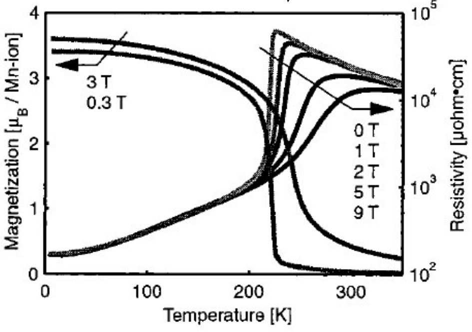
Spatial Electronic Phase Separation in Manganites

Bulk Crystal
$La_{0.7}Ca_{0.3}MnO_3$



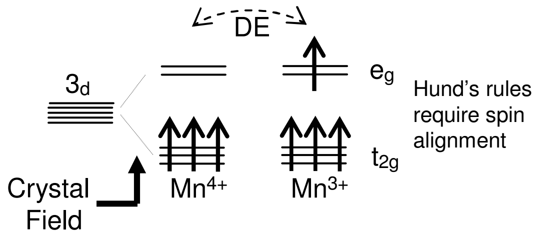
Coupled metal-insulator/ferromagnetic-paramagnetic transition

Zero field R-T curve

- below T_c → metallic ($d\rho/dT > 0$) → "scattering" as T↑
- above T_c → insulating ($d\rho/dT < 0$) → thermally activated

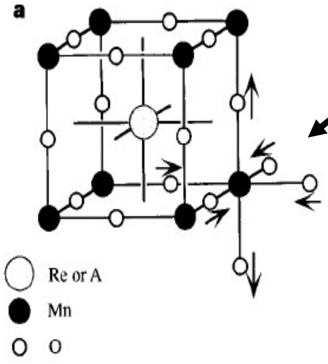
Below Tc

- spins aligned → ferromagnetic ↔ double exchange
- mixed valence via doping
- conduction via hopping

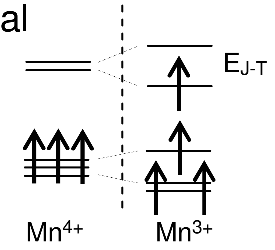


Above Tc

- spin disorder → paramagnetic → electron scattering
- dominated by polarons (electron-phonon coupling)
  - → electron on Mn distorts O-Mn octahedral
  - → potential minimum
  - → self-trapped electrons



Jahn-Teller Distortion



spatial electronic phase separation

→ coexisting but spatially distinct insulating & metallic domains

→ broadens R-T peak

Colossal magneto resistance (CMR)

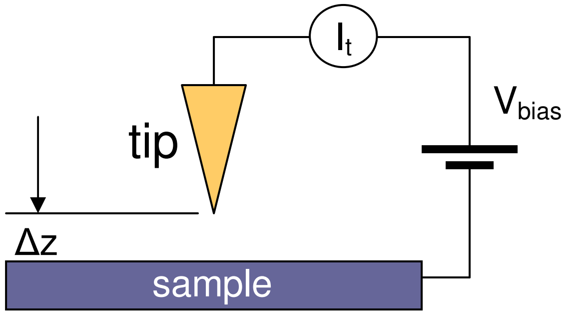
applied magnetic field → align spins → decrease PM (insulating) & increase FM (metallic) → R↓

Scanning Tunneling Spectroscopy (STS)

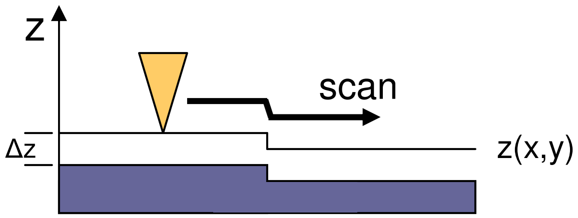
- tunneling current given by,

$$I_t(\Delta z) = I_0(V_{bias}, DOS)\; e^{-2\kappa \Delta z}$$

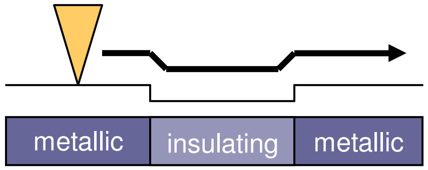
Δz	tip-surface distance
V_{bias}	tip-surface potential difference
DOS	tip & sample density of states
κ	proportional to surface work function



- STM topography
  - fix V_{bias} maintain $I_{set} = I_t$
  - adjust tip height, z, while scanning across surface
  - electronically homogeneous sample, z(x,y) values map topography
  - inhomogeneous sample, changes in DOS modify I_0
  - insulating material may require minimum V_{bias}



topography



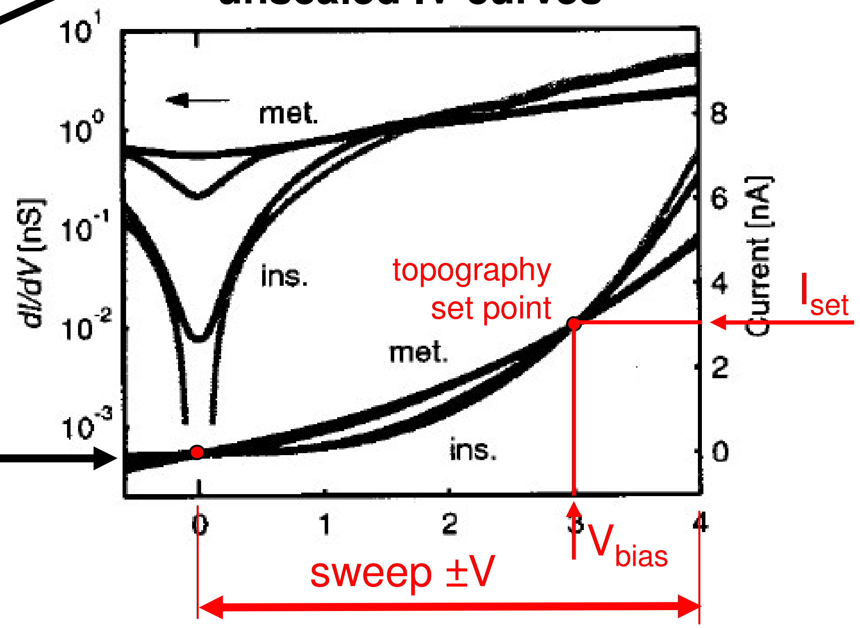
inhomogeneities

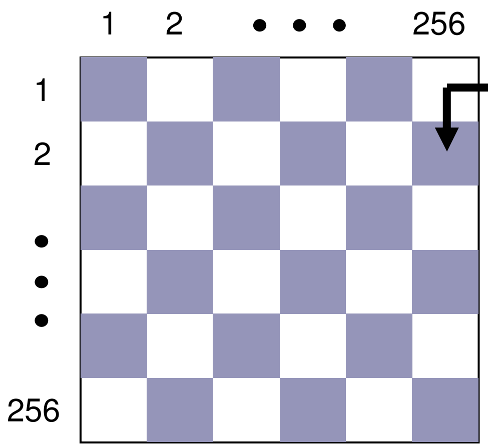
Scanning Tunneling Spectroscopy

$$I_t(\Delta z) = I_0(V_{bias}, DOS)\boxed{e^{-2\kappa\Delta z}}$$

- STS → measure sample DOS
  - scan topography
  - at each pixel take I-V
    - stop scanning→x,y fixed
    - feedback off →Δz fixed
    - sweep bias ±V
    - measure I_t
    - differentiate I-V curve for dI/dV

unscaled IV curves





one I-V per pixel

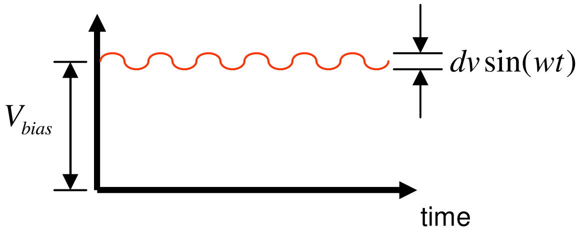
- Conductance map
  - determine criteria
    - dI/dV at V_{bias}
    - dI/dV at zero volts
    - gap in dI/dV
  - assign to each pixel

Conductivity Map

Measure dI/dV Directly

- modulate bias with small sinusoidal voltage

  $$V_{bias} + dv\sin(wt)$$



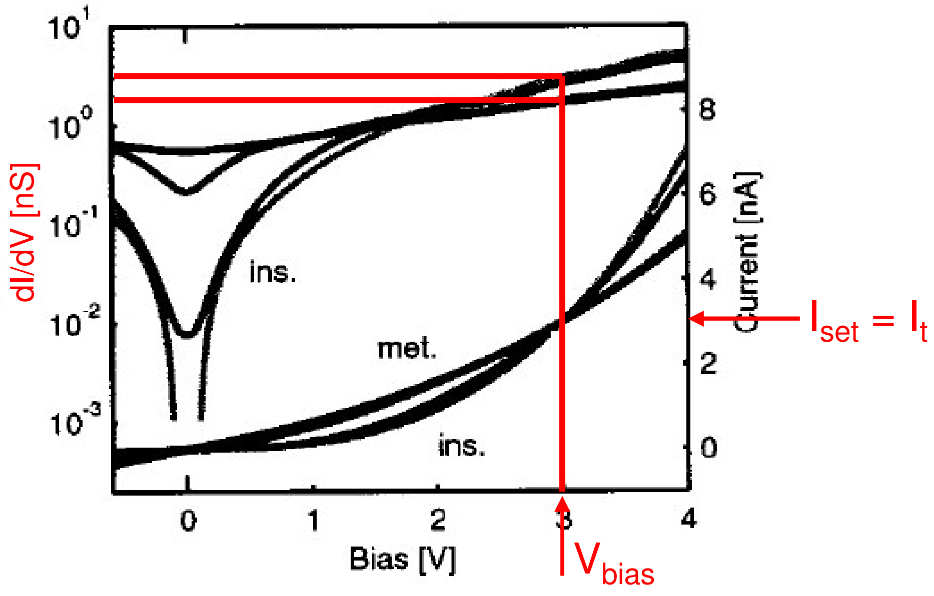
- scan topography

  $\omega >> BW_{FEEDBACK}$ → feedback cannot react

- lock-in amplifier measures dI/dV

  $V_{bias} >> dv$ → measure dI/dV directly

- with each pixel, record both topography and lock-in output



“Standard”Lock-In Technique

- bias modulated with small sinusoidal voltage

$$V_{bias} + dv\sin(wt) \rightarrow I_t = f(V_{bias} + dv\sin(wt))$$

- for small dv, tunneling current, I_t, can be approximated,

Taylor Series

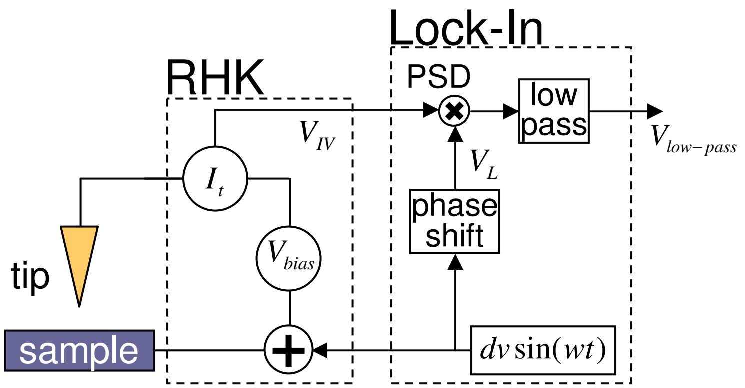
$$I_t\left(V_{bias} + dv\sin(wt)\right) \approx I(V_{bias}) + \left.\frac{dI}{dV}\right|_{V_{bias}} dv\sin(wt)$$

- IV converter measures tunneling current

$$V_{IV} = A_{IV} I_t(V_{bias} + dv\sin(wt)),\ \ A_{IV} \approx 1v/nA$$

- lock-in shifts reference signal phase

$$V_L \sin(\omega_L t + \theta)$$



- lock-in PSD multiplies V_{IV} and V_L

$$V_{psd} = V_{IV} V_L \sin(\omega_L t + \theta) = \left[A_{IV} I(V_{bias}) + A_{IV} \left.\frac{dI}{dV}\right|_{V_{bias}} dv\sin(wt)\right] V_L \sin(\omega_L t + \theta)$$

$$= A_{IV} I(V_{bias})\ V_L \sin(\omega_L t + \theta) + \tfrac{1}{2} A_{IV} \left.\frac{dI}{dV}\right|_{V_{bias}} dv\ V_L \cos\left[\underline{(\omega - \omega_L)t} - \theta\right] - \tfrac{1}{2} A_{IV} \left.\frac{dI}{dV}\right|_{V_{bias}} dv\ V_L \cos\left[\underline{(\omega + \omega_L)t} + \theta\right]$$

- for $\omega = \omega_L$,

$$V_{psd} = A_{IV} I(V_{bias})\ V_L \sin(\omega_L t + \theta) + \tfrac{1}{2} A_{IV} \left.\frac{dI}{dV}\right|_{V_{bias}} dv\ V_L \cos[\theta] - \tfrac{1}{2} A_{IV} \left.\frac{dI}{dV}\right|_{V_{bias}} dv\ V_L \cos[2\omega_L t + \theta]$$

phase

- lock-in low-pass filter eliminates all ac components

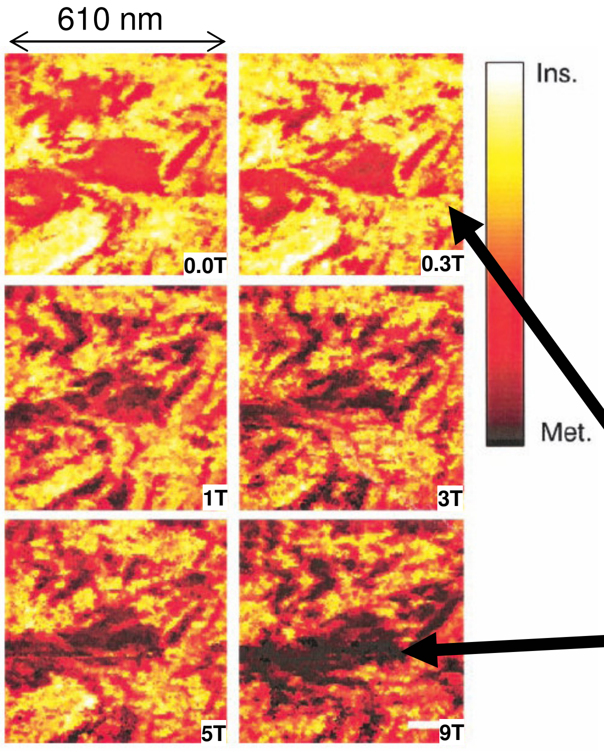
$$V_{low-pass} = \tfrac{1}{2} A_{IV} \left.\frac{dI}{dV}\right|_{V_{bias}} dv\ V_L \cos[\theta] \xrightarrow{DualPhase} \tfrac{1}{2} A_{IV} \left.\frac{dI}{dV}\right|_{V_{bias}} dv\ V_L$$

slope

→ $\omega_{NOISE} \neq \omega$ rejected

Earlier Results: Matthias

STS in Applied Magnetic Field

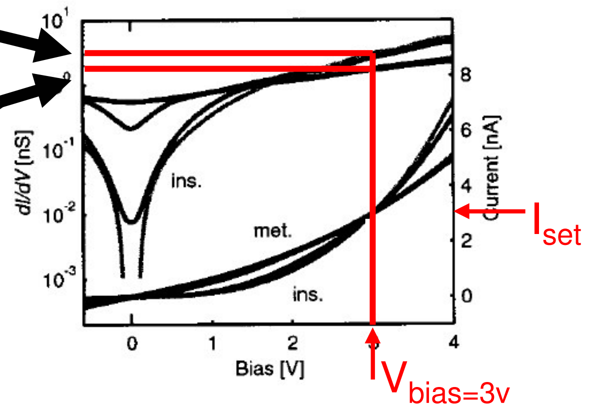


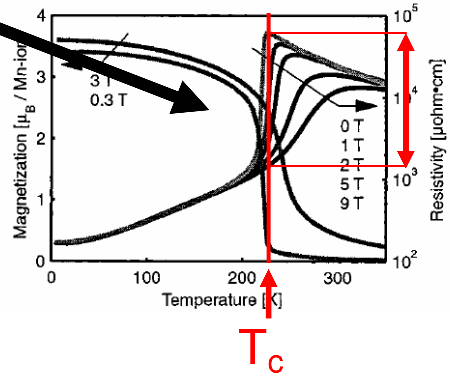
Material

- $La_{0.7}Ca_{0.3}MnO_3$ (10-100 nm) on $SrTiO_3$
- $YBa_2Cu_3O_y$ template for low-resistant contact
- STO → tensile strain

Method

- conductance map with lock-in, V_{bias}=3v
- light = insulating
- dark = metallic
- just below Tc to maximize CMR
- measured in PPMS



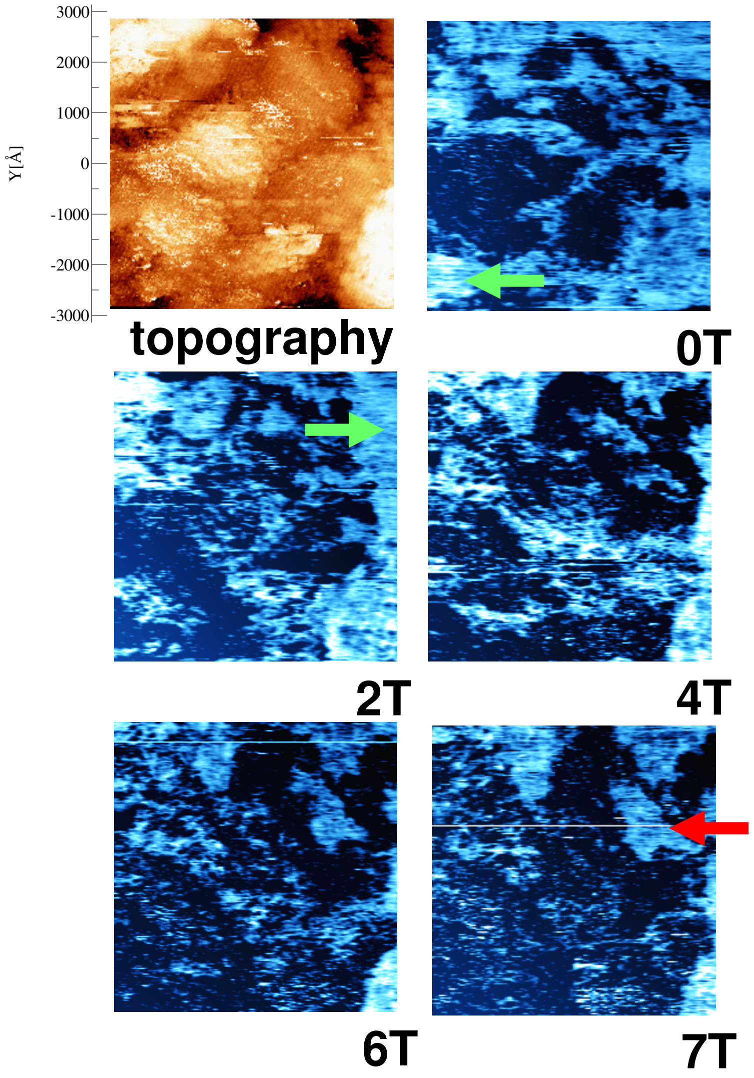


Observations

- increase applied magnetic field → more dark area
  - →insulating regions to metallic
  - →metallic percolation paths
  - →reduction in macroscopic resistivity
  - ↔CMR

Recent Results

STS in Applied Magnetic Field



V_{bias} = 2.0v, I_{set} = 200pA; $A_{lock-in}$ = 24mv, f =1.9kHz

Material

- $La_{0.7}Ca_{0.3}MnO_3$ (100 nm) on Nb-doped $SrTiO_3$ → strained (~tensile 0.6%)
- Nd doped enhance STO conduction
- sample L407

Method

- conductance map with lock-in, V_{bias}=2v
- light = insulating
- dark = metallic
- T=50K
- measured in He gas

no tunneling
$V < 2.0v$

Observations

- similar to Matthias
- limited correlation to topography
- increased AMF → increased metallic area (←)
- some increase of insulating area (←)
- **reversible? reproducible?**

not topo or
defect

Other Results: Becker *et al.*

STS with Varied Temperature

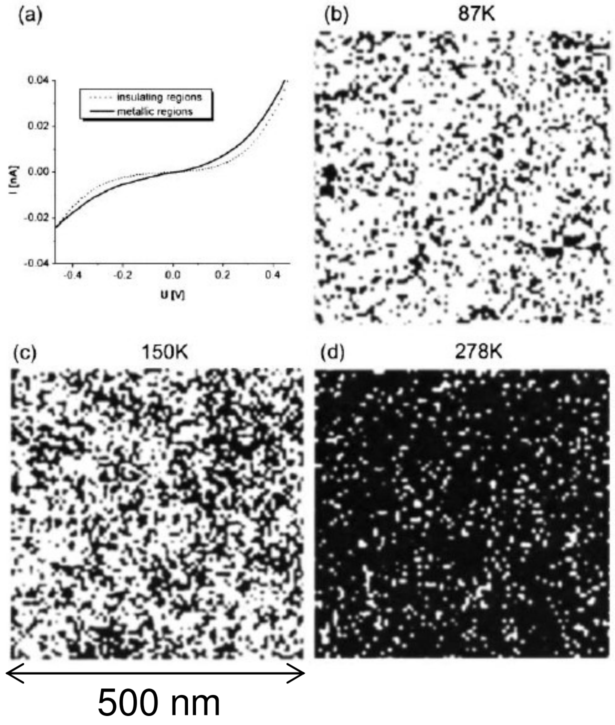
Material

- $La_{0.7}Sr_{0.3}MnO_3$ (50 nm) on MgO → epitaxial
  → strained (~compressive 8%)

Method

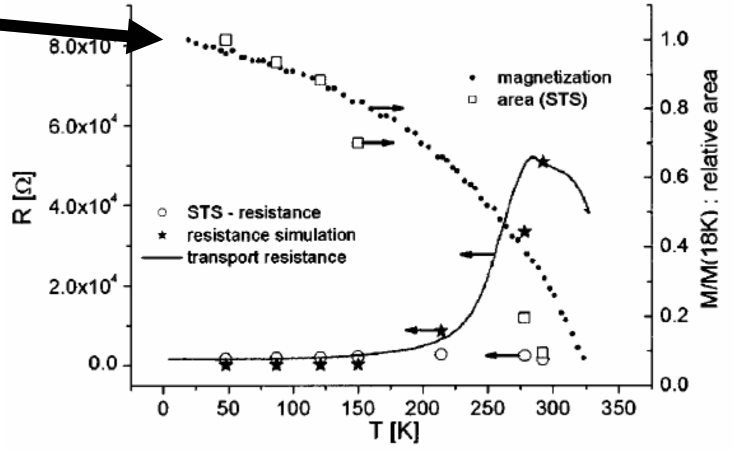
- full I-V
  - I-V sweep ±0.6v with Vbias=2v
  - every 5th pixel
  - fit 5th-order polynomial
  - slope at V = 0.0
  - spatially smoothed
- insulating/metallic threshold criteria
  - dI/dV < 5.9e-3 nA/v → insulating → black
  - dI/dV > 5.9e-3 nA/v → metallic → white
  - magnetization **:** metallic domain area
- measured in UHV with cut Pt-Ir tip, rapid cool to 50K

to avoid
oxygen loss



Observations

- claim correspondence between area and magnetization
- metallic region mean tunneling conductance does not explain
  R-T peak (○)
- but resistor network simulations demonstrate R-T peak (*)
- **inhomogeneities → MIT**



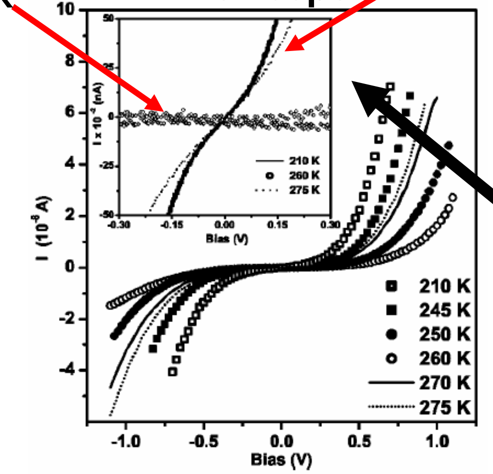
Other Results: Mitra *et al.*

STS with Varied Temperature

I-V Sweeps

260K

210K & 275K



Material

- $La_{0.7}Ca_{0.3}MnO_3$ (50 nm) on $NdGaO_3$
- LCMO epitaxial and strain free on NGO

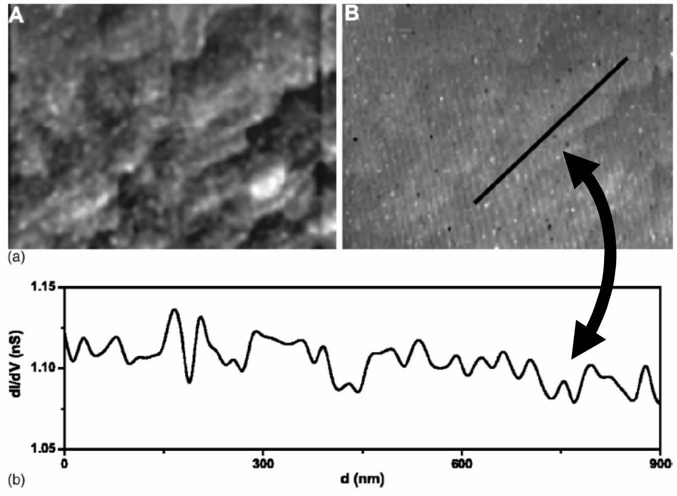
Method

- I-V (not conductance map)
- lock-in conductance map with Vbias=100mV
- measured in HV with Pt-Ir tip

Observations

- strong suppression of tunneling current at T_c = 268K
- strain free → no electronic phase separation T=265K
- topography with step (0.4 nm) & terrace structure
- sharp MIT & low residual resistivity → “quality film”
- **R-T peak explained by changes to DOS**

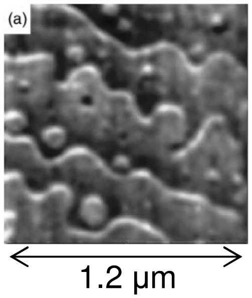
Topography **Conductance Map**



Matthis

PS on LCMO single crystal

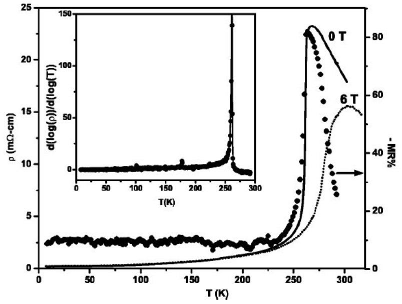
broad R-T peak on 15 nm film



T = 300K & 100K

V_{bias} = 100mV

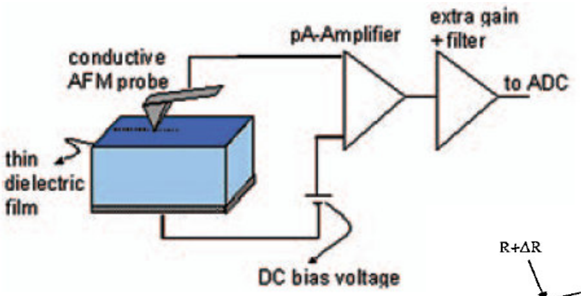
I_t = 0.5 nA

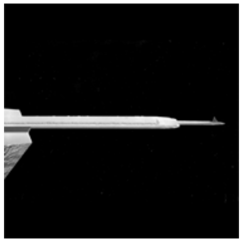


Other Methods: Conducting AFM

C-AFM → measure topography & spectroscopy independently

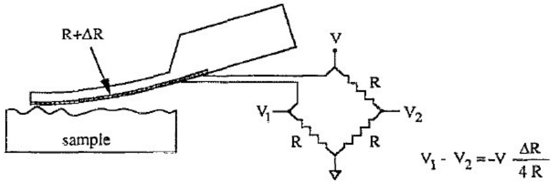
- contact AFM for topography
- apply V_{bias} to conducting tip
- measure current





Problems

- tip wear removes conductive coating
- commercially available conductive tips use laser to measure deflection → remote alignment difficult



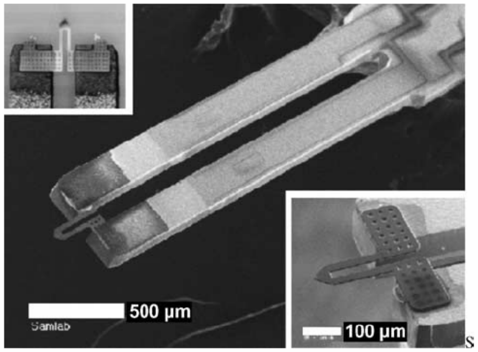
Piezoresistive (Tortonese *et al.*)
Available from Veeco

Solutions

- use conductive diamond tip coating
- modify commercial piezoelectric & piezoresistive tips
  - piezoresistive → contact AFM → I-V
  - piezoelectric → non-contact AFM → $\langle I_t(z,A)\rangle \approx \dfrac{I_t(z,0)}{\sqrt{4\pi\kappa_t A}}$

dynamic → changes in strain

- make conductive AFM with quartz tuning fork (piezoelectric)

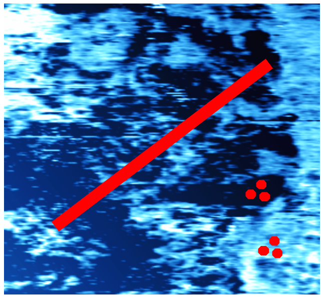


Piezoelectric (Akiyama *et al.*)
Available (?) from NanoWorld

Next Steps

STM

- Immediate
  - further investigate tip etching — etched tungsten, Pt-Ir
  - reproduce results with varied Temp & AMF
  - measure full I-V (every pixel, along line or selected spots) →
  - miscut substrate (STO or NGO or ?) — what will show step-edge induced strain
- Medium-Term
  - improvements to STM → vibration isolation, “residual” 50Hz
  - atomic resolution



AFM

- Immediate
  - investigate (modified) commercial AFM tips
  - improvements to our AFM
- Medium-Term
  - conductive AFM at RT with our existing AFM — need current amplifier
- Longer-Term
  - low-temperature AFM