

Gaps and pseudogaps in perovskite rare earth nickelates

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We report on tunneling measurements that reveal the evolution of the quasiparticle state density in two rare earth perovskite nickelates, NdNiO₃ and LaNiO₃, that are close to a bandwidth controlled metal to insulator transition. We measure the opening of a sharp gap of ~30 meV in NdNiO₃ in its insulating ground state. LaNiO₃, which remains a correlated metal at all practical temperatures, exhibits a pseudogap of the same order. The results point to both types of gaps arising from a common origin, namely, a quantum critical point associated with the T = 0 K metal-insulator transition. The results support theoretical models of the quantum phase transition in terms of spin and charge instabilities of an itinerant Fermi surface. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4907771]

Second order or continuous T = 0 K Mott transitions are believed to be tied to many interesting phenomena, such as marginal Fermi liquid behavior and quantum spin liquid states.^{1–4} A continuous quantum phase transition (QPT) is *quantum critical*, which implies the presence of characteristic energies that vanish on approaching the transition point from either direction. On the side for which the ground state is insulating, several obvious energy scales exist, such as the single-particle gap, or the critical temperature for a thermally driven metal-insulator transition (MIT) and/or magnetic ordering transition. On the metallic side of the T = 0 K Mott transition, one has a correlated metallic state without a gap or a T > 0 K transition; in this regime, it is more challenging to find evidence for a low energy scale associated with Mott physics.

The rare earth perovskite nickelates^{5,6} with chemical formula $RNiO_3$ are a canonical class of transition metal oxides exhibiting a bandwidth controlled Mott transition⁷ that is controlled by the size of the rare earth ion R,⁸ which tunes the Ni e_g bandwidth. The two materials studied here, LaNiO₃ and NdNiO₃, sit on opposite sides of the T = 0 K transition (see Fig. 1): LaNiO₃ remains metallic at all practical temperatures, whereas NdNiO₃ is an antiferromagnetic insulator at 0 K, exhibiting a thermally driven MIT at high temperatures.

Here, we use electron tunneling spectroscopy to investigate the low energy scale on both sides of the T = 0 K QPT. Tunneling probes the single particle density of states in correlated electron systems,⁹ with a fine energy resolution over a wide temperature range. We show that in NdNiO₃, a sharp gap of ~30 meV develops at low temperature. The gap broadens but persists as a *pseudogap*, i.e., a depression of the tunneling conductance, to temperatures above the MIT. Furthermore, LaNiO₃ shows a similar pseudogap feature, *despite* its metallic behavior. The characteristic temperatures at which these features appear and the energy (voltage) scale of the features themselves are comparable, and both are much smaller than the e_g bandwidth and Coulomb energy U (~4 eV¹⁰), suggesting a continuous or nearly continuous nature of the T = 0 K bandwidth controlled Mott transition.

Coherently strained, 16.5-nm-thick epitaxial NdNiO₃¹¹ films and 30-nm-thick epitaxial LaNiO₃¹² films were grown on (001) LaAlO₃ by RF magnetron sputtering. Transmission electron microscopy of the NdNiO₃ film showed that ~20% of the area was an unknown NiO_x phase. X-ray diffraction

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FIG. 1. $RNiO_3$ phase diagram near the QPT, after Torrance *et al.*⁸ The temperature axis is scaled so that the transition temperature coincides with that observed in the films under investigation.

showed the majority phase to be epitaxial NdNiO₃. Resistance versus temperature measurements were obtained on the films before processing and used as a bench mark indicator of potential damage during processing. A schematic top view of the 4-terminal tunnel devices is shown in Fig. 2. They were fabricated by evaporating ~1 nm of Al *over the entire film*. The Al covered *R*NiO₃ films were heated again for 30 min in pure oxygen at 600 °C to form the Al₂O₃ tunnel barrier and to ensure that the film remained in a fully oxidized state. The films were patterned by scribing through openings in a mask and an insulator was deposited through the same areas to mitigate potential shorts to the Al counter electrodes in the areas physically abraded by the mini-scribe. Al counter electrodes were deposited by thermal evaporation through another shadow mask, resulting in 4 tunnel junctions on each 5×5 mm² square chip. Electrical connection was made by In soldering to the ends of the inscribed strip of the *R*NiO₃ and the ends of an Al counter electrode. Electrical measurements were made with a Keithley source-meter while the test device was mounted on the cold finger of a closed cycle refrigerator that could reach 7.5 K. Four-terminal measurements mitigate complications that would mask the tunnel conductance by the series resistance of the film, which rises dramatically for NdNiO₃ below the MIT.



FIG. 2. A schematic of the tunnel junctions for a 4-terminal measurement of conductance. It also allows a two-terminal measurement of the conductance of the film that is one electrode of the tunnel device.



FIG. 3. Sheet resistances of the NdNiO₃ and LaNiO₃ films, in the actual tunneling devices under test, as a function of temperature.

Figure 3 shows that the epitaxial NdNiO₃ film is metallic (positive temperature coefficient of resistance) until it undergoes a sharp, hysteretic transition to an insulating state.¹¹ The resistance ratio for these films is ~10⁶. The resistance versus temperature for the film after processing was essentially the same as that measured before the Al/oxidation processing. The two terminal measurement in the tunnel junction arm exhibited the same ~10⁶ resistance rise, hysteresis, and transition temperatures of the preprocessed film. The transition temperature (T_{MIT} ~ 100 K on cooling) is smaller than for bulk ceramic samples,^{13,14} which is believed to be due to substrate induced coherency strains.^{6,15–22} The hysteretic region indicates the coexistence of insulating and metallic domains,^{6,18,23} with the sharp rise in resistance at ~100 K, marking the temperature at which the insulating region is greater than ~¹/₂ the area, so that the conducting domains no longer percolate. At ~70 K and below, while metallic regions exist, the film is predominantly insulating.^{6,18}

We note that the transition to the insulating state in thin film NdNiO₃ is very sensitive to substrate,²⁴ growth conditions, and processing. Indeed, the NdNiO₃ film studied here, deposited on LaAlO₃, exhibits a strong hysteretic transition whereas the nominally same film/substrate discussed by Liu *et al.*²⁴ shows none. We emphasize here that the lateral transport and the tunneling spectroscopy are carried out on the film that is integral to the tunnel junctions.

The epitaxial LaNiO₃ film exhibits a room temperature resistivity of ~0.15 m Ω cm and a resistance ratio [R(300 K)/R(7.5 K)] of approximately 5,¹² similar to bulk.¹³ Like the NdNiO₃ film, the LaNiO₃ film exhibited essentially no significant change in resistance vs temperature following the 1 nm Al/oxidation processing. Resistance versus temperature departs from T,² Fermi liquid behavior, above ~40-50 K. One can infer that the film behaves "Fermi liquid"-like at low T while the high temperature resistance approaches values typical of a saturating metal.²⁵

Figure 4 shows the tunneling conductance versus bias for the NdNiO₃ film taken upon cooling. Below the transition temperature the tunneling conductance at the Fermi energy (zero bias) drops by several orders of magnitude while it is strongly enhanced on either side of the gap. We cannot be certain that the tunnel barrier is Al_2O_3 or a more complex barrier formed with the film surface. More important, nor can we be certain that the tunneling is not simply sensing an interfacial region. We mitigate these concerns by noting in Figure 5 that the zero bias tunneling conductance exhibits hysteresis that mirrors the hysteresis in the lateral transport. The lateral transport and tunneling conductance are probing electron states in the same regions of the film.

The energy resolution in tunneling is $\sim 3k_BT$, which corresponds to 10 meV at 50 K. The tunnel conductance between 50 and 100 K shows a depletion of the density of states below a many-body correlation gap, which tends to conserve state density by transferring states above the gap. These experimental features are analogous to normal-metal/superconductor tunnel junctions.²⁶ As the temperature is lowered, the zero-bias conductance continues to fall, and the tunneling conductance is strongly suppressed. At 7.5 K, the thermal smearing is negligible. There are no metallic NdNiO₃



FIG. 4. (a) Tunneling conductance (logarithmic scale) as a function of voltage for NdNiO₃ versus voltage at various temperatures (measured on cooling). Note the increase in tunneling conductance at elevated voltages, outside the evolving energy gap, as the film becomes insulating. The tunneling conductance completely collapses at the lowest temperatures. (b) Same data as in (a) but normalized to the conductance at 140 K.

inclusions at this temperature, and the tunneling conductance exhibits a sharp turn-on at ~±15 meV. This is a clear indication of a true spectral gap in the insulating state. The gap is an order of magnitude smaller than *a prior* estimate of 200 meV based on optics.²⁷ It is comparable in energy to the scale of the critical temperature of the metal-insulator transition. Taking $T_{MIT} = 100$ K, and the gap $\Delta = 15$ meV, one calculates $\Delta/k_BT_c = 1.7$, which is strikingly close to the mean field, BCS, value.²⁶ This suggests the MIT is driven by excitations of electrons on the scale of the gap, and not much farther from the Fermi energy, and that a mean-field description might apply. At the lowest temperatures, the tunnel conductance collapses outside the gap region as well. Unfortunately, at the lowest temperatures, despite the 4-terminal tunnel device used here, the sheet resistance of the NdNiO₃ film limits the accessible range of voltage drops, so the energy scale of the transfer of state density well outside the gap cannot be determined.

The observation of a well-defined gap in the state density of NdNiO₃ is expected, in the clean limit of an antiferromagnetic insulator. It, nevertheless, differs qualitatively from results obtained by infrared conductivity (even on the same films²⁸) and photoemission measurements,^{29–33} which show a suppression of states near the Fermi energy but no hard gap. It is important to note that tunneling and optical spectroscopies are fundamentally different probes of the excitations of the Mott insulator; tunneling spectroscopy probes the spectrum of single quasi particle states,⁹ while optical conductivity³⁴ measures the coherent (collective) response in the far infrared and incoherent response in the near infrared. The difference between the tunneling spectra and optical spectra should provide theoretical constraints into the nature of the excitations of the correlated ground state.

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FIG. 5. Zero bias tunneling conductance exhibits hysteresis that mirrors the hysteresis in the lateral transport.

Furthermore, the depression in the tunneling spectrum is visible even at temperatures *above* the MIT. This can be seen more clearly in Fig. 4(b), which plots the tunneling conductance normalized to the curve at T = 140 K. The conductance is progressively suppressed between 140 K and 100 K. This is a *pseudogap*, similar to that observed in other correlated materials, in particular, the under-doped cuprates. In the cuprates, the origin of the pseudogap is hotly debated, with proposed origins including preformed superconductivity, charge or spin order, and more exotic scenarios.

The intrinsic nature of a pseudogap feature in NdNiO₃ is further supported by the observation of a very similar effect in LaNiO₃, shown in Fig. 6. At elevated temperatures, the tunneling conductance (dI/dV) exhibits moderate voltage dependence. Below 100 K, the tunneling conductance is depressed over a relatively narrow range of bias voltage (~30 mV), which is especially clear when the low temperature conductance is normalized [Fig. 6(b)]. The depression of the zero bias conductance saturates at low temperature. This is consistent with the fact that LaNiO₃ remains metallic at all temperatures, maintaining a non-zero density of states at the Fermi level.

Given that the LaNiO₃ films investigated here show no evidence of a MIT in the in-plane transport, it is reasonable that the pseudogap is associated with the correlated nature of the metallic state. Broadband infrared conductivity has observed substantial mass enhancement, by approximately \sim 3 times the band structure mass.^{35,36} From the heavy effective mass *m*^{*}, one might naively expect an enhanced rather than suppressed tunneling conductance, since the thermodynamic density of states is inversely proportional to *m*^{*}, but this may be compensated in the single particle density of states, probed by tunneling, by the quasi-particle renormalization factor *Z*. In the Gutzwiller approximation or dynamical mean field theory,³⁷ which neglects momentum dependence of the self-energy, these effects cancel, and the tunneling conductance is neither suppressed nor enhanced. The suppression observed here, therefore, indicates non-trivial momentum dependent self-energy effects.

Electron-electron interactions acting in concert with disorder can also give rise to a gap in tunneling,³⁸ and, indeed, has been reported for LaNiO₃.^{39–41} Far from the metal insulator transition, this produces a singularity in the density of states at the Fermi energy that behaves as $N(E) = N(0) \left(1 + \left[(|E - E_F|)/\Delta\right]^{1/2}\right)$. The scaling factor, Δ , is as large as ~0.58 eV,⁴⁰ which is more than an order of magnitude larger than the energy scale of the pseudo-gap shown in Figs. 4 and 6. Furthermore, the depression in tunneling conductance cannot be fit to the aforementioned



FIG. 6. (a) Tunneling conductance for LaNiO₃ as a function of voltage at various temperatures. (b) Same data as in (a) but first normalized to data at 200 K and then scaled so that the value is one at -75 meV.

voltage dependence. For these reasons, we exclude a disorder-driven gap in the LaNiO₃ films in our experiments.

The results reported here have implications on the theory of the bandwidth-tuned QPT. The observation of a pseudogap in the tunneling density of states for NdNiO₃ and LaNiO, on both sides of the bandwidth-tuned Mott transition in the nickelates, suggests that the pseudogaps are associated with proximity to the T = 0 K MIT. The energy scales of these pseudogaps, determined both from the voltage scale of the conductance suppression and the onset temperature, are comparable and are small compared to the microscopic energy scales of the problem. In particular, the gap in the insulating NdNiO₃ is only \sim 30 meV. The smallness of the gap presents a challenge to local pictures of the gap formation, such as site selective Mott transitions,^{42–44} in which the natural energy scales are of order of the e_g bandwidth 1-2 eV,³¹ the hybridization of the nickel d and oxygen p states, and the on-site Coulomb repulsion U of order ~4 eV.¹⁰ Instead, the small gap supports theoretical models^{45,46} that are based on an itinerant electron liquid for which the incipient instability, be it related to spin and/or charge, arises from a relatively narrow range of states around the Fermi energy. The consistency of the Δ/k_BT_c ratio suggests a mean field model based on such a narrow set of states. These observations are not inconsistent with the proposition that the T = 0 K metal-insulator transition is nearly continuous or quantum critical, and that the pseudogap energy scales probe the (nearly) quantum critical region that emerges from this point, as suggested in Fig. 1.

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