Chapter 4

Mid-gap states and phase-phonons in \( \text{K}_{0.3}\text{Mo}_{1-x}\text{W}_x\text{O}_3 \)

4.1 Introduction and literature review

In chapter three we have presented a Raman study of blue bronzes, focusing on the collective and vibrational excitations. Raman spectroscopy alone is not enough to fully address the vibrational features associated with the charge-density-wave (CDW) formation, also the infrared-activity of phonons will be influenced by the CDW formation. The quasi-particle excitations, vibrational degrees of freedom and their interactions leading to the collective-excitations can be addressed in an infrared study. The infrared-active phasons, quasi-particle excitations, phonons and the excitations due to intra-gap states (so-called mid-gap states which are discussed in later sections) might reveal their spectral features in an infrared study. One may also address the phonons arising due to unit cell-doubling and symmetry changes. In centrosymmetric media Raman and infrared activity are mutually complimentary and hence both are essential to fully address the vibrational features. We have performed polarization and temperature dependent infrared reflectivity measurements to reveal the vibrational features consequent upon the formation of the CDW in \( \text{K}_{0.3}\text{Mo}_{1-x}\text{W}_x\text{O}_3 \).

First we discuss some previous infrared studies on \( \text{K}_{0.3}\text{MoO}_3 \). Frequency-dependent conductivity measurements were reported in the CDW state of \( \text{K}_{0.3}\text{MoO}_3 \) and \( \text{K}_{0.3}\text{Mo}_{1-x}\text{W}_x\text{O}_3 \) in the radio-frequency, microwave, millimeter-wave and infrared spectral range [1]. In contrast with conventional semiconductors, where
only phonon lines appear in the spectral range below the single-particle gap, in the CDW state one can observe a variety of phenomena which contribute to the optical features in an extremely wide spectral range \((10^{-3} - 10^{12}) \text{ Hz}\). Several distinct features associated with the electrodynamics of the CDW ground states have been observed in the optical spectra.

It is convenient to discuss the response of the CDW in terms of different spectral ranges. The high frequency down to the middle infrared (MIR) (ie., between \(10^3 \text{ and } 10^5 \text{ cm}^{-1}\)), the far-infrared (FIR) (ie., between 10 and \(10^3 \text{ cm}^{-1}\)), and the low-frequency spectral range (ie., between \(10^{-2} \text{ and } 10 \text{ cm}^{-1}\)). In the high frequency range there are interband transitions which typically involve the \(d\) states of \(\text{Mo}\) and the \(p\) and \(s\) states of the \(\text{MoO}_6\) octahedral units. In the MIR range there is a sharp absorption edge which is the Peierls gap (or CDW gap). The FIR part of the reflectivity shows many sharp lines and two distinct resonances; one at 3 \(\text{ cm}^{-1}\) and the other at 40 \(\text{ cm}^{-1}\). The strong resonance at about 3 \(\text{ cm}^{-1}\) was ascribed to the so-called phason-mode of the CDW collective excitation. It is worth to remember that the phase-mode of the CDW is expected to be ideally a zero-frequency excitation (ie., it costs ideally no energy to excite phasons); however it’s interactions with the lattice, lattice-imperfections and pinning centers effectively shift it’s energy to a finite value. The dynamics of this mode is characterized by a large effective mass \(m^*\), consequently the spectral weight of the collective mode is small, of the order of \(m_b/m^*\); where the subscript \(b\) stands for the band mass.

It should be noted that the band mass, \(m_b\) is already renormalized and hence is larger than the free electron mass.

The second resonance at 40 \(\text{ cm}^{-1}\) was not identified, however, it was ascribed to a "collective bound state" of the CDW. It is worth to mention that this resonance cannot be ascribed to any other expected CDW excitations like amplitudon mode, longitudinal optical phason, zone-boundary acoustic phason, or any other mode originating from defects or vacancies [2, 3]. The possibility of amplitudon mode is discarded since it is only Raman active, except when there is no inversion symmetry. Also, the amplitudon mode frequency (56 \(\text{ cm}^{-1}\) : see chapter three) is different than the observed resonance. An optical phason arises due to a periodicity \(\lambda = \pi / k_F\) leading to a \(q = 2k_F\) optically active phason. This possibility is also discarded since the resonance occurs in \(\text{K}_{0.3}\text{MoO}_3\) and another CDW material (\(\text{TaSe}_4\)) at almost the same energy whereas the effective masses corresponding to the resonances are very different. From the calculated values of the frequency of the "longitudinal optical phason" (if it is optically active), it differs by an order of magnitude than the observed resonance at 40 \(\text{ cm}^{-1}\). Hence, this possibility is also excluded. Thus the second resonance at 40 \(\text{ cm}^{-1}\) remains
In the FIR region sharp phonons appear which are due to a coupling of the lattice distorted phonons with the fluctuations of the modulated electron density. These phonons are called phase-phonons [4]. The CDW state is not a prerequisite for this effect [5] since it requires only electronic density fluctuation with a lattice distortion, however, in CDW state it arises inevitably due to phason-phonon coupling.

In the E // b (electric field of the incoming light being parallel to the b-direction or along the CDW formation) the large oscillator strength associated with phonon modes in the CDW state was ascribed to the phase-phonon coupling. This description was consistent with the theoretical considerations of phase-phonons by Rice [4] (discussed in chapter three). In the same study they [3] also observed the single particle gap at 1024 cm$^{-1}$ and discussed the spectral features of the latter. While the broad and prominent features associated with the CDW formation were addressed in this study, phonons which are influenced by CDW formation were not addressed. This is particularly true for the infrared-active phonons in the in the perpendicular direction (E⊥b).

A Raman and infrared study by Nestor E. Massa [6] focused on the possible presence of midgap states inside the main Peierls gap in K$_{0.3}$MoO$_3$ and Rb$_{0.3}$MoO$_3$. A mid-gap state is a discommensuration or soliton-like structure in the electron density modulation. The study addressed triplets of excitations which were observed in the Peierls state just below the main Peierls gap for polarization perpendicular to the CDW direction. Below the main Peierls gap two sets of triplets (one around 590 cm$^{-1}$ and another around 950 cm$^{-1}$) were assigned to the midgap exciton-polaritons. The presence of these features even at room temperature was interpreted in terms of pre-transitional Peierls fluctuations indicating the presence of a pseudo-gap. However, these assignments were found to be incorrect [7] since the midgap states and the Peierls fluctuation effects are expected to be observable along the metallic direction only. Moreover, similar excitations have been observed for the semiconducting compound K$_{0.33}$MoO$_3$ [8] and in the insulator MoO$_3$ [9] where Peierls transition does not occur.

In another study [7] the far-infrared reflectance of Rb$_{0.3}$MoO$_3$ for both polarizations (E∥b) and (E⊥b) at 300 K and 9 K were presented. Below the Peierls temperature ($T_P$ =180 K) for the E∥b polarization the existence of a Peierls gap and midgap states were observed along with phase phonons. For the E⊥b polarization, 41 phonons were detected at 9 K. Many optical phonons, which became infrared-active as a result of coupling with the CDW below $T_P$ were observed. Fitting the optical conductivity ($\sigma$) obtained by means of a Kramers-Kronig (KK)
transformation of the reflectance data lead to an estimate of the CDW gap of around 1010 cm$^{-1}$ with the presence of a high-density of midgap states.

Travaglini and Wachter [10] have explored the optical response of the CDW system $K_{0.3}MoO_3$ focusing mainly on the collective modes (mostly phasons) of the CDW state of the material. In the far-infrared region at 5K a very strong polarization dependent phonon spectrum was observed. This structure reaching reflectivity values of 97% was assigned to the oscillation of the pinned Fröhlich charge-density-wave or phason mode. It is worth to note that in this study the measured phason energy is much different than the study of Degiorgi et al.,. The FIR resonance at 60 cm$^{-1}$ is assigned as the phason whereas in Degiorgi’s study it is the 3 cm$^{-1}$ mode. Considering the fact that the phason is a nearly zero-energy mode one tends to believe that the 3 cm$^{-1}$ mode is the phason. Probably the resonance at 60 cm$^{-1}$ in the study of Travaglini et al., corresponds to the unidentified feature near 40 cm$^{-1}$ in the study of Degiorgi et al.,. In the same study by Travaglini et al., optical constants were calculated by means of the KK relations. The results were compared with the predictions of the mean-field (MF) theory. While at room temperature the reflectivity parallel to CDW-axis ($E\parallel b$) was metallic-like (i.e., $R \rightarrow 1$ as $\omega \rightarrow 0$) with a plasma edge at about 1.3 eV (10 485 cm$^{-1}$), at 5K the metallic-like reflectivity turned into a semiconductor like spectrum exhibiting a large number of phonons in the far-infrared region ($\omega < 700$ cm$^{-1}$). In the optical conductivity along the b-direction a gap (rather a midgap) was observed at $\Delta$ (where $2\Delta$ is the main Peierls gap). The presence of the midgap state is consistent with the theoretical proposal of Machida and Nakano [11]. In a quasi-1D material which develops an incommensurate CDW there exist several energy gaps (midgaps) inside the Peierls gap. The position (with respect to conduction band or valence band) and the magnitude of such midgap states depend on the band filling and the electron-phonon coupling strength. In the section below we will briefly discuss the formulation and properties of midgap states.

4.1.1 Energy-gap structure in a quarter-filled band

The energy-gap structure of the single-particle excitation spectrum near the Fermi level is one of the most fundamental quantities in solid state physics. This determines many physical properties like conductivity, optical response etc. In ordered systems like CDW or SDW (spin-density-wave) materials it was generally believed that even in the incommensurate state there exists a single energy-gap structure near the Fermi level. As it is discussed in Chapter three, a commensurate CDW state has a gap in the phason dispersion spectrum since the phase of the density wave with respect to the underlying lattice is "locked". This naturally
makes the condensation energy as a function of the phase variable. Thus, any small variation in the phase would reflect in a corresponding change in the condensation energy. Here, "incommensurate" is used in a restricted sense. In other words, we are dealing with a situation where there is a small but finite incommensurability. We refer to it as nearly commensurate state. Commensurability or incommensurability may come from two factors. One, at a given temperature commensurability may be achieved by band-filling, another, when a band filling is close to commensurate state, one can achieve a incommensurate to commensurate transition at a certain temperature. For example, \( K_{0.3\text{MoO}_3} \) is a nearly 3/4 filled system which undergoes an incommensurate to commensurate transition at \( T = 100 \text{K} \) [12] which is also found in our Raman study (chapter three). It has been well established that there exists a gap in the single particle spectrum when there is a Peierls transition, called the Peierls gap. It was generally believed that there can be an additional energy gap inside the main Peierls gap only in a strictly commensurate state. This assumption was proved to be incorrect by Machida [11] thus establishing that depending on the filling factor (half-filling, quarter-filling etc) there exist several mid-gap states below the main Peierls gap. In the same study the position of the midgap states were predicted together with the exact nature of the midgap band. It is worth to ask for the origin of the midgap states in an incommensurate CDW system.

When an electron band of 1D-metal is just a third-filled, the trimerized lattice distortion takes place in the ground state because of the Peierls instability. In the quarter-filled case the Peierls distortion is due to a quadrimerized lattice distortion. This opens a gap at the Fermi level, which is called a Peierls gap. This Peierls gap inevitably has higher harmonics since it has to satisfy the self-consistency condition [11]. The physical meaning of self-consistency is that "there exists not a single gap but many higher harmonics of the gap". Thus the problem boils down to diagonalizing the mean-field Fröhlich Hamiltonian in one dimensional in a self-consistent way. A complete theoretical formulation of the procedure is given by Machida et al., [11, 13]. We will not discuss the details here.

The results of the calculations for perfect third filled and quarter filled cases are shown in figure 4.1.

The magnitude of the midgap depends upon the commensurability parameter. For small incommensurability it is found near the valence band (see fig 4.1), upon increasing the incommensurability the midgap gradually increases in energy, eventually approaching the conduction band.

Thus the midgap band in the one third filled case is approximately 0.1 times the main Peierls gap from the valance band (figure 4.1). As the incommensurabil-
Figure 4.1: Left panel: Bandstructures in the perfect (a) one third-filled and (b) one quarter-filled cases drawn in the reduced-zone scheme. Right panel: Energy band structure for nearly one third-filled case (a) high incommensurability, (b) low incommensurability [11]. [Reprinted figure with permission from Masahiro Nakano and Kazushige Machida. Phys. Rev. B 33, 6718 (1986). Copyright(1986) by the American Physical Society.]
ity increases the position of the midgap band is moved towards the nearest main band (valence or conduction band).

The midgap band was proposed to result from a soliton [14] (discommensuration) lattice structure. Thus in half-filled band case the mid-gap state is situated at the center of the Peierls gap. This theory has been found to be applicable in the case of another orthorhombic CDW system $TaS_3$ [15] in which possible electronic transitions across the midgap states were found. Sharp absorption lines at energies of $\sim 62$ and $125$ meV ($500$ and $1008$ cm$^{-1}$) inside the fundamental absorption edge; $\sim 184$ meV ($1484$ cm$^{-1}$) were observed at temperature just above the commensurate-incommensurate lock-in transition temperature, $98$ K. Thus the orthorhombic incommensurate-CDW material $TaS_3$ has been found to have at least two midgap states below the main Peierls gap serving as the first proof of the presence of midgap states in an incommensurate CDW material. Since blue bronze also undergoes an incommensurate-to-commensurate transition (or "lock-in" transition) [16] experiments were proposed to verify the presence of the midgap states near the "lock-in" transition. While theoretically the position of the midgap states were predicted, to observe it experimentally one needs to achieve nearly commensurate (temperature close to the commensurate-incommensurate transition) situation in which the bandwidth of the midgap state is narrow enough to be easily observable.

4.2 The key issues

The main objective of this work is to address the following issues. 1) To address the infrared active phonons in the CDW states in $K_{0.3}Mo_{1-x}W_xO_3$ ($x = 0$ and $1$), 2) to search for midgap states and to address changes in the gap-structure upon doping, 3) to search for traces of pre-transitional fluctuations in the phonon spectrum for $E \parallel b$ polarization.

4.2.1 Why to dope W?

It is worth to consider the possible or expected effects of doping in $K_{0.3}MoO_3$. There can be two kinds of doping in $K_{0.3}MoO_3$: alkali doping (doping with Rb) and tungsten doping. It has been known from previous studies [14] that the charge-density-wave develops a gap in the single particle spectrum in the conduction band. In $K_{0.3}MoO_3$ it has been known from band structure studies [17] that the conduction band of $K_{0.3}MoO_3$ is composed of admixture of "O-2p" and "Mo
4$d^{10}$ orbitals. By substituting $Rb$ for $K$ disorder can be introduced on the alkali sublattice. This type of doping is not expected to affect the electronic properties pertaining to the formation of the CDW since the conduction properties are mainly due to the Mo-O octahedra which form the one-dimensional electronic conduction path along the b-axis. Moreover, $Rb_{0.3}MoO_3$ and $K_{0.3}MoO_3$ have isomorphic structures and nearly identical properties including the sliding CDW behavior and hence observed differences in the properties of pure and alkali doped samples can be attributed merely to alkali disorder. However, the effect of tungsten doping is expected to produce a strongly perturbing influence by directly disrupting the number of overlapping Mo $d_{z^2}$ orbitals near the W-impurity site, large effects are expected on the CDW onset temperature and on the threshold field for the nonlinear transport. The above speculative ideas were supported by the previous studies by Schneemeyer et al. [18] and S. Yue et al. [19] in which a detailed doping dependent transport study has been performed. In these studies it has been shown that the effects of tungsten doping strongly influenced the CDW transition temperature and Pauli susceptibility. It was also observed that the effect of tungsten substitution was indeed stronger when compared to that due to alkali substitution. One of the important observations was the reduction of the CDW gap in the W-doped samples. It is interesting to understand whether the doped W atoms contribute to the energy gap structure as midgap states. Since a large tungsten doping ($\approx 10\%$) is found to produce large detrimental effects on the CDW characteristics (like the CDW transition temperature), 1% W doping would be optimal to observe the "crossover temperature" effects. Such "crossover temperature" (from a sharp transition to an almost no transition) were observed in the above mentioned studies also. As mentioned before infrared spectroscopy is an efficient tool to address the vibrational properties, phase-phonons, and also the quasiparticle excitations across the Peierls gap. The following section describes the experimental set up and the experimental procedure adopted in the present study.

### 4.3 Experimental set-up

The reflectivity experiments were performed on a standard Bruker IFS 66v/S FT-IR spectrometer equipped with various light sources to cover a large frequency region. In far-infrared range ($<700$ cm$^{-1}$) the light source used was a mercury lamp or a globar source with a mylar bream-splitter of 6 µm thickness. A liquid helium cooled bolometer was used as the detector. The spectral resolution was 1 cm$^{-1}$ which is sufficient to address various IR-active phonons. The measure-
ments in the FIR range were performed with polypropylene foil as the cryostat-window which transmits in the given frequency range. In the mid-infrared range (700-8000 cm\(^{-1}\)) a globar source was used with a KBr beam-splitter. A liquid-nitrogen-cooled MCT (Hg-Cd-Te or Mercury Cadmium Telluride) was used as a detector. The spectral resolution was 4 cm\(^{-1}\). In the MIR region the window of the cryostat was KBr.

The samples of \(K_{0.3}MoO_3\) and \(K_{0.3}Mo_{1-x}W_xO_3\) (\(x=0.01\)) were grown in the group of C. Kuntscher, University of Stuttgart, Germany. The CDW transition temperatures, \(T_{CDW}\) of \(K_{0.3}MoO_3\) and doped ones were determined from the DC resistivity measurements [19]. For the pure sample \(T_{CDW} = 179.2\) K and for the 1% W-doped one \(T_{CDW} \approx 140\) K, which matches with the values in literature [14] and demonstrates good quality of the samples. The samples were polished in order to get a good surface of optical quality. The sample holder was made of copper and designed in the shape of a cone. The sample was attached at the "vertex-side" of the cone to avoid the unwanted reflection of light from the sample holder reaching the detector. The focusing mirrors in the sample chamber were aligned such that the incident light falls on the sample perpendicular to its surface.

One of the key factors in infrared measurements is to align the crystallographic axis of the sample with respect to the polarization of the incoming light. The light coming from the sources discussed before is unpolarized. Since a single polarizer cannot serve in all the frequency regions one needs to change the polarizer so as to suit the particular frequency region. During this process determining the optical axis of the polarizer with respect to the desired crystallographic axis of the given sample is crucial. In other words, the polarizer is calibrated with respect to the desired axis of the sample. This is done as follows, which is based on the magnitude of anisotropy of the sample. For a given unknown orientation of the sample we measure the reflectivity for three rotations of the polarizer (say, 0, 45 and 90\(^\circ\)). Given the fact that the b-axis (in the present case of \(K_{0.3}MoO_3\)) is in the plane of the sample and it is more reflecting than in the perpendicular direction, we can identify the "maximum reflectivity" among the three measured angle of rotation of the polarizer. When we find "the correct" b-axis we check it by rotating the polarizer 45 degrees on either side (suppose that 0 degree of the polarizer scale corresponds to the b-axis, then the reflectivity corresponding to +45 and -45 rotation should match exactly). This procedure is found to be working well in the case of extremely anisotropic systems.

This allows one to determine the orientation of the crystal axes with respect to the polarization of the incoming light, thus allowing to perform polarization-dependent measurements. The sample holder was properly fixed to the cryostat
which allows us to vary the temperature from 4K to 300K. The cryostat was pumped to achieve high-vacuum (10^{-7} torr) in order to avoid any possible condensation of the water on the sample.

The temperature dependent reflectivity-measurements were performed by cooling the sample by passing liquid helium in a controlled manner. The temperature was stabilized by optimizing both the helium flow and temperature of the heater. To measure the absolute reflectivity of any sample one needs a reference sample, with respect to which the reflectivity of the sample has to be measured. We used an in-situ gold evaporation technique in which appropriate amount of gold is evaporated onto the sample surface. Thus, first reflectivity of the sample, S(\omega), is measured at each desired temperature. Then gold is evaporated on the sample as a thin layer of a few micrometers. After that the reflectivity, G(\omega), is measured for the gold evaporated sample for the same temperatures as done for the bare sample. The absolute reflectivity of the sample at a given temperature is then given by S(\omega)/G(\omega). A detailed description of the technique of reflectivity measurements with gold evaporation can be found in [20].

4.4 Reflectivity of K_{0.3}Mo_{1-x}W_xO_3 (x = 0 and 0.01) at high and low temperatures

Low energy excitations in solids appear in the frequency rage 1-8,000 cm^{-1} or in other words the FIR and MIR regions. Some of these excitations characterize a particular phase of the material (for example, the pinned phase mode characterizing the CDW state of the material ) and appear in reflectivity measurements [1, 3, 21, 22]. We start our discussion with the reflectivity at room temperature and at a low temperature (T_{CDW}=180 K for K_{0.3}MoO_3 and 145 K for K_{0.3}Mo_{0.99}W_{0.01}O_3).

First let us concentrate on the reflectivity of the pure compound in E||b polarization which is shown in the top-right plot of figure 4.2. At room temperature K_{0.3}MoO_3 is a quasi-ID metal and hence shows metallic-like reflectivity, reaching as large as 85 % near 150 cm^{-1}. The reflectivity increases with decreasing frequency as it is expected for metals. One may notice a large number of small-amplitude features in the FIR region at T = 290 K. These are nothing but the precursor of the phase-phonons which indicate the presence of a pseudo-gap at room temperature. This pseudo-gap eventually develops into a Peierls gap as the temperature is decreased to T_{CDW} from above. The existence of such pre-transitional fluctuations were also reported in previous studies on K_{0.3}MoO_3 [8, 23]. It is worth to remember that such pre-transitional Peierls fluctuations were also found
Figure 4.2: Reflectivity of $\text{K}_{0.3}\text{Mo}_{1-x}\text{W}_x\text{O}_3$ ($x=0$ and 0.01) for $E\parallel b$ below and above the CDW transition
in our Raman study (Chapter three).

At 6 K, far below the CDW transition, three interesting observations can be made. First, At 900 cm\(^{-1}\) and above a mid-infrared band is formed with a plasma frequency of about 10,000 cm\(^{-1}\) (≈1.2 eV). Second, even in the metallic direction (ie., \(E_{||}b\)) the reflectivity in the FIR region has many distinct sharp features, and finally there is a suppression in the reflectivity in the FIR region, near \(\omega \approx 150\) cm\(^{-1}\).

From the previous studies on \(K_{0.3}MoO_3\) it has been well established that there is a CDW transition at 180 K [3, 8, 10, 14] which allow us easily to attribute the appearance of the MIR band (the structure from 900 to 9000 cm\(^{-1}\)) to the formation of the CDW gap (Peierls gap). In general, a MIR band may be formed through various channels like charge-density-wave [1, 24], spin-density-wave or superconducting [21] states and polaron formation [25].

The appearance of phonons for \(E_{||}b\) in the CDW state is consistent with the lattice distortion accompanied by the phase-phonon coupling which was first proposed by Rice [4]. The phase phonons originate from the coupling of the conduction band electrons to the various components of the lattice distortion. The origin of phase phonons is discussed in chapter three. From a general point of view the appearance of phonons along \(E_{||}b\), a metallic direction, below a metal to insulator transition is a signature of strong electron-phonon interaction [26].

The observed suppression of the reflectivity in the FIR region hints to the presence of a gap in the single particle spectrum or in other words it reflects the insulating behavior. Thus the metal-to-insulator transition is through the Peierls channel and resulting in a CDW ground state. The suppressed reflectivity also shows up as reduced optical conductivity (discussed in the next section) and suggestive of the Lee, Rice and Anderson picture of developing a pseudogap [27]. The suppression of the reflectivity is due to a strongly reduced density of states near the Fermi-level. This strongly reduces the absorption and virtually gives the effect of an energy gap, which is often called a pseudo-gap. The signatures of a pseudogap can be observed as precursors when the temperature is approaching the metal-insulator transition from above, which is due to the strong Peierls fluctuations. Correspondingly, for temperatures slightly above [up to the mean-field transition temperature] the \(T_{CDW}\), the features that are the characteristics of the charge-ordered state, for instance phase-phonons, may be visible. The presence of a pseudogap well above the phase transition temperature seems to be a generic feature of low dimensional systems which develop a 3D-charge ordering.

The reflectivity of \(K_{0.3}Mo_{0.99}W_{0.01}O_3\) above and below \(T_{CDW}\) are shown in the bottom-plots of figure 4.2, which shows similar features as that of \(K_{0.3}MoO_3\) with
quantitative differences. The reflectivity at room temperature, for example at 150 cm$^{-1}$, is slightly smaller than that of K$_{0.3}$MoO$_3$ implying that the doped material has a slightly reduced metallicity. The reduced metallicity in the doped sample may not be attributed to a reduced electron density since tungsten is isoelectronic (with Mo). However, the presence of impurities may effectively reduce the scattering time of electrons or in other words enhance the rate of collisions ($\sigma_{DC} = ne^2/\tau/m$). This is consistent with previous study [28] in which 3 % W doped samples showed very small scattering times, almost 3 orders of magnitude smaller than for the pure samples.

At lower temperature, T = 25 K, the doped sample shows similar characteristics as that of the pure one.

The reflectivity in E$\perp$b (insulating direction) at low and high temperatures for both K$_{0.3}$Mo$_{1-x}$W$_x$O$_3$ (x=0 and 0.01) are shown in figure 4.3.

In the E$\perp$b direction there is no charge-density-wave ordering, however, there is a semiconducting gap. Although there is no CDW gap one may notice that the infrared active phonons are strongly influenced by the formation of the CDW gap, consequently, they become sharper at low temperature.

In both compounds below 1000 cm$^{-1}$ many sharp phonons are present at low temperature whereas at room temperature they become broader. While at temperatures well below $T_{CDW}$ most of the phonons get sharper because of the unavailability of decay channels whereas the phonons centered near 900 cm$^{-1}$ (see figure 4.3) show only a little temperature dependence.

After discussing briefly the main features of reflectivity spectra in both pure and doped samples of K$_{0.3}$MoO$_3$ we proceed to the analysis of the optical conductivities.

The experimental reflectivity data are fitted using the RefFit program. The program gives a model conductivity corresponding to the "best-fit" spectrum of the experimental reflectivity spectrum. This procedure should be distinguished from the conventional Kramers-Kronig transformation.

4.4.1 Optical conductivity

The optical conductivity of K$_{0.3}$MoO$_3$ for E$\parallel$b and E$\perp$b at T = 6 K and T = 290 K are shown in figure 4.4. The optical conductivity is obtained by fitting the experimental reflectivity data and calculating the optical conductivity with the help of a program called RefFit [29]. At room temperature the $\sigma_1$ for E $\parallel$ b is featureless whereas below $T_{CDW}$, T = 6 K a rich variety of excitations can be seen. The spectral features in $\sigma_1$ closely match those of the previous study by Degiorgi [1]. By comparing the $\sigma_1$ for E $\perp$b at T = 6 K and 290 K it is evident
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Figure 4.3: Reflectivity of $K_{0.3}Mo_{1-x}W_xO_3(x=0 \text{ and } 0.01)$ measured with $E \perp b$ below and above the CDW transition
Figure 4.4: The optical conductivity of K$_{0.3}$MoO$_3$ for E||b and E $\perp$ b at T = 6 K and T = 290 K.
that at low temperatures the phonons get sharper and also new phonons appear due to the metal-insulator transition. We discuss the $\sigma_1$ for $E \parallel b$ at $T = 6$ K. There are three prominent features which contribute to $\sigma_1$. The strongest one is from 800 cm$^{-1}$ and above which is nothing but the single particle gap or the CDW gap ($2\Delta$). This absorption is due to the excitation of the electronic quasi-particles from the CDW condensate across the CDW gap. This absorption band is absent in the $E \perp b$ spectrum. It is worth to mention that the magnitude of the CDW gap is uncertain. The gap $2\Delta$ has been estimated at 800 cm$^{-1}$ from transport measurement [30] and magnetic measurement [31], 1050 cm$^{-1}$ from tunneling spectroscopy [32] and 1400 cm$^{-1}$ from a fit of the infrared spectrum [1].

The second prominent feature is seen around 500 cm$^{-1}$, which was attributed to the so-called midgap states in the previous study [7]. Followed by the discussion in the next section, we claim that this is not a midgap.

The phase phonons which appear as sharp peaks in the optical conductivity have been analyzed in the previous study [7] in terms of their oscillator strength, frequency and linewidths.

The spectral features of $\sigma_1$ in $E \perp b$ is different from that in the $E \parallel b$ case. Many sharp phonons are observed. The triplets of phonons around 900 cm$^{-1}$ were also observed in previous studies [7, 33]. These triplets were interpreted as arising due to the internal vibrations of oxygen atoms inside an octahedron. They were also observed in another quasi-1D non-CDW conductor $K_{0.33}MoO_3$ (also called red bronze) [34] and in $MoO_3$ [9]. These triplets cannot be attributed to vibrations arising due to the three inequivalent Mo sites in $K_{0.3}MoO_3$ since they are also observed in the red bronze which has only two Mo sites and also in $MoO_3$ which has only one. As pointed out by Travaglini et al.,[34] the octahedron point group $O_h$ contains a triply degenerate $T_{1u}$ mode and due to the distorted octahedra in these materials the degeneracy is removed resulting in the splitting of three levels. These triplets are also found in a similar “CDW-type” material, $\beta$-$Na_{0.33}V_2O_5$ around the same energy [35]. The modes corresponding to Mo atoms appear at lower energies (around 300 cm$^{-1}$) as they are of heavier mass than Oxygen. A complete phonon-analysis in terms of mode-assignment is difficult in materials like $K_{0.3}MoO_3$ which has a very complicated crystal structure and a large number of atoms in the unit cell.

In the following section we discuss the effects of tungsten doping on the CDW gap. As mentioned earlier, the effect of tungsten doping is considered to be in the “strong-pinning” limit as it is detrimental to the formation of the CDW and consequently reduces the $T_{CDW}$ (145 K). This effect of reduction of the $T_{CDW}$ is consistent with the general claim that the impurities shift the transition tempera-
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ture to lower values [18, 19]. The real part of the optical conductivity, $\sigma_1$, at $T = \ldots$

![Graph showing optical conductivity](image)

Figure 4.5: The optical conductivity of $K_{0.3}Mo_{1-x}W_xO_3 (x = 0.01)$ and $K_{0.3}MoO_3$ for $E \parallel b$ $T = 25$ K. The lines at the bottom represent the background optical conductivity. The arrows indicate the single particle gap in each case.

25 K for $E \parallel b$ is shown in figure 4.5, together with the $\sigma_1$ of $K_{0.3}MoO_3$ for a close comparison. The effect of 1 % W doping is reflected in the slight reduction of the magnitude of $\sigma_1$ in the over all frequency range. In contrast to the case of $K_{0.3}MoO_3$, the intensity of the phase-phonons are reduced drastically. Due to the larger mass of W when compared to the Mo one can expect a considerable reduction in the oscillator strength, also the frequency of the modes which involve W vibrations eventually shift to a slightly lower values than those vibrations which
involve Mo. This effect unresolves the individual contributions. One more difficulty is that the phonons of very low oscillator strength are difficult to fit. To get the best fit one has to approximate a tiny bunch of small-amplitude phonons as a “single broad” feature. When we compare the $\sigma_1$ of $K_{0.3}MoO_3$ and the doped compound one can notice that the CDW gap is shifted to a lower frequency. Particularly, in the pure compound there is a clear “dip” in $\sigma_1$ near 750 cm$^{-1}$ whereas in the doped case the “onset” of the CDW gap starts at a lower frequency, about 500 cm$^{-1}$. This shows that there is a clear but partial destruction of the Fermi surface near 2$k_F$. The second interesting observation is that the peak of the single particle absorption band is shifted towards a higher frequency (about 800 cm$^{-1}$) in the doped case. This is in contrast with the earlier doping-dependent infrared reflectivity measurements on $K_{0.3}MoO_3$ [36]. In this study they observed that the magnitude of the peak decreased with increasing the W doping. Based on this observation it was claimed that the optical gap is irrelevant to the Peierls transition. While in principle, the optical gap is determined by the low-frequency onset of the optical conductivity rather than the peak position itself, the above claim seems to be incorrect. In the present study the peak position in the doped sample shifts towards the higher frequency, which is not related to the magnitude of the gap.

4.5 A comparison with the Raman spectrum

A comparison of the Raman spectrum [of chapter three] and the infrared spectrum is made in figure 4.6. Due to the presence of an inversion symmetry in blue bronze the phonon modes are observed either in the infrared spectrum or in the Raman spectrum but not in both.

It is worth to compare the Raman spectrum with the infrared spectrum for $E \parallel b$ which may question the existence of definition of the so-called phase phonons. As mentioned earlier the phase phonons were defined by Rice [4, 5] as the modes that are incorrectly present in the metallic (or along the CDW) direction and absent in the perpendicular direction. It is worth to mention that in the previous studies all the phonons which were observed for $E \parallel b$ below $T_{CDW}$ were attributed to phase phonons. We claim that this is not true. To exemplify, the mode at 525 cm$^{-1}$ is seen for both $E \perp b$ and $E \parallel b$, which is not a phase phonon by definition. This mode is originating due to the folding-up of the Brillouin-zone for temperatures below $T_{CDW}$. In $K_{0.3}MoO_3$ the appearance of the 525 cm$^{-1}$ mode and other modes which are “similar” to this mode are not phase phonons but they are zone-folding modes. While the existence of phase phonons require either a CDW transition associated with a lattice distortion or only lattice distortion, the
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Figure 4.6: The Raman spectrum and the infrared spectrum of \(K_{0.3}MoO_3\) are compared.
zone-folding modes by definition, are due to the folding of the Brillouin-zone which is associated merely with a metal-insulator transition. The relevance of phase-phonons is debatable.

After discussing the phase phonons and zone-folding modes we try to address the presence of the so called mid-gap states in $K_{0.3}MoO_3$ in the following section.

4.5.1 Midgap band?

Below the CDW gap (800 cm$^{-1}$) the contributions to the optical conductivity for $E || b$ in the CDW state of $K_{0.3}MoO_3$ can come from two sources. One, due to single particle excitations across the CDW gap. From the optical conductivity plot in figure 4.4 it can be easily noticed that the single particle excitations starts near 800 cm$^{-1}$ and extends for frequencies above. The second contribution may come from the theoretically proposed [4] phase phonons which appear as sharp small amplitude peaks in the optical conductivity. As mentioned in the introduction, there are two previous studies [7] and [6] which addressed the problem of the midgap states. In [6] the midgap state was assigned to the wrong polarization ($E$⊥$b$) where there is no Peierls gap at all. In [7] a relatively broad structure near 600 cm$^{-1}$ in the optical conductivity for $E || b$ was found and attributed to the excitations from the CDW condensate to the midgap state. It is worth to note that in our study the structure near 600 cm$^{-1}$ is well resolved into three peaks as shown in figure 4.7.

The feature at 525 cm$^{-1}$ is found both for $E || b$ and $E$⊥$b$ and hence we ascribe it to a phonon rather than the so called midgap state claimed in the previous studies [6, 7]. Note that the feature at 525 cm$^{-1}$ is also not a phase phonon since it is present in the $E$⊥$b$ polarization, whereas phase phonons are present only for light polarized parallel to the metallic direction. Further evidence may come from the bottom plot in figure 4.7 in which the optical conductivity is plotted for the three selected temperatures. The behavior of the second peak (marked by dashed arrow in the top plot) is very much similar to that of the phonon at 525 cm$^{-1}$. It undergoes temperature broadening and considerable reduction in the spectral weight which is similar to the expected phase phonon behavior. Based on these grounds we claim that the presence of midgap states in $K_{0.3}MoO_3$ is very much questionable.
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Figure 4.7: Top: The optical conductivity of $K_{0.3}MoO_3$ for $E||b$ and $E\perp b$ at $T = 6$ K in the region of expected "midgap", Bottom: Optical conductivity of $K_{0.3}MoO_3$ for the selected temperatures for $E||b$ showing the evolution of "midgap"
4.6 Discussion and summary

There are three main outcomes of our study. First; the relevance of phase-phonons in $K_{0.3}MoO_3$, second; the effect of W doping on CDW state, and third; absence of the mid-gap band. We discuss them in the following paragraph.

The optical conductivity of $K_{0.3}MoO_3$ in the CDW state in $E||b$ shows many sharp lines some of them are phase phonons. All the phonons which appeared in $E||b$ were attributed to phase phonons in the previous studies [1, 3, 7] which is not completely true. By definition, the phonons which become active only in $E||b$ (or metallic direction) are correctly called phase phonons [4, 5]. For example, the phonon at 525 cm$^{-1}$ is not a phase phonon since it is observed for both $E||b$ and $E\perp b$. We did not find sufficient evidence to conclude the previous claims [6, 7] that ”there exists atleast one midgap state inside every Peierls gap” which was originally proposed by Machida et al., [11]. It would be worth to discuss the connection between the so called phase phonons and the proposed midgap states. The phase phonons arise due to the coupling of phase oscillations of electron density (not necessarily CDW type) to the lattice. The midgap state arises due to some particular band fillings and necessarily there should be a CDW state or a Peierls gap. Neutron diffraction experiments can effectively address the question of midgap states which was attempted by Fujishita [11]. This study also could not come out with positive opinion about the presence of midgap states in $K_{0.3}MoO_3$. Further experiments on similar materials are essential to understand the midgap states.

From figure 4.3 it is evident that the doping of W does not change the phonon spectrum in the $E\perp b$ case whereas in $E||b$ it considerably affects the phonon spectrum and also the absolute value of reflectivity. Thus doping the transition metal W affects the phonon properties in the chain direction as it is expected. Tungsten doping reduces the room-temperature reflectivity in the FIR region due to the scattering of the carriers from impurities.

We also observed the pre-transitional Peierls fluctuations which eventually develop into a CDW gap.

Bibliography


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