Rice University

Nanostructure Investigations of Nonlinear Differential Conductance in NdNiO$_3$ Thin Films

by

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Abstract

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Transport measurements on thin films of NdNiO$_3$ reveal a crossover to a regime of pronounced nonlinear conduction below the well-known metal-insulator transition temperature. Surprising evolution of the transport properties is observed at temperatures well below this transition, which appears consistent with a gradual formation of a gap in the hole-like Fermi surface of this strongly correlated system. A model of Landau-Zener breakdown fails to describe the $I(V)$ characteristics at high temperatures, where Ohmic transport dominates, but becomes increasingly more appropriate as the temperature approaches 2 K.
Many thanks to my advisor, Doug Natelson, for his guidance and mentorship that have made this research successful and helped me to grow as a scientist.

I am also grateful to the other two members of my committee, Prof. Du and Prof. Biswal, for taking their valuable time to evaluate this thesis.

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In this whole process of getting to Rice, it probably didn’t hurt that my parents were a librarian and a teacher, and once upon a time survived grad school themselves. Thanks, Mom and Dad.

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## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>iii</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Motivation</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Metal-Insulator Transitions</td>
<td>3</td>
</tr>
<tr>
<td>1.3 The Rare Earth Nickelates</td>
<td>6</td>
</tr>
<tr>
<td>1.4 Scope of the Present Work</td>
<td>8</td>
</tr>
<tr>
<td>2 Methods</td>
<td>9</td>
</tr>
<tr>
<td>2.1 Thin Film Growth and Device Fabrication</td>
<td>9</td>
</tr>
<tr>
<td>2.2 Transport Measurement Techniques</td>
<td>11</td>
</tr>
<tr>
<td>3 Results</td>
<td>13</td>
</tr>
<tr>
<td>3.1 Resistivity</td>
<td>13</td>
</tr>
<tr>
<td>3.2 $I(V)$ and $dI/dV$ vs. $V$ Measurements</td>
<td>14</td>
</tr>
<tr>
<td>3.3 Understanding the Nonlinear Transport</td>
<td>17</td>
</tr>
<tr>
<td>4 Discussion</td>
<td>21</td>
</tr>
<tr>
<td>4.1 Landau-Zener Breakdown</td>
<td>22</td>
</tr>
<tr>
<td>4.2 Back-to-Back Schottky Diodes</td>
<td>25</td>
</tr>
<tr>
<td>4.3 Space-Charge-Limited Current</td>
<td>26</td>
</tr>
<tr>
<td>4.4 Electric-Field-Driven Breakdown</td>
<td>28</td>
</tr>
</tbody>
</table>
5 Conclusions 30

A Supplementary Technical Information 32

References 34
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Mott-Hubbard and charge-transfer gap formation</td>
<td>5</td>
</tr>
<tr>
<td>1.2</td>
<td>Lattice distortion in LuNiO$_3$</td>
<td>6</td>
</tr>
<tr>
<td>2.1</td>
<td>SEM image of device</td>
<td>10</td>
</tr>
<tr>
<td>2.2</td>
<td>Measurement circuit diagrams</td>
<td>12</td>
</tr>
<tr>
<td>3.1</td>
<td>Temperature-dependent resistivity</td>
<td>15</td>
</tr>
<tr>
<td>3.2</td>
<td>$I(V)$ and $dI/dV$ vs. $V$ isotherms</td>
<td>18</td>
</tr>
<tr>
<td>3.3</td>
<td>Zero-bias resistance as a function of device length</td>
<td>20</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic diagram of Landau-Zener breakdown</td>
<td>23</td>
</tr>
<tr>
<td>4.2</td>
<td>Landau-Zener model fits of experimental $I(V)$ data</td>
<td>25</td>
</tr>
<tr>
<td>4.3</td>
<td>Comparison of $I(V)$ curve models</td>
<td>27</td>
</tr>
<tr>
<td>4.4</td>
<td>Plots of $dI/dV$ vs. $E$</td>
<td>29</td>
</tr>
<tr>
<td>A.1</td>
<td>Schematic of summing amplifier design</td>
<td>33</td>
</tr>
</tbody>
</table>
Strongly correlated materials (SCMs) deviate from the predictions of single-particle band structure calculations, by which the electronic properties of many materials can be adequately described. In SCMs, competing electronic ground states often result from interactions between electrons, and between electrons and the crystal lattice. Metal-insulator transitions (MITs), often accompanied by structural or magnetic ordering changes, are manifestations of this competition. These are of fundamental interest and could potentially prove useful for technological innovation. This category of materials has been the focus of a wide variety of recent investigations [1, 2, 3, 4, 5, 6] seeking to understand both the physical properties of the correlated state, as well as the complex dynamics that control the electron-electron interactions in solids.

1.1 Motivation

The challenges presented by SCMs were not brought to prominence until the late twentieth century. In many conventional materials, single-particle band structure calculations (e.g., using the independent electron approximation) can be employed successfully to predict the electronic properties of metals (e.g., Cu, Au), semiconduc-
tors (e.g., Si, GaAs), and insulators (e.g., diamond) to fair precision. This approach avoids the (impossible) task of solving an N-electron problem exactly, where N is the number of electrons in the system. In this simplified picture, the Schrodinger equation is solved for a single quasiparticle (which can be electron-like or hole-like) of effective mass \( m^* \), which takes into account the interaction of the electron and crystal lattice (as well as the average interaction with all other electrons, employing a self-consistent solution procedure such as the Hartree-Fock method) without actually considering these interactions individually.

Bloch’s theorem states that the solution to the one-particle Schrodinger equation can be written as a wavefunction of the form

\[
\psi_k(r) = u_k(r)e^{ik \cdot r}
\]  

This is the product of \( u_k(r) \), which has the periodicity of the lattice, and a plane wave. Note that \( k \) is the electron’s wavevector (and \( p = \hbar k \) its crystal momentum).

This Bloch function (or its reciprocal-space form) can be used to calculate the dispersion relation, \( E(k) \); a complementary piece of information, the number of electrons per energy band, can be deduced from the number of valence electrons per unit cell. From this simple treatment, it can be predicted whether a crystal will be insulating or metallic in the zero-temperature limit. Specifically, if a band is left only partially full (requiring an odd number of electrons per unit cell), or if two full bands overlap, then excitations of infinitesimally low energy are possible, giving rise to metallic properties. If on the other hand all bands are left exactly full or empty (requiring an even number of electrons per unit cell) and energy gaps exist between bands, then the crystal is predicted to be insulating.[7]

While this approach is adequate for many materials and, indeed, is directly responsible for the development of a large part of modern computing and telecommunications
technology, it does not work in all cases. Failures of this approach started to become apparent in the second quarter of the twentieth century (especially in transition metal compounds with partially filled $d$-bands [8]), when it was discovered that materials like NiO,[9] Fe$_3$O$_4$,[10] and, later, VO$_2$ [11, 12] presented great disagreements between theory and experiment. NiO, for instance, was predicted to be metallic but experimentally found to be insulating; VO$_2$ and Fe$_3$O$_4$ exhibit large metal-insulator transitions which are likewise not anticipated by single-particle theory. The fact that these simple theoretical results are so inadequate for SCMs was, and remains today, a powerful impetus to develop better theories and empirical understanding.

1.2 Metal-Insulator Transitions

The present thesis will consider one principal consequence of strong correlations: the metal-insulator transition. As the name suggests, MIT materials are characterized by a phase transition from metallic to insulating behavior, which can commonly be driven by parameters such as temperature, pressure, or doping. Insulating characteristics are the result of the formation of an energy gap that prohibits infinitesimally-low-energy excitations; the specific physical mechanism responsible for the development of this gap depends on the energetics of any particular system, including types of constituent atoms and crystal structure. Three important MIT classifications are: Mott-Hubbard systems, charge-transfer systems, and charge-ordered (or charge-disproportionation) systems. These three classes of behaviors are most often found in compounds, especially transition metal oxides.[13, 14]

In Mott-Hubbard systems, the gap is thought to arise from the Coulomb interaction energy $U$, which causes splitting of a half-filled band (often a $d$-band) into filled (lower) and empty (upper) Hubbard bands. The lower Hubbard band sits below the Fermi level and the upper Hubbard band above $E_F$, with a finite gap separating the
two. A cartoon of this process is shown in Fig. 1.1(a).

A charge-transfer gap is formed when a half-filled (again, often a $d$-) band likewise splits into upper and lower Hubbard bands, but in this case, the separation between the resulting upper and lower bands is larger. The minimal energy gap $\Delta$, then, lies between the empty upper Hubbard band and a distinct band, often a filled $p$-band of oxygen. This process is depicted in Fig. 1.1(b).

Finally, charge ordering (alternatively known as charge disproportionation) describes a system in which adjacent regions of the same type of atoms (e.g., the Ni atoms in NiO$_6$ octahedra of RNiO$_3$) have alternating, distinct oxidation states. This can result from lattice distortions that drive the transition, [15, 16] as such lattice distortions lead to an effective doubling of the unit cell. This causes the band filling to switch from half full to a filled valence and empty conduction band. A crystal structure diagram showing this type of lattice distortion in LuNiO$_3$ is shown in Fig. 1.2.

In attempts to determine the origins of MITs in real materials, investigators turn to a variety of experimental methods such as spectroscopic ellipsometry [17], neutron or synchrotron-based-x-ray diffraction studies, [15], and resonant x-ray scattering.[18]
Figure 1.1: Energy band diagrams of two kinds of metal-insulator transition mechanisms: (a) Mott-Hubbard transition, in which the $d$-band splits (into the upper and lower Hubbard bands) due to “turning on” the interaction $U$. The energy gap then lies between these upper and lower Hubbard bands. (b) Charge transfer transition, in which the splitting between upper and lower Hubbards bands is larger, and the energy gap is instead between the filled $p$-band and empty upper Hubbard band. Diagram reproduced from [13].
Figure 1.2: Crystal structure of monoclinic LuNiO$_3$, with Lu shown as spheres and the NiO$_6$ octahedra shown in two shades of gray. Each shade represents a different Ni oxidation state (3+$\delta$, 3-$\delta$), and the distortion is evident in the tilting of the two groups of octahedra in opposite directions away from the vertical $c$-axis. Diagram reproduced from [16].

1.3 The Rare Earth Nickelates

The rare earth perovskite nickelates RNiO$_3$, where R is a rare earth ion, are model systems for studying strong correlation behavior. All members of the RNiO$_3$ family except for LaNiO$_3$ exhibit a metal-insulator transition driven by electronic correlations. [19, 20] In 1971, Demazeau and collaborators synthesized bulk RNiO$_3$ compounds for the first time and discovered that the electronic and structural properties could be tuned by the choice of rare earth ion. [21, 19] Interest in such compounds was renewed in the late 1990s when investigations (encouraged by the discovery of high-temperature superconductivity in the cuprate compounds) yielded improved bulk
synthesis techniques. [19] Although superconductivity was not discovered in RNiO$_3$ compounds, investigators successfully demonstrated control of the MIT by addition of electrons or holes via chemical doping. [22] Due to the difficulty in preparing large, bulk single crystals,[23] more recent studies have focused primarily on epitaxial thin films, in which parameters such as material thickness and strain (via choice of substrate) can be tuned deterministically during growth to modify the material properties. [24, 25, 26]

One such compound, NdNiO$_3$ (NNO), has been the subject of a decades-long debate regarding the mechanism of its metal-insulator transition, specifically whether the low-temperature insulating phase results from formation of a Mott [17] or charge-transfer gap,[14] or is perhaps due to long-range charge ordering. [18, 27, 28] Bulk polycrystalline samples exhibit a first-order MIT at $\sim 200$ K [29, 14, 30] that separates the orthorhombic, metallic, paramagnetic state at high temperatures from the low-temperature monoclinic, insulating, antiferromagnetic phase. [27, 28] Once synthesis and doping techniques had been established, investigators sought additional means of altering the MIT. Ionic liquid gating, [25, 31] as well as modulation doping, [20] have been explored as methods for controlling the transition temperature and conductivity (with one eventual goal of producing a Mott-field-effect transistor), but these have not been shown to completely suppress the MIT in NNO. A recent study [28] by Hauser and collaborators employed complementary Hall coefficient and Seebeck measurements to determine that the high-temperature coexistence of a large hole Fermi surface and small electron pocket gives way to a low-temperature pseudogap in the hole Fermi surface, leaving only the electron-like carriers to participate in transport. A forthcoming report from Allen and collaborators details tunneling measurements on thin NNO films that reveal the formation and evolution of a pseudogap at temperatures below $T_{MIT}$. [32] Further investigation of this low-temperature pseudogap
is therefore warranted.

1.4 Scope of the Present Work

In this work, we employ nano- and micro-structure-based electronic transport to study the nature of the low-temperature insulating state in thin films of NNO. The advantages of this approach are twofold: the film thickness and substrate material can be chosen to tune the lattice strain, and a small lateral distance between deposited metal contacts allows the system to be driven by comparatively high electric fields established by applying modest voltages. Current-voltage ($I(V)$) characteristics offer a remarkable abundance of information about the system and make it possible to monitor the temperature-dependent electronic properties. A brief overview of the fabrication and measurement techniques employed in these experiments is given in Chapter 2.

In Chapter 3, we describe in detail our observation of a smooth, gradual crossover from Ohmic to non-Ohmic transport that accompanies the MIT, as well as the non-linear transport properties that continue to evolve richly at low temperatures, well below $T_{MIT}$. Extrinsic, potentially complicating factors, such as contact resistance and self-heating, are discussed and ruled out based on their inconsistency with the experimental results.

In Chapter 4, we consider three candidate models to analyze our experimental $I(V)$ data: Landau-Zener breakdown (LZB), back-to-back Schottky diodes, and space-charge-limited current, and find the best agreement using the LZB model, especially at the lowest temperatures.

Finally, in Chapter 5, we conclude with an outlook for future work.

The contents of this thesis are largely based on work published in November, 2014.
2.1 Thin Film Growth and Device Fabrication

Epitaxial NNO thin films were grown by RF magnetron sputtering on LaAlO$_3$ (LAO) substrates, which present a small lattice mismatch of approximately $-0.5\%$ for NNO (the smallest mismatch possible with available single-crystal substrates), resulting in compressive strain. [34, 25] The samples were characterized by x-ray diffraction (XRD) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) to verify the film thickness and crystallinity, similar to a previous work. [28] The film growth and initial characterization were done at the University of California, Santa Barbara, by Evgeny Mikheev in the group of Prof. Susanne Stemmer.

Three film thicknesses were studied: 3.85 nm, 10 nm, and 16 nm. Planar multi-contact devices were defined by electron-beam lithography (EBL), followed by electron-beam evaporation of metal contacts (2 nm Ni and 50 nm Au) and liftoff. A second step of EBL defined a protective mask for reactive ion etching with BCl$_3$, or wet etching with hydrochloric acid. For the samples prepared by wet etching, the contacts used for electrical measurements were deposited after the etching step in order
to avoid acid damage to the Ni adhesion layer. In this case, only one initial metal contact was deposited before etching and grounded during subsequent EBL in order to dissipate excess charge. Due to sample-to-sample variation with wet etching, as well as the additional EBL step required to preserve the contacts, we conclude that reactive ion etching is the preferred etching method.

The resulting device geometry consisted of a narrow ($\sim 5 - 10 \mu m$) strip of film, isolated from its surroundings by the insulating substrate, and several pairs of interdigitated contacts with separation lengths between $\sim 100$ nm and $6 \mu m$. A scanning electron microscopy (SEM) image of such a device is shown in Fig. 2.1. Each metal contact shown extends beyond the image border to a large ($\sim 300 \mu m$ side length) pad where electrical contact can be made by wire bonding with Au wire.
2.2 Transport Measurement Techniques

All devices were measured in a Quantum Design Physical Property Measurement System (PPMS), a commercial $^4$He cryostat capable of reaching a base temperature of 1.8 K (on a good day!), equipped with a 9 T superconducting magnet. Both low-frequency lock-in techniques as well as dc characterization were employed in these experiments. Lock-in measurements are preferred due to their superior ability to reject unwanted electrical noise, allowing a higher signal-to-noise ratio. Excitation frequencies below $\sim 100$ Hz are sufficiently low to be treated as essentially the “dc limit,” and consideration of any high-frequency properties of the circuit is not necessary.

Measurement of the temperature-dependent resistivity allowed estimation of $T_{MIT}$. Simultaneous current-voltage ($I(V)$) and differential conductance ($dI/dV$ vs. $V$) measurements were performed by superimposing a small ac excitation on a variable dc bias using a summing amplifier. Schematics of the circuits used for measurements are shown in Fig. 2.2, and a schematic of the summing amplifier is included in Appendix A.
Figure 2.2: (a) Schematic of ac circuit used for four-terminal resistance measurements. An ac current source is provided by a ballast resistor in series with the oscillator output (voltage) of a lock-in amplifier, and the current is essentially constant provided that $R_{ballast} \gg R_{device}$. The device (labeled DUT, device under test) current is measured with the same lock-in, sometimes with an additional preamplifier stage prior to lock-in measurement. A second lock-in is required to measure the voltage drop across the inner contacts. From these two measured quantities, the resistance can be calculated using Ohm’s law. A National Instruments data acquisition card (DAQ) converts the analog output signals from the amplifiers to a digital format, and a computer records the data. For a dc measurement, the ac source is replaced with a dc voltage source, and the current and voltage are measured with dc amplifiers.

(b) Schematic of circuit used for simultaneous $I(V)$ and $dI/dV$ vs. $V$ measurements. The summing amplifier (S.A.) superimposes a small ac voltage ($dV$) onto a variable dc bias before applying the combined voltage across the device (DUT). A current preamplifier outputs a voltage proportional to the current, which is then separated into dc ($I$) and ac ($dI$) components for data recording.
Chapter 3

Results

3.1 Resistivity

The first measurement to be performed was one of resistivity as a function of temperature. This basic experiment provided a groundwork of information about the metal-insulator transition temperature, broadness of the transition, temperature hysteresis, and low-temperature behavior.

Temperature-dependent resistivity data for three film thicknesses, collected using four-probe measurements, are shown in Fig. 3.1. Between room temperature and 100 K, the resistivity decreases with increasing thickness for the three films (from 1 mΩ-cm to 0.5 mΩ-cm at 300 K), and a positive linear slope as a function of temperature in this region is consistent with metallic conduction. An upturn in each curve marks $T_{MIT}$, below which the slope $\frac{d\rho}{dT}$ is negative down to low temperatures, indicating insulating behavior. Taking $T_{MIT}$ to be the temperature at which the resistivity reaches its minimum value upon cooling from room temperature, the transition temperature values for each thickness are approximately 138 K (3.85 nm film), 100 K (10 nm film), and 90 K (16 nm film). The reduced value of $T_{MIT}$ compared to the bulk value and the observed smoothness of the MIT are characteristic of thin film samples [24, 25]
and are likely due to the strain imposed by the substrate. This interfacial strain is known to distort the Ni-O-Ni bond angles, leading to modifications of band width, resistivity, and other aspects of correlation physics.[35, 36, 37, 38]

At intermediate temperatures, a clear hysteresis between the warming and cooling curves is visible for the 10 nm and 16 nm samples, while the hysteresis is comparatively small for the 3.85 nm sample, probably due to its greater sensitivity to strain effects. [24] At $T = 2$ K, the 3.85 nm and 16 nm films have similar resistivity values on the order of 100 m$\Omega$ cm; it is unclear why the 10 nm film’s resistivity at this temperature is so much larger. This film was prepared under different growth conditions (200 mTorr total sputter pressure, instead of the 300 mTorr pressure used for the other two films). The MIT has been found to show great sensitivity to growth and post-processing conditions, which probably explains the higher resistivity of the 10 nm film.

### 3.2 $I(V)$ and $dI/dV$ vs. $V$ Measurements

To study the transport properties in the insulating state, $I(V)$ and $dI/dV$ vs. $V$ curves were collected at selected temperatures, with particular focus on temperatures below $\sim 20$ K. $I(V)$ curves for three film thicknesses measured at selected temperatures are shown in the left column of Fig. 3.2, along with their corresponding $dI/dV$ vs. $V$ curves in the right column. Above $T_{MIT}$, the $I(V)$ curves are Ohmic, as expected for a system with metallic resistivity properties, but become increasingly nonlinear as the temperature is reduced below $T_{MIT}$. When the temperature is above $\sim 50$ K, the practically accessible range of bias voltages is typically very small if the current is to be limited to several $\mu$A to avoid detectable Joule heating. High-bias (and therefore high source-drain electric field) data at these temperatures are dominated by self-heating and are therefore not shown.
Figure 3.1: Temperature-dependent resistivity of NNO films of three different thicknesses. Each sample undergoes a metal-insulator transition upon cooling. When the samples are subsequently warmed, a clear hysteresis is observed in the 10 nm and 16 nm films’ data, while the hysteresis in the 3.85 nm data is comparatively small and not visible at this scale. A second upturn is present in each curve below $T_{MIT}$, near 5 K.
At sufficiently low temperatures that the temperature hysteresis is negligible, the $I(V)$ curves show rich evolution of their nonlinearity as the temperature is varied, even though one might naively expect that the material would be nearly fully gapped. Previous work has suggested the coexistence of metallic and insulating domains below $T_{MIT}$, with conduction made possible by percolation through metallic domains. [34, 28] A second upturn in the temperature-dependent resistivity curve below $T_{MIT}$ testifies to a possible loss of conduction channels. There is, however, no evidence of conduction taking place through discrete domains, as was previously reported in, e.g., vanadium dioxide films [39] or manganese nanowires,[40] other strongly correlated systems with pronounced metal-insulator transitions.

The differential conductance $dI/dV$ allows closer scrutiny of this nonlinear behavior. The $dI/dV$ vs. $V$ curve for each film thickness is suppressed about $V = 0$ when $T < T_{MIT}$, and the suppression becomes stronger with decreasing temperature. The curve for the 3.85 nm film has such a dip in the conductance which becomes noticeably sharper as the temperature is reduced from 50 K to 1.8 K. Even at this low temperature, $dI/dV$ is not flat near zero bias, but rather has a relatively sharp minimum at $V = 0$. The 16 nm film’s dip near $V = 0$ deepens smoothly with decreasing $T$, starting at 10 K down to 2 K. Its $dI/dV$ curve is also not flat at 2 K near zero bias, but instead has a rounded dip. The 10 nm film, which is significantly more insulating at low temperatures than the other two films, exhibits markedly different $dI/dV$ behavior. As the sample is cooled, $dI/dV$ has a smoothly rounded dip at 20 K; at 10 K, there is instead a sharp cusp at zero bias; at 5 K, a flatter region near $V = 0$ appears; and at 2K, the curve has two well defined regions at low bias: an apparent gap flat below $\sim 230$ mV, and a roughly linear voltage dependence at high bias (above $\sim 1$ V), connected by smooth curves. The zero bias suppression of the conductance is suggestive of the formation of a pseudogap as the temperature is reduced.
3.3 Understanding the Nonlinear Transport

Apparently nonlinear $I(V)$ behavior can result from self-heating in certain situations, particularly in nanoscale samples at low temperatures. Based on the absence of behavior that would be expected in the case of significant Joule heating, this scenario seems unlikely in the present work.

Severe local heating would be expected to cause the temperature in the channel between the source and drain electrodes to rise well above the measured substrate temperature. At steady state, the channel temperature is maintained (above the substrate temperature) by the power dissipated while a bias voltage is applied. At progressively lower substrate temperatures, the thermal path for dissipation should become worse, which would be expected to cause the effective channel temperature at low substrate temperature to be at least as large as at higher substrate temperatures. This, in turn, could cause the $I(V)$ curves to saturate or cross when a large bias is applied.

However, no saturation of the $I(V)$ or $dI/dV$ vs. $V$ curves is apparent at high bias, nor do the high-bias conductances at widely different nominal temperatures overlap. In addition, the temperature dependence of the zero-bias conductance indicates that an increase in the current (or differential conductance) of the magnitude observed at the highest applied voltage bias for each film thickness, would require the material temperature to rise by tens of K if this were a heating-induced effect.

The lack of high-bias saturation at low $T$ of $dI/dV$ vs. $V$, coupled with the striking thickness-dependent differences in $dI/dV$ vs. $V$ and absence of hysteresis, leads us to believe that the nonlinear conduction properties are in fact characteristic of the material and not due to self-heating. In future studies, pulsed measurements could be employed in order to mitigate or better characterize any effects of self-heating.

It is important to analyze the contribution of contact resistance, which could be
Figure 3.2: $I(V)$ (left column) and $dI/dV$ vs. $V$ (right column) isotherms for 3.85 nm, 10 nm, and 16 nm film thicknesses at selected temperatures. Below $T_{MIT}$, as the temperature is reduced, $I(V)$ becomes increasingly nonlinear, and $dI/dV$ vs. $V$ develops a dip around zero bias. The specific shape of this dip evolves with temperature and depends upon the sample thickness, likely due to the different strain configurations. The observed suppression of the conductance near zero bias may be due to the formation of a pseudogap that grows with decreasing temperature.
non-Ohmic, to the nonlinear conduction behavior described above. There are two approaches available: four-terminal measurements, which become difficult for very resistive samples; and the transmission line method.\cite{41, 42} The present multi-contact sample design is readily compatible with the latter approach, permitting study of the films’ electrical properties as a function of inter-electrode distance (the device length, $L$). Fig. 3.3 shows plots of zero-bias resistance (extracted from the $I(V)$ curves) as a function of device length for each film thickness at $T = 2$, $5$, and $10$ K. Since these data were collected using a two-terminal method, there is some contribution from contact resistance, which can be determined from the $L \to 0$ intercept. The values estimated from this intercept are small compared to the total two-terminal zero-bias resistance at low $T$.

The linear fit shown in Fig. 3.3 is clearly not the best possible fit for these low-$T$ data, and even has an unphysical negative $y$-intercept in some cases. This issue arises in a variety of device situations, \textit{e.g.}, organic field effect transistors, where it is most often interpreted as a consequence of the uncertainty in the linear fit, due to the large scatter in the resistance of the long devices.\cite{43}

In light of this interpretation, it is reasonable to conclude that the two-terminal $I(V)$ and $dI/dV$ vs. $V$ curves are indeed primarily measurements of the NNO film itself and not contact limited; in fact, the contact resistance becomes less important at low $T$ as the bulk resistivity increases, as indicated by the $\rho(T)$ curves in Fig. 3.1.
Figure 3.3: Zero-bias resistance as a function of device length for each film thickness at selected temperatures. The red lines are linear fits to the experimental data (full circles). A superlinear trend is visible at the lowest temperatures measured for each thickness; the data become more linear at higher temperatures.
The experimental $I(V)$ curves contain a great deal of information in a compact measurement, which can potentially offer insights into the electronic structure of NNO’s insulating state. The great challenge lies in extracting useful physical information from the measured nonlinear $I(V)$ curves, for which there is no well-established universal procedure. This stands in contrast to the related case of finite-bias tunneling spectroscopy, which in the appropriate circumstances can provide a direct way to measure the local density of states.

Here, the most direct approach is to consider a variety of transport mechanisms and compare expected behavior in those situations to the present results. Three $I(V)$ fitting models are considered, each linked to a distinct transport mechanism: (1) a model of Landau-Zener breakdown of the insulating state; (2) a back-to-back Schottky diode model; and (3) a space-charge-limited current model. Our results are most consistent with (1), while attempts to use (2) and (3) did not produce reasonable fits. Even model (1) is only appropriate at low bias and low temperature, becoming less accurate as $V$ or $T$ increases.
4.1 Landau-Zener Breakdown

The Landau-Zener breakdown model uses the following expression (after the result of Oka and Aoki [44]) to approximate $I$ vs. $V$:

$$I = -AV\ln(1 - e^{-\frac{V_0}{V}})$$  \hspace{1cm} (4.1)

This model is the correlated-system analogue of Landau-Zener breakdown in a conventional band insulator, in which case an applied electric field causes tunneling between the valence and conduction bands, resulting in dielectric breakdown that proceeds exponentially as long as the field is maintained.[45, 44]

Here, electric-field-driven breakdown instead occurs when a charge carrier can gain enough energy from the electric field as it crosses a unit cell to become excited above the correlation gap. This process is illustrated schematically in Fig. 4.1, showing the effective distortion of the band structure caused by the applied electric field. The LZB model is expected to match the experimental results best at low temperatures, when the system is fully gapped and Ohmic transport becomes negligible.
Figure 4.1: Schematic diagram of Landau-Zener breakdown in a correlated system, with energy $\omega$ plotted against spatial coordinate $R$. The applied electric field causes the band structure to “tilt,” which results in the valence and conduction bands both touching the zero-energy level. These points are separated by a spatial distance $R_2 - R_1$, which is the length scale over which a charge carrier gains sufficient energy to overcome the correlation gap. Diagram reproduced from [46].

The scaling factor $A$ sets the overall curve slope, while $V_0$ represents a threshold voltage (or electric field), above which the current increases rapidly. Fig. 4.2a shows fits of the experimental $I(V)$ curves using this model for each film thickness at selected temperatures. Fitting parameters $A$ and $V_0$, which are plotted against temperature in Fig. 4.2b, were chosen for best agreement between the fit and the experimental data at low bias. The model typically provides the best fit at low bias and low temperatures, becoming less satisfactory at higher bias and temperatures. The overall quality of the fits was approximately the same for all film thicknesses. The model’s assumption of a threshold voltage (or field), below which there is very limited conduction, is only consistent with the experimental $I(V)$ curves at the lowest temperatures (near
2 K). At higher temperatures (5 K and above), the slope of the $I(V)$ curve is non-zero and approximately linear close to zero applied bias. This suggests that the temperature evolution of the Fermi surface gapping is incomplete at temperatures above approximately 2 K, and the kink found in the resistivity curves near $\sim$5 K may mark a crossover to the LZB regime. It is important to note that while other LZB models for $I(V)$ exist, model (1) provides the best agreement with this experiment. (As an example of such an alternative, a model of LZB presented by Eckstein et al.,[47] is found to be less adequate than (1), as shown briefly in Fig. 4.3.)
4.2 Back-to-Back Schottky Diodes

An alternative model worth considering in the case of contacts between metals and gapped material is that of Chiquito et al., which describes back-to-back Schottky diodes and has been reported to explain the \( I(V) \) behavior of one-dimensional semiconductor SnO\(_2\) nanobelts contacted by various metals. \[48\] In this case, the nonlinear effects observed are primarily due to the work function of the metal used to
contact the semiconductor, which is a situation well described as a Schottky interface, at the two ends of a narrow strip of otherwise ballistic conductor. The model can adequately account for a range of work functions for commonly used contact metals, as well as describe asymmetric behavior that results from microscopic differences between two nominally identical contacts on the same device, for samples measured at and above room temperature. When we attempted to adapt this result to model our $I(V)$ curves obtained at temperatures below 100 K, we found that a kink in the fit near the origin (which is small when the temperature parameter is of order 300 K) becomes the dominant feature over the relevant range of bias voltage ($< 1$ V). We conclude that this model is not valid for the present situation. This is not wholly unexpected, recalling that for the present case the transmission line analysis showed that the effects of contacts are relatively small.

### 4.3 Space-Charge-Limited Current

Finally, one could imagine that a model of space-charge-limited current, in which charge traverses a nominally insulating region (vacuum or solid state), might be salient to the present situation. In the space-charge-limited current picture, the bulk medium is sufficiently insulating that charge entering the medium can “pile up” near one contact, creating a non-uniform charge distribution and altering the electric field environment. For the thin film case, Grinberg *et al.* calculate that the current density $J$ should be proportional to $V^2$. [49] When applied to the present case, this model systematically fails to match the experimental data, with the fit falling below at low bias and above at high bias (see Fig. 4.3).
Figure 4.3: Examples of $I(V)$ curve fits to 16 nm film data using three trial models: The LZB model of Oka and Aoki,[44] an alternative LZB model of Eckstein et al.,[47] and a space-charge-limited current model.[49] The first LZB fit is qualitatively the best; the second LZB fit is nearly as good at low bias but noticeably fails at high bias, and the space-charge-limited current fit systematically fails at both low and high bias.
4.4 Electric-Field-Driven Breakdown

One further consideration regarding the breakdown process is whether the relevant parameter is the voltage bias or the electric field. The LZB model assumes that the electric field, established by the voltage drop across a characteristic distance of the lattice, causes the breakdown process to occur. If electric-field driven breakdown is indeed the cause of the nonlinear differential conductance, signatures should be visible in the transport data. In order to check for evidence of this, $dI/dV$ was plotted considering the independent variable to be the electric field $E$, defined as the dc bias divided by the inter-electrode distance. Plots of $dI/dV$ vs. $E$, shown in Fig. 4.4, demonstrate that the data from various gap sizes collapse onto a common curve shape for 3.85 nm sample at $T = 1.8$ K and for the 10 nm sample at $T = 2$ K and 5 K, but not for higher temperatures, or for the 16 nm sample at any measured temperature. The observed overlap in $dI/dV$ vs. $E$ supports the conclusion that the electric field is indeed the parameter responsible for breakdown in the nearly-fully-gapped, low-temperature state in the presence of sufficiently large strain. The 16 nm sample, which likely has comparatively lower strain overall, may require even lower temperatures for the pseudogap to fully develop.
Figure 4.4: Plots of $dI/dV$ vs. $E$ for each sample thickness at $T = 1.8$ or 2 K, 5 K, and 10 K. When plotted against $E$, the curves for the 3.85 nm sample at $T = 1.8$ K and for the 10 nm sample at $T = 2$ K and 5 K overlap well. This overlap disappears at higher temperature, and does not appear for the 16 nm sample at any measured temperature.
We have explored the electronic properties of NdNiO$_3$ thin films via nano- and micro-scale transport measurements. These experiments show a nonlinear regime below the nominal metal-insulator transition temperature. A transmission line analysis demonstrates that contact effects are not dominant and must not be chiefly responsible for the observed nonlinear transport, especially at low temperatures. Self-heating is likewise determined not to be an important source of the nonlinearity based on the observed evolution of the transport properties with bias and temperature. The evolution of the $I(V)$ and $dI/dV$ vs. $V$ curves suggests that the gapping of the Fermi surface upon cooling is not complete until the temperature is well below $T_{MIT}$. Below $T = 2$ K, when conduction is no longer Ohmic, a Landau-Zener breakdown model designed for strongly correlated systems (with electric field, rather than bias voltage, as the driving parameter) is adequate to describe the $I(V)$ curves. The $dI/dV$ vs. $E$ curves of the two most resistive samples support this conclusion at low temperatures.

The nonlinear transport observed in these systems is a compact representation of the complex physical phenomena that govern correlated conduction processes, and yet these transport data are not readily decomposed to provide a complete physical picture. The ideal model, explaining the crossover from Ohmic transport to breakdown,
and taking into account the effects of intrinsic transport properties, self-heating, and contacts, does not exist. Lacking such a universal theoretical approach, we can still narrow the range of possible explanations for nonlinear transport by way of systematic measurements (here, e.g., $I(V)$ curves as a function of length and temperature). Additional and complementary information could potentially be obtained from transport measurements at even lower temperatures (at which the NNO films should be even more gapped), pulsed measurements (to study the effects of self-heating), and crystal-orientation-dependent measurements (to study any anisotropy in the transport).
Figure A.1: Schematic of summing amplifier design.

LF412CP (dual 411) used for all op-amps.
First two stages built on one op-amp; the third is on a second op-amp.
The 412 takes +/- 3.5 to 18 V supplies; lock-in preamp power is nice for this.
References


