

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

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M. Niewczas  - PPMS instrument

G. Luke , Paul Dube  -- Oxford MagLab & SQUID instruments, helium supply

H. Dabkowska , A. Dabkowski , J. D. Garrett , - floating zone & Bridgeman growth

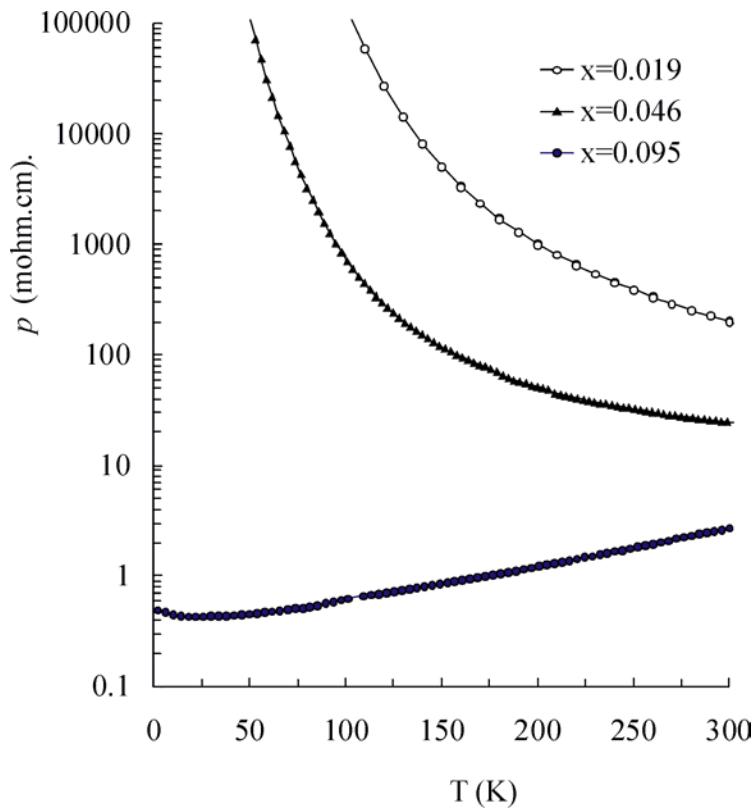
I. Swainson , L. Cranswick  - neutron diffraction

J. Yang , J. Hwang , T. Timusk  - Optical measurements

NSERC

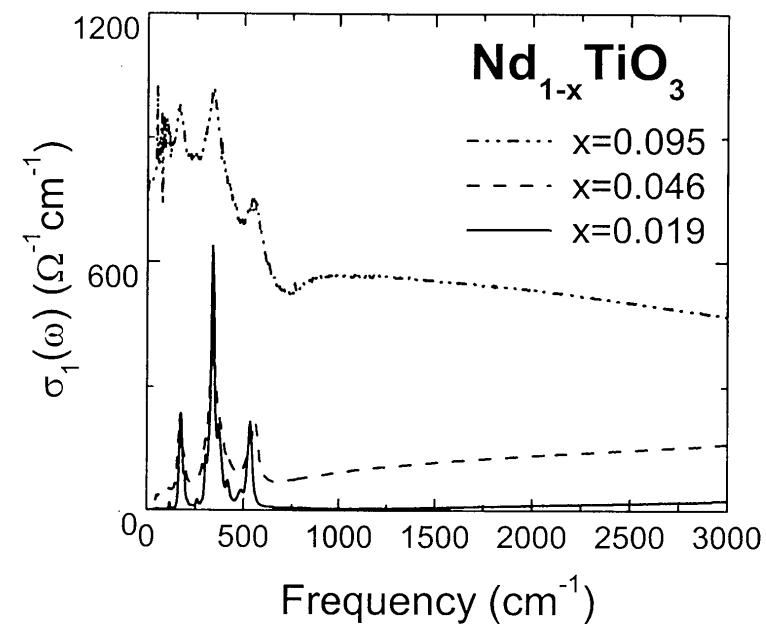
Metals vs Insulators: polar opposites

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



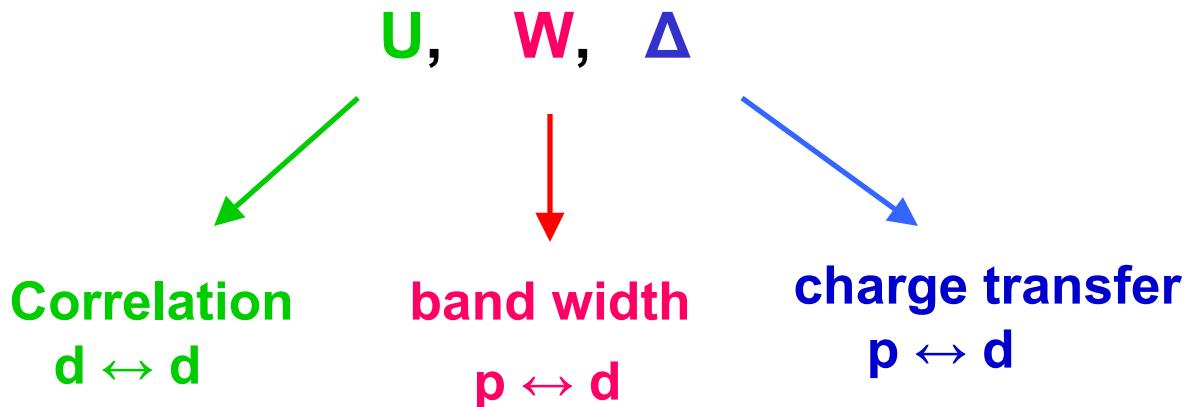
← Electrical transport

Optical →

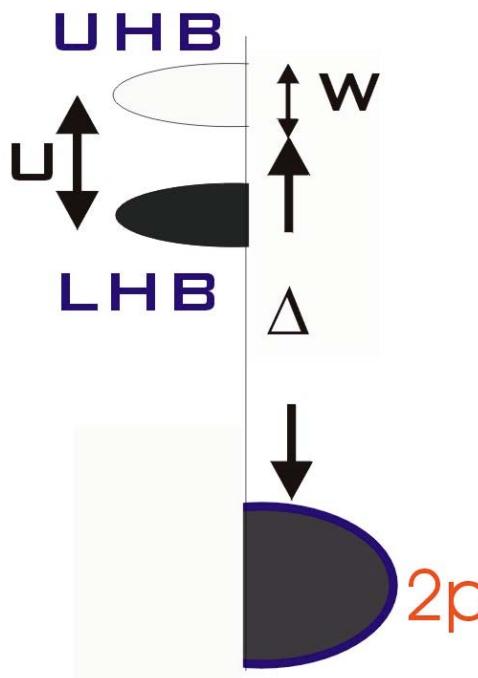


Metals vs Insulators : Electronic Structure

Zaneen, Sawatsky, Allen

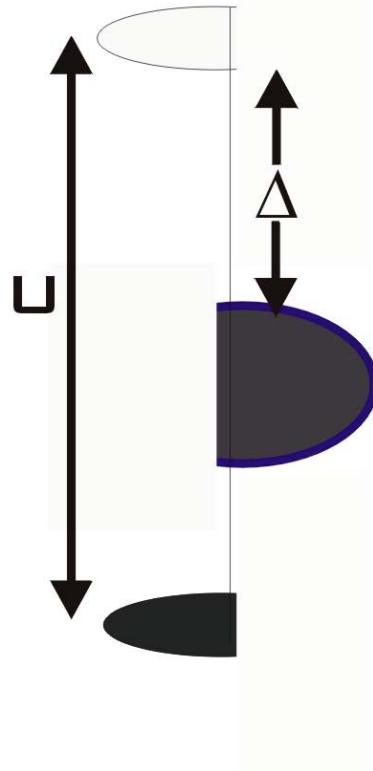


If U is neglected,(traditional band theory)
nearly all TMO's should be
metallic. In fact most are insulating.



$\Delta > U > W$

M-H



$U > \Delta > W$

CT

U/W a correlation index. For $U/W > 1$ d electrons localized and an insulator results.

A metallic state obtains when:

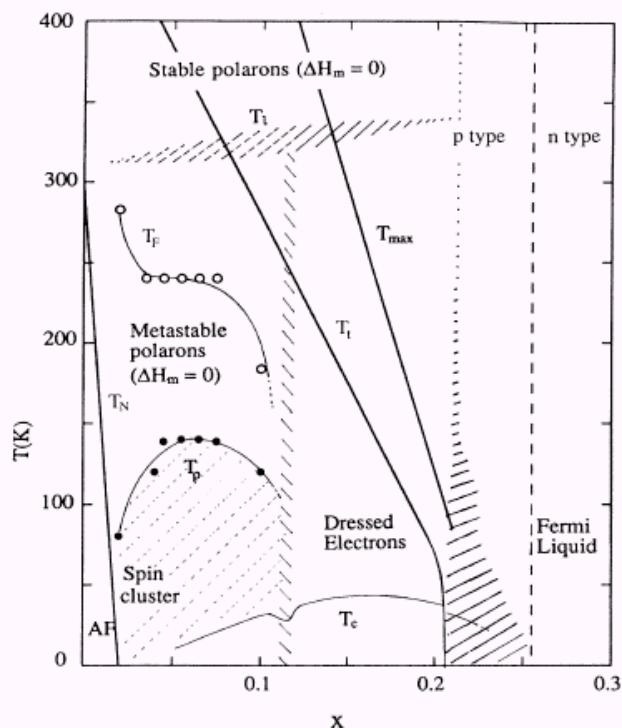
M-H $W > U$

CT $W > \Delta$

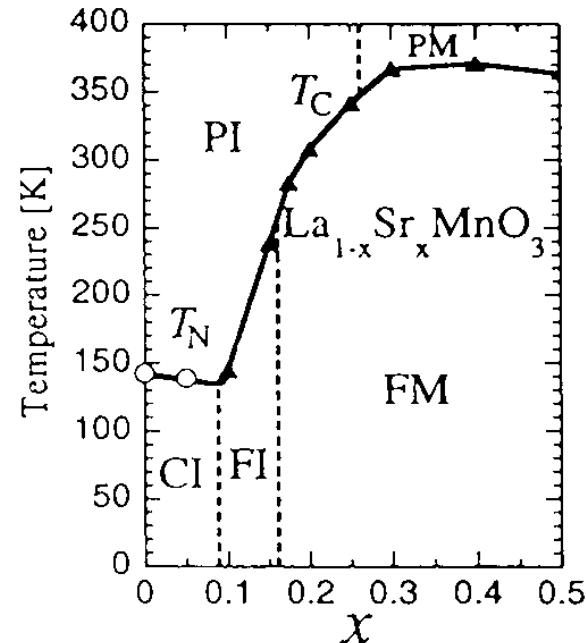
**Most I / M transitions are induced by “doping”
of either M-H or CT insulators.**

Two famous examples:

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



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



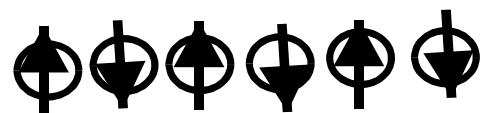
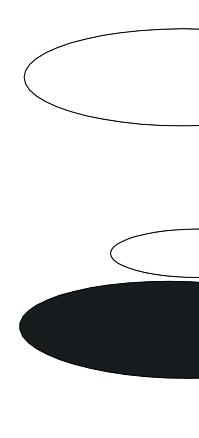
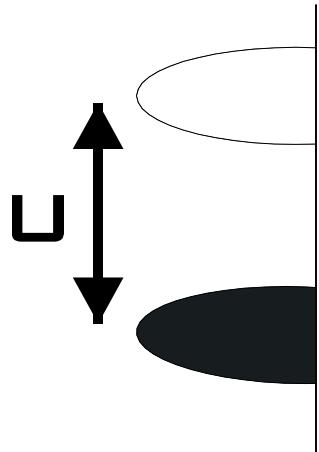
Schiffer et al PRL 75 (1995)

Goodenough et al PRB 47 (1993)

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

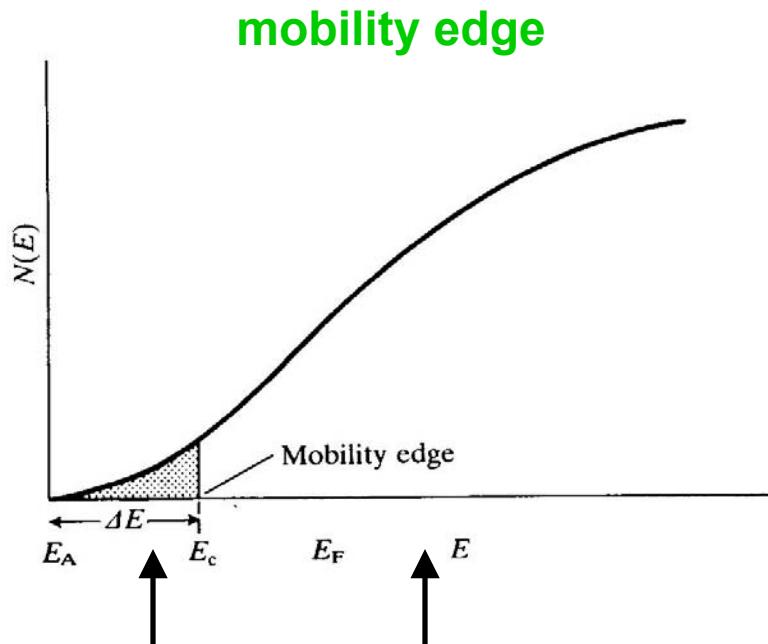
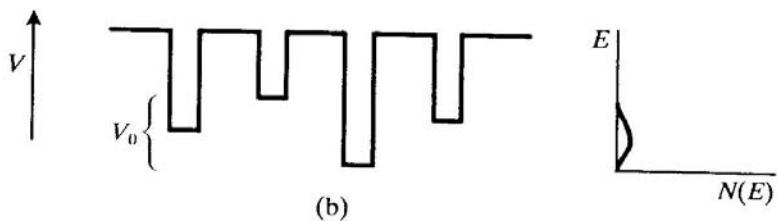
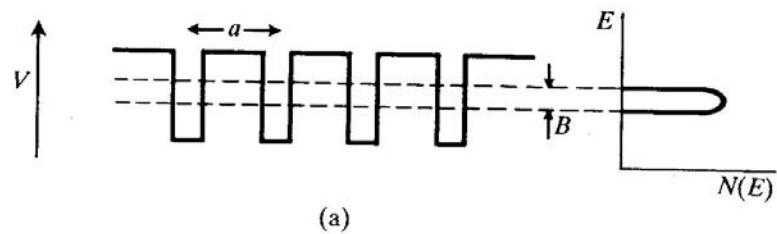


Add one more electron:
cost = U

Add one more electron:
cost $\ll U$

What is the role of disorder?

(Anderson Phys.Rev.109(1958)1492)
 (N. Mott "Conduction in Non-Crystalline Materials" Oxford, 1987)



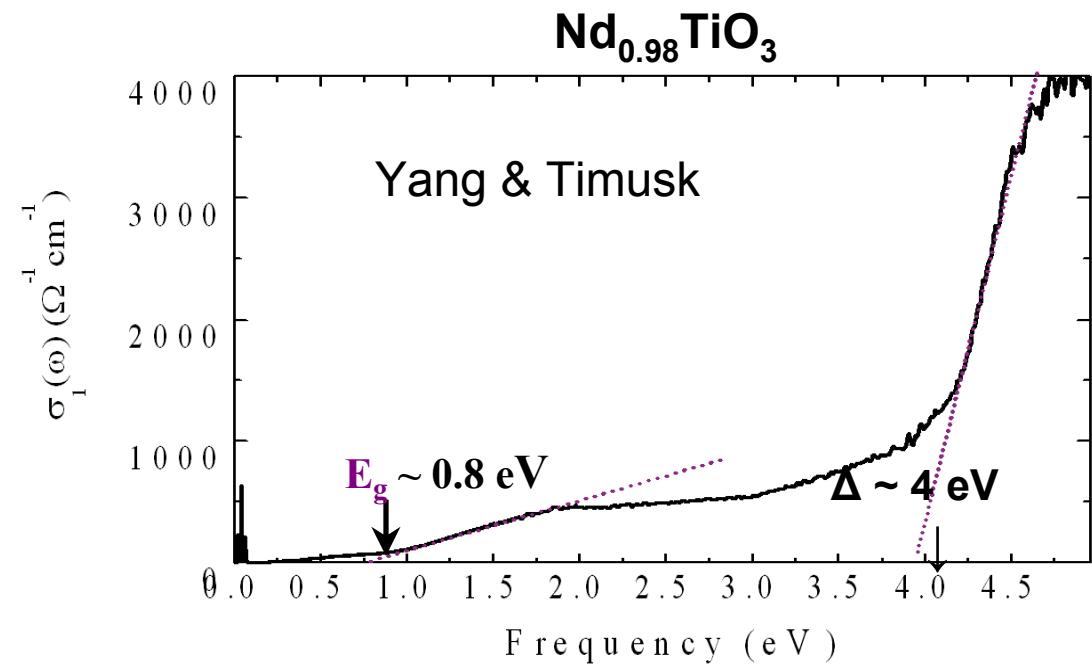
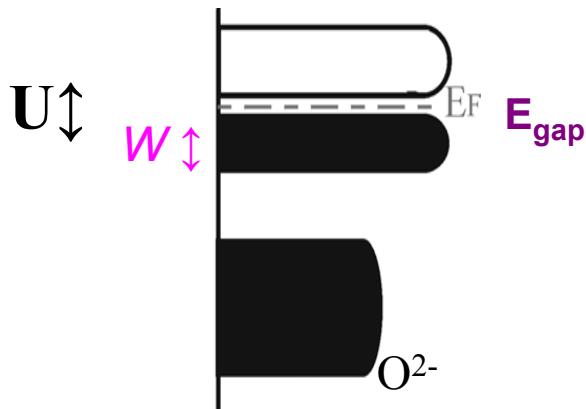
Random potential, V_0
 $B = TB$ band width

- (1) $B \gg V_0 \rightarrow$ standard band
- (2) $B \ll V_0 \rightarrow$ localization
- (3) $B \sim V_0 \rightarrow$ 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

NdTiO₃ electronic structure MHI



$$U = 4.0 \text{ eV}$$

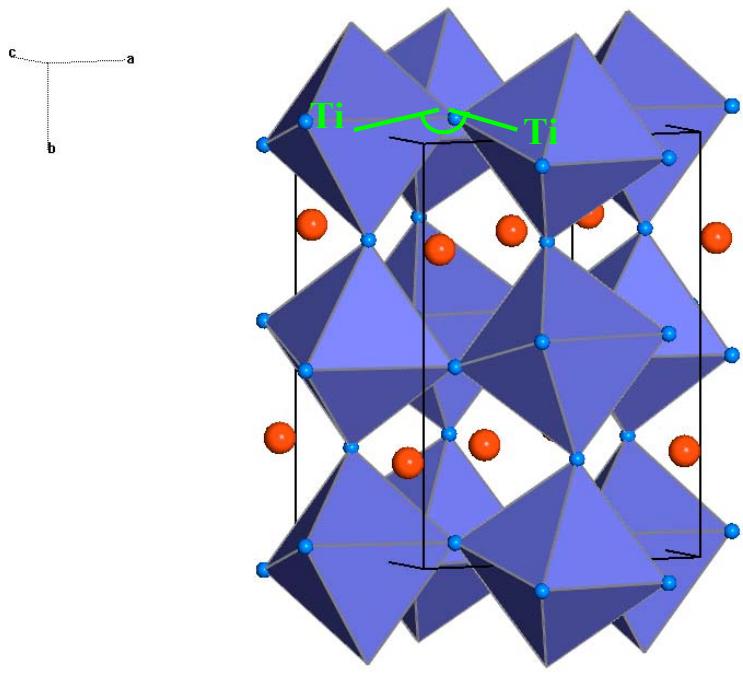
[Tokura, et al. Phys. Rev. B 56, (1997), 10145]

$$W \sim 3 \text{ eV}$$

$$E_g \sim 0.8 \text{ eV}$$

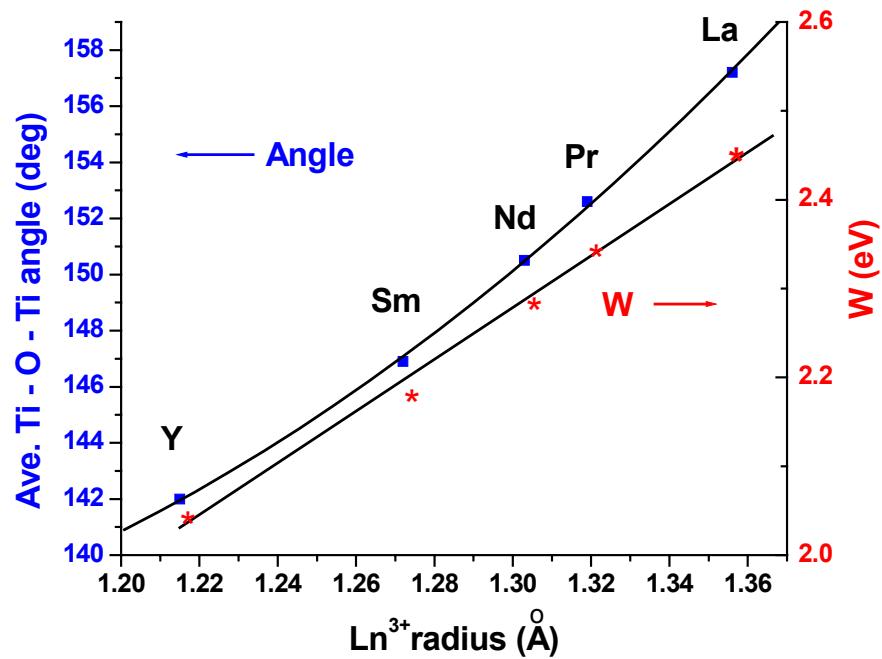
Tunable U/W

Pnma LnTiO_3



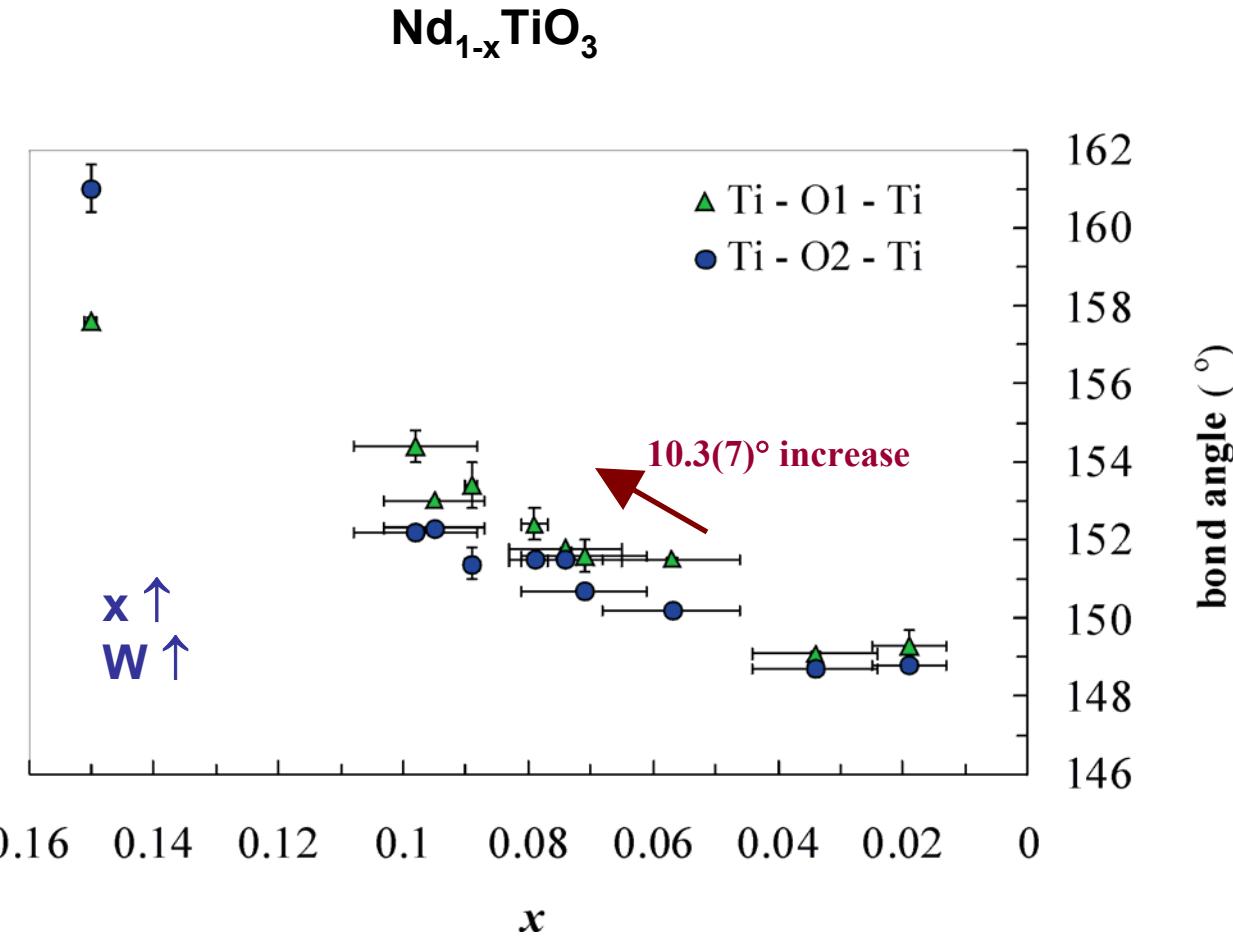
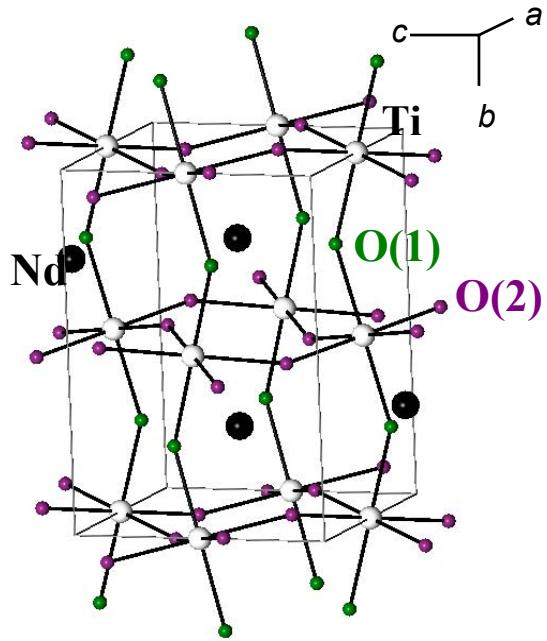
Tune
ave. Ti – O – Ti angle
and W

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

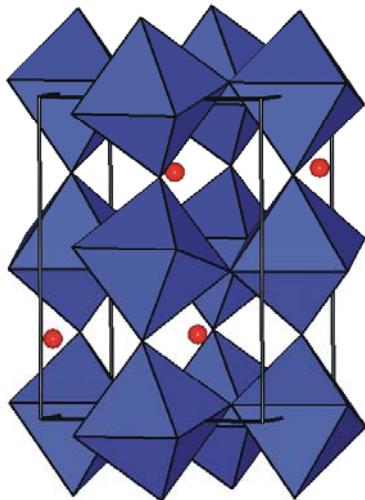


U/W ↑ as Ln^{3+} radius ↓

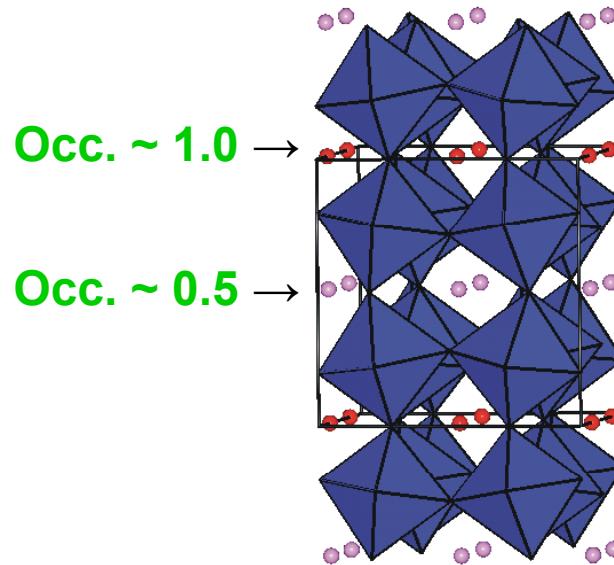
Tunable U/W , contd.



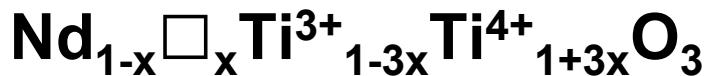
Doping mechanism



Pnma: random Nd^{3+} vacancies
 $0.00 < x < 0.20$



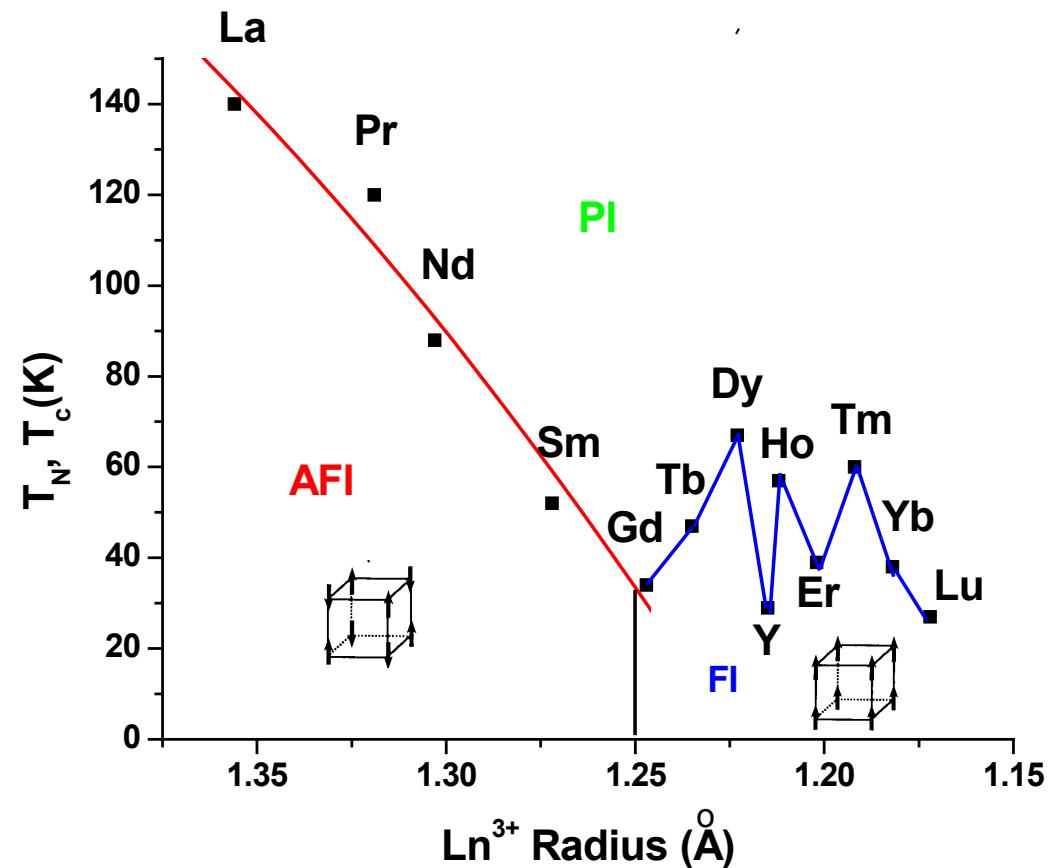
Cmmm: ordered Nd^{3+} vacancies
 $0.25 < x < 0.33$



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

Remarkable Magnetic Properties

LnTiO_3 Magnetic Order: abrupt AF → F

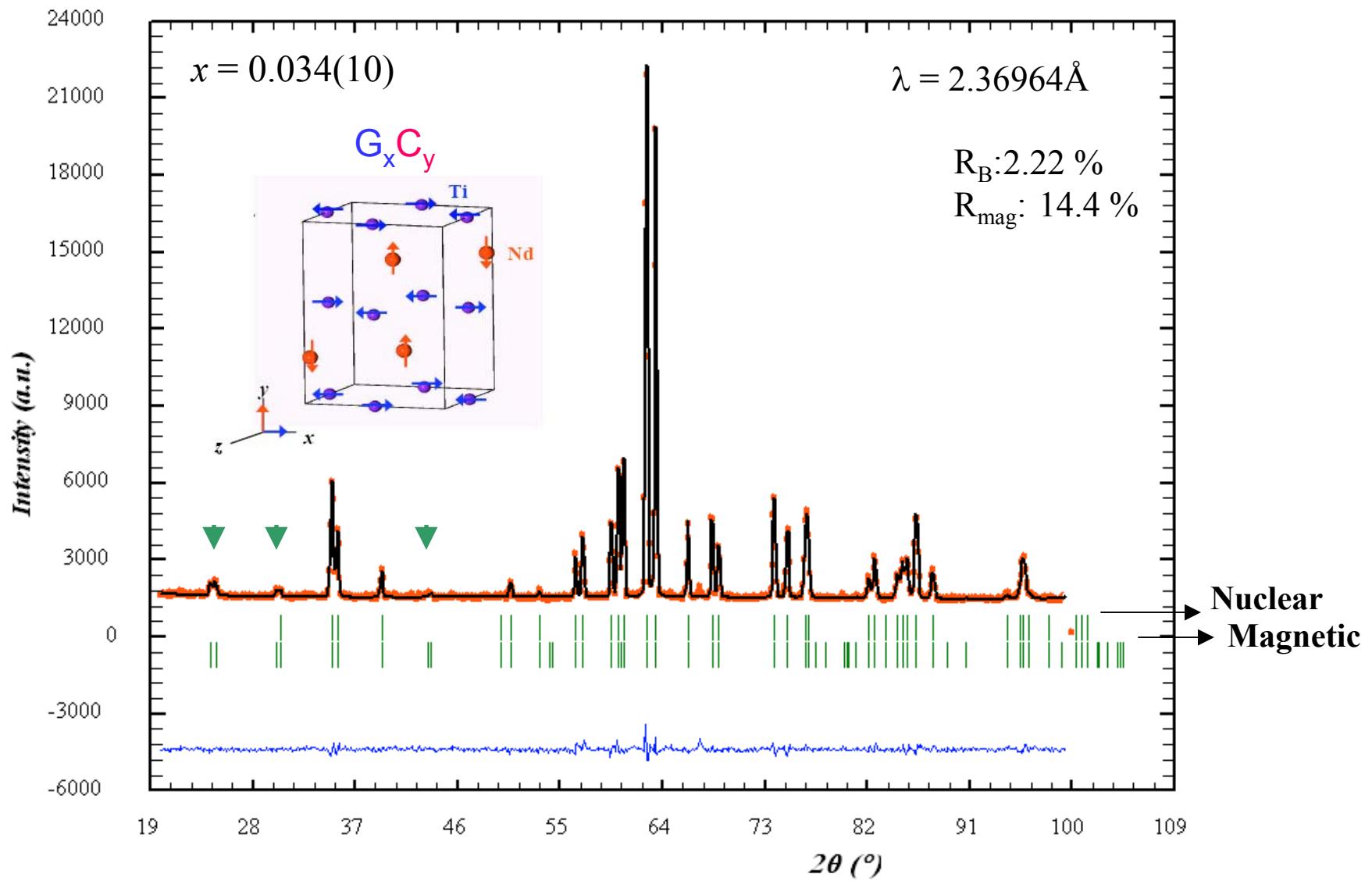


Among M-H AFI's

NdTiO_3 has largest
U/W
(except SmTiO_3
but Sm is not
neutron friendly!!)

σ_{abs} (Sm) = 5670 barns

σ_{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.

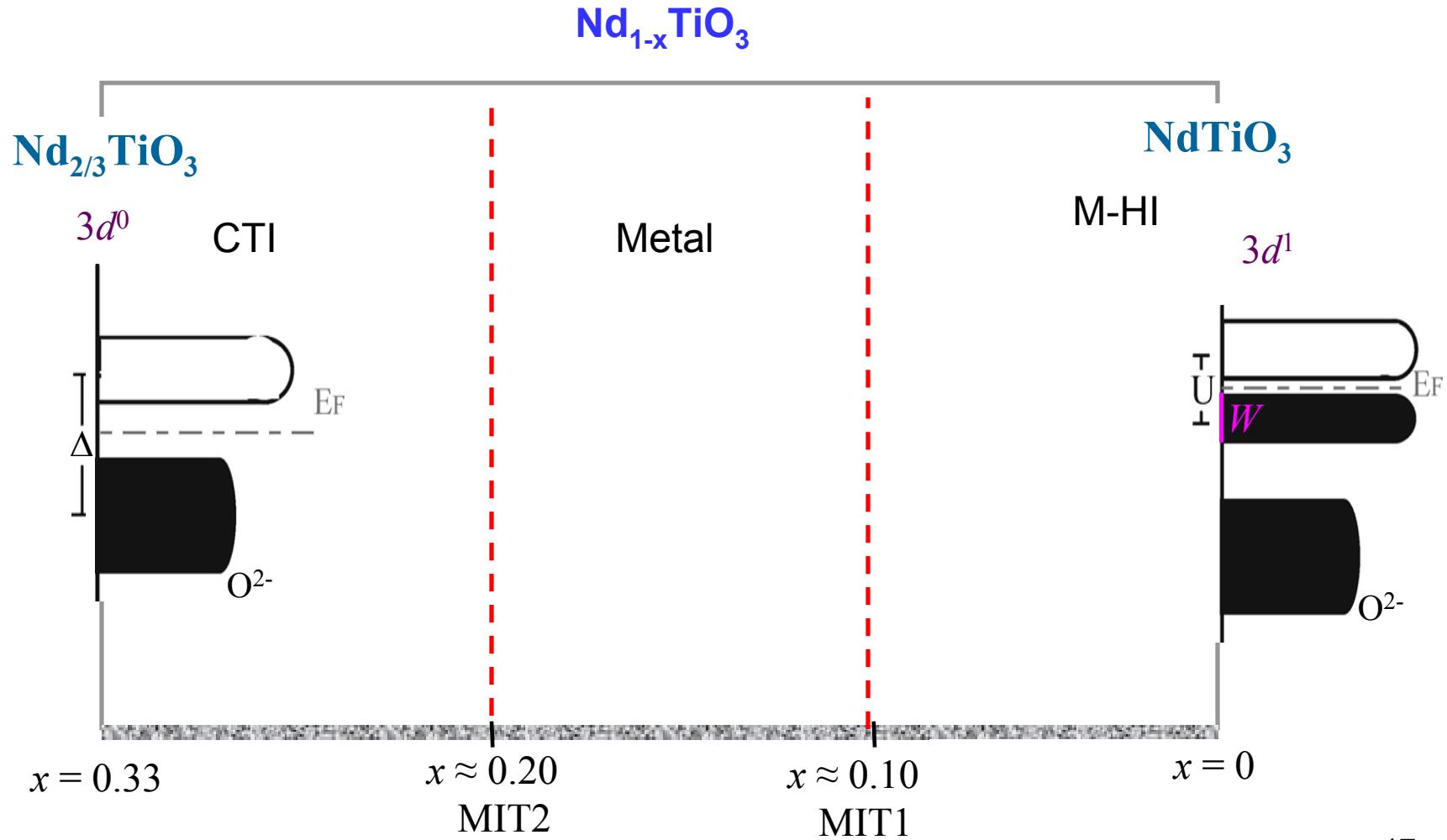
For a recent attempt to explain both see:

M. Mochizuki and M. Imada, J. Phys. Soc. Japan 73 (2004) 1833

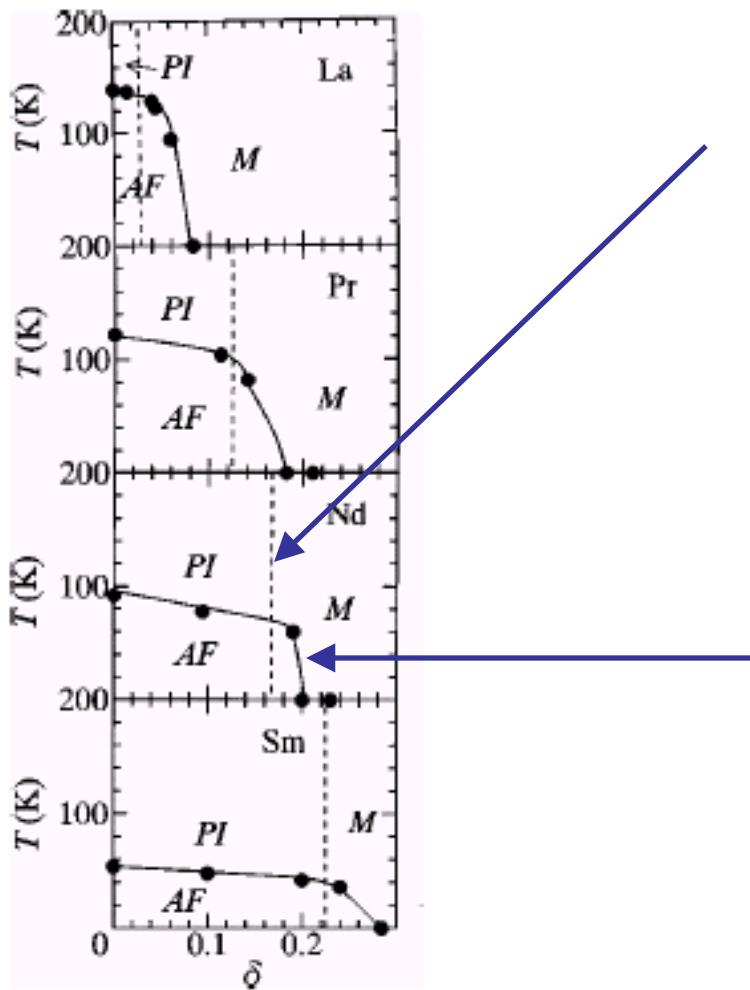
Previous Studies have located the MIT's, approximately.

[*G. Amow et al, JSSC 155 (2000)*]

[$Nd_{1-x}Ca_xTiO_3$ *Katsufuji et al. PRB 56 (1997)*]



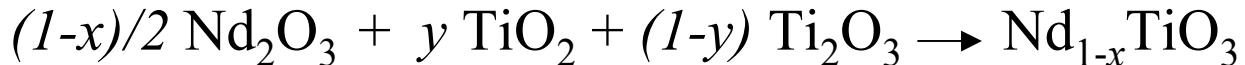
Detailed study of the MIT (Mott Transition) near $x = 0.10$



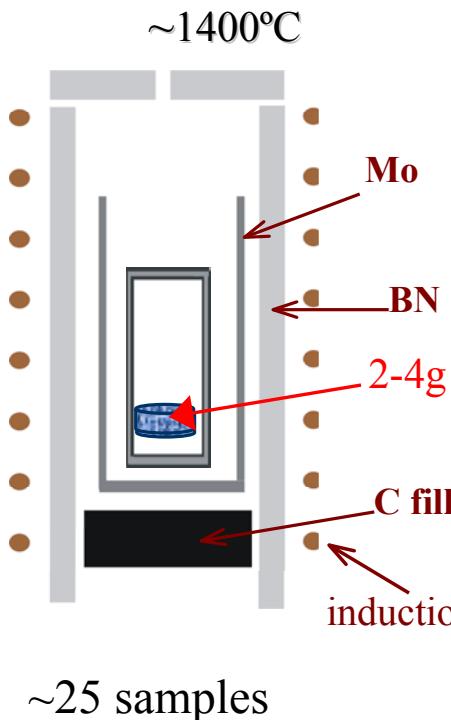
Questions to answer:

- 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 ?

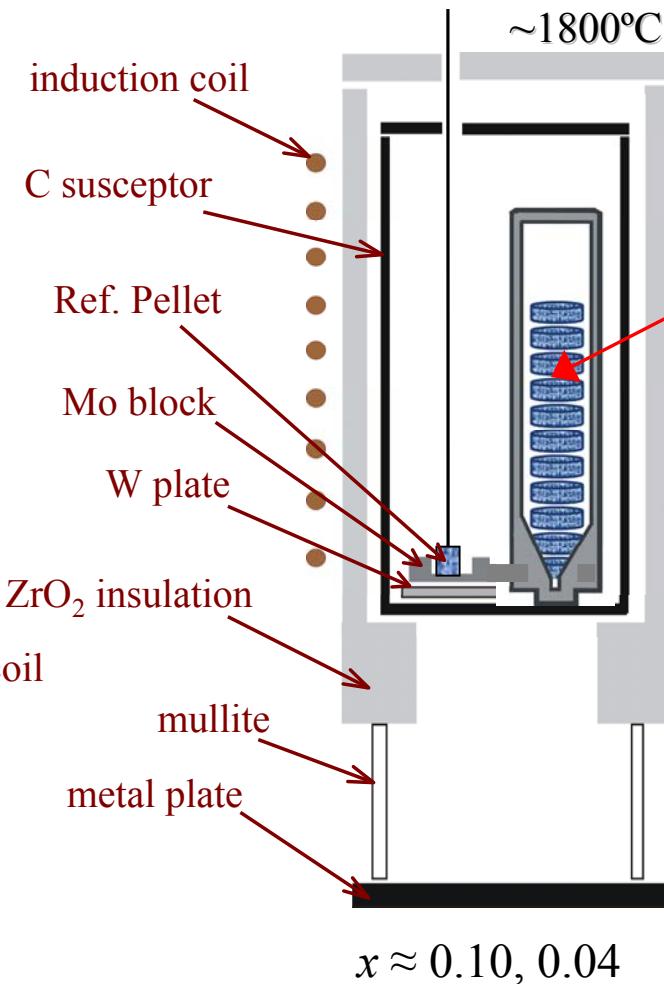
- **Synthesis**



(a) **Polycrystalline samples**



(b) **Bridgeman method**



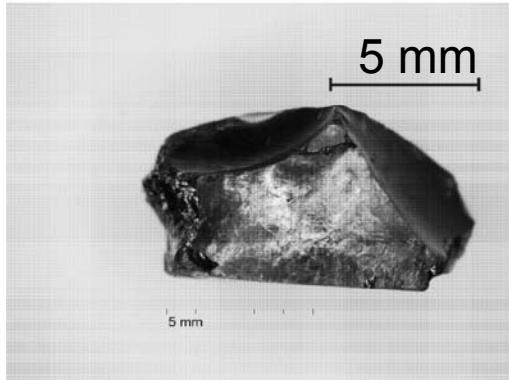
(c) **FZ method**



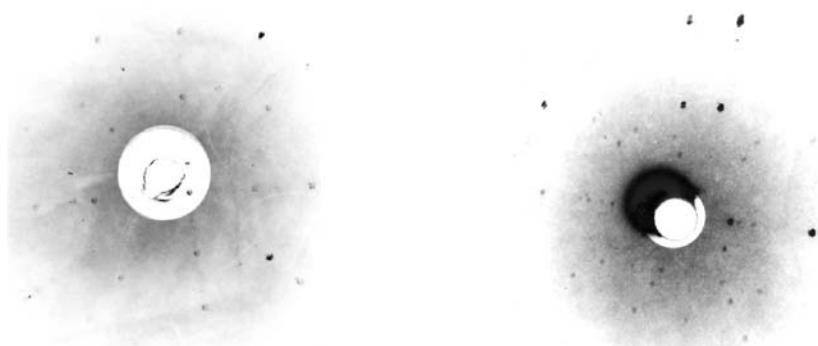
$x \approx 0, 0.15, 0.20$

Bridgeman crystals

$x = 0.10$



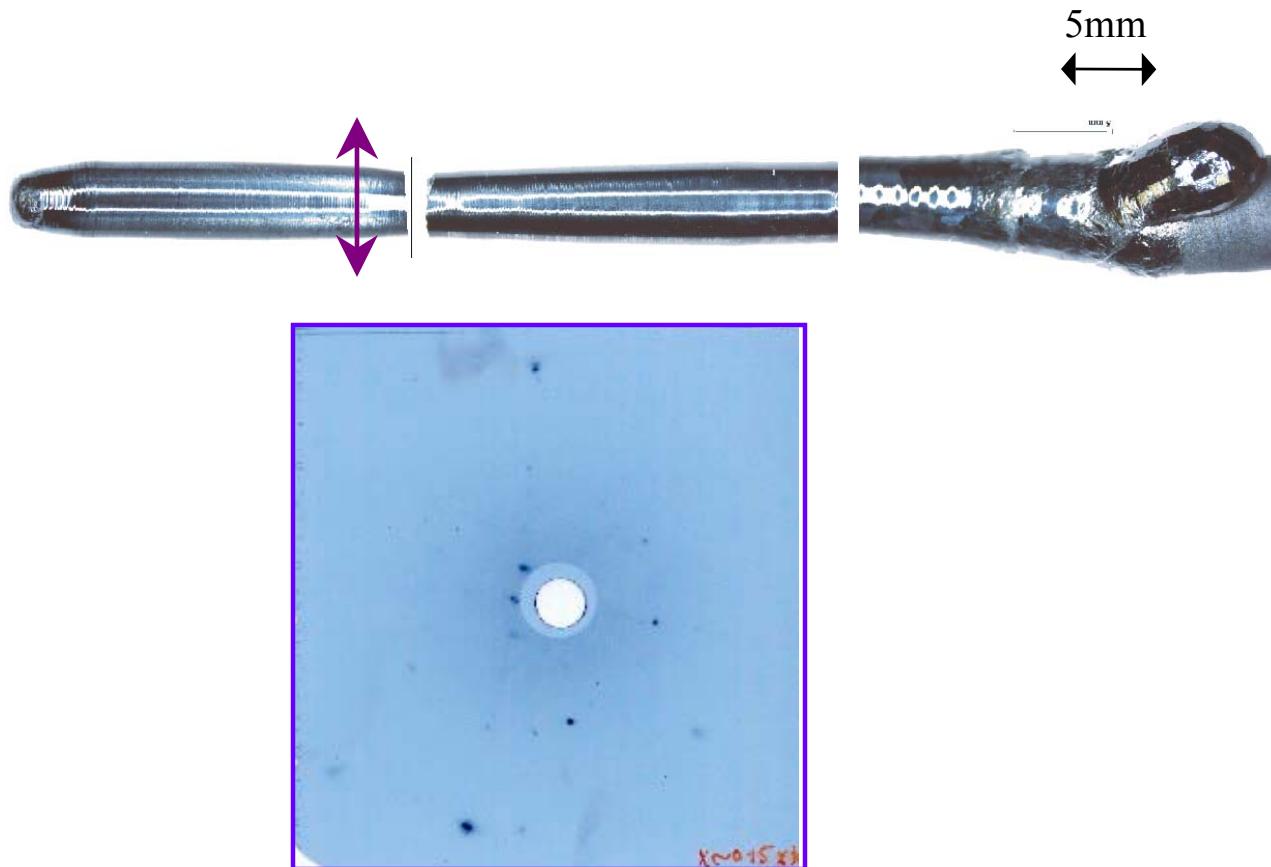
$x = 0.04$



$$5 \text{ mm} = 5 \times 10^6 \text{ nm}$$

Floating Zone Crystal

$$x \approx 0.15$$



Compositional Analysis

a. Find Nd/Ti ratio → x

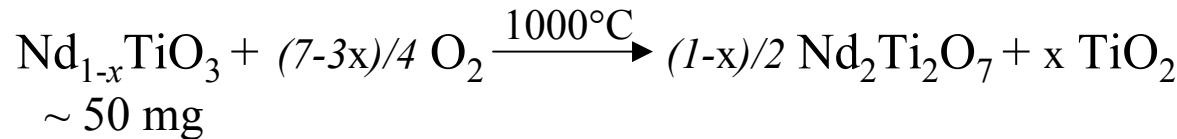
Neutron Activation Analysis (~ 100 mg)

Isotopes: ^{151}Nd , ^{51}Ti

($t_{1/2} = 12.44 \text{ min}$, 5.76 min)

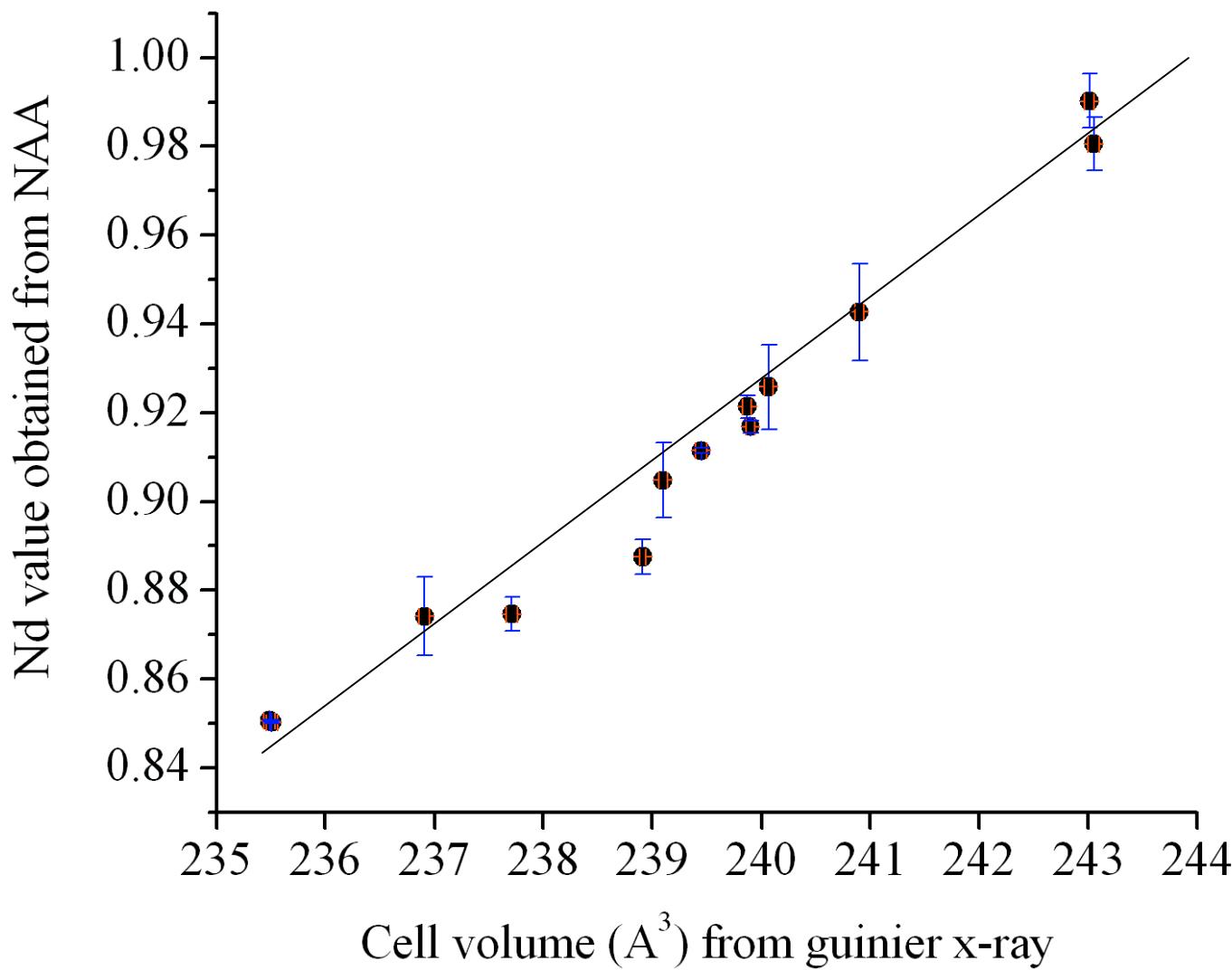
b. Find $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio → x

ThermoGravimetric Analysis



Results from a and b consistent to ~ 0.5%

c. Unit cell volume (Guinier x-ray data) scales with x



Sample characterization critical for LnTiO₃ phases !!!

LnTiO₃ easily oxidized to Ln_{1-x}TiO₃

ex. “LaTiO₃” - T_N = 125K , poor metal

(MacLean and Greedan, Inorg.Chem. 20 (1981)) 1025.

Currently accepted: T_N = 150K, insulator

“NdTiO₃” - T_N = 0 !!!

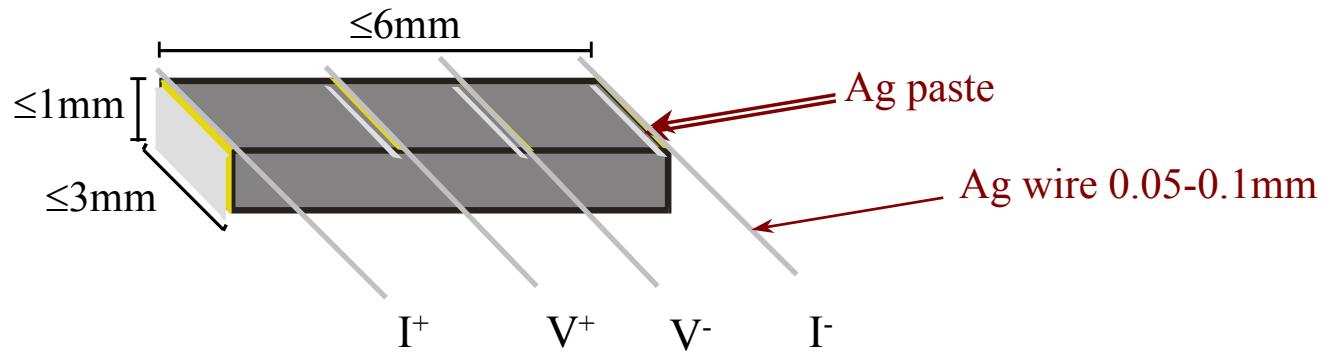
(Greedan, JMMM 44 (1984) 299)

Currently accepted: T_N = 100(5) K

(Amow and Greedan, JSSC 121 (1996) 443.)

Electrical Transport

Resistivity



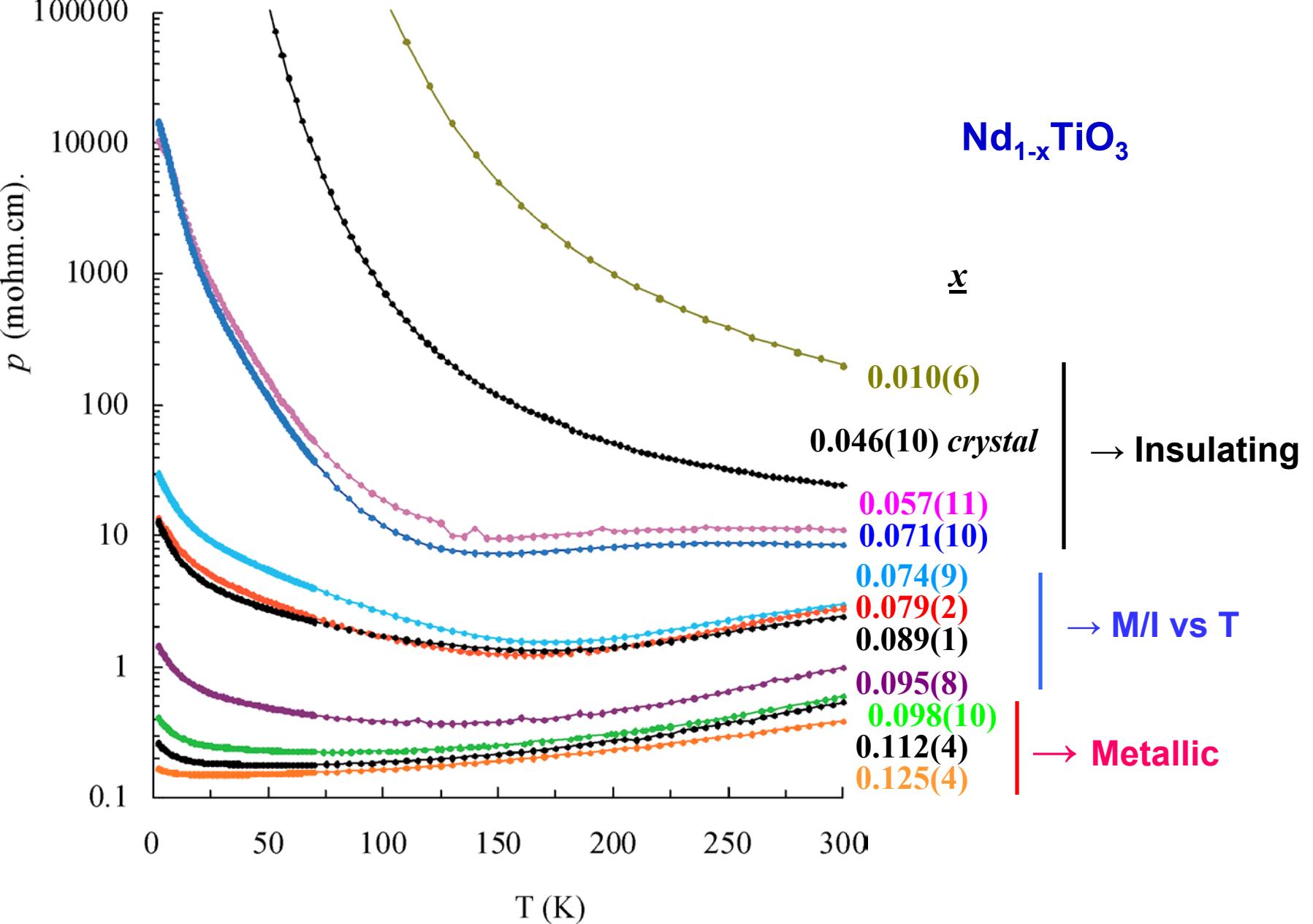
$$\rho = \frac{RA}{l}$$

$x = 0.33$



$x = 0$

25



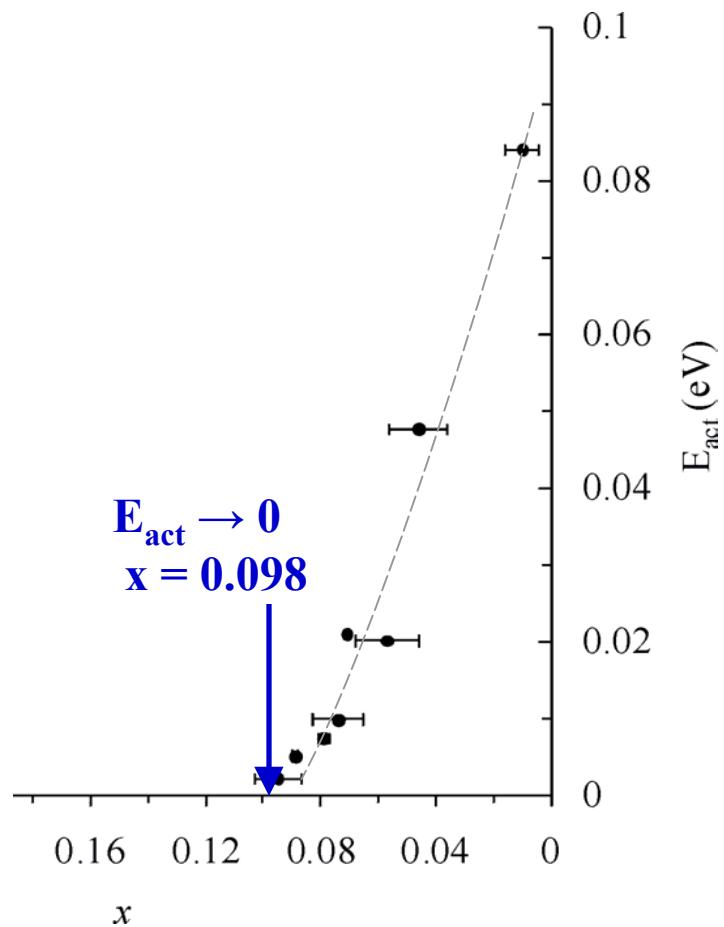
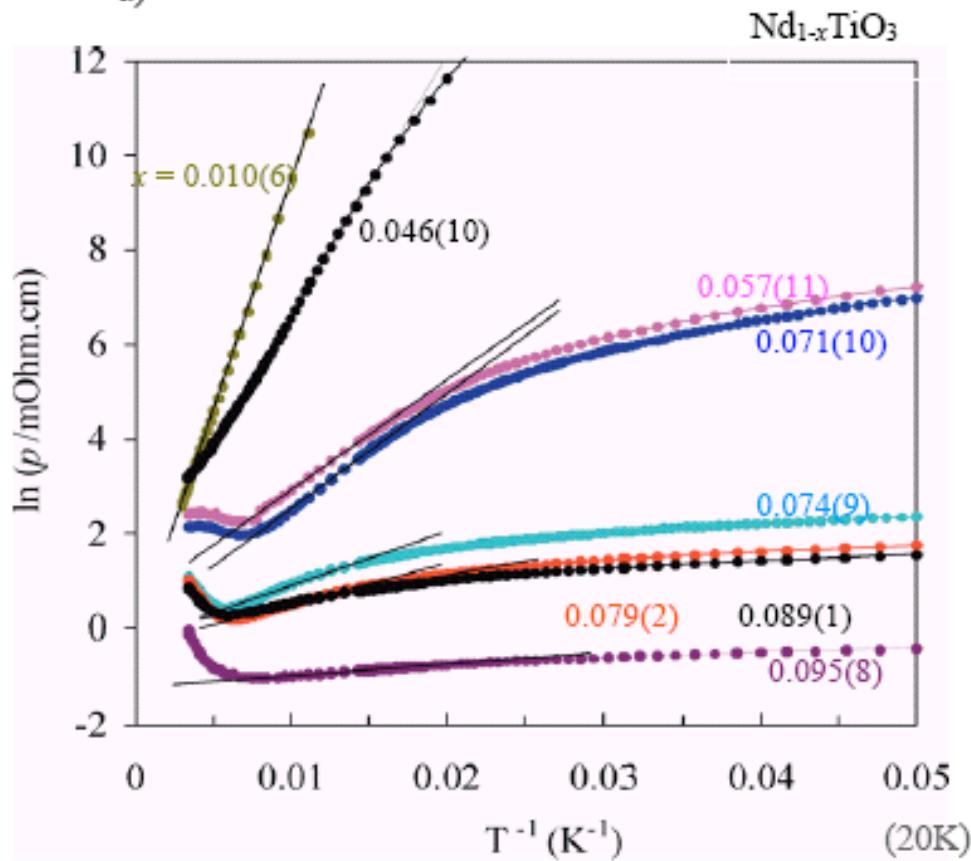
$x = 0.33$

$x = 0$

26

Arrhenius

$$\rho = \rho_0 \exp(E_{\text{act}} / k_B T)$$

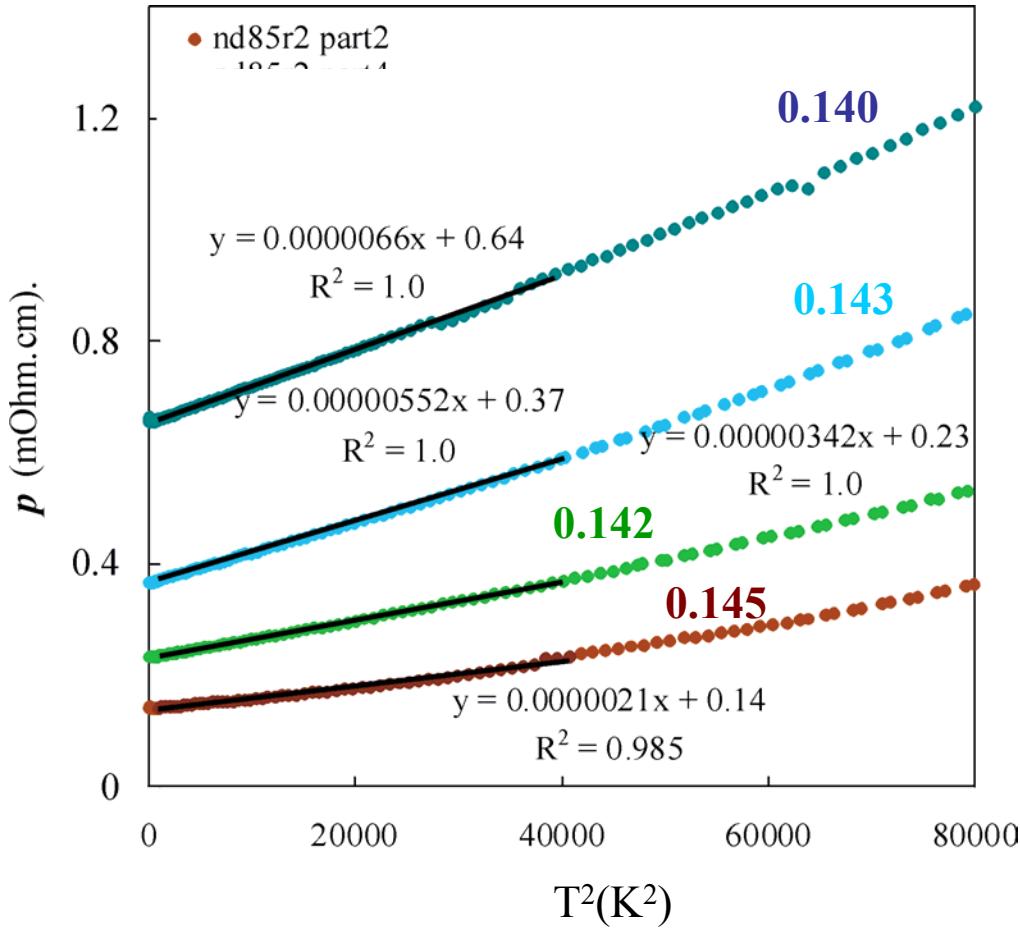


Note: $E_{\text{act}} \ll \text{M-H gap} \sim 0.8 \text{ eV}$. Mid-gap states involved

$x = 0.33$



$x = 0$



Fermi Liquid

$$\rho(T) = \rho_0 + AT^2$$

A is a measure of correlation/ carrier mass.

Kadowaki/Woods: $A^2/\gamma \sim \text{const.}$, $\gamma \sim (m^*)^{3/2}$

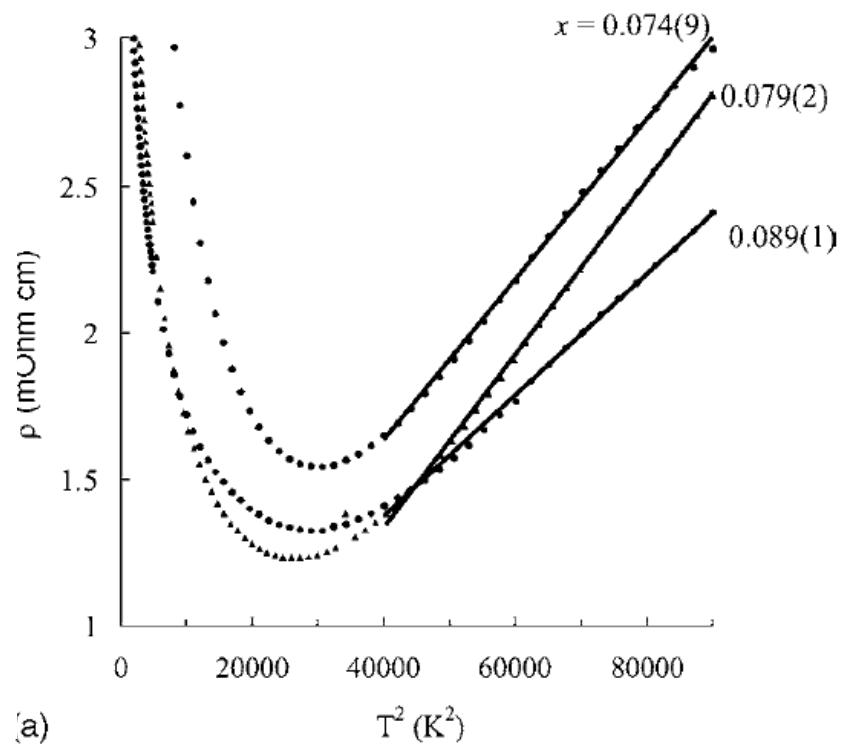
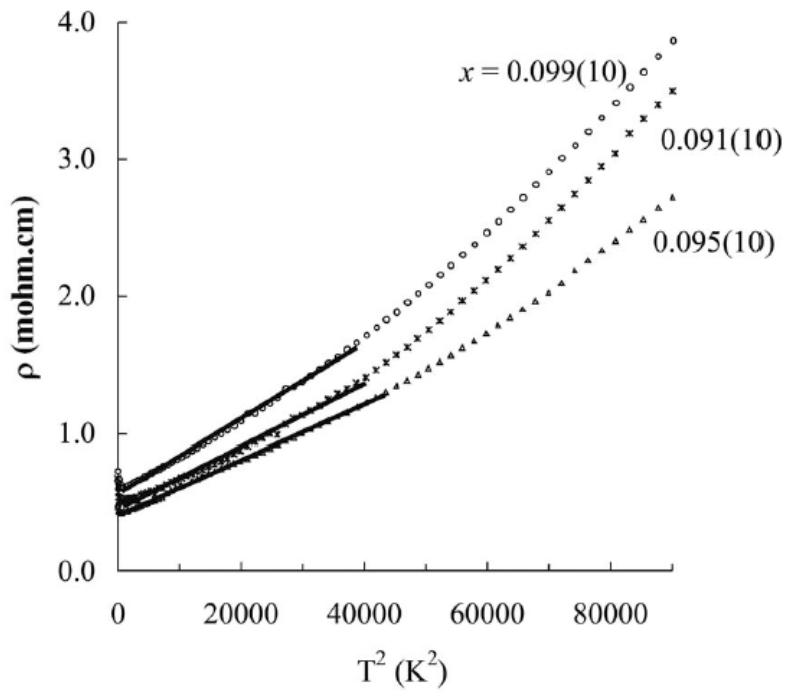
$x = 0.33$

$x \sim 0.2$

$x \sim 0.1$

$x = 0$





(a)

$x = 0.33$

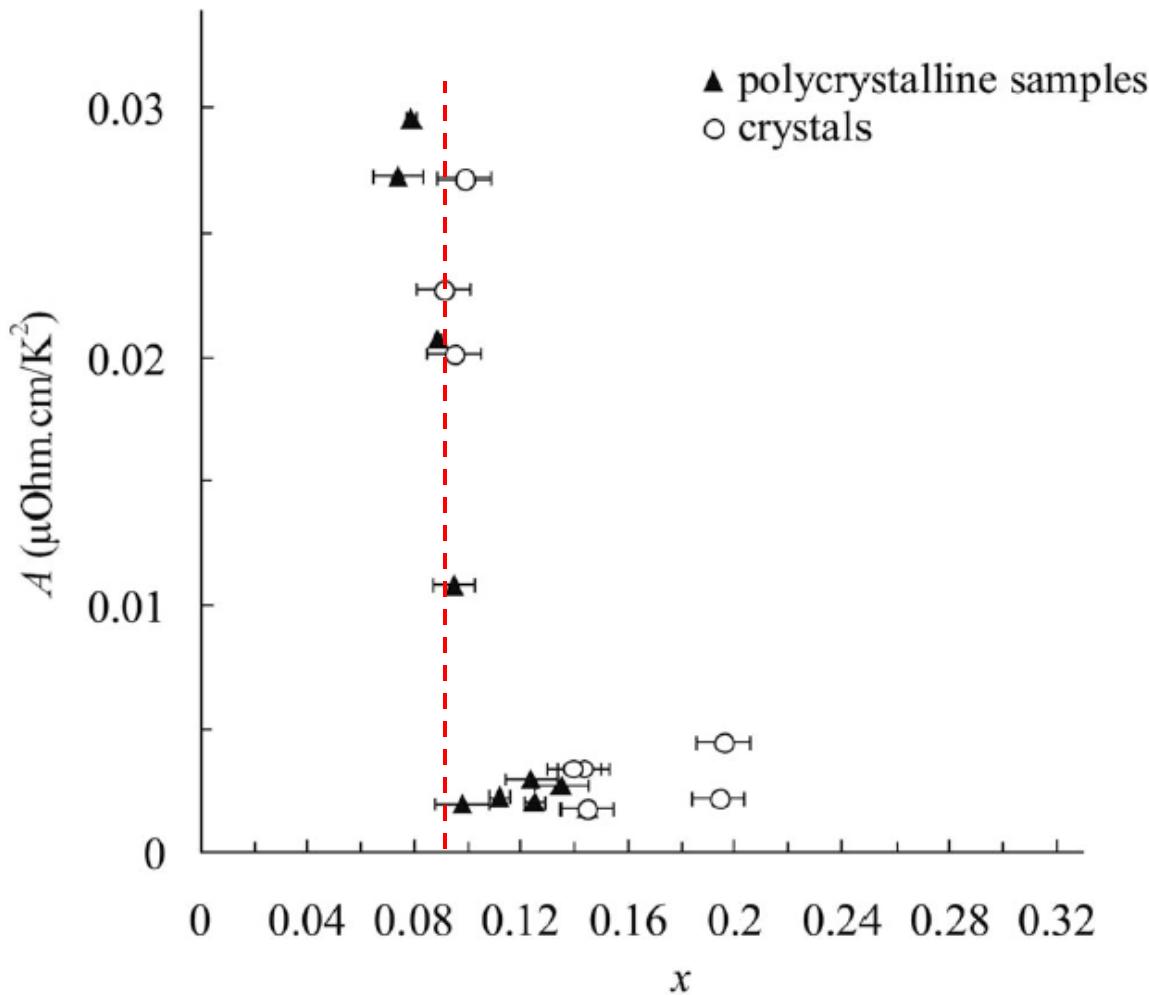
$x \sim 0.2$

$x \sim 0.1$

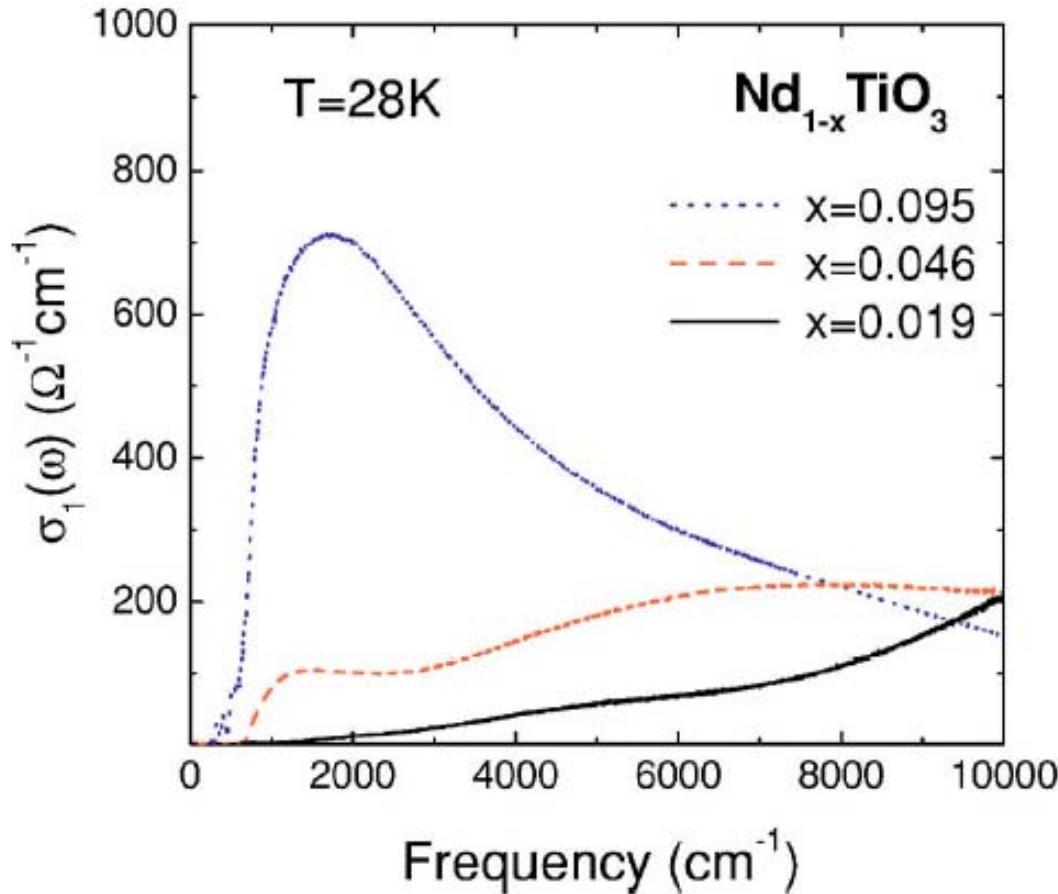
$x = 0$



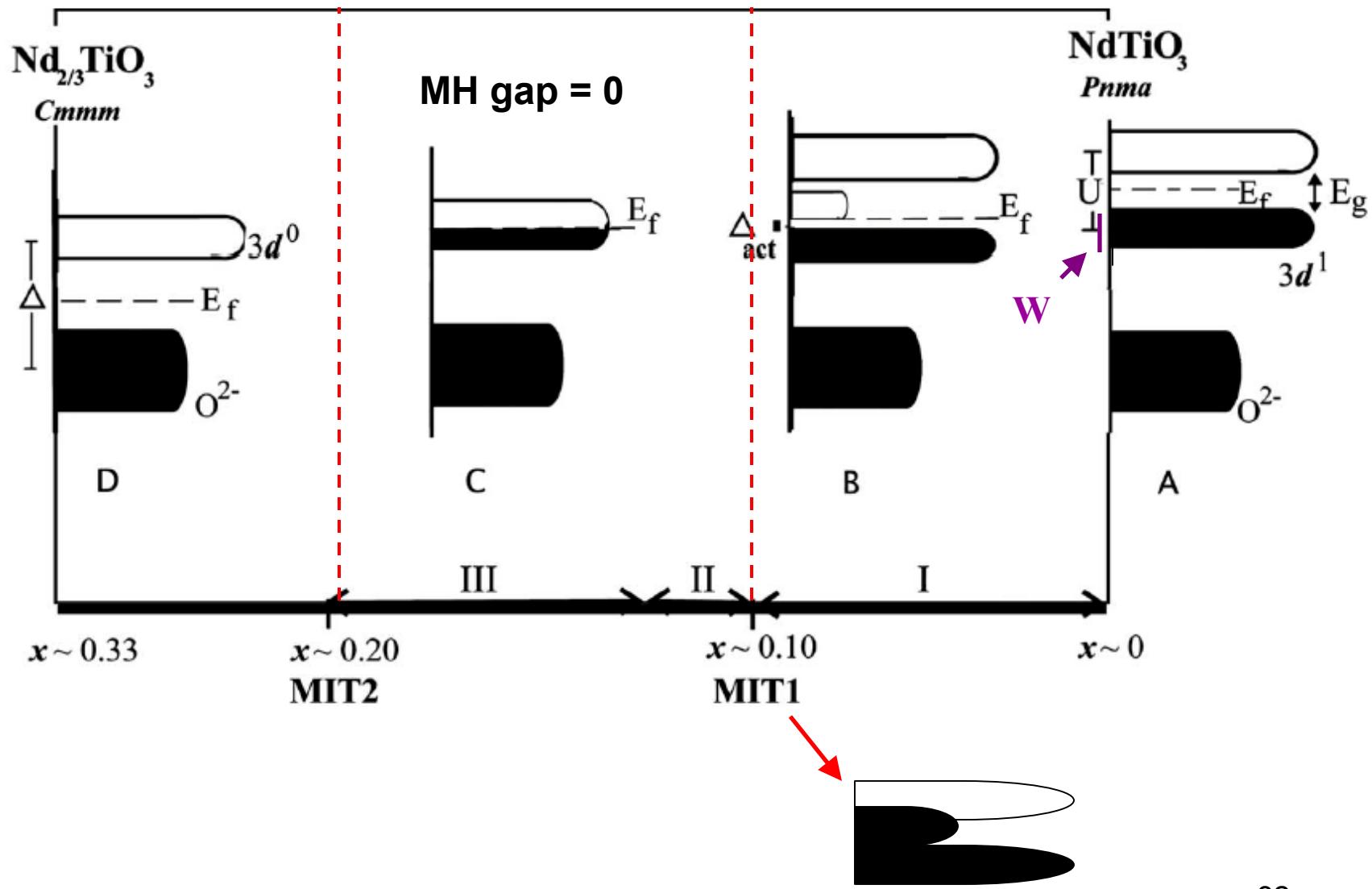
A (and m*) greatly enhanced at MIT1 boundary!!



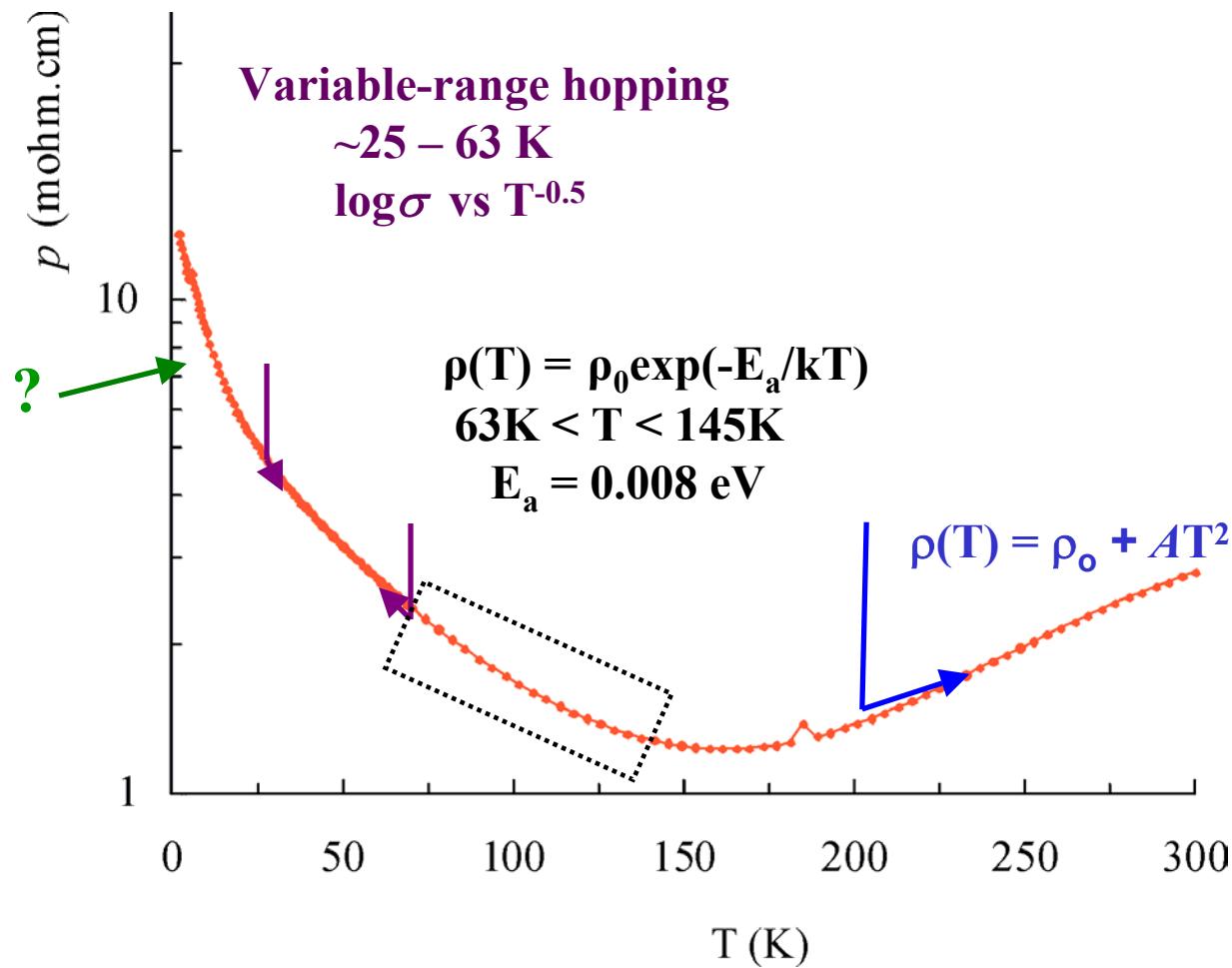
Finite MH gap at MIT1



Conclusion: MIT1 results when mid-gap band overlaps the UHB



x = 0.079

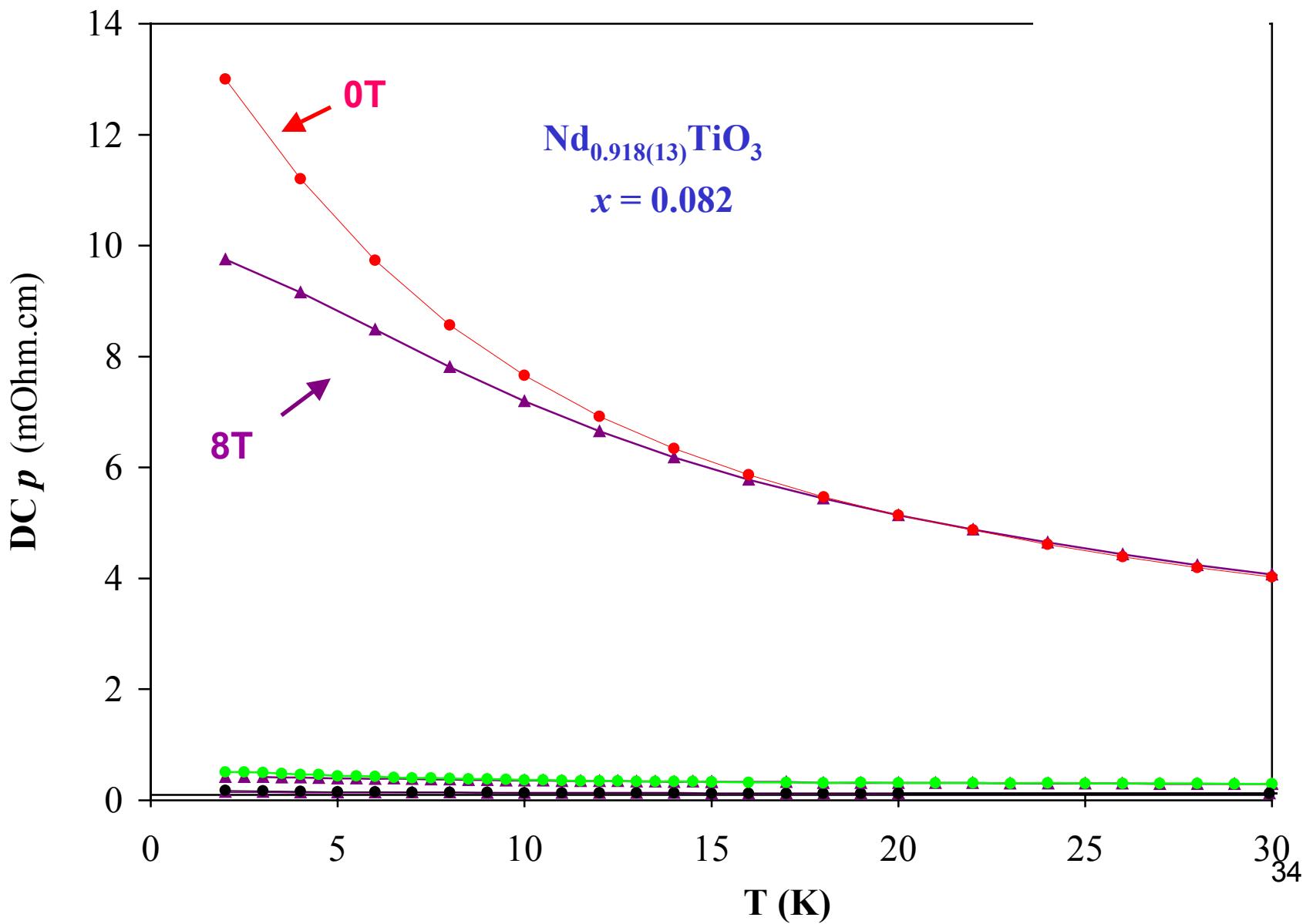


0.057(11) ≤ x ≤ 0.079(2)

x = 0.33

x = 0

Weak magneto-resistance. Due to scattering by Nd³⁺ moments which order @ 1K ?



How is disorder manifested?

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

$$\sigma = A \exp(-(T_0/T)^n)$$

n = 1/4 (Mott-Davis)

Mott&Davis, “Electronic Processes ...” Oxford(1971)p42

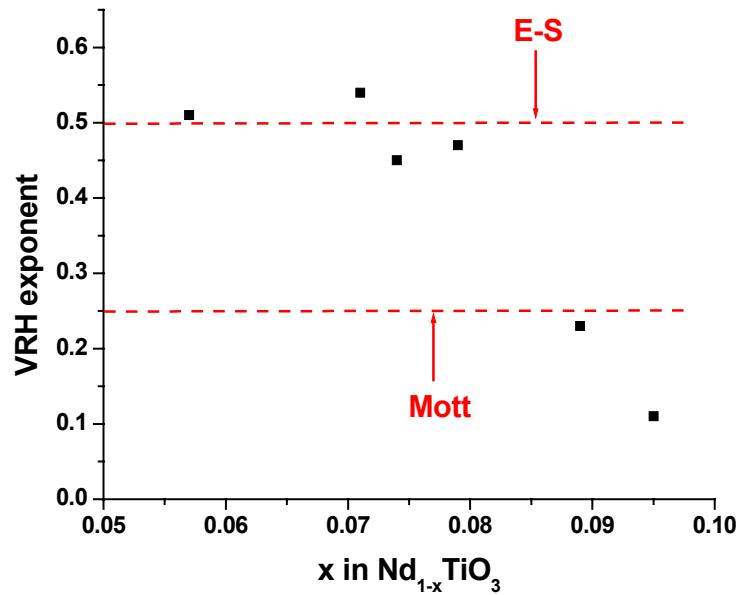
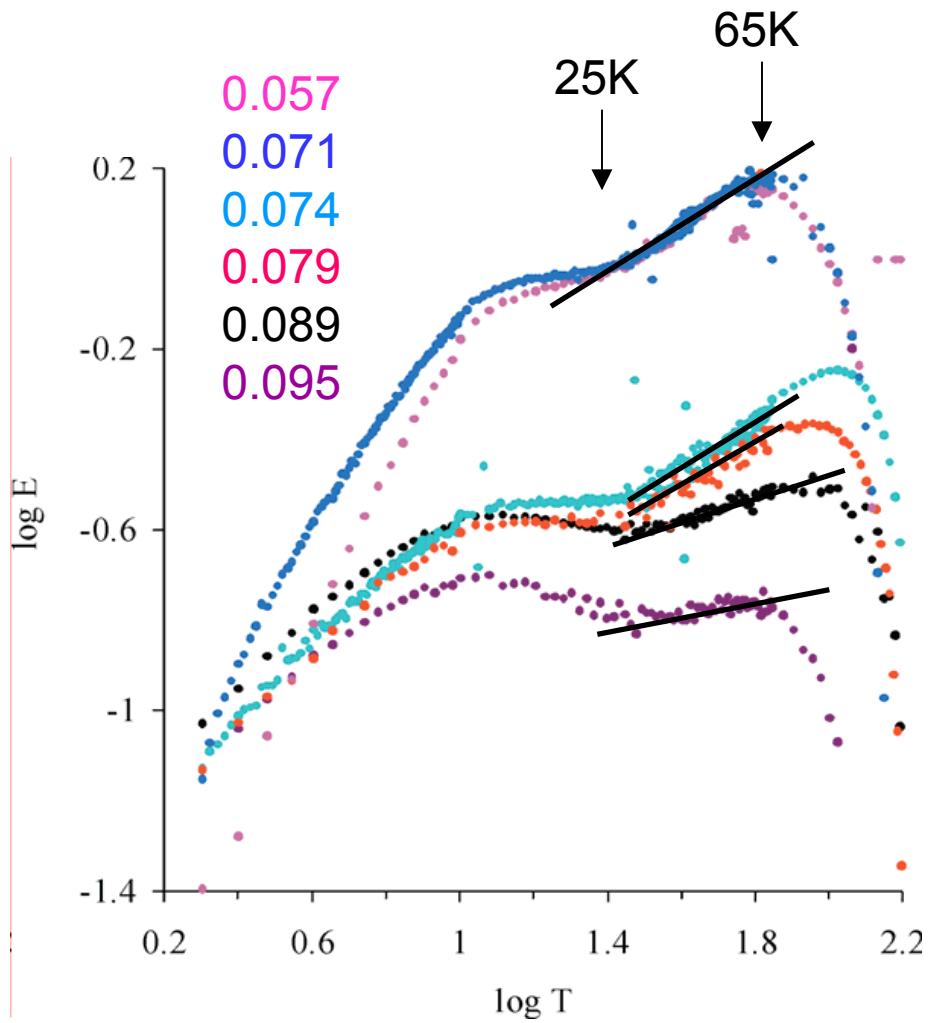
**n = 1/2 (with correlation)
E-S**

Efros,Shklovskii
J.Phys.C8(1975)L49

Use Hill/Zabrodskii method to distinguish exponents

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

Hill,Phys. Stat. Sol.A35(1976)K29
Zabrodskii,Sov.Phys.Semic.11(1977)345



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

Magnetic Properties

- Determine T_N (T_c) vs x

For which x does T_N vanish?

- Determine Ti^{3+} ordered moment vs x

For which x does the moment vanish?

- Correlation with transport properties ?

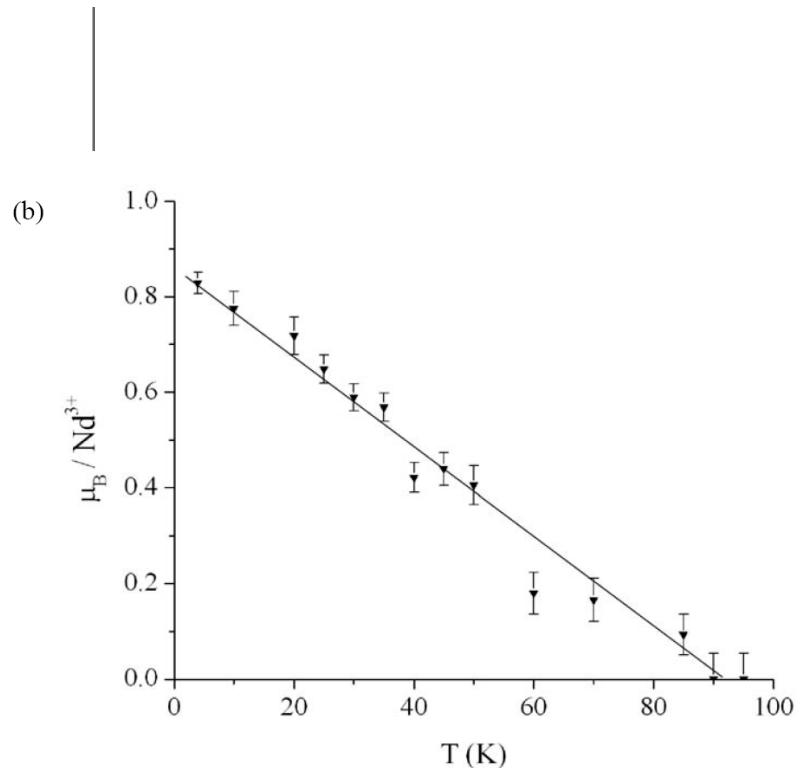
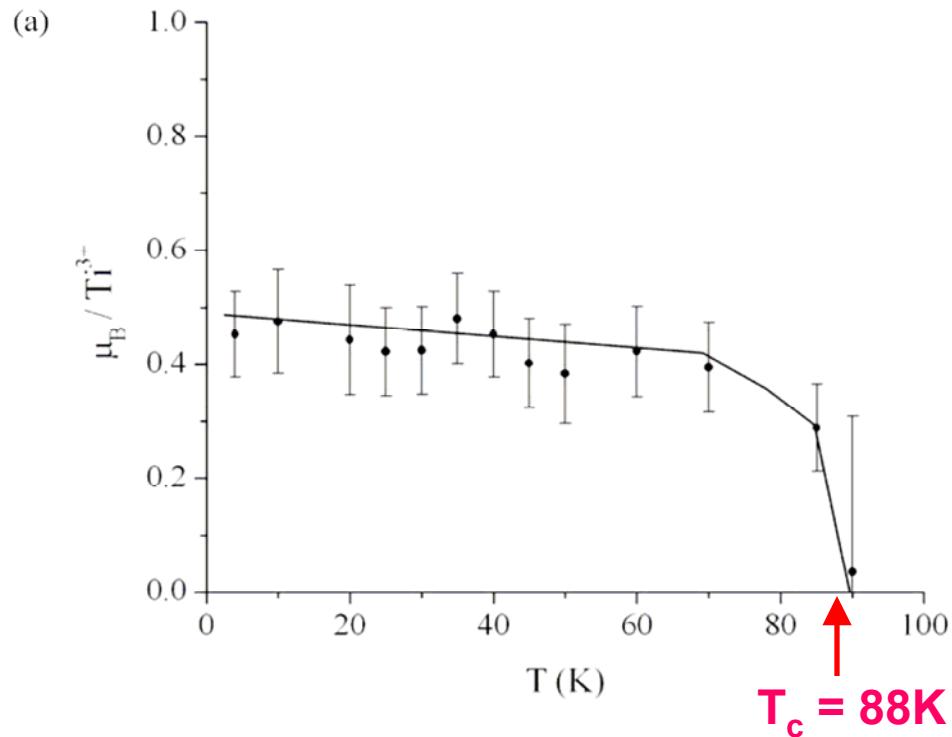
Five ways to measure T_N

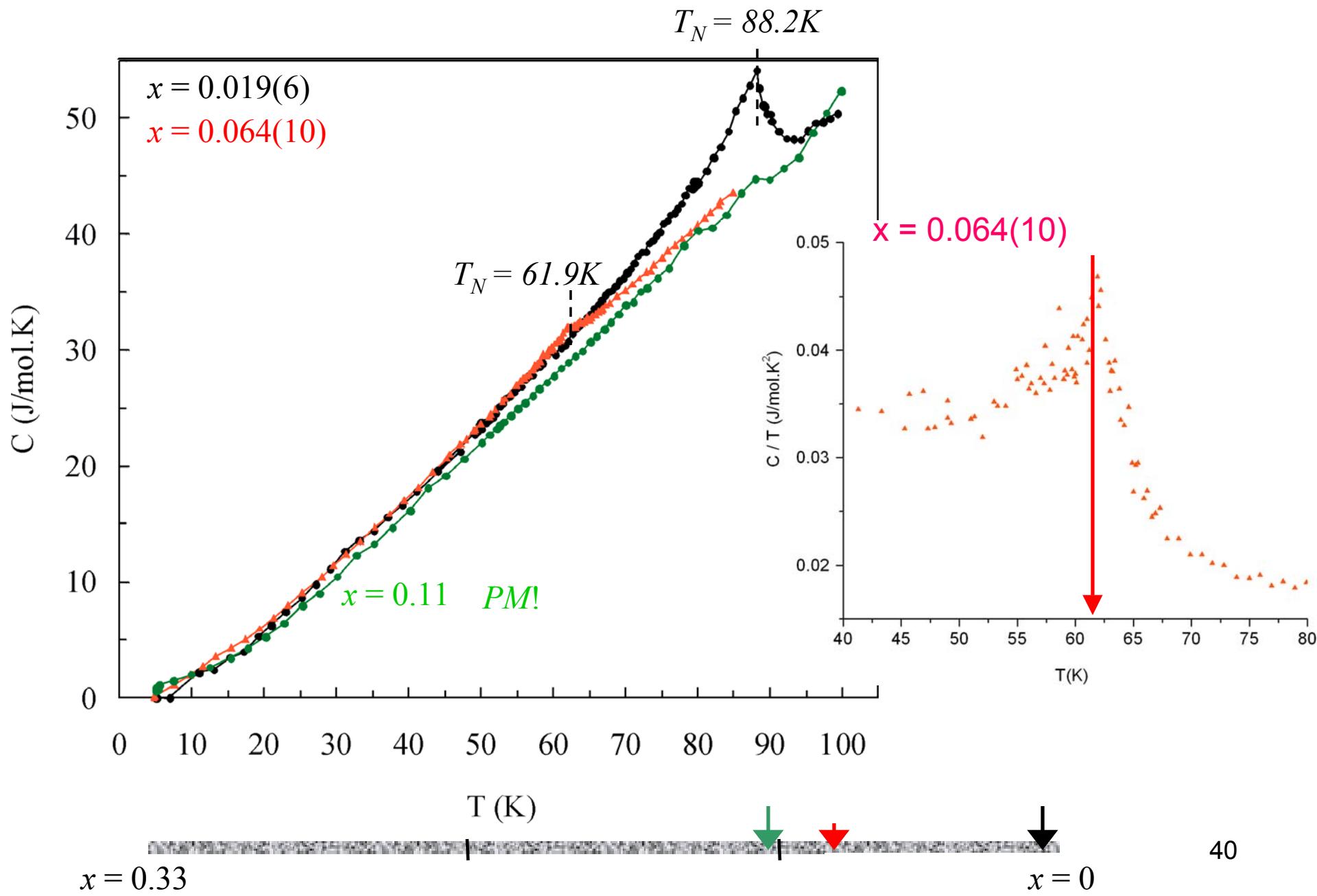
- Neutron diffraction vs T \Rightarrow reliable but slow
- ZFC/FC divergence in M/H vs T
(NdTiO_3 is a canted moment AF \Rightarrow unreliable, sensitivity to
 - develops a weak F moment magnetic micro structure below T_N)
- M_{sat} vs T in ZF \Rightarrow slightly better but still unreliable
- C_p vs T \Rightarrow best (but time consuming)
- “Fisher’s” heat capacity: $d(\chi T)/dT \Rightarrow$ fast and reliable

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

Neutron Diffraction

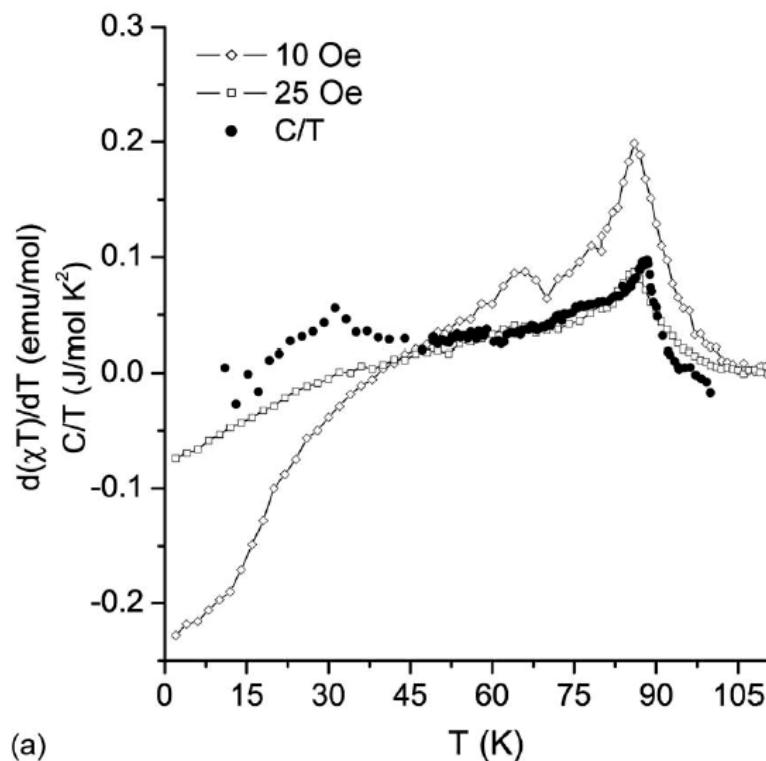
$$x = 0.019(6)$$



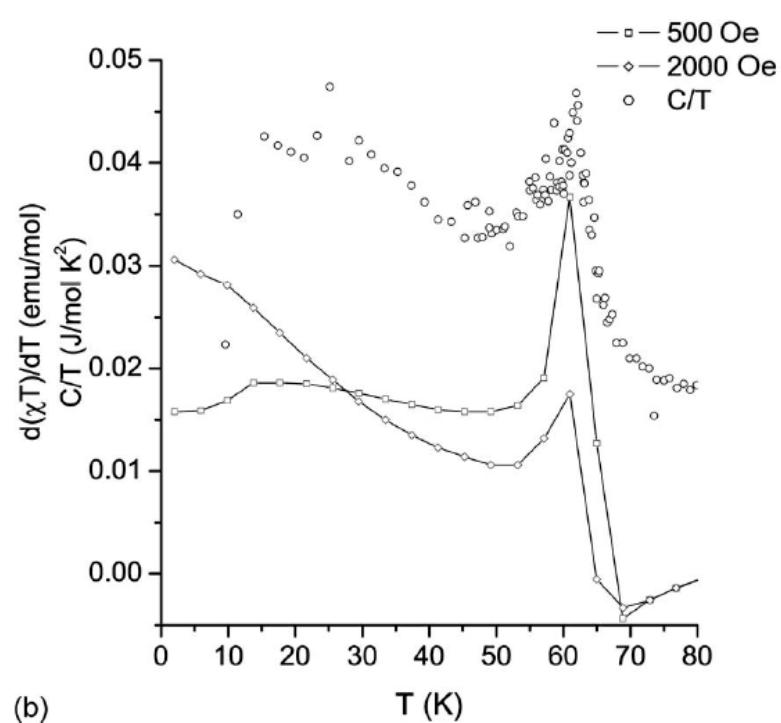


Compare “real” heat capacity with Fisher’s heat capacity $d(\chi T)/dT$ vs T

$$x = 0.019(6)$$

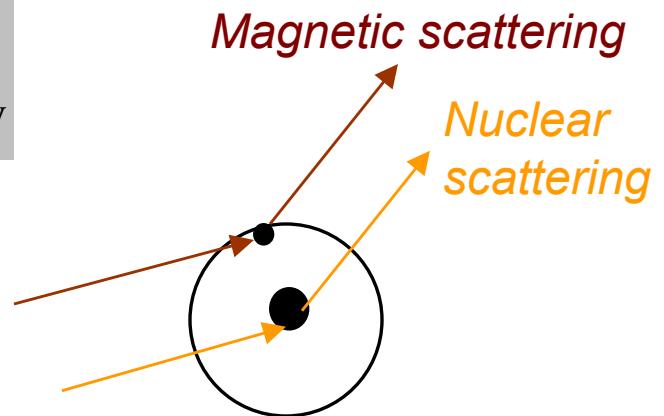


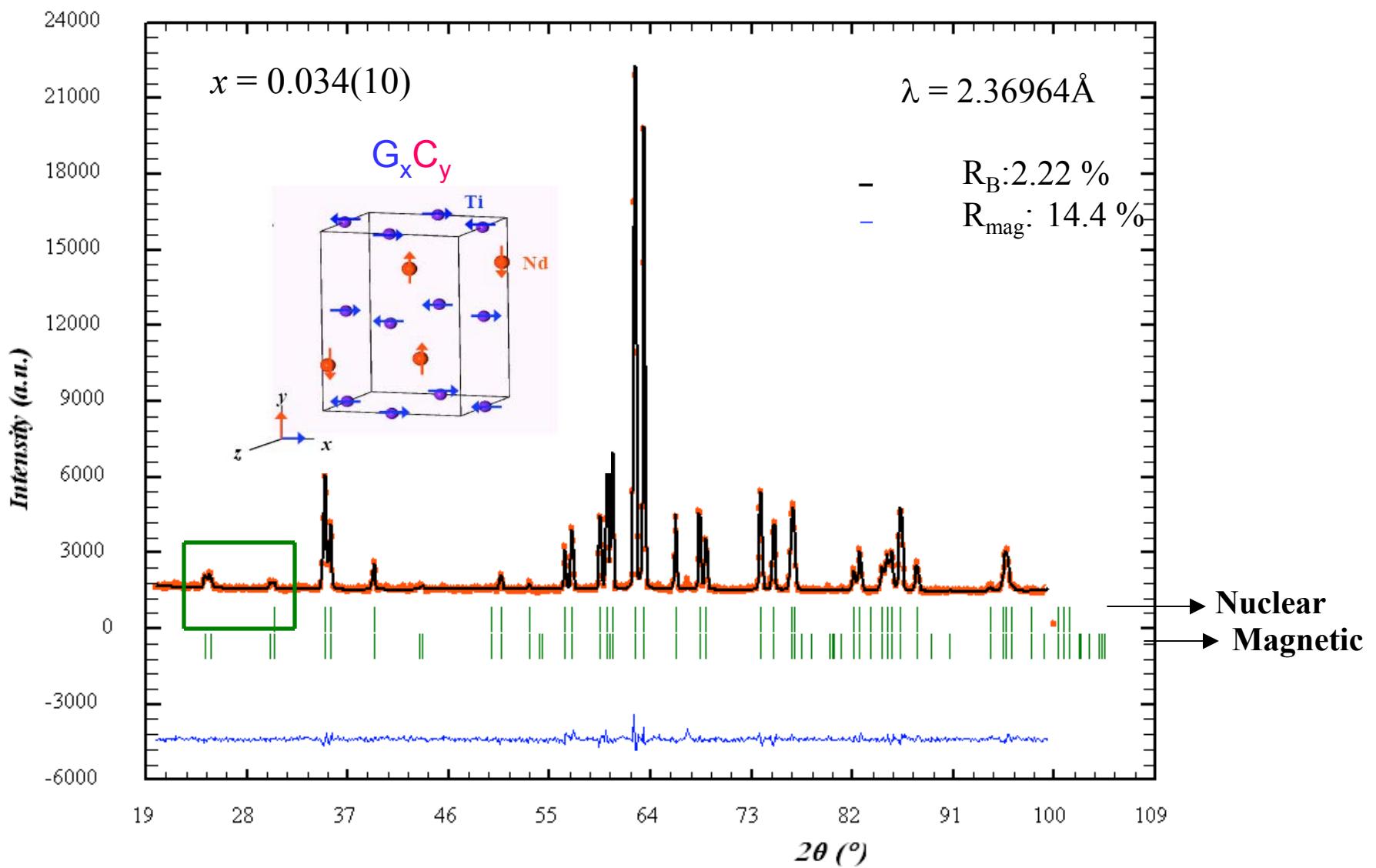
$$x = 0.064(10)$$

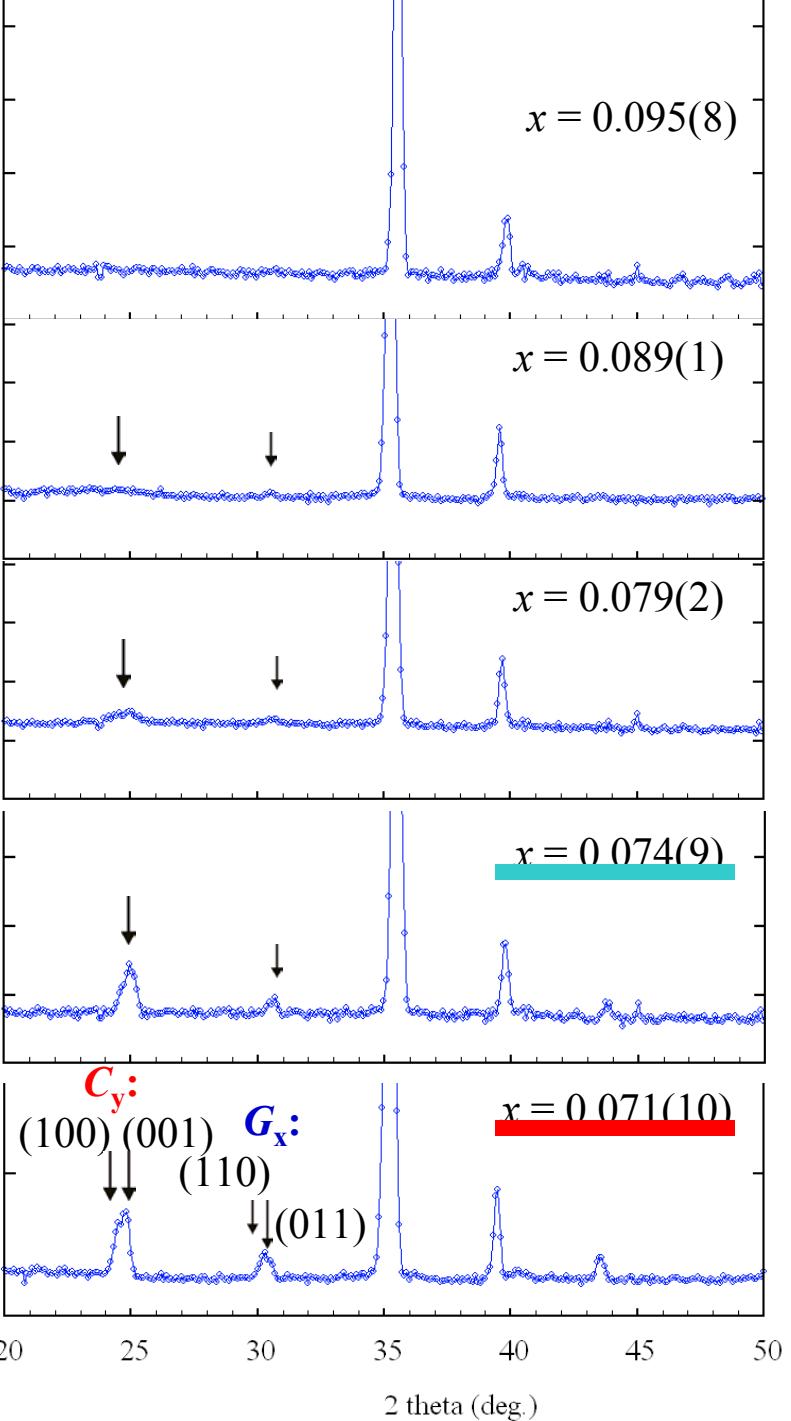


Neutron diffraction

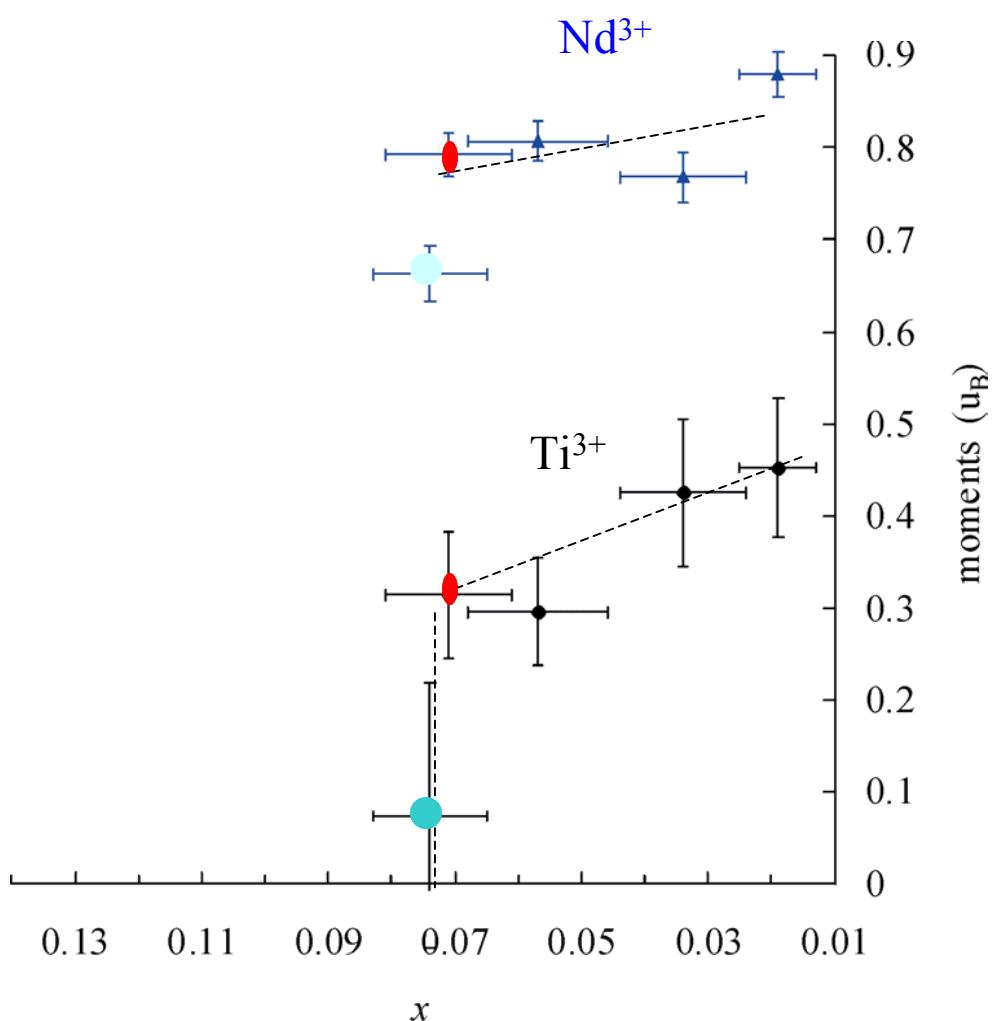
- $\lambda \sim \text{\AA}'s$
- Neutrons are scattered by nuclei
- Neutrons ($S = 1/2$) interact with unpaired spin density



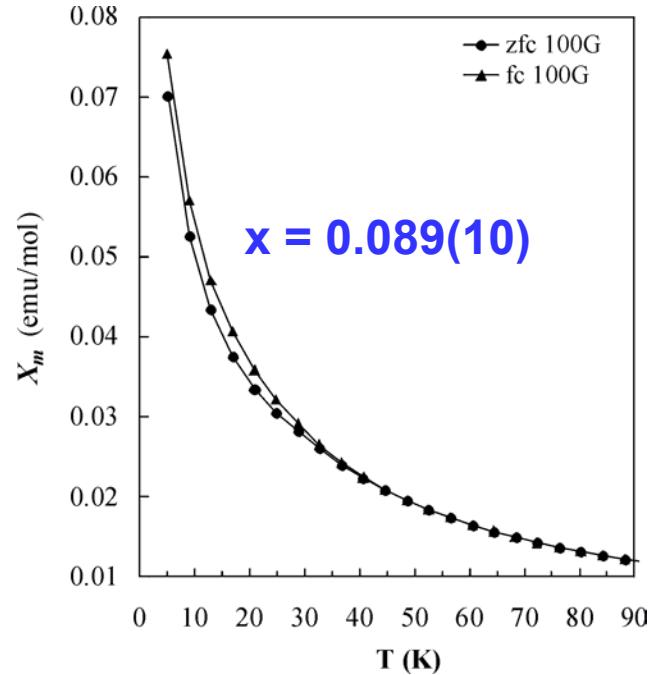
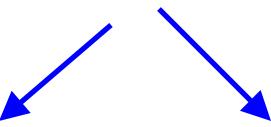
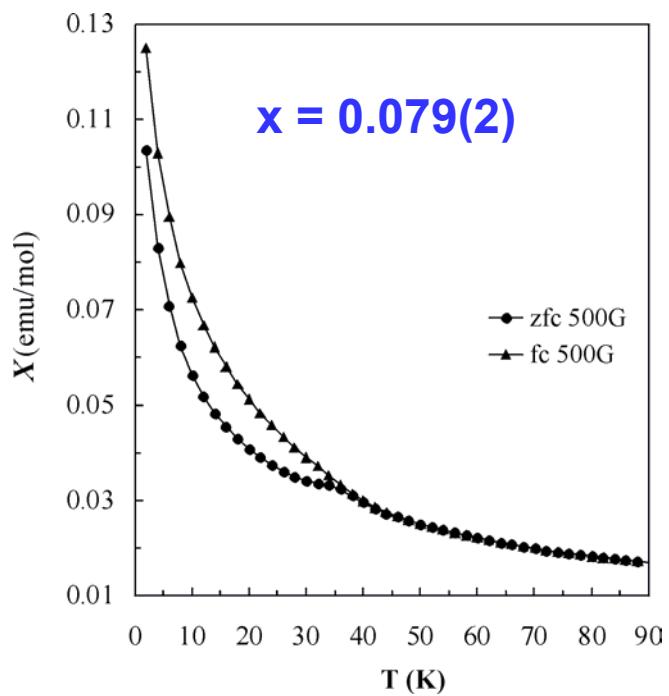




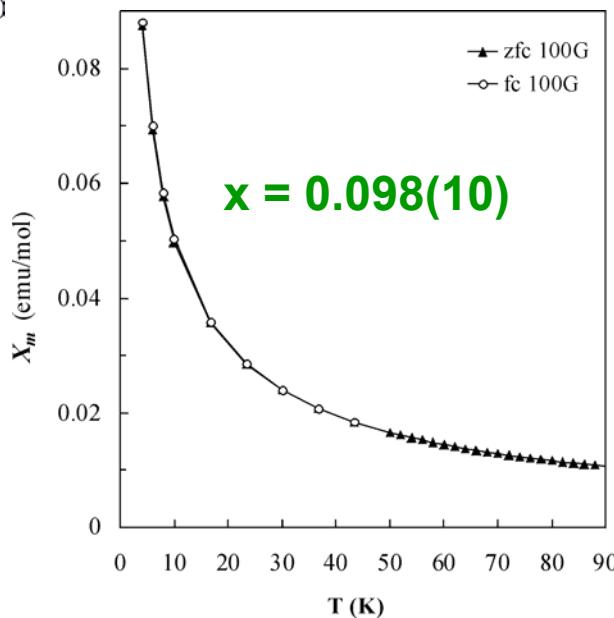
LRO: $x \leq 0.071(10)$
 SRO: $0.074(9) \leq x \leq 0.089(1)$
 PM: $x = 0.095(8)$



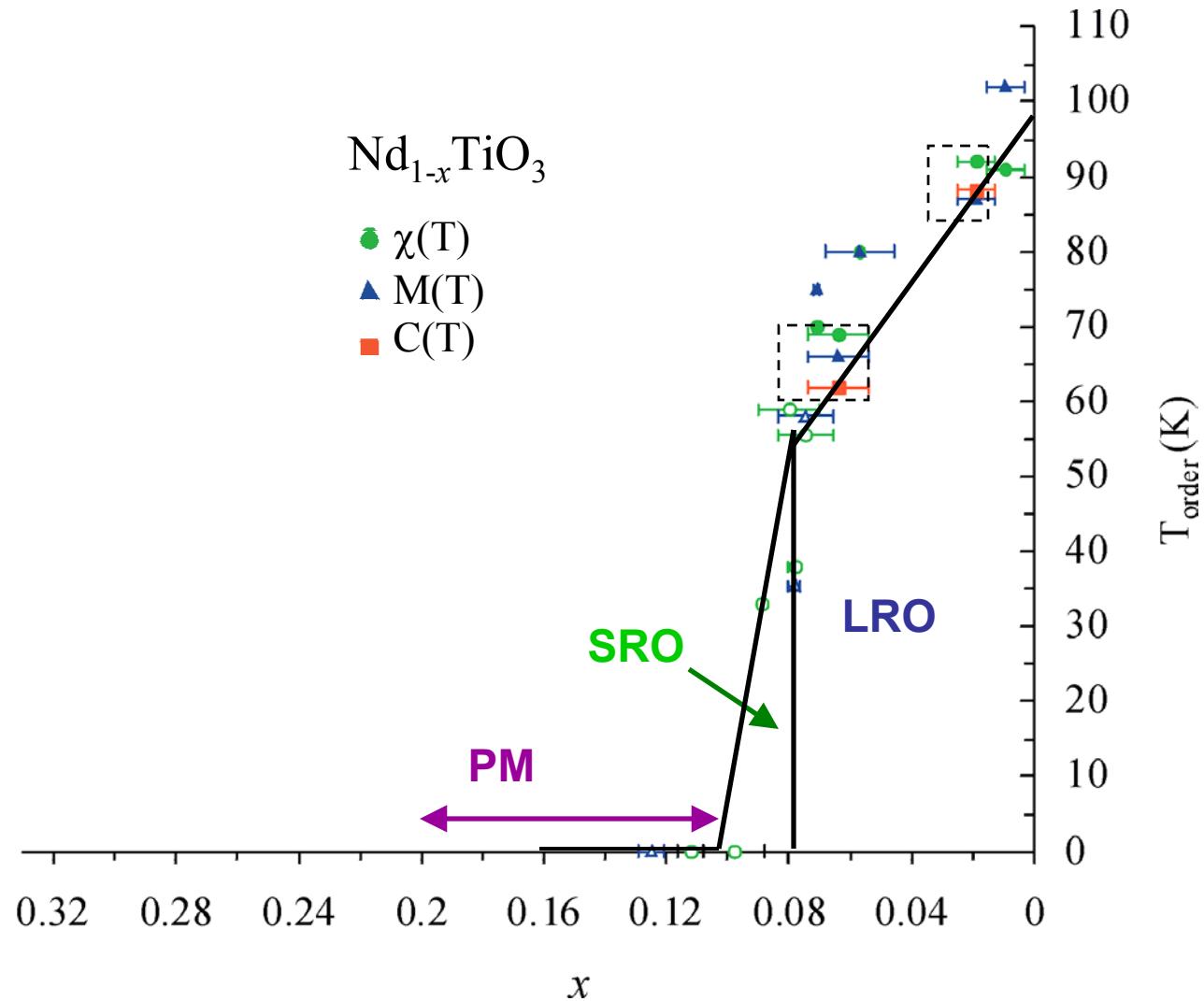
spin-glass-like



paramagnetic



Magnetic phase diagram



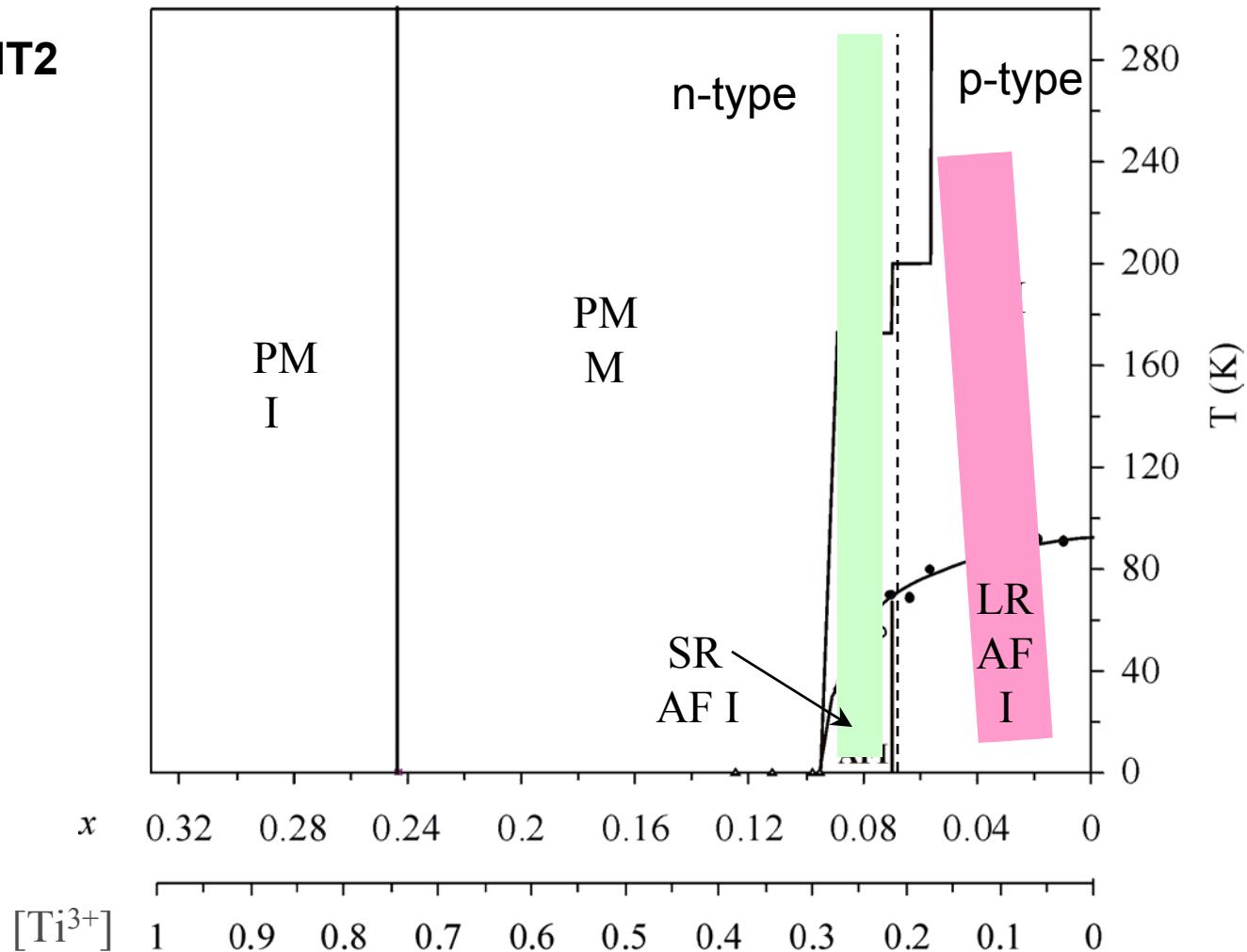
The phase diagram for $\text{Nd}_{1-x}\text{TiO}_3$

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

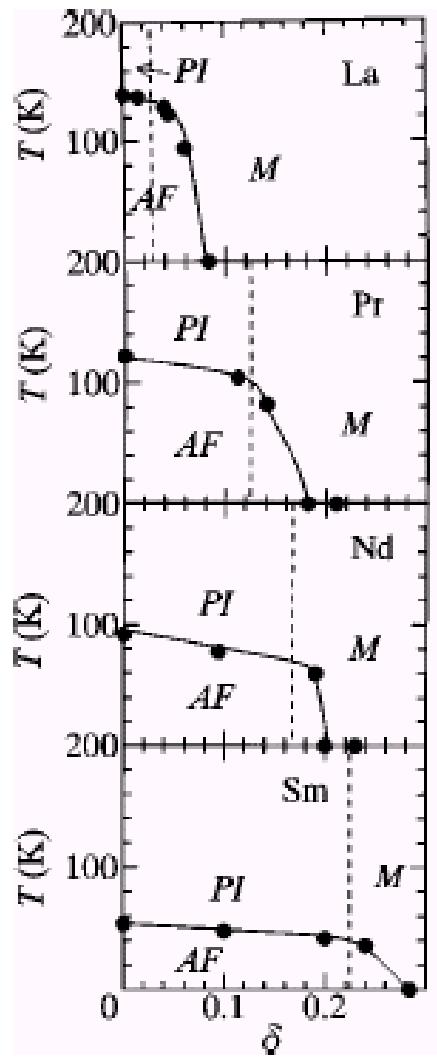
$0.074(9) \leq x < 0.089(1) \rightarrow$ SR AFI/PI/PMM Anderson Localization

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

$x = 0.243(10) \rightarrow$ MIT2



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



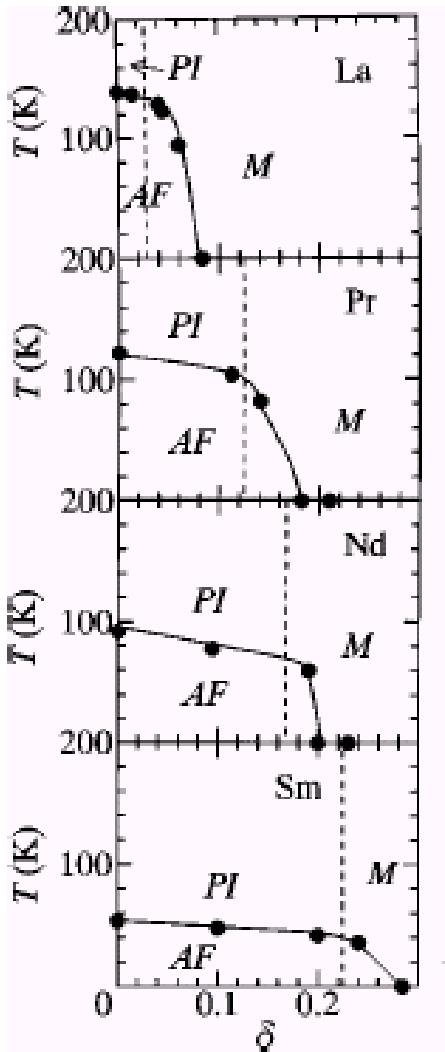
hole conc.

Summary and Conclusions

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

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

Summary and Conclusions contd.



- determined magnetic structure of NdTiO_3 , unequivocally (high resolution powder data) : $\text{G}_x\text{C}_y \pm$
- traced T_c vs x accurately - first time for a hole- doped MH AFI \pm
- shown abrupt collapse of ordered moment on Ti^{3+} @ $x = 0.074 \pm$
- found SRO AF regime bridging collapse of ordered moment and onset of metallic behaviour, $x = 0.095$ (first observation) \pm
- AF metallic state does not exist for $\text{Nd}_{1-x}\text{TiO}_3!! \pm$

Athena S. Sefat

PHYSICAL REVIEW B 73, 195125 (2006)

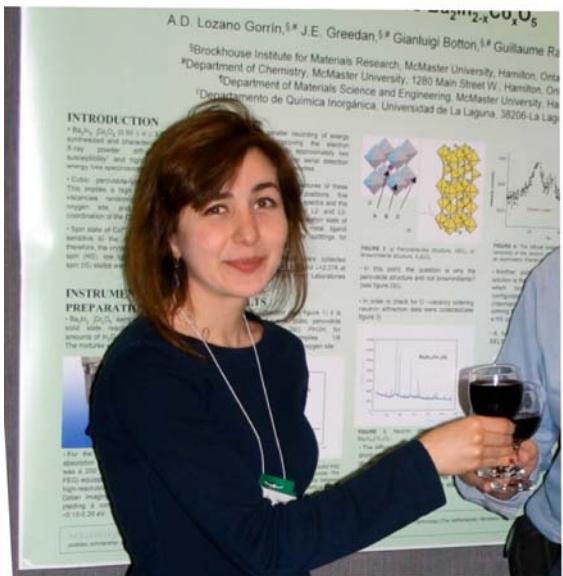
Temperature-dependent optical spectroscopy studies of $\text{Nd}_{1-x}\text{TiO}_3$

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PHYSICAL REVIEW B 74, 104419 (2006)

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

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PHYSICAL REVIEW B 74, 104418 (2006)

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

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

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Gianluigi A. Botton^{a,d,e}, J.E. Greedan^{a,b}

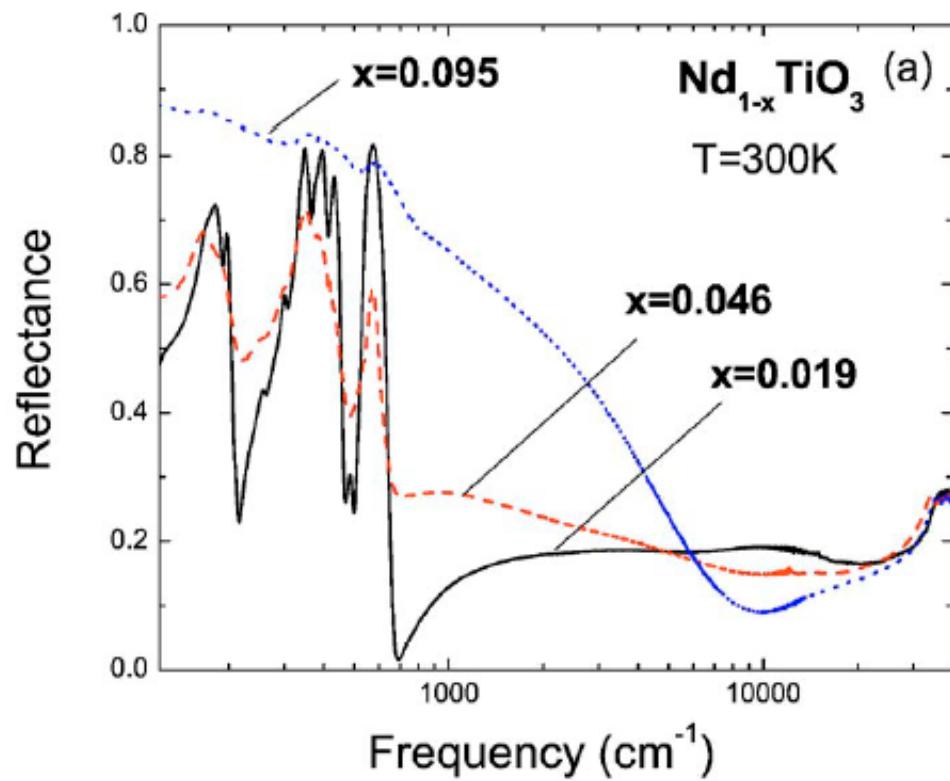
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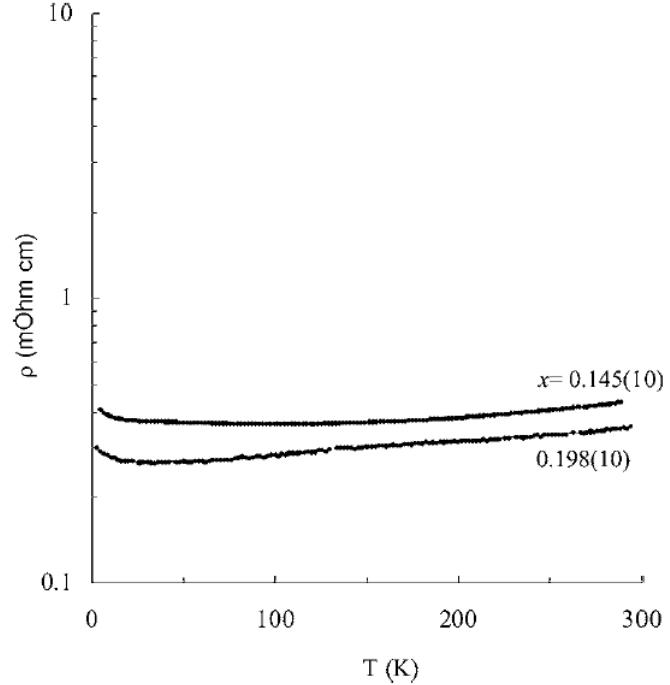


FIG. 11. The $\rho(T)$ for two $\text{Nd}_{1-x}\text{TiO}_3$ polycrystalline samples. Note the presence of upturns at low temperatures.

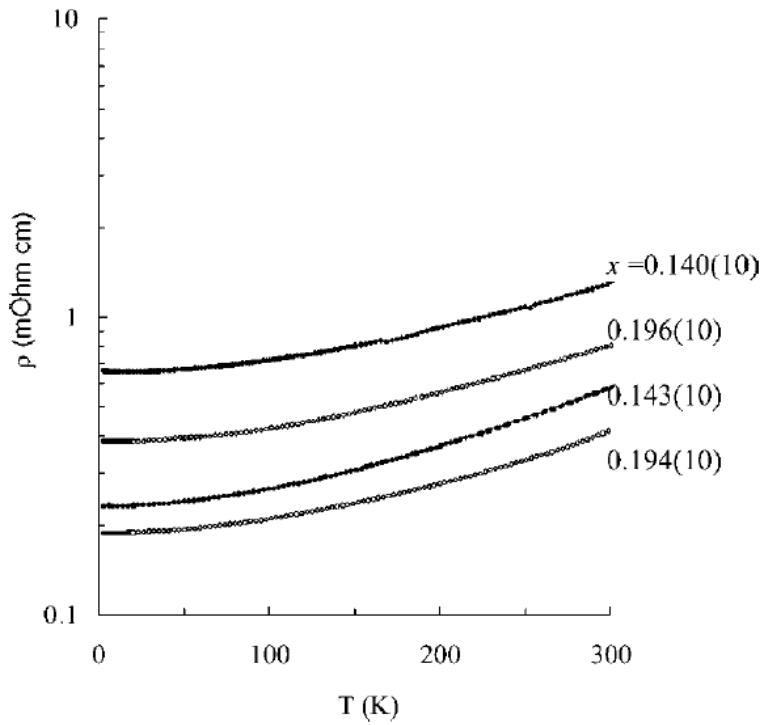


FIG. 12. The electronic resistivity vs temperature for single-crystal pieces with $x \sim 0.15$ and 0.20 compositions in $\text{Nd}_{1-x}\text{TiO}_3$. Note the absence of upturns at low temperatures.