Anatomy of the Mott Transition in Nd$_{1-x}$TiO$_3$: Hole-doping of an Antiferromagnetic Mott-Hubbard Insulator

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NSERC
Metals vs Insulators: polar opposites

Nd$_{1-x}$TiO$_3$

Electrical transport

Optical

Graph showing the electrical transport and optical properties of Nd$_{1-x}$TiO$_3$ for different values of $x$. The graphs depict the temperature dependence of the electrical resistivity and optical conductivity for varying $x$ values.
Metals vs Insulators: Electronic Structure

Zaneen, Sawatsky, Allen

$U, \ W, \ \Delta$

Correlation $d \leftrightarrow d$

Band width $p \leftrightarrow d$

Charge transfer $p \leftrightarrow d$

If $U$ is neglected, (traditional band theory) nearly all TMO’s should be metallic. In fact most are insulating.
A metallic state obtains when:

\[ M - H \ W > U \]

CT \ W > \Delta

\[ \Delta > U > W \]

\[ U > \Delta > W \]

\[ U/W \] a correlation index. For \( U/W > 1 \) d electrons localized and an insulator results.

A metallic state obtains when:

\[ M - H \ W > U \]

CT \ W > \Delta
Most I / M transitions are induced by “doping” of either M-H or CT insulators.

Two famous examples:

La$_{2-x}$Sr$_x$CuO$_4$ - “hole-doping” of an AF CTI

La$_{1-x}$Sr$_x$MnO$_3$ - “hole-doping” of an AF CTI?

Goodenough et al PRB 47 (1993)

Schiffer et al PRL 75 (1995)
Modifications to ZSA due to hole doping of a M-H insulator

(1) new states within M-H gap

(2) introduction of disorder - another localization mechanism

(3) changes in W due to structural changes
(bond angles/bond lengths)
U/W will decrease in general with hole doping
New states near top of LHB

Add one more electron:
\[ \text{cost} = U \]

Add one more electron:
\[ \text{cost} \ll U \]
What is the role of disorder?
(Anderson Phys. Rev. 109(1958)1492)

Random potential, $V_0$
$B = $ TB band width
(1) $B \gg V_0 \rightarrow$ standard band
(2) $B \ll V_0 \rightarrow$ localization
(3) $B \approx V_0 \rightarrow$ mobility edge
Choosing a M-H AF insulator to study: NdTiO$_3$

- $d^1$ MH AFI analog of the $d^9$ CT AFI cuprates
  (well characterized as M-H AF I)

- perovskite Pnma
  control of U/W via Ln$^{3+}$ radius

- convenient hole doping mechanism via Nd$^{3+}$ vacancies

- neutron friendly

- previous studies for comparison/contrast
NdTiO$_3$ electronic structure MHI

$U = 4.0 \text{ eV}$


$W \sim 3 \text{ eV}$
$E_g \sim 0.8 \text{ eV}$
Tunable U/W

Pnma LnTiO₃

Tune

ave. Ti – O – Ti angle and W

D.A. MacLean et al JSSC30(1979)
T. Katsufuji et al PRB56(1997)

U/W ↑ as Ln³⁺ radius ↓
Tunable U/W, contd.
**Doping mechanism**

\[ \text{Nd}_{1-x}\text{TiO}_3 : \quad 0.00 < x < 0.33 \]

\[ \begin{align*} 
\text{Pnma: random Nd}^{3+} \text{ vacancies} \\
0.00 < x < 0.20
\end{align*} \]

\[ \begin{align*} 
\text{Cmmm: ordered Nd}^{3+} \text{ vacancies} \\
0.25 < x < 0.33
\end{align*} \]

\[ \text{Occ. } \sim 1.0 \rightarrow \quad \text{Occ. } \sim 0.5 \rightarrow \]

\[ \text{Nd}_{1-x} \square_x \text{Ti}^{3+}_{1-3x} \text{Ti}^{4+}_{1+3x} \text{O}_3 \]

\[ 1 \square = 3 \text{ holes (Ti}^{4+}) \]

[Amow et al JSSC 155(2000)177]
Remarkable Magnetic Properties

**LnTiO$_3$ Magnetic Order:**
abrupt AF → F

Among M-H AFI’s

NdTiO$_3$ has largest U/W (except SmTiO$_3$ but Sm is not neutron friendly!!)

$\sigma_{\text{abs}}$ (Sm) = 5670 barns

$\sigma_{\text{abs}}$ (Nd) = 50.5 barns
\[ \text{Nd}_{0.966(10)} \text{TiO}_3 \]

\[ \mu_{\text{Nd}^{3+}}: 0.77(3) \mu_B \]

\[ \mu_{\text{Ti}^{3+}}: 0.43(8) \mu_B \]

Note the very small ordered moment on Ti\(^{3+}\). For \( S = 1/2 \) expect ~ 1 B.M.
The phase diagram of slide # 14 and the anomalously small Ti$^{3+}$ ordered moment have been known since the 1980’s but have largely eluded explanation.

For a recent attempt to explain both see:

Previous Studies have located the MIT’s, approximately.

[G. Amow et al, JSSC 155 (2000)]
[Nd$_{1-x}$Ca$_x$TiO$_3$  Katsufuji et al. PRB 56 (1997)]
Detailed study of the MIT (Mott Transition) near $x = 0.10$

**Questions to answer:**

- Mott Transition at discrete $x$ or a range of $x$?
- Does the MH gap collapse at the MIT? (or is the mid-gap band involved?)
- What is the role of disorder?
- Do the magnetic properties ($T_N$, Ti$^{3+}$ ordered moment) track exactly the transport properties?

$\text{Ln}_{1-x}\text{Ca}_x\text{TiO}_3$: Katsufuji et al
• **Synthesis**

\[(1-x)/2 \text{Nd}_2\text{O}_3 + y \text{TiO}_2 + (1-y) \text{Ti}_2\text{O}_3 \rightarrow \text{Nd}_{1-x}\text{TiO}_3\]

<table>
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<tr>
<th>Single crystals</th>
<th>Polycrystalline samples</th>
<th>Bridgeman method</th>
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<td>(a)</td>
<td>(b) bridgeman method</td>
<td>(c) FZ method</td>
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- **Polycrystalline samples**
  - ~1400°C
  - Mo block
  - BN
  - 2-4g
  - C fill
  - ~25 samples
  - C susceptor
  - W plate
  - ZrO₂ insulation
  - induction coil
  - metal plate
  - mullite
  - x ≈ 0.10, 0.04

- **Bridgeman method**
  - ~1800°C
  - 10-12g
  - Ref. Pellet
  - 5-8 cm seed
  - 10-12 cm feed
  - x ≈ 0, 0.15, 0.20

- **FZ method**
  - ~1800°C
  - 10-12g
  - 5-8 cm seed
  - 10-12 cm feed
  - x ≈ 0, 0.15, 0.20

- Synthesis
  - Single crystals
Bridgeman crystals

\[ x = 0.10 \quad \text{and} \quad x = 0.04 \]

5 mm = 5 x 10^6 nm
Floating Zone Crystal

\[ x \approx 0.15 \]
Compositional Analysis

a. Find Nd/Ti ratio $\rightarrow x$

Neutron Activation Analysis ($\sim 100 \text{ mg}$)

Isotopes: $^{151}\text{Nd}$, $^{51}\text{Ti}$

(t$_{1/2}$ = 12.44 min, 5.76 min)

b. Find Ti$^{3+}$/ Ti$^{4+}$ ratio $\rightarrow x$

ThermoGravimetric Analysis

$\text{Nd}_{1-x}\text{TiO}_3 + (7-3x)/4\ \text{O}_2 \xrightarrow{1000^\circ C} (1-x)/2\ \text{Nd}_2\text{Ti}_2\text{O}_7 + x\ \text{TiO}_2$

$\sim 50 \text{ mg}$

Results from a and b consistent to $\sim 0.5\%$
c. Unit cell volume (Guinier x-ray data) scales with x

![Graph showing the relationship between cell volume and Nd value obtained from NAA. The x-axis represents the cell volume (Å³) from Guinier x-ray data, and the y-axis represents the Nd value obtained from NAA. The data points are shown with error bars, and a linear trend line is fitted to the data.]
Sample characterization critical for LnTiO$_3$ phases !!!

LnTiO$_3$ easily oxidized to Ln$_{1-x}$TiO$_3$

ex. “LaTiO$_3$” - $T_N = 125$K, poor metal


Currently accepted: $T_N = 150$K, insulator

“NdTiO$_3$” - $T_N = 0$ !!!!

*(Greedan, JMMM 44 (1984) 299)*

Currently accepted: $T_N = 100(5)$ K

*(Amow and Greedan, JSSC 121 (1996) 443.)*
Electrical Transport

Resistivity

\[ \rho = \frac{RA}{l} \]

\( x = 0.33 \)

Ag paste

Ag wire 0.05-0.1mm
Nd$_{1-x}$TiO$_3$ → Metallic → Insulating → M/I vs T → Metallic

$\rho$ (mohm.cm).

T (K)

$x = 0.33$

$x = 0$
Arrhenius

\[ \rho = \rho_0 \exp(\frac{E_{\text{act}}}{k_B T}) \]

Note: \( E_{\text{act}} \ll \text{M-H gap} \sim 0.8 \text{ eV}. \) Mid-gap states involved
Fermi Liquid

\[ \rho(T) = \rho_0 + AT^2 \]

A is a measure of correlation/ carrier mass.
Kadowaki/Woods: \( A^2/\gamma \sim \text{const.}, \ \gamma \sim (m^*)^{3/2} \)
A (and m*) greatly enhanced at MIT1 boundary!!
Finite MH gap at MIT1

Conclusion: MIT1 results when mid-gap band overlaps the UHB
$\text{Nd}_{2/3}\text{TiO}_3$

$Cmmm$

$3d^0$

$O^{2-}$

$\Delta$

$\triangledown$

$x \sim 0.33$

$\text{MIT2}$

$\text{MH gap} = 0$

$\Delta_{\text{act}}$

$E_f$

$I$

$\text{NdTiO}_3$

$\text{Pnma}$

$3d^1$

$O^{2-}$

$\uparrow E_g$

$x \sim 0$

$\text{MIT1}$

$x \sim 0.10$

$x \sim 0.20$

$x \sim 0.33$
\[ \rho(T) = \rho_0 \exp\left(-\frac{E_a}{kT}\right) \]

Variable-range hopping
\(~25 - 63\ K\)
\(\log \sigma \text{ vs } T^{-0.5}\)

\[ 0.057(11) \leq x \leq 0.079(2) \]

\[ \rho(T) = \rho_o + AT^2 \]
Weak magneto-resistance. Due to scattering by Nd$^{3+}$ moments which order @ 1K?

$\text{Nd}_{0.918(13)}\text{TiO}_3$

$x = 0.082$
How is disorder manifested?

• Suppression of metallic state
• VRH, (variable range hopping) at low T

\[ \sigma = A \exp\left(-\frac{T_0}{T}\right)^n \]

\[ n = \frac{1}{4} \text{ (Mott-Davis)} \]

\[ n = \frac{1}{2} \text{ (with correlation) \ E-S} \]

Use Hill/Zabrodskii method to distinguish exponents

• define \( E = -(1/T)[d(\log\sigma)/d(1/T)] \)
• \( \log E = A + n\log T \)

Disorder plays major role in the localization of carriers in Nd$_{1-x}$TiO$_3$ for $0.057 < x < 0.089$. 

E-S

Mott
Magnetic Properties

• Determine $T_N$ ($T_c$) vs $x$

  For which $x$ does $T_N$ vanish?

• Determine $\text{Ti}^{3+}$ ordered moment vs $x$

  For which $x$ does the moment vanish?

• Correlation with transport properties?
Five ways to measure $T_N$

- Neutron diffraction vs $T$ ⇒ reliable but slow

- ZFC/FC divergence in M/H vs $T$
  (NdTiO$_3$ is a canted moment AF ⇒ unreliable, sensitivity to
  – develops a weak F moment magnetic micro structure
  below $T_N$)

- $M_{sat}$ vs $T$ in ZF ⇒ slightly better but still unreliable

- $C_p$ vs $T$ ⇒ best (but time consuming)

- “Fisher’s” heat capacity: $d(\chi T)/dT$ ⇒ fast and reliable

[M.E. Fisher Philos. Mag. 7 (1962) 1789]
Neutron Diffraction

\[ x = 0.019(6) \]

\( T_c = 88 \text{K} \)
$T_N = 88.2K$

$x = 0.019(6)$
$x = 0.064(10)$

$x = 0.11 \quad PM!$

$x = 0.33$

$x = 0$
Compare “real” heat capacity with Fisher’s heat capacity
\( d(\chi T)/dT \) vs \( T \)

\[ \chi = 0.019(6) \]

\[ \chi = 0.064(10) \]
Neutron diffraction

- $\lambda \approx \text{Å’s}$
- Neutrons are scattered by nuclei
- Neutrons ($S = 1/2$) interact with unpaired spin density

Magnetic scattering
Nuclear scattering
$x = 0.034(10)$

$\lambda = 2.36964 \text{Å}$

- $R_B: 2.22\%$
- $R_{mag}: 14.4\%$

G\textsubscript{x}C\textsubscript{y}

Nuclear

Magnetic
\[
\begin{align*}
\text{LRO: } & x \leq 0.071(10) \\
\text{SRO: } & 0.074(9) \leq x \leq 0.089(1) \\
\text{PM: } & x = 0.095(8)
\end{align*}
\]
$x = 0.079(2)$

spin-glass-like

$x = 0.089(10)$

paramagnetic

$x = 0.098(10)$
Magnetic phase diagram

\( \text{Nd}_{1-x}\text{TiO}_3 \)

- \( \chi(T) \)
- \( M(T) \)
- \( C(T) \)

\( x \)

\( T_{\text{order}} \) (K)
The phase diagram for Nd$_{1-x}$TiO$_3$

$x \leq 0.071(10)$ LR AFI/PMI

$0.074(9) \leq x < 0.089(1)$ → SR AFI/PI/PMM Anderson Localization

PM metal at $x = 0.098(10)$: [Ti$^{3+}$] = 71(4)\% or 29\% hole doping

$x = 0.243(10)$ → MIT2
Ln$_{1-x}$Ca$_x$TiO$_3$: Katsufuji et al

Summary and Conclusions

Compare Nd$_{1-x}$TiO$_3$ and Ln$_{1-x}$Ca$_x$TiO$_3$

- Mott transition occurs over a small range of $x$
- unambiguous role for disorder-induced localization ‡

hole conc.
Summary and Conclusions contd.

- determined magnetic structure of NdTiO$_3$, unequivocally (high resolution powder data): G$_x$C$_y$
- traced T$_c$ vs x accurately - first time for a hole-doped MH AFI
- shown abrupt collapse of ordered moment on Ti$^{3+}$ @ x = 0.074
- found SRO AF regime bridging collapse of ordered moment and onset of metallic behaviour, x = 0.095 (first observation)
- AF metallic state does not exist for Nd$_{1-x}$TiO$_3$!!
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Temperature-dependent optical spectroscopy studies of Nd$_{1-x}$TiO$_3$

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Anderson-Mott transition induced by hole doping in Nd$_{1-x}$TiO$_3$

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Effect of hole doping on the magnetic properties of the Mott-Hubbard antiferromagnetic insulator Nd$_{1-x}$TiO$_3$

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High-resolution EELS study of the vacancy-doped metal/insulator system, Nd$_{1-x}$TiO$_3$, $x = 0$ to 0.33.

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FIG. 11. The $\rho(T)$ for two $\text{Nd}_{1-x}\text{TiO}_3$ polycrystalline samp
Note the presence of upturns at low temperatures.

FIG. 12. The electronic resistivity vs temperature for single-crystal pieces with $x \sim 0.15$ and 0.20 compositions in $\text{Nd}_{1-x}\text{TiO}_3$. Note the absence of upturns at low temperatures.