The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
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1936-5

Advanced School on Synchrotron and Free Electron Laser Sources and their Multidisciplinary Applications

7 - 25 April 2008

IR spectroscopy and microscopy in material science

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IR spectroscopy and microscopy in material science

A. Perucchi

Outline - Selected applications of IRSR in solid state physics

- Superconductivity
  1. Optical properties of superconductors
  2. The two gaps of superconducting MgB_2
  3. Pump-probe experiments in the far-infrared on Pb film

- High-pressure measurements
  1. Tuning the Peierls instability on RE dichalchogenides
  2. Inducing Metal to Insulator Transition: the example of VO_2

- Imaging in solid state physics
  1. Electric field induced phase transition in VO_2 films
  2. IR Imaging of phase separation

Advantages of IRSR

Brightness gain →

- Small samples
- Extreme experimental conditions (high pressure, high magnetic field)
- Spatial resolution (microscopy)

Flux gain in the THz range →

- ≈ 10 with incoherent IRSR
- > 10^4 with coherent IRSR (CSR)

see next talk

Pulsed structure →

- Time resolved spectroscopy (≈10 ps)
- Pump-probe

Superconductivity

Superconductivity today

1. Looking for new materials
   - 1986: High-T_c cuprates
   - 1990: C_{60} fullerene
   - 2000: MgB_2
   - 2003: $Na_xCoO_2 \cdot 3H_2O$
   - 2004: B-doped diamond

2. Understanding new materials

Superconductivity is ruled by low-energy electrodynamics:

- Superconducting gap : THz-range
- Spectral weight of condensate and penetration depth:THz-range
- Mediators of pairing (phonons, etc.): Far-infrared
- Range of sum rules: Far-, Mid-, or Near-infrared
- Free-carrier conductivity above T_c: Infrared

Magnetic levitation

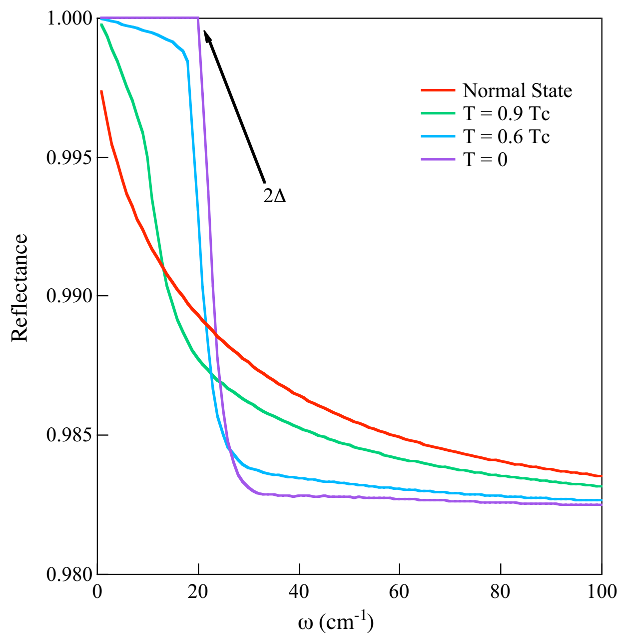
MALEV in Shanghai (liquid-He cooled)

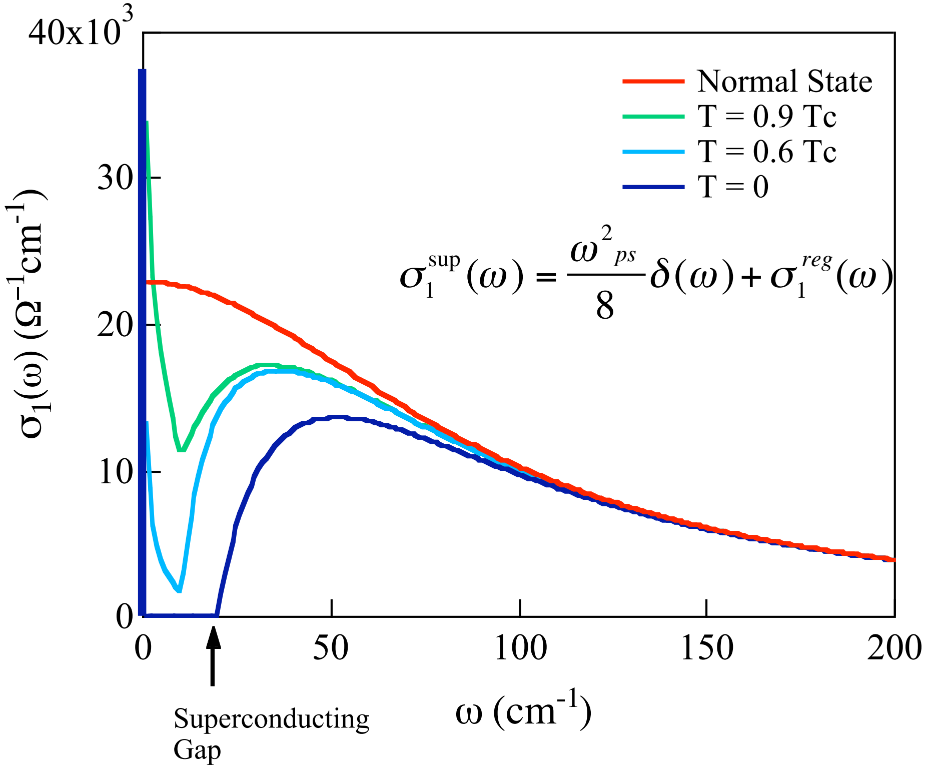
Lifting a Sumo wrestler (LN_2 cooling)

Basic optics of superconductors

Minimum excitation energy:
Cooper-pair breaking 2Δ

Superconducting gap observed if:
•sample in the dirty-limit ($2\Delta < \Gamma$)
•Cooper pairs in s-wave symmetry

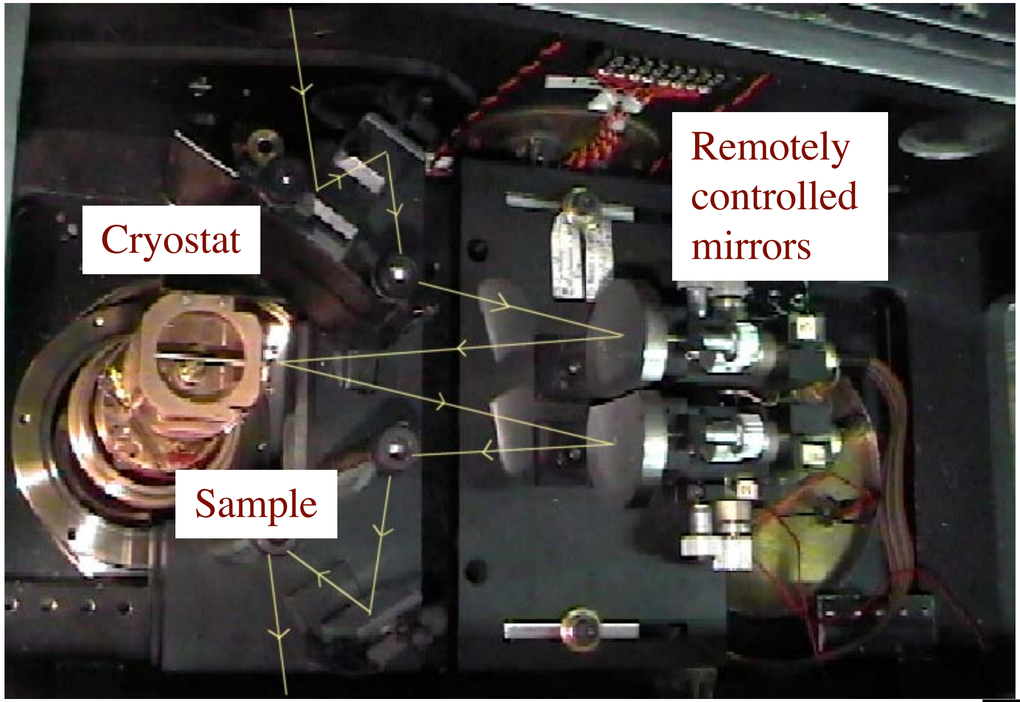




$\int [\sigma_1(\omega, T>Tc) - \sigma_1(\omega, T<Tc)]\, d\omega = \omega^2_{ps}/8 = n_s e^2/m^* \dashrightarrow \lambda = c/\omega_{ps}$

Ferrel-Glover-Tinkham Rule

Reflectivity set-up



Reference:

gold evaporated *in situ*

Reflectivity:

$R = I_R^{crys} / I_R^{gold}$

$\Downarrow$

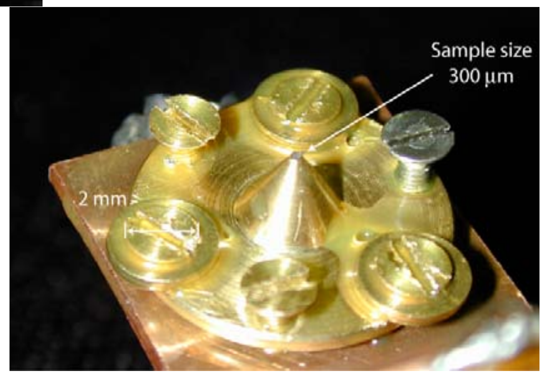
Kramers-Kronig transf.

$\Downarrow$

optical conductivity

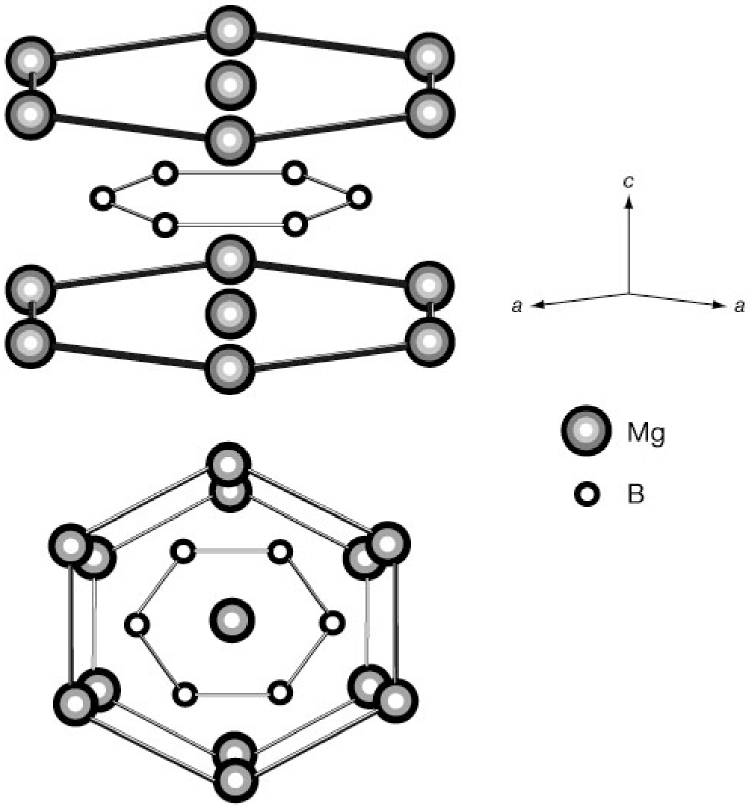
$\sigma(\omega)$

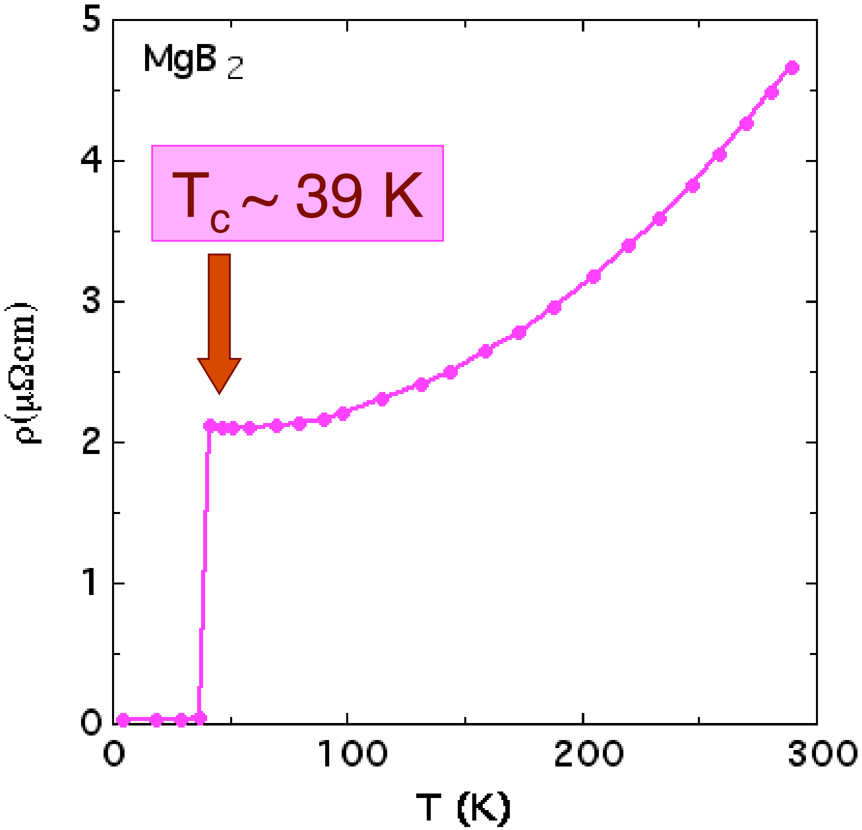
Single crystals may be very small:



The 39 K superconductor MgB_2

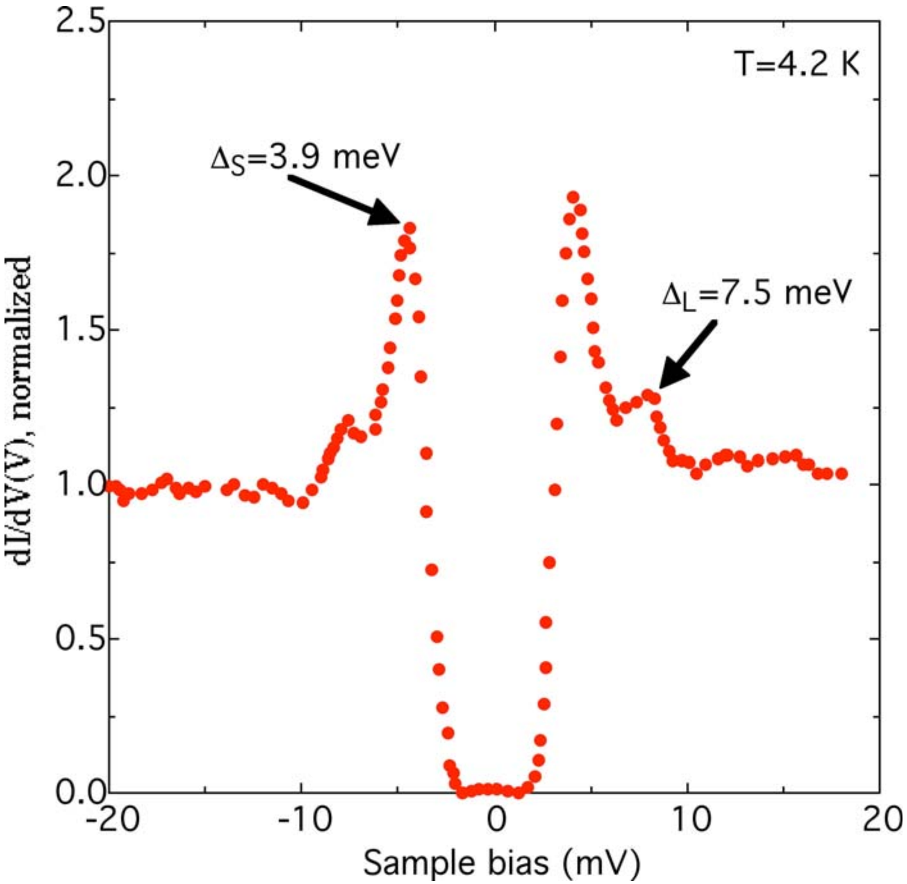
Space group P6/mmm
a=3.086 Å
b=3.542 Å

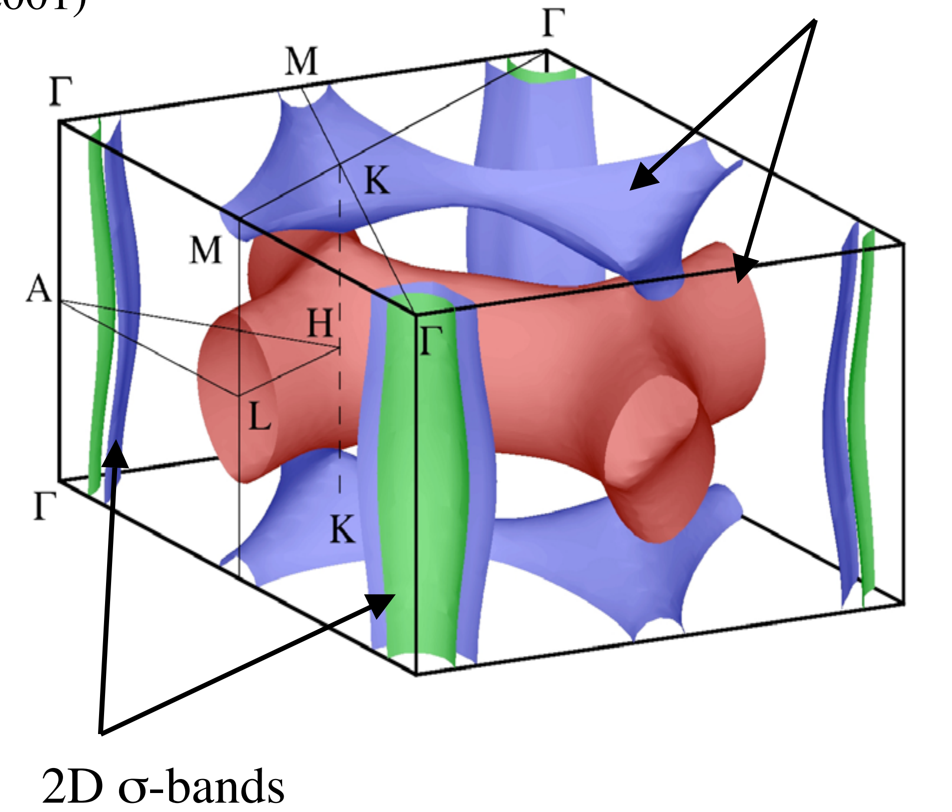




Multiband superconductivity in MgB_2

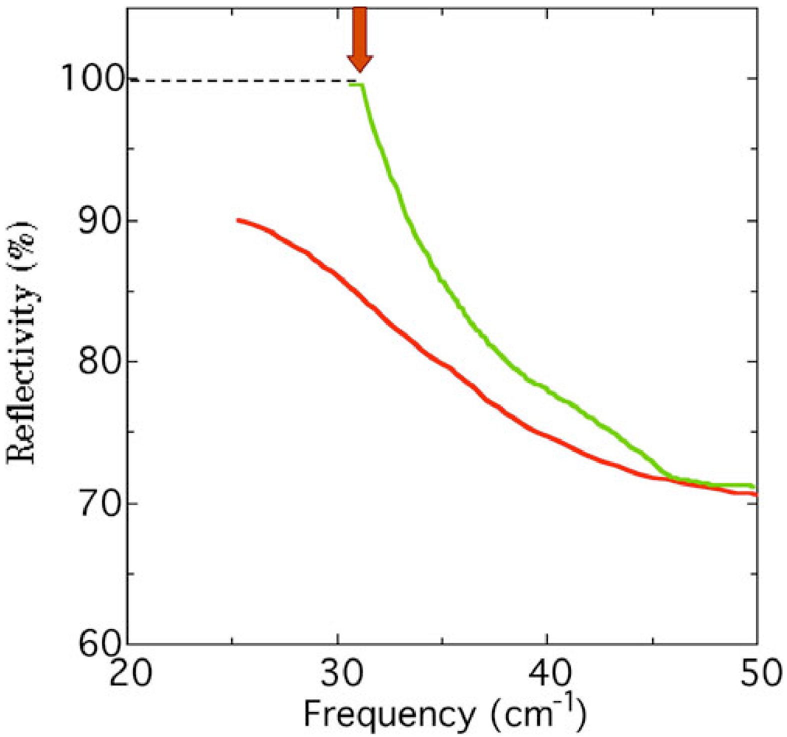
Giubileo *et al*. Phys. Rev. Lett. **87**, 177008 (2001)

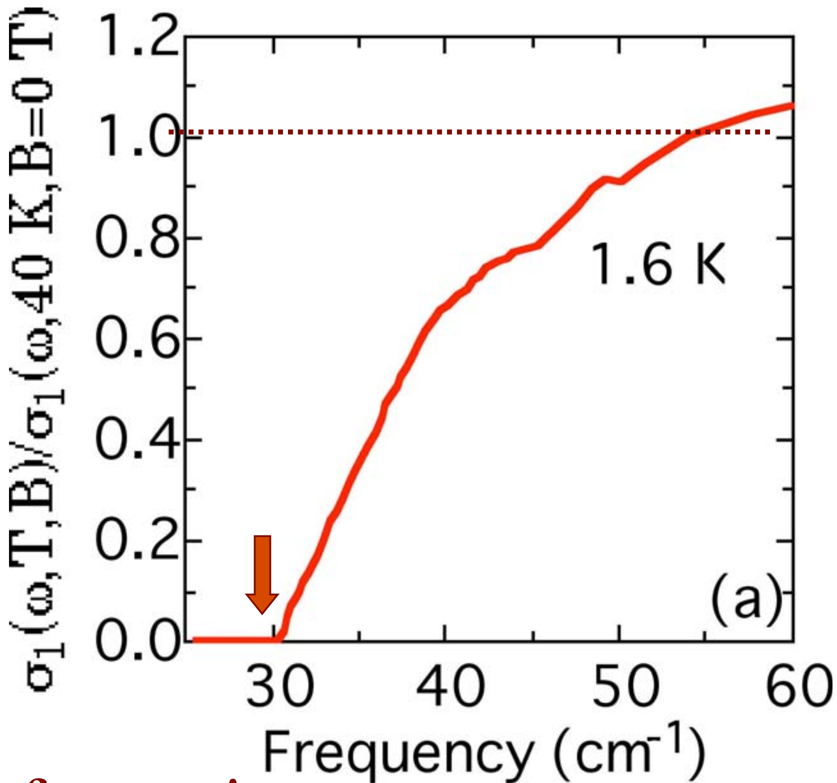




Kortus *et al*. Phys. Rev. Lett. **86**, 4656 (2001)

Reflectivity of MgB_2 measured with a conventional source (Hg-lamp)

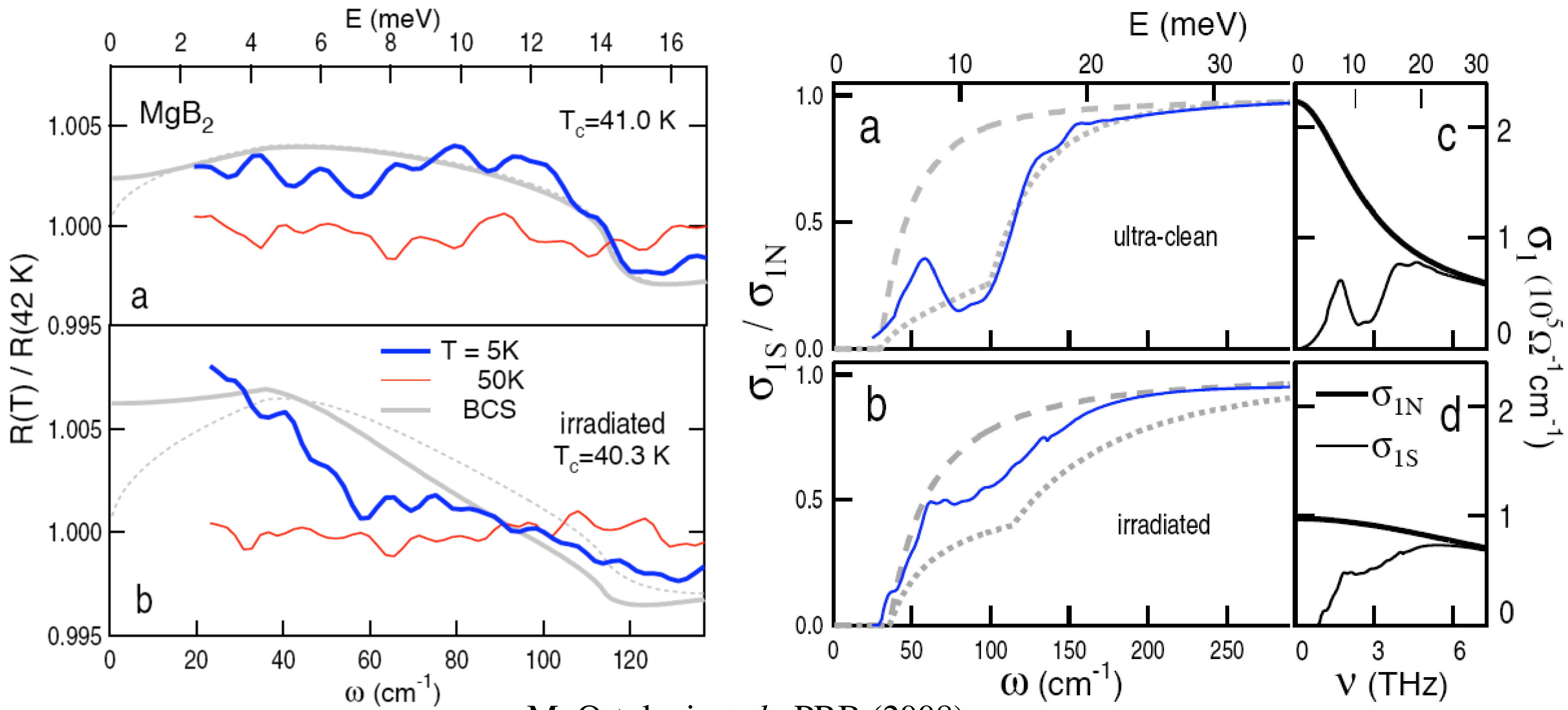




One single gap feature!

A. Perucchi *et al.*, PRL **89**, 097001 (2002)

A synchrotron study of MgB_2 on ultra-clean films



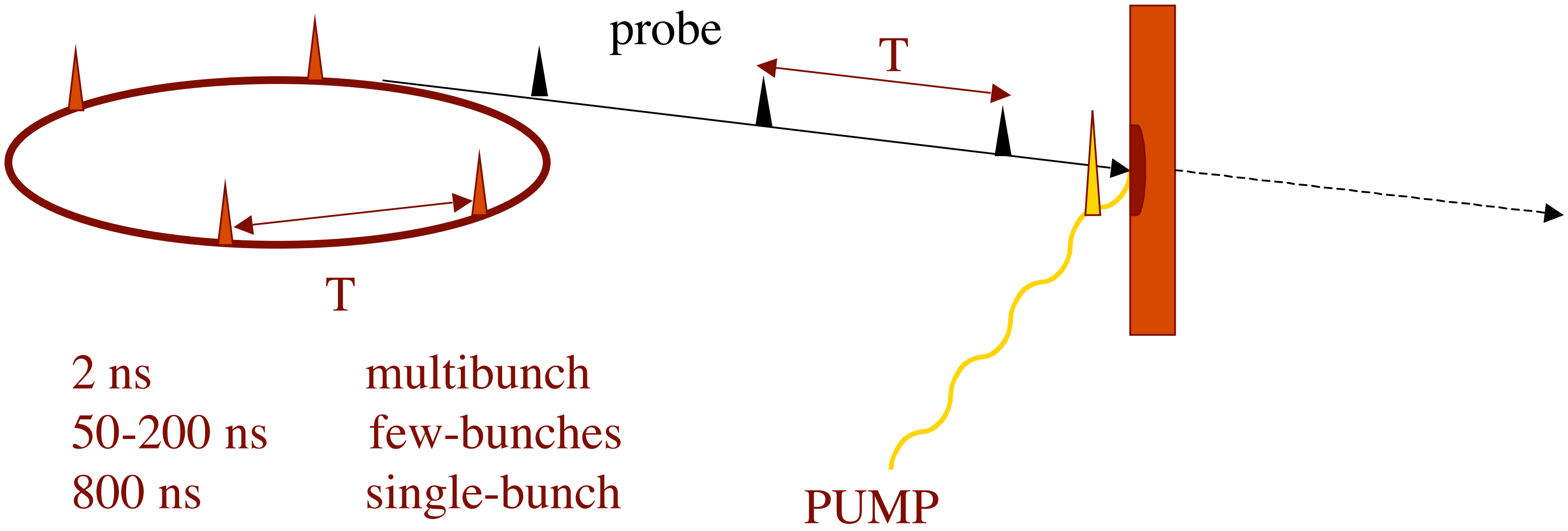
M. Ortolani *et al.*, PRB (2008)

The π-gap feature is enhanced by impurities

To observe the σ-gap a very high signal to noise ratio is needed!

(ΔR<0.5% @ THz frequencies)

Pump-probe experiments

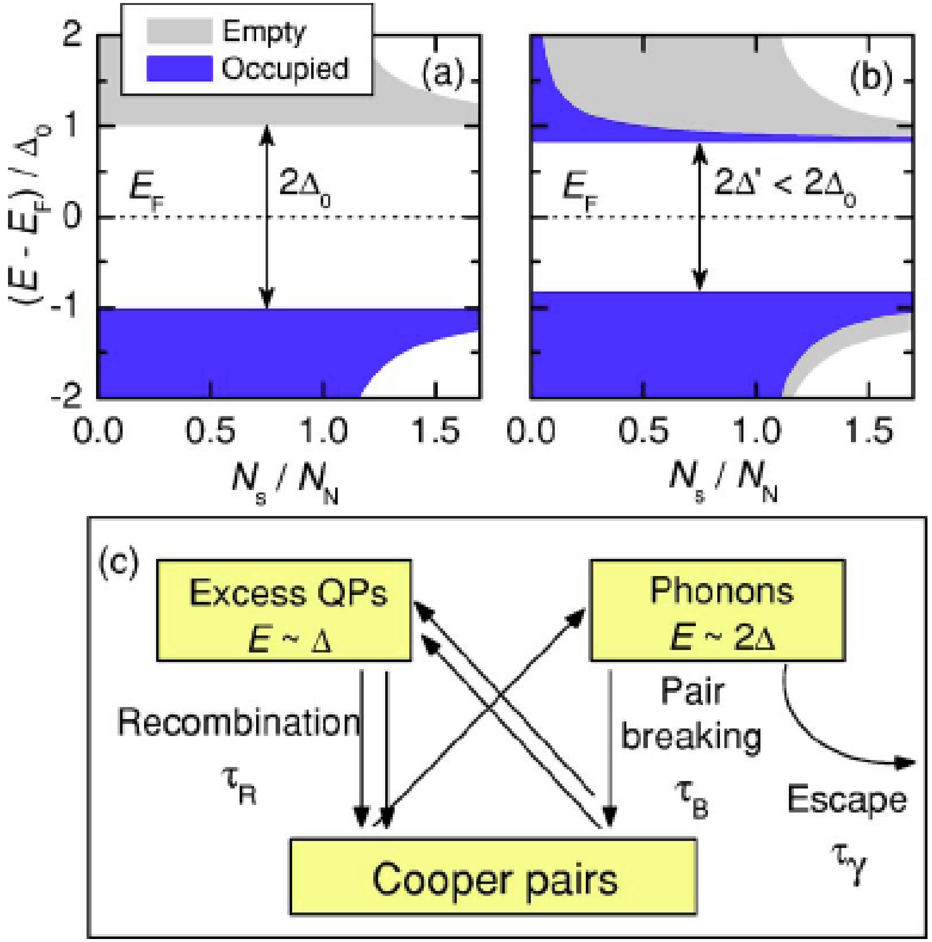


2 ns	multibunch
50-200 ns	few-bunches
800 ns	single-bunch

Temporal resolution is determined by:
- Synchrotron beam pulse-width Δt
- Pump pulse-width (fs laser)
- Jitter

Δt is typically 10's of ps, but can be reduced to below 1 ps under special conditions as low-α (cfr. next talk) or femtoslicing

Pump-probe experiments



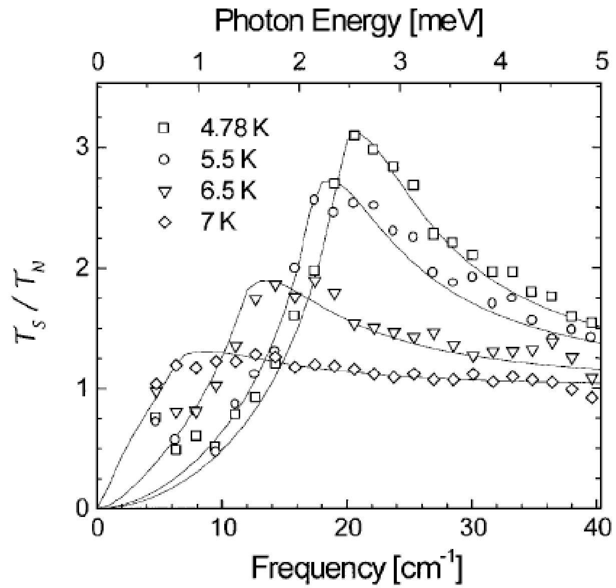
1. Pump photons ($h\nu > 2\Delta_o$) break Cooper pairs thus creating high energy (>> E_F) QP's
2. Very quickly (<ps) QP's relax to lower energies and accumulate at the gap edge (b)
3. Recombination into Cooper pairs dominated by the phonon bottleneck effect (c)

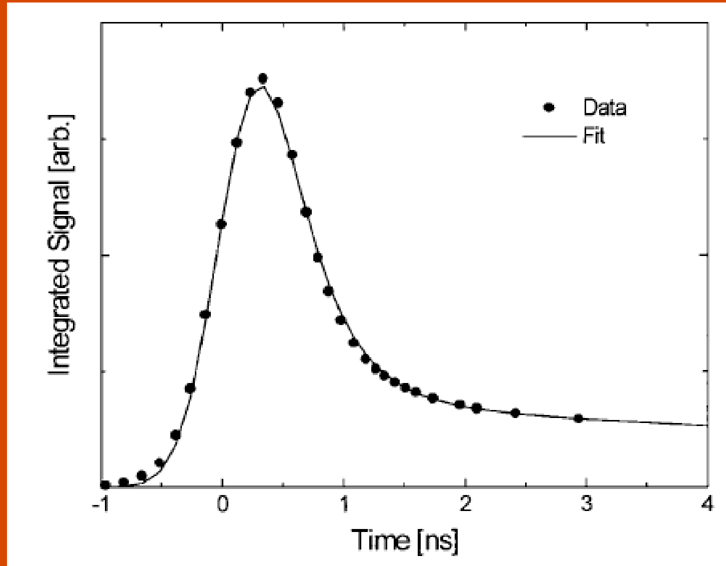
From Rothwarf-Taylor equations

$$\tau_{eff} = \tau_\gamma \left(1 + \frac{\tau_R}{2\tau_B}\right)$$

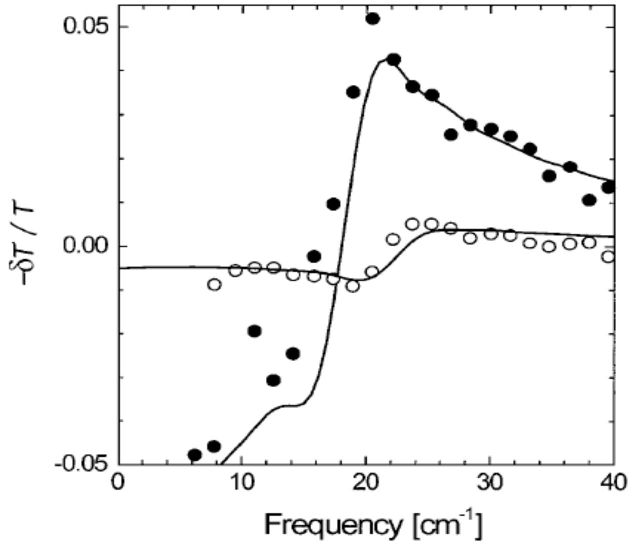
G. L. Carr *et al.*, PRL **85**, 3001 (2000)

Pump-probe experiments on Pb film





- Long relaxation (20 ns): extrinsic effect (heating)
- Short relaxation (250 ps): consistent with Rothwarf and Taylor model



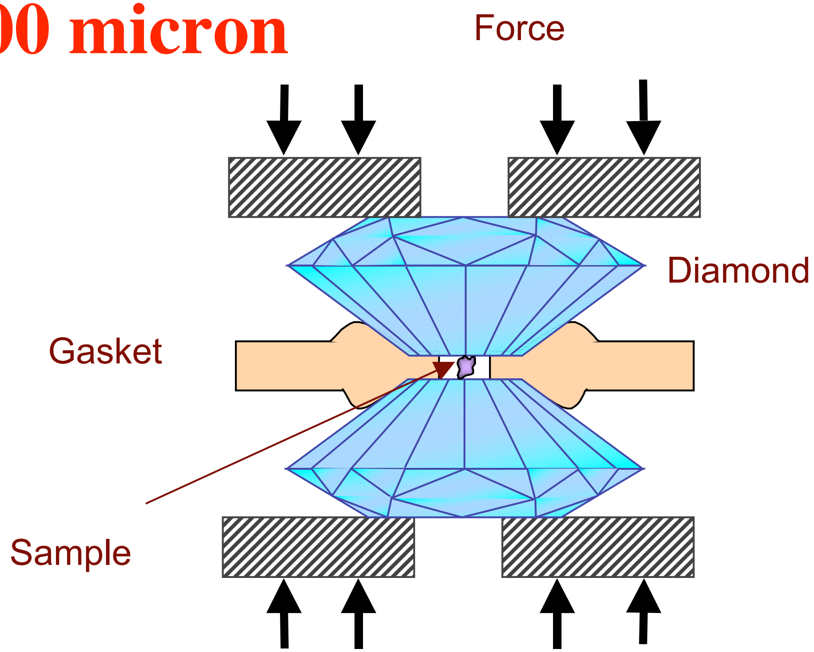
Time resolved frequency-dependent data demonstrate a gap reduction of 0.6% at 0.4 nJ pump pulse energy (empty circles) and 3% for 1.8 nJ (full circles)

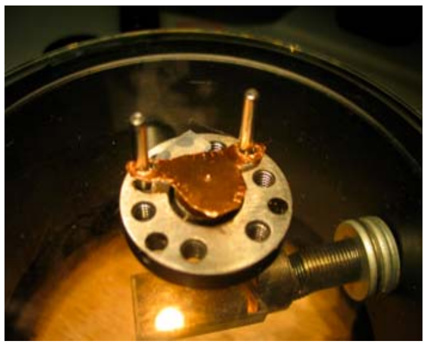
G. L. Carr *et al.*, PRL **85**, 3001 (2000)

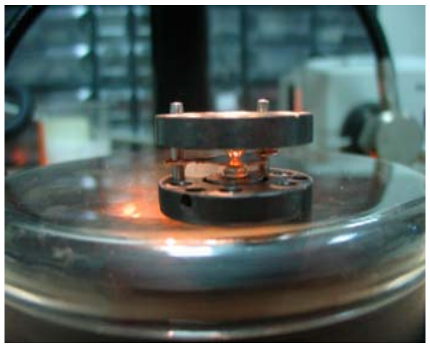
High Pressures

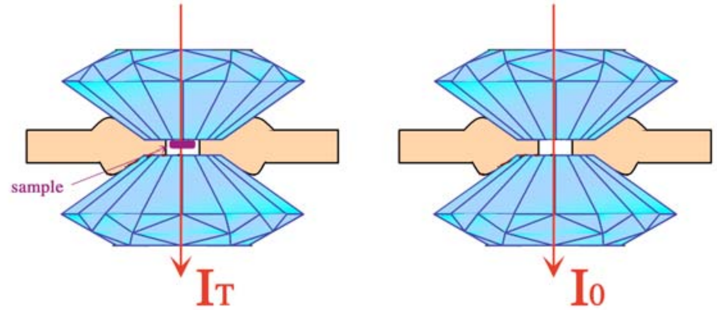
Diamond Anvil Cell (DAC)

Sample size
<100 micron



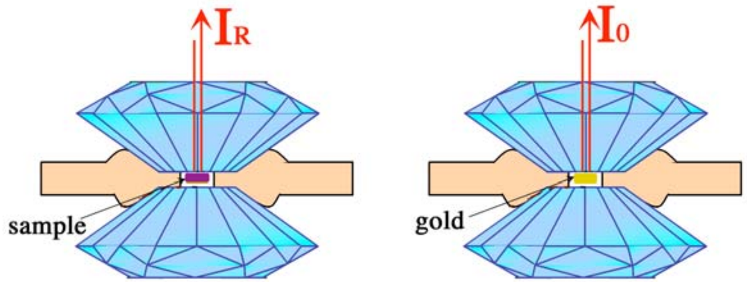






$$T = I_T / I_0$$

$$\text{Op.D.} = -\ln(T) = \alpha d$$



$$R_{dia/sam} = I_R / I_0$$

Infrared measurements at high pressure

Infrared spectroscopy is a bulk, contactless technique which probes both electronic and phononic excitations over a broad energy range

Transmission Measurement:
Op.D= - ln (I/I_0)
Since $I=I_0 \exp(-\alpha d)$ one has Op.D= α d
Determination of the absorption coefficient

Reflectivity Measurement:

$$R_{sd} = \left| \frac{(n+ik)-n_d}{(n+ik)+n_d} \right|^2$$

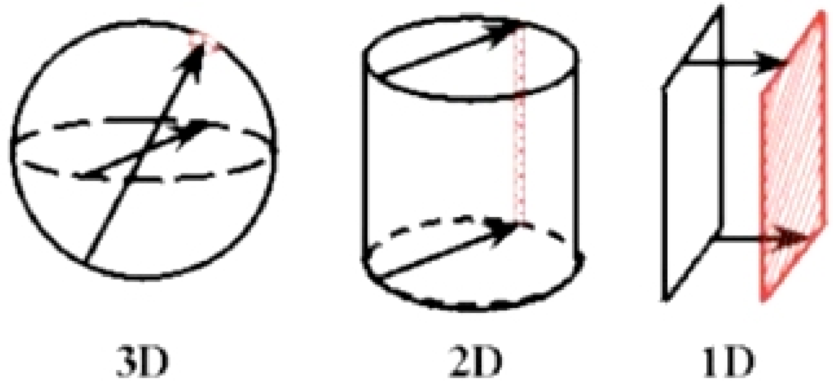
1 measured quantity

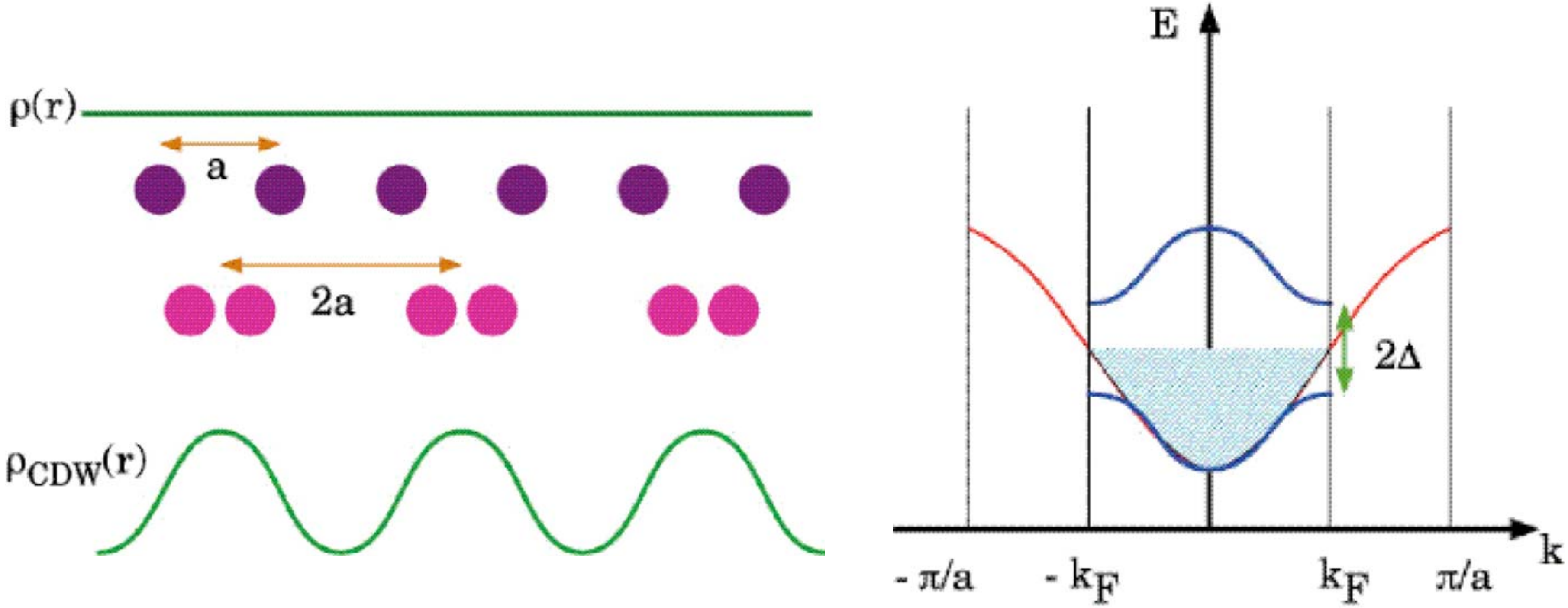
2 optical constants to be determined

With n_d=2.43 being the diamond refractive index

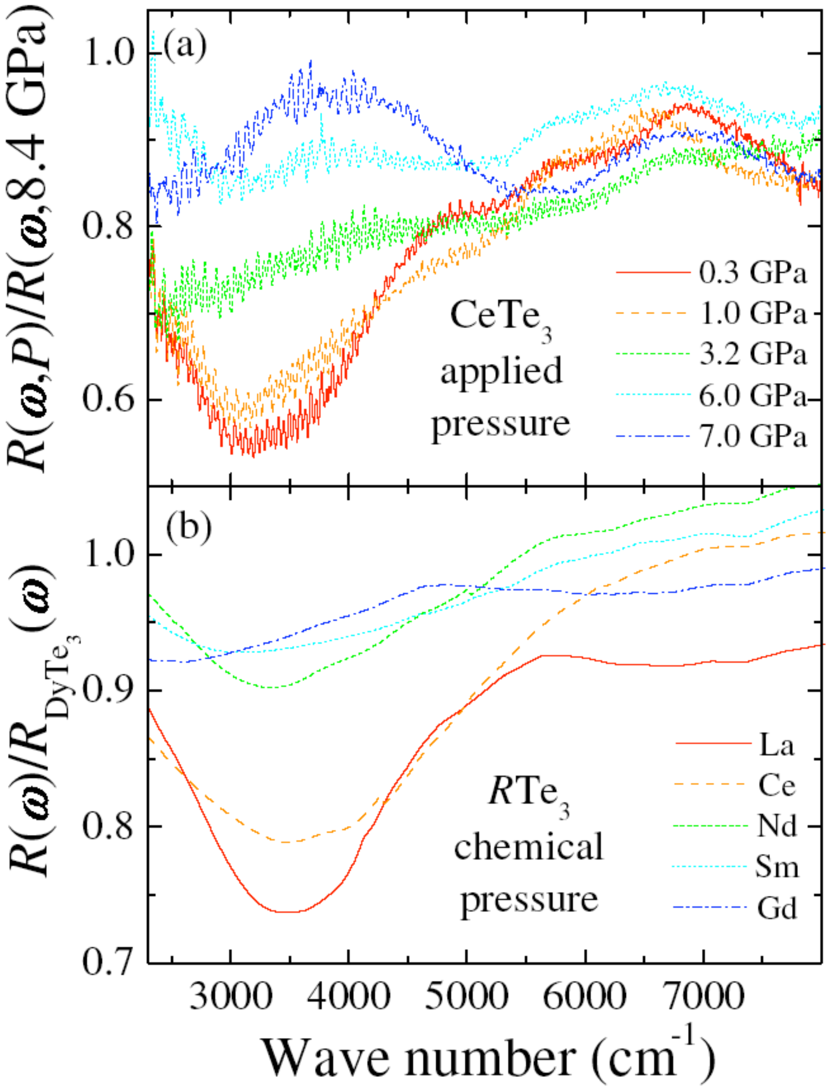
The full determination of the optical constants can be achieved through:
- Simultaneous measurement of R and T
- Lorentz-Drude fitting
- Kramers-Kronig Transformations

Nesting wavevectors and the Peierls transition





Hydrostatic pressure vs. chemical pressure

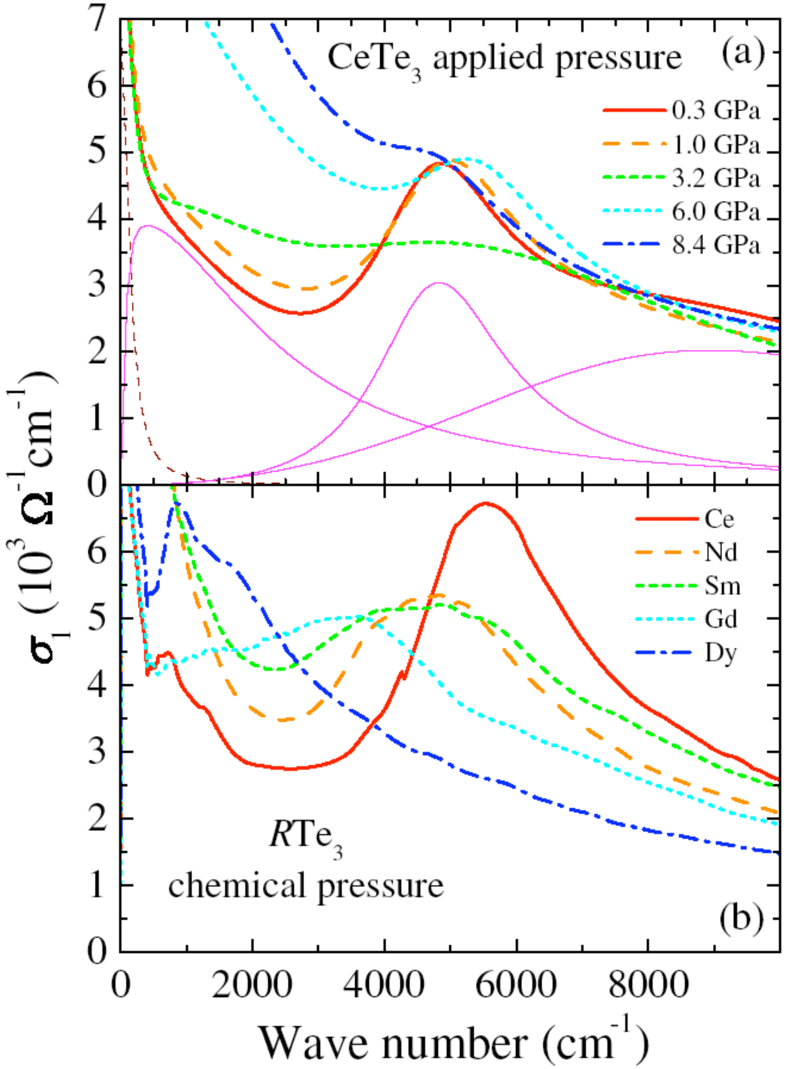


A. Sacchetti *et al.*, PRL **98**, 026401 (2007)

With increasing P, R(ω) increases between 2000 and 5000 cm^{-1}

The same kind of behavior is observed by applying chemical pressure (substitution of the Rare Earth ion).

Optical conductivity

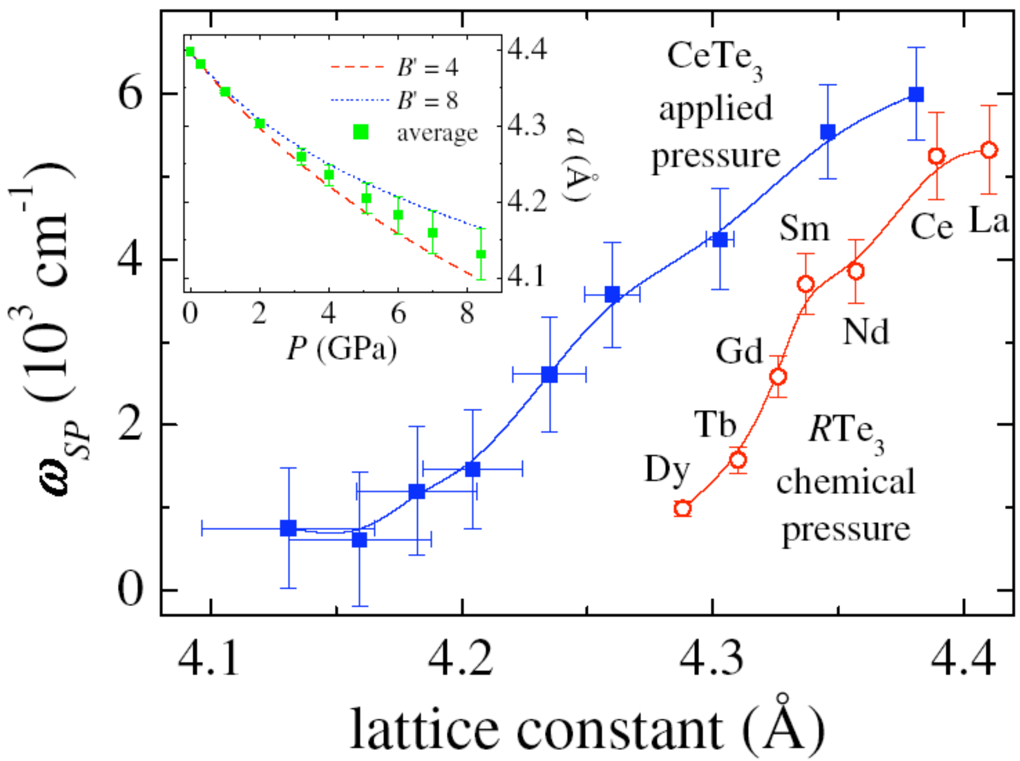


A. Sacchetti *et al.*, PRL **98**, 026401 (2007)

The optical conductivity is recovered through a fitting of the reflectivity data.

It is then possible to give an estimate for the single particle-gap energy.

Single-particle gap



A. Sacchetti *et al*., PRL **98**, 026401 (2007)

β is known from specific heat

$$\beta = (2\pi^2/5)k_B(2\pi \cdot k_B/hv_s)^3$$

➡ v_s = 1923 m/s

$B_0 = \rho v_s^2$, ρ=6873 kg/m^3

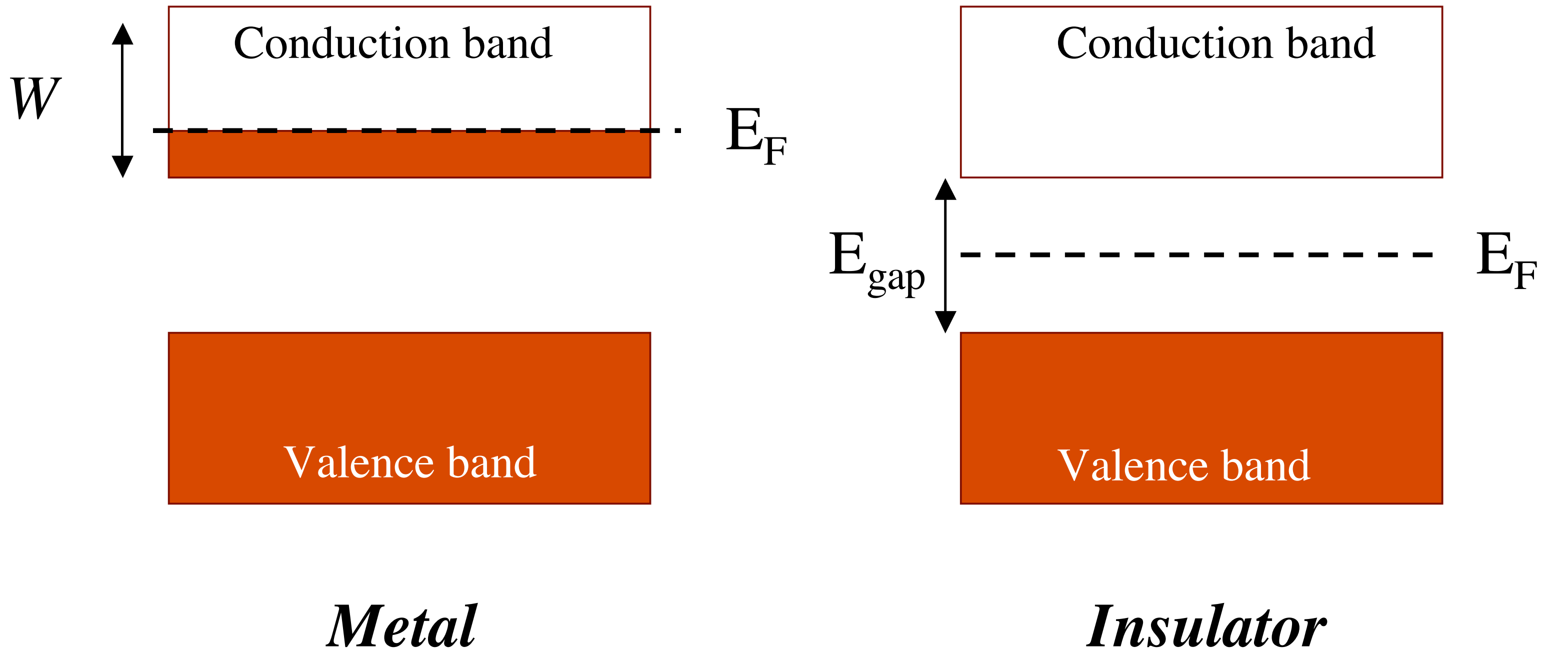
➡ B_0 = 25 GPa

$$B(P) = B_0 + B'P$$

$$V(P) = V(0)\left(1 + \frac{B'}{B_0}P\right)^{-1/B'}$$

➡ $\alpha(P) = \alpha(0) \times [V(P)/V(0)]^{1/3}$

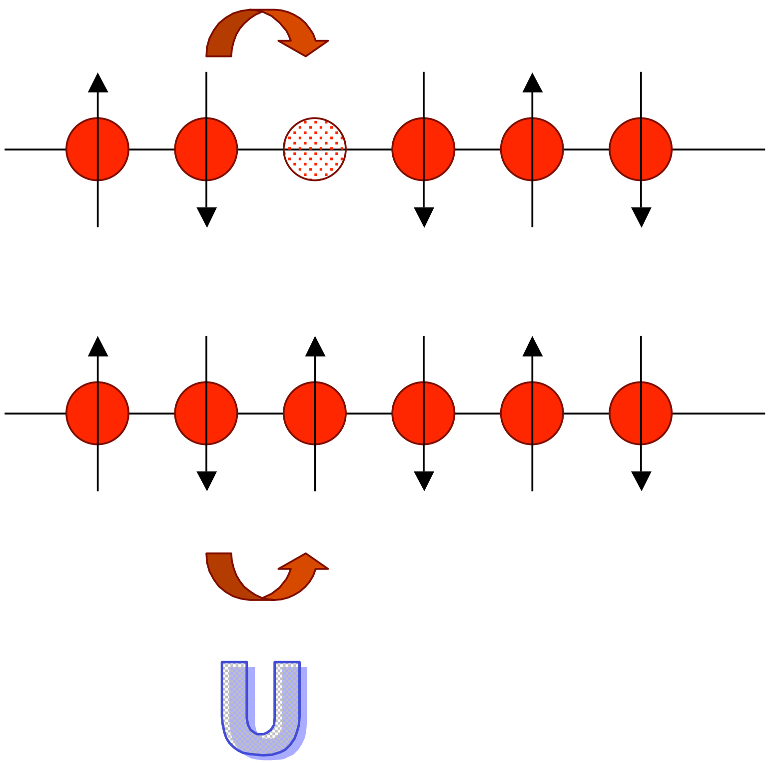
Band insulators

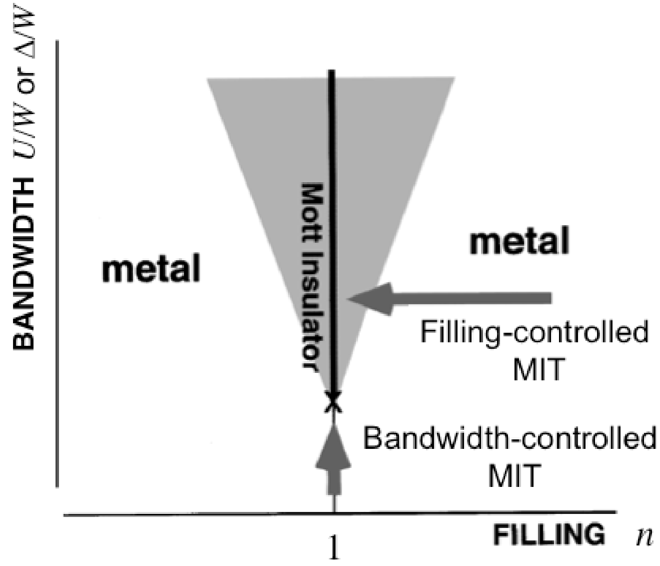


The band theory is properly defined in the one-electron approximation, i.e. when W is much larger than other electronic energy scales

$$W >> U, e-ph$$

Mott-Hubbard insulators





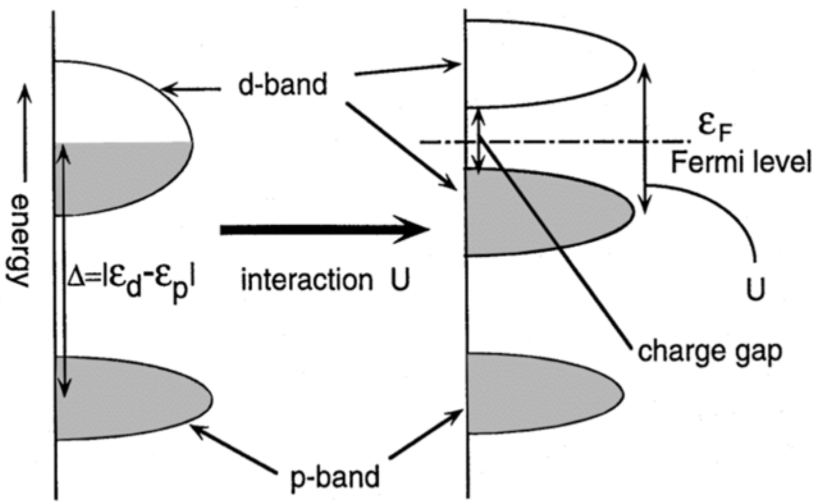
U prevents double on-site occupancy
the opening of a gap in the
spectra of excitations is induced

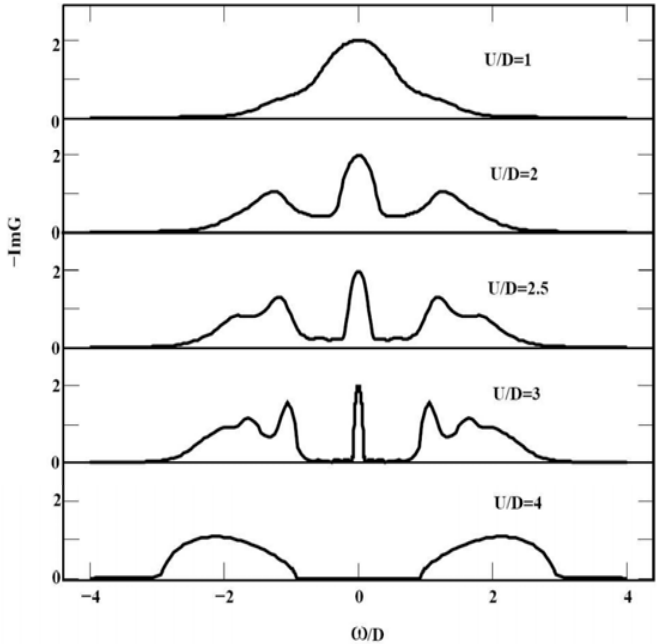
$$H = -t \sum_{<i,j>,\sigma} c^{\dagger}_{i,\sigma} c_{j,\sigma} + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow}$$

Electron-electron interaction and insulator to metal transition (MIT)

Electronic correlation: failure of band model

Hubbard model





Pressure may increase the W/U ratio inducing a MIT

W: bandwidth or kinetic energy (strongly dependent on atomic distances)
U : coulomb repulsion

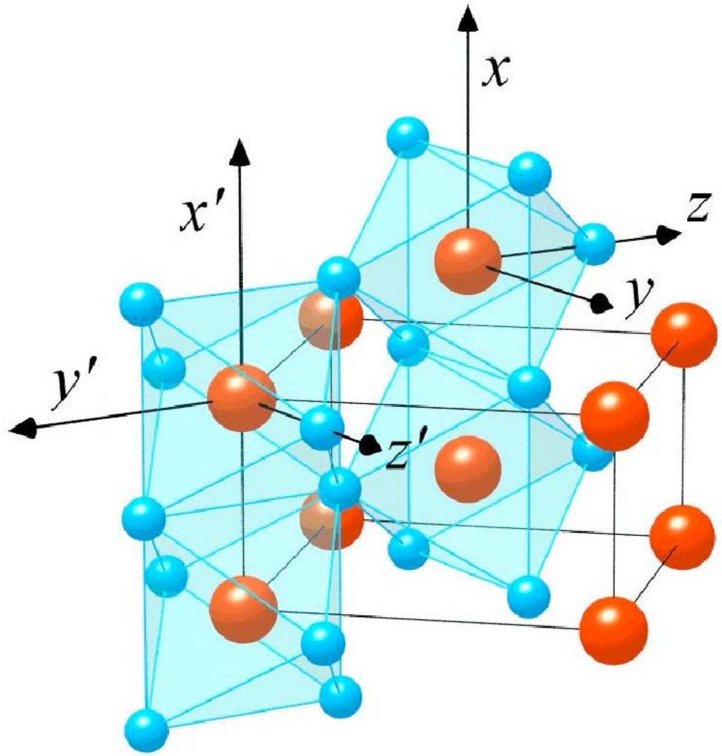
The metal-insulator transition in VO_2

T<340 K

Insulating monoclinic (M1) phase
Dimerization and tilting of V pairs
MIR Optical gap

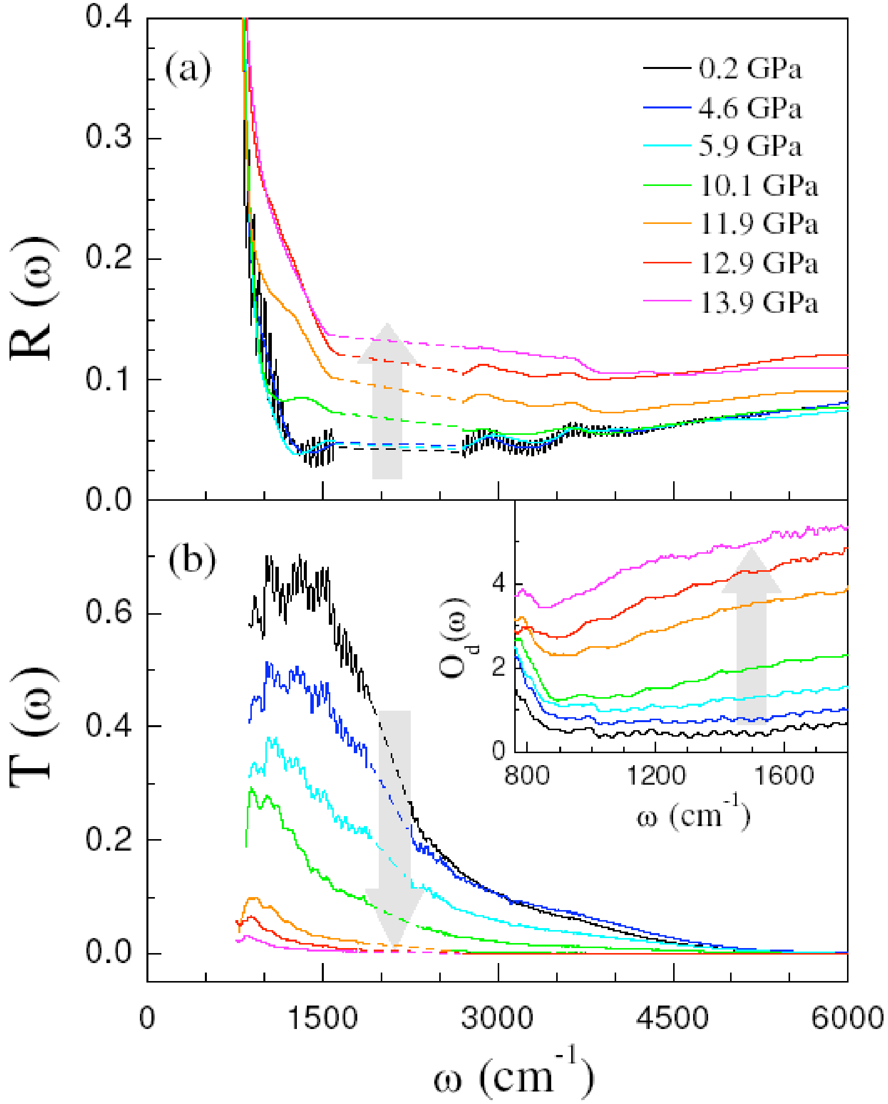
T>340 K

Metallic rutile (R) phase
With a resistivity jump of several order of magnitude



Rutile structure (picture taken from V. Eyert)

P-dependent reflectance and transmittance of VO_2

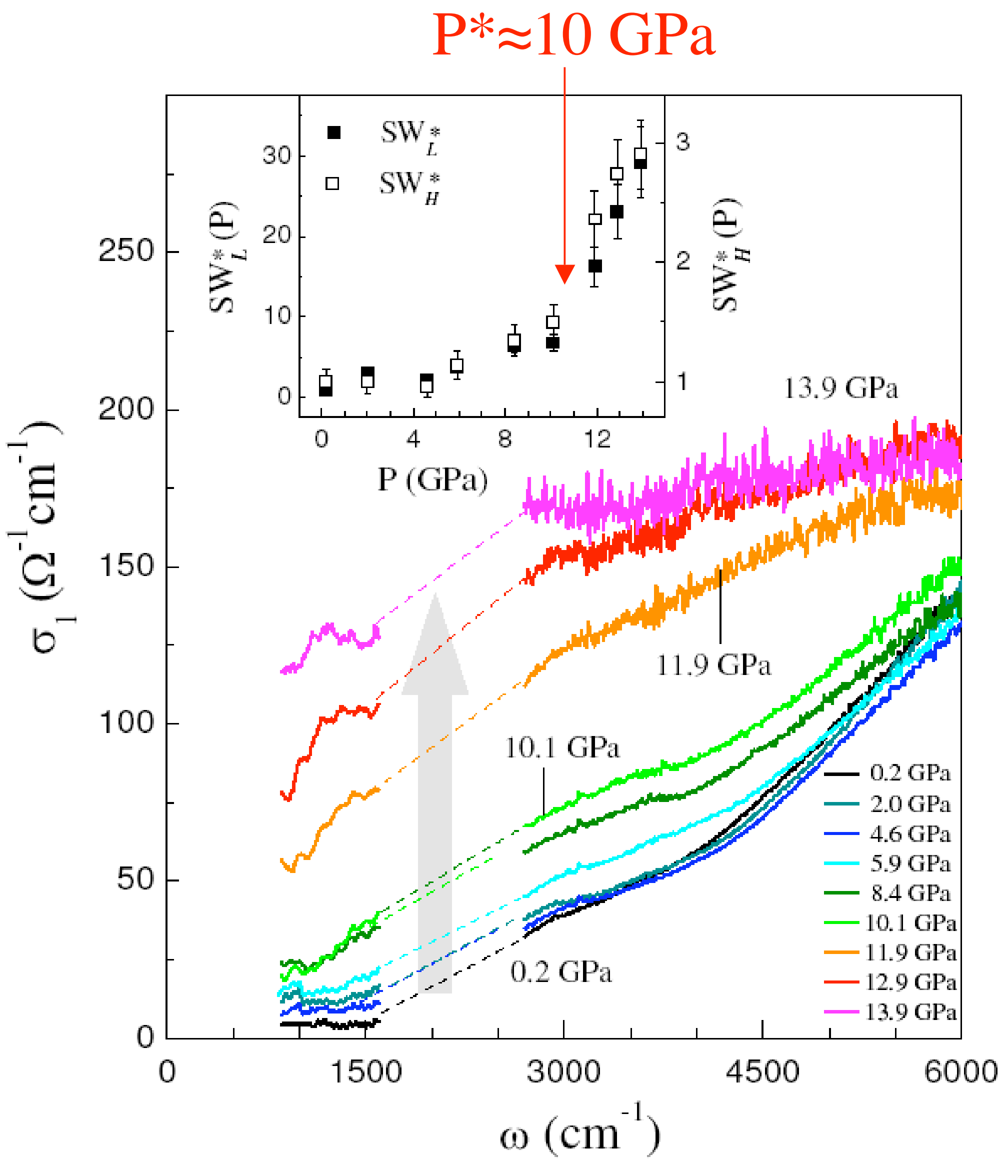


E. Arcangeletti *et al.*, PRL **98** 196406 (2007)

R(ω) increases above 10 GPa

T(ω) continuously decreases

Optical conductivity of VO_2 under high pressure

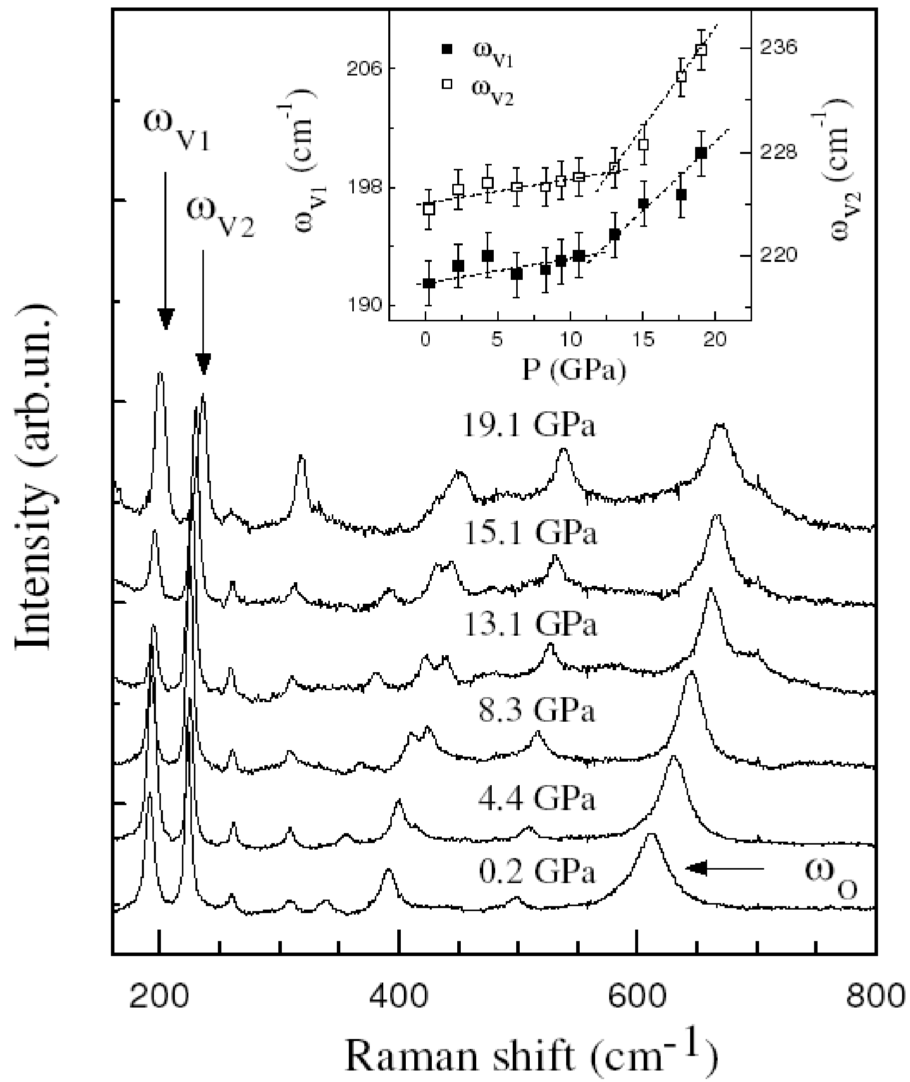


E. Arcangeletti *et al.*, PRL **98** 196406 (2007)

For P<P* the optical gap decreases in energy

For P>P* the gap seems to be completely closed $\sigma_1(\omega) \to 0$ for $\omega \to 0$

Raman spectroscopy on VO_2 under high pressure



E. Arcangeletti *et al.*, PRL **98** 196406 (2007)

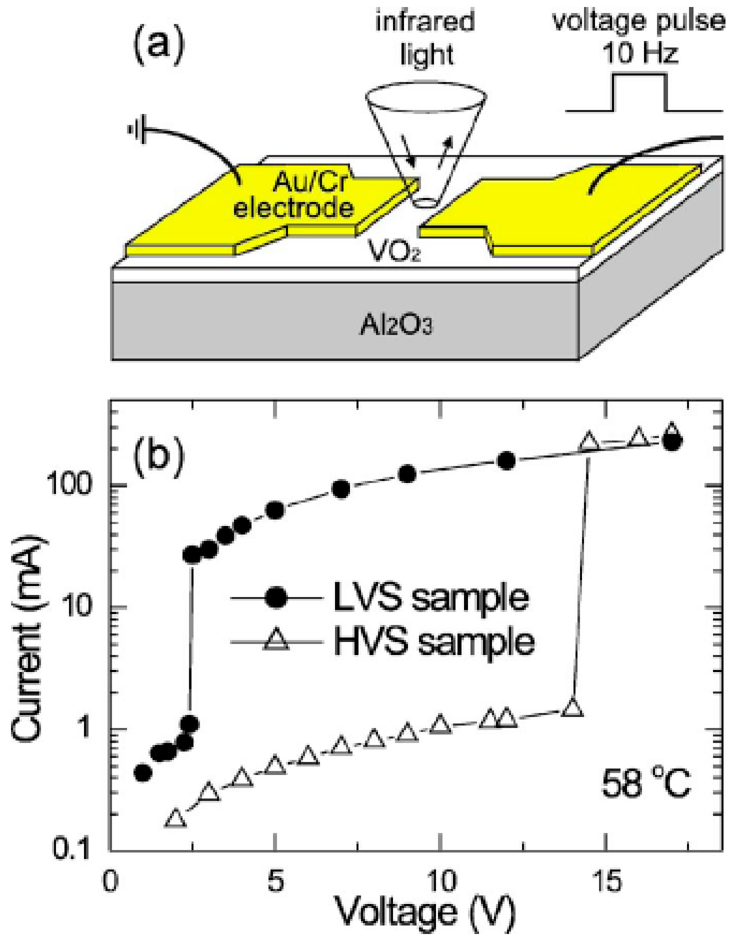
Phonon frequency hardening above P*=10 GPa without significant changes in the peak pattern

Two regimes:
P<P*: weak P-dependence
P>P*: rearrangements of V chains within a monoclinic framework

New high-P monoclinic phase ?

Imaging

Electric field induced phase transition in VO_2



Study of the temporally and spatially resolved optical response.

Temporal resolution on the *μs* time-scale is achieved through the fast response of the MCT (HgCdTe) detector.

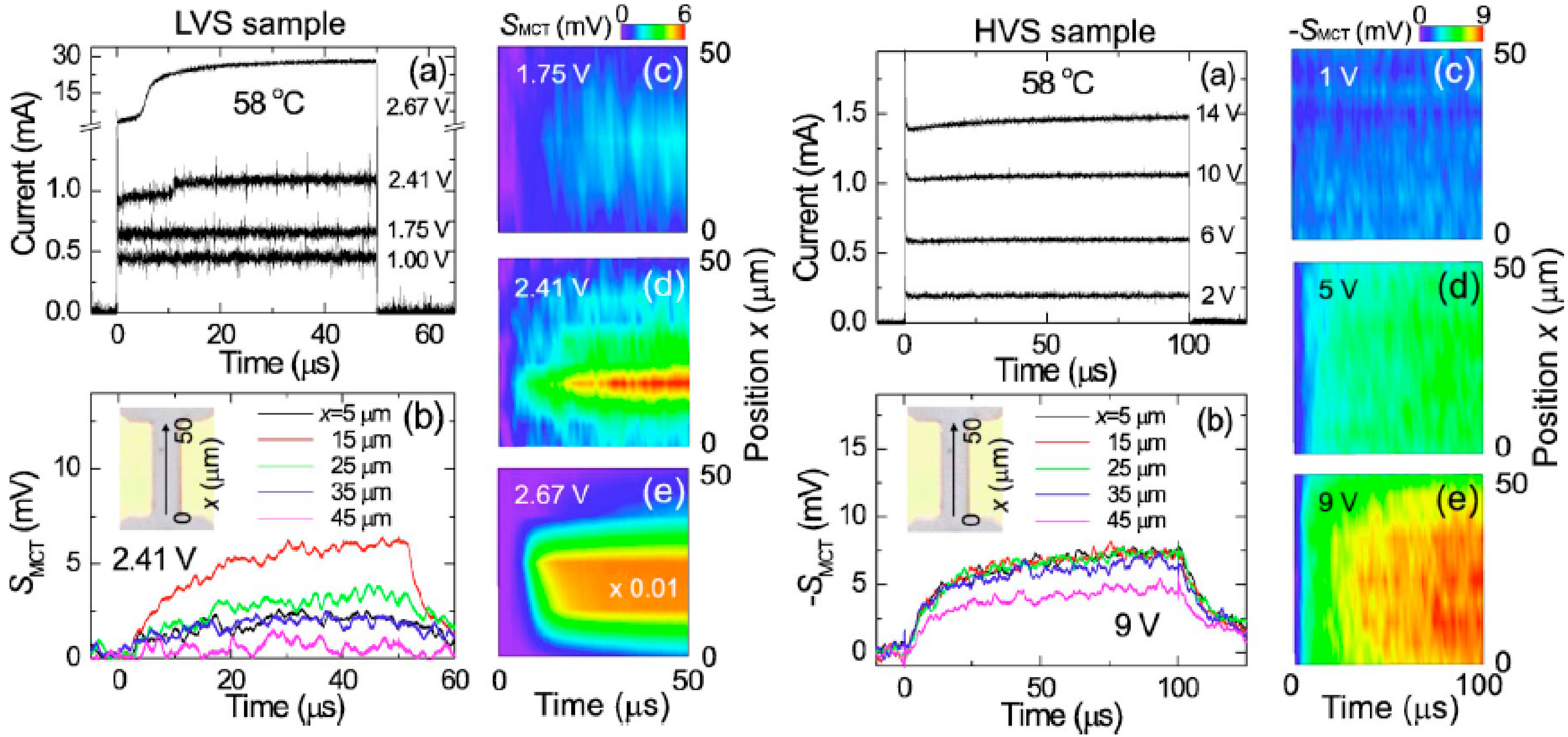
→ No role for Synchrotron in this case: the pulsed structure of synchrotron is useful to reach *ns* and below.

Spatial resolution (5 *μm*) is obtained by coupling IR synchrotron radiation with a microscope.

→ **Role for Synchrotron Brightness Gain**

J.-S. Lee *et al.,* Appl. Phys. Lett. **91,** 133509 (2007)

Electric field induced phase transition in VO_2



The spatially resolved optical response permits to explain the differences in voltage switching in terms of sample inhomogeneities which favor the creation of conducting paths (possible role of oxygen deficiencies).

J.-S. Lee *et al.,* Appl. Phys. Lett. **91,** 133509 (2007)

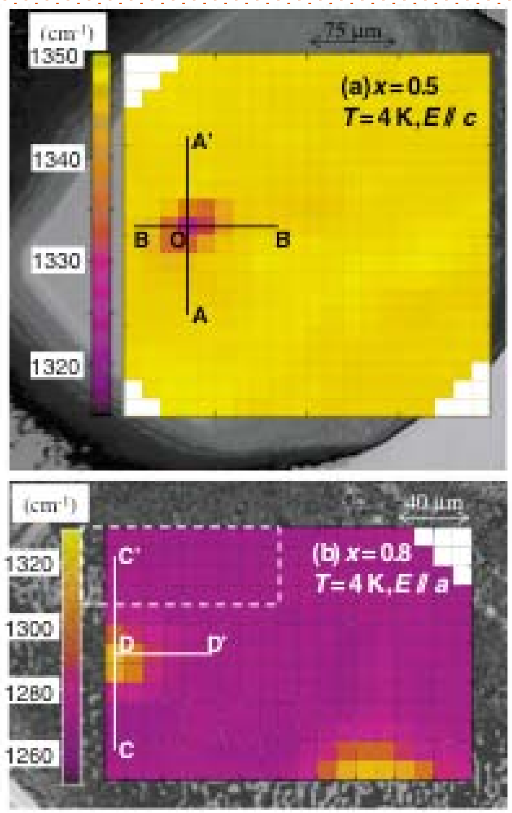
Microscopy in solid state physics

The frequency of the υ_3 (a_g) phonon mode gives indication on the metallic nature of κ-(BEDT-TTF)$_2$X.

This enables imaging of phase separation on the micrometer scale.

T. Sasaki *et al*. PRL **92**, 227001

Imaging of phase separation in κ-(BEDT-TTF)$_2$X



Acknowledgements

The SISSI@ELETTRA group

:

D. Eichert
M. Kiskinova
S. Lupi
F. Morgera
R. Sopracase
L. Vaccari

P. Calvani and **A. Nucara,**
L. Baldassarre
IRS Group, University of Rome
“La Sapienza”
& CNR-INFM Coherentia
M. Ortolani and **U. Schade**
Synchrotron BESSY II Berlin
P. Postorino
HP Group, University of Rome
“La Sapienza”
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and many others…….