2139-34

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

26 April - 7 May, 2010

IR spectroscopy and microscopy in material science
Electrodynamics at high pressures of strongly correlated electron systems

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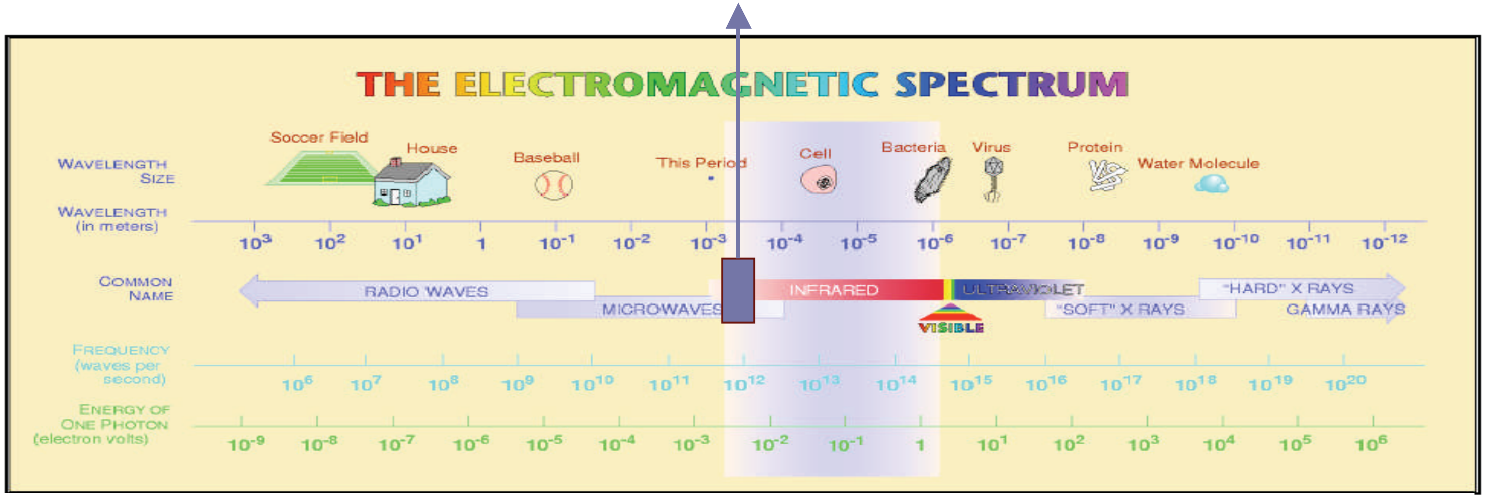
Outline - Selected applications of IRSR in solid state physics

- IR light and IR synchrotron radiation
- Basics of IR spectroscopy in condensed matter physics
  1. From Reflectivity to Optical Conductivity
  2. The Lorentz-Drude Model
- High-pressure measurements
- Strongly Correlated Electron Systems
  1. Pressure-Induced Insulator to Metal Transition in VO_2
  2. The complexity of V_2O_3
  3. Pressure vs Alloying effects in NiS2
  4. Tuning a CDW instability in RE dichalchogenides

Electromagnetic Spectrum

The “Terahertz gap”, Collective Excitations in Macromolecules and exotic electronic materials



IR Units: 200 cm^{-1}=300 K= 25 meV = 50 μm = 7 THz

FIR MIR NIR

Phonons;
Drude absorption;
Gaps in superconductors;
Molecular Rotations

Molecular Vibrations
(“Fingerprints”);
Electronic excitations
(polarons, CDW gaps,
d-bands)

Molecular Overtones and
Combinations bands;
Excitons;
Gaps in semiconductors

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)

lecture by S. Lupi on May 7

Pulsed structure →

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

Basics of infrared spectroscopy in condensed matter physics

Refractive index and Optical constants

Complex refractive index

$$\tilde{N} = n + ik$$

Real refractive index
(Snell's law, dispersion)

Extinction coefficient
(absorption)

$$\tilde{N} = \sqrt{\tilde{\varepsilon}(\omega)}$$

$$\varepsilon_1 = n^2 - k^2,$$
$$\varepsilon_2 = 2nk$$

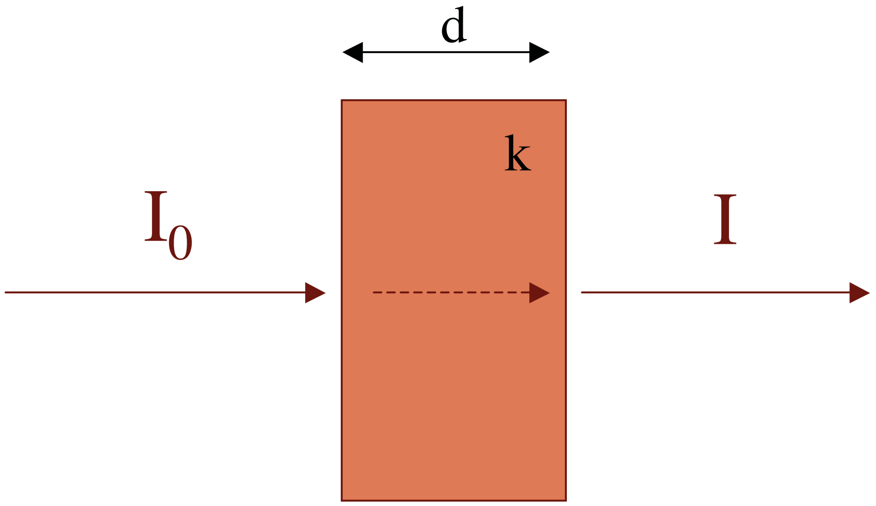
Complex dielectric constant

$$\tilde{\sigma} = i\frac{\omega}{4\pi}(1 - \tilde{\varepsilon})$$

$$\sigma_1 = \frac{\omega\varepsilon_2}{4\pi},$$
$$\sigma_2 = (1 - \varepsilon_1)\frac{\omega}{4\pi}$$

Complex optical conductivity

Absorbance, Optical Density and the Lambert-Beer's law



$$I = I_0 \exp(-\alpha d)$$

$$A = -\log\left(\frac{I}{I_0}\right)$$

$$Op.D. = -\ln\left(\frac{I}{I_0}\right)$$

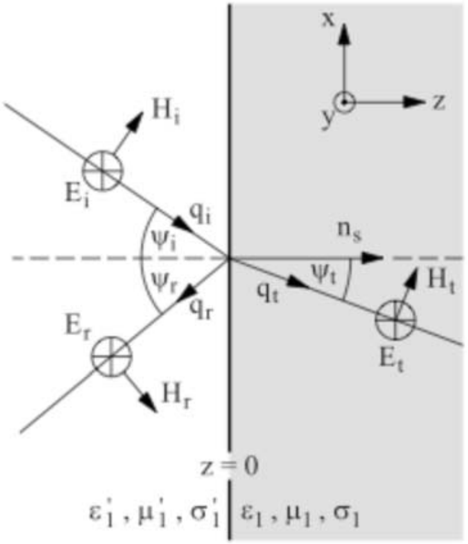
$$\boxed{\alpha = {}^{Op.D.}\!/_{d} = {}^{2k\omega}\!/_{c}}$$

Optical Reflectivity

From Maxwell to Fresnel equations

$$\hat{t}_\perp = \frac{E_{0t}}{E_{0i}} = \frac{2\mu_1 \cos\psi_i}{\mu_1 \cos\psi_i + \sqrt{\hat{N}^2 - \sin^2\psi_i}} \qquad \hat{t}_\parallel = \frac{E_{0t}}{E_{0i}} = \frac{2\mu_1 \hat{N} \cos\psi_i}{\hat{N}^2 \cos\psi_i + \mu_1\sqrt{\hat{N}^2 - \sin^2\psi_i}}$$

$$\hat{r}_\perp = \frac{E_{0r}}{E_{0i}} = \frac{\mu_1 \cos\psi_i - \sqrt{\hat{N}^2 - \sin^2\psi_i}}{\mu_1 \cos\psi_i + \sqrt{\hat{N}^2 - \sin^2\psi_i}} \qquad \hat{r}_\parallel = \frac{E_{0r}}{E_{0i}} = \frac{\hat{N}^2 \cos\psi_i - \mu_1\sqrt{\hat{N}^2 - \sin^2\psi_i}}{\hat{N}^2 \cos\psi_i + \mu_1\sqrt{\hat{N}^2 - \sin^2\psi_i}}$$



By normal incidence … and at vacuum interface

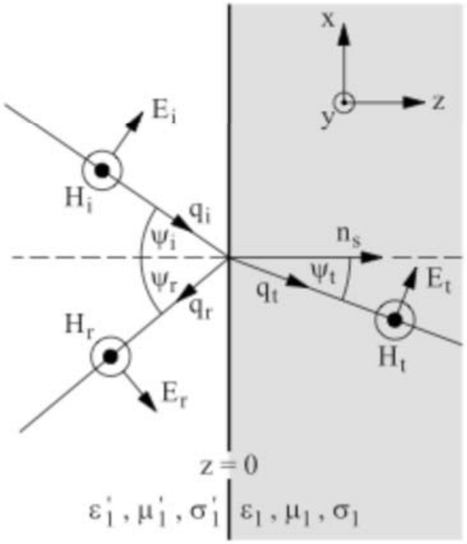
$$\tilde{r} = \frac{\tilde{N}' - \tilde{N}}{\tilde{N}' + \tilde{N}}$$

$$R(\omega) = \left|\tilde{r}(\omega)\right|^2 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

$$R(\omega) = \frac{I_s(\omega)}{I_0(\omega)}$$

← Sample

← Reference (Au, Al, Ag, …)



Kramers-Kronig Transformations

Following causality principle, the real and imaginary part of any linear response function are univocally determined through Kramers-Kronig Transformations

$$\tilde{r}(\omega) = \sqrt{R(\omega)}\exp\left[i\vartheta(\omega)\right] \longrightarrow \chi(\omega) = \ln\left(\tilde{r}(\omega)\right) = \ln\sqrt{R(\omega)} + i\vartheta(\omega)$$

$$\vartheta(\omega) = -\frac{2\omega}{\pi} P\int_0^\infty \frac{\ln\sqrt{R(\omega')}}{\omega'^2 - \omega^2}\,d\omega'$$

To this aim one should measure R(ω) over the broadest energy range:
Extrapolation procedures are also used both at high and low frequencies

The Lorentz-Drude model

$$\frac{d^2x}{dt^2}+\gamma\frac{dx}{dt}+\omega_0{}^2x=-\frac{e}{m}E_{loc},$$

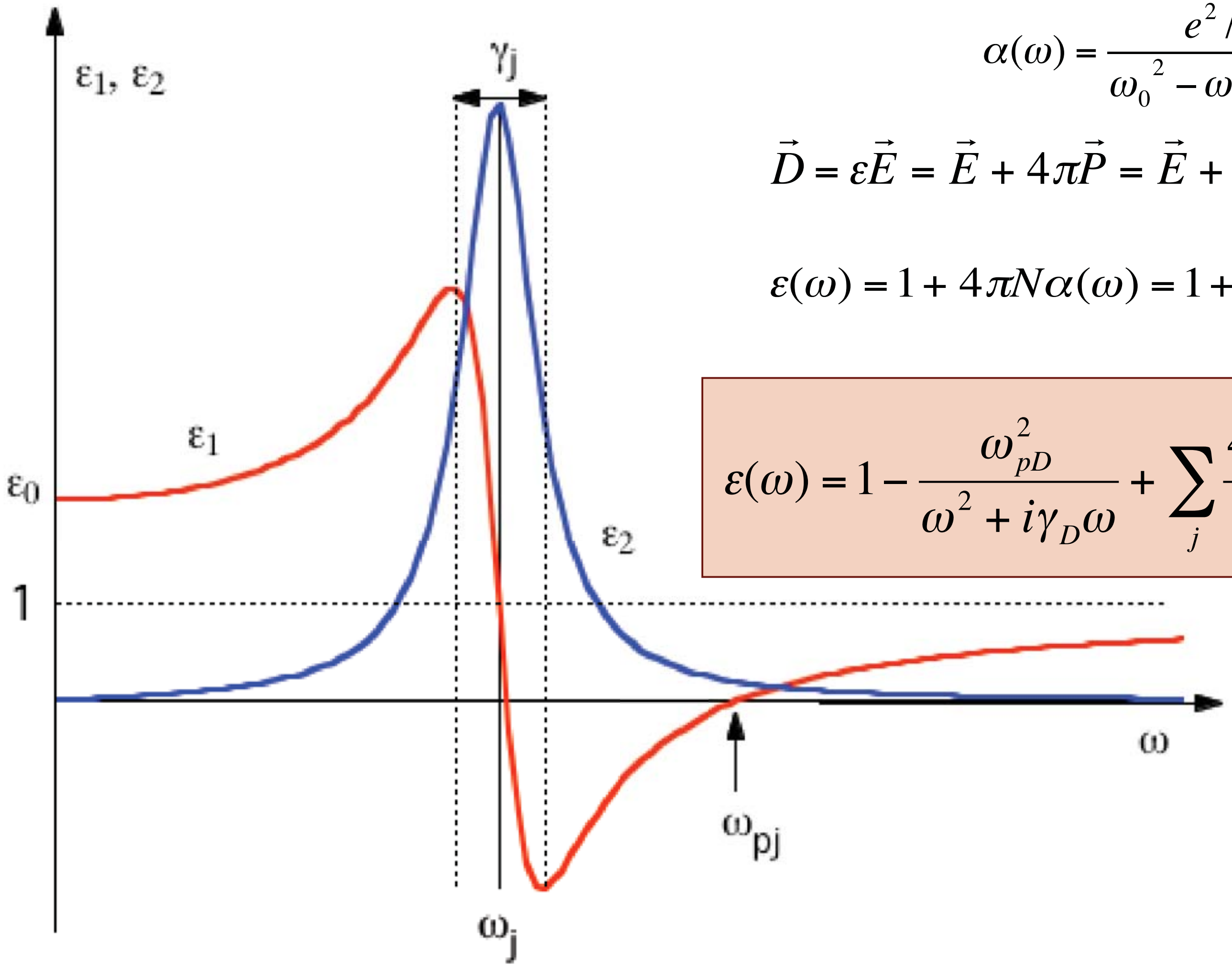
$$\vec{P}_e=-e\vec{r}=\alpha(\omega)\vec{E}_{loc},$$

$$\alpha(\omega)=\frac{e^2/m}{\omega_0{}^2-\omega^2-i\gamma\omega}$$

$$\vec{D}=\varepsilon\vec{E}=\vec{E}+4\pi\vec{P}=\vec{E}+4\pi N\vec{P}_e=(1+4\pi N\alpha)\vec{E}$$

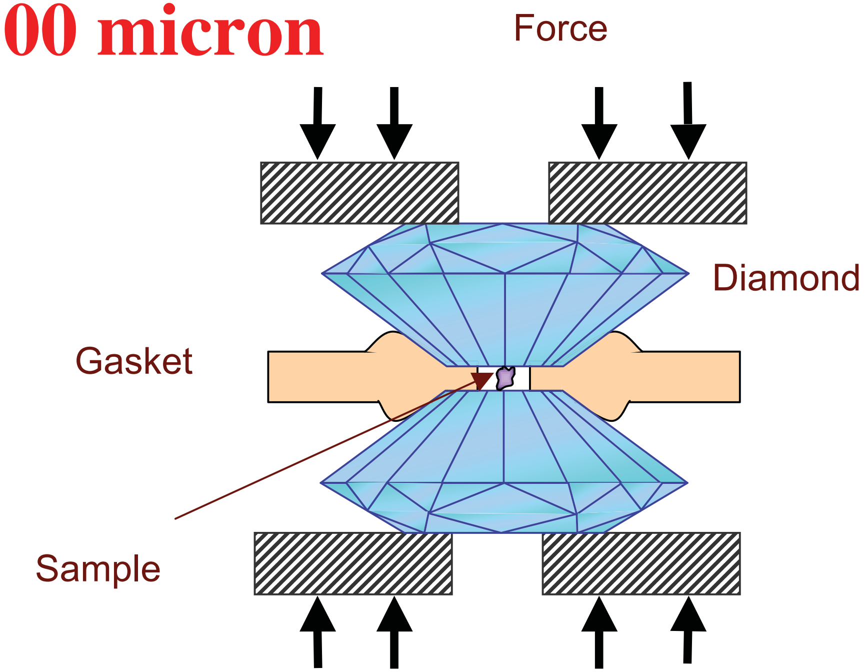
$$\varepsilon(\omega)=1+4\pi N\alpha(\omega)=1+\frac{4\pi Ne^2}{m}\frac{1}{(\omega_0^2-\omega^2)-i\gamma\omega}$$

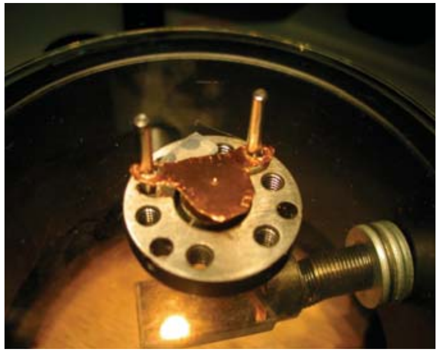
$$\boxed{\varepsilon(\omega)=1-\frac{\omega_{pD}^2}{\omega^2+i\gamma_D\omega}+\sum_j\frac{4\pi N_je^2}{m}\frac{1}{(\omega_j{}^2-\omega^2)-i\gamma_j\omega}}$$

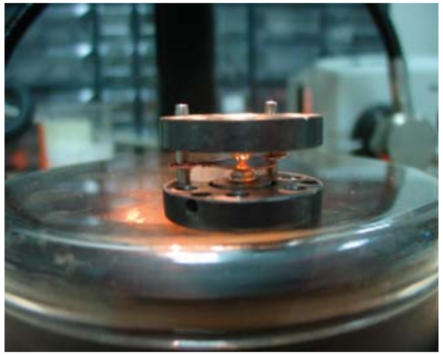


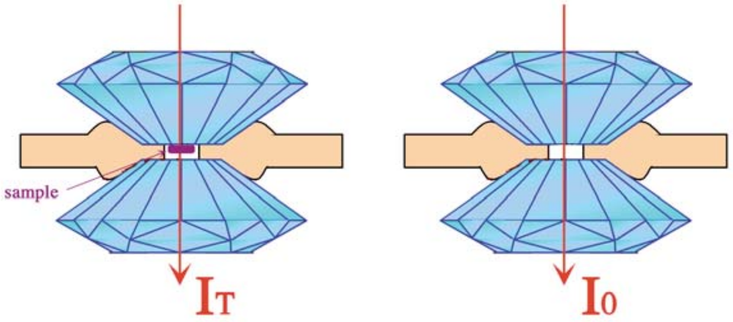
Diamond Anvil Cell (DAC)

Sample size
<100 micron

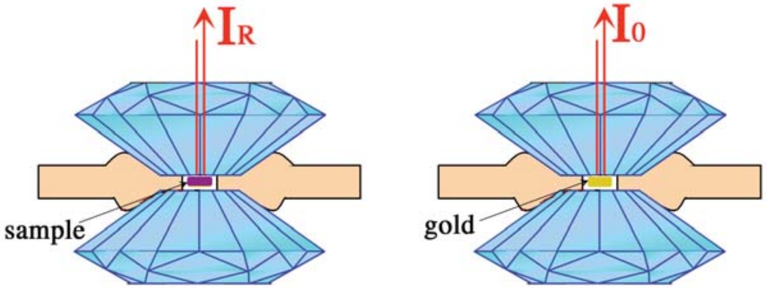








$$T=I_T / I_0$$
$$\text{Op.D.} = -\ln(T) = \alpha d$$



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

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

1 measured quantity

Reflectivity Measurement:

2 optical constants
to be determined

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

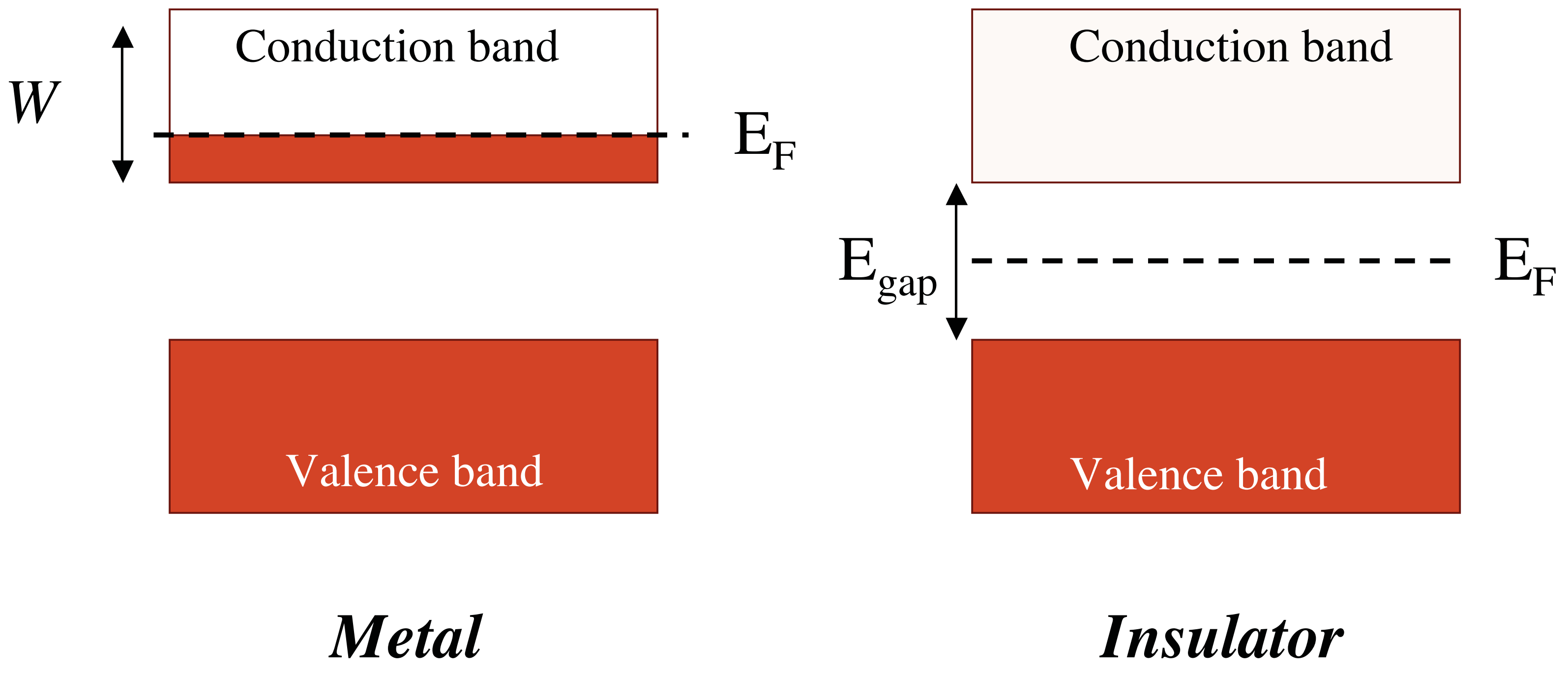
With n_d=2.43 being the diamond refractive index

The full determination of the optical constants can be achieved through:

- Simultaneous measurement of R and T
- Lorentz-Drude fitting
- Kramers-Kronig Transformations

Electrodynamics at high pressures of strongly correlated electron systems

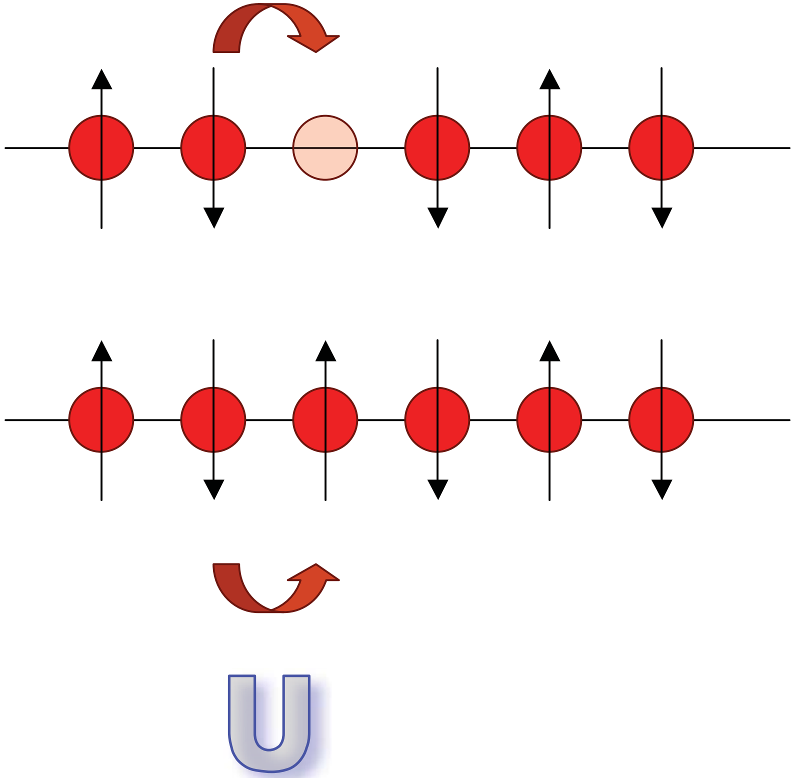
Band insulators

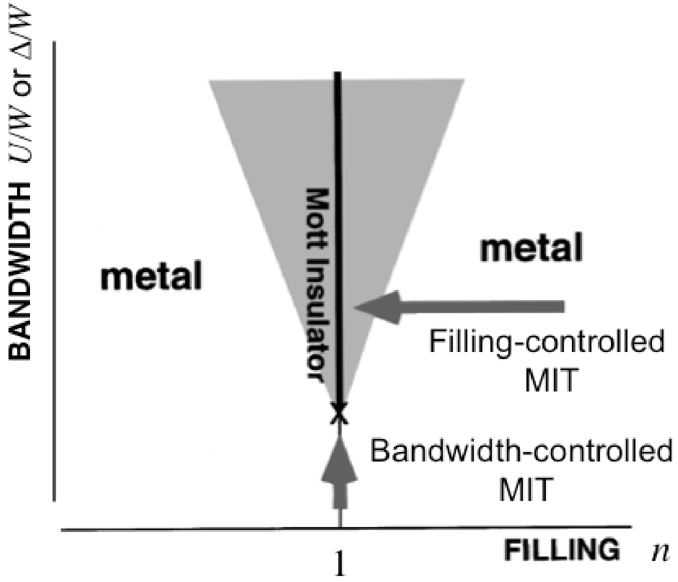


The band theory is properly defined in the one-electron approximation, i.e. when W is much larger than other electronic energy scales

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

Mott-Hubbard insulators





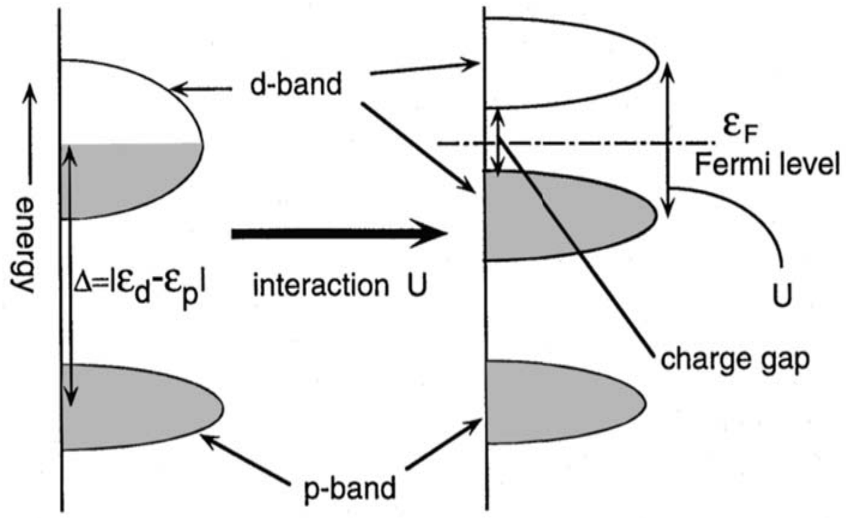
U prevents double on-site occupancy
the opening of a gap in the
spectra of excitations is induced

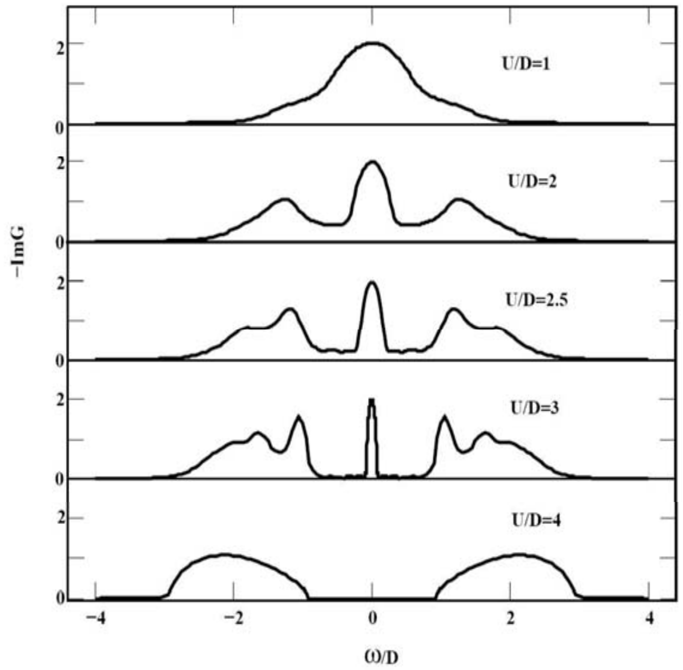
$$H = -t \sum_{<i,j>,\sigma} c^{\dagger}_{i,\sigma} c_{j,\sigma} + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow}$$

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

Electronic correlation: failure of band model

Hubbard model



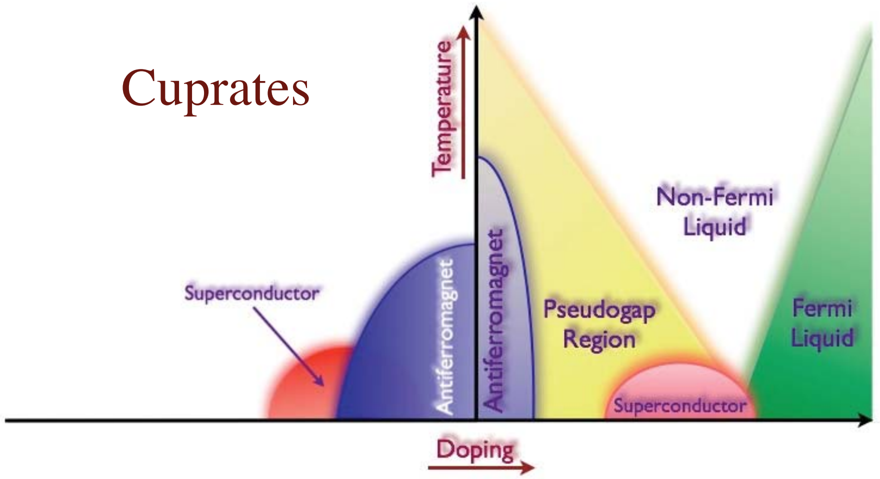


Pressure may increase the W/U ratio inducing a MIT

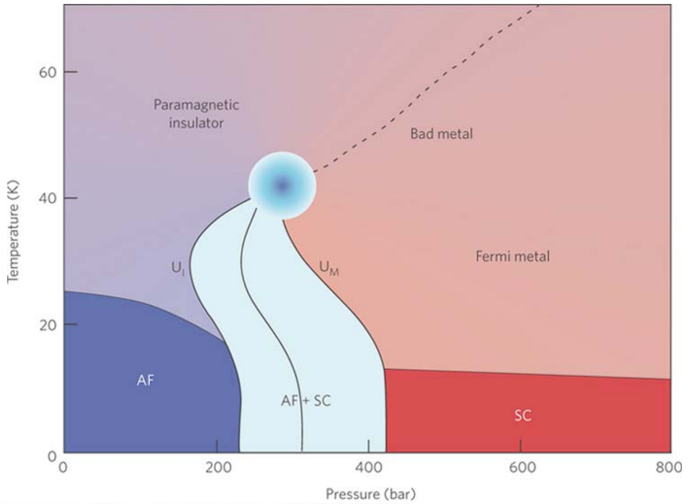
W: bandwidth or kinetic energy (strongly dependent on atomic distances)
U : coulomb repulsion

Strongly correlated electron systems

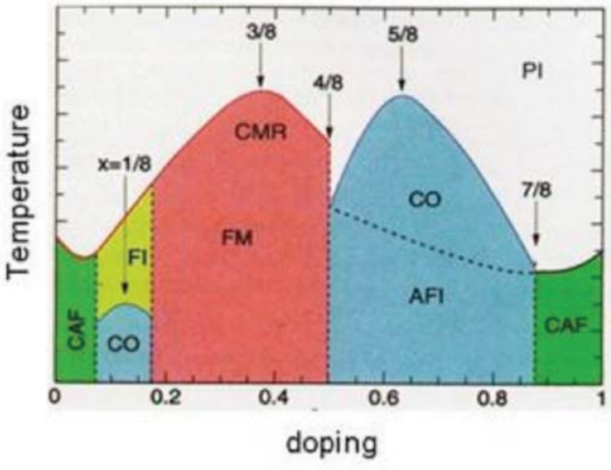
Cuprates

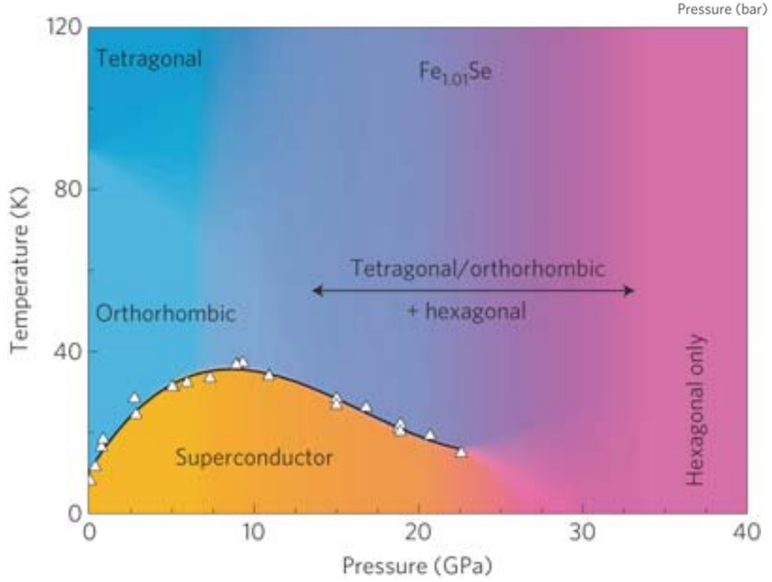


Mott insulators
(V203, Bechgaard salts, NiS2)



Manganites



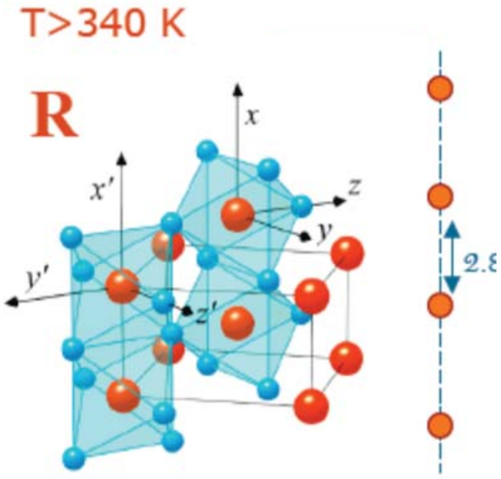


FeSe

P-Induced Insulator to Metal Transition in Vanadium Dioxide - VO_2

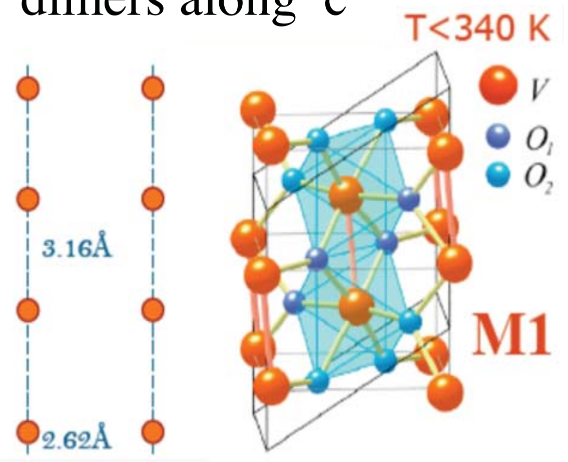
The metal-insulator transition in VO_2

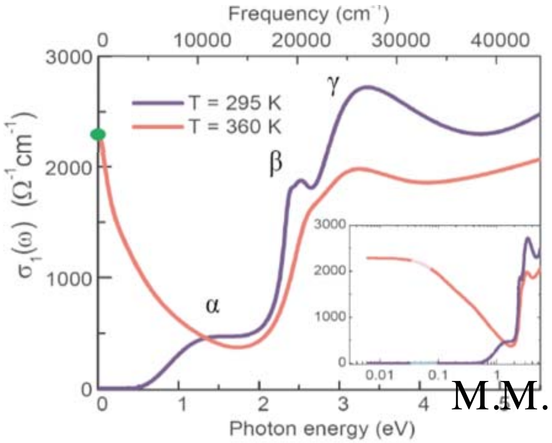
Metal



T-dependent MIT at T_{MIT}= 340 K
Concomitant lattice modification
from a low-T monoclinic (M1)
phase to a high-T rutile (R) phase.
<u>Both phases are non-magnetic</u>

Insulator
dimers along c





M.M. Qazilbash et al, PRB 2007

Strong Interplay between electron-lattice and electron-electron interactions

Driving MIT mechanism Hubbard or Peierls?

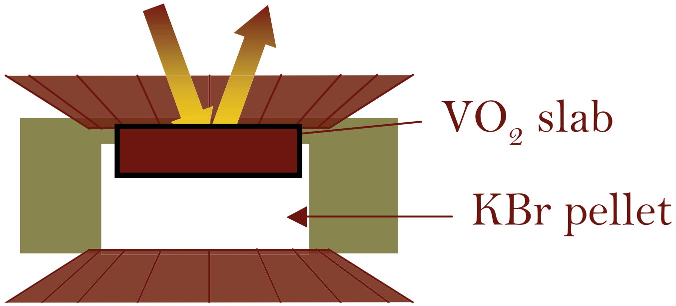
High Pressure may disentangle the two mechanisms

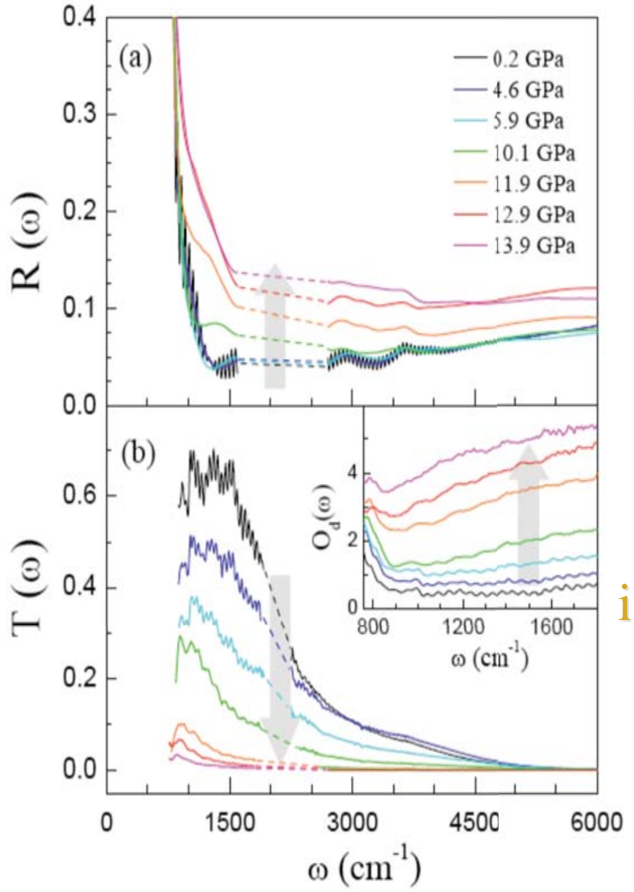
<u>Chosen techniques</u>: IR and Raman

so to monitor independently electronic and structural changes

P-dependent reflectance and transmittance of VO_2

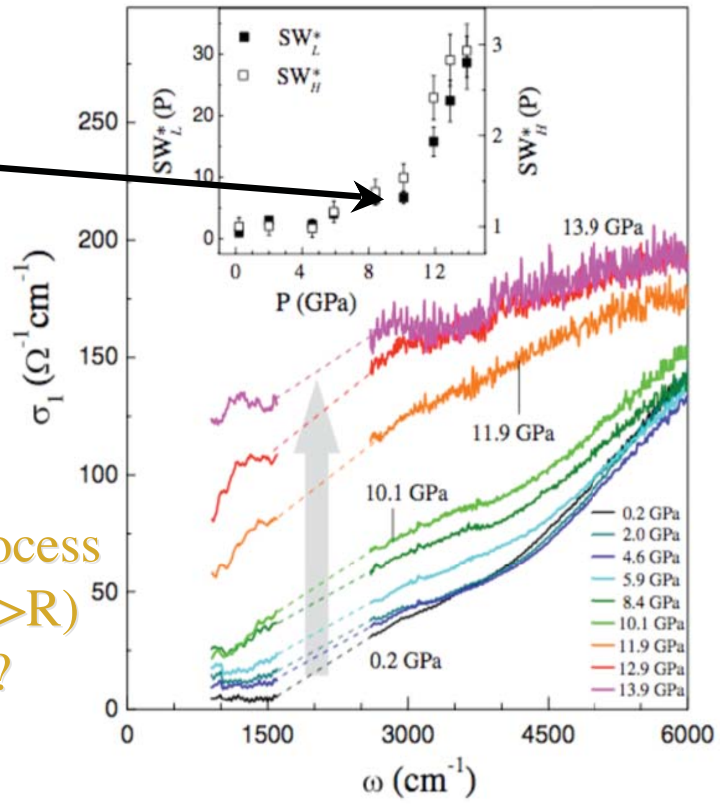
Simultaneous measurements of reflectance and transmittance at 300 K in the M1 monoclinic insulating phase on a thin VO_2 sample





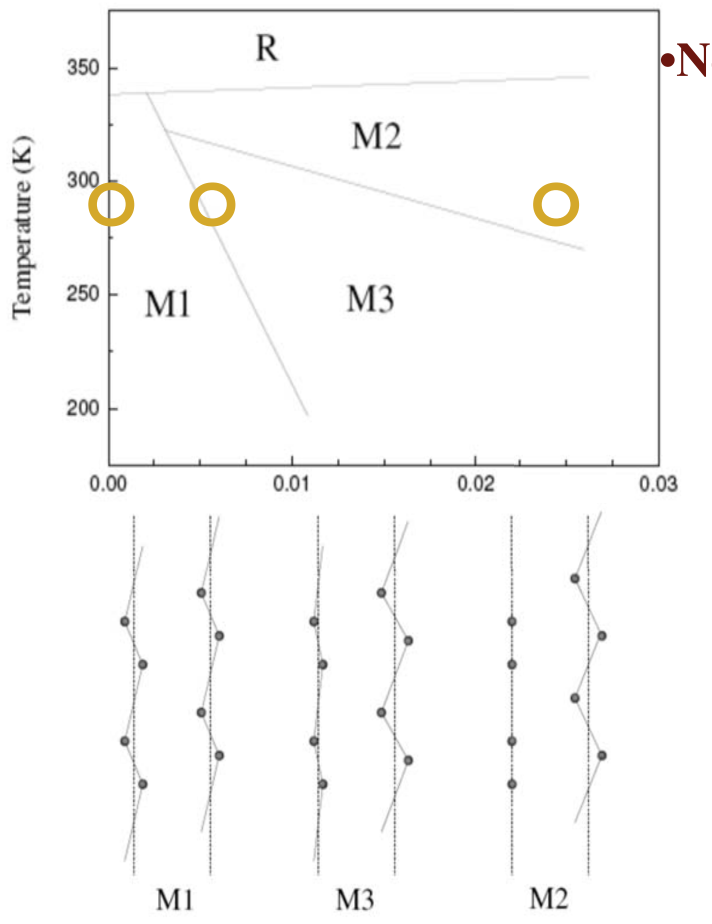
Onset of a metallization process around 10 GPa

Main question: is the metallization process associated to a (M1-->R) symmetry change?



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

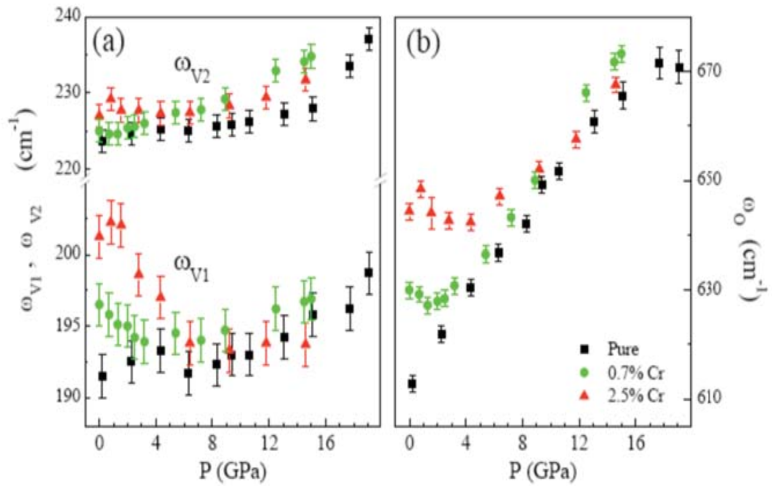
Optical conductivity of VO_2 under high pressure

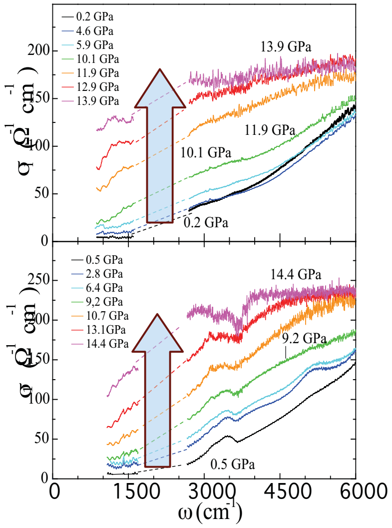


pristine Cr=0.7% Cr=2.5%

•Different extent of Peierls distortion

•Negligible effects on electronic properties at P=0



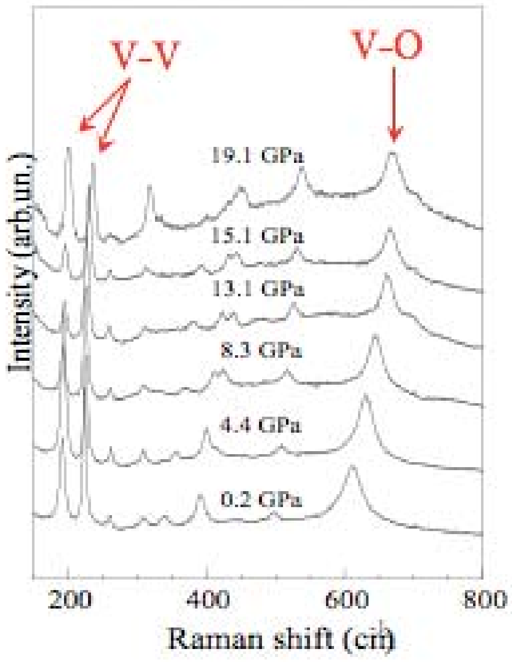


• Structural transition and MIT decoupled at high pressure

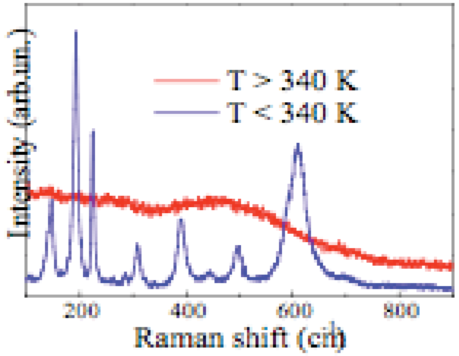
•Weakened relevance of Peierls distortion in leading the MIT in favours of electronic correlation

• Strong impact on theoretical models

Raman spectroscopy on VO_2

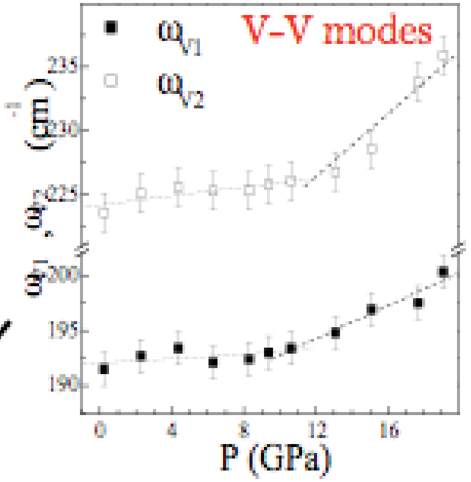


- M1 phase: 18 Raman active modes
- R phase: 4 broad band



Raman spectroscopy is a good technique to study structural transition in VO_2

Monoclinic phase is stable up to 19 GPa (up to 39 GPa from XRD, L. Malavasi et al, unpublished)



Anomalous behaviour of low frequency modes

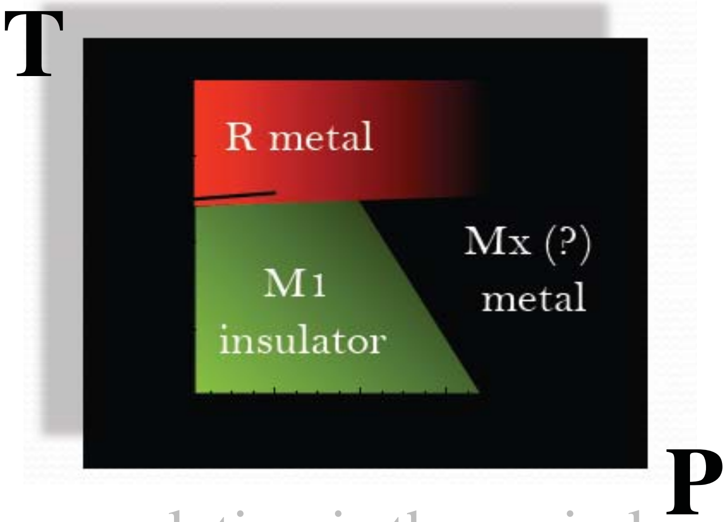
Subtle rearrangement of V-V chains

New Monoclinic metallic structure?

Raman spectroscopy on VO_2 under high pressure

Insulator to metal transition and monoclinic to rutile transition are decoupled at high pressure

Metallization process in a new Mx monoclinic structure

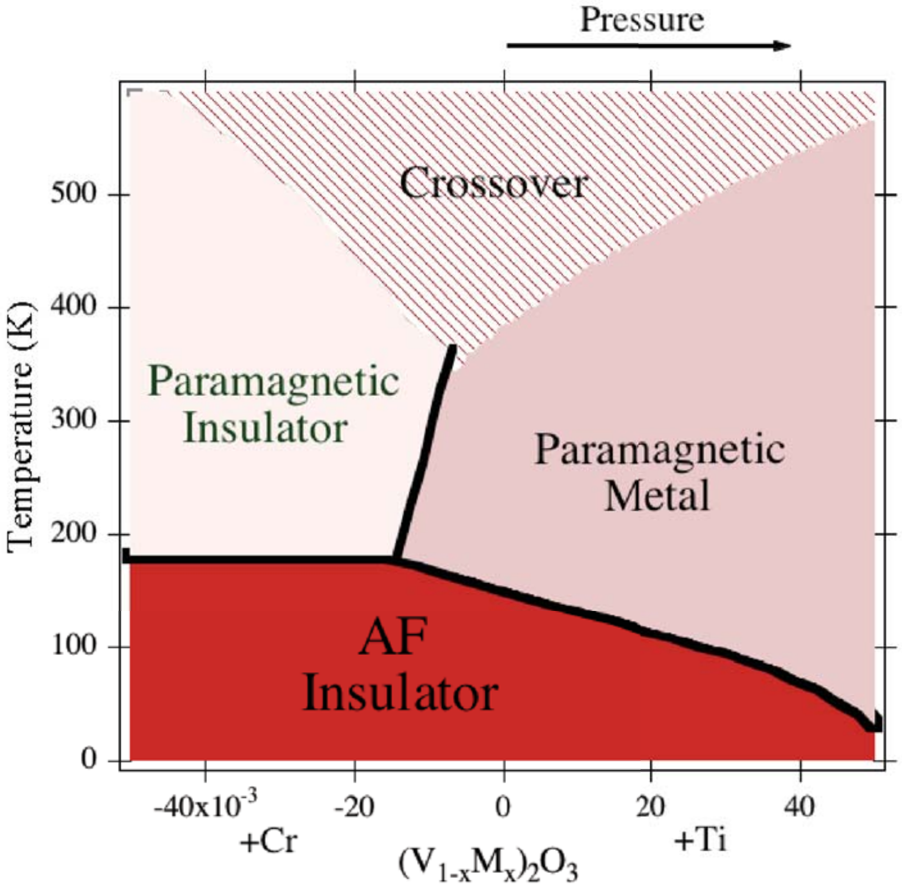


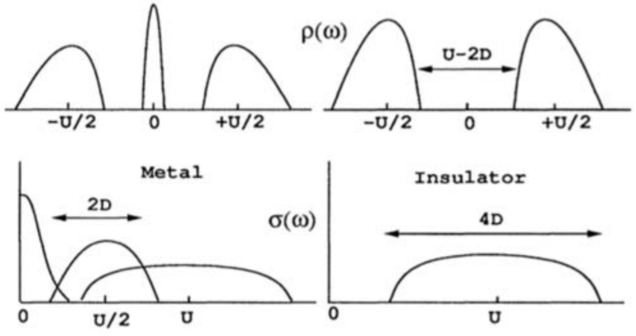
Electron correlation is the main localization mechanism (at least at high-P) in VO_2

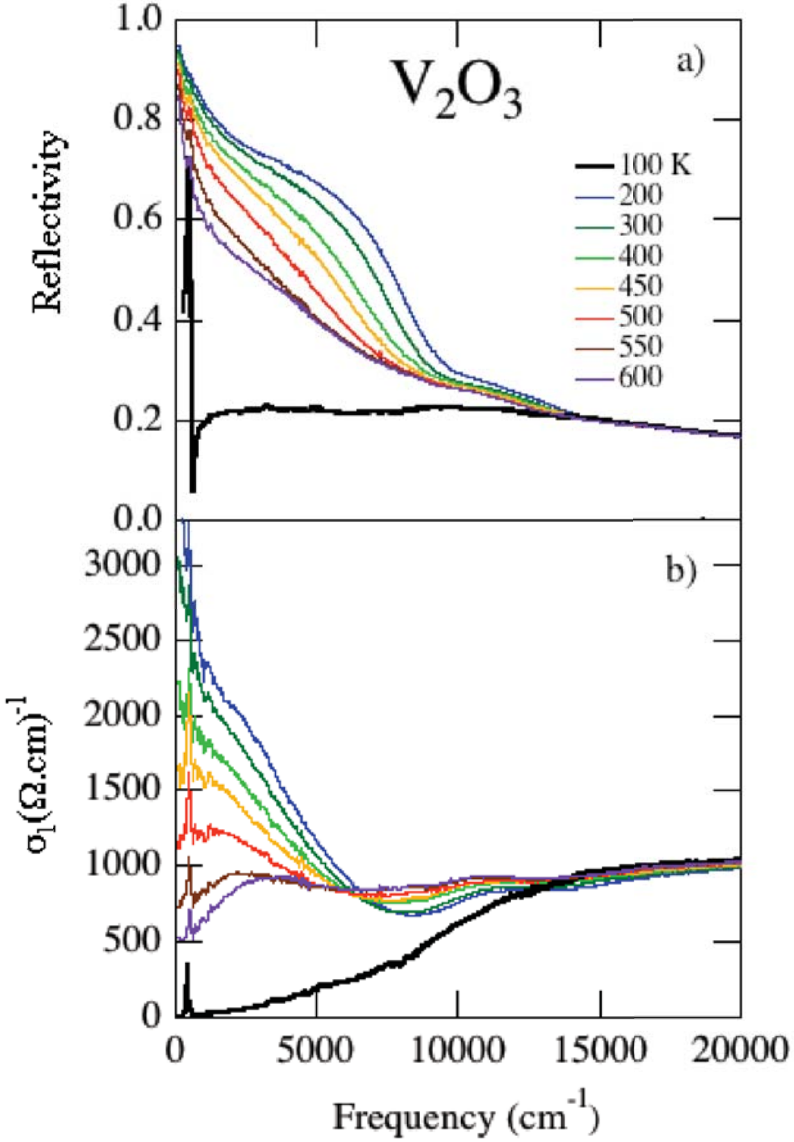
E. Arcangeletti et al, PRL98, 196406 (2007)
C. Marini et al, PRB 2008

The complex phase diagram of Vanadium Sesquioxide - V_2O_3

Vanadium Sesquioxide - V_2O_3

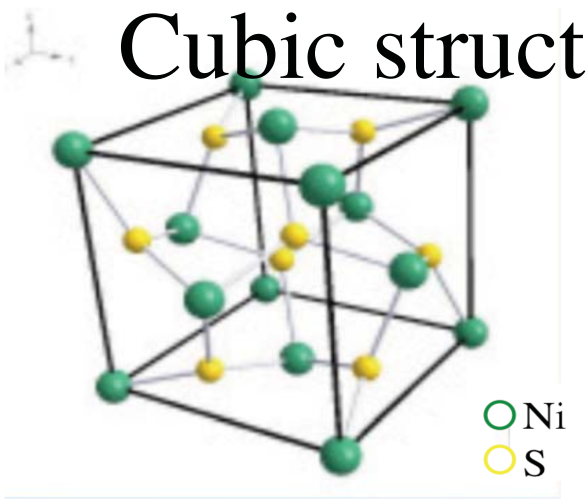






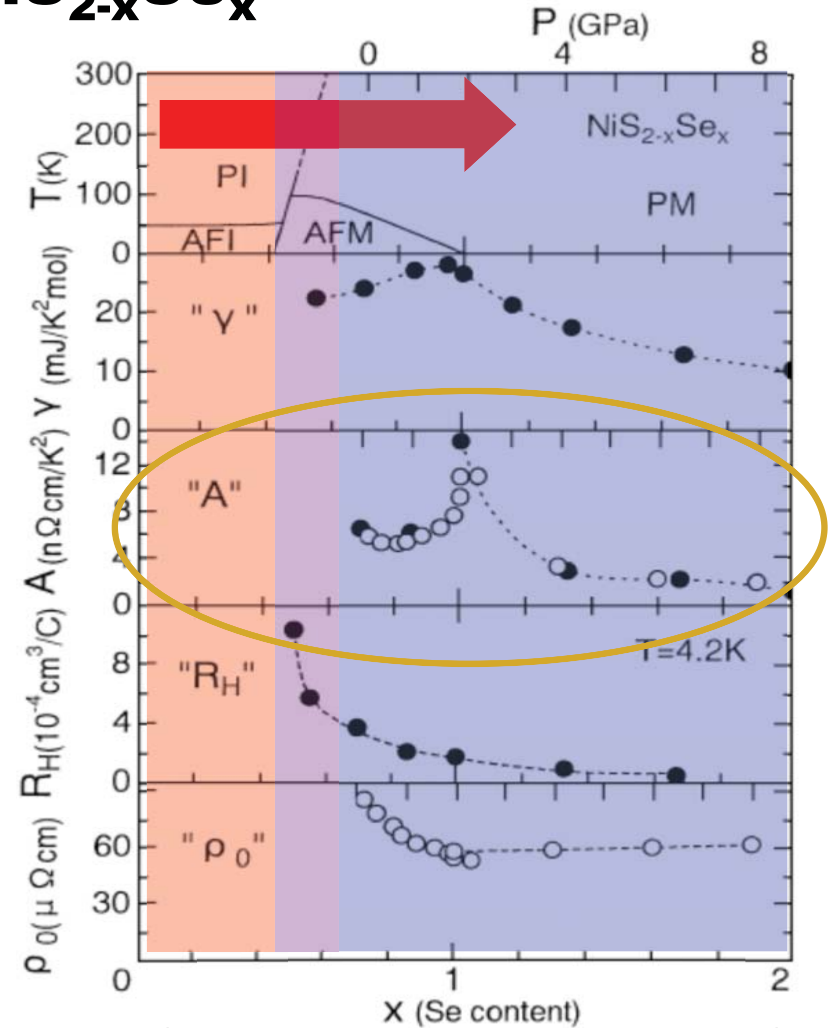
Pressure vs Alloying effects in Nickel Disulfide - NiS_2

Ni pyrite and its Se alloys $NiS_{2-x}Se_x$



Simple cubic structure
Homogeneous $NiS_{2-x}Se_x$ solution
No structural transition!
Charge Transfer Insulator

$$\rho = \rho_0 + A \cdot T^2$$

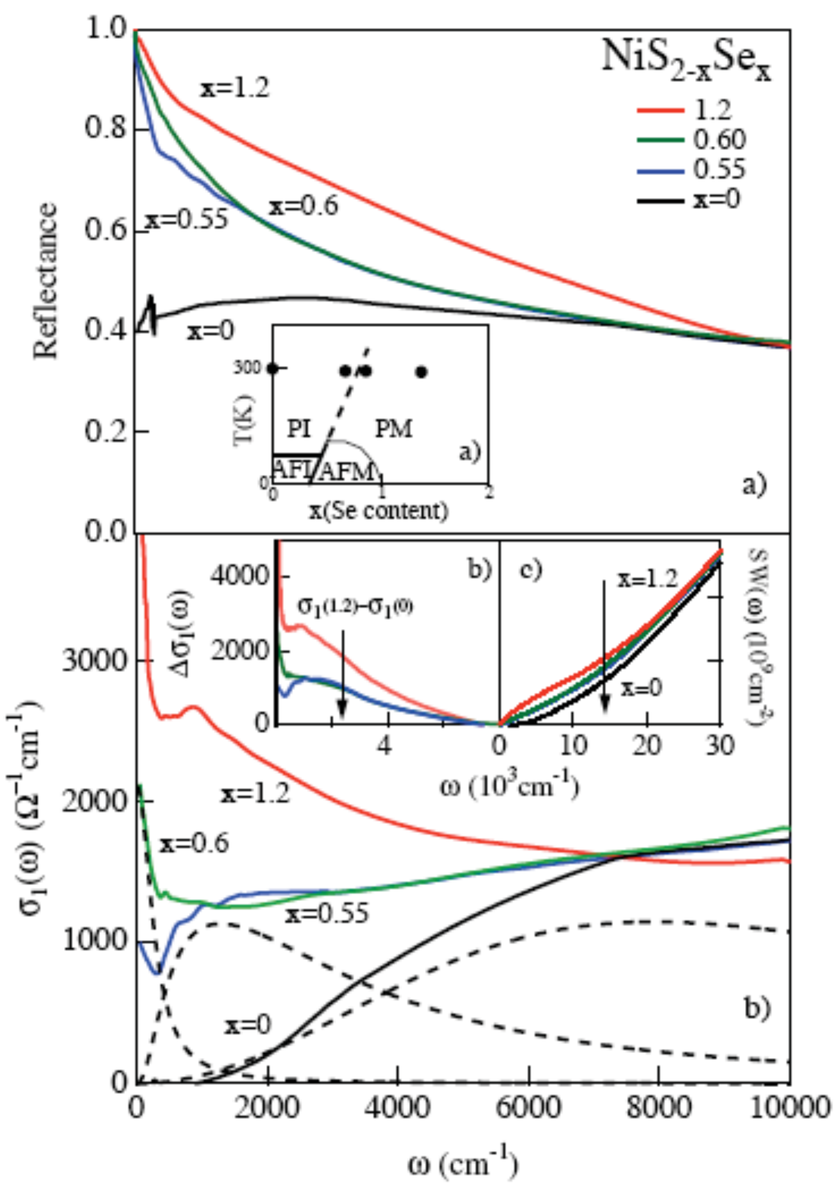


NiS_2 insulator → $NiSe_2$ metal

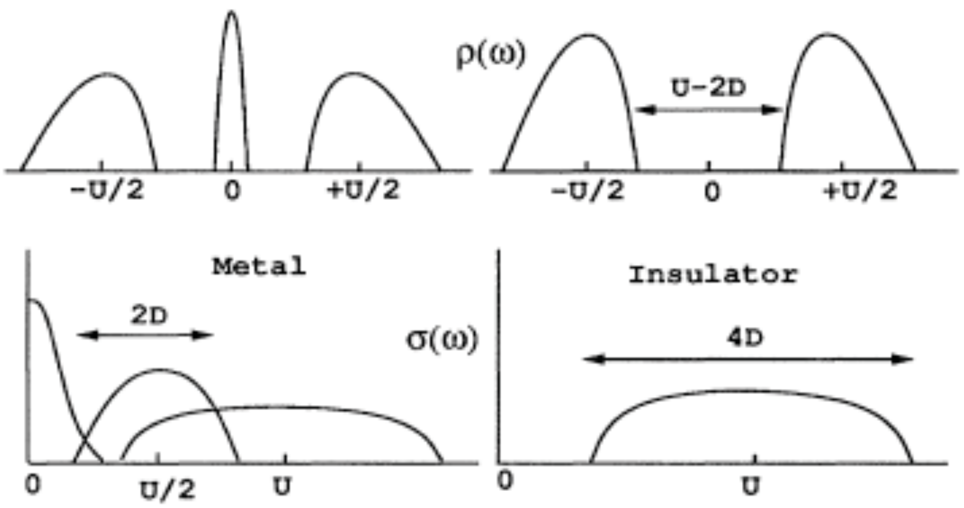
Se increases bandwidth while expanding the lattice!
Surprising similarities in the T-x, T-P phase diagrams

S.Miyasaka et al, J. Phys. Soc. Jpn. 69, 3166 (2000)

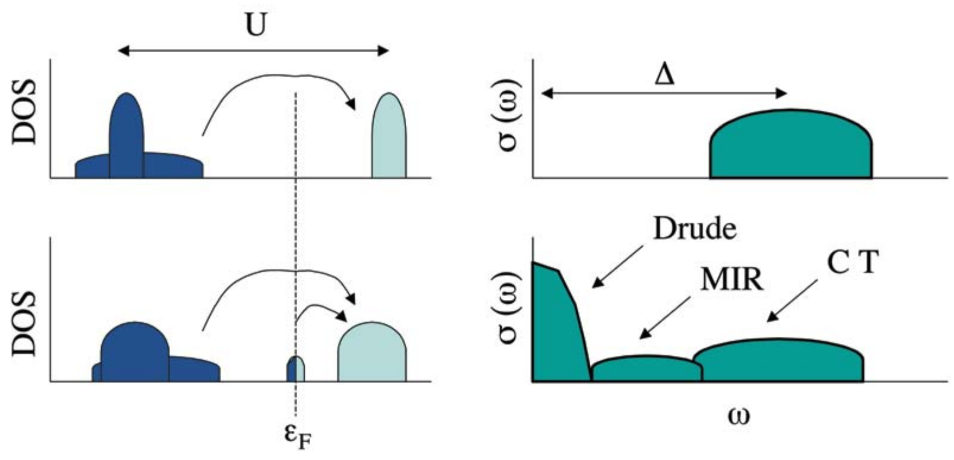
Coherent vs Incoherent excitations in $NiS_{2-x}Se_x$



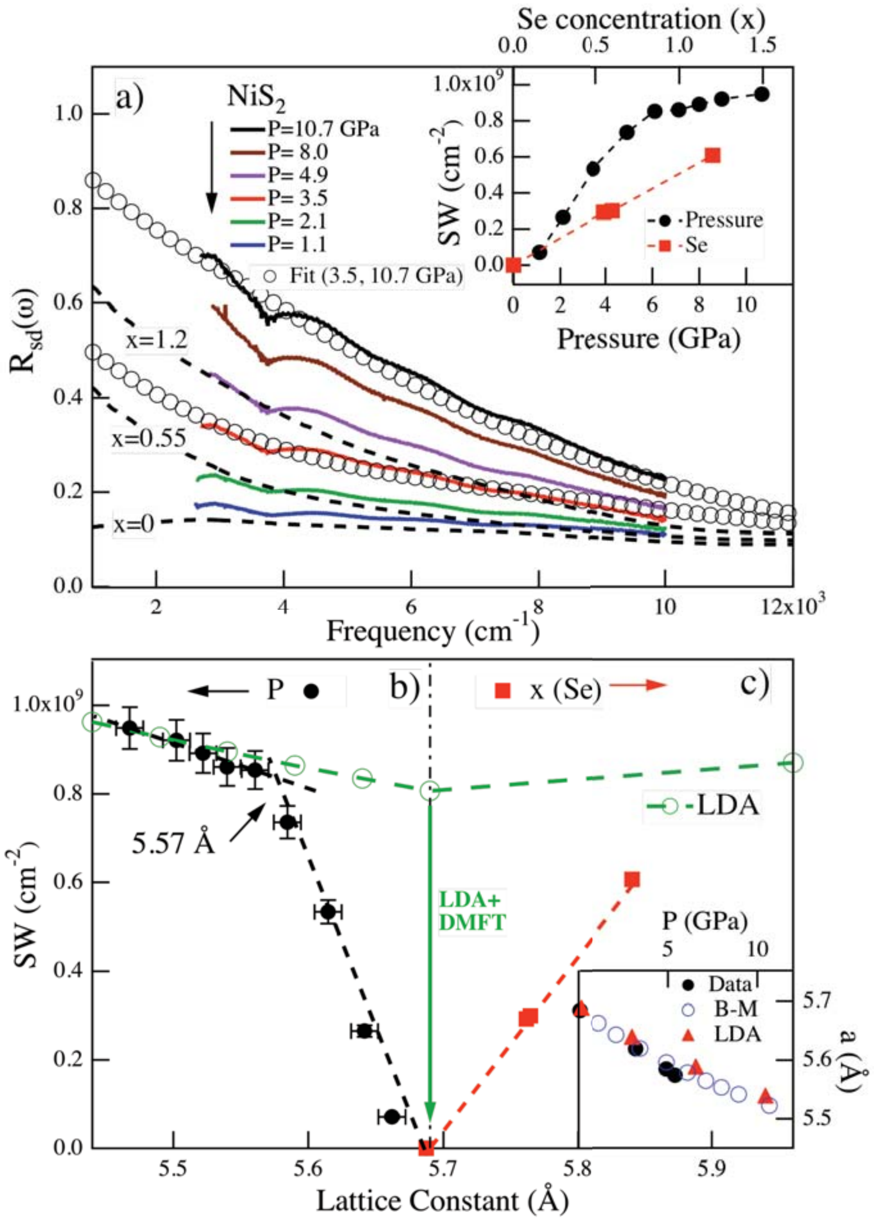
Mott-Hubbard

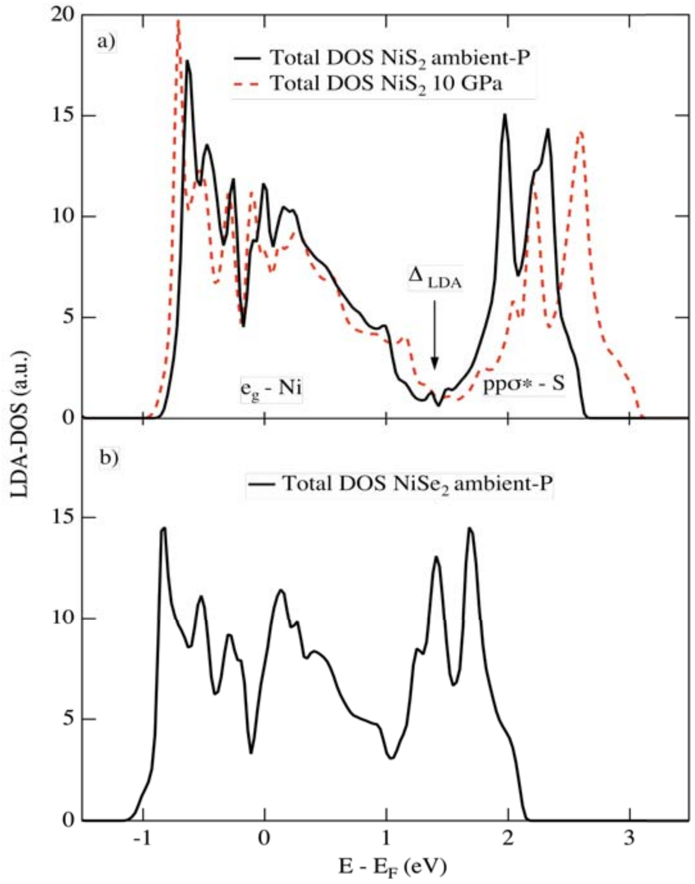


Charge Transfer



Bandwidth vs CT controlled transition





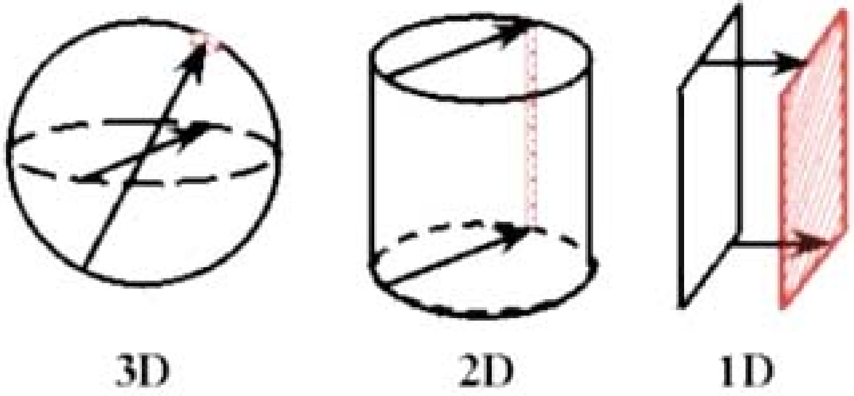
Two different MITs:

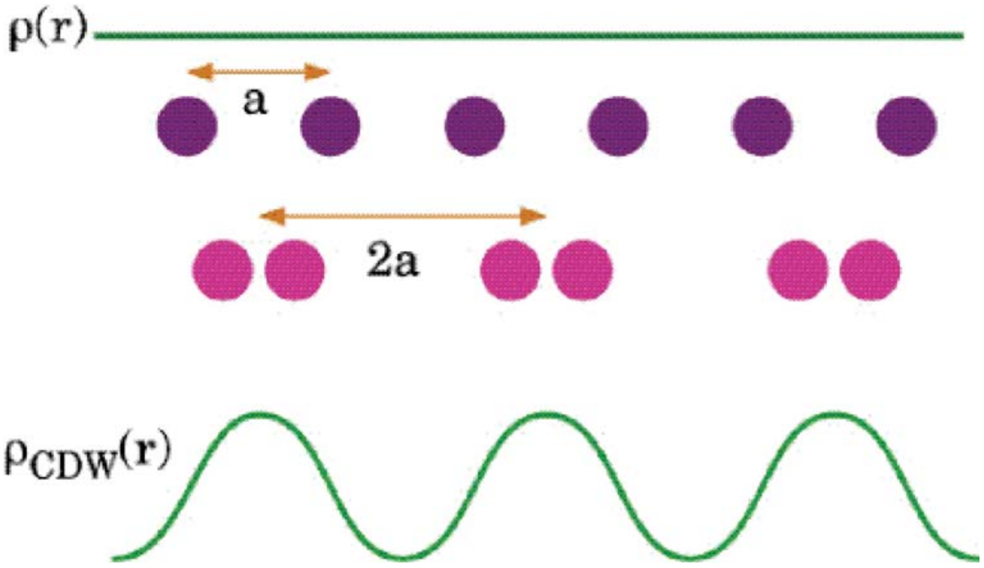
1) under pressure, W/Δ = const. and W/U decreases, triggering the MIT;

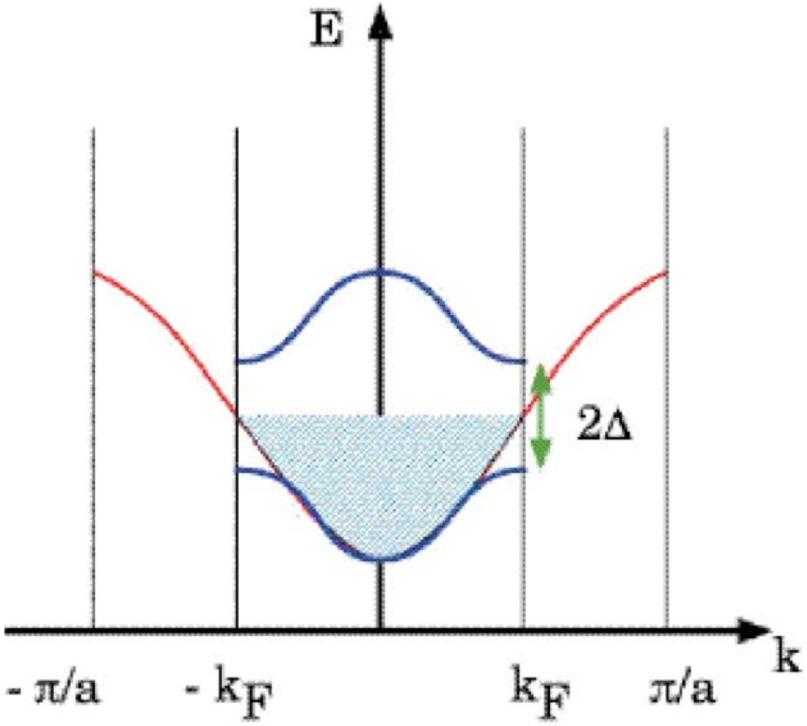
2) Se alloying: W/U = const. whereas W/Δ increases inducing the MIT;

Tuning a CDW instability in Rare-Earth Dichalchogenides

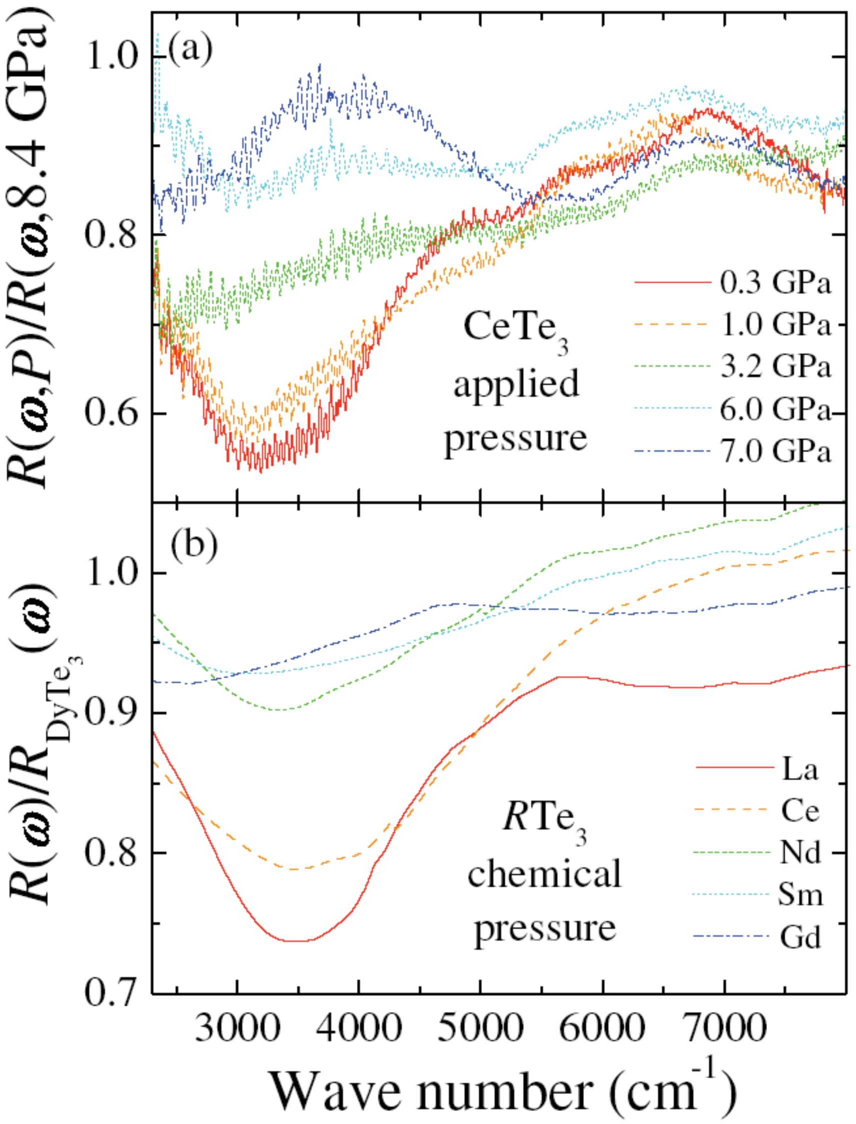
Nesting wavevectors and the Peierls transition







Hydrostatic pressure vs. chemical pressure

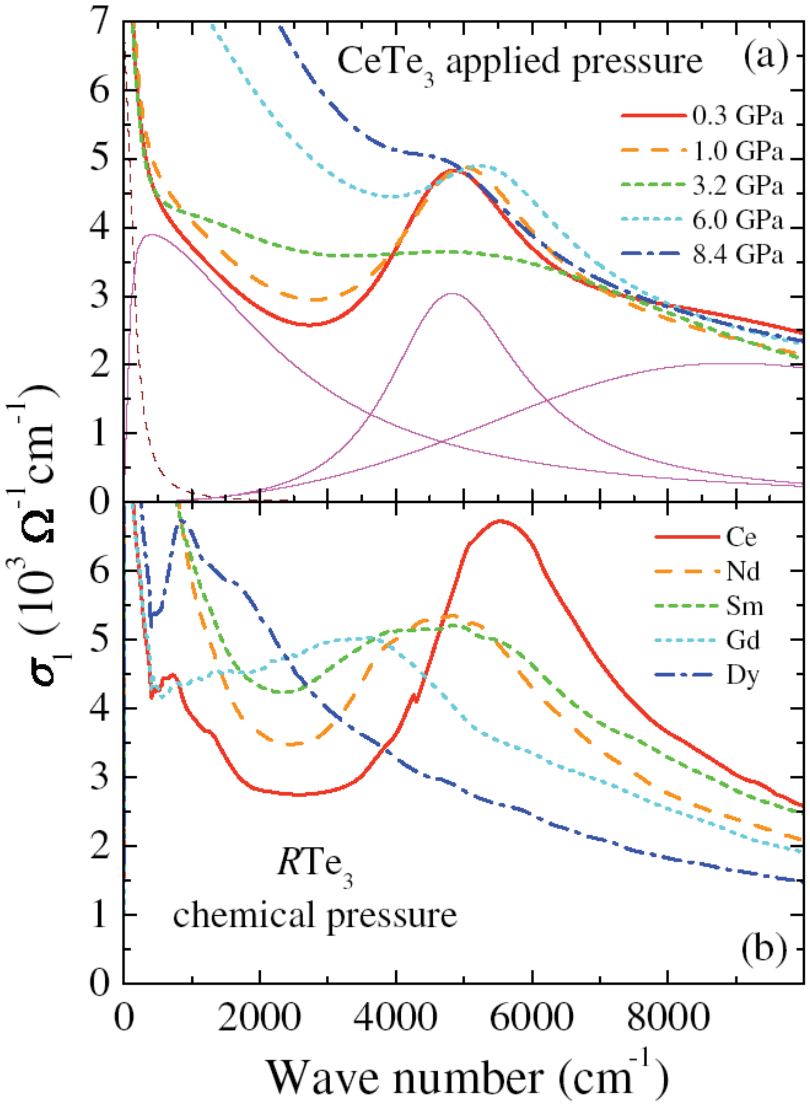


A. Sacchetti *et al*., PRL **98**, 026401 (2007)

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

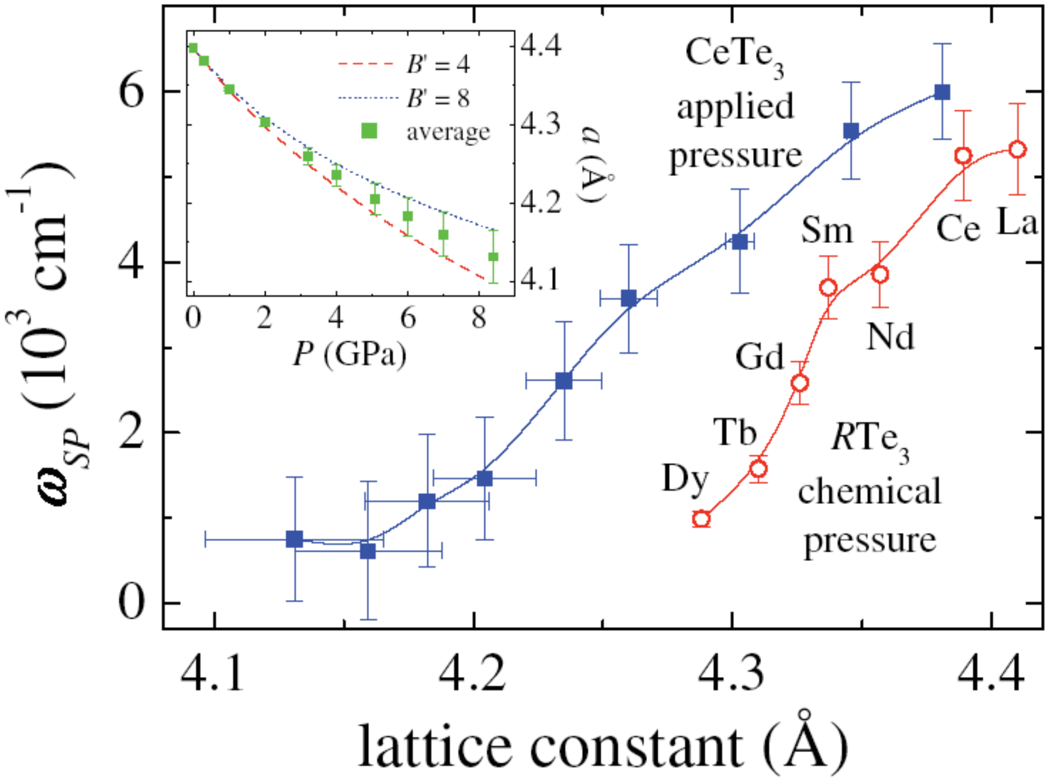


A. Sacchetti *et al*., PRL **98**, 026401 (2007)

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/m³

➡ B_0 = 25 GPa

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

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

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

The high pressure measurement permits to study the evolution of the SP gap as a function of the lattice parameter **by using one single sample.**

Pressure vs. Alloying

VO_2

Cr-doping changes structure within the insulating phase but does not affect electronic properties. Independently on the level of Cr-doping Pressure drives a metallic monoclinic phase

V_2O_3

Besides expanding the lattice, Cr-doping induces phase separation. Pressure drives a more homogeneous metallic phase but does not completely restore the pristine V_2O_3 homogeneous metallic state. Pressure vs doping scaling does not hold

NiS_2

Se expands the lattice contrary to Pressure

Se drives metallicity through a reduction of Δ: merging of Ni-e_g and chalchogen ppσ bands

Pressure increases bandwidth of Ni-e_g

$CeTe_3$

Pressure and Rare Earth substitution have the same effect on CDW:

Reduced nesting because of increased 3-D character

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