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LETTER TO THE EDITOR

Tunnelling studies on sodium tungsten bronzes near the metal–insulator transition

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Abstract. We present measurements of tunnelling conductances (at $T = 4.2$ K) of point contact and planar junctions formed on sodium tungsten bronze single crystals as the carrier concentration is changed through the metal–insulator (MI) transition. We find that the junction conductance is $\propto |V|^{1/2}$ on the metallic side, and that as the MI transition is approached, the voltage dependence becomes deeper and changes to a linear dependence ($\propto |V|$) in the critical region. We interpret this observed behaviour as being due to evolution of short-range screened Coulomb interactions (giving rise to a square-root cusp in the density of states) in the disordered metallic phase into an Efros–Shklovskii-type Coulomb gap in the insulating phase. The possibility of breakdown of normal Fermi-liquid-like behaviour in the critical region is discussed.

Alkali metal tungsten bronzes form an interesting class of oxide systems which range from metallic to insulating as the concentration of alkali metals is varied [1]. They have the general formula M_xTO_n in which relatively electropositive alkali metal atoms (M) are inserted into a more or less covalent network TO_n formed of oxygen and a transition element (T). In addition to showing interesting features associated with metal–insulator (MI) transitions, they also show superconductivity in tetragonal or hexagonal phases. Generally, incorporation of alkali metal also produces a rich variety of crystallographic phases depending on the concentration of the alkali metal.

MI transitions in sodium tungsten bronzes (Na_xWO_3) have been extensively studied in the past using techniques such as conductivity, thermopower, NMR, Hall effect and specific heat studies [1, 2]. Na_xWO_3 (with $x > 0.5$) has a cubic perovskite structure in which the WO_6 octahedra occupy the corners of the cube. The Na^+ ions are incorporated in the interstitials and each Na atom donates one electron to the empty hybridized 5d orbitals of tungsten, which forms an impurity conduction band [1]. It is believed that the MI transition occurs in the conduction band. With lower sodium concentration ($x < 0.4$), the cubic phase cannot be retained. In order to stabilize the cubic phase and facilitate the study of the MI transition in this system, Ta is substituted for W, giving rise to Ta-compensated Na_xWO_3 with the general chemical formula $Na_xTa_yW_{1-y}O_3$ [3]. The substitution of Ta produces charge carrier compensation and $(x-y)$, instead of x, becomes the measure of the net carrier concentration. It has been shown that the MI transition occurs in cubic $Na_xTa_yW_{1-y}O_3$ at a critical composition $(x-y)_c \simeq 0.19$ [2]. Recently, conductivity measurements have been made on these systems (with composition close to the critical value) down to 0.1 K [4]. The measurements showed the following interesting features:

(i) the existence of metallicity with zero-temperature conductivity, $\sigma(T=0) \ll \sigma_{\text{Mott}}$ (the Mott minimum metallic conductivity);

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(ii) corrections to $\sigma(T)$ due to strong electron–electron interactions;

(iii) evidence for correlated hopping in a Coulomb gap in the insulating side (close to the critical composition) with $\ln(\sigma) \propto (-T_0/R)^{1/2}$. Close to the critical composition, values of T_0 as low as 50 K have been detected using $\sigma(T)$ measurements down to 0.3 K.

In the context of the MI transition in the sodium bronze system, we would like to raise a rather important question, which we elaborate now. In disordered insulators, the electronic states at the Fermi energy E_F are localized due to disorder. Because these states cannot carry a current, they are unable to screen the electron–electron interaction, which retains its long-range $1/r$ form. Coulomb interactions have a large effect on the electronic structure of disordered insulators and lead to a Coulomb gap in the single-particle density of states $g(E)$, which is that for adding an extra electron or hole to the ground state and allowing no relaxation of the localized electrons [5]. The Coulomb gap is a 'soft' gap, which means that $g(E) = 0$ only at $E = E_F$. Evidence for a Coulomb gap in the insulating side of the $Na_xTa_yW_{1-y}O_3$ system has been obtained from photoemission studies [6, 7] where it was observed that a soft gap does indeed open up in the density of states $g(E)$ at the Fermi level E_F. Using a classical model based on long-range Coulomb interaction of the type $E_0 a_0/r$ (where a_0 is the lattice spacing and E_0 is the Coulomb energy between adjacent sites given by $E_0 = (e^2/4\pi\varepsilon_0\kappa a_0)$; e is the electronic charge, κ is the static dielectric constant and ε_0 is the permittivity in free space), it was shown that the density of states calculated theoretically matched well with the experimentally observed photoemission results [8]. The existence of a gap introduced by long-range Coulomb interaction in the insulating side of the sodium bronze system is thus well established. We must point out that oxides with higher carrier concentration are more prone to the formation of a Coulomb gap. In doped semiconductors, the inter-change separation is much larger, and the DC dielectric constant is often fairly high as a result of which the energy scale of the gap formation is much less.

An interesting question can be posed: on the insulating side, a Coulomb gap originating from long-range Coulomb interaction is seen; is it possible to see a precursor of the Coulomb gas in $g(E)$ on the metallic side itself, given the fact that one observed strong electron–electron interaction from conductivity measurements below 10 K? This question, though posed in the context of this particular system, has general and broader consequences in the area of MI transitions in disordered systems, in particular when one considers the role of Coulomb interactions.

It is known from studies on disordered solids that disorder-induced electron–electron interaction leads to a cusp-like singularity in $g(E)$ at E_F with $g(E) \propto |E - E_F|^{1/2}$ [9]. Electron tunnelling experiments are ideally suited to probing such effects in the density of states near the Fermi level, as the tunnelling conductance $G(V)$ at low voltages is generally assumed to be a measure of the density of states $g(E)$ within a thermal smearing factor of a few times k_BT [10]. Past tunnelling experiments on amorphous Nb:Si [11], granular Al films [12], amorphous In_xO_y films [13], Au:Ge [14] etc have demonstrated the existence of a $|V|^{1/2}$ dip in the tunnelling conductance near zero bias, which has been taken as a signature of the singularity in the single-particle density of states $g(E)$ that we discussed earlier. Recently we found evidence for this behaviour in metallic transition metal perovskites ($LaNi_{1-x}Co_xO_3$) also [15]. In this case, the system undergoes a MI transition for $x > 0.65$, and electron tunnelling experiments on this oxide system brought to light certain interesting aspects. It was found that, as the MI transition is gradually approached from the metallic side, the tunnelling conductance $G(V)$ does not maintain the theoretically predicted $|V|^{1/2}$ dependence throughout but instead seems to follow the relation [15, 16]

$$G(V) = G_0(1 + |V/V^*|^n) \tag{1}$$

where G_0 is the zero-bias conductance, eV^* is some energy scale, to be discussed later, and $0.4 \leqslant n \leqslant 1$. On the insulation side (i.e. $x > 0.65$) the exponent $n > 1$, as is expected from theories that take into account the long-range Coulomb repulsion in disordered insulators. (However, the exponent n well into the insulating side cannot be relied upon, as tunnelling conductance may not be representative of the density of states in the insulating regime.) It should be pointed out here that the electron–electron interactions on the metallic side are of the screened Coulomb short-range type, characterized by a screening length κ. As the MI transition is approached, the correlation length ξ diverges and the static screening breaks down, and so κ also diverges. The important question is that of how this breakdown of screening leads to long-range Coulomb interaction in the insulating side. In other words, the singularity in $g(E)$ on the metallic side may continuously open up as a soft Coulomb gap on the insulating side. It is the purpose of the present investigation, in the context of the sodium tungsten bronze system, to see whether such a phenomenon occurs. Although sodium tungsten bronzes are among the most widely studied systems in the context of MI transitions, ours is the first tunnelling study.

The reasons for choosing this particular system for the present study are the following:

(i) the availability of good single crystals;

(ii) the absence of magnetic ions—magnetic ions could raise the possibility of magnetic scattering and hence obscure the origin of the tunnelling conductance anomaly at zero bias [10].

The $Na_xTa_yW_{1-y}O_3$ single crystals were grown by the electrolytic reduction method and details are described elsewhere [17]. Typical metallic crystals were about 3 mm^2 in size, but near the transition the samples were much smaller. (One crystal of the series, ($x = 0.34$, $y = 0.16$) was donated by M Dubson.) Electron tunnelling experiments were carried out in both point-contact-type and barrier-type junctions at 4.2 K using normal metallic and superconducting counter-electrodes. The crystal surfaces were mechanically polished and chemically cleaned prior to the junctions being made. Electrochemically etched Au tips were used to make point contact junctions, and the polished surface of a small Pb ball was pressed against the surface to form barrier-type junctions. (Out attempts to make barrier junctions using evaporated Pb have not proved successful so far, given the small crystal size. However, we have reasons to believe that studies made on such junctions will not give results that are any different.) In either case, the native oxide on the surface of the samples served as the tunnel barrier. The dI/dV–V characteristics were measured directly using a modulation technique. Details of the cryostat design and instrumentation have been described in an earlier publication and are also given elsewhere [18, 19].

Figure 1 shows the normalized $G(V)$ curves for three samples of $Na_xTa_yW_{1-y}O_3$ single crystals at 4.2 K as the values of x and y are tuned to cross from the metallic to the insulating regime. The data are normalized with respect to G(100 mV) and shifted for clarity. The compositions of curves (a) and (b) are on the metallic side of the MI transition while sample (c) lies at the critical region but on the insulating side. It is for this sample that the conductivity $\sigma(T)$ showed a correlated hopping behaviour with

$$\ln(\sigma) \propto (-T_0/T)^{1/2}$$

for $T < 4$ K and with $T_0 \simeq 50$ K [4]. The tunnelling curve of tetragonal $Na_{0.3}WO_3$ in the normal state is also qualitatively similar to those of the cubic samples. Although we do not have a $G(V)$ curve for a sample well into the insulating side with the exponent n much greater than 1, one can see the trend of the tunnelling exponent, i.e. n increases gradually

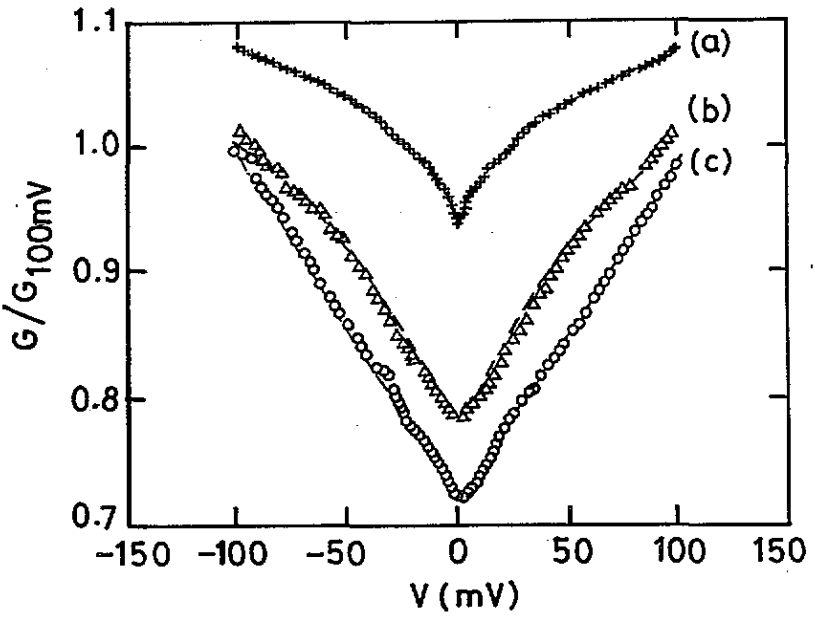

Figure 1. Normalized tunnelling conductance curves for Au–$Na_xTa_yW_{1-y}O_3$ junctions at 4.2 K. The curves are shifted relative to each other for clarity and the $G(100\ \text{mV})$ values are: (a) 8 mS; (b) 12 *mS*; and (c) 1 *mS respectively. The samples are:* (a) $x = 0.6$, $y = 0.0$; (b) $x = 0.6$, $y = 0.1$; and (c) $x = 0.34$, $y = 0.16$. All three are cubic systems with (a) and (b) on the metallic side and (c) just on the insulating side of the transition. Fits generated using (1) are represented by the dashed lines. The values of V^* and n obtained for all the tunnelling curves are listed in table 1.

from around 0.5 to 1 as the MI transition is approached. The behaviour is very similar to the data on $LaNi_{1-x}Co_xO_3$ samples reported by us before [16]. It should be mentioned here that past studies on two disordered systems (Nb:Si [11] and granular Al [12]) indicated that $n > 0.5$ only on the insulating side of the transition, but $n \simeq 0.5$ even close to the critical composition. However, in the case of Au:Ge alloy [14], the data clearly show n changing from 0.5 to 1 as the MI transition is approached, and $n > 1$ beyond on the insulating side. This gradual change of n from 0.5 to 1, however, was not highlighted in that report. Our observation of this continuous change in the tunnelling conductance exponent close to the MI transition emphatically stresses the need for looking at the density of states close to the transition carefully: in particular, the development of the '$E^{1/2}$' behaviour in the screened Coulomb region into a Coulomb gap in the insulating region.

In addition to the fact that the exponent n changes (see figure 1), it can be seen that as one goes from curves (a) to (c) the zero-bias dip deepens (or in other words, the ratio $G(0)/G(100)$ decreases). This is most probably the signature of the anticipated fact that it is the square-root anomaly on the metallic side that evolves into the Coulomb gap on the insulating side. If a soft gap does indeed open up in the DOS ($g(E)$) beyond the MI transition, then $G(V)$ should be zero at zero bias. But we see a finite conductance at $V = 0$. This could mean that in these systems, $g(E)$ is strictly not zero at $E = 0$. However, we are inclined to take a more conservative view and suggest that this finite zero-bias conductance is due to leaks or microshorts, which are almost unavoidable in point contact junctions or even planar junctions formed on a non-ideal native oxide barrier. Our contention is that

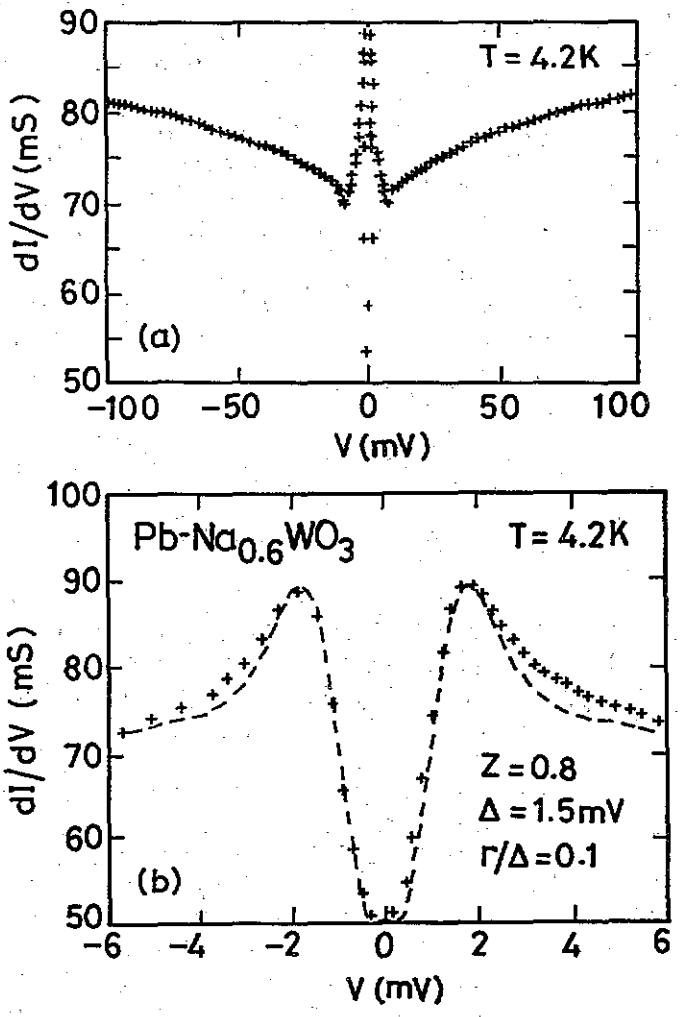

Figure 2. (a) The tunnelling conductance of the Pb–$Na_{0.6}WO_3$ junction at 4.2 K. The structure near zero bias is due to superconductivity of Pb. (b) An expanded portion of the bias voltage range −6 to 6 mV, to illustrate the gap of Pb clearly. The dashed curve is the fit generated using our modified BTK model with the fitting parameters also shown in the panel.

the leaks just provide an arbitrary ohmic shift to the zero-bias conductance, and that any change in dI/dV with V is preserved in its original form. In fact, clear superconducting gaps of Pb were seen when Pb was pressed against the oxide surface, although a finite zero-bias conductance is still present, indicating a non-ideal barrier. Figure 2(a) shows typical tunnelling conductance data for Pb–$Na_{0.6}WO_3$ junction at 4.2 K. The superconducting gap (Δ) of Pb is clearly seen close to zero bias, demonstrating that electron tunnelling is the dominant mechanism of conduction. Figure 2(b) shows an expanded portion of the voltage bias range −6 to 6 mV of the data in figure 2(a) to identify the gap of Pb clearly. This region can be modelled using a modified BTK model [20] suggested by us, where one uses the Pb gap Δ, lifetime broadening parameter Γ and barrier strength Z as fitting parameters. The fit is shown in figure 2(b) along with the values of relevant parameters. The important

point we would like to stress is that the junction conductances of both the point contact and the Pb counter-electrode pressed junctions (for bias $|V| > \Delta$) are very similar. One thus cannot assign these observed features to artefacts of any particular type of junction.

Table 1. Values of n and V^* obtained by fitting the observed conductance data using the expression given in (1). Note that V^* decreases as n increases, and $n \simeq 1$ for the sample that lies in the critical regime just on the insulating side of the MI transition.

JUNCTION	n	V^*(meV)	
Au-$Na_{0.6}WO_3$	0.44	4090	↑
Au-$Na_{0.6}Ta_{0.1}W_{0.9}O_3$	0.69	530	Cubic
Au-$Na_{0.34}Ta_{0.16}W_{0.84}O_3$	1.04	260	↓
Au-$Na_{0.3}WO_3$ (T_c=1.3K)	0.73	430	Tetragonal

In table 1, we present the values of V^* and n for the oxide system obtained by fitting the experimental $G(V)$ curves using expression (1). Comparing equation (1) with the functional form for the tunnelling density of states suggested by McMillan [21], we can take the parameter V^* to be associated with correlation in some way. It should be noted that V^* decreases and n increases as one approaches the insulating side from the metallic side. Physical insight into the parameter V^* and whether this represents an intrinsic energy scale associated with the oxide system are areas that should be investigated further.

In doing tunnelling experiments in highly disordered solids, a natural question arises: it is correct to assign all the observed features in $G(V)$ to $g(E)$? The answer to this rather persistent question is still uncertain. First, in oxides the nature of the surface can be different from that of the bulk. Junctions formed on such surfaces can have strong inelastic scattering of electrons in the barrier. The existence of such scattering can give rise to a linear tunnelling conductance, as has been shown recently by Kirtley and Scalapino [22]. However, the similarity of behaviour observed for different types of oxide suggests that an origin of these effects based on specificity of the oxide surface (such as magnetic scattering) may not be a likely mechanism. It may also happen that the total junction current contains contributions from both elastic and inelastic processes. Second, in these junctions we have for one electrode a disordered metal that is on the verge of becoming insulating with localized electrons. The finite lifetime of electrons in such electrodes can break the simple relationship of $g(E)$ with $G(V)$ and, more importantly, a part of the applied bias may extend into the bulk. The extent of the quantitative contribution of such effects is not known. Recently, in the context of marginal Fermi liquid (MFL) phenomenology [23], it was shown that a linear tunnelling conductance (as seen in high-T_c oxides) can arise from tunnelling matrix elements only where there are no special features of $g(E)$, and this depends on the form for the self-energy [24]. It is correct to say that close to the MI transition the electron lifetime is severely limited and that there may be breakdown of the applicability of the normal Fermi liquid description. As a result, similar effects postulated in MFL theory can also arise naturally. We think that unless these issues are resolved one must exercise caution in identifying $G(V)$ with $g(E)$ without any modification, and it remains a challenge

to explain these data. The important and interesting facts are the gradual evolution of $G(V)$ as the MI transition is approached from the metallic side and that there is a *linear* tunnelling conductance in the critical region.

The normal-state tunnelling conductances of high-T_c oxide superconductors (cuprates and bismuthates) show a linear variation with bias voltage. This 'linear' conductance has been one of the most keenly debated topics of recent times and the arguments are as yet unresolved. Our observation of a linear tunnelling conductance in the critical regime of MI transitions in normal perovskite oxides is rather interesting in this context. This study raises two important issues of a fundamental nature:

(i) is the linear tunnelling conductance a general behaviour associated with a critical regime where the conventional Fermi liquid description breaks down and

(ii) do all high-T_c oxide superconductors (which invariably show a linear normal-state conductance) lie in a critical regime characterized by a behaviour that is not Fermi liquid like?

We urge that more experiments should be done on disordered perovskite oxides and oxygen-doped as well as transition-metal-doped oxide superconductors to investigate these issue.

In conclusion, we present evidence for a depletion of the density of states $g(E)$ at the Fermi level E_F of the sodium tungsten bronze system obtained from electron tunnelling experiments on the metallic side. As the MI transition is approached, the tunnelling exponent increases from 1/2 to 1 and this singularity becomes deeper, eventually merging with the Coulomb gap on the insulating side. We point out that this evolution of a Coulomb gap from a precursor in the metallic state cannot be explained using existing theories of MI transitions, and raise extremely interesting questions regarding the nature of Coulomb interactions close to the MI transition.

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