Infrared spectroscopy and nanoscale imaging of the metal-insulator phase transition in vanadium dioxide

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Department of Physics
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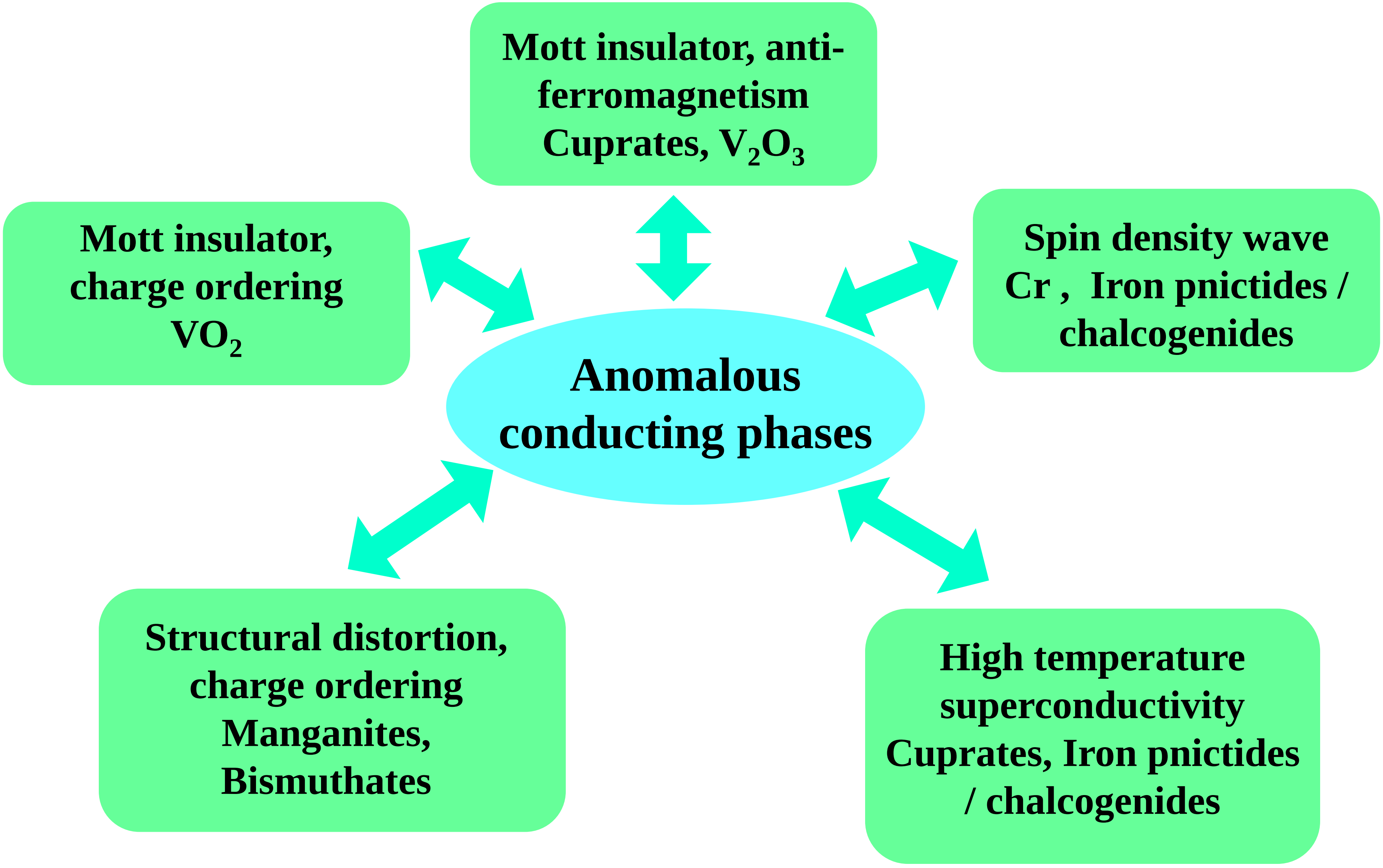
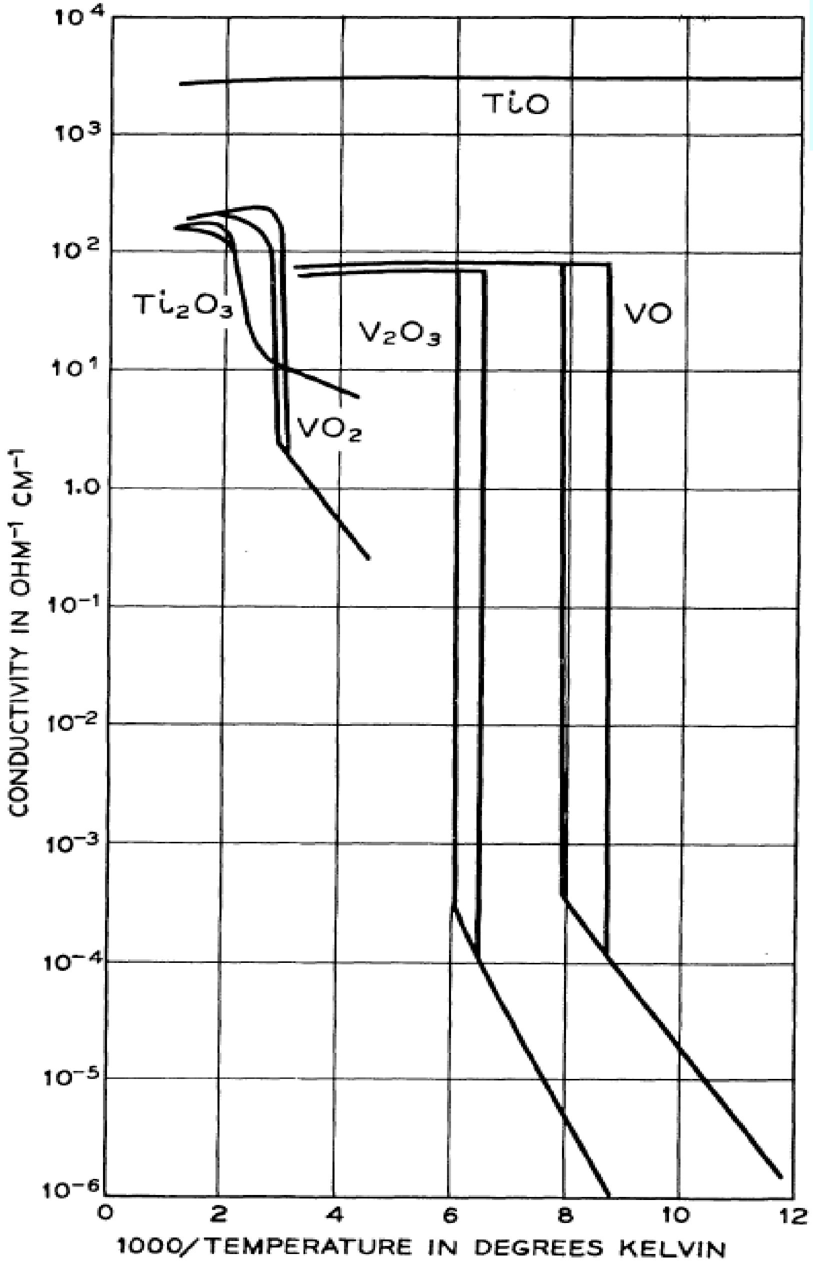
Electronic Structure Workshop 2013
College of William & Mary

A grand challenge

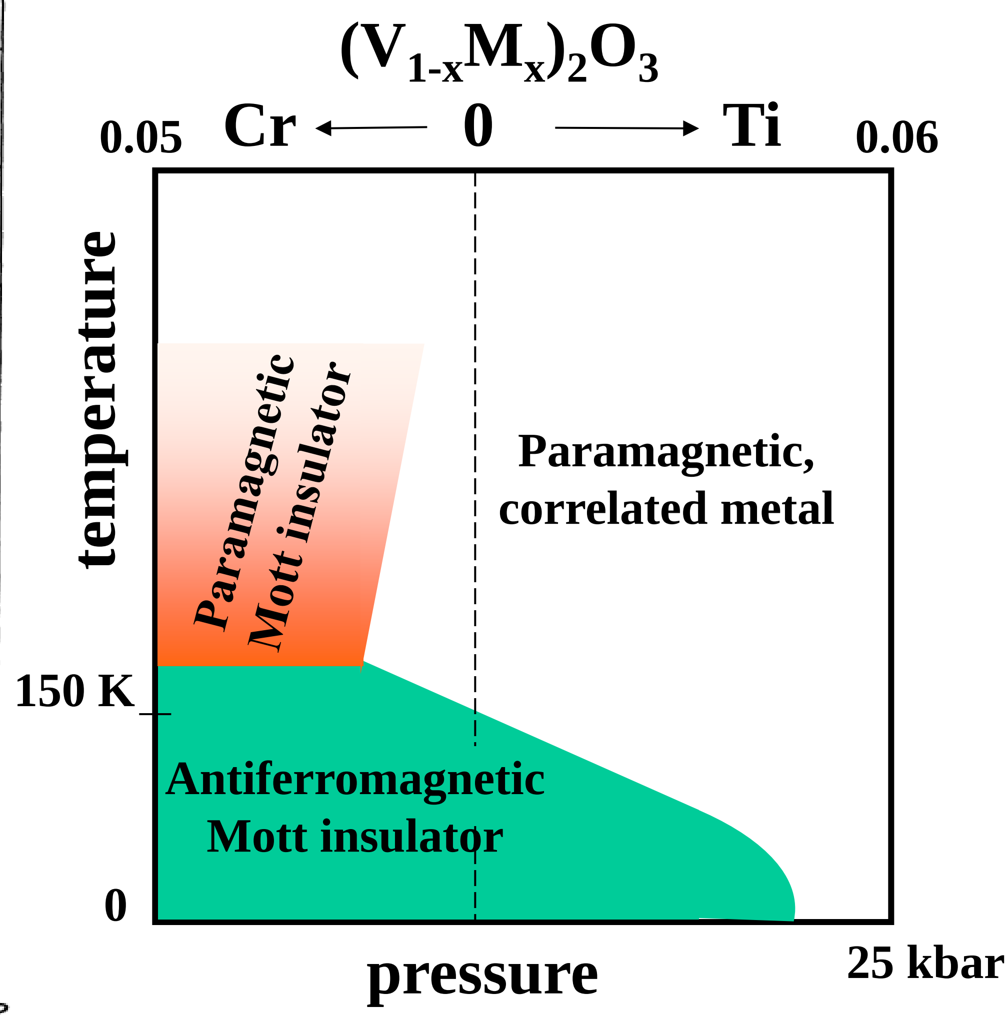


Oxides of vanadium and titanium

Metal-insulator transitions in correlated binary oxides



F. J. Morin, Phys. Rev. Lett. 3, 34 (1959)

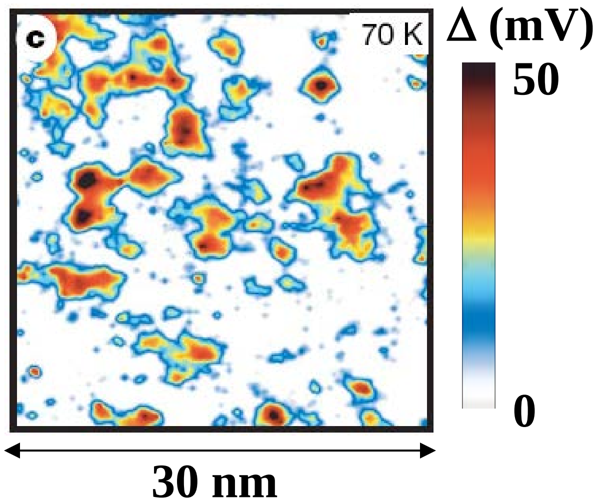


Inhomogeneities and Correlated Electron Matter

Cuprates: tunneling

Gomes et al., Nature 447, 569 ('07)

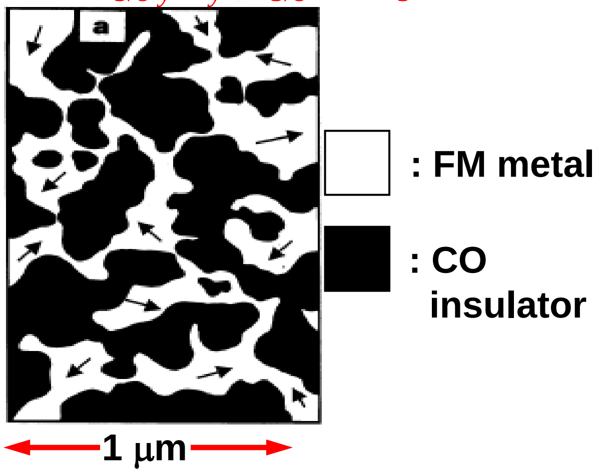
Over-doped Bi-2212



Manganites: el microscopy

M.Uehara, S.Mori, C.H.Chen, S.W.Cheong, Nature 399 560 (1999)

$La_{5/8-y}Pr_yCa_{3/8}MnO_3$ (y=0.375)



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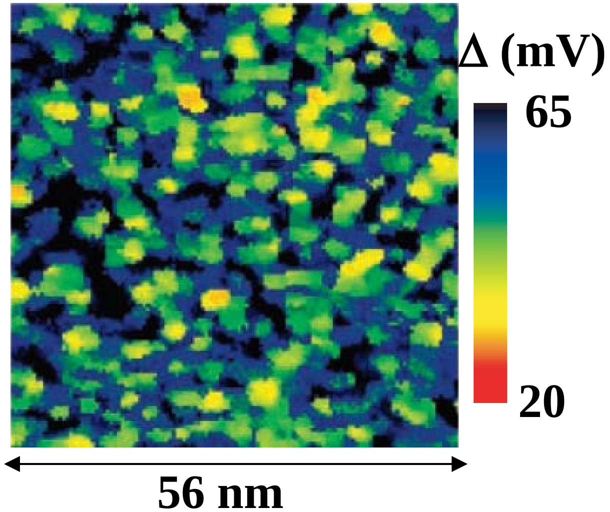

Manganites: MFM

L.Zhang et al, Science 298 805 ('02)

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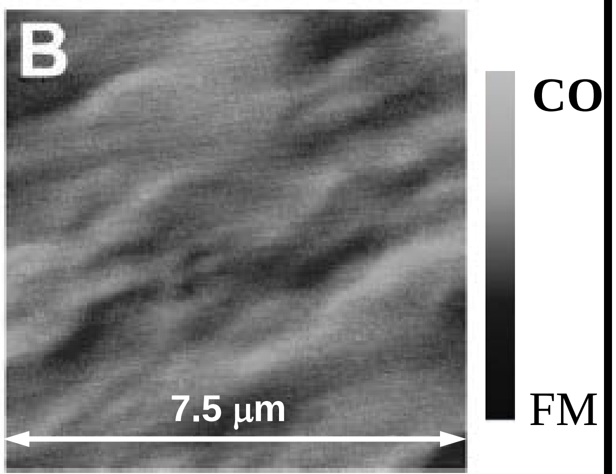

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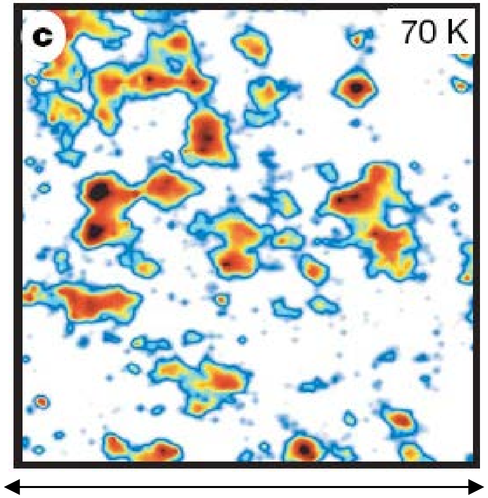

30 nm

Manganites: el microscopy

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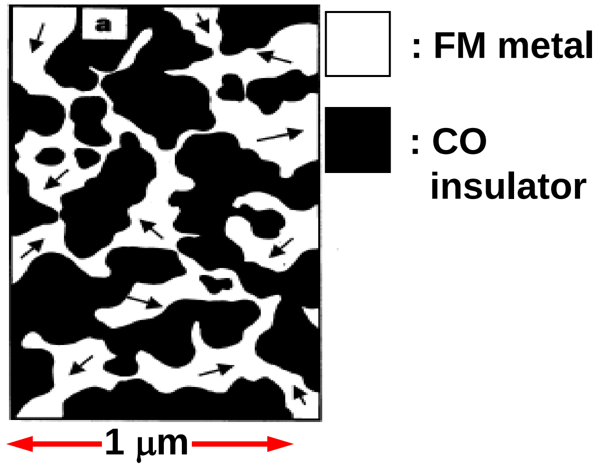

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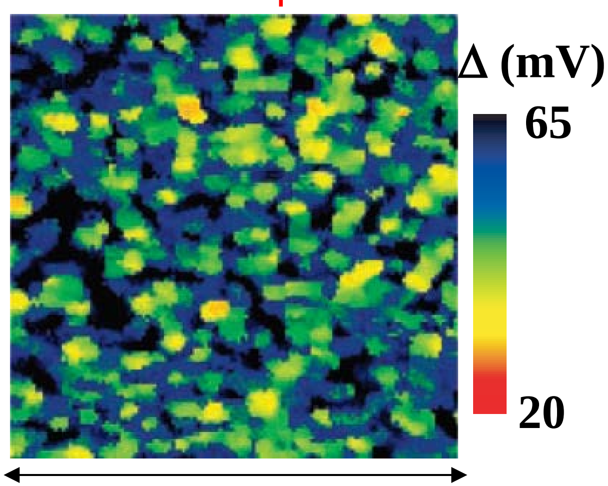
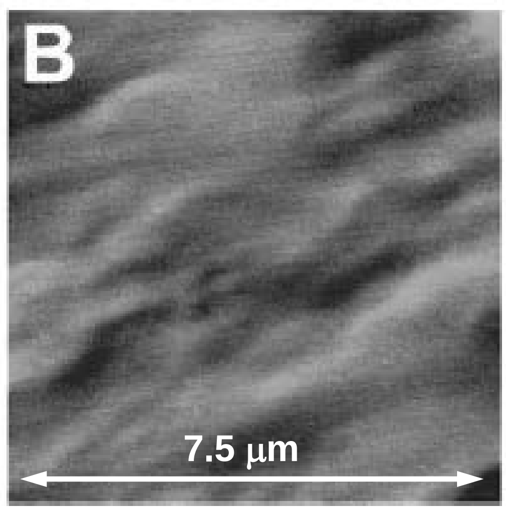


56 nm

Manganites: MFM

L.Zhang et al Science 298 805 (02)



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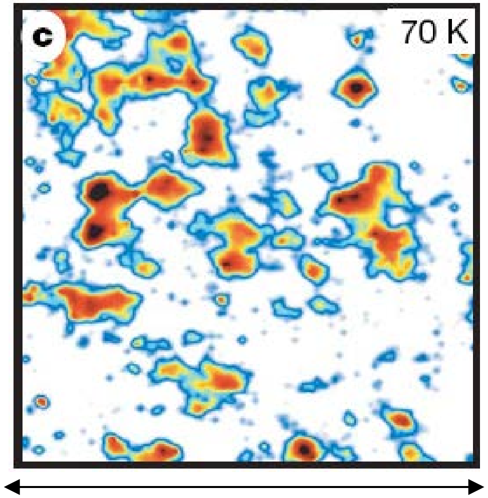

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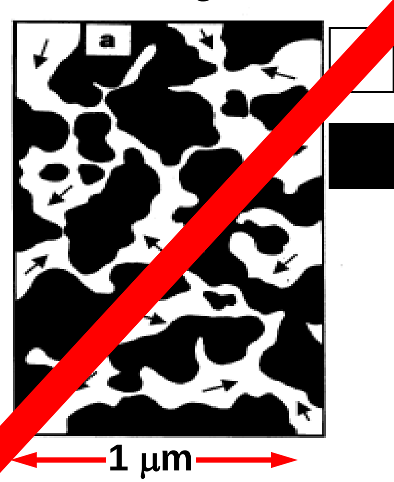

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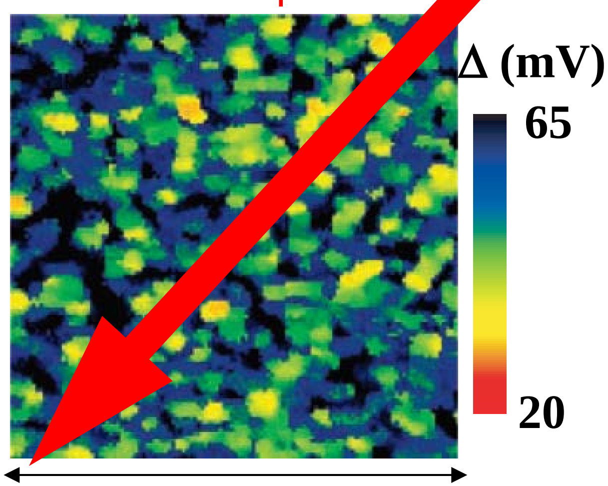

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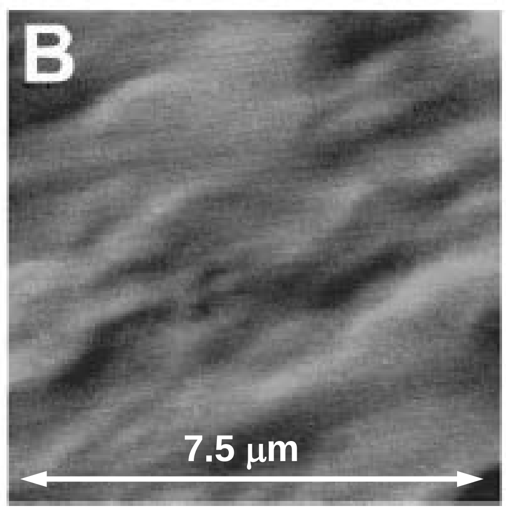


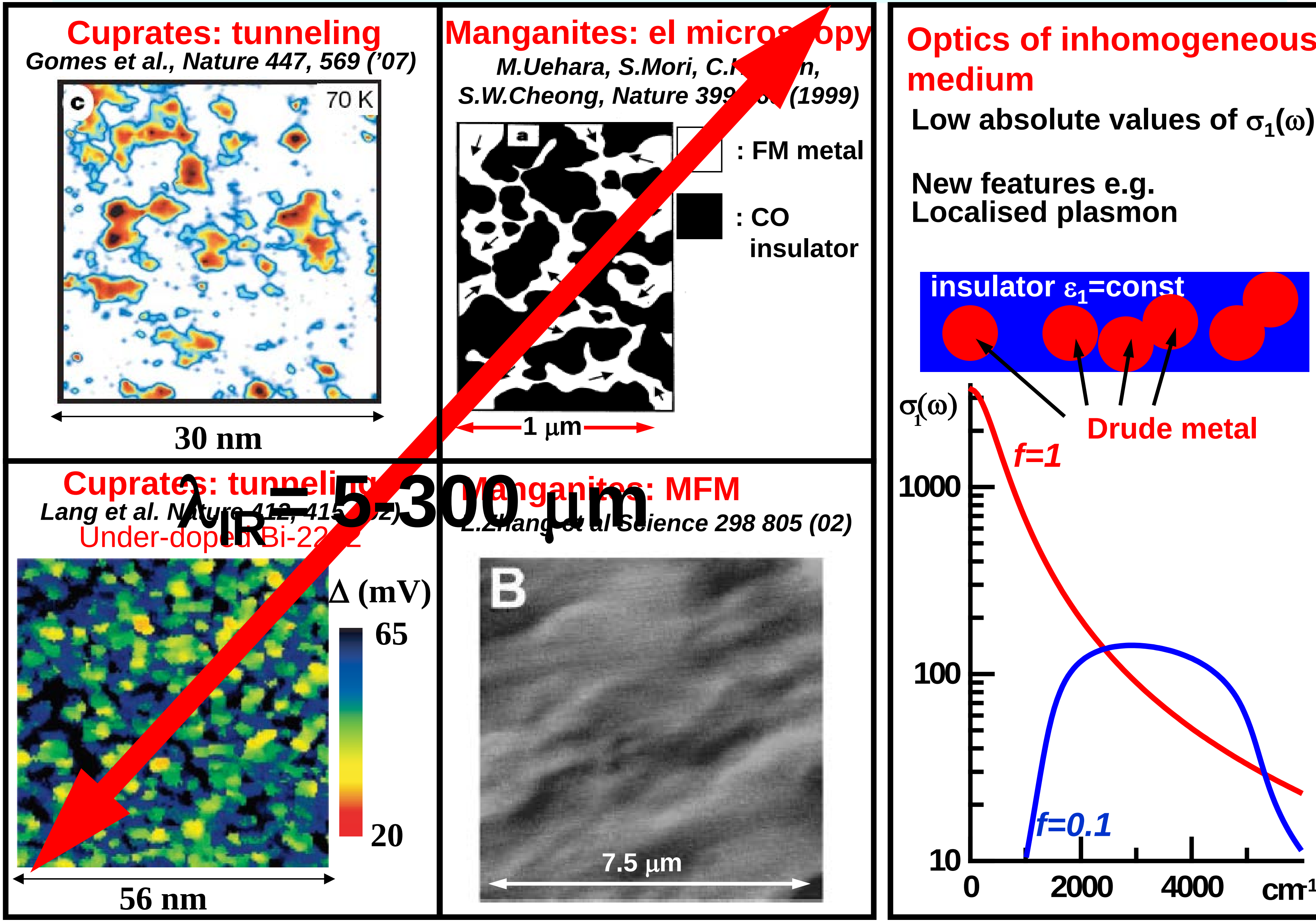
λ_{IR} = 5-300 μm

Optics of inhomogeneous medium

Low absolute values of $\sigma_1(\omega)$

New features e.g.
Localised plasmon

Inhomogeneities and Correlated Electron Matter



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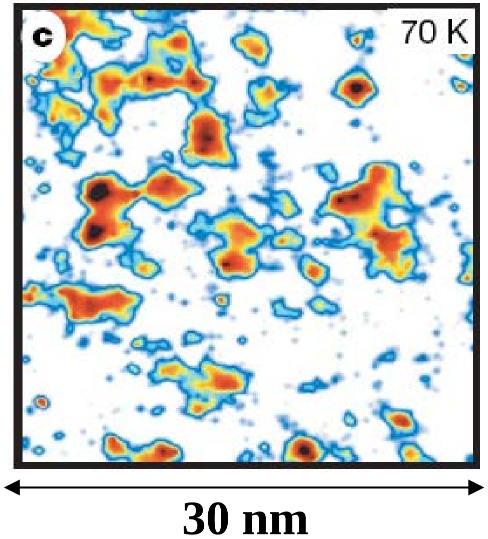
Gomes et al., Nature 447, 569 ('07)



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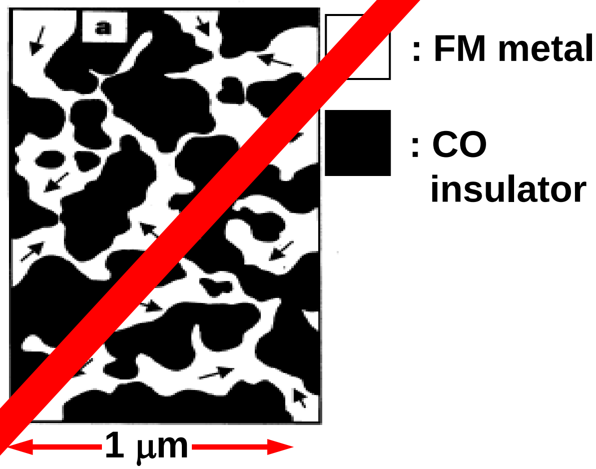

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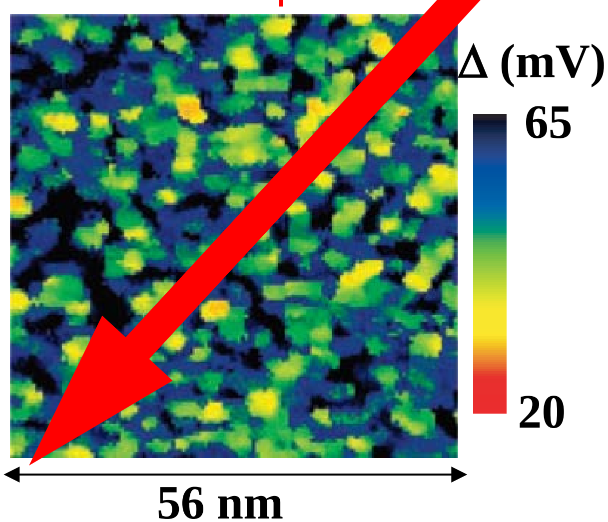

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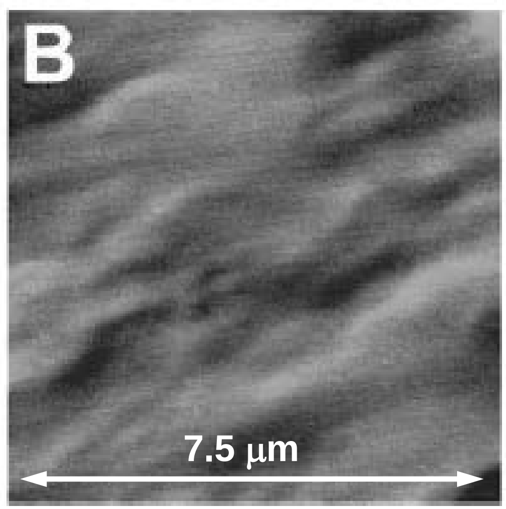

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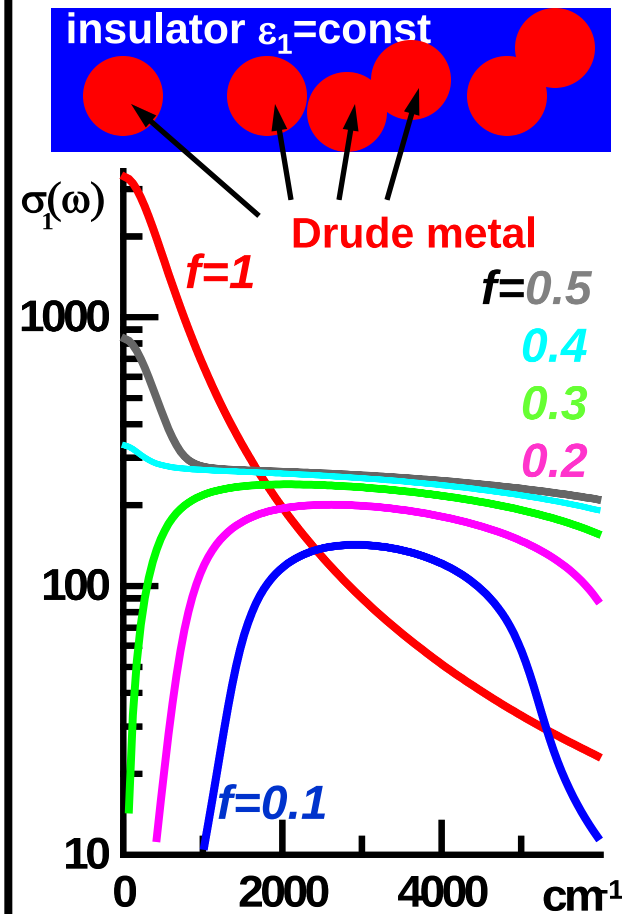
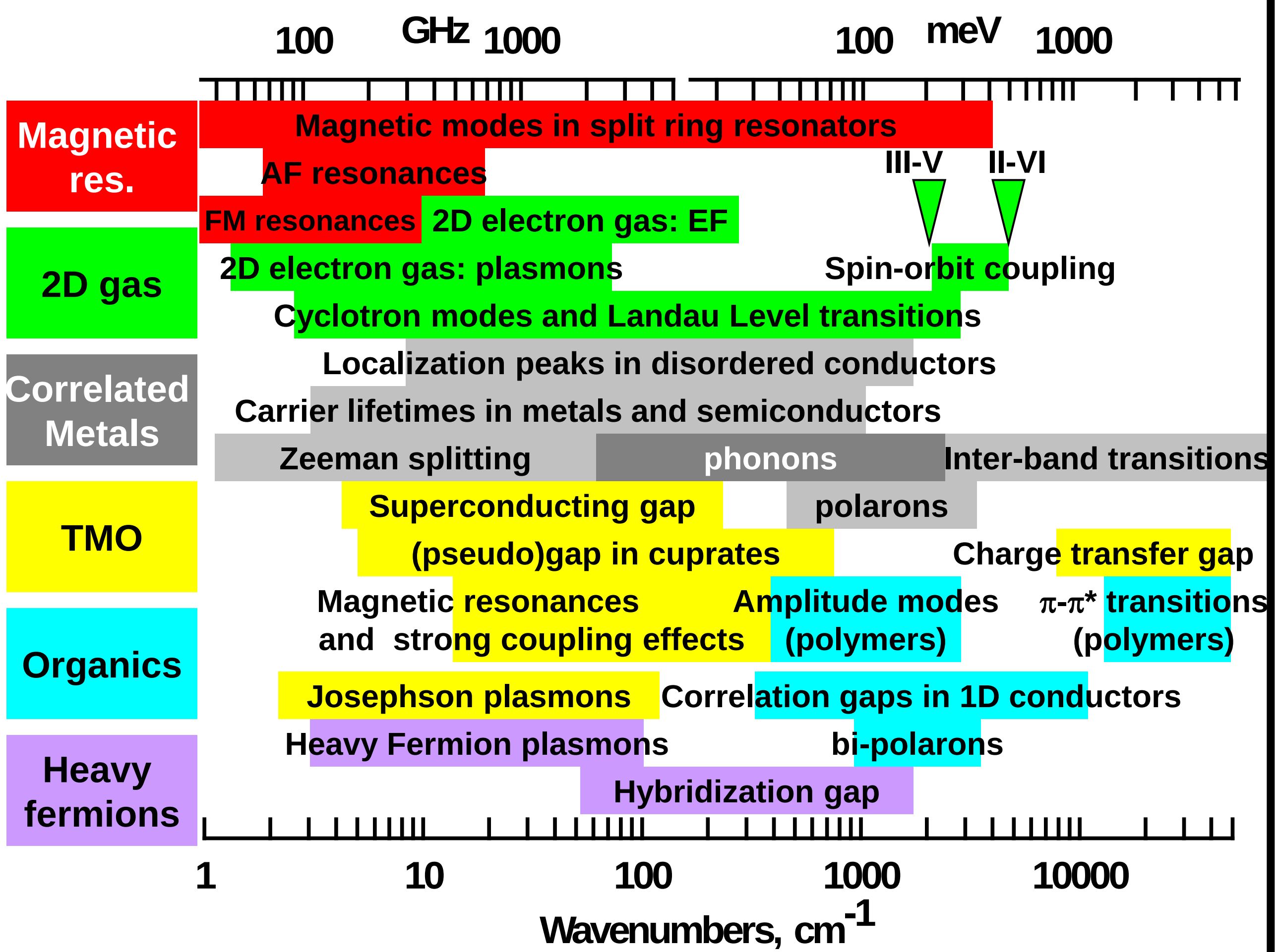
Localised plasmon

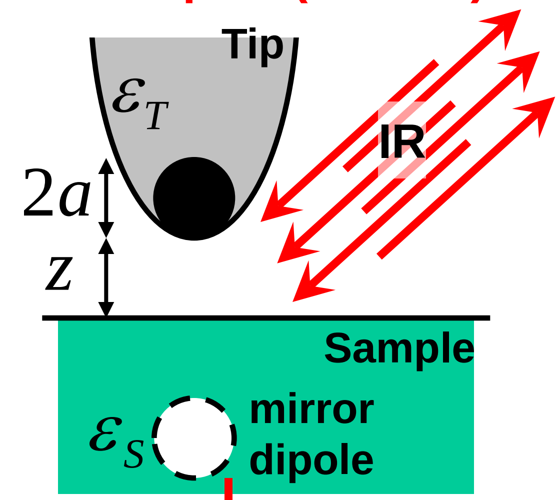


Infrared optics at the nano-scale



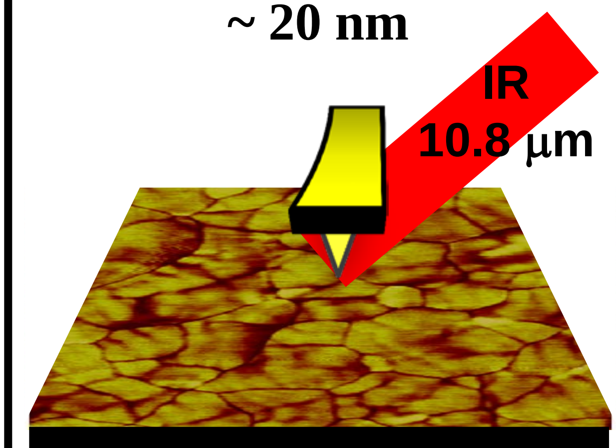
D.N.Basov and T.Timusk Reviews of Modern Physics 77, 721 (2005)
S.V. Dordevic and D.N. Basov Annalen der Physik 15, 545 (2006)

Scattering Near field IR microscope (s-SNIM)



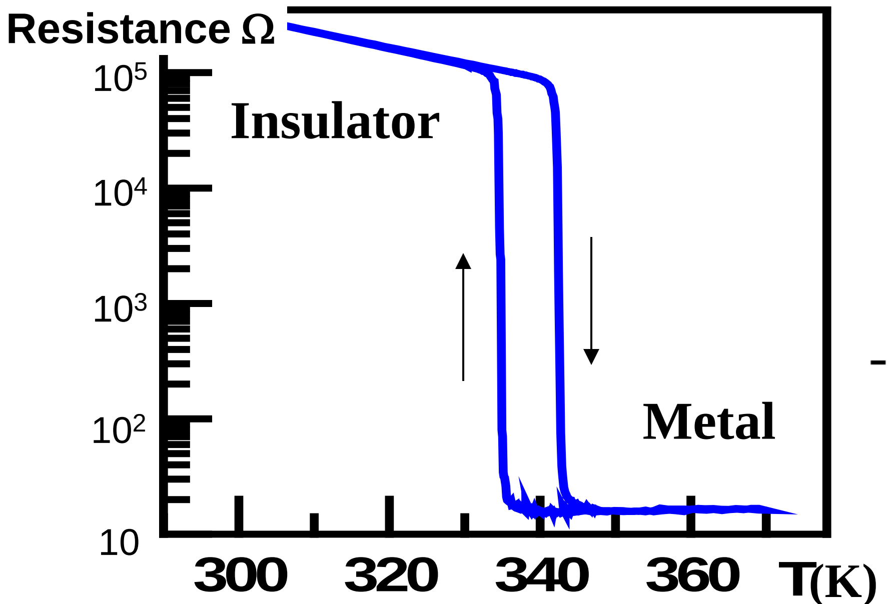
$\varepsilon_1, \varepsilon_2$ @ ω_{laser}

Spatial resolution
~ 20 nm

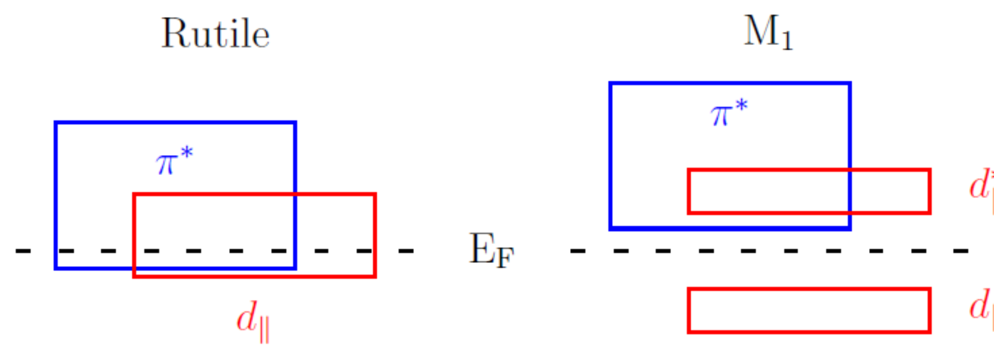


F.Keilmann J. El. Micr. 53, 187 (2004)

First Order Metal-insulator Transition in VO_2



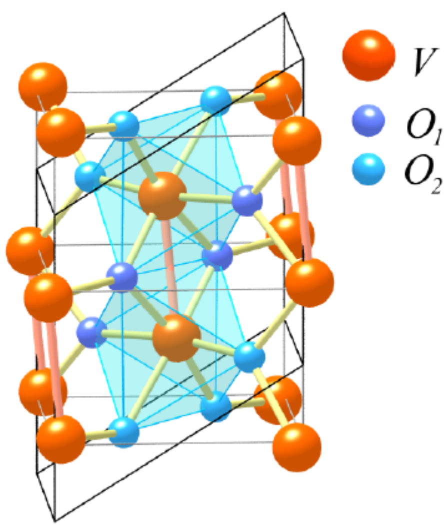
Band diagram

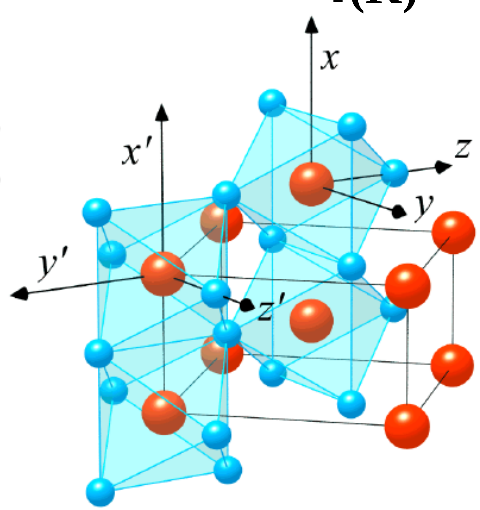


Nature of the energy gap ?

V-V dimerization (Peierls instability)

Electronic correlations (Mott physics)





Monoclinic M_1 insulator

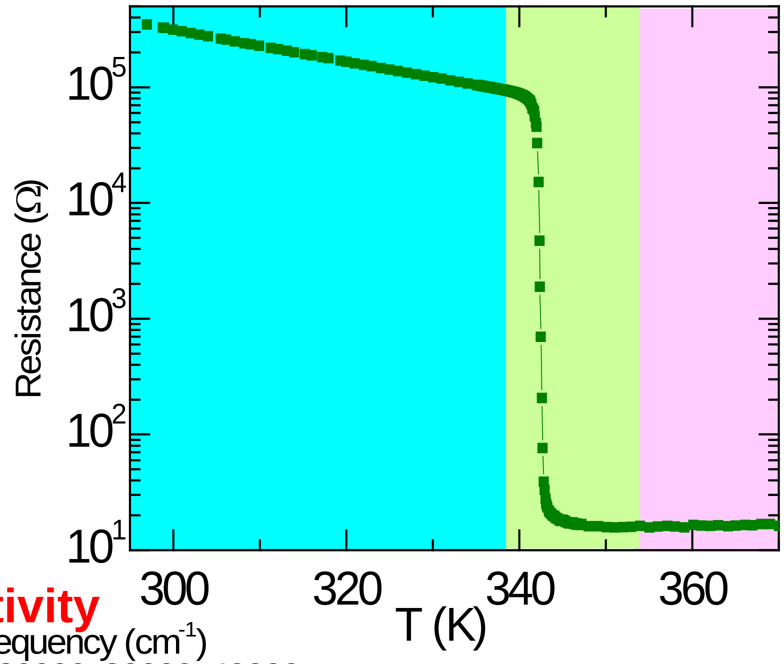
Rutile metal

V. Eyert, Ann. Phys. (Leipzig) 11, 650 (2002)

VO_2 : Correlated insulator, correlated metal

dR/dT < 0

Monoclinic insulating

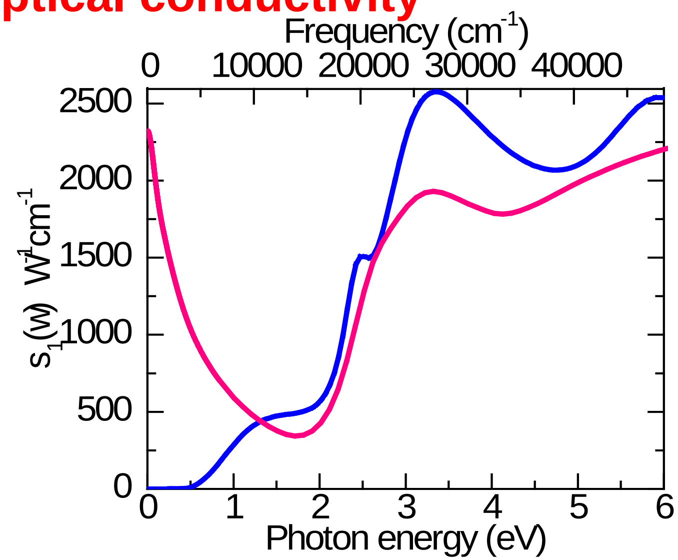


dR/dT > 0

Rutile metallic

Nature of the metallic phase in the transition region ?

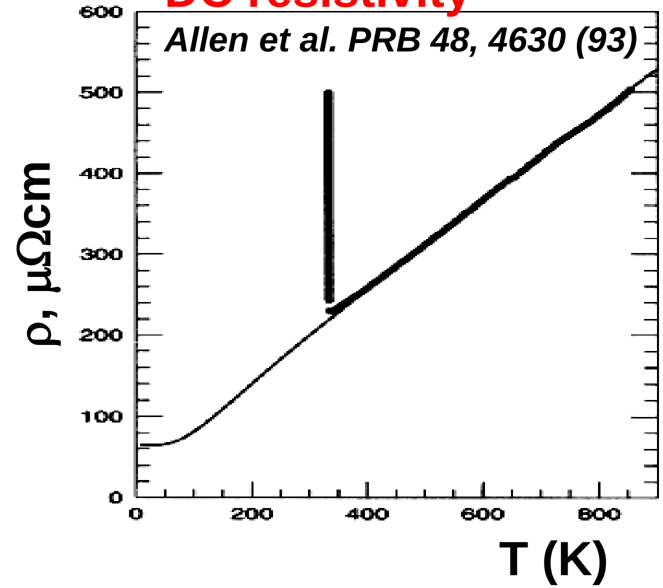
Optical conductivity



Changes in $\sigma_1(\omega)$ up to 6 eV

Mott physics

DC resistivity



M. M. Qazilbash *et al.*, PRB 74, 205118 (2006)

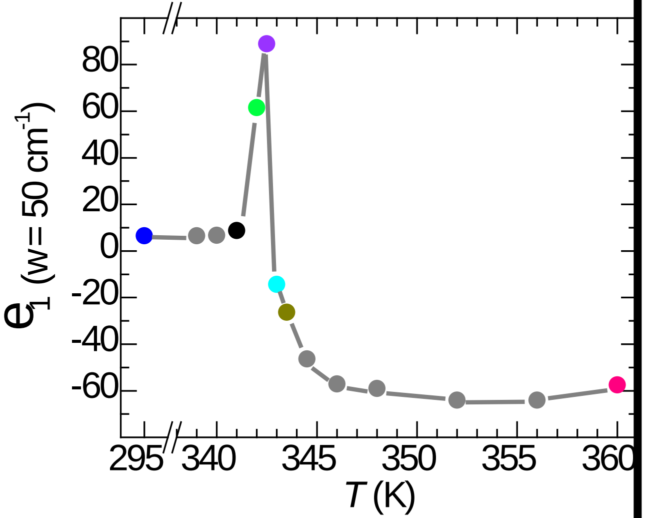
In the metal-insulator transition regime of VO_2

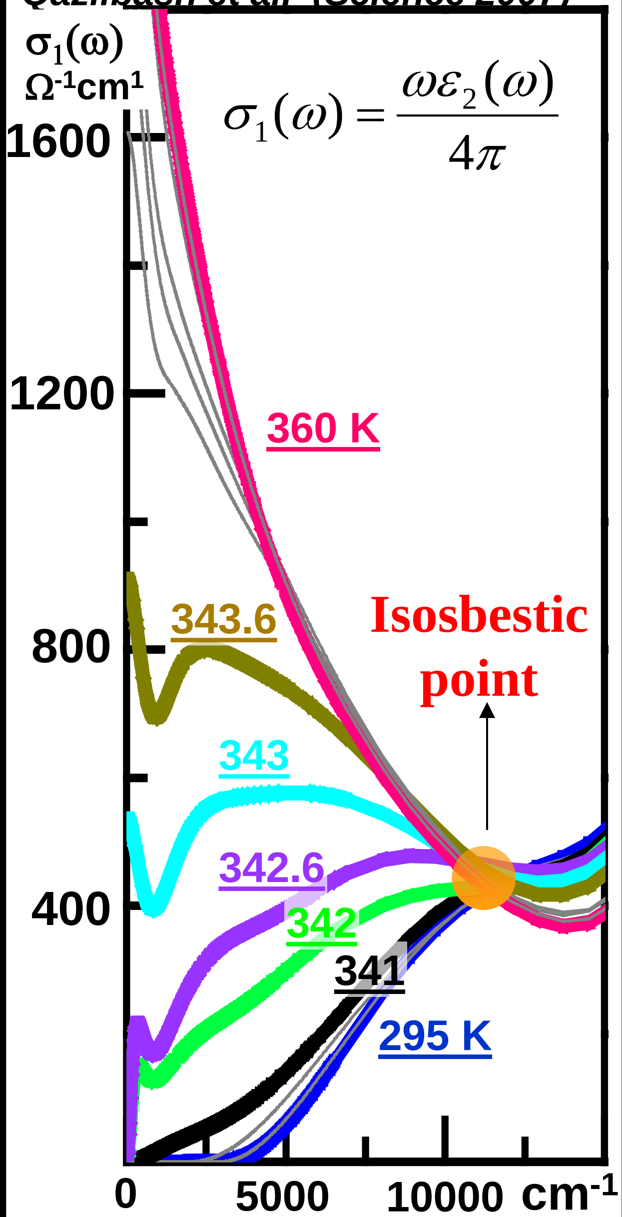
VO_2 film 100 nm on sapphire substrate

Ellipsometry
(400 – 15000 cm^{-1})

Reflectance
(40 – 660 cm^{-1})

$$\varepsilon_1(\omega), \varepsilon_2(\omega)$$





$$\sigma_1(\omega) = \frac{\omega \varepsilon_2(\omega)}{4\pi}$$

- **spectral weight fills up gap**
- **isosbestic point**

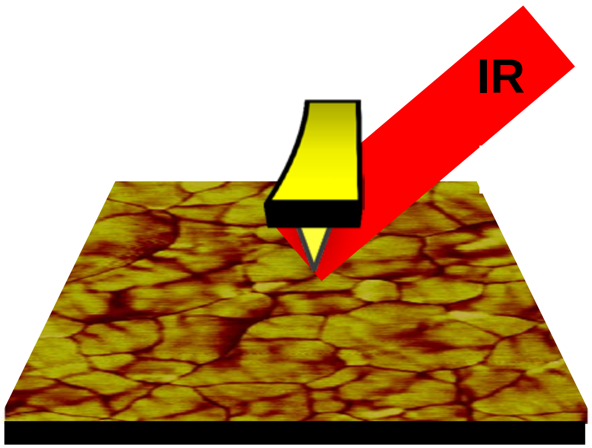
Similar to other Mott systems

percolation

M. M. Qazilbash *et al.*, Science 318, 1750 (2007)

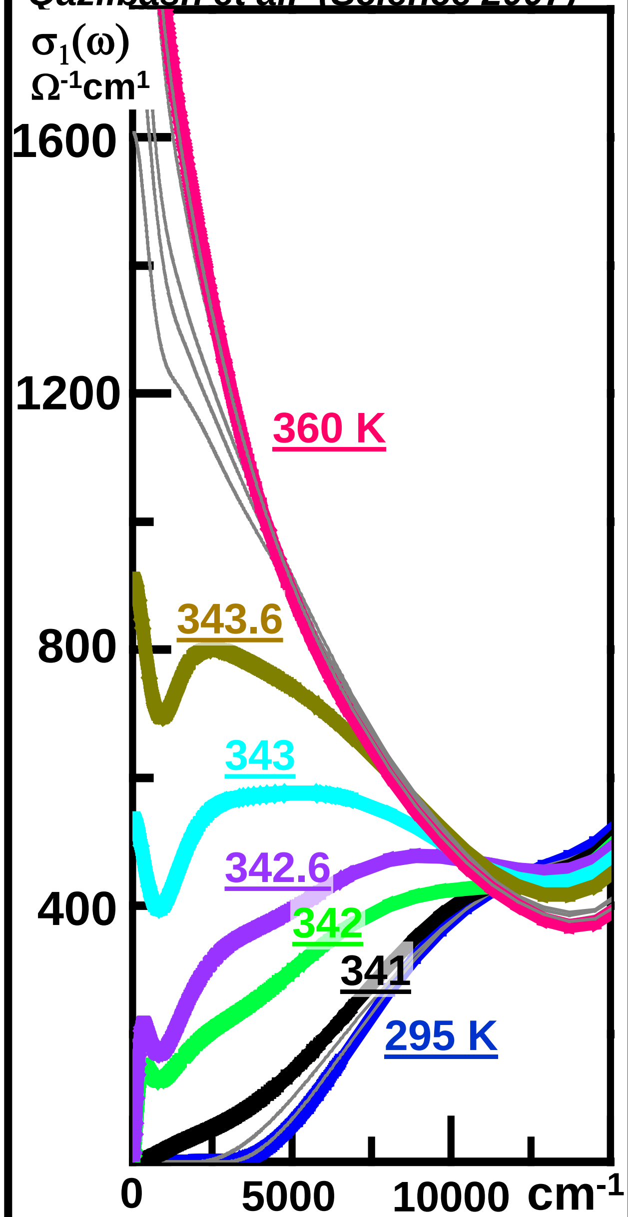
Direct observation of inhomogeneity in VO_2

IR nanoscopy



Zooming on $\sigma_1(\omega)$ near T_c

Qazilbash et al. (Science 2007)



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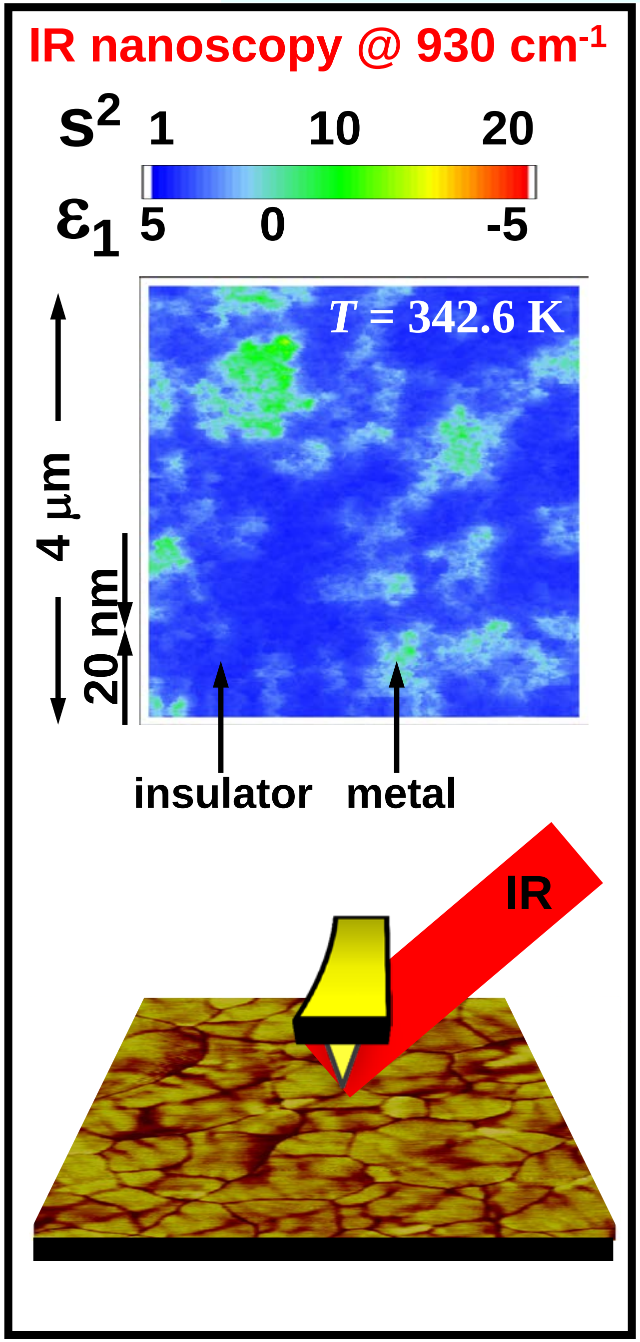

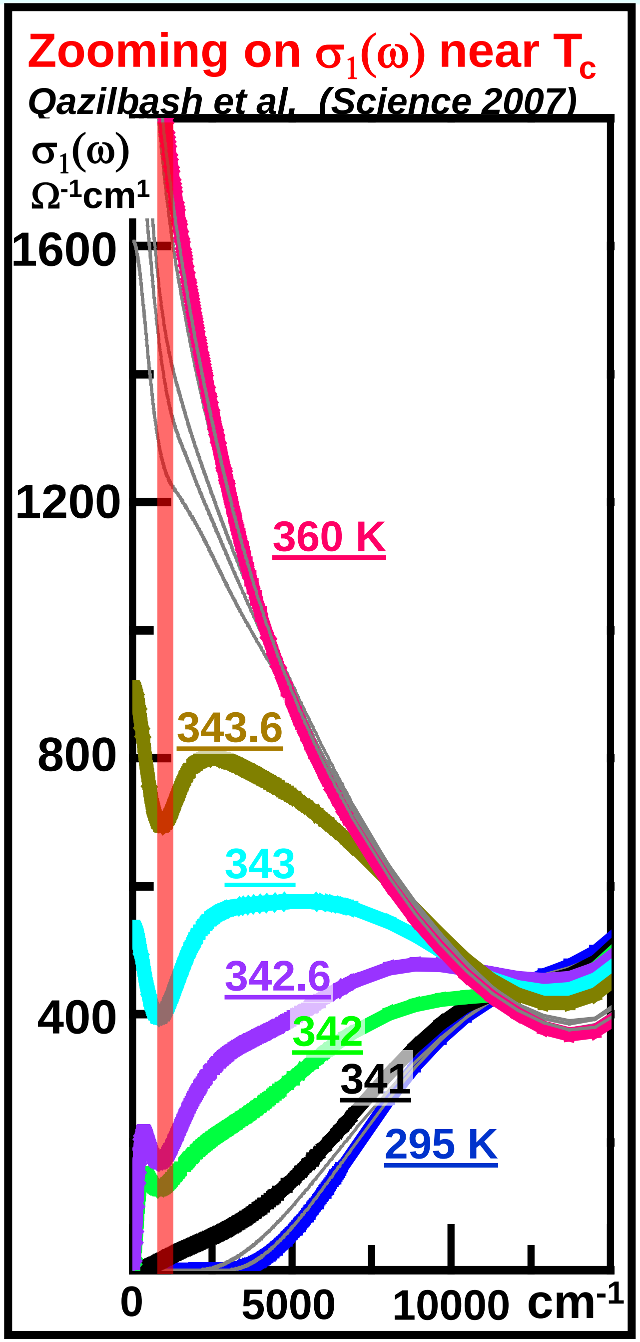

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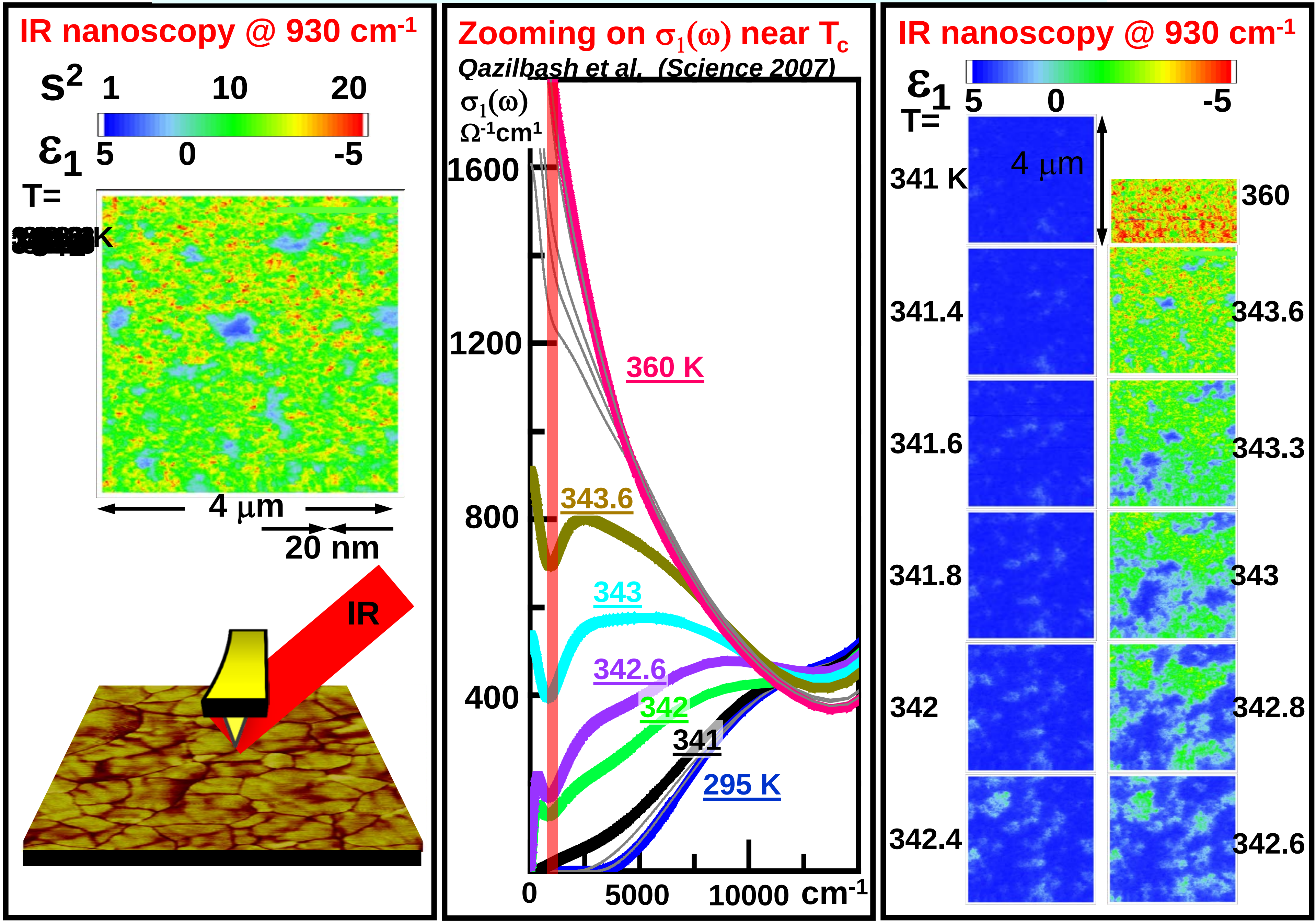
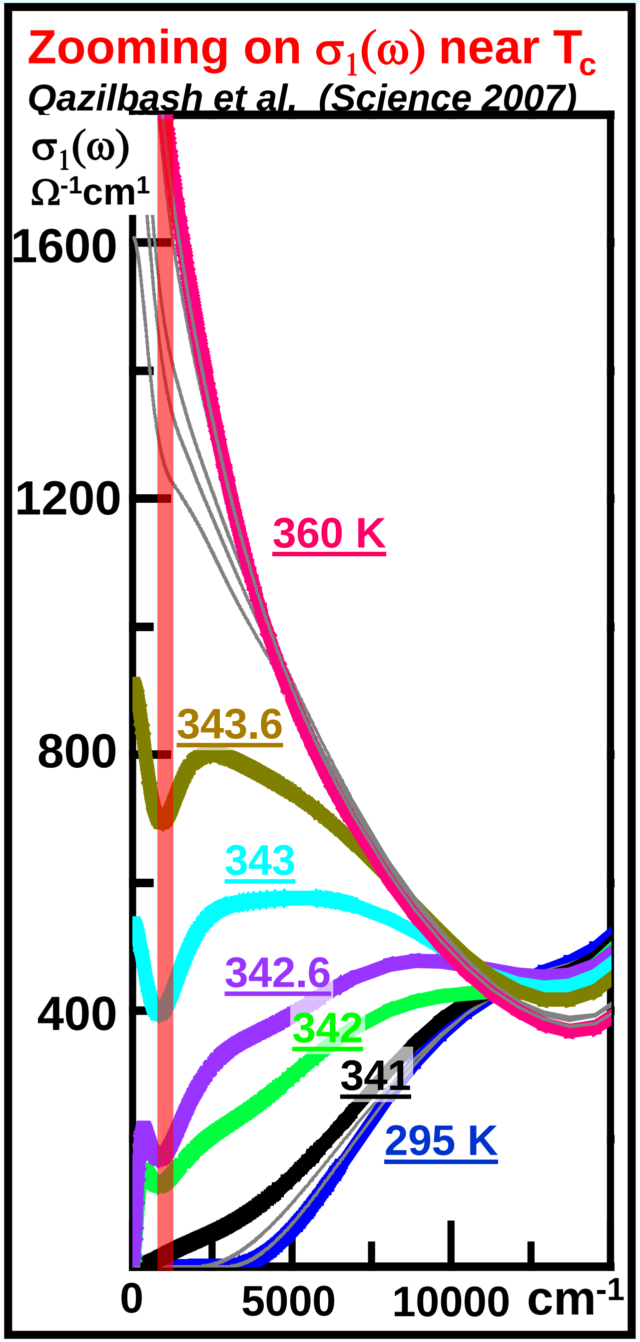


Inhomogeneity in VO_2

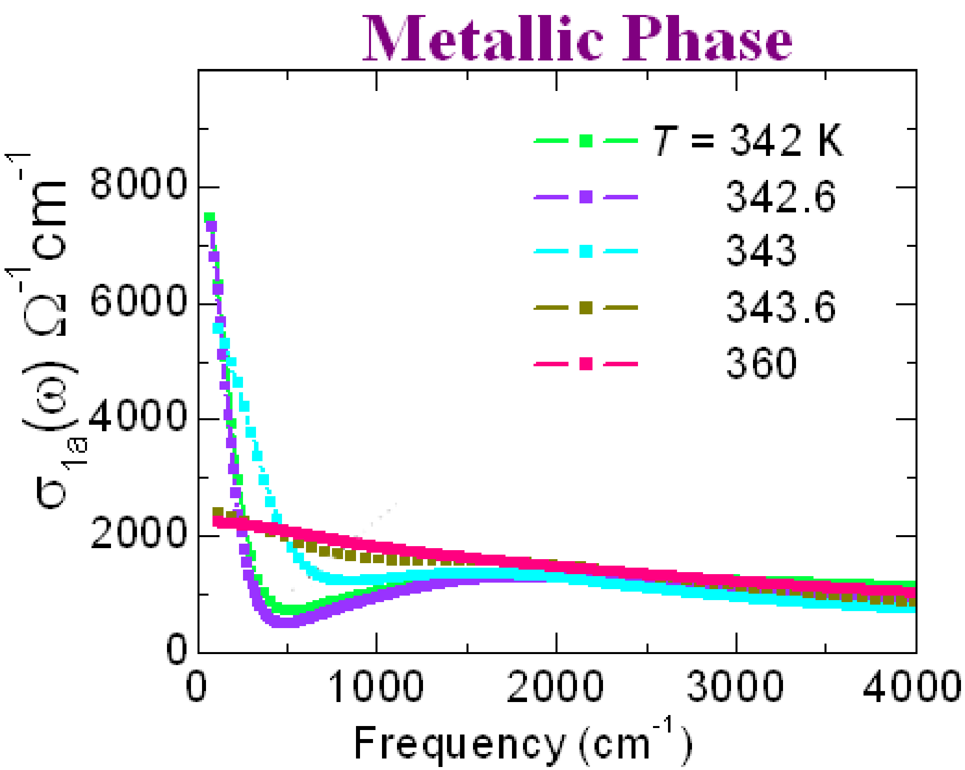
Infared nanoscopy @ 930 cm^{-1}

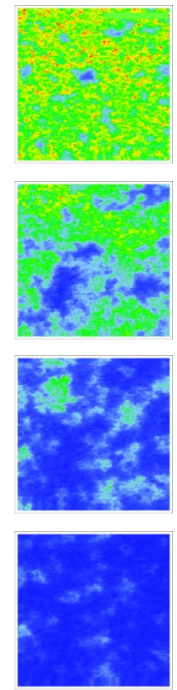


Broad-band spectra of metallic puddles ?

Effective medium approach to inhomogeneity in VO_2

Bruggeman Effective Medium Theory to determine broadband infrared properties of metallic phase





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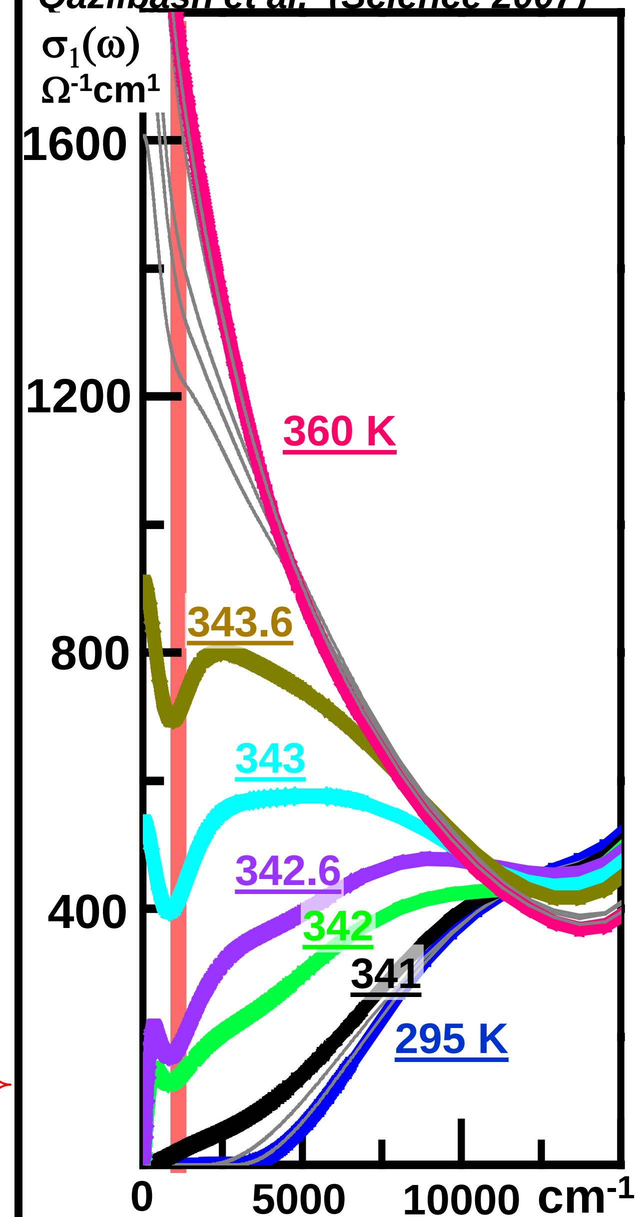
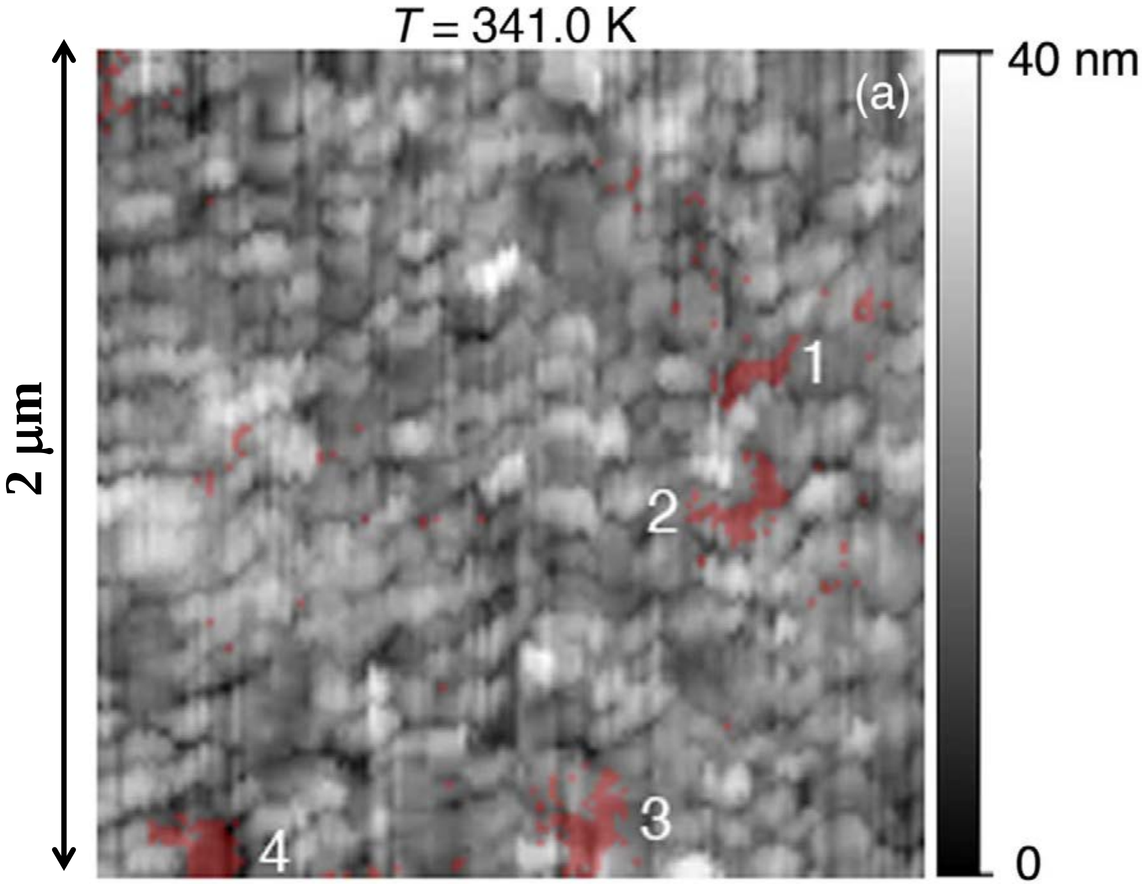
Qazilbash et al. (Science 2007)



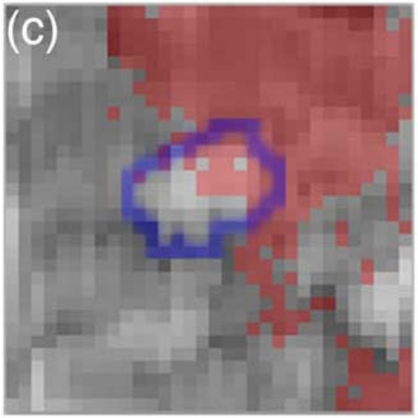
Optical conductivity of metallic islands is different from T = 360 K rutile metallic phase

Strong correlations
Finite size effects
Strain fields
Grain boundaries

Film morphology and metallic regions



Metallic regions (red)
superimposed on topography



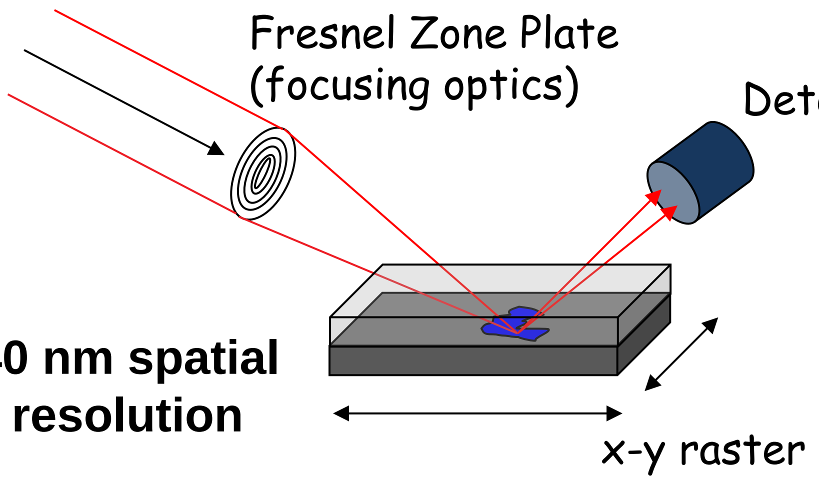
Phase coexistence
in single grain

Metallic regions nucleate at or near grain boundaries and crevices

A. Frenzel *et al*,
Phys. Rev. B 80, 115115 (2009)

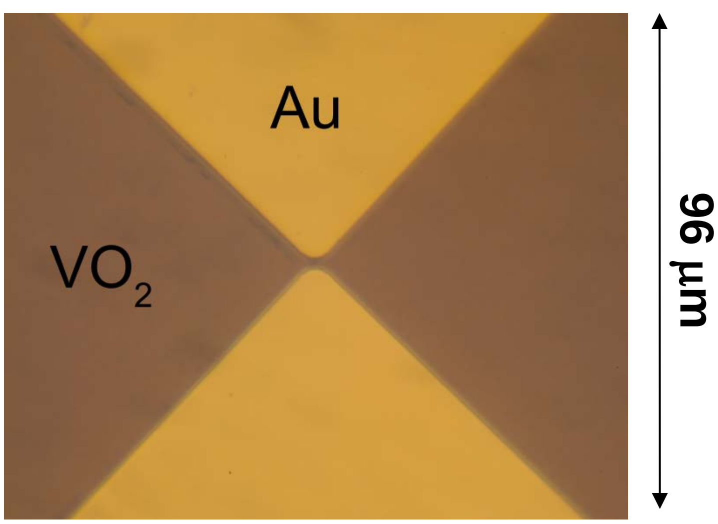
Structural change: Nanoscale x-ray diffraction

Imaging nanoscale domains by X-ray nanoprobe, Argonne National Lab

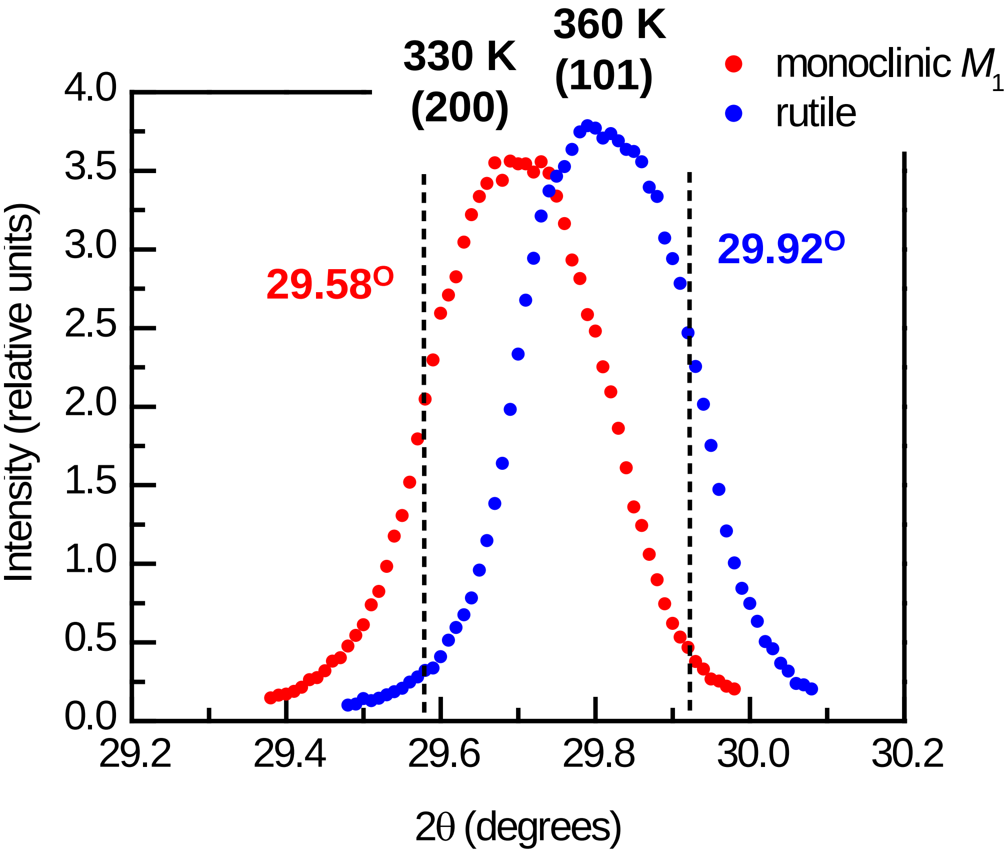


40 nm spatial resolution

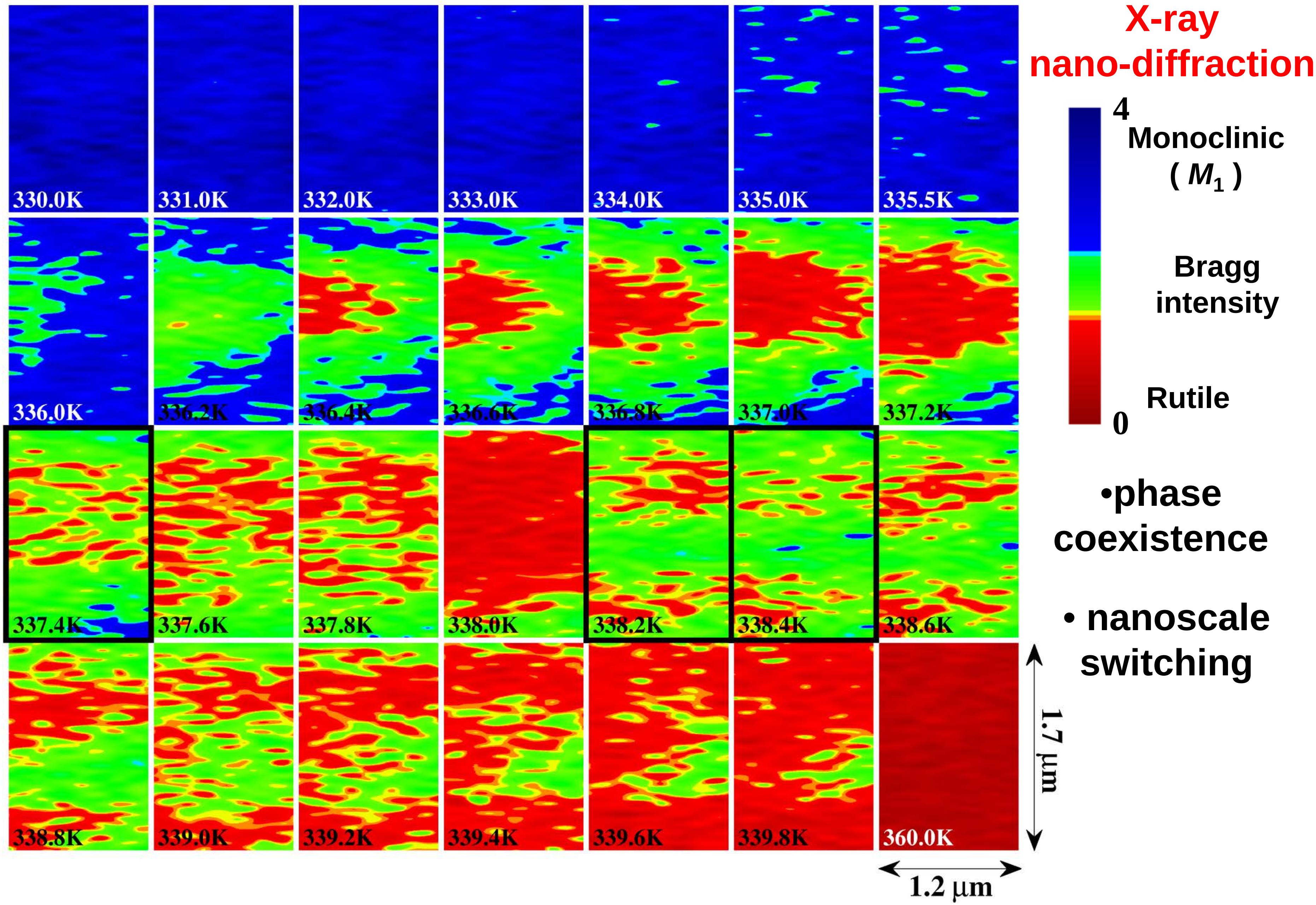
VO_2 device



Bragg diffraction



Non-monotonic, metastable structural changes

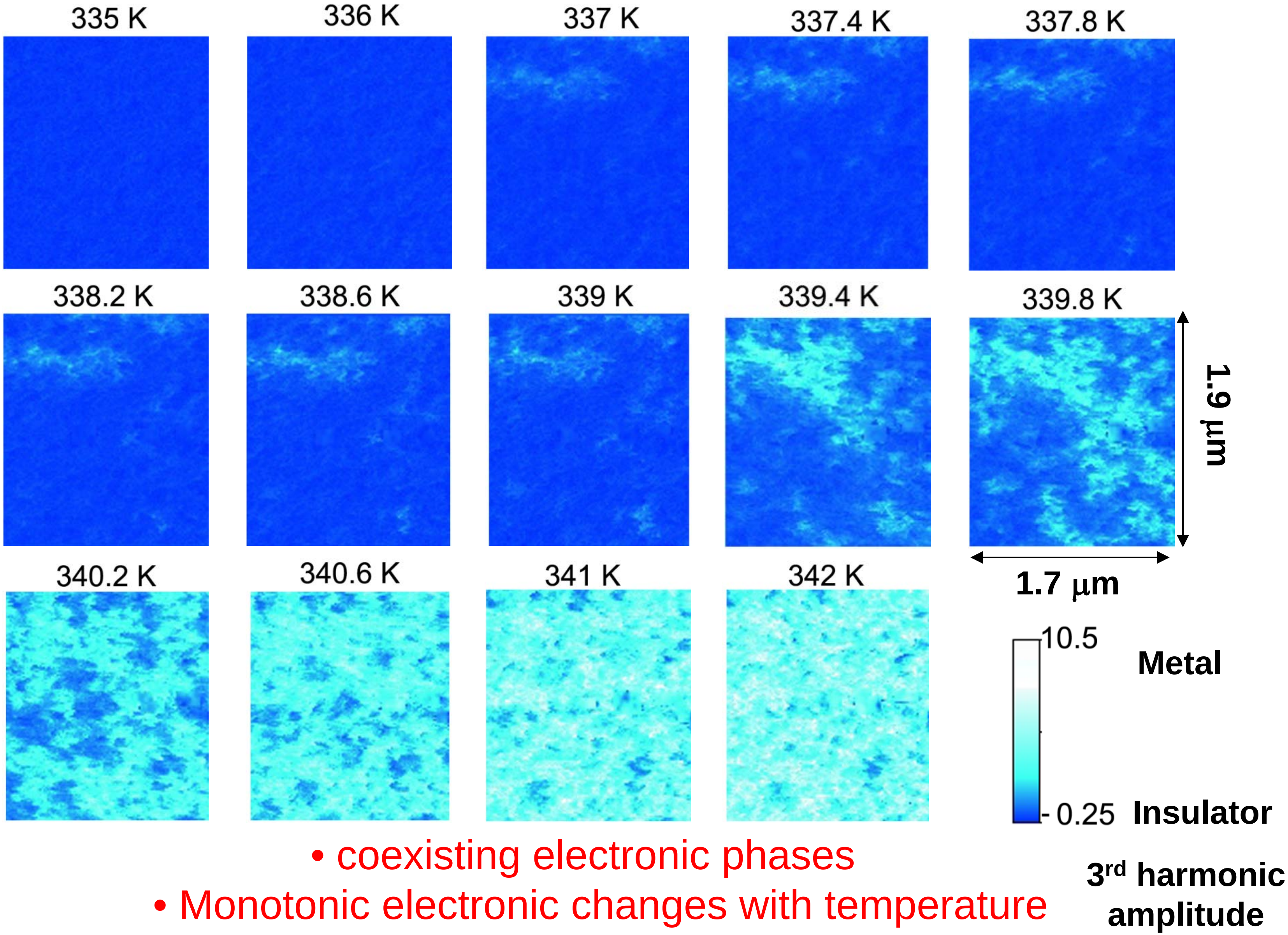


• phase coexistence

• nanoscale switching

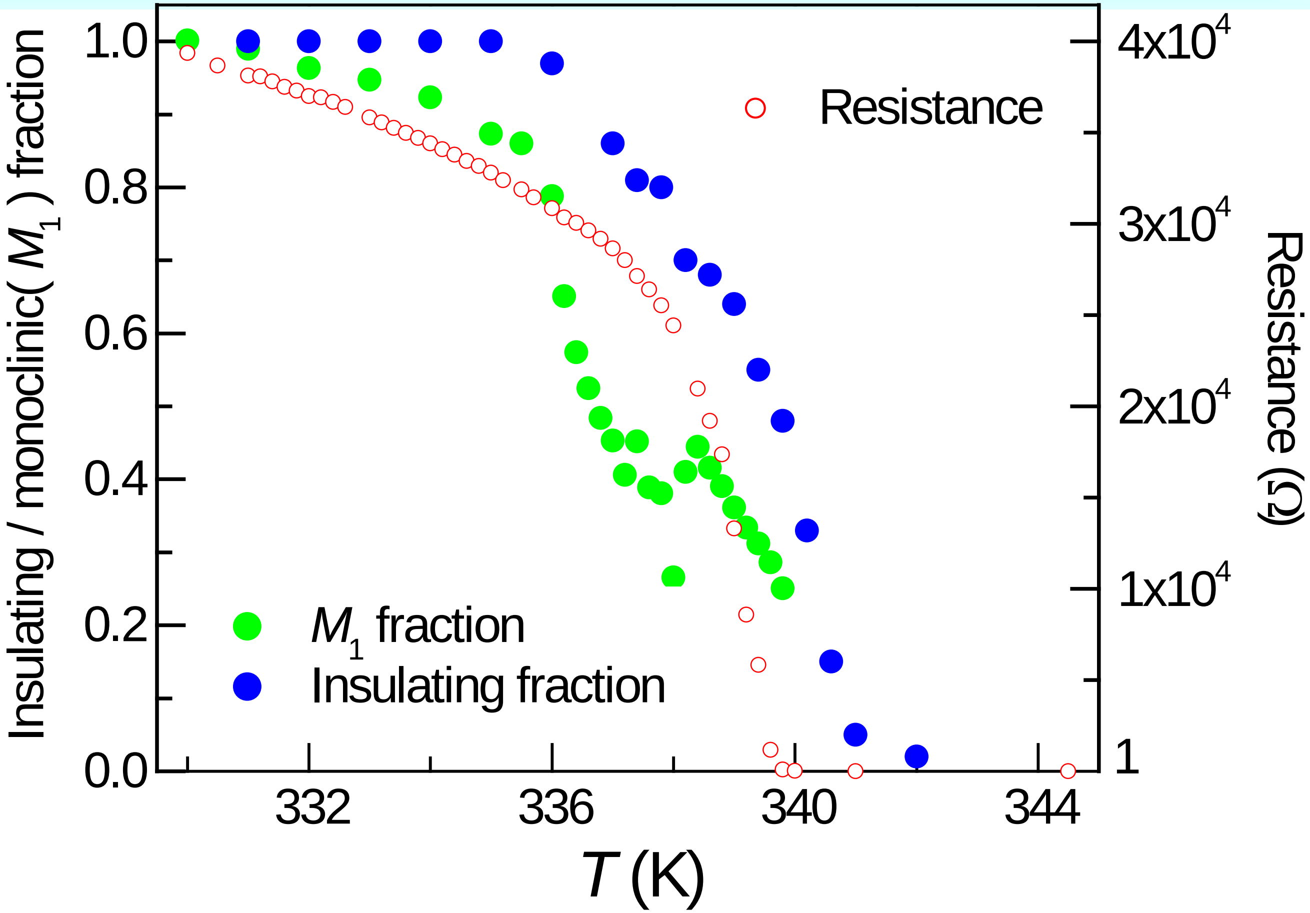
Monotonic electronic changes

Near-field infrared microscopy



- coexisting electronic phases
- Monotonic electronic changes with temperature

Nanoscale decoupling of electronic and structural transitions



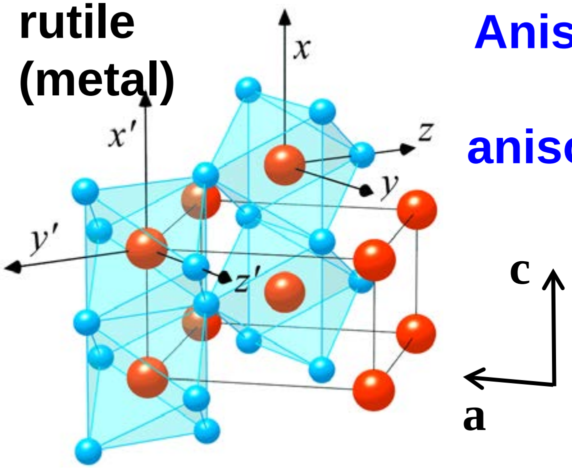
Qazilbash et al., Phys. Rev. B 83, 165108 (2011)

- **Monotonic electronic evolution, non-monotonic structural evolution**
- **Nanoscale decoupling between electronic and structural changes**
- **Metallic state possible in a non-rutile structure**

Intrinsic anisotropy of VO_2

Role of anisotropy in the metal-insulator transition (MIT) and the lattice instability

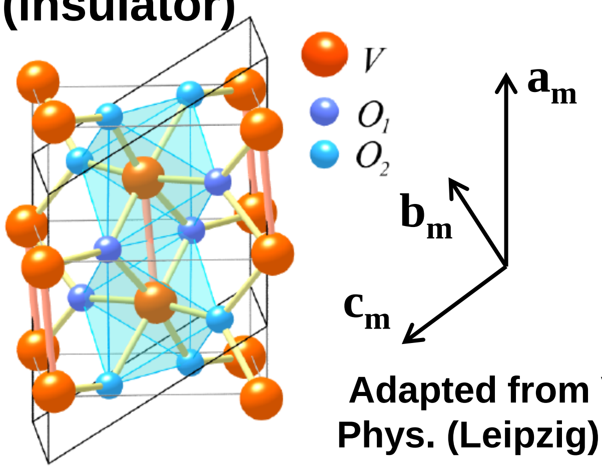
Tetragonal, rutile (metal)



Anisotropic lattice structures and directional dependence of *d*-orbitals suggest anisotropic electronic and phonon properties

Polarized infrared spectroscopy on single crystalline VO_2 samples for anisotropic optical constants

Monoclinic M_1 (insulator)



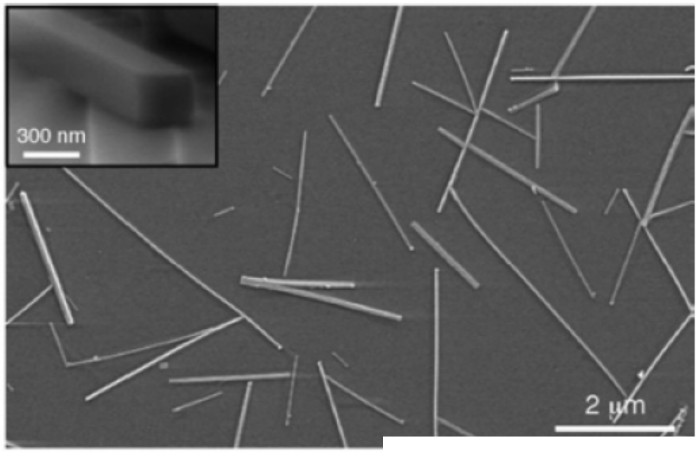
Adapted from V. Eyert, Ann. Phys. (Leipzig) 11, 650 (2002)

Challenge

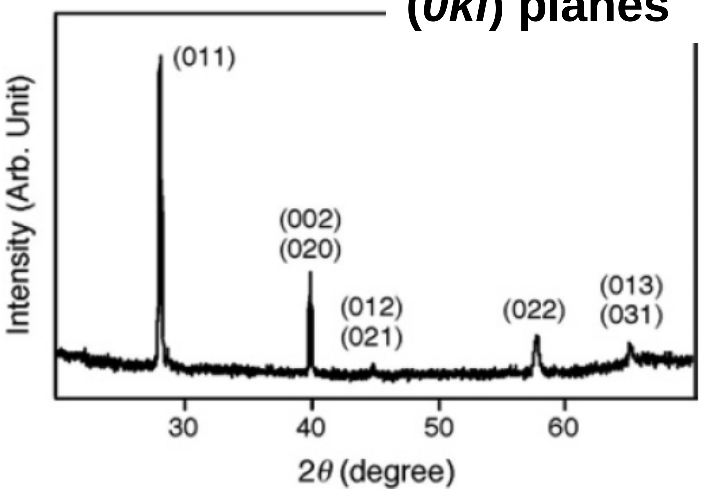
In bulk crystals:

- **Macroscopic cracks across MIT**
- **Domains with twinning about a_m axis i.e. b_m, c_m axes interchanged**

VO_2 single crystalline nano-rods and nano-platelets



(*0kl*) planes



Grown by vapor transport method

Monoclinic a_m axis (and rutile c-axis) along the long axis of nanorods

- **Single domain (no twinning)**
- **Do not break across Tc**
- **Strained near Tc and above Tc**

Guiton *et al*., J. Am. Chem. Soc. 127, 498 (2005)

Infrared micro-spectroscopy with polarized light on VO_2 micro-crystalline platelets

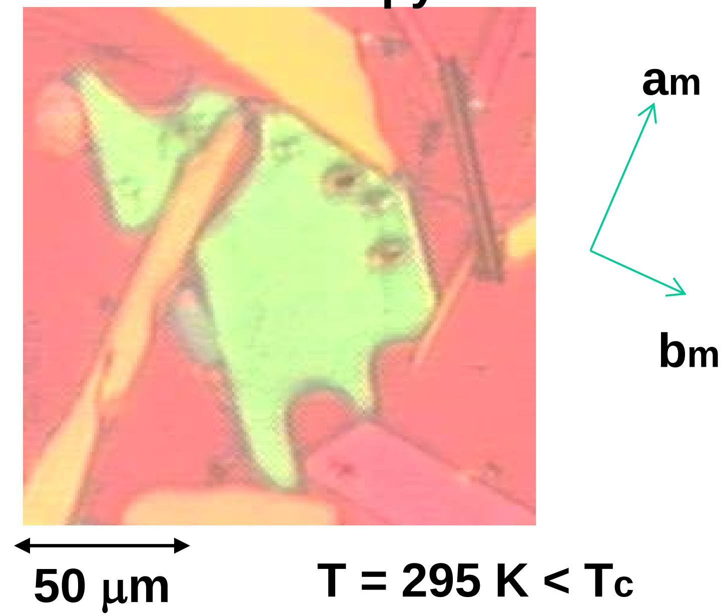
Samples grown by David Cobden's group (Univ. of Washington)

20 μm

T ~ Tc ~ 340 K

Phase coexistence

Biggest crystal chosen for infrared microscopy

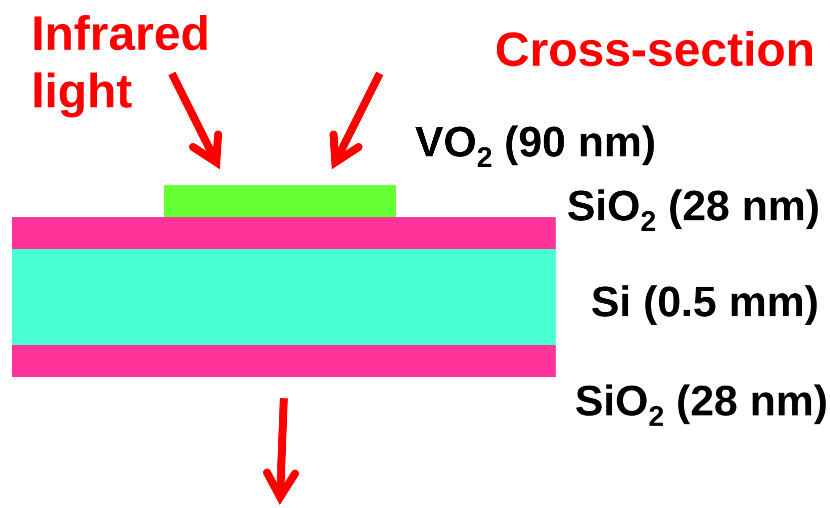


T = 295 K < Tc

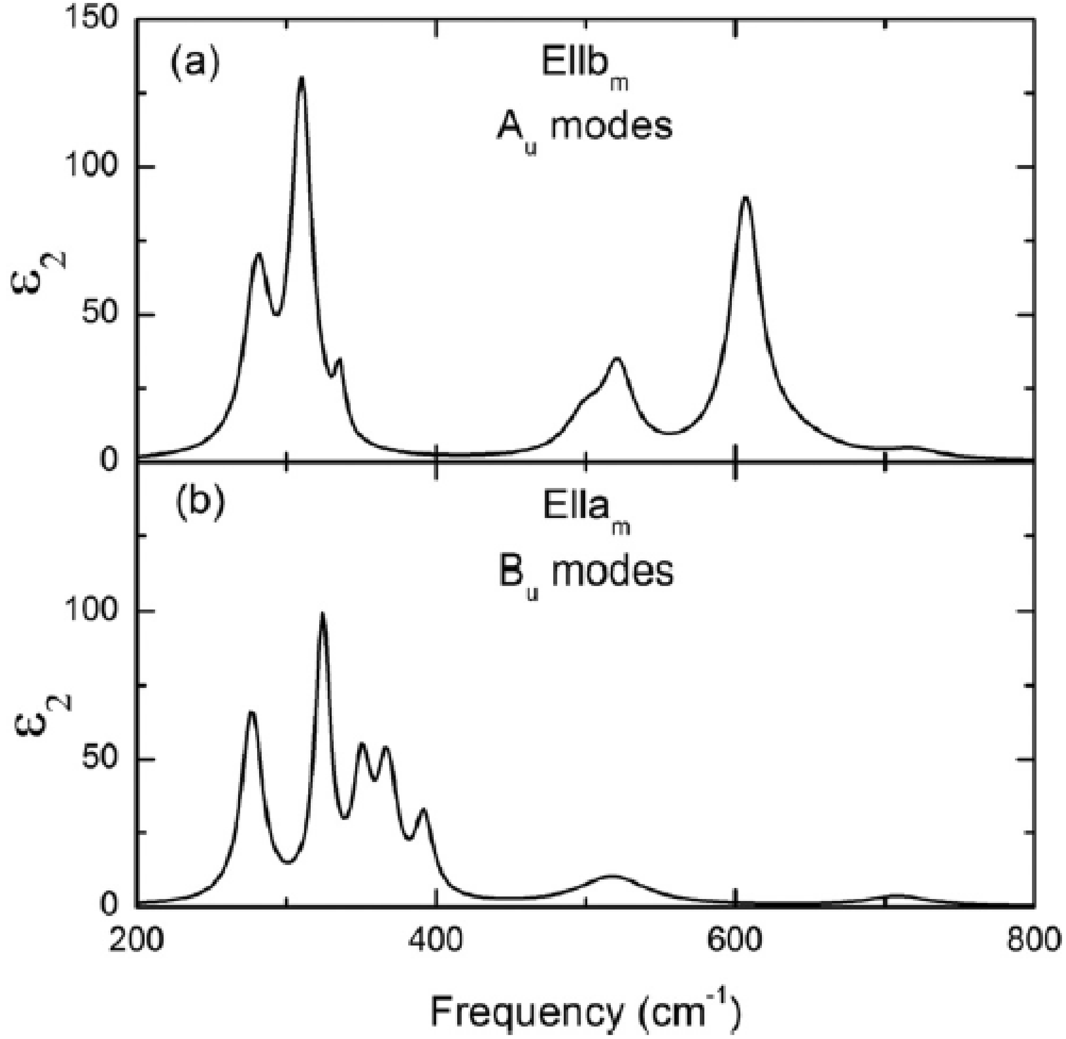
Infrared micro-spectroscopy at NSLS, Brookhaven National Lab

- 200 cm^{-1} to 6000 cm^{-1}
- Resolution 2-4 cm^{-1}

Cross-section



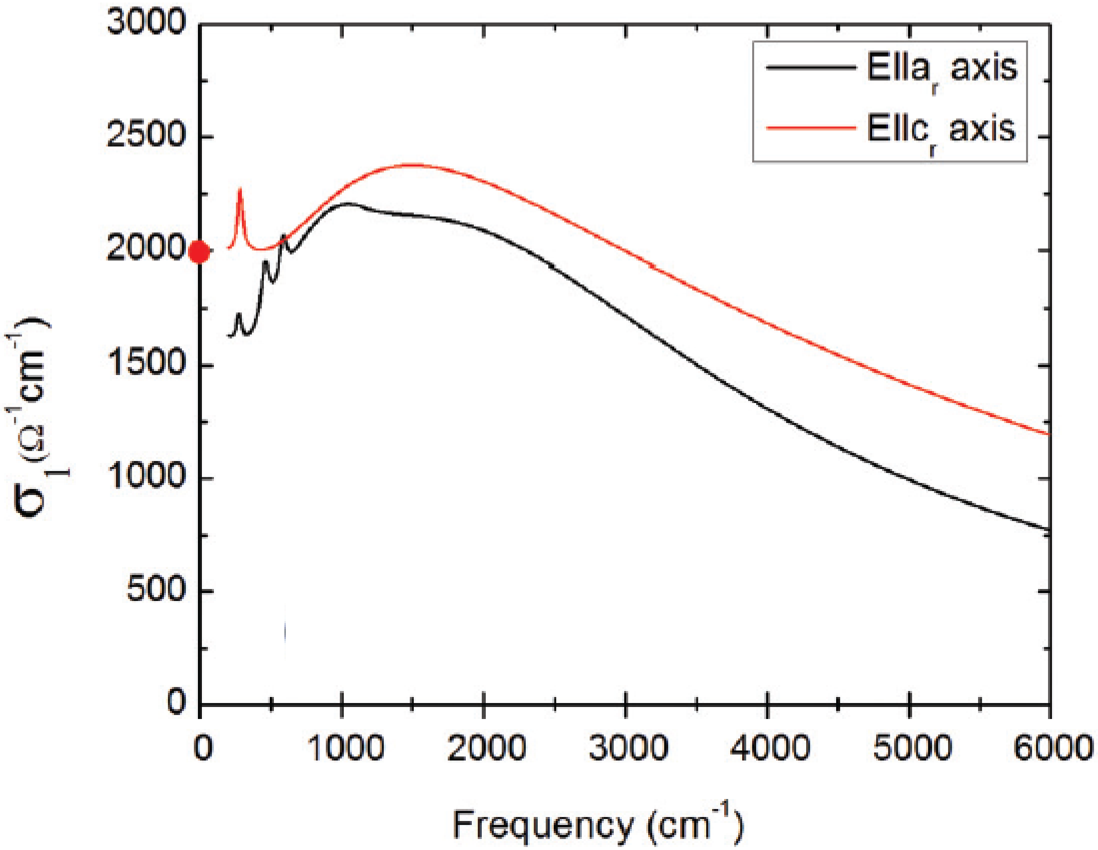
Infrared-active phonons in M_1 insulating phase



- **Measured true anisotropy of infrared-active phonons**
- **Good agreement with DFT+U calculations**

T. J. Huffman *et al*, PRB 87, 115121 (2013)

Infrared electronic and phonon response of rutile metal



- **First measurement of infrared active phonons in rutile metal**
- **Weak anisotropy of the electronic response despite V-V bonding along c-axis and V-O-V bonding along a-axis**
- **A_{2u} phonon is only stable in DFT+U for U > 4 eV**

T. J. Huffman *et al*,
PRB 87, 115121 (2013)

Outlook

- **Development of local probes for nanoscale imaging and spectroscopy**
  - **broadband near-field infrared spectroscopy**
  - **x-ray diffraction < 5 nm spatial resolution at NSLS 2**

- **Single-domain, untwinned samples of correlated materials provide access to intrinsic, anisotropic properties**

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