

## Metal-insulator transition in perovskite oxides: Tunneling experiments

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In this paper we have investigated the composition-driven metal-insulator (MI) transitions in two  $ABO_3$  classes of perovskite oxides ( $LaNi_xCo_{1-x}O_3$  and  $Na_xTa_yW_{1-y}O_3$ ) in the composition range close to the critical region by using the tunneling technique. Two types of junctions (point-contact and planar) have been used for the investigation covering the temperature range  $0.4 \text{ K} < T < 4.2 \text{ K}$ . We find that in both classes of materials the junction conductance  $G(V)$  [ $=dI/dV$ ] decreases near the zero-bias region as the MI transition is approached. However, there is a fairly strong thermal-smearing effect near the zero-bias region for  $|V| < 10k_B T/e$ .  $G(V)$  has been found to follow a power law of the type  $G(V) = G_0(1 + \{|V|/V^*\}^n)$  with  $V^* = \text{const}$  and with  $n = 0.5$  for samples in the weak-localization region. However, as the critical region of the MI transition is approached  $G_0 \rightarrow 0$  and  $n \rightarrow 1$ . We also find that for samples lying in the weak-localization region  $\Delta = eV^*$  has a well-defined dependence on  $\sigma_0$ , the zero-temperature conductivity. The observed behavior can be explained either as a manifestation of depletion of density of states at the Fermi level as the MI transition is approached or as a manifestation of strong inelastic scattering in the junction region.

### I. INTRODUCTION

A number of interesting phenomena are seen in the transport and thermodynamic properties of disordered solids at low temperatures, which originate from the enhanced Coulomb interactions between electrons in the presence of disorder.<sup>1,2</sup> In a large class of solids, the metal-insulator (MI) transition can be *predominantly* disorder driven and it can be achieved by changing the electronic concentration by doping or chemical substitution. Even if the MI transition is disorder driven (i.e., Anderson transition) Coulomb interaction plays a major role. This is expected to be stronger as one approaches the critical region of the MI transition.

In the metallic side and in the regime of weak localization (WL), two observable behaviors (mentioned below) are generally taken as the signature of these many-body Coulomb effects. In three-dimensional systems (the type we are dealing with here), the electrical conductivity  $\sigma(T)$  at low temperatures ( $T < 5 \text{ K}$ ) is given as

$$\sigma(T) = \sigma_0 + \delta\sigma(T) = \sigma_0 + \alpha\sqrt{T}, \quad (1)$$

where  $\sigma_0$  is the zero-temperature conductivity and  $\alpha$  is a constant. In the WL regime,  $\delta\sigma(T)$  is typically a small fraction of  $\sigma_0$  for  $T < 5 \text{ K}$ . Second, the single-particle density of states at the Fermi level  $g(\epsilon)$ , is given as

$$g(\epsilon) = g(E - E_F) = g_0[1 + |\epsilon/\Delta|^{0.5}], \quad (2)$$

where  $\Delta$  is called the correlation gap.<sup>1,2</sup>

In the past, the correctness (as well as the limitations) of the above theories have been well established through studies in a number of different weakly localized three-dimensional systems at low temperatures.<sup>3-9</sup> Some of these studies also included investigations of  $g(\epsilon)$  through tunneling studies, though such studies are fewer.<sup>6-9</sup> The

behavior of  $g(\epsilon)$  as described through Eq. (2) gives rise to a cusplike dip at  $V=0$  in the tunneling conductance  $G(V)$  when such disordered metals form one of the electrodes of the tunnel junction. [ $G(V)$  denotes the dynamic conductance  $dI/dV$  at bias  $V$ .]

Applicability of the above concepts and theories in the context of electronic transport in metallic oxides is a problem of current interest. It is only recently that these issues are being raised; in particular, in the context of MI transitions in them.<sup>10-13</sup> In a large class of oxides, like the transition-metal oxides, one gets MI transition by varying the composition of constituent elements or the oxygen stoichiometry.<sup>14</sup> The existence of high-temperature superconductivity in these materials have given rise to a special interest in the normal-state properties of perovskite transition-metal oxides, which form an interesting class of correlated and disordered electronic system. Metallic oxides have rather high electron densities ( $10^{21} - 10^{22} \text{ cm}^{-3}$ ) even near the MI transition and rather low  $\sigma$  (at 300 K,  $\sigma = 10^2 - 10^4 \text{ S/cm}$ ). This implies a low electron diffusivity  $D = 10^{-1} - 10^{-3} \text{ cm}^2\text{s}^{-1}$ . It can be seen that such a low diffusivity is well below the classical limit  $D = \hbar/3m_{\text{eff}}$  ( $m_{\text{eff}}$  is the effective mass of the electrons). A low  $D$  is expected to enhance the Coulomb interaction in these oxides. Recently, these have been investigated in certain oxides at low temperatures.<sup>10-13</sup> In the context of this paper, we draw attention to our recent work on the oxide system  $LaNi_xCo_{1-x}O_3$  (Ref. 13), which we refer to here as I. In I, we studied the conductivities  $\sigma(T)$  of oxides belonging to this system at low temperatures ( $0.1 \text{ K} < T < 10 \text{ K}$ ) with  $x$  close to  $x_c$ , the critical composition for the MI transition, and have shown the limits of applicability of current theories. The  $LaNi_xCo_{1-x}O_3$  system is metallic for  $x \geq 0.35$ . Below 2 K ( $0.1 \text{ K} < T < 2 \text{ K}$ ),  $\sigma(T)$  follows the power law<sup>15</sup>

$$\sigma(T) = \sigma_0 + \delta\sigma = \sigma_0 + \alpha T^m, \quad (3)$$

with  $0.3 < m < 1$  and  $m \rightarrow 1$  as  $x \rightarrow x_c$ . We have also confirmed that such power-law conductivities [Eq. (3)] are seen for other  $ABO_3$  class of oxides in the metallic side of the MI transition.<sup>16</sup>

In this paper, we would like to investigate the MI transition in these oxides from a different viewpoint. We would like to ask the following questions

(i) Whether the interaction would cause a modification in  $g(\epsilon)$  of these solids as expected in Eq. (2).

(ii) What happens to this particular form of  $g(\epsilon)$  as the critical region is approached from the metallic side ( $x \rightarrow x_c$ ).

In the metallic side of the transition and somewhat away from the critical composition, we have screened the Coulomb interaction. One can still treat the electrons in the framework of Fermi-liquid theory. As the critical region is approached, the electrons are going to get localized and the charge relaxation time diverges. In the insulating side, one has long-range Coulomb repulsion, which opens up a soft gap in  $g(\epsilon)$ , which is known as the Coulomb gap.<sup>17</sup> We felt a study of this system will give us the opportunity to investigate experimentally if the  $\sqrt{\epsilon}$  singularity in  $g(\epsilon)$  as given by Eq. (2) becomes deeper and shows any sign of evolution to a Coulomb gap. It must be pointed out that some of the previously reported tunneling measurements in disordered systems, like Nb-Si, granular Al (Ref. 6) and Au:Ge (Ref. 7) probed this particular issue near the critical region of MI transition and found evidence for depletion in  $g(\epsilon)$  as the MI transition is approached. [There are theories of disordered interacting electronic systems in the framework of Fermi-liquid theory.<sup>18</sup> However, we know of no theory that can explain this continuous evolution in  $g(\epsilon)$  as the MI transition is approached.] In the perovskite oxides that we are considering here, the interparticle charge separation  $r_s$  is of the same scale as the lattice spacing  $a_0$ . As a result, the scale of Coulomb energy,  $E_0 = e^2 / (4\pi\epsilon_0\kappa r_s)$  ( $\kappa =$  static dielectric constant), is much larger in these materials compared to that in the doped semiconductors. We can, thus, expect that the effect of Coulomb interactions on  $g(\epsilon)$  will be quite large in these materials when the critical region of the MI transition is approached.

With the above objective, we have carried out tunneling studies on the system  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  for different values of  $x > x_c$  in the temperature range  $0.4 \text{ K} < T < 4.1 \text{ K}$ . We have also studied another perovskite-oxide tungsten-bronze system  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$ , which shows MI transition for  $(x - y) \geq 0.19$ . A preliminary report of the tunneling data on the tungsten-bronze system have been published by us before.<sup>19</sup> The conductivity studies in this system to low temperatures and near the critical composition can be found in Refs. 12 and 20.

Both systems studied by us belong to the  $ABO_3$  class of perovskite oxides.<sup>14</sup> They are essentially cubic in structure. The  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  system has a small distortion from the cubic structure while in the tungsten bronze, the cubic structure has been stabilized for  $x < 0.4$  by Ta substitution.

In the following parts of the paper, we will present the results and discuss the implications. Tunneling conduc-

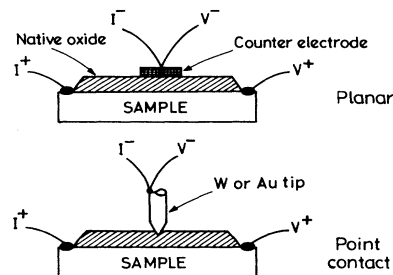


FIG. 1. Schematics of the configurations of the electrodes for measurement of  $G(V)$ .

tance  $G(V)$  is supposed to give the density of state  $g(\epsilon)$  and it has been used in the past to study  $g(\epsilon)$  of disordered electronic systems.<sup>6-9</sup> We will also discuss our concern if the direct correspondence between  $G(V)$  and  $g(\epsilon)$  remains valid in such highly disordered metals. We feel that some of the issues raised here have general implications on tunneling studies on disordered solids. We will point this out in our discussions.

## II. EXPERIMENT

The tunneling experiments were carried out in both point-contact type and barrier-type junctions with different counter electrodes. For point-contact junctions, we used W and Au tips. While for barrier junctions, we used Ag and Pb. Natural oxide has been used as the barrier for the planar junctions. This procedure has been found to work well with even high  $T_c$  oxides.<sup>21</sup> The planar-junction data were taken in the temperature range 0.4–4.1 K in a  $\text{He}^3$  cryostat. The point-contact data were taken at 4.2 K by immersing the sample in liquid He. The junctions were formed at 4.2 K using a differential screw and a piezoelectric-tube combination. The details of the experimental setup are given elsewhere.<sup>22,23</sup>

The  $G-V$  data were taken by a dc method (numerical differentiation of  $I-V$  data) or by a modulation technique using a lock-in amplifier.<sup>23</sup> The complete experiment was automated through a PC/AT personal computer. The four-terminal junctions were so made that the voltage drop occurs at the junction. In Fig. 1 we show the configurations of the electrodes.

The  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  samples used were polycrystalline in nature. The details of sample preparations and the characterization are given in I. For one sample of this class ( $x = 1$ ), it was possible to obtain an epitaxial film on the  $\text{LaAlO}_3$  substrate by laser ablation.<sup>24</sup> We obtained data on the film with both geometries. For the  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  system we used single crystals, which were grown by a method similar to that described in Ref. 20.

## III. RESULTS

In Fig. 2, we show the data taken at 4.1 K by the point-contact method. It can be seen that the junction

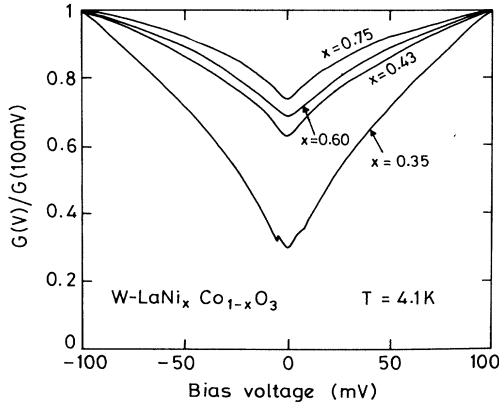


FIG. 2. Normalized conductance  $G(V)/G(100 \text{ mV})$  for the system  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  for different compositions. Data taken at 4.1 K with tungsten tip.

conductance  $G(V)$  shows a dip near the zero-bias ( $V \cong 0$ ) region. For comparison in Fig. 3 we show the data on the epitaxial film of  $\text{LaNiO}_3$  taken with a Au point contact. The data taken on the epitaxial film and the polycrystalline samples are nearly identical. In Fig. 4, we show the conductance  $G(V)$  taken with a planar junction using Ag as the counter electrode at 4.1 K. The qualitative as well as to some extent the quantitative similarity of the two data sets can be seen from the data presented in Figs. 2 and 4. From the planar-junction data, at 4.1 K we find that the normalized zero-bias conductance  $G(V=0)/G(V=200 \text{ mV})$  decreases from 0.65 for the most metallic sample ( $x=0.75$ ) to 0.05 for the sample at the critical composition ( $x=0.35$ ). If a soft gap indeed opens up in the insulating side at the MI transition so that  $g(\epsilon=0)=0$ , then the junction conductance  $G(V=0)$  should be nearly zero for the  $x=0.35$  sample if  $G(V)$  does represent  $g(\epsilon)$ . The small though finite conductance  $G(V=0)/G(V=200 \text{ mV}) \cong 0.05$  observed in the sample at the critical composition may mean that  $g(\epsilon)$  is strictly

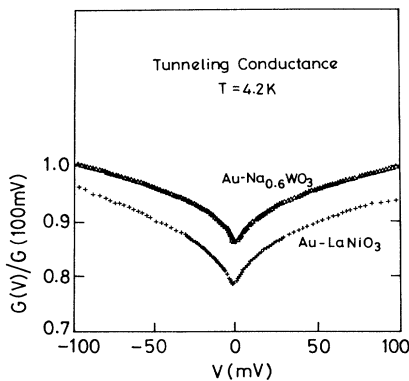


FIG. 3. Normalized conductance  $G(V)/G(100 \text{ mV})$  for epitaxial  $\text{LaNiO}_3$  film and  $\text{Na}_{0.6}\text{WO}_3$  single crystal. Data taken with Au tip at  $T=4.2 \text{ K}$ .

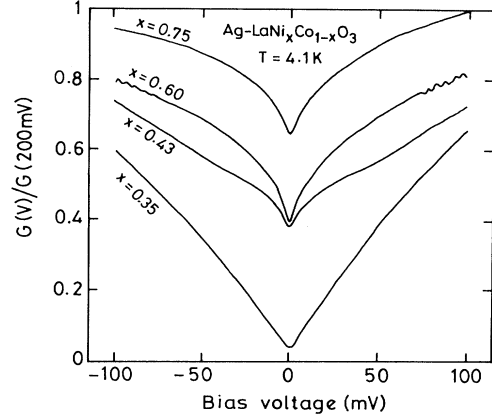


FIG. 4. Normalized conductance  $G(V)/G(200 \text{ mV})$  for the system  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  for different compositions. Data taken using planar-junction configuration with Ag as counter electrode at  $T=4.1 \text{ K}$ .

not zero at  $\epsilon=0$ . However, we are inclined to take a more conservative view and suggest that this finite  $G$  at zero bias is due to leaks or microshorts, which are somewhat "inevitable" in these junctions. For the point-contact junction on the same material (Fig. 2), we find that  $G(V=0)/G(V=100 \text{ mV}) > 0.1$ . This is understandable because point-contact junctions are more prone to leaks. It is, therefore, likely that the nonzero  $G(V=0)$  for the  $x=0.35$  sample is a sign of leakage and this value is then a measure of the leak in these junctions. One can then conclude that in junctions on samples with higher  $x$  ( $\geq 0.43$ ) where  $G(V=0)/G(V=200 \text{ mV})$  is much larger than this value (0.05–0.1), the contribution of the leaks to the measured conductance is much smaller. Another interesting observation is that the junction  $G-V$  curves are symmetrical and they show no rectifying behavior.

In Fig. 5, we show the planar-junction data at 0.4 K.

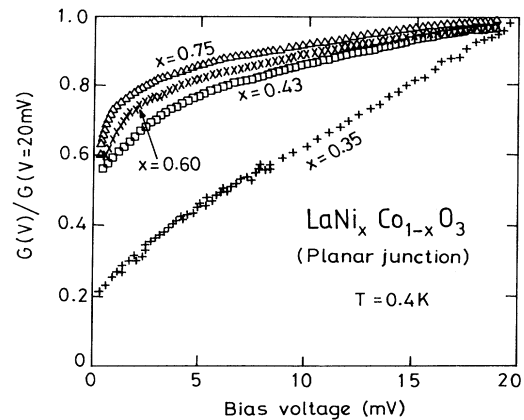


FIG. 5. Normalized conductance  $G(V)/G(20 \text{ mV})$  for the system  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  for different compositions. Data taken at 0.4-K planar-junction configuration using Ag as counter electrode.

To avoid heating, the junction bias is restricted to  $\pm 20$  mV. It can be seen that the dip in  $G(V)$  near the zero bias becomes deeper at lower temperatures. To appreciate this, in Fig. 6 we show the  $G-V$  curves at three temperatures for three samples. It can be seen that the temperature dependence becomes more prominent and the dip in  $G(V)$  becomes deeper as the MI transition is approached (lower  $x$ ). Similar tunneling data were also obtained on  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  single crystals with Au point contact at 4.2 K. For details of this system we refer to our earlier publication.<sup>19</sup>

Based on the data presented above, we summarize below the main observations:

(1) A cusp shows up in  $G(V)$  as  $V \rightarrow 0$  and this is *qualitatively different* from what one observes in a conventional MIM junction. For all the samples, the  $G(V)$  can be expressed in the general form

$$G(V) = G_0 [1 + (|V|/V^*)^n], \quad (4)$$

for  $|V| < 50$  mV. The exponent lies in the range  $1 > n > 0.5$  and  $V^*$  is a constant. Keeping in tune with Eq. (2), if we identify the  $G(V)$  as representing  $g(\epsilon)$  we can identify  $V^*$  with  $\Delta/e$  in the special case when  $n = 0.5$ . In Fig. 7(a), we have plotted the "tunnel" ex-

ponent  $n$  as a function of  $x$  for the  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  and in Fig. 7(b) we show the same for the  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  system as a function of  $(x-y)$ . For both systems,  $n \rightarrow 1$  as the critical region is approached.

(2) The ratio  $G_0/G(V=200 \text{ mV})$  becomes smaller as  $x$  decreases and the MI transition is approached.

(3) The essential features of the  $G(V)$  curves are unaltered on cooling but the thermal smearing near the zero-bias region decreases progressively and the singularity at  $V=0$  becomes sharper and deeper.

In the next section we will explore the likely implications of our observations. Before that, we would like to mention a few problems one invariably faces in working with this type of solids. These problems are related to the nature and quality of the junctions.

We have already pointed out that the junctions we have are not of the "canonical leak-free" variety of tunnel junctions. We have also put an estimate on the leak or microshort contribution to the  $G(V)$  of such junctions, and concluded that for junctions formed on the tungsten-bronze materials and on the  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  series with  $x \geq 0.57$  the dominant contributions are not from leaks. We have to accept these difficulties as a part of the reality when working with this type of oxides.

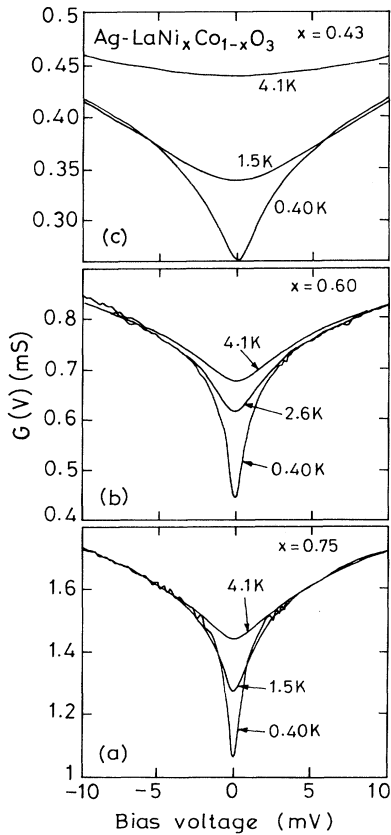


FIG. 6.  $G(V)$  for three compositions (of the system  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ ) taken at three different temperatures. Data taken in planar-junction configuration with Ag as counter electrode.

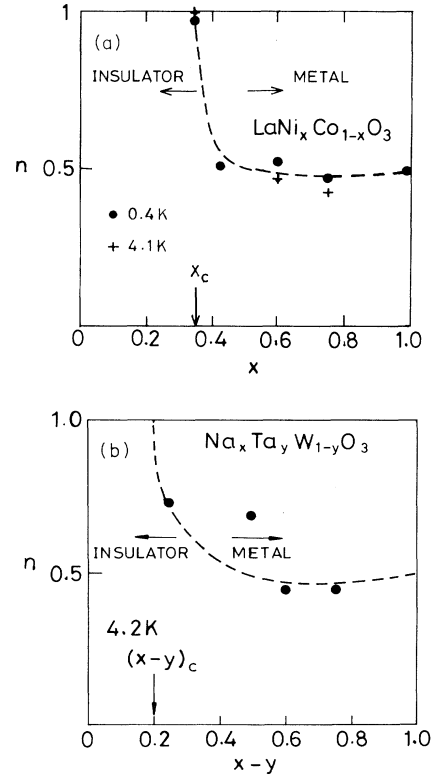


FIG. 7(a) Change in "tunnel" exponent  $n$  [see Eq. (4)] for  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  as a function of  $x$ . Data obtained at two temperatures. (b) Change in tunnel exponent  $n$  [see Eq. (4)] for  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  as a function of  $(x-y)$ . Data obtained at 4.2 K. In both figures, the arrow marks the critical composition. The dotted line is a guide to the eye only.

This is similar to the case of high  $T_c$  oxides where very few junctions reported in the literature are of low-leak type.<sup>21</sup> However, some level of information can be obtained from them if we are cautious. Below we present two sets of data to show the extent of “faith” we can have on such junctions.

First, we show that  $G(V)$  is definitely not measuring the bulk conductance. To show this, we have measured the magnetoresistance (MR) of these junctions at 4.2 K in a field up to 7 T. In the bulk, these samples show giant negative isotropic MR when  $x \cong x_c$ , which at low  $T$  can be as high as 70% or more.<sup>15,25</sup> However, we find no such magnetic-field effect in the junction conductance. This is important because it shows that the voltage drop across the junction is almost nearly the applied bias and it does not involve a drop across the bulk of the sample. (This possibility exists because the samples are resistive.)

Second, one can indeed see the gap of Pb when Pb is used as a counter electrode, although the observed  $G(V)$  near the gap region is severely smeared out. In Fig. 8, we show the  $G(V)$  curves obtained on LaNiO<sub>3</sub> and tungsten bronze Na<sub>0.6</sub>WO<sub>3</sub>. In the single crystal Na<sub>0.6</sub>WO<sub>3</sub>, the conductivity of the material is very high ( $2.12 \times 10^4$  S/cm at 4.2 K) and one can see a fairly good peak in  $G(V)$  for  $V \cong \pm \Delta_{\text{pb}}/e$ . In LaNiO<sub>3</sub>, which has less conductivity ( $8 \times 10^3$  S/cm at 4.2 K), the feature near the gap region is much broader. We think of it as a signature of finite lifetime of electronic states in the oxides. Such a smearing of the Pb gap had been seen in the junctions formed on boron-doped silicon for concentration of boron more than the critical concentration of the MI transition.<sup>26</sup> This smearing of the Pb gap was explained as due to the finite lifetime of electron states in the doped semiconductor. We followed a similar approach to analyze our data, but used the Blonder-Tinkham-Klapwijk (BTK) expression for transport through the junction.<sup>27</sup> The usual BTK expression for the current in a  $N$ - $S$  junction is

$$I = C_n \int_{-\infty}^{+\infty} [f(\epsilon - eV) - f(\epsilon)] [1 + A(\epsilon) - B(\epsilon)] d\epsilon, \quad (5)$$

where  $A(\epsilon)$  and  $B(\epsilon)$  are the Andreev and normal reflection coefficients given as Ref. 27.  $f(\epsilon)$  is the usual Fermi function. The modification made by us is to use a modified Fermi function  $f_{\text{mod}}(\epsilon)$ , which allows a finite width of the electronic states as given below:

$$f_{\text{mod}}(\epsilon) = \int_{-\infty}^{+\infty} f(\epsilon') \frac{(\Gamma/2\pi)}{(\epsilon - \epsilon')^2 + (\Gamma/2)^2} d\epsilon', \quad (6)$$

where  $f(\epsilon)$  is the usual Fermi distribution function and  $\Gamma$  is a measure of the width of the broadening. We used  $f_{\text{mod}}(\epsilon)$  from Eq. (6) instead of  $f(\epsilon)$  in Eq. (5). This modified BTK theory has now been used to obtain a fit for the  $G(V)$  curves. For the Pb-Na<sub>0.6</sub>WO<sub>3</sub> junction, we obtain  $\Delta = 1.5$  eV,  $\Gamma = 0.1$  eV, and  $Z = 0.98$ . In the Pb-LaNiO<sub>3</sub> junction, we get  $\Delta \mp 1.5$  eV,  $\Gamma = 0.65$ , and  $Z = 1.8$ , showing large broadening in this junction. The parameter  $Z$  is the barrier parameter and  $Z = 0$  for an ideal barrierless junction.<sup>27</sup> As the barrier increases,  $Z$  increases. The above fit shows that though not very good but reasonable quality planar junction can be formed on these materials.

#### IV. DISCUSSIONS

##### A. Density of states $g(\epsilon)$ and the junction conductance $G(V)$

Following conventional practice and wisdom we assign the variation of  $G(V)$  with  $V$  as the variation of  $g(\epsilon)$  with  $\epsilon$ . We comment on the validity of such assignment afterwards. For a junction with no inelastic scattering at the barrier as  $T \rightarrow 0$ , we have

$$G(V) \propto G_0 g(\epsilon). \quad (7)$$

This relation assumes a nearly featureless density of states (DOS) at  $E_F$  for the counter electrode. If the above assumption is not valid,  $G(V)$  will be a convolution of the DOS of the two electrodes forming the junction. If Eq. (7) is indeed valid in these junctions, then the cusplike singularity in  $G(V)$  is a reflection of the cusp in  $g(\epsilon)$  and the value of  $n$  deserves attention. According to theories of electron-electron interactions in disordered systems,<sup>1,2</sup>  $n = 0.5$ . For the more metallic samples (in the WL regime), we find that the prediction is indeed valid [i.e., Eq. (2) is obeyed]. However, the new observation is that  $n$  evolves continuously as the critical region is approached ( $x \rightarrow x_c$ ). We think that one likely explanation is that the observed variation of  $G(V)$  as the MI transition is approached reflects the nature of  $g(\epsilon)$  close to  $\epsilon = 0$  as the system evolves from a screened Coulomb interaction-dominated metallic system to a long-range Coulomb interaction-dominated insulator, which has a Coulomb gap.

There is a range of validity of Eq. (2). The interaction corrections are valid when  $(k_F l)^3 \gg (E/E_F)$ , thus, the theories are expected to be valid well inside the metallic region and away from the critical region of the MI transition. For the oxides studied by us,  $E_F = 0.2$  eV. For the samples in the transition region,  $k_F l \cong 1$  or even less. As

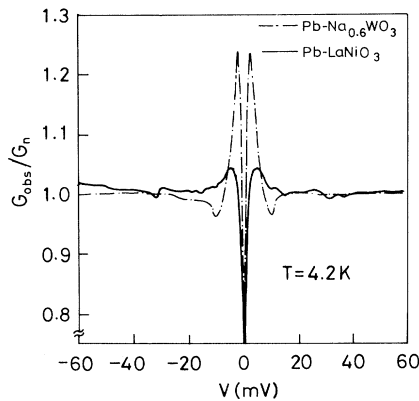


FIG. 8. Normalized tunneling curves of Pb-LaNiO<sub>3</sub> and Pb-Na<sub>0.6</sub>WO<sub>3</sub> junctions at 4.2 K. The native oxide on the surface is the barrier.  $G_n$  has been obtained by fitting  $G$  for  $V > 20$  mV with  $\sqrt{V}$  relation.

a result, we should expect deviation from the theories<sup>1,2</sup> for bias in excess of 100 mV. It is likely that the evolution of  $n$  from 0.5 to 1 signals the onset of the breakdown of the above theories. The role of strong correlation in determining the normal-state tunneling conductance of high  $T_c$  cuprates is a topic of current interest.<sup>28</sup> It is not unlikely that strong correlation is the origin of the behavior observed by us also. The generality of the observation of a cusplike dip in  $G(V)$  near zero bias in a large number of oxides (and not in cuprates alone) is a point that needs particular attention.

### B. Comparison with photoelectron spectroscopy

It will be good to compare our data on  $G(V)$  with the photoelectron-spectroscopy data, which also can give information on the density of states near  $E_F$ . Fortunately, such data are available on both the systems studied by us.

Recently the  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$  system has been studied extensively for the entire composition range  $1 > x > 0$ .<sup>29</sup>  $\text{LaNiO}_3$  is analyzed as a  $p$ - $d$  metal with states at  $E_F$  having extensive metal  $3d$  as well as oxygen  $2p$  character.  $\text{Ni}(3d^7)$  donates one electron to the  $p$ - $d$  hybridized conduction band. The  $\text{LaCoO}_3$  with  $\text{Co}(3d^6)$  in the low-spin state has been found to be a charge-transfer insulator. The occupied and the unoccupied DOS near  $E_F$  show systematic changes as the composition is varied. As the system moves towards the insulating side (smaller  $x$ ), there is depletion in the DOS at  $E_F$ . In the insulating region ( $x < 0.35$ ), a small soft gap does open up in the DOS, which has been interpreted as an evidence for Coulomb gap in the system.<sup>29</sup> The resolution of the photoelectron-spectroscopy data are at a much coarser scale. But combining our data  $G(V)$  and the photoelectron-spectroscopy data it seems that a gap does open up in the DOS at  $E_F$  as the critical region is approached.

For the Na-doped (and Ta-substituted)  $\text{WO}_3$  system, there is clear evidence from ultraviolet photoemission spectroscopy (UPS) that a soft gap does open up in the DOS and there is depletion in the DOS in the metallic side.<sup>30</sup> The data in the insulating region had been fitted to a simulation based on a model of Coulomb gap and good agreement had been found with the observed spectrum.

A comparison of our data on  $G(V)$  and the photoelectron-spectroscopy data both suggest a depletion in  $g(\epsilon)$  and our assignment of  $G(V)$  with  $g(\epsilon)$  seems to be in the main correct. It will be definitely good to have similar studies done on other oxide systems to verify the generality of our remarks.

### C. Finite temperature effects

In Fig. 6, we have shown the temperature dependence of  $G(V)$ . In Fig. 9, we have shown the temperature variation of  $G_0(T)$  and conductivity  $\sigma$  in a relative scale. It can be seen that while the temperature variation of  $G_0$  is much stronger than that of  $\sigma$  in the more metallic samples, near the transition they become comparable.

The correction to  $g(\epsilon)$  at a finite temperature  $T$  due to the electron-electron interaction is given as<sup>1</sup>

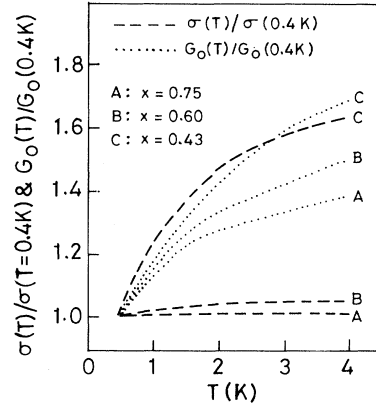


FIG. 9. Relative temperature dependence of conductivity  $\sigma$  and zero-bias conductance  $G_0$  for three different compositions of the system  $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ . These have been normalized at 0.4 K.

$$\delta g(\epsilon, T) \propto g_0 \left[ 1 + \frac{1}{24} (\pi k_B T / \epsilon)^2 \right] (\epsilon / \Delta)^{0.5}, \quad (8)$$

where  $\delta g(\epsilon, T)$  is the correction to the bare DOS. At finite temperature, the tunneling conductance is obtained from the following relation:<sup>1</sup>

$$\frac{\delta G(V)}{G_0} = \frac{1}{4k_B T} \int_{-\infty}^{+\infty} \frac{\delta g(\epsilon, T)}{g_0} \zeta(\epsilon, eV, k_B T) d\epsilon, \quad (9)$$

where  $\zeta = \cosh^{-2}[(\epsilon - eV)/2k_B T] + \cosh^{-2}[(\epsilon + eV)/2k_B T]$ .

A calculation of  $G(V)/G_0$  for different  $T$  obtained from Eqs. (8) and (9) are shown in Fig. 10. It can be seen that the thermal-smearing effect in the calculated  $G(V)$  starts for  $|V| < 7k_B T/e$ . The observed  $G(V)$  curves show the thermal-smearing effect for  $|V| < 10k_B T/e$  for the most metallic samples and it becomes even more serious for samples closer to the critical region of MI transition.

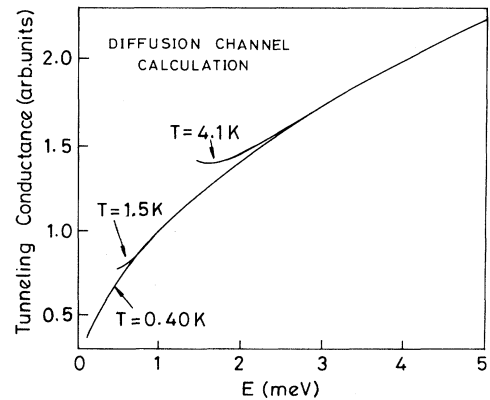


FIG. 10. Tunneling conductance  $[G(V)/G_0]$  calculated from Eqs. (8) and (9) for three temperatures.

This means that the temperature dependence of  $g(\epsilon, T)$  as given in Eq. (8) is not enough to describe the data. The extra temperature dependence of  $g(\epsilon, T)$  or it may mean that we have the onset of scattering (inelastic) taking place in the junction region as the sample moves closer to the MI transition region. In any case, we think that the strong temperature dependence of  $G(V)$  is an interesting observation and it calls for a closer look at the question of tunneling in disordered solids with high resistivity, which are close to the MI transition.

#### D. The correlation gap $\Delta$

For samples in the WL regime,  $\Delta$  in Eq. (2) has the meaning of a correlation gap, which measures the strength of the electron-electron interactions in the presence of disorder. It will be interesting to see how  $\Delta$  develops as a function of the zero-temperature conductivity  $\sigma_0$ . In Fig. 11, we have plotted our data for both the oxide systems. For comparison we have also plotted the data of Ref. 6 on granular Al/Al<sub>2</sub>O<sub>3</sub> films as well as on Ni-Si alloy films. To our knowledge, these are the only data where the comparison of  $\sigma_0$  and  $\Delta$  has been made. We find that for oxide samples,  $\Delta \propto \sigma_0$  over a wide range of conductivity. For the Nb-Si system,  $\Delta \propto \sigma_0^2$  for  $\sigma_0 > 50$  S/cm whereas for  $\sigma_0 < 50$  S/cm  $\Delta \propto \sigma_0$  seems to be a better choice. It can be argued if a simple and general dependence is to be expected between  $\Delta$  and  $\sigma_0$ . It is quite likely that the dependence of  $\Delta$  on  $\sigma_0$  depends on the details of the systems and, in particular, on the details of the interactions.<sup>15</sup> As a result though a general functional form of the type  $\Delta \propto \sigma_0^p$  is expected, different systems depending on the nature of interactions may have different  $p$ .

#### E. Alternate explanations and cautionary remarks

In the above discussions, the assumption is that the dominant contribution to  $G(V)$  arises from  $g(\epsilon)$ . Two questions immediately arise. First, junctions formed on oxide surfaces can have strong inelastic scattering. The existence of such scattering can give rise to a  $G(V)$  linear in  $|V|$  (i.e.,  $n=1$ ) as has been shown recently.<sup>31</sup> In general, the contribution of the inelastic processes in the barrier is given by

$$G(V) \propto \int_0^{eV} F(\hbar\omega) d(\hbar\omega), \quad (10)$$

where  $F(\hbar\omega)$  is the spectral density of the inelastic excitations, which scatter the electrons. In general for  $G(V) \propto V^n$ , we have  $F(\hbar\omega) \propto (\hbar\omega)^{n-1}$ . Thus, for  $n=1$  i.e.,  $F = \text{constant}$ , we have  $G(V) \propto V$ . However, if  $n < 1$  as in the case of our samples, we have  $F(\hbar\omega)$  diverging as  $\omega \rightarrow 0$ . Physically it is difficult to realize a scattering process that will have a diverging spectral density  $F(\hbar\omega)$  as  $\omega \rightarrow 0$ . It may, however, happen that the observed  $G(V)$  is a combination of both elastic process [giving  $n=0.5$  following Eq. (2)] and inelastic process (with  $n=1$ ); the inelastic process wins over as the MI transition is approached. Such a process can, *in principle* explain the ob-

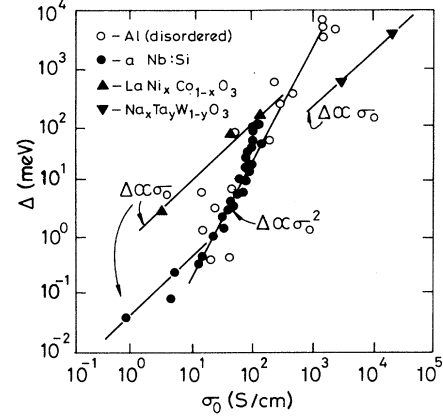


FIG. 11. Dependence of correlation gap  $\Delta$  on zero-temperature conductivity  $\sigma_0$  for four systems. Data of Nb:Si and Al(disordered) are from Ref. 6.

served evolution of  $n$  as the MI transition is approached.

Secondly, we have here a junction where one electrode has electrons with very small diffusivity and on the verge of getting strongly localized (insulator). It will imply a very short lifetime of any electronic state. The finite lifetime of electrons in these highly disordered electrodes can break the simple relation of  $G(V)$  and  $g(\epsilon)$  as given in Eq. (5). The extent of the quantitative contribution of such an effect is not very clear at this moment. But this particular issue definitely deserves attention when one works with such highly disordered solids.

We, in this paper, offered a certain viewpoint as an explanation of our observations. We have also pointed out alternate explanations. It is difficult to rule out any of these possibilities.

To summarize, we have studied at low temperatures the composition-driven MI transition in a class of metallic perovskite oxides ( $ABO_3$ ) with almost cubic structure by using the tunneling technique. We find that, in general, the junction conductance  $G(V)$  gradually deepens near the zero-bias region as the MI transition is approached and the  $G(V)$  follows a power-law behavior with bias  $V$  given by Eq. (4). The exponent evolves gradually from 0.5 in the WL regime to nearly 1 as the critical region of the MI transition is approached. We think that this trend either represents the evolution of the density of states  $g(\epsilon)$  (modified by the Coulomb interaction) as the MI transition is approached or it is a manifestation of strong inelastic scattering in the junction region.

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