

Point contact spectroscopy and temperature dependence of resistivity of metallic Sodium Tungsten Bronzes - Role of optical phonons

N. Gayathri*

Department of Physics,

Indian Institute of Science, Bangalore 560012, India

A. K. Raychaudhuri†

National Physical Laboratory,

Dr. K.S.Krishnan Marg, New Delhi, India

Abstract

In this paper we report the results of electrical resistivity ($1.5 \leq T \leq 300\text{K}$) and point contact spectroscopy (PCS) measurements on single crystals of metallic sodium tungsten bronze with varying sodium content. We have shown that the electron-phonon coupling function as measured through PCS can explain quantitatively the large temperature dependence of resistivity ρ seen in these materials over the entire temperature range. The electron-phonon coupling function shows predominately large peaks for phonon frequency range of $30 \text{ meV} \leq \omega \leq 100 \text{ meV}$ which match well with the calculated optical phonons for WO_6 octahedron. The integrated electron-phonon coupling constant λ from this data is $\approx 0.25\text{-}0.45$, depending on the Na content.

*email: gayathri@physics.iisc.ernet.in

†email: arup@csnpl.ren.nic.in

I. INTRODUCTION

Electrical conduction in oxides, in particular, in metallic transition metal oxides is a topic of current interest^{1,2}. Over the last decade three classes of phenomena (namely superconductivity, colossal magnetoresistance and insulator-metal transition) have kept the oxides in the center stage. For the high T_c cuprates even the normal state resistivity with a linear temperature dependence is an unresolved issue. While the problem is most severe in the high T_c cuprates the temperature dependence of the resistivity in the other transition metal oxides have a number of interesting features in store. To be specific in this paper we are concerned with normal (i.e, non-superconducting) metallic oxides which show the $\rho(T)$ as in a metal (i.e, $d\rho/dT > 0$) and would like to investigate whether the temperature dependence of ρ can be understood quantitatively. In this context two important observations are noteworthy. First, in these oxides the resistivity even in the metallic state is quite high and second, the magnitude of the temperature dependence of resistivity, $\Delta\rho(T)(= \rho(T)-\rho_0$, where ρ_0 is the residual resistivity) is also very high. In fact, incomparison to conventional metals and alloys, where the $\Delta\rho$ (often $\leq 100\mu\Omega\text{cm}$) arises from electron-acoustic phonon scattering, the $\Delta\rho$ in the metallic oxides can be considered giant. If the source of the extra $\Delta\rho$ in oxides is scattering of electrons by phonons then it is clear that there must exist a source of large density of phonons in these oxides. Such a contribution has been found in certain oxides. It was shown in oxides like $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (superconductor with $T_c \approx 17\text{K}$ at $x \approx 0.47$) and $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ (superconductor with $T_c \approx 22\text{K}$) that the scattering from optical phonons in these materials make a significant contribution to the temperature dependence of ρ in the normal state³. These studies obtained the phonon data from the superconducting tunneling spectroscopy which gives the Eliashberg function $\alpha^2F(\omega)$ and used it to calculate the resistivity. This investigation is a very good beginning in the quantitative understanding of the temperature dependence of the resistivity of metallic oxides. This study, however, had one big drawback. Most of the data were on polycrystalline thin film or bulk pellets. Also the samples used for the tunneling data were not the same as those used for the resistivity

studies. In order to improve upon this, we did a complete investigation with single crystalline Sodium Tungsten Bronze system (Na_xWO_3) and used the same sample for both the resistivity measurement and the phonon spectra measurement from which the Eliashberg function $\alpha^2F(\omega)$ can be obtained for calculation of the resistivity. In this investigation we take a fresh look into the problem in order to see that the large temperature dependence of the resistivity seen in the metallic oxides indeed arise from the electron-optical phonon scattering. By making the investigation on a different and somewhat simple metallic oxide system we also establish the generality of the phenomena.

Our experiment contains essentially two distinct parts: (1) measurement of the resistivity ρ over the temperature range $1.5 < T \leq 300\text{K}$ and (2) measurement of the phonon spectra (i.e, $\alpha^2F(\omega)$) using the technique of point contact spectroscopy done at 4.2K. We then use the experimental phonon spectra to calculate the temperature dependence of the resistivity.

The point contact spectroscopy (PCS) was first used by Yanson⁴ to obtain the phonon spectrum (PS) of conventional metals and dilute alloys from the non-linear current voltage characteristics of the point contact junction. This spectroscopy has the main merit that, it can give the function $\alpha_{pc}^2F(\omega)$ which is simply related to the Eliashberg function $\alpha^2F(\omega)$ (electron-phonon interaction function) for any metal including those with very weak electron-phonon coupling. The relation between $\alpha_{pc}^2F(\omega)$ and $\alpha^2F(\omega)$ is essentially a factor which depends on the geometry of the junction formed between the tip and the sample^{5,6} as discussed later on. This method enables one to derive the phonon spectrum of those metals which are not superconducting. We have thus used this technique to obtain the $\alpha_{pc}^2F(\omega)$ and use this function to fit the resistivity of the metallic sodium tungsten bronzes. It must be pointed out that this is the first time the phonon spectra is being studied using PCS technique in this type of metallic oxides.

II. THE SODIUM TUNGSTEN BRONZE SYSTEM

The sodium tungsten bronze system, (Na_xWO_3) , investigated in this work is a 3-dimensional cubic perovskite oxide. The corner sharing WO_6 octahedra forms a 3-dimensional network in WO_3 which is an insulator because the conduction band formed by the overlap of oxygen 2p and W 5d orbitals is empty. On addition of Na, it contributes one electron per Na atom and the conduction band gets filled. For $x > 0.2$ the system makes a transition to a metallic state. However, the cubic structure is stabilized only for $x > 0.4$. This material is very similar to ReO_3 which may be the most metallic of all oxides and in single crystalline form can be comparable to copper². In our system for $x = 0.9$ the residual resistivity, $\rho_0 = 3\mu\Omega\text{cm}$ which is more metallic than many conventional metallic alloys. Thus varying x (and hence the electronic concentration) one can go from a good metallic state to an insulating state. The sodium tungsten bronze system (Na_xWO_3) has been well studied because of this composition driven metal-insulator transition seen in this system⁷⁻¹⁰. This system has an additional feature that when W is substituted by Ta, the empty 5d orbitals of Ta compensates for the electrons being introduced by Na. This reduces the carrier density and also introduces a large disorder. One can thus see the effect of the disorder on the resistivity much like one does in a conventional alloy. On introduction of Tantalum in the tungsten site the chemical formula can be written as $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$.

To summarize, the tungsten bronze system used by us has three distinct advantages : (1) the oxide is a simple oxide with a cubic structure, (2) the metallic state can be tuned to different electron densities by changing x and (3) the Ta substitution allows a way to introduce disorder into the system. The above three features thus gives us a good system in which we can make a comprehensive investigation.

III. EXPERIMENTAL DETAILS

The samples studied were single crystals of composition $x=0.9$, 0.75 , 0.63 and one sample with Ta substitution with composition $x=0.6$ and $y=0.1$ ($x - y=0.5$). The single crystals were grown by electrochemical growth from molten bath of sodium tungstate and tungstic oxide. Details of the sample preparation and characterization are given in the reference^{9,11}. We essentially followed the same technique.

The effective carrier concentration n_{eff} as a function of x or $(x - y)$ is given by the relation $n_{eff} = (x - y)/a_0^3$, where a_0 (the cubic cell dimension) follows the empirical relation $a_0=0.0820x+3.7845 \text{ \AA}^{12}$. The values of n_{eff} calculated using the above relation and that obtained by Hall measurements¹³ are tabulated in table I. $n_{eff}(\text{exp})$ is larger in comparison to $n_{eff}(\text{cal})$ by few tens of percent. In particular this discrepancy is larger for low n_{eff} . The reason for this discrepancy (while it is not very large) can be the assumption of the free electron formula for obtaining n_{eff} from the Hall coefficient.

The resistivity of the samples were measured from 1.5K to 300K using four probe low frequency bridge technique¹⁵. The contacts to the samples were made by first depositing Au and leads were attached using silver paint or silver epoxy. Pre-cleaning of the surface before deposition of the Au is very crucial in this case. The dimension of the samples were less than 2mm x 2mm x 0.1mm. Because of the finite size of the contacts on the sample, the error in the measurement of the absolute resistivity is about 10%. The resistances of the samples measured varied between 1.0m Ω -5.0 Ω . We could measure the resistance value with a precision of 5 $\mu\Omega$.

The point contact spectroscopy was done at 4.2K in a dipper type¹⁶ cryostat using Au as the tip to make the point contact. The tip was formed by electrochemical etching of Au wire using a solution of HCl, HNO₃ and HF in the ratio 3:2:1. We used an ac bias of 5-10 V for etching the Au wire. The I-V characteristics of the Au-sample point contact junction were taken by a ac modulation method. This directly gives the conductance (dI/dV) of the junction as a function of V. The bias used were upto 125mV. The junction was in contact

with the liquid Helium bath at 4.2K and hence there is no possibility of temperature drifts when the I-V characteristics were obtained. Typical junction resistances were adjusted to the order of 5-20 Ohms using a differential screw. The surface of the samples were carefully cleaned just before mounting the sample and were subjected to minimum exposure to the atmosphere to avoid contamination of the surface.

IV. RESULTS

A. Resistivity

Figure 1 shows the resistivity of the samples as a function of temperature over the entire temperature range. The temperature dependence of the resistivity is like a metal and $d\rho/dT > 0$. It can be seen that the resistivity varies by a large amount by changing the value of x . In particular the Ta substitution can lead to a big jump in ρ . The value of the residual resistivity are given in table I. The residual resistivities of the samples agree well with the pervious reported values^{8,13}. In figure 2 we show the variation of $\rho(4.2\text{K})$ as a function of x (for $x > 0.5$) obtained by other investigators¹⁴ on single crystals and data obtained from our single crystals. For samples with $x \leq 0.6$ the residual resistivity generally varies within a factor of 2 depending on the extent of disorder. The exact value of $\rho(4.2\text{K})$, however does not affect our experiment or the conclusions.

The temperature dependence till 300K (i.e, $\Delta\rho(300\text{K})$) for the low resistivity samples are nearly 15-25 $\mu\Omega$ cm. While for the Ta substituted sample this can be as large as 88 $\mu\Omega$ cm. There is an interesting anomaly to the trend at $x=0.75$ so that the room temperature resistivity of this sample is actually lower than that of the $x=0.9$ sample. This arises because of partial ordering of Na atoms as has been seen previously¹³. We will see that this also affects $\Delta\rho(300\text{K})$. A detailed discussion on this issue is beyond the scope of the paper. Using a free electron model we estimate the mean free path at the two temperatures. The elastic mean free path l_0 as well as the in-elastic mean free path l_{in} at 300K (giving rise

to $\Delta\rho(300K)$) are shown in the table I. The elastic mean free path varies strongly as x is varied and for the Ta-substituted sample $l_0/a_0 \approx 2$. For the most metallic sample ($x=0.9$), $l_0/a_0 \approx 145$. Thus in the range of the composition studied, the electrons are not on the verge of localisation. Most importantly we are in a position to assess the strength of inelastic scattering quantified by l_{in}^{-1} in the presence of varied l_0 while keeping the system chemically unaltered. In comparison to variation of l_0 with x the variation of l_{in} is not that severe. Interestingly the Na ordering in $x=0.75$ leads to a drastic increase in l_{in} .

B. Point Contact Spectra

In figure 3 as an example we show the second derivative d^2I/dV^2 obtained from an experimental dI/dV - V curve for $x=0.75$. We also show the dI/dV curve for the sake of completeness. Here dI/dV decreases as $|V|$ is increased and it is a sign of "metallic" point contact. The voltage axis directly gives the phonon energy in eV and as stated earlier d^2I/dV^2 gives a measure of the phonon density of states. Essentially d^2I/dV^2 arises from inelastic scattering of electrons by the phonons. For the other samples the curves were similar and we donot show them to avoid over crowding of data. As a comparison we show that data taken on Au (figure 3(a) inset) which acts as reference to show the differences in the PS of the two classes of metals. For conventional metals the maximum phonon energy is often < 20 meV. For oxides there is a large density of phonons at energies beyond 20 meV. It will be our attempt to see whether the phonons seen in the point contact spectroscopy can give rise to the necessary electron-phonon scattering so that the temperature dependence of the resistivity can be explained. This requires a qualitative analysis of the experimental PCS data to obtain the spectral function $\alpha_{pc}^2 F(\omega)$. It is important to note that the thermal smearing ($\approx 3k_B T = 1$ meV at 4.2K) is much small compared to the phonon energies which are relevant for our work. As a result we will not apply any correction to our experimentally obtained spectra and treat them as essentially the zero temperature spectra.

V. ANALYSIS AND DISCUSSION

A. Analysis of Point Contact Spectroscopy data

The phonon spectrum can be obtained from the second derivative of the I-V characteristics of the point contacts from the relation¹⁷

$$\frac{d^2I}{dV^2} = -\frac{2\pi e^3}{\hbar} \Omega_{eff} N(0) \mathcal{F}(eV) \quad (1)$$

where $\mathcal{F}(eV)$ is the spectral function related to the strength of the inelastic interaction which gives rise to the features in d^2I/dV^2 , Ω_{eff} is an effective volume of phonon generation within which the inelastic scattering takes place, $N(0)$ is the density of states at the fermilevel. When phonons cause the inelastic scattering $\mathcal{F}(eV) = \alpha_{pc}^2 F(\omega)$ which is related to the Eliashberg function $\alpha^2 F(\omega)$ by a form factor⁶. In the measurement of this electron-phonon interaction by means of point contact, there is a considerable background which is due to the scattering due to non-equilibrium phonons. Taking this into account the final expression used for obtaining the $\alpha_{pc}^2 F(\omega)$ is given by

$$\frac{d^2I}{dV^2} = const \times \left(\alpha_{pc}^2 F(eV) + \kappa \int_0^{eV} \frac{\alpha_{pc}^2 F(\epsilon)}{\epsilon} d\epsilon \right) \quad (2)$$

In the case of a heterocontact the spectrum is given by the sum of phonon spectrum (PS) in both the electrodes¹⁸. We have used Au as one of the electrodes and the PS of Au has features between 10 and 17 meV (see inset of figure 3(a)). By subtracting the PS of Au one can easily identify the PS of the other electrode. The value of the constant (*const*) depends on the regime (ballistic or diffusive) we are working in and this is characterized by the Knudsen number $K \equiv l_0/r$, where r is the diameter of the contact region¹⁷. For hetero-junctions like ours where electrons in one electrode (like Au) have a very large mean free path, the l_0 of the electrons in the electrode with higher ρ_0 limits the Knudsen number K . In table II the relevant junction parameters are given. Thus the most metallic samples with $K > 1$ ($x=0.9$ and 0.75) lie in the ballistic regime, the $x=0.63$ sample with $K \sim 1$ is in the transition regime and the Ta substituted sample with $K \ll 1$ lies in the diffusive regime.

The difference between the two cases comes in the effective volume of the contact Ω_{eff} in which the inelastic scattering takes place and which contributes to the non-linearity in the I-V characteristics¹⁷. For $x = 0.63$ and $x=0.6;y=0.1$ samples, the necessary corrections were applied to take into account that the point contacts were diffusive. In the case of the ballistic regime, the volume $\Omega_{eff} = 8r^3/3$ and in the diffusive case $\Omega_{eff} = \pi r^2 l_0/4$, where l_0 is the elastic mean free path of the electron. All the relevant numbers of the point contact junctions are given in Table II. Eqn. 2 was used to obtain the $\alpha_{pc}^2 F(\omega)$. The constant κ was determined using the fact that the observed spectrum coincides with the background function for $eV > \hbar\omega_{max}$ ¹⁸. ω_{max} was chosen to be 125 meV. The above integral equation has been inverted to obtain the $\alpha_{pc}^2 F(\omega)$ which will be the total of the contributions from both the electrodes. Since $\alpha_{pc}^2 F(\omega)$ is independent of the contact details, we have subtracted the PS of the Au from this data which contributes a small peak at $\omega \approx 10\text{meV}$ and 17meV as shown in the inset of figure 3(a). The resultant is the phonon spectra of the sample alone. In figure 4(a) we have plotted the phonon spectra obtained by inverting the d^2I/dV^2 data for $x=0.9, 0.75$, and 0.63 . The curves have been shifted for the sake of clarity. It can be seen that there are distinct features at energies between 40-80 meV. We were able to resolve the spectrum into 6 major peaks by using peak analysis tools. For one spectrum the contributions are marked by dotted lines and peak positions by arrows. The frequencies where the peaks occur were essentially unchanged when we vary x , but there was a small but distinct increase in the spectral weights of the peaks. In figure 4(b) we have shown the spectral weights ($\alpha_{pc}^2 F(\omega)$) of some of the peaks marked in figure 4(a) for $x=0.9, 0.75$ and 0.63 . The peaks 4 and 6 show a constant increase as a function of x but peaks 2 and 5 show a dip at $x=0.75$. This sudden decrease at $x=0.75$ leads to lower electron-phonon coupling constant and thus can be related to the low $\Delta\rho$ value observed for this composition (see table I).

Before making any mathematical analysis we would first like to establish that the temperature dependence of resistivity $\Delta\rho(T)$ or the inelastic mean free path l_{in} really arises from the phonons particularly from those in the spectra beyond 20meV. For most conventional

metals the strongest contribution of the phonon spectrum comes from phonons within $\omega \leq 20\text{meV}$. The oxides thus differ from the conventional metals in the fact that a large density of vibrational states extend upto 100meV . The electron phonon coupling constant λ is given by⁵

$$\lambda = 2 \int_0^{\omega_{max}} \frac{\alpha^2 F(\omega)}{\omega} d\omega \quad (3)$$

From the experimental curve we obtain $\alpha_{pc}^2 F(\omega)$. We can connect $\alpha^2 F(\omega)$ and $\alpha_{pc}^2 F(\omega)$ by a factor G ($\alpha_{pc}^2 F(\omega) = G\alpha^2 F(\omega)$). The factor G depends on the contact characteristics and it can be calculated knowing the mean free path l_0 and the contact dimension r ⁶. For the ballastic regime the value is a constant $G = 0.25$. For the diffusive regime the value is given by the relation $G = ((K-1)/2K) + (1/4K^2) \times \ln(1+2K)$. The values obtained for our samples are given in Table II. Using this corrected $\alpha^2 F(\omega)$, we can obtain the value of λ . If the inelastic scattering of electrons arise from the phonons then l_{in}^{-1} (which is a measure of the scattering strength) should increase monotonically with λ . In figure 5 we plot $l_{in}^{-1}(300\text{K})$ as a function of λ . This clearly brings out that l_{in}^{-1} is indeed closely related to λ . This confirms that the source of the inelastic scattering are the phonons in particular those with $\omega > 20\text{meV}$ which have a very large spectral weight in the range $\omega \approx 40-80 \text{ meV}$. The value of λ for weak coupling metals like Cu, Na etc. is ≈ 0.15 . For strong coupling Pb, $\lambda = 1.34$. The oxide superconductors mentioned in section I have a λ of about 1.0. Comparing the values of λ obtained in our samples, we can say that the electron-phonon coupling strength is weak to intermediate ($\approx 0.2-0.4$). In the next section we make a quantitative evaluation of ρ from the phonon data and compare it with the experiment.

B. Analysis of resistivity using the PCS

The temperature dependence of the resistivity $\Delta\rho(T)$ can be calculated using the formula derived by Ziman, in terms of the $\alpha_{tr}^2 F(\omega)$ (electron-phonon transport coupling function)⁵

$$\Delta\rho(T) = \frac{16\pi^2}{\omega_p^2 k_B T} \times \int_0^{\omega_{max}} \frac{\hbar\omega\alpha_{tr}^2 F(\omega)}{(\exp[\hbar\omega/k_B T] - 1)(1 - \exp[-\hbar\omega/k_B T])} d\omega \quad (4)$$

where ω_p is the plasma frequency. The transport coupling function differs from the Eliashberg function $\alpha^2 F(\omega)$ only by a factor analogous to the relation between $\alpha_{pc}^2 F(\omega)$ and $\alpha^2 F(\omega)$. Work by Allen and co-workers¹⁹ provides a basis for using $\alpha^2 F(\omega)$ instead of $\alpha_{tr}^2 F(\omega)$ in the above formula. We thus replace $\alpha_{tr}^2 F(\omega)$ by $\alpha^2 F(\omega)$ in eqn.4. As mentioned in the previous section, $\alpha^2 F(\omega) = (1/G)\alpha_{pc}^2 F(\omega)$, hence using the value of G given in table II, we can evaluate the temperature dependence of the resistivity using eqn 4. The only unknown parameter in eqn 4 is the plasma frequency ω_p which we use as a fit parameter.

The resistivity obtained for the samples, were fitted using the above relation for the temperature dependent part. The fit are given in figure 6(a)-(d). The maximum fit error are given in table III. It is interesting to see that the data can be fitted with the experimental $\alpha_{pc}^2 F(\omega)$ over the whole temperature range for all the samples. The maximum fit error $\leq \pm 0.5\%$. The fit error was random and showed no systematic deviation either at low T or high T. The fit thus can be considered excellent because the only free parameter available is the plasma frequency ω_p which appears as a multiplicative factor only. The prefactor ω_p obtained in the above relation from the ρ data is listed in table III ($\omega_p(\text{exp})$). The table also contains the values of ω_p as observed experimentally by electron energy loss spectroscopy (LEELS) which we call $\omega_p(\text{obs})$ ²⁰.

For all the samples the value of ω_p obtained from the resistivity data $\omega_p(\text{exp})$ (eqn 4) and that obtained from LEELS $\omega_p(\text{obs})$ agree to better than 20% -30%. We think that this is a very good agreement given the fact that they are obtained from two widely different techniques. There is, however, a systematic difference. $\omega_p(\text{exp})$ is always lower than $\omega_p(\text{obs})$. One reason for this could be that while $\omega_p(\text{exp})$ is obtained from the bulk measurements, $\omega_p(\text{obs})$ is obtained from the surface sensitive LEELS. In these materials the Na has a tendency to diffuse to the surface. This makes the surface somewhat Na rich compared to the bulk and thus the n_{eff} at the surface can be somewhat larger than that in the bulk. We feel this makes $\omega_p(\text{obs})$ systematically larger than $\omega_p(\text{exp})$.

For the sake of completeness we would like to investigate whether instead of analysing $\rho(T)$ using the complete phonon spectra we use a discrete frequency approach. In this case

we take a Bloch-Gruneisun type of electron-acoustic phonon interaction characterized by a Debye temperature θ_D ²² and an electron-optic phonon contribution characterized by a temperature θ_E ²³. The resulting ρ is given by

$$\rho(T) = \rho_0 + A \left(\frac{T}{\theta_D} \right)^5 \int_0^{\theta_D/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} + B \frac{\theta_E}{T} \sinh^2(\theta_E/2T)^{-1} \quad (5)$$

Results of such a fit is given in the table IV. A typical fit shown in figure 7 for x=0.9 sample. For comparison we have plotted the fit error obtained using eqns 4 and 5 in figure 8. It is clear that eqn 5 can be used to fit the ρ vs T curve but the extent of agreement is poorer compared to that obtained from eqn 4. The value of θ_D obtained is close to what one expects for these oxides. From the specific heat data²¹ on these materials the values of θ_D are ≈ 300 - 400K. The value of $k_B\theta_E \approx 55$ - 80 meV. This corresponds very well to some of the peaks in the phonon spectrum (figure 4a).

Though the values of θ_D and θ_E are reasonable, the resistivity can definitely be better explained by the complete phonon spectrum rather than assuming the above expression 5 to be valid.

C. Effect of Ta substitution

It can be seen from figure 1 that even a small (10%) substitution of W by Ta leads to a large change in $\rho(T)$. Between the $x=0.63$ and $x=0.6$ $y=0.1$ samples, n_{eff} differ by $\approx 20\%$. But the change in ρ_0 is by a factor of more than 6 and that in $\Delta\rho(300K)$ by a factor of nearly 2. The empty Ta orbitals at random sites thus act as a strong source of disorder in the system leading to substantial electron scattering which brings down the elastic mean free path l_0 to just twice the cubic unit cell dimension. The comparison of $x=0.63$ and $x=0.6$ $y=0.1$ sample will thus be like comparing a "metal" and a "substitutional alloy".

Our concern in this paper is the temperature dependent part $\Delta\rho(300K)$ which changes by nearly a factor of 2 and the inelastic mean free path $l_{in}(300K)$ which is also quite small ($\approx 27\text{\AA}$) in the Ta substituted samples. We would like to see whether the changes to $\alpha^2 F(\omega)$

brought forward by Ta substitution can also explain the temperature dependent part. This is an important test of our work that the $\Delta\rho(300\text{K})$ can be quantitatively explained by the observed $\alpha^2F(\omega)$ even when there is large substitutional disorder and the elastic mean free path is very small.

In figure 8 we show the $\alpha_{ph}^2F(\omega)$ for the two samples. Ta has very similar mass as W. In the region $\omega \approx 40 - 60$ meV there is a large enhancement of $\alpha^2F(\omega)$ and the peaks have moved towards higher ω . The enhancement of the $\alpha_{ph}^2F(\omega)$ in the region $\omega \approx 40 - 60$ meV makes the λ go up by a factor of 1.5. This causes the l_{in} to go down by a factor of 1.75. Thus we see that the resistivity enhancement $\Delta\rho(T)$ can be explained by the enhancement of electron-phonon interaction in the Ta substituted sample. This can be put into a simple description that whenever a large change occurs in the phonon spectrum a comparable change is also seen in the inelastic mean free path. Our above extensive analysis quantitatively establishes the fact that the temperature dependence of ρ in these oxides can be explained by the electron-phonon interaction. These modes mostly occur in the range 40 - 100 meV. We next discuss the origin of these modes and establish that they are optic modes.

D. The optic modes

WO_3 is a polar crystal which has a basis consisting of differently charged ions. When Na is added, the empty conduction band is filled but the polar basis lattice remains unchanged. Na_xWO_3 can be considered as a polar metal, which we can define as polar substance (WO_3) with a partially filled conduction band. The structure of the WO_3 (ReO_3 structure), is a vacant structure, where the oxygen ions can oscillate with large amplitudes (lower energy). The frequency of this oscillations correspond to the optical modes of the lattice vibrations. In a polar crystal, the optical vibrations are accompanied by a displacement and a deformation potential leading to polarisation. The total polarisation leads to a displacement which causes a strong coupling between the electrons and the optical phonons²⁴. The optical mode in WO_3 corresponds to a temperature of 600K or 50 meV²⁵. As Na is doped into the system, the Na

occupies the vacant space and the amplitude of the oscillation of the oxygen ions decreases. This increases the energy corresponding to the oscillations. This shifts the spectral weight of the different peaks towards higher values of ω (see figure 4a). The phonon frequencies of Na_xWO_3 mostly arise from the WO_6 octahedra and thus are similar to WO_3 . The phonon dispersions in WO_3 has been calculated²⁴ and we use this as an identification guide to our experimental spectra. In WO_3 the highest calculated acoustic mode frequencies (at the zone boundary) is ≈ 25 meV. The lowest peak in $\alpha^2F(\omega)$ occurring below 30 meV (i.e, peak #1) is likely to arise from the acoustic phonons. The lowest calculated optical mode frequency (at zone center) ≈ 33 meV. Thus all the peaks of $\alpha^2F(\omega)$ for $\omega > 30$ meV are from optical phonons. At the zone center the calculated phonon frequencies are 33 meV and 77 meV for $\omega < 100$ meV. At the zone boundary, the phonon frequencies are calculated to be around $\omega \approx 55, 75, 85, 115$ meV where the exact position depends on the symmetry directions. The calculation of electron-phonon interaction parameters show that it is wave vector (q) dependent and also symmetry dependent²⁴. The resulting $\alpha^2F(\omega)$ will have to be determined by an integration of all q using the phonon dispersion curve. Such a calculation is beyond the scope of this paper. We only note that in most symmetry directions the calculated electron-phonon interaction parameters reaches a high value for $q\pi/a_0 > 0.5 - 0.75$. As a result peaks in $\alpha^2F(\omega)$ are expected to occur for values of phonon frequencies intermediate between those calculated for the zone center ($q=0$) and zone boundaries ($q\pi/a_0=1$). We find that the observed peaks in $\alpha^2F(\omega)$ indeed occur between these limits. Also the splitting into longitudinal and transverse optical modes leads to a maximum of 5 distinct frequencies in the range $30\text{meV} < \omega < 100\text{meV}$. This also matches with our observation. This establishes clearly that the peaks in $\alpha^2F(\omega)$ indeed are related to the indentifiable optical phonon frequencies of the WO_3 structure. In insulating WO_3 the electron-optical phonon coupling is quite strong due to the polar nature of the material. However, on introduction of Na as x increases the material becomes conducting which leads to screening of the interaction which reduces the electron-optical phonon coupling.

The Ta substitution in place of W leads to an increase in the $\alpha^2F(\omega)$ for ω lying in

the range 40-60 meV. The $\alpha^2 F(\omega)$ remains unaltered in the other frequency range. This is rather interesting and allows us to draw some interesting conclusions. The phonon dispersion calculations show that the lowest optical phonon branches describe a displacement field in which the W(or Ta) atom moves in one direction and the oxygen atoms move in the other direction. This leads to a large dipole moment and large electron-lattice coupling. This will therefore depend strongly on the charge on the W-site and the screening associated with the atomic charges. When Ta is substituted for W, there is a hole on the W-site. This reduces significantly the screening and the coupling constant is strongly enhanced. This explains the increase in the value of the λ in the case of Ta substituted sample ($x=0.6$ $y=0.1$) compared to the $x=0.63$ sample.

VI. CONCLUSION

In this paper we have brought out the role of optical phonon modes of simple perovskite oxides in the resistivity. The phonon spectra, better still the electron-phonon spectral frequencies were directly measured by point contact spectroscopy. We find that, there are distinct phonon modes at energies between 40-80 meV in the phonon spectrum ($\alpha^2 F(\omega)$) obtained using point contact spectroscopy. Using this phonon spectrum we are able to explain the temperature dependence of resistivity of the metallic sodium tungsten bronzes. We have obtained the values of λ the electron-phonon coupling constant. Comparing this with the values obtained for other conventional metals and superconductors, we can conclude that the electron-phonon interaction in this system is in the weak coupling limit. It may not induce superconductivity but this has significant influence on the temperature dependence of resistivity. The paper is quantitative and clearly shows that the large temperature dependence of ρ seen in these class of oxides essentially arises from interaction with optical phonons.

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FIGURE CAPTIONS

Figure 1 Resistivity of the $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$ samples.

Figure 2 $\rho_{4.2K}$ values obtained from our investigation and Ellerbeck et.al.¹⁴

Figure 3 Point contact spectra. **(a)** d^2I/dV^2 for $x=0.75$ obtained at $T=4.2\text{K}$. **Inset** shows the Phonon spectra of Au. **(b)** dI/dV obtained by modulation technique for the same sample ($R_0 \approx 5\Omega$).

Figure 4 (a) The point contact electron-phonon interaction function $\alpha_{pc}^2 F(\omega)$ obtained using eqn 2. The peaks have been marked following the multiple peaks analysis. **(b)** The spectral intensity of some of the peaks as a function of composition x .

Figure 5 The inverse of inelastic mean free path at 300K (l_{in}^{-1}) as a function of the electron phonon coupling strength (λ).

Figure 6(a-d) The fit to the resistivity using eqn.4 for the samples. The only fit parameter is ω_p tabulated in table II.

Figure 7 (a) Fit to the resistivity using eqn.5 for $x=0.9$ sample. **(b)** Fit error (%) for the two fitting schemes ((a) eqn.4 and (b)eqn.5 for $x=0.9$ sample).

Figure 8 $\alpha^2 F(\omega)$ for $x=0.63$ and $x=0.6; y=0.1$ samples. The difference in the spectral intensities clearly indicate greater electron-phonon interaction strength (characterized by λ) for the Ta substituted sample.

TABLE I

Composition		n_{eff} (calc)	n_{eff} (exp) ¹³	ρ_0	$\Delta\rho(300K)$	l_0	$l_{in}(300K)$
x	y	/cm ³	/cm ³	$\mu\Omega$ cm	$\mu\Omega$ cm	Å	Å
0.9	-	1.57×10^{22}	1.95×10^{22}	3.20	25.3	550	70
0.75	-	1.32×10^{22}	1.60×10^{22}	6.95	15.3	288	130
0.63	-	1.12×10^{22}	1.49×10^{22}	47.01	42.0	45	47
0.6	0.1	8.91×10^{21}	1.18×10^{22}	330.10	88.0	7.5	27

TABLE II

Composition		R^\dagger	K^\ddagger	G^*	r^b
x	y	Ω			Å
0.9	-	5.0	5.0	0.25	110
0.75	-	3.0	1.7	0.25	134
0.63	-	15.0	0.5	0.19	90
0.6	0.1	18	0.09	0.053	83

† : Junction resistance

‡ : Knudsen number

* : Correction evaluated using expressions from ref[6]

b : Contact dimension calculated using $r = (4\rho l/3\pi R)^{1/2}$ for Ballistic regime and Wexler's interpolation formula for the diffusive regime. (ρ and l are of the sample, since the contact resistance is limited by the sample because of its higher resistivity).

TABLE III

Composition	$\omega_p(\text{exp})$	$\omega_p(\text{obs})^{20}$	Fit error
	eV	eV	
$x=0.90$	2.58	3.14	$\pm 0.4\%$
$x=0.75$	2.83	3.02	$\pm 0.4\%$
$x=0.63$	2.23	2.97	$\pm 0.5\%$
$x=0.6$ $y=0.1$	2.13	2.77	$\pm 0.3\%$

TABLE IV

Composition	ρ_0	A	B	θ_D	θ_E	Fit error
	$\mu\Omega$ cm	$\mu\Omega$ cm	$\mu\Omega$ cm	K	K	
$x=0.90$	3.17	74.55	16.94	356.4	916.6	$\pm 4.0\%$
$x=0.75$	7.00	42.37	7.09	334.6	756.1	$\pm 2.5\%$
$x=0.63$	47.05	67.21	18.62	252.4	645.7	$\pm 2.5\%$
$x=0.6$ $y=0.1$	330.14	296.19	33.94	328.2	855.2	$\pm 1.5\%$

TABLE CAPTIONS

Table I The important parameters obtained from the transport measurements.

Table II Parameters from the point contact junctions for all the samples used in calculating the true $\alpha^2 F(\omega)$.

Table III Comparison of plasma frequencies obtained by our method and LEELS²⁰ along with the maximum fit error obtained using eqn.4 to fit the resistivity.

Table IV Parameters obtained from the fit of resistivity to eqn 5.



















