Ordering and low energy excitations in strongly correlated bronzes
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Chapter 5

Disorder induced structural transitions in $K_{0.3}WO_3$

5.1 Structural properties

Tungsten bronzes are nonstoichiometric compounds with the general formula $M_xWO_3$, where $M$ is an alkali metal and $0 < x < 1$. These materials undergo one or more structural phase transitions when $x$ is varied from 0 to 1, high $x$ values show high symmetry and low $x$ values show low symmetry [1] at room temperature. A common characteristic of these materials is the corner-bounded $WO_6$ octahedra with the alkali ions occupying the interstitial sites (see figure 5.1). The phases observed for different $M$ ions as a function of the concentration $x$ is shown in figure 5.2. For example, the potassium tungsten bronze exhibits two kinds of structures. For $x$ values between 0.2 and 0.3 it is hexagonal and for $x$ ranging from 0.3 to 0.7 it exhibits a tetragonal structure. The vertical lines indicate the range of $x$ values for which the same structure (indicated by the corresponding symbol) is observed. Since the parental compound $WO_3$ has a lower symmetry with a monoclinic structure [1] the tungsten bronzes may be considered to be high symmetry forms of $WO_3$ stabilized by the presence of the alkali ions [1]. Magneli [4] has shown that the hexagonal structure consists of six-membered rings forming channels and the tetragonal-I structure consists of five-membered rings forming channels as shown in fig. 5.1. At concentration $x = 0.33$ there are two $M$ atoms per unit cell and all channels are filled.

Superconductivity in these materials has been observed as early as 1964 [5]. The hexagonal K, Rb and Cs bronzes were found to be superconducting with $T_c$ near 1.5 K [6]. The $Tl$ compound, $Tl_{0.33}WO_3$, was also found to be hexagonal and
superconducting [7]. One of the reasons why these materials attained considerable interest is that they offer a playground to study how the normal and superconducting states react to the filling of the conduction band, as this can be adjusted by varying the $M$ stoichiometry. This is because the parental compound WO$_3$ is an insulator with an empty $d$ band hybridized with the oxygen $2p$ band. The role of the alkali atoms, $M$, is to donate their $s$ electrons to the host conduction band giving rise to metallicity and eventually a superconducting transition [2, 8]. The striking feature of these compounds is that one can have a control over the superconducting properties (such as $T_c$) by adjusting both the band filling through variation of the stoichiometry, as well as the lattice dynamical properties [7], by changing the alkali ion.

The class of tetragonal bronzes containing the alkali atoms $Na$ and $Li$ are relatively well studied [5, 9]. Many studies were focused at the metal-nonmetal transition in distorted perovskite $Na_{0.25}WO_3$ with $x = 0.25$, which suggest that the transition is due to localization in a pseudogap between a sodium-induced $W$
5.2 Physical properties and some questions

One of interesting properties of the hexagonal $M_x$WO$_3$ (for $M$=K and Rb) is that it shows a resistivity anomaly \cite{2} which is strongly dependent on the concentration of the metal ion. Figure 5.3 (left panel) shows the temperature dependence of the resistivity of $K_x$WO$_3$ for $0.18 \leq x \leq 0.32$. The most striking feature of the data is the $x$ dependent anomalous "hump" whose onset is indicated by the arrows in Fig 5.3. The onset temperature, $T_B$, as a function of the composition $x$ is shown in the right panel of figure 5.3. One can notice that $T_B$ is highest for the composition $x = 0.25$. For $K_{0.3}$WO$_3$ $T_B$ is around 180 K. A very similar
Chapter 5. Disorder induced structural transitions in $K_{0.3}WO_3$

Figure 5.3: Left panel: Temperature dependence of the resistivity of $K_xWO_3$ for $x = 0.18$ to $0.32$. Right panel: The temperature at which the anomaly is observed for different $x$ values, the lines indicate the temperatures ($T_B$) corresponding to the resistivity anomaly and the symbols represent the temperatures at which the structural phase transitions were observed in neutron scattering [10]. *(Note: The structural phase transitions and the resistivity anomaly occur at the same temperatures. [Reprinted figure with permission from L. H. Cadwell*, R. C. Morris, and W. G. Moulton. Phys. Rev. B 23, 2219 (1981). Copyright(1981) by the American Physical Society]*)
behavior is also found in Rb compounds. Based on these observations Cadwell [2] suggested that these anomalies are associated with some type of phase transition. Though the exact nature of the phase transition was not recognized in their study some models were suggested. The conduction mechanism and the band structure near the fermi level in the hexagonal tungsten bronzes are mainly arising from the tungsten 3d $t_{2g}$ and oxygen 2p $p\pi$ orbits in the $WO_3$ octahedra [11]. Qualitatively, the presence of the resistivity anomaly is dependent on the kind of the alkali metal ion; in Cs$^+$ compounds no resistivity anomaly was observed; in Rb$^+$ compounds a weak anomaly exists; and in K$^+$ the anomaly is strong. In addition, measurements of the resistivity of the mixed crystals of Cs$_x$Rb$_y$WO$_3$ for 0.2 < x+y < 0.3 as a function of temperature [2] have indicated that the transition decreases in temperature and broadens as the Cs concentration increases before disappearing at high Cs concentrations. The proposed interpretation of this was that the size of the metal ion is the controlling parameter. It was known that the size of the metal ion determines the crystal structure of the WO$_3$ lattice in the tungsten bronzes. Thus in going from the large Cs$^+$ ion to the small K$^+$ ion the open space in the octahedral channels increases (In other words the larger Cs$^+$ ion fills the space between the octahedral channels more efficiently than the smaller K$^+$ ion). This would imply that K$^+$ ions are less tightly bound to the WO$_3$ lattice and hence have more mobility. This argument is supported by the specific heat studies [12] which showed that the coupling constant of the Cs$^+$ ions to the lattice is more than twice that of the smaller Rb$^+$ ions. Thus the correlation of the transport properties with ion characteristics was well established, however, the detailed mechanism was still unclear. At this point it would be worth to remember that the behavior of the resistivity (which resembles the plots in figure 5.3) looks very similar to that of some materials with a CDW ground state (for example NbSe$_3$) having two CDW transitions [13]. Since the CDW transition is associated with a doubling of the unit cell which may very well be observed in x-ray scattering experiments, its natural to look for temperature dependent changes in the lattice parameter. Understanding the resistivity anomaly by the experimental data was complicated by the observation that x-ray diffraction studies showed no abrupt changes in the lattice parameters as a function of temperature to an accuracy better than 0.0025Å [2]. It is possible that a distortion smaller than this could result in the observed property changes provided the Fermi surface lies in a region of a rapidly changing density of states [14, 15]. This is true for the case of tetragonal tungsten bronzes [14]. Though a formation of charge-density-wave (CDW) could exhibit a resistivity anomaly as shown in Fig. 5.3 it is difficult to understand the behavior of $T_B$ with x since in general disorder tends to drive the CDW transition
down in temperature [16] which contradicts the experimental observations, particularly for \( x \neq 0.25 \) in the right panel of figure 5.3. It seems likely that ordering of the Rb\(^+\) and K\(^+\) ions near \( x=0.25 \) plays a role in the formation of a CDW-like state. Although, x-ray diffraction experiments would be an ideal tool to check the possibility of the ordering the fact that the x-ray scattering cross section of Rb is only 1 % of that of W, makes it more difficult. No direct experimental evidences exist to support the CDW formation in the hexagonal tungsten bronzes. The fact that the critical concentration, \( x = 0.25 \), at which the maximum in \( T_B \) is observed, is approximately the same for both the Rb and K compounds could support the assumption that the metal ions undergo some sort of ordering. While the x-ray scattering studies have failed to witness some kind of phase transition near \( T_B \) a more convincing neutron study by Sato et al., [17] clearly indicated two structural phase transitions. In the neutron scattering measurements some new superlattice peaks appeared at \( S = 205 \) K and grow upon decreasing the temperature. The structural phase transition temperature \( T_S \) agrees reasonably well with \( T_B \) (of figure 5.3). This clearly indicated ordering of the metal atoms (Rb,K) along the \( c \) direction. Thus the resistivity anomaly observed by Cadwell et al., can now be explained based on the physics which involves a doubling of the unit cell along the \( c \) direction. Since the doubled unit cell contains four Rb sites, \( x=0.25 \) corresponds to exactly one alkali atom per unit cell, thus explaining the origin of the resistivity anomaly. This transition is essentially an order-disorder transition in which at low temperatures the metal atoms tend to order. A fully ordered state is possible for the composition \( x=0.25 \), in which case the transition of first order type [18]. The order-disorder transition is expected to show long-period structures due to a random distribution of sites. The loosely bound nature of the alkali metal ion in the channels of the octahedra leads to the occurrence of phonon modes which are almost independent vibrational motion of the alkali metal atoms leading to the so-called local mode behavior. Indeed a nearly dispersionless phonon branch has been observed in Rb\(_{0.3}\)WO\(_3\) at an energy of 5.5 meV (44 cm\(^{-1}\)) [17]. This branch reflects the local mode character of the Rb atoms within the host cage. When the octahedral cages are fully occupied (for \( x = 0.33 \)) local mode-behavior may not be expected since there is a long-range ordering. In this case, a finite dispersion of the modes corresponding to the M atoms is expected.

In the same study by Sato et al., a second transition has also been observed near room temperature which is accompanied by an optical phonon softening at the center (\( \Gamma \)-point) of the Brillouin-zone. This second order phase transition is due to a distortion of the WO\(_3\) host cage of \( M_xWO_3 \). A recent study [19] has pointed out that this octahedral distortion may arise due to a Jahn-Teller (J-T)
distortion. This argument can be supported on the following grounds. The valence electronic configuration of atomic W is 5d^{4}6s^{2}. In the parental compound WO_{3} the ionic configuration W has lost all its valence electrons. Indeed solid WO_{3} is an insulator. Thus, as mentioned earlier, the origin of superconducting properties is due to the M atoms which dope electrons into the 5d conduction band. Due to the octahedral crystal field the energy associated with the \( t_{2g} \) orbitals of W is lower than the \( e_{g} \) orbitals. In the hexagonal tungsten bronzes the symmetry is \( D_{6h}^{3} \) and the \( t_{2g} \) orbitals are further split into the lowest doublet (\( d_{x^2-y^2}, d_{yz} \)) and an upper singlet \( d_{xy} \). Thus when there is no further distortion of the octahedra the electrons in the lowest doublet will reside in a doubly degenerate orbital site. This electronic configuration is subject to a J-T distortion. At high enough electron doping (x), the J-T distortion may eventually become cooperative.

Below certain critical concentration, which is not known at present, the J-T distortion is noncooperative and remains local. This J-T distortion is a second order transition resulting in the softening of corresponding phonon modes. Similar effects have been found in the case of SrTiO_{3}, a perovskite system [20].

Apart from the above mentioned transport properties the \( M_x \)WO_{3} (M = K, Rb, Tl, Cs) bronzes also undergo a superconducting transition [2] at very low temperatures (\( T_{c} = 1-4 \) K), which is shown in figure 5.4. Substantial variation in \( T_{c} \) was observed both with respect to composition x and also with respect to the kind of M ion. The observed variation of \( T_{c} \) with x is not monotonous and hence does not seem to be consistent with the BCS theory. This is enough to create surprise since most of the low \( T_{c} \) superconductors obey the BCS theory. Sato et al., [17] tried to explain this behavior by assuming that there is an additional contribution to the electron-phonon coupling parameter due to the structural excitations arising from the vacancies of the alkali metal atom, which was called "local structure excitation". Dependence of \( T_{c} \) on the species of M (K,Cs,Rb,Tl) was also observed experimentally [7]. The possibility that the superconducting transition temperature within a group of materials could be raised substantially by varying lattice dynamical properties attracted many researchers. Due to a small subgroup (the modes due to the alkali metal) of the lattice modes the \( T_{c} \) varied considerably thus showing the general possibility of optimizing \( T_{c} \) in other similar systems by varying lattice-dynamical properties. In the same study it was observed that the \( T_{c} \) varied as \( m^{-1/2} \), where \( m \) is the mass of the alkali atom. It was shown that the special phonons arising due to the alkali ion are responsible for altering the superconducting transition temperature (to several K). The results were explained qualitatively considering two factors. The first is the loose binding of the alkali atoms, which cause the electron-phonon coupling parameter related to the alkali
Chapter 5. Disorder induced structural transitions in $K_{0.3}WO_3$

Figure 5.4: Variation of the superconducting transition temperature as a function of composition $x$ [18] for $Rb_xWO_3(K_{0.3}WO_3$ shows similar behavior [17]), the monotonously decreasing dash-dotted curve is the expected behavior in the absence of vacancy ordering. [Reprinted figure with permission from R. Brusetti, P. Haen, and J. Marcus. Phys. Rev. B 65, 144528 (2002). Copyright(2002) by the American Physical Society]

metal atom alone to be fairly large and hence results in a relatively large $T_c$. The second factor could be that in low-$T_c$ materials the Coulomb repulsion of electrons has been just slightly overbalanced by the electron-phonon interaction due to the octahedral network. The further increase in the electron-phonon interaction due to the phonons arising from the alkali metal atom can cause an increase in the $T_c$. A recent study by Brusetti et al.,[18] explained the observed behavior of $T_c$, the dip near $x = 0.25$ in figure 5.4, as due to the ordering of the $Rb$ atoms for $x \approx 0.25$. The ordering of the $Rb$ atoms leads to a reduction in the density of states at the Fermi level. This destabilizes the superconducting state but has a minor effect on the resistivity of the normal state. Thus the ordering of the alkali metal atoms are found to be detrimental to the superconducting transition.

Further discussions on the superconducting properties can be found in [2, 7, 17, 18].

The claim that the alkali metal ions are loosely bounded to the $WO_3$ lattice and
have considerable freedom to move is supported by heat capacity measurements [12, 21] in which it was shown that at low temperatures $M_xWO_3$ compounds have a large excess heat capacity over that of WO$_3$ itself. It was shown that the excess heat capacity can be fit as arising from vibrations of the $M$ atoms. In Tl compounds these modes were observed directly by neutron scattering measurements [7]. Relatively dispersionless modes or Einstein modes associated with the $M$ atoms are found at an energy of about 0.6 THz (20 cm$^{-1}$) and 1.3 THz (43 cm$^{-1}$) which is shown in the fig. 5.5.

Though the above mentioned studies give a hint about the presence of a phase transition together with rich physics involving vibrational dynamics coupled with electronic degrees of freedom the exact nature of the transition is not understood completely. Such electron-phonon dynamics can be studied using Raman scattering. The long standing question whether the hexagonal $M_xWO_3$ may undergo a CDW transition due to the ordering of the metal atoms can also be addressed in a Raman study. Raman spectroscopy is a convenient tool to unravel not only the

![Graph showing neutron diffraction peaks at 0.6 THz (20 cm$^{-1}$) and 1.3 THz (43 cm$^{-1}$) for TI$_{0.33}WO_3$ and WO$_3$, with no peaks for pure WO$_3$.](image-url)
vibrational properties but also their possible coupling with electronic degrees of freedom.

5.2.1 The key-issues

This study is done to address the following key issues. First, to verify experimentally the possibility of a Charge-Density-Wave (CDW) formation. As speculated in many previous studies [2, 7, 17] doubling of the unit cell along the hexagonal axis (c-axis) together with a possible gap opening near the Fermi surface was thought to be due to a CDW formation. Second, to study the structural properties to address the issue of the so-called "local structural excitation" and the possible ordering of alkali sub-lattice.

5.2.2 The crystal structure controversy

The $M_xWO_3$ bronzes have been a subject of controversy with respect to their room temperature structure. The most complete structural analysis has been done for $x = 0.27$. The space group P6$_3$/mcm ($D_{6h}^3$) suggested by Magneli [4] was found to be inadequate [17]. Sato et al., carried out a thorough structural analysis for the composition $x = 0.27$. In this study the final R-factor (weighted profile) is about 11 % while the statistically expected R-factor is 4 % for the hexagonal symmetry which best suits (among the other possibilities). The origin of the discrepancy lies in accommodating the metal atom (K and Rb) in the lattice. Another reason for the unsatisfactory fitting could be that the calculation was done for average structures and the local shifts of the oxygen atoms near the vacant sites were not included. Although, a firm conclusion about the space group has not been made the hexagonal symmetry is retained with a precision of $10^{-4}$ [17], which is consistent with the obtained lattice parameters (c/a ratio). The exact crystal structure of the material remains unsolved till now.

5.3 Raman spectra of $K_{0.3}WO_3$ at low and high temperature

Figure 5.6 shows the Raman spectra of $K_{0.3}WO_3$ at $T = 40$ K and $T = 275$ K for the polarization (cc) (ie., along the hexagonal axis), which denotes the direction of the electric vector of the incoming and the outgoing light being parallel to the c-axis of the crystal. The Raman spectra in the polarization (aa) at $T = 40$ K and $T = 275$ K are shown in figure 5.7. The spectrum in the cross polarization
Chapter 5. Disorder induced structural transitions in $K_{0.3}WO_3$

Figure 5.6: Raman spectra of $K_{0.3}WO_3$ at two different temperatures. (xy) indicates the polarization of the incoming and the scattered light being parallel to the x-axis and y-axis respectively of the crystal. The spectra are shifted vertically for clarity.
Figure 5.7: Raman spectra of $K_{0.3}WO_3$ in the (aa) configuration at $T = 40\,\text{K}$ and $275\,\text{K}$. The spectra are shifted vertically for clarity.
configuration (ac) shows no measurable signal (see figure 5.6). In the T = 275 K spectrum in (cc) configuration there are four strong modes whose central frequencies are 35 cm\(^{-1}\), 50 cm\(^{-1}\), 83 cm\(^{-1}\) and 201 cm\(^{-1}\). One can also notice a few weaker and broader modes with the central frequencies 157 cm\(^{-1}\), 247 cm\(^{-1}\), 278 cm\(^{-1}\), 337 cm\(^{-1}\) and 383 cm\(^{-1}\). At this point it’s worth to recall the previous study by Scott et al., [22] in which no Raman features were observed in the hexagonal Rb\(_{0.3}\)WO\(_3\) compound. Only a broad feature near 650 cm\(^{-1}\) was observed. The absence of any Raman lines was interpreted as due to a smaller unit cell size when compared to the tetragonal Na counterparts. This is rather surprising since our study clearly shows the presence of many phonon lines. In the case of (aa) polarization configuration (figure 5.7) only a very strong \(A_g\) mode at 83 cm\(^{-1}\) is observed, whereas at low temperatures many new modes are seen. Most of our discussion will be focused on the (cc) polarization Raman spectra. It is well known from the retrospective studies [3, 23] that the internal vibrations appear at higher frequencies than the vibrations that involve a rigid tilt or any other forms of octahedral displacements. Based on these grounds, the higher frequency modes that are mentioned above might very well be due to the internal vibrations of the octahedra. Since such vibrations may couple strongly to the metal atom, \(K\), they relax their energy quickly and hence appear as broad features. To support this argument further, in the Raman spectrum of the parental compound WO\(_3\) [22] the W-O stretching modes near 400 cm\(^{-1}\) are much sharper due to the absence of this type of relaxation.

In the low temperature spectrum (figure 5.6) many interesting observations can be made. 1) new Raman active modes appear, 2) the modes get sharper, 3) the sharp mode at 60 cm\(^{-1}\) is associated with an asymmetric tail of about 40 cm\(^{-1}\) linewidth (Full Width at Half Maximum) towards the low frequency side of the spectrum. To understand these features we carry out a detailed temperature dependent study.

### 5.4 The temperature dependent Raman spectra of K\(_{0.3}\)WO\(_3\)

Figure 5.8 shows the temperature dependent Raman spectra of K\(_{0.3}\)WO\(_3\). In the low temperature spectra there are about 28 modes where as at high temperature (T>200 K) there are about 12 modes. The modes marked with arrows in the T = 70 K spectrum are the new modes that appear below T \(\approx\) 200 K. The linewidth of the new modes increases with increasing the temperature and they disappear above 200K. The high-temperature modes show a temperature dependent linewidth broadening along with a downshift in their frequency. The most
Figure 5.8: Raman spectra (cc) of $K_{0.3}WO_3$ at various temperatures. Note: The spectra are shifted vertically for clarity.
striking feature of the temperature dependent Raman spectra of K$_{0.3}$WO$_3$ is the temperature dependent behavior of the feature at the low frequency, i.e., the dynamics of the band observed between 25-60 cm$^{-1}$. At low temperatures (T = 3 K to 40 K) a sharp mode is observed at 60 cm$^{-1}$, together with a tail towards the lower frequency side. As the temperature is increased two interesting observations can be made. First, the intensity of the 60 cm$^{-1}$ mode grows with temperature up to about 170 K and second, the low frequency tail gradually gains strength and grows in to a prominent peak at T = 250 K. We proceed by first analyzing the strong low frequency feature which undergoes enormous changes with increase in temperature.

5.4.1 The local modes

In figure 5.9 a “zoom-in” view of the low frequency band and the two other modes for the two temperatures is plotted. In the first glimpse the shape of the low frequency band (30-60 cm$^{-1}$) in the T = 40 K spectrum appears to have a Fano line shape (Breit-Wigner) [24–26]. A Fano resonance [27] may result from the interference in the scattering from a continuum of states and an embedded discrete level. The spectrum of light scattered from the discrete state is strongly modified due to this coupling. The continuum of excitations may, for instance, result from an electronic continuum or from a continuum of phonon states.

Even though the spectrum at T = 40K can be fitted using a Fano-formula it is clear that the T = 4K spectrum definitely cannot be fitted in this way. This leads us to believe that the low frequency band has no contribution from Fano effects. A more convincing and supportive argument to discard the possibility of Fano resonance is the strong evidence of disorder in these kind of materials [3]. Although in principle the presence of lattice disorder does not discard the possibility of Fano-processes, the presence of disorder has been found to influence strongly the Raman line shapes in a similar way as the Fano-effect does. For example, in the case of the intercalated compound Ag$_{0.33}$TiS$_2$ the disordering of the Ag atoms leads to a strong modification of the Raman spectra at low temperatures [28, 29]. The Raman line shape of these compounds resemble a Fano-line shape. The asymmetry is indeed due to the disorder of a particular kind of atom in the lattice which is loosely bound to the host lattice. It was suggested by Sato [17] that most of the properties of $M_x$WO$_3$ compounds resemble that of the intercalated compounds. For example, there exist order-disorder transitions and long range periodic structures. The phonon dynamics were found to be similar to that of intercalated graphite systems which also display local-mode behavior.

In the T = 4K spectrum of figure 5.9 one can notice at least four A$_g$ phonon
Figure 5.9: The modes at 45 cm$^{-1}$, 52 cm$^{-1}$, 60 cm$^{-1}$, 70 cm$^{-1}$ and 97 cm$^{-1}$ are due to the local modes of K atoms. Note that the modes marked by arrows are resolved reasonably well in the T = 4 K spectrum.
modes at energies 45 cm$^{-1}$, 52 cm$^{-1}$, 60 cm$^{-1}$, 70 cm$^{-1}$ and 97 cm$^{-1}$; among which two of them, the 60 cm$^{-1}$ and the 97 cm$^{-1}$ are strong ones. At this point it is worth to mention that, in the neutron scattering study of the member compound $Tl_{0.3}WO_3$ by Kamitakahara [7] there are two broad dispersionless Einstein modes observed at energies 0.6 THz and 1.3 THz (20 and 43 cm$^{-1}$ respectively). Since these features were not observed for the parental compound WO$_3$, they were ascribed to the local modes of the alkali atoms (see figure 5.5). In the $Tl$ compound all these modes were observed at slightly lower energies due to the heavier mass of $Tl$ ion. Accordingly, by doing a harmonic approximation the square root of the ratio of the mass of the K to $Tl$ is $\sqrt{M_K/M_{Tl}}=0.4373$, which matches closely with the measured frequency ratio $\frac{\omega_T}{\omega_K}=20/45 = 0.44$, considering the fact that the spectral feature found in the neutron study was very broad. Thus the 45 cm$^{-1}$ mode in our study corresponds to the $\approx 20$ cm$^{-1}$ of $Tl$ compound. Another strong mode at 97 cm$^{-1}$ would corresponds to the 43 cm$^{-1}$ mode (the second peak in figure 5.5) in the case of $Tl$. The other modes, 60 cm$^{-1}$, 52 cm$^{-1}$ and 70 cm$^{-1}$ correspond to the first broad structure around 20 cm$^{-1}$ in figure 5.5. These modes were not well resolved in the neutron diffraction study [7] reflecting a better resolution of our Raman spectrum. Table 5.10 gives a comparison of the modes found in the neutron [7] and our Raman study.

In the neutron scattering study of Rb$_x$WO$_3$ by Sato et al., [17] a very broad feature of about 40 cm$^{-1}$ width with central frequencies of about 44 cm$^{-1}$ and 48 cm$^{-1}$ was observed at T = 35 K and it gained strength at higher temperatures. Our claim that the modes in the frequency range 45 cm$^{-1}$ to 97 cm$^{-1}$ (see figure 5.9) are the dispersionless Einstein modes; is consistent with the above mentioned neutron studies. The $x=0.25$ composition together with the doubling of the unit cell, which was reported in the study by Sato [17] and Cadwell [2], corresponds to one $M$ atom per unit cell. At some low temperature this composition may undergo a perfect order-disorder transition while the composition other than this value corresponds to an imperfect order-disorder transition. A local mode corresponding to a particular site occupation gives rise to a discrete well defined vibrational frequencies whereas a distribution of occupancies gives rise to a broad features. For example, in the case of Rb$_{0.27}$WO$_3$ [17] a diffuse broad feature having a peak energy of about 5.5 meV (44 cm$^{-1}$) was found in the inelastic neutron scattering measurements. Thus the loosely bound $K$ atoms together with the non-stoichiometry accounts for the observed broad features at low energy. Since this is driven by a structural excitations of the $K$ sublattice this is often called local-structure-excitation (LSE). For the reasons given in the next section we call the low frequency band a LSE-band.
Chapter 5. Disorder induced structural transitions in $K_{0.3}WO_3$

<table>
<thead>
<tr>
<th>Neutron $\omega_{Tl}$ (cm$^{-1}$)</th>
<th>Raman $\omega_K$ (cm$^{-1}$)</th>
<th>$[M_K/M_Tl]^{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 ($\Delta \omega \sim 10-30$ cm$^{-1}$)</td>
<td>45</td>
<td>0.43</td>
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<td>52</td>
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<td>70</td>
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<td>43 cm$^{-1}$</td>
<td>97</td>
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Figure 5.10: Table showing the $Tl$ modes observed in neutron scattering [7] compared with our Raman modes of $K$ atoms. $\Delta \omega$ represents the "broadness" of the feature in the neutron study.

5.4.2 The Local-Structure-Excitations: Order-disorder transition

The temperature dependence of the LSE band is plotted in figure 5.11. The left plot shows un-normalized Raman intensity and the right plot shows the spectra normalized by the factor $(1+n(\omega,T))$ in order to remove the temperature dependence. One can notice enormous changes with increasing temperature. The following observations can be made. 1) The 45 cm$^{-1}$ and 52 cm$^{-1}$ modes broaden enormously and merge in to the broad continuum, 2) the mode at 60 cm$^{-1}$ broadens and softens as the temperature is increased 3) above 100 K a new mode evolves at 35 cm$^{-1}$, 4) At 170 K both the 60 cm$^{-1}$ and 35 cm$^{-1}$ modes have almost equal Raman strength, 4) above T = 170 K the 35 cm$^{-1}$ mode grows strongly while the 60 cm$^{-1}$ mode remain almost unchanged. Although the minor features of the temperature dependent LSE band is not trivial to analyze due to the presence of an increasing continuum together with the complicated shape, the two strong features at 35 cm$^{-1}$ and 60 cm$^{-1}$ can be further analyzed by fitting them to a Lorentzian lineshape. The results of the fit are displayed in figure 5.12.

The frequency of the 60 cm$^{-1}$ mode does not vary much until 100 K. For higher temperatures it softens by about 20 % while the 35 cm$^{-1}$ mode softens...
Figure 5.11: Temperature dependent behavior of the LSE-band for various temperatures. Right-panel: The spectra are normalized by \(1+n(\omega,T)\) where, \(n(\omega,T) = 1 / (e^{\omega/T} - 1)\).

Note: The spectra are shifted vertically for clarity. The arrow at the right side indicates the temperature-chronology of the spectra from bottom to top.
Figure 5.12: Temperature dependent frequencies and linewidths of the 35 cm\(^{-1}\) mode and the 60 cm\(^{-1}\) mode.
only by 4% upon increasing temperature. The softening of the 60 cm\(^{-1}\) mode continues up to about 170 K. The linewidth of the 35 cm\(^{-1}\) mode decreases from 12 cm\(^{-1}\) to 4 cm\(^{-1}\) with increase in temperature which shows that this mode is stable at higher temperatures. The linewidth of the 60 cm\(^{-1}\) mode increases steadily until \(T \approx 170\) K and saturates above. It is interesting to note that the temperature at which the frequencies and the linewidths of the two modes saturate, i.e., \(T \approx 170\) K corresponds to the temperature \(T_B\) of the order-disorder transition for \(K_{0.3}WO_3\), as shown in the right panel of figure 5.3. This implies that these two modes are associated with the order-disorder transition and consequently with the previously reported resistivity anomalies. The mode at 60 cm\(^{-1}\) softens about 20% as shown in figure 5.12, which indicates that this might be the soft mode of the order-disorder transition. The softening takes place from 170 K to 100 K. At \(T = 4\) K the modes 45 cm\(^{-1}\), 52 cm\(^{-1}\) and 60 cm\(^{-1}\) are relatively sharp, indicating a "frozen-in" nature of the modes, i.e., a frozen-in disordered state. The ordering of \(K\) sublattice may result in a doubling of the unit cell as proposed by Brusetti et al., [18]. A perfect ordering is possible for the composition \(x = 0.25\) which corresponds to one alkali atom per unit cell. As one goes away from this composition there will be disorder. Due to the nonstoichiometry of the alkali atom sublattice there are vacancies (unoccupied sites). At low temperatures these vacancies are localized in a given region resulting in a relatively less disorder giving rise to a reduced Raman intensity. Thus at low temperatures the \(K\) sublattice order due to which sharp modes corresponding to the \(K\) atoms are observed. Recent results of differential scanning calorimetric measurements on \(Rb_{0.25}WO_3\) [18] have shown that only for \(x = 0.25\) the order-disorder transition is first order. As the temperature is increased the vacancies can distribute randomly pertaining to a disordering of the \(K\) sublattice giving rise to a broad continuum. These observations are consistent with the lattice-gas theory [29] which was invoked to describe the order-disorder transition in the intercalate compound \(Ag_{0.33}TiS_2\). The main outcome of the theory is that away from the order-disorder transition temperature, there exists a broad distribution of vibrational frequencies. As \(T \rightarrow T_c\) this continuum becomes narrower and may interfere with the zone-folded phonons. Thus similar to the intercalate compounds, \(K_{0.3}WO_3\) also gives a strong continuum due to a random distribution of site occupancies. A dramatic enhancement to the Raman signal at higher temperatures could be due to an arbitrary distribution of \(K\) atoms which may break the translational symmetry thus relaxing the Raman selection rules. Thus at high temperatures the observed increase in the Raman activity of the LSE band is due to the breaking of the translational symmetry arising from the disorder in the \(K\) sublattice. When the translational symmetry is broken due to
the effects like disorder (or impurities) the \( k \approx 0 \) selection rule for the scattering process is relaxed giving rise to an enhanced Raman signal.

Another interesting consequence of breaking translational symmetry is worth to consider. According to the Goldstone theorem [30, 31] there exists a massless particle if a continuous symmetry is spontaneously broken (The theorem was originally meant for particle physics). In condensed matter state the massless particle corresponds to a collective excitation with frequency \( \omega \rightarrow 0 \). Thus the observation of the soft mode, \( 60 \text{ cm}^{-1} \), (although the softening is incomplete) in our study may corresponds to the proposed collective excitation. However, we propose a detailed structural analysis of \( M_x\text{WO}_3 \) compounds to confirm this claim. The first observation of the collective structural excitation in a crystalline solid was observed by Kendziora et al., [32] in the superconducting pyrochlore \( \text{Cd}_2\text{Re}_2\text{O}_7 \). This material showed cubic-to-tetragonal structural phase transition at \( 200 \text{ K} \) which was accompanied by the manifestation of a peak in the Raman spectrum with \( \text{B}_1 \) symmetry and with divergent intensity.

After presenting the temperature dependent Raman spectra of the ”local modes” it is worth to discuss their implications with respect to the local structure excitations. We have shown that the local modes due to the loosely bound alkali atoms (also Tl) reveal their spectral features in the Raman spectra. If there exists disorder arising due to non-stoichiometry the excitations between the local states may give rise to the so-called local structure excitations (LSE). The concept of LSE is a general subject matter of materials which have many minima in their local ground state configuration. These minima are separated by a small energy and by a potential barrier. The excitations between these local states are called local structural excitations [33]. Transition between these states may be caused by electrons or phonons [5]. LSEs have significant effects on the electron and phonon properties if their excitation energy and the barrier between their states are sufficiently small to be activated, for instance, by temperature. LSEs were mainly observed in high-\( T_c \) superconductors which are significantly influenced by dynamical lattice instabilities. These dynamical lattice instabilities were proposed to play a significant role in pairing in high-\( T_c \) superconductors. These materials exhibit more than one phase as a function of temperature, pressure, or composition [34]. The best examples are the occurrence of the composition-dependent structural phase transitions in \( M_x\text{WO}_3 \) bronzes as shown in figure 5.2 (see introduction). Dynamical fluctuations/transitions between these local states are important if they can be excited easily. In addition defects and nonstoichiometry introduce randomness in to the energy differences between these local states. Defects were found to induce nucleation of more than one phase [35–38]. Although this is an extreme possibil-
ity, they may randomly modify the local potential barrier and the energy separation between two phases [33]. It should be noted that the local phases may not always correspond to phases realized macroscopically but rather may be occupied only locally. This is clearly exemplified by the temperature-dependent LSE-band in figure 5.11. For $T \leq 70 \text{ K}$, the $60 \text{ cm}^{-1}$ mode has a larger intensity whereas the $35 \text{ cm}^{-1}$ mode is hardly visible. As temperature is increased the $35 \text{ cm}^{-1}$ mode grows and at $T \approx 170 \text{ K}$ both the modes attain the same strength. Further increasing temperature the $35 \text{ cm}^{-1}$ mode grows beyond the $60 \text{ cm}^{-1}$ mode and finally both the modes become broader near room temperature. Thus at low temperatures the $60 \text{ cm}^{-1}$ mode is dominant and at high temperatures the $35 \text{ cm}^{-1}$ mode becomes dominant. These two modes exemplify the two local ground state configurations or they are two LSEs. Thus in the present case the order-disorder transition is driven by LSEs. The temperature-dependent LSE-band is pictorially shown in figure 5.13.

Further we claim that the two modes, $35 \text{ cm}^{-1}$ and $60 \text{ cm}^{-1}$, represent two different local phases due to the following reasons. The $35 \text{ cm}^{-1}$ mode does not exist for temperatures below $T \approx 100 \text{ K}$ and the $60 \text{ cm}^{-1}$ mode is considerably sharper indicating a frozen-in state. At high temperatures, the $60 \text{ cm}^{-1}$ mode tends to vanish whereas the $35 \text{ cm}^{-1}$ mode gains strength. This indicates that these two modes represent two different phases (at least locally) of the material, however, whether these two phases are realized macroscopically is not clear yet.

Figure 5.13 can be understood as follows. There are at least two local ground state configurations. At low enough temperatures the $60 \text{ cm}^{-1}$ excitation is sharper reflecting the stability of the phase. As the temperature is increased the potential barrier between the local minima is reduced allowing for the tunnelling between the states, consequently near $170 \text{ K}$ we observe equal strengths for both the modes. A further increase in temperature results in a further reduction of the potential barrier thus making the $60 \text{ cm}^{-1}$ unstable. However, a lower energy excitation i.e., the $35 \text{ cm}^{-1}$ mode can be stable with the newly occupied local ground state.

While the low frequency Raman spectra revealed the physics mostly driven by the local structural excitations the high frequency Raman spectra may give valuable information about the phonon modes associated with the octahedral host cage. The previous studies by Sato et al., [17, 18] predicted that the energetics of the octahedral distortion are coupled with the $K$ modes it would be interesting to observe them in the Raman spectra. Pertaining to the vibrational dynamics two kinds of phonons are observed in our Raman spectra as can be seen in figure 5.8. One, the high-T modes which sharpen as temperature is decreased and second,
Chapter 5. Disorder induced structural transitions in $K_{0.3}WO_3$

The interplay between the two local phases

![Diagram](image)

Figure 5.13: A diagrammatic representation of the tunnelling between the two phases derived from figure 5.11.

the new modes that appear below $T \approx 200$ K. A gradual temperature dependent variation of the frequencies and linewidths of these modes point towards the presence of a second-order phase transition. We proceed with the following section by discussing the high-T modes.

5.5 The high-T modes and the zone-folding modes

The temperature dependent Raman spectra of $K_{0.3}WO_3$ showed two interesting features. First, appearance of the new modes (marked by arrows in figure 5.8) and second, a strong renormalization of the high-T modes. Specifically, the high-T modes undergo strong changes in their frequency and linewidth. It has been reported in various studies [39, 40] that the high-T modes can be strongly influenced by second order transitions like superconducting or charge-density wave transitions. For example in the CDW material TaS$_3$ the normal mode at 283 cm$^{-1}$ showed a systematic shift in its frequency with temperature which resembled the behavior of the temperature dependent order parameter. Similar behavior was also observed in the superconducting compound Nb$_3$Sn. In otherwords, the temperature dependent frequency shifts were different for temperatures above and below $T_c$. These studies have indicated that the phonon self energies are sensitive to the changes in the electronic structure. A stronger support to this claim
comes from the Raman study [41] of the high-T\textsubscript{c} superconductor YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7−δ} in which the change in the superconducting gap due to Zn doping was reflected in the self energies of the high-T modes. Since these changes in the self-energy of the vibrational modes can be associated with the temperature dependent order parameter their behavior may indicate the presence of a phase transition.

While the above mentioned studies [39, 40] indicate that some high-T modes couple to the order parameter which originate from the coupling between e − e and/or e − h (electron-electron and/or electron-hole) in some cases there could be lattice contributions also. For example, in the case of the ferroelectric compound Ba\textsubscript{x}Sr\textsubscript{1−x}TiO\textsubscript{3} (ferroelectric for x=1) there exists an order-disorder transition, [42] depending on the concentration of Ba atoms, which has a soft mode. The soft mode in this material is of displacive type. In this compound the A\textsubscript{1} mode at 150 cm\textsuperscript{−1} shows softening up to the phase transition temperature and then almost saturates.

First we examine the behavior of some strong high-T modes which indicate the presence of a second-order phase transition.

Figure 5.14 shows the temperature dependent frequencies of three modes at 219 cm\textsuperscript{−1}, 96 cm\textsuperscript{−1}(aa) and 439 cm\textsuperscript{−1}. All these modes show a systematic decrease with increasing the temperature until about T = 210 K and saturate above. The 96 cm\textsuperscript{−1} mode of (aa) polarization shifts about 13 cm\textsuperscript{−1} and the 219 cm\textsuperscript{−1} mode shifts about 16 cm\textsuperscript{−1} and the 439 cm\textsuperscript{−1} mode shifts by only small amount. The saturation of the frequency shift above this temperature is a striking feature. This gradual frequency change with temperature together with the saturation above 210 K would strongly indicate the presence of a second order phase transition near T = 210 K.

Many of the new modes which appear below T \approx 210 K, that are marked by arrows in figure 5.8. are too weak to be considered for further investigations, however, the temperature dependent frequency, linewidth and integrated intensity of the modes at 128 cm\textsuperscript{−1}, 258 cm\textsuperscript{−1} are considerably interesting.

The temperature dependent frequency shift of the mode at 258 cm\textsuperscript{−1} is shown in the first plot in the left panel of figure 5.15. The frequency of this mode shifts linearly to lower values from 258 cm\textsuperscript{−1} to 255 cm\textsuperscript{−1} as the temperature is increased and it’s integrated intensity vanishes above T = 200 K, as shown in the third column-first plot in figure 5.15. The mode 258 cm\textsuperscript{−1} shows similar linear frequency softening with increasing temperature. The integrated intensities of the two modes show a systematic decrease with increasing the temperature and vanishes for temperatures above T \approx 200 K. The linewidth of these two modes increase with increasing the temperature and tend to diverge near T = 200 K.
Figure 5.14: The temperature dependent frequency shift of the modes at 96 cm$^{-1}$ (aa), 219 cm$^{-1}$ (cc) and 439 cm$^{-1}$ (cc). The thick line in the top-plots are guide to eye. The arrow mark indicates the temperature-chronology of the plots.
Figure 5.15: The temperature dependent frequency, linewidth and integrated intensities of two of the new modes in the (cc) configuration.
Particularly, the enormous linewidth enhancement from $\approx 2$ to $8 \text{ cm}^{-1}$ of $258 \text{ cm}^{-1}$ mode indicates the presence of an effective relaxation channel involving strong electron-phonon or anharmonic interactions. The observations that the integrated intensities of these modes vanish and the tendency of their linewidths to diverge near $T = 200 \text{ K}$ very much indicate the presence of a second order phase transition.

### 5.6 Discussion and summary

In the present chapter we have presented a Raman study on the hexagonal bronze, $\text{K}_{0.3}\text{WO}_3$. The essence of the study can be framed in three parts and they are, the LSEs, order-disorder transition and the second-order phase transition. We discuss the outcome of our study as follows. At very low temperature, $T \leq 4 \text{ K}$, we observed sharp Raman features. The modes at 45 cm$^{-1}$, 52 cm$^{-1}$, 60 cm$^{-1}$, 70 cm$^{-1}$ and 90 cm$^{-1}$ were seen in the previous neutron scattering measurements as relatively broad features [7, 17]. These modes could very well be due to the ordering, though not perfect, of the metal atoms, $K$ in the hexagonal tunnel formed by the arrangement of the octahedra.

It should be noted that except for the composition $x=0.25$ a perfect ordering is not possible even with the speculated [12] doubling of the unit cell along the $c$-axis. By increasing the temperature the modes become broader giving rise to LSE mode. This broad feature very much resembles the inelastic x-ray scattering data which was measured by Sato et al., [17]. The appearance of the sharp features due to the partial ordering of the alkali metal atom together with the observed broadening at slightly higher temperatures agree qualitatively with the theoretical predictions of the lattice-gas model [29] for order-disorder transitions. At the temperature $T_B$ ($\approx 170 \text{ K}$), which corresponds to the previously reported resistivity anomaly [2, 18], the $K$ atoms start to order. Since for $x \neq 0.25$ the order-disorder transition is not of first order considerable softening is observed for the LSE band. Sharpening of the $K$ sublattice modes (45 cm$^{-1}$, 52 cm$^{-1}$ and 60 cm$^{-1}$) at $T = 4 \text{ K}$ indicates that there must be a change in the lattice constant possibly unit cell doubling.

The temperature dependent dynamics of the LSE band is mostly driven by effects due to disorder.

The temperature dependent LSE band indicated a gradual shift in the peak position from high-frequency side to low-frequency side. This probably indicates that, pertaining to the ordering scheme of $K$ atoms, there exist at least two energetically favorable minima in the free energy between which the occupancy changes
as a function of temperature. A composition dependent Raman study at various temperatures may provide further evidence for the speculated ordering scheme [17] of the metal atoms. We discard the possibility of an alternative mechanism to explain the broad low frequency asymmetric tail in terms of Fano-effect, since as it can be observed from the temperature dependent Raman data that at higher temperatures the lineshape does not resemble the Fano-shape. This drives us to interpret the low frequency data as due to disordering of the metal atom.

The second interesting observation is the presence of a second order phase transition near \( T = 200 \) K. Starting from the lowest temperature measured, as the temperature is increased their frequencies soften (figure 5.15) together with the enhancement in their linewidth. For example, the 219 cm\(^{-1}\) mode shows a systematic frequency downshift up to \( T = 210 \) K and saturates above. The linewidths of many modes saturate for temperatures above \( T = 200 \) K which very much implies that some decay channel is closed above this temperature. This hints the presence of most probably a second order phase transition near \( T_c \approx 200 \) K. After establishing the presence of the second order transition in \( K_{0.3}WO_3 \) it would be interesting to ask what is the nature of the phase transition?. The most often speculated type was the CDW transition [2] which might emerge due to the ordering of the metal atom along the c-axis together with the doubling of the unit cell at low temperatures. If at all there is a CDW transition one might observe the so-called Raman-active amplitudon(AM)-mode due to the transverse oscillation of the charge-density-wave. Generally, the AM mode is observed at very low frequencies due to it’s strongly coupled nature of the mode. In the (cc) configuration the presence of the broad feature due to the disorder makes the observation of the speculated AM mode, if it exists, less probable. If at all there exists a CDW due to the ordering of the metal atoms in the c-axis this would lead to a disordered and weak CDW due to the nonstoichiometry of the material. These observations allow us to discard the possibility of the CDW transition in \( K_{0.3}WO_3 \). The observed second order phase transition is most likely due to the distortion of the octahedra of Jahn-Teller type. Finally, we remark on one interesting observation pertaining to the LSE band. The Raman spectrum of the LSE band at room temperature is dramatically different from that of \( T = 275 \) K. It undergoes further over all reduction in the Raman intensity while going from 275 K to 300 K, together with a slight increase in the frequency. We observed this behavior for three independent measurements. We do not understand this behavior fully. We speculate that this could be due to a stabilization of the octahedral distortion together with a rearrangement of the alkali sublattice as suggested in [18]. A composition and alkali atom (K,Rb) dependent Raman study is necessary to fully understand the
observed behavior.

**Bibliography**


Chapter 5. Disorder induced structural transitions in $K_{0.3}WO_3$


