducer that drives the ultrasonic wave. The frequency doubling crystal LBO is used to achieve the necessary power densities which is generally not available from a cw-pumped laser. The third main component of the Hurricane is stretcher and compressor. The ultra short pulses have a very high saturation fluorescence which can lead to self focusing. This problem can be solved by using a stretcher...
and a compressor combination. When a pulse is stretched it’s peak power is distributed over a relatively large area and hense it’s power density is lowered. This lower power density reduces the possibility of damage due to self focusing. The pulse stretching and compression uses diffraction gratings. Thus the Hurricane Ti:Sapphire regenerative amplifier is designed to amplify individual pulses from a mode-locked Ti:Sapphire laser. Typically an input pulse of energy only a few nanojoules can be amplified to over 1 mJ. The output pulse from the hurricane is with an energy of 750 µJ and a pulse width of 120 fs operating at 1 kHz. Contrast to the 80 MHz repetition rate which was used in the case of [20], we used 1 kHz. This low repetition rate allows the sample to relax completely before the next pulse arrives, thus minimizing the heating effect due to the pile-up of pulses.

2.2.4 Description of The TOPAS

To get laser pulses of continuously tunable wavelengths one needs an energy conversion technique. A widely adopted method is based on an optical parametric generation that uses a non-linear crystal like Lithium triborate (LBO). The optical parametric generation is the inverse process of the sum frequency generation. In optical parametric generation a photon of certain frequency is split into two photons of lower frequencies.

The TOPAS (Travelling wave Optical Parametric Amplifier of Superfluorescence) operation is based on a second order nonlinear optical process - three photon parametric interaction in noncentrosymmetric crystals. The frequency matching condition to be satisfied is $\omega_3 = \omega_1 + \omega_2$, where the subscripts 3, 1 and 2 corresponds to the pump pulse, and the other two parametric waves are called the signal and the idler. The parametric light converters can be tuned over wide frequency range. A pair of signal and the idler can be amplified efficiently if the phase-matching condition below

$$n_3\omega_3 = n_1\omega_1 + n_2\omega_2$$

is satisfied simultaneously with frequency matching condition. The frequency of the idler and the signal can be tuned continuously by changing the indices $n_1$, $n_2$, and $n_3$ controlling the crystal orientation, it’s temperature, pressure or electric field applied to the crystal. TOPAS also uses the principle of sum/difference frequency generation and second harmonic generation to cover a wide frequency region ranging from the far-infrared to the UV range. The output of the ”Hurricane” (the 800 nm pulse) is fed into the frequency converter TOPAS. The optical scheme of TOPAS is presented in the figure 2.3. From the figure one can easily notice that there are five passes in which the input pump beam travels. In the first pass (A1-M1) the diameter of the input pump beam is reduced by spherical
telescope and further focused by a cylindrical lens in order to generate superfluorescence in the nonlinear crystal. The iris aperture A1 controls the intensity of the pump beam. The beam splitters BS1 and BS2 couple the beam to fourth and the fifth pass. In the second pass the weak superfluorescence signal is amplified by several orders. These two stages act as preamplifiers and shape the beam. In the third pass (BS2-M3-M3'-M4-GP-M5-NC-DG-M7) a fresh pump-beam coming from by BS2 passes through the nonlinear crystal and incident on the grating. The grating generates the parametric signal in the fourth pass. The angular alignment of grating is done through the software supplied by the company "LIGHT CONVERSION". The fifth pass starts from the beam splitter BS1 and forms the parametric seed beam for the power amplifier. This parametric seed beam is overlapped in space and time with the fresh pump beam on the mirror M11. The temporal alignment is done by adjusting the mirror M10 and moving the delay (not shown in the figure) and looking for the increase of the signal at the output of the TOPAS.

Figure 2.3: The Optical plan of TOPAS describing the beam-pass. Codes: A: Iris aperture, BS:Beam splitter, L:Lens, CL:Cylindrical lens, M:Mirror, CM:Cylindrical mirror, NC:Nonlinear crystal, TD:Time delay, DG:Diffraction Grating, GP:Glass plate (used here as a time delay compensator).
2.2.5 Coherent Amplitudon and few questions

After giving a brief overview of the mechanism of coherent excitations we wonder what would be the generation and decay mechanism of the so called collective mode viz, amplitudon-mode (AM) of the well known and well studied charge-density-wave system K$_{0.3}$MoO$_3$. Recently, coherent oscillations of AM have been observed as a modulation of the reflectivity in K$_{0.3}$MoO$_3$ [20]. This opens up a channel to study the real-time dynamics of the AM using femtosecond time-resolved pump-probe spectroscopy. The questions like what underlying mechanism generates the coherent AM, what is its life time, what are the dephasing mechanisms and what is the role of the quasi-particles and more importantly its response to the various wavelengths of pump-pulse are not hitherto answered in the literature of femtosecond physics of K$_{0.3}$MoO$_3$. An important issue here is the role of coherence which is essential to observe the excitations in real-time.

2.3 The Transient Reflectivity of K$_{0.3}$MoO$_3$

The transient reflectivity response, $\Delta R/R$ of blue bronze measured using the standard pump-probe technique is shown in figure 2.4. The pump-pulse arrives at time $\delta t = 0$, where $\delta t$ is the time delay between the arrival of the pump and the probe at the surface of the sample. As seen from the figure 2.4, the $\Delta R/R$ response contains a sharp change in the reflectivity followed by a non-exponential decay (decay time $\approx 0.5$ ps) on which distinct oscillations are superimposed. The Fourier transformation of the oscillations, as seen in the inset of the figure, shows that there are three coherent modes with energies 1.67 THz, 2.25 THz and 2.5 THz.

In contrast to these observations at $T = 4.2$K the $\Delta R/R$ above $T = 180$ K shows only a sharp increase followed by a fast exponential decay (decay time $< 180$ fs) as shown in figure 2.5. No coherent reflectivity oscillations were observed above 180 K.

2.4 Data analysis and Discussion

It is relatively straightforward to analyze the oscillatory part of the $\Delta R/R$. While all these three modes are observed in the CDW state of the material the mode at 1.67 THz is found to be a soft-mode from Raman measurements (discussed in the next chapter). It’s frequency shifts towards lower values and finally vanishes as the temperature is approached to $T_{CDW}$ from below. We also observed an enormous
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Figure 2.4: Transient Reflectivity response of $K_{0.3}MoO_3$. Inset: Fourier Spectrum showing the amplitudon mode at 1.67 Thz, and two zone folded phonons at 2.25 Thz and 2.5 Thz.

broadening in the full width at half maximum of this mode (often called linewidth) and tends to diverge with increasing the temperature towards $T_{CDW}$. Based on these observations this mode is assigned to the amplitudon mode (AM) which is arising due to a transverse oscillation of the coupled electron-lattice system. The energy of this mode matches well with the previous time resolved and Raman measurements [20, 21]. The two coherent phonons could very well be ascribed to the new phonon modes activated in the CDW-state due to the folding of the Brillouin-zone below $T_{CDW}$. All these three modes are observed as $A_g$ modes (or fully symmetric breathing modes) in the Raman measurements shown in the figure 2.7.

To understand the origin of the transient dynamics the $\Delta R/R$ response shown in the figure 2.4 is fitted using Matlab by convoluting the cross-correlation of the pump and the probe with the various contributions.

$$\frac{\delta R}{R} = Ae^{(-t/\tau_{QP})^n} + Be^{-(t/\tau_L)} + \sum_j A_je^{-(t/\tau_j)} \cos(\omega_j t + \phi_j)$$  \hspace{1cm} (2.1)
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Based on the reasons given below the terms in the equation can be interpreted as follows. The first term is due to the quasi-particle decay, the second term is due to the lattice cooling and the third term denotes the coherent amplitudon oscillation and the two coherent phonons.

Table 2.1: Various decay times in ps extracted from the fit equation for $\Delta R/R$. The subscripts $QP$, $AM$, $Ph1$ and $Ph2$ refer respectively to Quasi-particles, Amplitudon, Phonon 1 and Phonon 2 respectively.

<table>
<thead>
<tr>
<th>Relaxation times(ps)</th>
<th>$A$</th>
<th>$B$</th>
<th>$\tau_{QP}$</th>
<th>$\tau_{cooling}$</th>
<th>$\tau_{AM}$</th>
<th>$\tau_{Ph1}$</th>
<th>$\tau_{Ph2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.53</td>
<td>0.12</td>
<td>0.6 ns</td>
<td>3.5</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

The parameters obtained from the fit are displayed in table [1] and the various constituents of $\Delta R/R$ are shown in figure 2.8. Based on the observations together with the parameters extracted from the fit the observed $\Delta R/R$ can be interpreted as follows. Since the energy of the pump pulse is much larger than the CDW gap ($\Delta_{CDW}=0.12$ eV [22]) we can expect that the optical pumping can excite quasiparticles across the Peierls gap (also called CDW gap in the present case). The experiments have been done in the high fluence limit (1-10...
mJ/cm$^2$) the pump pulse therefore creates a large number of quasi-particles from the CDW-condensate (About $10^{15}$ QPs per pulse, assuming each photon creates about $E_{pump}/2\Delta \approx 50$ QPs, and about $10^{14}$ photons absorbed per pulse). After the photoexcitation the internal thermalization among the excited electrons (often called hot carriers) occurs on the time scale of about 30 fs [20] and our temporal resolution is not enough to observe this effect. However, when the thermalized electrons reach near the Fermi level the relaxation is delayed due to the presence of the gap. (The mechanism of this "delayed relaxation" is presented in the next section). In the response $\Delta R/R$ the sharp initial change in the reflectivity is due to the presence of the electronic quasi-particles above the CDW gap. After about 0.5 ps the transient reflectivity relaxes back due to the decay of the quasi-particles across the gap. The observed quasi-particle decay is not a simple exponential one as in the case of [20] but its rather a stretched exponent as described in the first term in equation [1] with the index power, $n = 0.5$. At room temperature a more fast quasiparticle decay of about 200 fs is observed which can be well fitted using an exponential decay. This shows that presence of the CDW gap hinders the fast relaxation of the excited quasiparticles where as when the gap is closed above $T_{CDW}$ a faster decay is observed.

After a picosecond the transient reflectivity relaxes back to about 80 percent of its initial value near $\delta t = 0$. The second slower exponent has a decay time of more than a nanosecond. This can be interpreted as heat diffusion due to phonon excitations. It is worth to recall that the slowest decay component was also observed in [20] and was ascribed to the phason-mode of the CDW state. They argued that the pinned phason-mode can contribute to the transient reflectivity as a long living component. Though this argument seems convincing in the first approximation our results contradict this. Our $\Delta R/R$ data at room temperature where there is no CDW-gap shows the presence of the long lived component as well which is evident from the figure 2.6. It is also observed in our data that the long living component (or $\Delta R/R$ at $t$ greater than 100 ps) is a linear function of the pump-power.

These observations suggest that this is likely a heating-effect rather than due to the presence of phasons. While, a minor contribution of phasons to $\Delta R/R$ below $T_{CDW}$ cannot be ruled out completely the major contribution comes from lattice heating.

It is interesting to note that the coherent amplitudon is very short lived when compared to the two coherent phonons. The typical life time of the coherent amplitudon mode measured in our experiment is about 3.5 ps where as the two other coherent phonons live more than 25 ps. While in [20] the amplitudon life time
was about 10 ps, it is worth to note that the pump-fluence used in their experiment was about 1000 times smaller than in the present case. The observed short lifetime of the coherent AM in our experiment can be due to the large number of quasi-particles excited as a consequence of a high pump-fluence used in the experiment. These quasi-particles can scatter from the coherent amplitudons through electron-phonon or electron-electron interaction thereby reducing the lifetime of the amplitudon mode. The magnitude of the effect $\Delta R/R$ is considerably larger than what was observed in Ref [20]. A huge $\Delta R/R$ as large as 10 percent, is observed in our case, where as they measured as low as $10^{-4}$. This is due to the large pumping power used in our experiments and the power dependence scales satisfactorily with the magnitude of the effects in the two cases. The collective modes, together with the change in reflectivity are observed when the pump-polarization was parallel to the direction along with which the CDW ordering develops or in other words, along the metallic direction.

If the observed three coherent modes can be principally considered as three closely spaced harmonic oscillators it may be possible to enhance or suppress one of them using a pulse train of properly tuned time-spacing. In the following
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Figure 2.7: The Raman spectrum showing AM and the two fully symmetric modes in $K_{0.3}MoO_3$.

section we present the results of such an attempt.

2.5 The Selective excitation of CDW in $K_{0.3}MoO_3$

Recently the feasibility of using the collective AM excitation of a CDW in combination with femtosecond-pulse laser beams to represent data written on the surface of a $1T-TaS_2$ crystal has been reported [23]. In this study they demonstrated that the switching of the AM on and off by suitably tuning the timing of the incident pump laser beam to a significant accuracy is possible. It was also shown that one can control the phase and amplitude of the collective AM mode by laser pulses and thus it can be used as a switchable THz optical modulator. Parallelly, we performed a similar study on $K_{0.3}MoO_3$ and found that among the three coherent modes one of them can be selectively enhanced while suppressing the other. Such a resonance enhancement has got some technical importance. One and the most interesting is to make ultrafast coherent-control data storage devices using coherent modes or coherent AM mode. If one of the coherent modes is considerably
long living, say >10 ps, by applying a Π pulse (a laser pulse that is out of phase with the coherent oscillation) one can switch between on and off states of the coherent mode. A longer life time of the coherent excitation allows one to store the data in terms of amplitude and phase of the oscillations. This can be used as a coherently controlled data processor.

In the experiment we excited first the system with a strong pump pulse of about 1 mJ/cm² which is divided equally in intensity into four pulses. The four pulses are consecutively delayed using a home-build optical delay which is made up of glass plates of suitably adjusted thickness. The thicknesses are adjusted so that the optical delay generated between each pulse is equal to \( nt_{AM} \), where \( n = 1 \) to 4 and \( t_{AM} \) is the period of the amplitudon mode. The optical delay stage that splits the pump pulse is attached to a rotating stage whose axis is horizontal to the optical table and perpendicular to the incoming laser pulse. The delay between the divided pulses can be tuned with a sub picosecond precision by adjusting the angle of the rotating stage. The rotation can make an oblique incidence to the incoming laser pulse thus can vary the thickness and hence the optical delay between the pulses.
2.6 Results and discussion

Fig. 2.9 shows the transient reflectivity for different pump power at \( T = 40 \text{ K} \). Together with the exponential relaxation components described in the previous section the other three components are damped oscillations with frequencies 1.67, 2.2, and 2.5 THz (56, 74, and 85 \text{ cm}^{-1}). All three resonances can also be clearly seen in the Fourier spectrum \( F(\nu) \) in Fig. 2.10. The inset in Fig. 2.9 depicts the dependence of the amplitudon frequency \( \nu_A \) and damping \( \Gamma_A \) upon the pump power. It is observed that the frequency of the AM mode weakly depends on the pump power. This shows that there is hardly any heating effect. The absolute values of \( \nu_A \) and \( \Gamma_A \) agree very well with previous Raman \([21, 24]\) and pump-probe experiments \([20]\).

Due to the non-linear power dependence of the amplitudon, discussed below, the Raman modes become well resolved at relatively high power only. This is probably the reason why they were not reported previously \([20]\). Another method to increase the sensitivity to particular modes is the use of a pulse train with a
Figure 2.10: Fourier spectrum of the transient response for the single pulse pump excitation (A), and the four pulse trains for two different pulse separations. Left inset: transient reflectivity, induced by four-pulse trains. Right inset: cross-correlation of the pump pulse train with the probe.

spacing tuned to the period of the mode. A typical pump-probe cross-correlation function of such a pulse train is shown in the right inset of Fig. 2.10. Fig. 2.10 shows a Fourier spectrum of a single pulse response at high power. When the train repetition rate is tuned to a resonance, we can suppress the other components as demonstrated by the 600 fs spectrum (i.e. tuned to $\nu_A$, the transient reflectivity for this experiment is shown in the left inset). Thus we were able to suppress the coherent mode of 2.23 THz while enhancing the AM mode. In the case of $1T$-TaS$_2$ crystal reported in [23] it was possible to reduce the amplitude of the coherent mode while in our experiment a full suppression of the 2.23 THz mode is possible. On and off states of the coherent state is more effectively achieved in our experiments which makes $K_{0.3}\text{MoO}_3$ a better and promising system for coherent controlled data processing.

Power dependent experiments were done with an intermediate tuning (500 fs) between the phonons and the amplitudon. From the Fig. 2.9 one can see that the oscillatory component, mainly determined by the amplitude mode, ini-
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Potentially increases with the pump power, reaches its maximum at -5 dB, and falls back at higher power. The amplitude of the 1.67 THz resonance normalized to the pump power, \( F(\nu_A)/P \) is plotted vs the pump power in the right panel of Fig. 2.9 together with the other two resonances. As can be seen, \( F(2.23 THz)/P \) and \( F(2.5 THz)/P \) remain fairly constant over a wide range of pump power. In contrast, \( F(\nu_A)/P \) shows a strong \( P \)-dependence, which results in a highly nonlinear relation \( F(\nu_A) \sim P \cdot \log P_0/P \), where \( P_0 \) is a constant.

It is unlikely that the observed effects are due to heating. Because \( \nu_A \) and especially \( \Gamma_A \) are strongly temperature dependent, they can serve as a measure of heating. From a comparison of the data in Fig. 2.9 to Raman and pump-probe data [20, 21] we conclude that the 4 % change in \( \nu_A \) and 30 % change in \( \Gamma_A \) observed in the present experiments would account for no more than 20 K change in temperature. And thus, the temperature of the sample remains well below the transition temperature 183 K and well below the mean-field limit of the decoupling of the amplitude and phase \( \sim 100 \) K [25].

The most probable candidate for the observed strong decrease of the amplitude response is the quasiparticle-amplitudon interaction. Quasiparticles (QP) excited by the pump pulse quickly relax to the single particle gap at \( k \sim k_F \), where they strongly scatter from the \( 2k_F \) periodic potential. Because the scattering occurs exactly by \( 2k_F \), the QP energy is unchanged and the scattering is inevitably elastic. This type of scattering would lead to a dephasing of the amplitudon excitations, consistent with the observed weak broadening of the amplitudon response as a function of the pump power.

After understanding the transient reflectivity dynamics of K\textsubscript{0.3}MoO\textsubscript{3} together with the observation of the coherent AM it is natural to quest for understanding the phenomenological origin of the AM mode. Unlike the relatively simple case of coherent phonons in the conventional semi-conductors the collective AM mode of a CDW material is rather a coupled electron-phonon oscillation. The photoexcitation of carriers is no more of a simple electronic form but rather they are vibronically coupled quasi-particles. This is because of the strongly coupled electron-phonon system involved in the formation of the CDW.

Pump fluence-dependent experiments can reveal interesting physics like the possibility of an optically induced phase transition. Presence of a large number of photoinduced quasiparticles above the CDW gap may possibly create a metallic state. In addition to that the transient dynamics of the photoinduced quasiparticles and coherent excitations can give insight in to the generation, decay and dephasing mechanism of coherent AM.

The next section describes the response of Quasi-particles to the varying pump-
2.7 The Quasi-particle dynamics

In superconductors (where there is electron-electron pairing) or in CDW systems (where there is electron-hole pairing) an ultrashort laser pump pulse first excites electron-hole pairs via an interband transition in the material. These hot carriers very rapidly release their energy by $e-e$ and $e-ph$ (electron-electron and electron-phonon) collisions and reach near the states close to the non equilibrium Fermi energy within $\tau_i = 10 - 100 \text{ fs} \left( \sim \hbar E_F / 2\pi E^2 \right)$.

This quick relaxation of carriers acts as an ultrafast single-particle (SP) injection pulse. The above processes are commonly observed in many materials including metals, semiconductors and superconductors [13, 26]. If a gap of CDW type or superconducting type is present in the single particle excitation spectrum, it inhibits the final relaxation step by creating a bottleneck, consequently the photoexcited carriers accumulate above the gap. This accumulation of photoexcited carriers above the CDW gap can induce transient changes in the reflectivity, $\Delta R/R$ of the probe-pulse by modulating the dielectric constant. This can be observed if the temporal width of the probe pulse is shorter than the final relaxation time of the SP excitations. The time scale and the various relaxation channels of SP-excitations or more generally here after called quasi-particle (QP) excitations (In a strongly correlated system like $K_{0.3}\text{MoO}_3$ it is more appropriate to address them as quasi-particles) are interesting since they reveal "how fast" or "how slow" the energy transfer takes place in the material. The CDW gap at $2k_F$ in the density of states and the consequent collective modes that originate from the fluctuation of the gap are phenomenologically related to the initial transient reflectivity peak ($\Delta R/R$). The e-ph relaxation becomes important when the QP energy is reduced to $E = \sqrt{E_F \hbar / 2\pi \tau_{e-ph}} \simeq 30 - 50 \text{ meV}$, assuming that the gap is of the order of 0.1 eV [27]. The observed bottleneck effect is a consequence of unavailability of relaxation channels near the gap. Because the final relaxation across the gap is suppressed the QP and the high energy phonons ($\hbar \omega > 2\Delta$) form a quasi-equilibrium. In superconductors the QP recombination is governed by the emission of $2\Delta$ phonons. For low laser powers a theoretical model exists to explain the number of quasi-particles excited as a function of laser power and temperature, however, in the high fluence limit, 1-10 mJ/cm$^2$, the theory is not adequate.

In the case of cuprate-superconductors the decay of the QP is through the incoherent excitations like the emission of $2\Delta$ phonons. This interpretation is adequate as long as the pump fluence is small enough to be considered as a weak
perturbation on the system. To probe the QP dynamics and the plausible ways that the photoexcited QPs decay, we have performed pump-fluence dependent measurements. The wavelength of the optical pump is tuned to the intraband plasma frequency of $K_{0.3}MoO_3$ (1150 nm) and the wavelength of the probe is fixed at 800 nm.

![Figure 2.11: $\Delta R/R$ for few pump fluences](image)

The pump fluence is varied from 1-10 mJ/cm$^2$. Few fluence dependent data are presented in the figure 2.11.

When the pump-fluence is increased the $\Delta R/R$ increases linearly due to the optical pumping of the quasiparticles above the CDW gap, which is expected from the theoretical models in literature [27]. A linear increase in the life time of the QPs is observed together with a decrease in the amplitude of the coherent AM mode. The decay time of the QP raises from 0.3 ps to 1.8 ps whereas the decay time of the coherent AM does not vary with the pump fluence. If the coherent AM are generated directly by the photons of the pump pulse one would expect a consequent increase in the amplitude of the coherent AM when the pump fluence is increased. The observation is contrary to this. This implies that the coherent AM are not directly coupled to the photons. These observations suggest that the lifetime of QPs has a strong influence upon the generation of the coherent AM.
The amplitude of coherent AM mode or hereafter called I(AM) decreases exponentially with the QP life time, where as, the life time of AM ($\tau_{AM}$) does not vary. This gives a subtle hint that the decrease of I(AM) may be due to either dephasing or interaction with the incoherent excitations most probably QPs. At this point we conclude that the long lived excited QPs have a detrimental influence on the coherent AM generation. While the photons do not directly couple to coherent AM it is natural to ask “whether the excited QPs couple to the coherent AM and generate them?”. One can do a “thought experiment” to investigate the generation of the coherent AM, which goes as follows.

### 2.7.1 Realizing a coherent excitation

In general, to excite a mode in a coherent way and to observe it experimentally one needs an excitation laser pulse of finite intensity and finite pulse width. The amplitude of a coherent mode is expected to vary linearly with the intensity of

![Graph](image_url)

Figure 2.12: Amplitude of the coherent AM decreases with increasing the quasi-particle life time. This shows a loss of coherence due to a delayed relaxation of the quasi-particles
the exciting source if the other competing interactions are absent. As a prerequisite, to observe a coherent mode one needs to have the pulse width of the pump-pulse to be considerably less than the time period of that mode. However, these fundamental assumptions couldn’t explain the reduction in the amplitude of the coherent AM with the increase in the pump fluence. This drives us to think the possibility of generation of the coherent AM by QPs. Ultrafast decay of the QPs can act as an injection pulse on the CDW state and can excite coherent AM. We model such a QP injection pulse as the product of the intensity of the QP peak, $I_{QP}$, ($\Delta R/R$ at zero time delay) and its full width at half maximum, $\tau_{QP}$, which is the decay of the QPs. Let’s abbreviate this term as $P_{QP}$. If the amplitude of the coherent AM is normalized with respect to $P_{QP}$ the resultant gives probability of the coherent AM generation due to the QP decay pulse, abbreviated as $I_{norm AM}$. We define a term called decoherence factor $= \tau_{QP}/t_{AM}$. If this term goes beyond unity the coherence is lost. The probability of the generation of coherent AM via ultrafast QP decay pulse is plotted against the decoherence factor in figure 2.12.

From the plot it is evident that when the raise in $\tau_{QP}$ reaches the $t_{AM}$ the $I_{norm AM}$ drops rapidly. This data has few consequences, in the sense that, it strongly questions the existing theories about the generation of coherent modes. Specifically, hitherto it was believed that the photons in the pump pulse generates the coherent AM. Our data indicates a possibility of an alternative mechanism of generating coherent AM via QPs relaxation. Phenomenologically, it can be understood as follows. The coherent AM are generated due to the ultrafast decay of the QPs. Thus the QP decay acts as a driving force in generating the coherent AM, which can be called a QP decay pulse. When the $\tau_{QP}$ increases (or the width of the QP-pulse becomes larger) the coherent amplitudons generated at different times add up in phase. This dephasing become pronounced when the $\tau_{QP}$ reaches the period of the coherent AM oscillations which is clearly seen in the figure 2.12.

### 2.7.2 Is the Two-Temperature-Model relevant?

A theoretical model is proposed to explain the $e - ph$ thermalization followed by the photoinduced change in reflectivity/transmission [28]. We discuss the relevance of the Two-Temperature-Model (TTM) in our data. The increase in the pump fluence is followed by the increase in the number of excited quasi-particles across the CDW gap which is at the cost of destructing the CDW state locally. Since we excite a large number of quasi-particles, a metallic-like state is formed and eventually relaxes back to the ground state as time evolves. It is a general tendency of a metallic system that the quasi-particle life time or electron-electron thermalization time increases with the increase of the pump laser fluence. This
can be explained on the grounds of the two temperature model (TTM) [28]. Here we briefly outline the features and outcome of the TTM. A solid system is divided into two subsystems, the conduction electrons with a temperature $T_e$ and the ionic lattice with a temperature $T_i$. When a metal is irradiated with an energetic laser pulse its electronic temperature is raised with respect to the lattice temperature. The TTM describes the heat flow between electrons and the lattice when $T_e > T_i$. The TTM assumes that immediately after the laser irradiation the hot electrons thermalize among themselves instantly. Now, the electron-phonon thermalization takes place with a typical time scale of about a picosecond in metals. TTM gives the time evolution of the electronic temperature as a function of the lattice temperature $T_i$ and the deposited laser energy density. At low pump fluences the electronic temperature is given by

$$T_e(t = 0) = \left( T_i^2 + \frac{2U_l}{\gamma} \right)^{0.5}$$

Where, $T_e(t = 0)$ is the peak electronic temperature at time $t = 0$, $U_l$ is the deposited laser energy density and $\gamma$ is the specific heat of the metal. The TTM also allows one to determine the electron-phonon coupling constant by measuring the electron-phonon relaxation time as follows.

$$\tau(T_e(0), T_i) \approx \gamma \frac{[T_e(0)+T_i]}{2g_{\infty}}$$

Where $\tau$ is the electron-phonon relaxation time and $g_{\infty}$ is the electron-phonon coupling constant.

In our case although this quasi-linear dependence of $\tau_{QP}$ qualitatively seems to be in agreement with the predictions of the Two Temperature Model (TTM)[28], we discard the applicability of TTM in this present system for the following reasons. First, TTM is meant for metals in which the electron-phonon coupling constant ($\lambda$, the dimensionless parameter which is proportional to $g_{\infty}^2$) is weak (typically 0.1). In a strongly correlated system like blue bronze, the ($\lambda$) is of the order of unity.

Second, TTM breaks down at low temperatures (In our case the temperature is always at 4.2 K) due to the fact that the time scales of electron-electron thermalization and electron-phonon thermalization are comparable.

The observed quasi-linear increase of $\tau_{QP}$ with the pump-fluence may have two origins. The photoexcited hot carriers exchange their energy among themselves and reach an equilibrium. For larger pump-fluences the number of photoexcited carriers increase and the initial energy relaxation becomes delayed. The other possibility is the one that is often observed in other low dimensional system such as quantum dots [29]. When the initial thermalization among the hot carriers takes place, the further energy relaxation is delayed due to the unavailability of the high energy phonons (phonons whose energy $> 2\Delta$). This is called "phonon
bottleneck” effect and it is mostly observed in low dimensional materials [29] and also in superconductors [? ].

As discussed earlier regarding the mechanism of the generation of the coherent phonons in materials, the discrimination between the two main mechanisms viz, DECP and TSRS, is done by analyzing the phase of the oscillations with respect to the auto-correlation signal between the pump and the probe pulses. The precision of this method is limited by the necessity to use very short pulses (of about 30-50 fs). Pertaining to this, our approach is more direct, in the sense that, we directly measure the absorption of light in to the material (by ellipsometry, as described in the next section) and calculate the amount of light absorbed at each wavelength. This directly gives the potential absorption states of the material.

Another motive of such an experiment is when we change the wavelength of the pump-pulse due to consequent change in the absorption coefficient of the material the number of QPs excited also vary. This allows one to understand the combined dynamics of QPs and coherent AM. In particular, the role of QPs in coupling to the coherent AM needs to be made more clear. In an absorbing material like $K_{0.3}MoO_3$ accessing various absorption states by varying the pump-wavelength can lead to a better understanding of the role of absorption of light in to the material. Also, the study of the response of the CDW collective modes with respect to various wavelengths of incident pump-pulse can probe various resonances. In the following section we discuss the $\lambda_{Pump}$-dependence of the collective modes and QPs in the CDW system $K_{0.3}MoO_3$.

### 2.8 The Wavelength Dependence

Before understanding the photoinduced changes in the reflectivity for various pump wavelengths, it may be essential to understand the origin of optical constants of the system. The optical constants at various wavelengths can give potential absorption states in the system. This can further give insights into the exact mechanism of the coherent AM generation. Figure 2.13 shows the optical constants measured using an ellipsometer with wavelength varying from 270 nm to 1700 nm. To our knowledge, this is the first experimental result at this wavelength range measured in blue bronze.

The initial sharp edge in $\epsilon_2$ raising from 500 nm and below is due to the ”p-d”-transition involving the electronic excitations from the Oxygen ”2p” to the Molybdenum ”4d” levels. The quotations are used to indicate that the levels are admixtures rather than pure ones. This is consistent with the photo-emission experiment done on blue bronze [30]. The broad asymmetric band around 1000
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nm is due to interband "d-d"-transition. Onwards the onset indicates single particle excitations [22]. The conduction band of $K_{0.3}MoO_3$ extends 2 eV below the Fermi level [30]. The actual zero crossing of $\varepsilon_1$ occurs at 1150 nm (1.08 eV) and indicates the plasma frequency which contradicts the previous measurements [31] where the plasma frequency was found to be at 800 nm (1.5 eV). However, at 800 nm the real part of the dielectric function goes very close to zero but never crosses zero in our samples.

In the figure 2.14 the $\Delta R/R$ response for a selected region of $\lambda_{Pump}$ shows that the transient response is strongly influenced by $\lambda_{Pump}$.

Figure 2.15 shows the amplitudon mode in blue bronze measured for various wavelengths of the pump pulse at a pump fluence of $1mJ/cm^2$. Amplitude (Peak-to-Peak) of the second AM oscillation is plotted against the pumping wavelength ($\lambda_{Pump}$) for each photon absorbed, thus including the correction for the differences in the penetration depths of various pump wavelengths. It is interesting to note that the coherent AM mode shows a resonating behavior. This implies
that the collective modes are sensitive to the absorption of photons from the pump pulse in the sample. The coherent AM mode seem to follow the total absorption curve, i.e., \((1 - R)(1 - e^{-\alpha z})\), where \(z\) is the thickness of the sample. The reflectivity is calculated using the optical constants obtained from ellipsometry measurements. But it doesn’t scales with the total absorption curve exactly. There is no strong peak at 1150 nm in the total absorption curve whereas the AM is resonant at 1150 nm (\(\omega_p\)).

A total enhancement is observed for all the features of the spectrum, like the initial \(\Delta R/R\) peak contribution, the Raman phonons, and also the amplitudon at \(\omega_p\). Two distinct enhancements can be recognized. The one at 1150 nm is close to the inter-band "d-d"-transition and situated exactly at the plasma frequency (figure 2.13) of \(K_{0.3}\MoO_3\).

The point on the onset at 600 nm matches well with a maximum in the absorption and again hints the importance of absorption of light into the material that was proposed in DECP. For a given pumping power, the oscillations vanish above 1550
nm but the quasi-particle contribution resulting from the initial sharp transient reflectivity persists. This implies strongly that in a highly absorbing CDW system like blue bronze, the absorption due to electronic excitation plays an important role in the manifestation of collective modes. It is worth to note that no change in frequency is observed for all the three oscillatory components of transient reflectivity. The decay-time of all the contributions to $\Delta R/R$ are fairly independent of the $\lambda_{\text{Pump}}$. The $\lambda_{\text{Pump}}$-dependent data can be understood as follows. When the $\lambda_{\text{Pump}}$ is varied there is a consequent change in the absorption coefficient of the material and hence different absorption states are available. The $\Delta R/R$ at $\delta t = 0$ is proportional to the number of QPs excited across the gap. We observed that the intensity of the coherent AM follows the magnitude of $\Delta R/R$. This can be taken as a further evidence for our proposition that an ultrafast decay of QPs generates the coherent AM. As mentioned in the section Quasi-particle dynamics the $I_{\text{QP}} * \tau_{\text{QP}}$ constitutes the QP-decay pulse. The QP-peak or $I_{\text{QP}}$ is a function of $\lambda_{\text{Pump}}$. By changing $\lambda_{\text{Pump}}$ the number of electronic excitations also change and

Figure 2.15: Amplitudon mode showing maxima at 1150 nm and 600 nm. The total absorption is also plotted for comparison.
as seen in the figure 2.15 the \( I_{AM} \) (the amplitude of coherent AM) follows the absorption curve. The physics behind the observed resonance at \( \omega_P \) becomes more obvious simply because at this particular frequency plasmons – polaritons can be excited and the latter can couple strongly to the QPs thus increasing the overall contributions to \( \Delta R/R \).

![Graph showing Intensity of coherent AM normalized with the QP-decay pulse](image)

Figure 2.16: Intensity of coherent AM normalized with the QP-decay pulse shows similar behavior

To make it more explicit the \( I_{AM} \) is normalized with respect to the QP-decay pulse and plotted against the wavelength of the pump-pulse. The results are plotted in the figure 2.16. Clearly, this shows that the coherent AM in \( K_{0.3}MoO_3 \) are generated by the ultrafast decay of the QP-pulse.

### 2.9 Discussion and Summary

The CDW material \( K_{0.3}MoO_3 \) has been studied since almost half a century. Nevertheless, it is still a subject of interest for various researchers. One of the main reasons for this continuing interest is that the advent of modern state of art techniques like time resolved femtosecond spectroscopy, coherent X-Ray diffraction
In the present work there are few important points worth discussing in the light of our data. First and foremost would be to consider the so-called optically induced phase transition which is fascinating from technological point of view and also interesting from the point of fundamental physics. For example, the generation of coherent excitations using ultra-short laser pulses may generate ultra-fast phase transitions with dynamics on the time-scale of the atomic motion which is best exemplified in the case of an organic molecular conductor (EDO-TTF)$_2$PF$_6$ [33]. At the present stage this photoinduced phase transition is a wonderful example of the fastest switching of macroscopic properties of a molecular material i.e., from insulator to metal.

In the case of the CDW material K$_{0.3}$MoO$_3$ which opens a gap at the Fermi surface the ground state (CDW state) inevitably has an empty conduction band. Thus a CDW to metallic transition would be possible by inter-band excitation of carriers across the Peierl’s gap provided the photo-excited-carriers have a long “life-time” of the order of several picoseconds to nanoseconds. The longest QP relaxation time, $\tau_{QP}$, that is observed is about 2 ps for the highest fluence (10 mJ/cm$^2$) used in the experiment.

The question whether such a delayed relaxation creates a transient-metallic state is addressed in our study. Two experimental observations can reveal the possible presence of such an optically induced phase transition. First, disappearance of the AM mode (which is the characteristic feature of the CDW state) at a certain pump fluence and at temperatures well below $T_{CDW}$ would imply that there is a phase transition from CDW state to a metallic state. Second, if the magnitude of $\Delta R/R$ at longer times (say above 100 ps) is not a linear function of the pump fluence then this would mean a phase transition. For example, in the case of $\alpha$-NaV$_2$O$_5$, a 2-dimensional spin ladder system, a long living $\Delta R/R$ (more than 150 ps) was ascribed to a change in the valence of vanadium ions that is induced by the pump-pulse [34]. This essentially would mean an optically induced charge-transfer type of phase transition. However, we did not observe any such effects in our experiments, which probably means that an optically induced phase transition in K$_{0.3}$MoO$_3$ is still far from experimental reality.

As it is evident from our data, in the high pump fluence regime (1-10 mJ/cm$^2$) the $\Delta R/R$ is quite complex and contains many contributions like quasi-particles, AM, coherent and incoherent phonons and possibly phasons. Though we observed two coherent phonons at 2.23 THz and 2.5 THz in our time resolved experiments due to their weaker intensity it was not possible to carry out any further investi-
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gations. The high pump-fluence (about $10^4 - 10^5$ times more than in [20]) may destroy the CDW state of the material locally. However, we did not find any evidence (like disappearing of the AM mode) for it. This drives us to interpret the observed fast decay ($\tau_{QP}$) in terms of the QP dynamics rather than CDW recovery dynamics. At high pump-fluences, analogous to the materials with a superconducting-gap, the quasi-particle relaxation in the CDW state cannot be described using a simple exponential decay whereas above $T_{CDW}$ the relaxation of quasi-particles can be modelled using an exponential decay. The stretched exponential behavior ($e^{(1 - t / \tau)^n}$) with an almost invariable power $n = 0.5$ implies that the relaxation is composed of a distribution of life-times indicating multiple relaxation processes.

Another important issue is the mechanism of generation of the coherent AM which is hopefully answered in this study. The ultrafast-decay of the photoexcited QPs generates the coherent AM, which is evident from our data.

At a fluence of 10 mJ/cm$^2$ the quasi-particle relaxation time is about 2 ps which is few times more than the period of the coherent amplitudon oscillation (0.5 ps). Consequently, the amplitude of the coherent amplitudon decreases as a result of the adding up of the AMs of different phases generated at different times. The proposition is further supported by the $\lambda_{Pump}$-dependent measurements in which by changing the $\lambda_{Pump}$ the $I_{QP}$ (the number of QPs) is consequently changed. The change of latter has a strong impact on the amplitude of the coherent AM. The amplitude of the coherent AM follows the QP peak ($\Delta R/R$ at $\delta t = 0$) implying that the photoexcited QPs couple strongly to the coherent AM, or in other words, the coherent AM couple to the real electronic absorption in the material. After realizing that the “Ultrafast decay of QPs generates coherent AMs” one may ask ”Whether DECP still works in $K_{0.3}MoO_3$?”. In other words whether the experimental results discard DECP?. The answer is “no”. In fact, our results goes one step further and proposes strongly that “The coherent AM is generated by the decay of QPs” which does not discard the mechanism of DECP in $K_{0.3}MoO_3$. Because, both the DECP and our results implies that the absorption of photons from the pump-pulse is very important. While DECP gives the “necessary condition” for the generation of coherent AM our results probes the “time-resolved-phenomenological” aspects of both generation and observing the coherent AM. Particularly, the interaction among the excited QPs and the generated coherent AM is revealed. This result on a CDW system like $K_{0.3}MoO_3$ can be considered as a starting point to study further.

An alternative mechanism to explain the observed “resonance” of $\Delta R/R$ at the plasma frequency is worth to mention. An overall enhancement in the $\Delta R/R$ at
the plasma frequency ($\omega_p = 1150$ nm) may be due to the excitation of either bulk or surface plasmons. The plasmons may couple to the coherent excitations like coherent AM or coherent phonons where such a process can be very well described by resonant Raman scattering. Thus a contribution from stimulated Raman scattering near $\omega_p$ could be possible together with the displacive excitation mechanism. However, a clear distinction between the two mechanisms (DECP and TSRS) is possible only by analyzing the phase of the coherent excitations with respect to the arrival of the pump pulse. Such a phase analysis certainly needs ultrashort pulses (20-50 fs).

Unlike the coherent phonons seen in $\Delta R/R$ the coherent AM is very short lived (3.5 ps). This fast decay of coherent AM could very well be due to scattering from electrons or quasi-particles. To support this proposition, previous results of Demsar et., al [20] measured the QP life time of about 10 ps using pump fluences much smaller (about 5 orders of magnitude lesser than in the present case) than the present study. Surprisingly, no dependence of $\tau_{AM}$ on the incident pump-fluence is found which probably implies that the magnitude of interaction or scattering probability has reached a saturation.

The enormous enhancement of the $\tau_{QP}$ below $T_{CDW}$ with increasing pump fluence leaves few physical questions like, 1. Whether the life time of the contributing processes like electron-electron thermalization or electron-phonon thermalization enhances with increasing number of the photoexcited quasi-particles?. The number of decay processes that contribute to the experimentally observed QP relaxation are $1/\tau_{QP} = 1/\tau_{e-e} + 1/\tau_{e-ph} + 1/\tau_{e-h}$, where the subscripts e-e, e-ph and e-h refers to respectively electron-electron thermalization, electron-phonon thermalization and electron-hole recombination (or the interband relaxation). However, above $T_{CDW}$ the quasi-particle life time does not increase even when the pump fluence is increased 10 times. This clearly shows that the so called "bottle-neck" effect observed in other similar gapped systems enhances with the increasing number of quasi-particles. However, the question "how exactly the QP life time varies with the initial photoexcited QP population above the CDW-gap?" can be addressed by using femtosecond pulses.

Based on the experimental data and the retrospective literature the essence of the outcome of the study can be summarized as follows. We have studied the charge density wave system $K_{0.3}MoO_3$ using variable energy pump-probe spectroscopy, ellipsometry, and inelastic light scattering (Refer to Chapter 3). The observed transient reflectivity response exhibits quite complex behavior, containing contributions due to quasi-particle excitations, coherent amplitudons, coherent phonons and possibly also due to phasons. We show that a selective excitation of
coherent AM is possible by tuning the delay between the two pump pulses to the period of the coherent AM. The coherent generation of amplitudon is found to become resonant when the pump energy approaches the interband plasmon energy. In addition it shows a tendency to be enhanced upon increasing linear absorption. Based on the experimental observations we propose that the mechanism of the coherent amplitudon generation is through the ultrafast decay of the excited QPs. We also discussed the role of quasi-particle dynamics in the dephasing of the coherent amplitudons. Finally, we observed coherent excitation of two fully symmetric phonons, which we assign to zone-folding modes of the charge density wave state.

Bibliography


Chapter 2. Coherent excitations in $K_{0.3}MoO_3$: Pump-probe spectroscopy


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