Neutron and Photon Spectroscopy

Part I : Introduction

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Outline

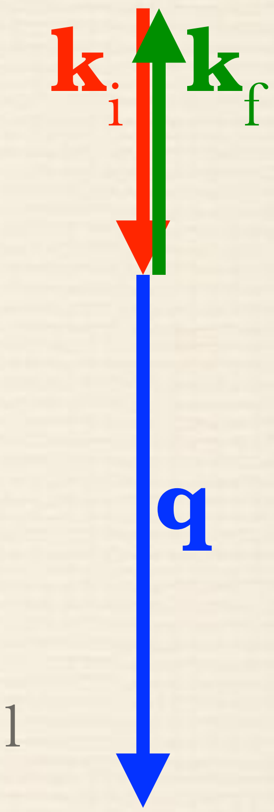
1.1 Basic of Inelastic Physics

Momentum Conservation

- Neutrons and photons Momentum : $\vec{p} = \hbar \vec{k}$

- Transfered Momentum : $\vec{q} = \vec{k}_i - \vec{k}_f$

$$\vec{q}_{min} = (k_i - k_f)\widetilde{k_i} \underset{\omega=0}{=} \vec{0} \qquad \vec{q}_{max} = (k_i + k_f)\widetilde{k_i} \underset{\omega=0}{=} 2\vec{k}_i$$



- Photons visible (λ~500nm - ħω~2.5eV) : k_i~10^{-3} $Å^{-1}$

  Photons X-Ray : (λ~14Å - ħω~900eV) : k_i~1 $Å^{-1}$

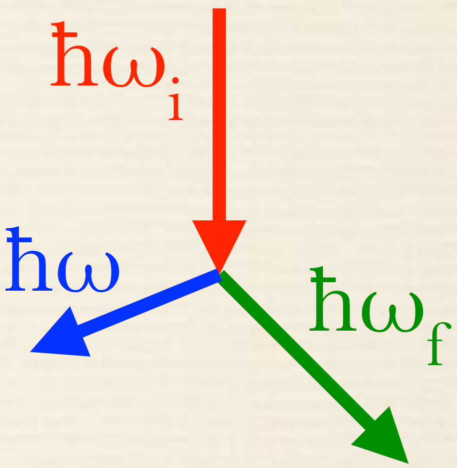
  Neutrons : (λ~2.36Å - ħω~15meV) : k_i~1 $Å^{-1}$

- Typical Brillouin Zone size (*a*~5 Å) : q_X~1 $Å^{-1}$

Energy Conservation

- Neutrons : $\hbar\omega_i = \frac{p_i^2}{2m} = \frac{\hbar^2 k_i^2}{2m}$

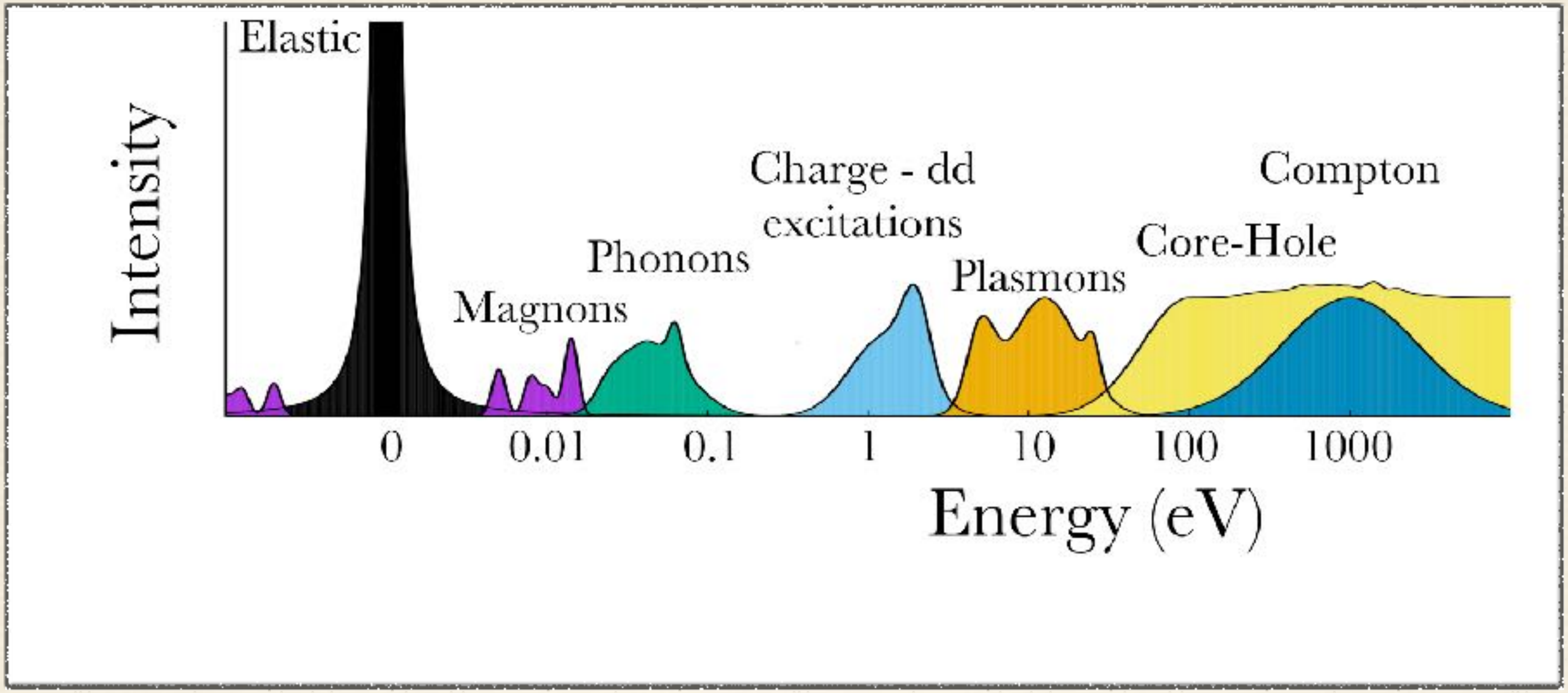
  Transfered energy : $\hbar\omega = \hbar\omega_i - \hbar\omega_f = \frac{\hbar^2}{2m}(k_i^2 - k_f^2)$



- Photons : $\hbar\omega_i = p_i c = \hbar c k_i$

  Transfered energy : $\hbar\omega = \hbar\omega_i - \hbar\omega_f = \hbar c(k_i - k_f)$

Energy Conservation



Excitation	Crystal Field	Magnon	Phonon	*d-d* & e^--*h*	Plasmon	Core hole
Energy	~ 1 meV	~ 10 meV	10-100 meV	~1 eV	~ 10 eV	0.1 - 100 keV

Energy Conservation

Technique	Brillouin	Raman	Neutrons Scattering	Infrared	IXS	RIXS
Probe	Photon (Visible)	Photon (Visible)	Neutron	Photon	Photon (X-ray)	Photon (X-ray)
Particule Energy	~1 eV	~1 eV	1 - 150 meV	1 - 100 meV	~10 keV	0.5 - 100 keV
Transfered Energy	0.01 - 1 meV	1 - 1000 meV	0.1 - 100 meV	1 - 100 meV	1 - 400 meV	-

Excitation	Crystal Field	Magnon	Phonon	*d-d* & e^--*h*	Plasmon	Core hole
Energy	~ 1 meV	~ 10 meV	10-100 meV	~1 eV	~ 10 eV	0.1 - 100 keV

Energy and Momentum

Energy and Momentum are connected through dispersion relation :

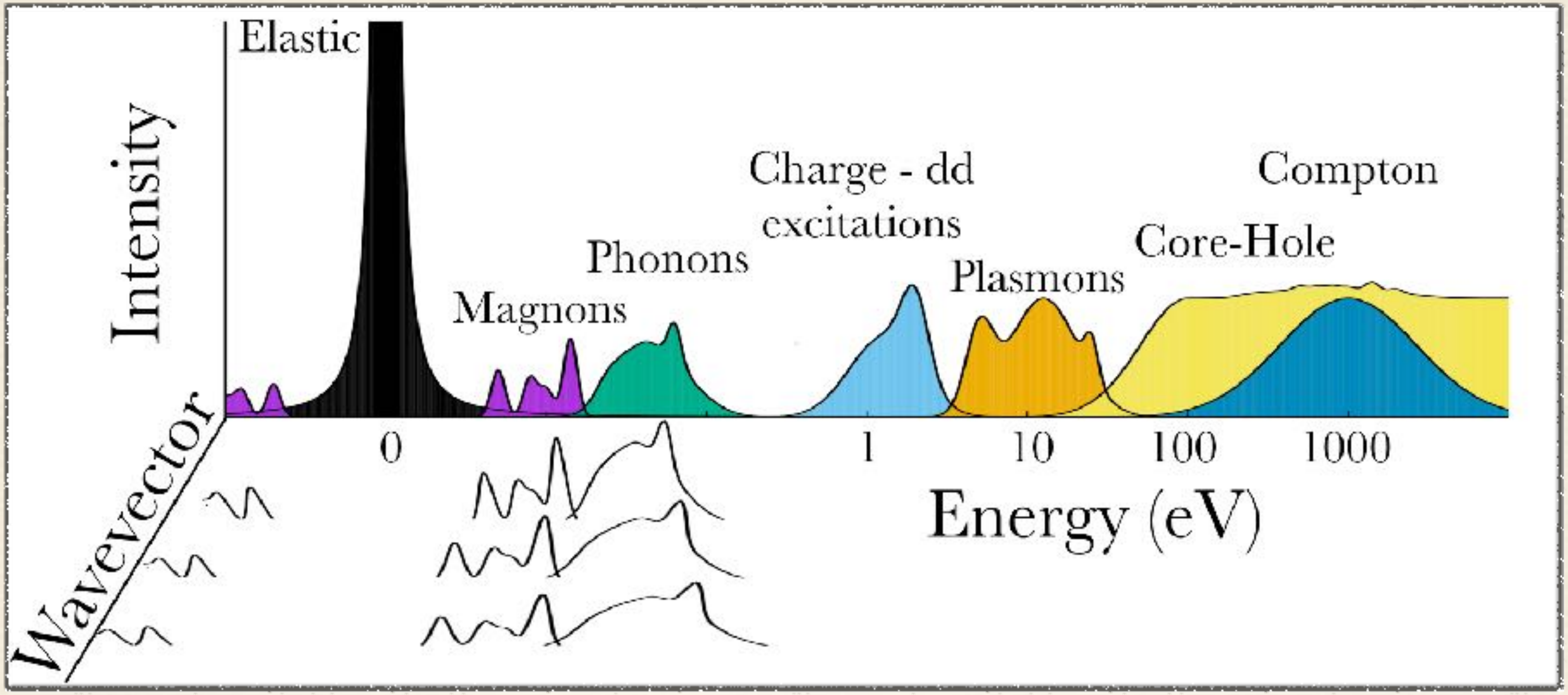
$$\omega(\vec{q})$$

For local excitations such as Crystal Field or Ising-like excitations, this dispersion relation may be constant :

$$\omega(\vec{q}) = \omega_0$$

This dispersion relation may be complex for collective modes such as Magnon, Phonons, etc… and is a fingerprint of the Hamiltonian parameters stabilizing the ground state.

Energy and Momentum



Excitation	Crystal Field	Magnon	Phonon	*d-d* & *e*⁻*-h*	Plasmon	Core hole
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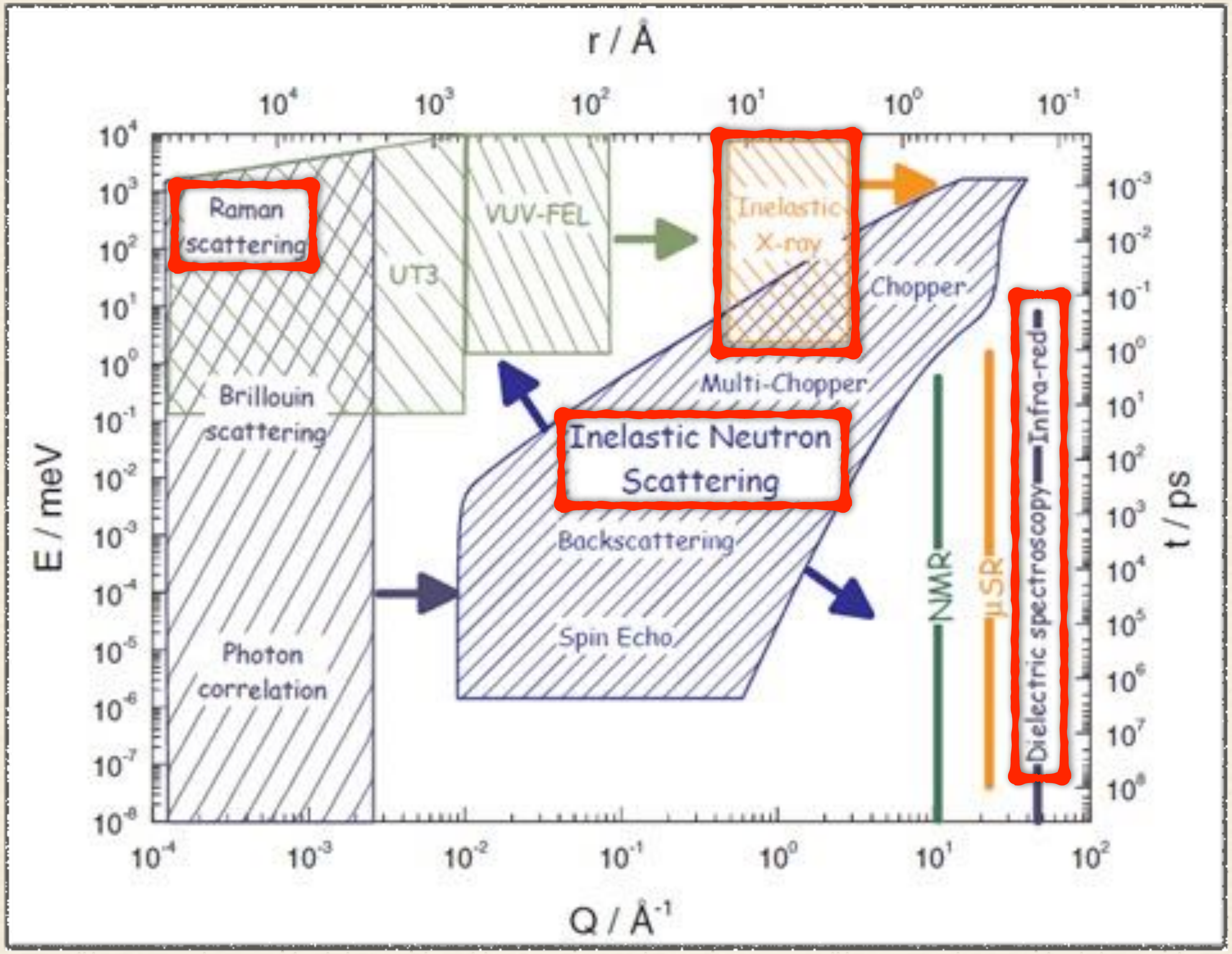
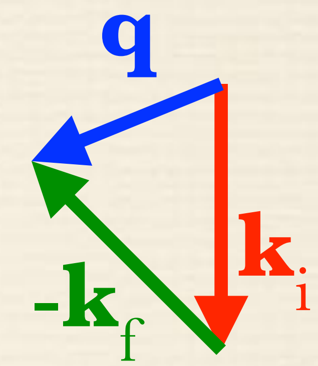
Energy and Momentum



Energy and Momentum

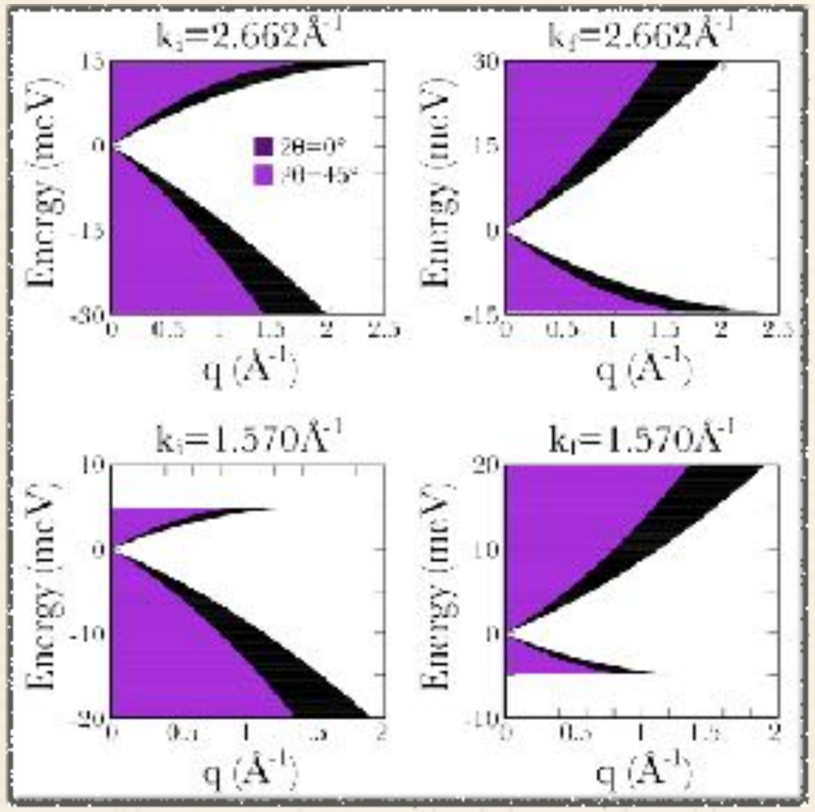
- Neutron kinematic limit (close the triangle)

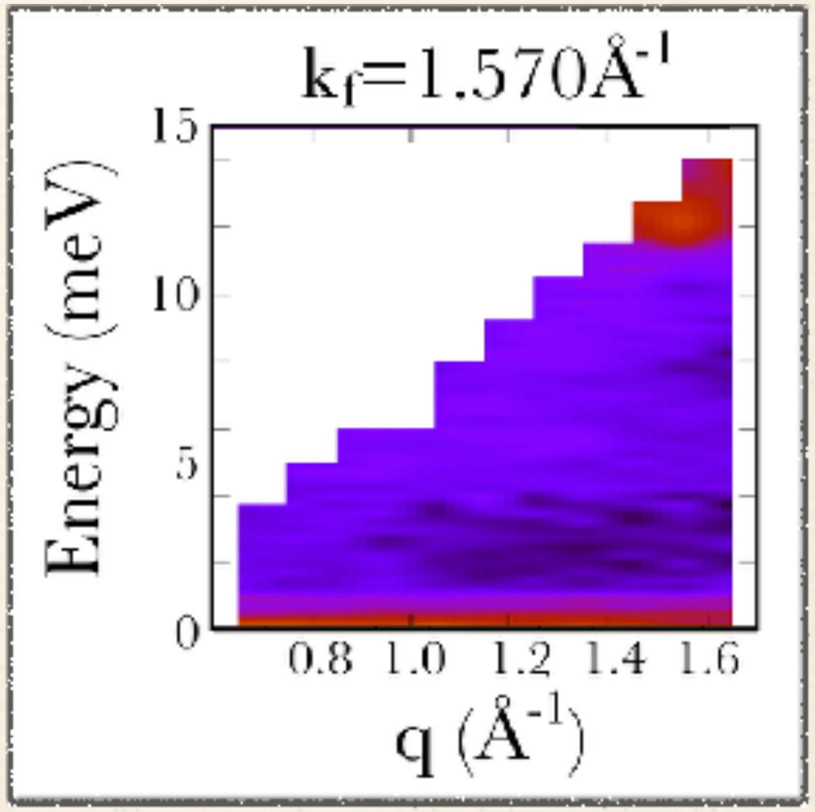


$$\vec{q} = \vec{k}_i - \vec{k}_f$$

$$\omega = \frac{\hbar^2}{2m}(k_i^2 - k_f^2)$$

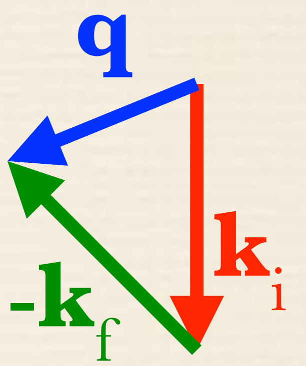
$$q = \sqrt{2k_i^2 - \frac{2m\omega}{\hbar} - 2k_i\sqrt{k_i^2 - \frac{2m\omega}{\hbar}}cos(2\theta)}$$





Energy and Momentum

- Photon kinematic limit (close the triangle)



$$\vec{q} = \vec{k}_i - \vec{k}_f$$

$$\omega = \hbar c(k_i - k_f)$$

$$q = \sqrt{\frac{\omega^2}{c^2} + 2k_i^2(1 - cos(2\theta)) - \frac{2k_i\omega}{c}(1 + cos(2\theta))}$$

- X-Ray : $\omega << ck_i \Rightarrow q \approx \sqrt{1 - cos(2\theta)}k_i$

Kinematic limit for X-Ray = Momentum Conservation

Spin Angular Momentum

- Neutron Spin Angular momentum $S_z = \pm\frac{\hbar}{2}$

  $\Delta S = 0$: Non Spin-Flip excitation
  $\Delta S = 1$: Spin-Flip excitation

- Photon Spin Angular Momentum $S_z = \pm\hbar$

  $\Delta M = 0$: Linear Polarization
  $\Delta M = -1$: Right Circular Polarization
  $\Delta M = +1$: Left Circular Polarization

1.2 Inelastic Scattering

Inelastic Neutron Scattering

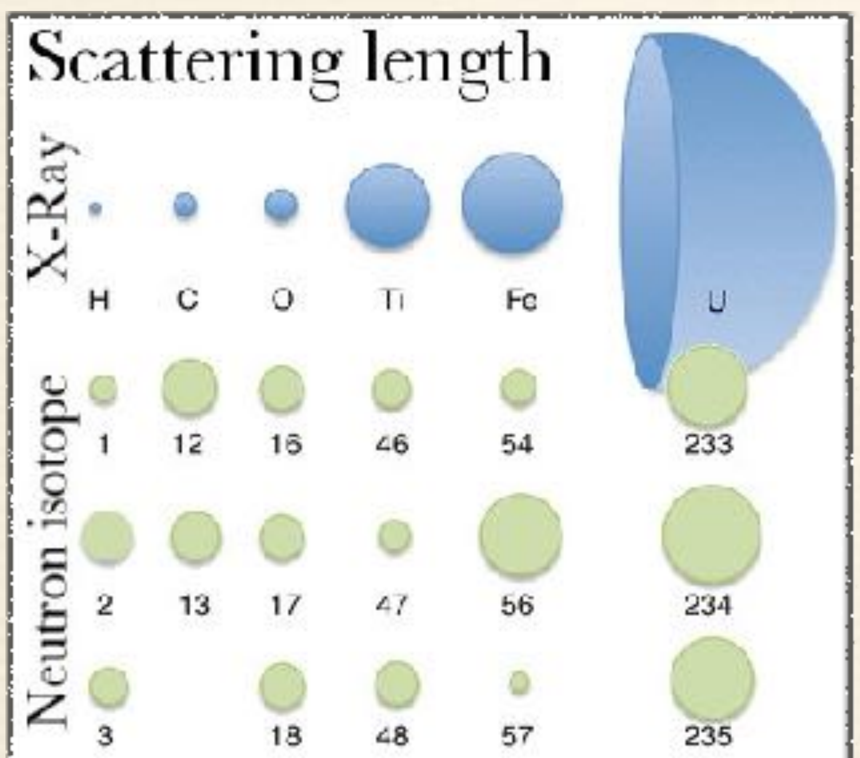
Interaction neutron-nucleus

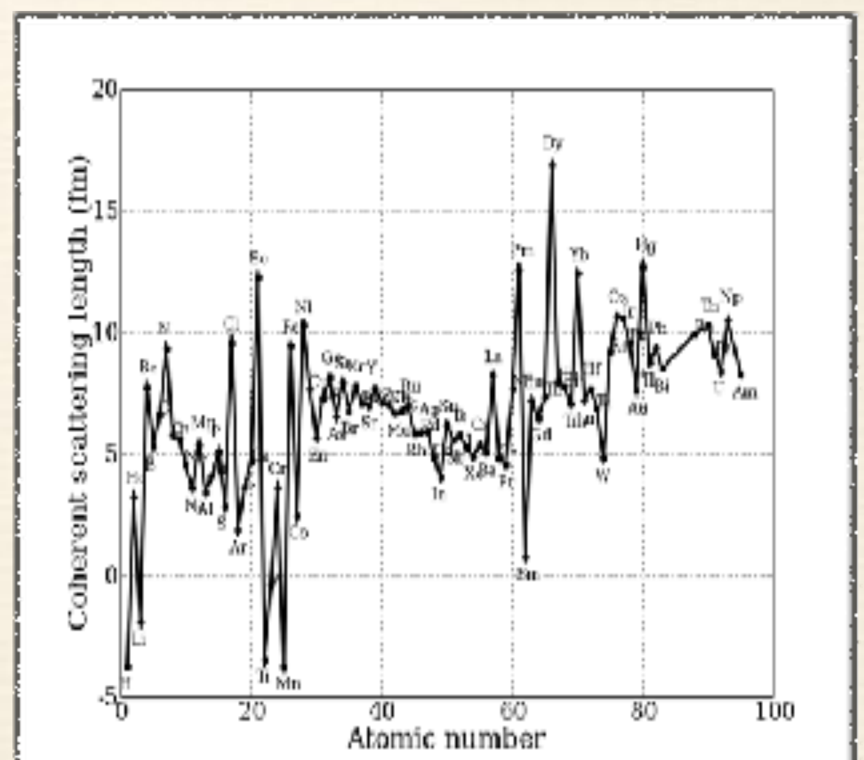
Fermi pseudo-potential for nuclear interaction

$$\mathcal{V}(\vec{r}) = \frac{2\pi\hbar^2}{m_n} b\delta(\vec{r} - \vec{R})$$

m_n : neutron mass

b : scattering length (complex and isotope-dependent)





Inelastic Neutron Scattering

Interaction neutron-nucleus

Fermi golden rule : $W_{i\to f} = \mathcal{P}_f \frac{2\pi}{\hbar} |\langle\psi_i|\mathcal{V}|\psi_f\rangle|^2$

$$|\psi_i\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}_i.\vec{r}} \qquad \int_V |\psi_i| d^3\vec{r} = \int_V |\psi_f| d^3\vec{r} = 1 \qquad \Phi_i = |\psi_i|^2 v = \frac{1}{V}\frac{\hbar k_i}{m_n}$$

$$|\psi_f\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}_f.\vec{r}}$$

$$\mathcal{P}_{f,d\Omega} = \frac{dn}{dE_f}\frac{d\Omega}{4\pi} = \frac{dn}{dV_k}\frac{dV_k}{dk_f}\frac{dk_f}{dE_f}\frac{d\Omega}{4\pi} = \frac{V}{(2\pi)^3} 4\pi k_f^2 \frac{m_n}{\hbar^2 k_f}\frac{d\Omega}{4\pi} = \frac{V k_f m_n}{(2\pi)^3\hbar^2} d\Omega$$

$$\frac{\partial\sigma}{\partial\Omega} = \frac{1}{\Phi_i}\frac{W_{i\to f,d\Omega}}{d\Omega} = \frac{k_f}{k_i} V^2 \left(\frac{m_n}{2\pi\hbar^2}\right)^2 |\langle\psi_i|\mathcal{V}|\psi_f\rangle|^2$$

$$= \frac{k_f}{k_i}\left|\sum_j b_j \int e^{i\vec{k}_i.\vec{r}}\delta(\vec{r}-\vec{r}_j)e^{-i\vec{k}_f.\vec{r}} d^3\vec{r}\right|^2$$

$$= \frac{k_f}{k_i}\left|\sum_j b_j e^{-i\vec{Q}.\vec{r}_j}\right|^2$$

Elastic Structure Factor F(Q)

X

Inelastic Neutron Scattering

Interaction neutron-nucleus

Fermi golden rule : $W_{i\to f} = \mathcal{P}_i\mathcal{P}_f\frac{2\pi}{\hbar}\left|\langle\psi_i|\mathcal{V}|\psi_f\rangle\right|^2\delta(\omega_i-\omega_f-\omega)$

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \frac{1}{\Phi_i}\frac{W_{i\to f,d\Omega,d\omega}}{d\Omega d\omega}$$

$$= \frac{k_f}{k_i}\sum_{a_1,a_2} b_{a_1}b_{a_2}\int_{-\infty}^{+\infty}\langle e^{i\vec{Q}.(\vec{R}_{a_1}(0)-\vec{R}_{a_2}(t))}\rangle e^{-i\omega t}dt$$

$$= \frac{k_f}{k_i}S(\vec{Q},\omega)$$

Dynamical Structure Factor

$$S(\vec{Q},\omega) = FT(G(\vec{r},t))$$

Pair correlation function

Time-dependent atomic position : $\vec{R}_a(t) = \vec{R}_c + \vec{r}_a + \vec{u}_a(t)$

$\mathbf{R}_c$: cell position, $\mathbf{r}_a$: atom position in the cell

Inelastic Neutron Scattering

Interaction neutron-cristal

Inelastic scattering cross-section :

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \frac{k_f}{k_i}\sum_{c_1,c_2} e^{i\vec{Q}.(\vec{R}_{c_1}-\vec{R}_{c_2})}\sum_{a_1,a_2} b_{a_1}b_{a_2}e^{i\vec{Q}.(\vec{r}_{a_1}-\vec{r}_{a_2})}\int_{-\infty}^{+\infty}\langle e^{i\vec{Q}.(\vec{u}_{a_1}(0)-\vec{u}_{a_2}(t))}\rangle e^{-i\omega t}dt$$

Thermodynamic average :

$$\langle e^{i\vec{Q}.(\vec{u}_{a_1}(0)-\vec{u}_{a_2}(t))}\rangle = e^{-W_{a_1}-W_{a_2}}e^{\langle\vec{Q}.(\vec{u}_{a_1}(0)-\vec{u}_{a_2}(t))\rangle}$$

$$= e^{-W_{a_1}-W_{a_2}}\left(\boxed{1}+\boxed{\langle\vec{Q}.(\vec{u}_{a_1}(0)-\vec{u}_{a_2}(t))\rangle + ...}\right)$$

Elastic Scattering **Inelastic Scattering**

$W_{a_1} = \frac{1}{2}\langle\left|\vec{Q}.\vec{u}_{a_1}(t)\right|^2\rangle$: Debye-Waller factor

$\vec{u}_{a,p}(t) = \sqrt{\frac{\hbar}{m_a\omega_p(\vec{q})}}e^{(i\vec{Q}.\vec{r}_a-\omega_p t)}\vec{\tilde{u}}_{a,p}$: harmonic phonon mode p

Inelastic Neutron Scattering

Phonons

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = N\frac{(2\pi)^3}{v_0}\sum_{\vec{G}\in RS}\delta(\vec{Q}-\vec{G})\left|\sum_a b_a e^{-W_a} e^{i\vec{Q}.\vec{r}_a}\right|^2$$

Elastic cross-section

$$+\frac{k_f}{k_i}\frac{(2\pi)^3}{v_0}\sum_{\vec{q}\in BZ}\delta(\vec{Q}-\vec{q}-\vec{G})\sum_p\left|\sum_a\sqrt{\frac{\hbar}{m_a\omega_p(\vec{q})}}b_a e^{-W_a} e^{i\vec{Q}.\vec{r}_a}(\vec{Q}.\vec{\tilde{u}}_{a,p})\right|^2$$
$$\times\left[(1+n_B(\omega_p(\vec{q}),T))\delta(\omega-\omega_p(\vec{q}))+n_B(\omega_p(\vec{q}),T)\delta(\omega+\omega_p(\vec{q}))\right]$$

Inelastic cross-section

Inelastic Neutron Scattering

Phonons

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = N\frac{(2\pi)^3}{v_0}\sum_{\vec{G}\in RS}\delta(\vec{Q}-\vec{G})\left|\sum_a b_a e^{-W_a}e^{i\vec{Q}.\vec{r}_a}\right|^2$$

$$+\frac{k_f}{k_i}\frac{(2\pi)^3}{v_0}\sum_{\vec{q}\in BZ}\delta(\vec{Q}-\vec{q}-\vec{G})\sum_p\left|\sum_a\sqrt{\frac{\hbar}{m_a\omega_p(\vec{q})}}b_a e^{-W_a}e^{i\vec{Q}.\vec{r}_a}(\vec{Q}.\vec{\tilde{u}}_{a,p})\right|^2$$

$$\times\left[(1+n_B(\omega_p(\vec{q}),T))\delta(\omega-\omega_p(\vec{q}))+n_B(\omega_p(\vec{q}),T)\delta(\omega+\omega_p(\vec{q}))\right]$$

Inelastic Structure Factor

Inelastic Neutron Scattering

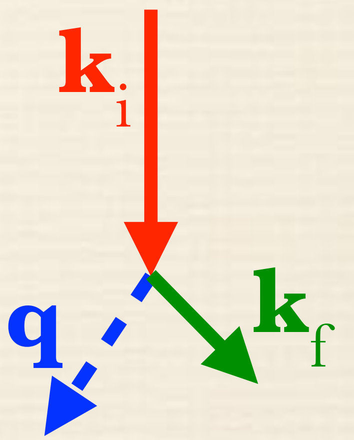
Phonons : creation and annihilation

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = N\frac{(2\pi)^3}{v_0}\sum_{\vec{G}\in RS}\delta(\vec{Q}-\vec{G})\left|\sum_a b_a e^{-W_a}e^{i\vec{Q}.\vec{r}_a}\right|^2$$

$$+\frac{k_f}{k_i}\frac{(2\pi)^3}{v_0}\sum_{\vec{q}\in BZ}\delta(\vec{Q}-\vec{q}-\vec{G})\sum_p\left|\sum_a\sqrt{\frac{\hbar}{m_a\omega_p(\vec{q})}}b_a e^{-W_a}e^{i\vec{Q}.\vec{r}_a}(\vec{Q}.\vec{\tilde{u}}_{a,p})\right|^2$$

$$\times\left[(1+n_B(\omega_p(\vec{q}),T))\delta(\omega-\omega_p(\vec{q}))+n_B(\omega_p(\vec{q}),T)\delta(\omega+\omega_p(\vec{q}))\right]$$

Energy conservation : creation process



Inelastic Neutron Scattering

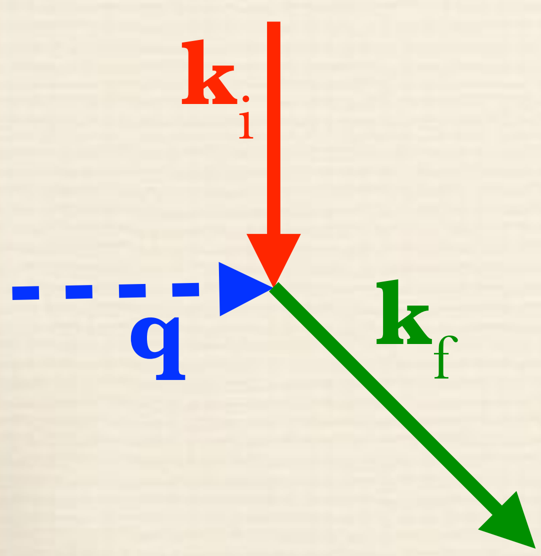
Phonons : creation and annihilation

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = N\frac{(2\pi)^3}{v_0}\sum_{\vec{G}\in RS}\delta(\vec{Q}-\vec{G})\left|\sum_a b_a e^{-W_a} e^{i\vec{Q}.\vec{r}_a}\right|^2$$

$$+\frac{k_f}{k_i}\frac{(2\pi)^3}{v_0}\sum_{\vec{q}\in BZ}\delta(\vec{Q}-\vec{q}-\vec{G})\sum_p\left|\sum_a\sqrt{\frac{\hbar}{m_a\omega_p(\vec{q})}}b_a e^{-W_a}e^{i\vec{Q}.\vec{r}_a}(\vec{Q}.\vec{\tilde{u}}_{a,p})\right|^2$$

$$\times\left[(1+n_B(\omega_p(\vec{q}),T))\delta(\omega-\omega_p(\vec{q}))+\boxed{n_B(\omega_p(\vec{q}),T)\delta(\omega+\omega_p(\vec{q}))}\right]$$

Energy conservation : annihilation process



Inelastic Neutron Scattering

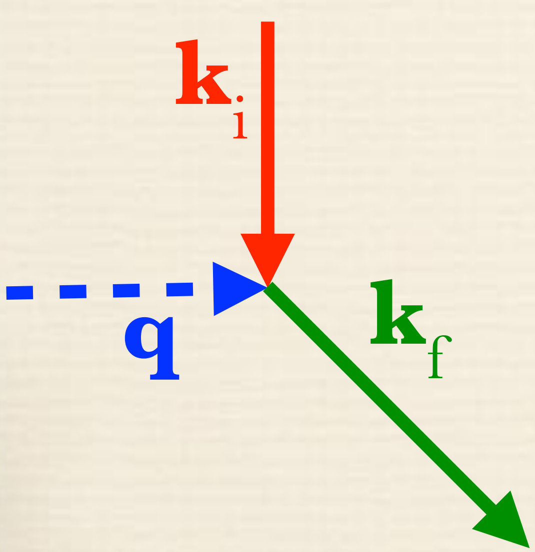
Phonons : creation and annihilation

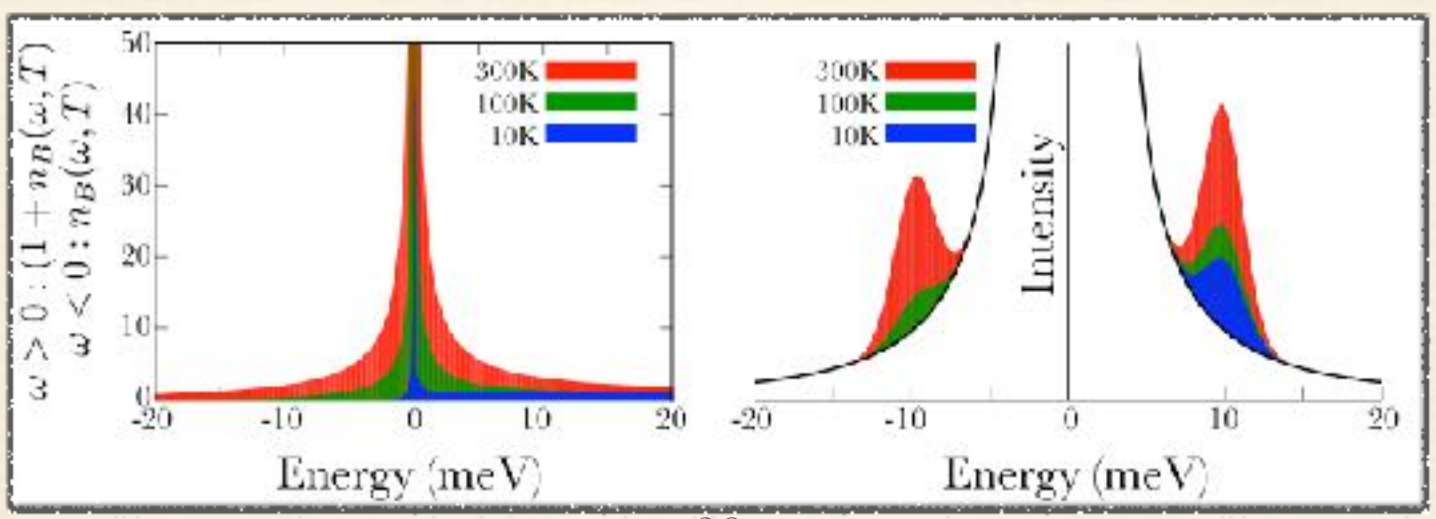
$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = N\frac{(2\pi)^3}{v_0}\sum_{\vec{G}\in RS}\delta(\vec{Q}-\vec{G})\left|\sum_a b_a e^{-W_a} e^{i\vec{Q}.\vec{r}_a}\right|^2$$

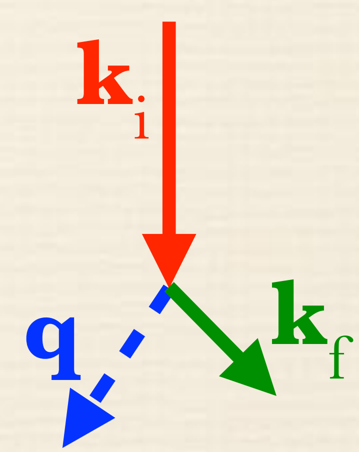
$$+\frac{k_f}{k_i}\frac{(2\pi)^3}{v_0}\sum_{\vec{q}\in BZ}\delta(\vec{Q}-\vec{q}-\vec{G})\sum_p\left|\sum_a\sqrt{\frac{\hbar}{m_a\omega_p(\vec{q})}}b_a e^{-W_a}e^{i\vec{Q}.\vec{r}_a}(\vec{Q}.\vec{\tilde{u}}_{a,p})\right|^2$$

$$\times\left[(1+n_B(\omega_p(\vec{q}),T))\delta(\omega-\omega_p(\vec{q}))+n_B(\omega_p(\vec{q}),T)\delta(\omega+\omega_p(\vec{q}))\right]$$

$n_B(\omega,T) = \dfrac{1}{e^{\frac{\hbar\omega}{k_B T}}-1}$: detailed balance factor







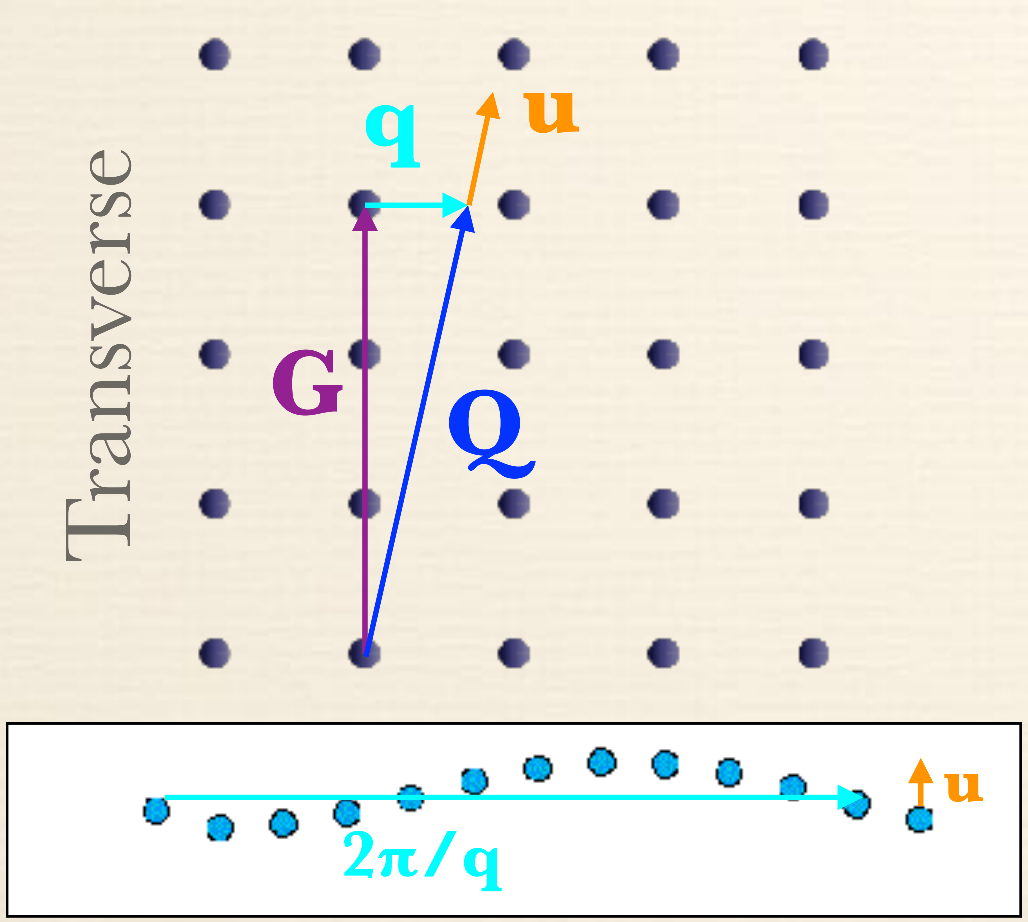
Inelastic Neutron Scattering

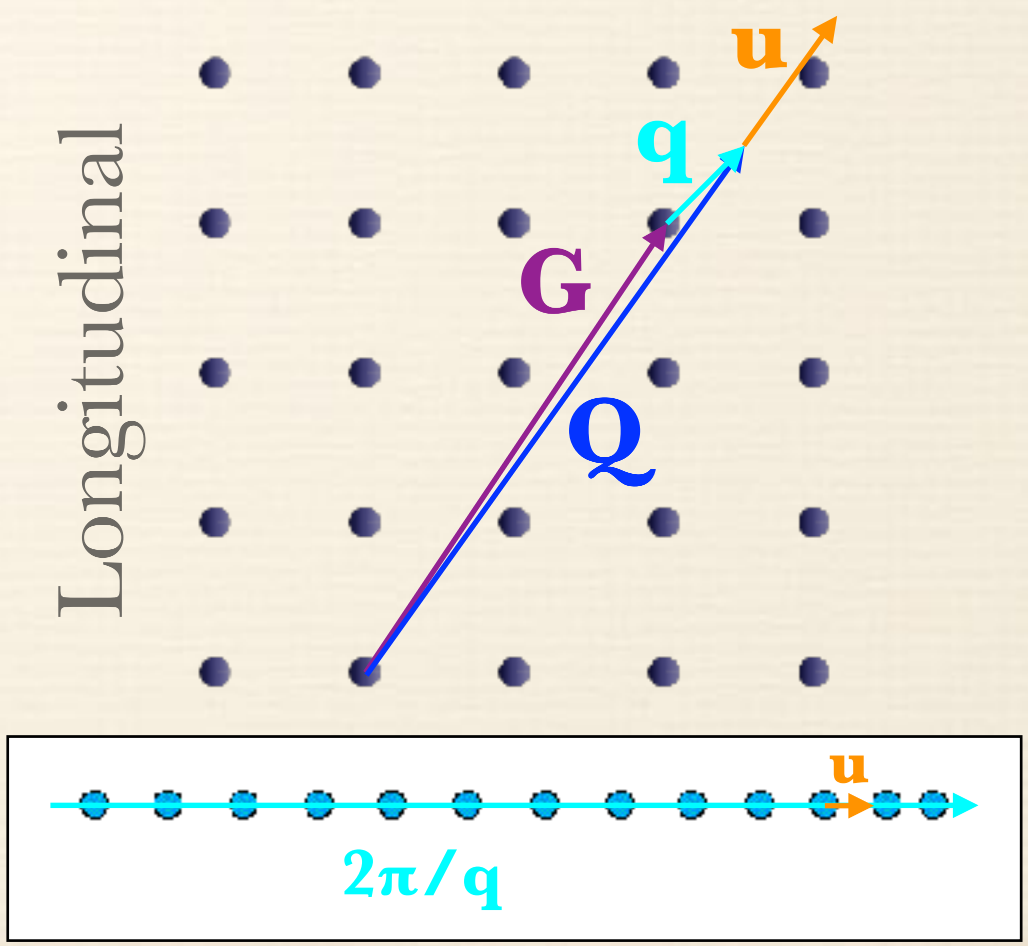
Phonons and polarization factor

$$\left.\frac{\partial^2\sigma}{\partial\Omega\partial\omega}\right|_{inel} = \frac{k_f}{k_i}\frac{(2\pi)^3}{v_0}\sum_{\vec{q}\in BZ}\delta(\vec{Q}-\vec{q}-\vec{G})\sum_p\left|\sum_a\sqrt{\frac{\hbar}{m_a\omega_p(\vec{q})}}b_a e^{-W_a}e^{i\vec{Q}.\vec{r}_a}(\vec{Q}.\vec{\tilde{u}}_{a,p})\right|^2$$

$$\times\left[(1+n_B(\omega_p(\vec{q}),T))\delta(\omega-\omega_p(\vec{q}))+n_B(\omega_p(\vec{q}),T)\delta(\omega+\omega_p(\vec{q}))\right]$$

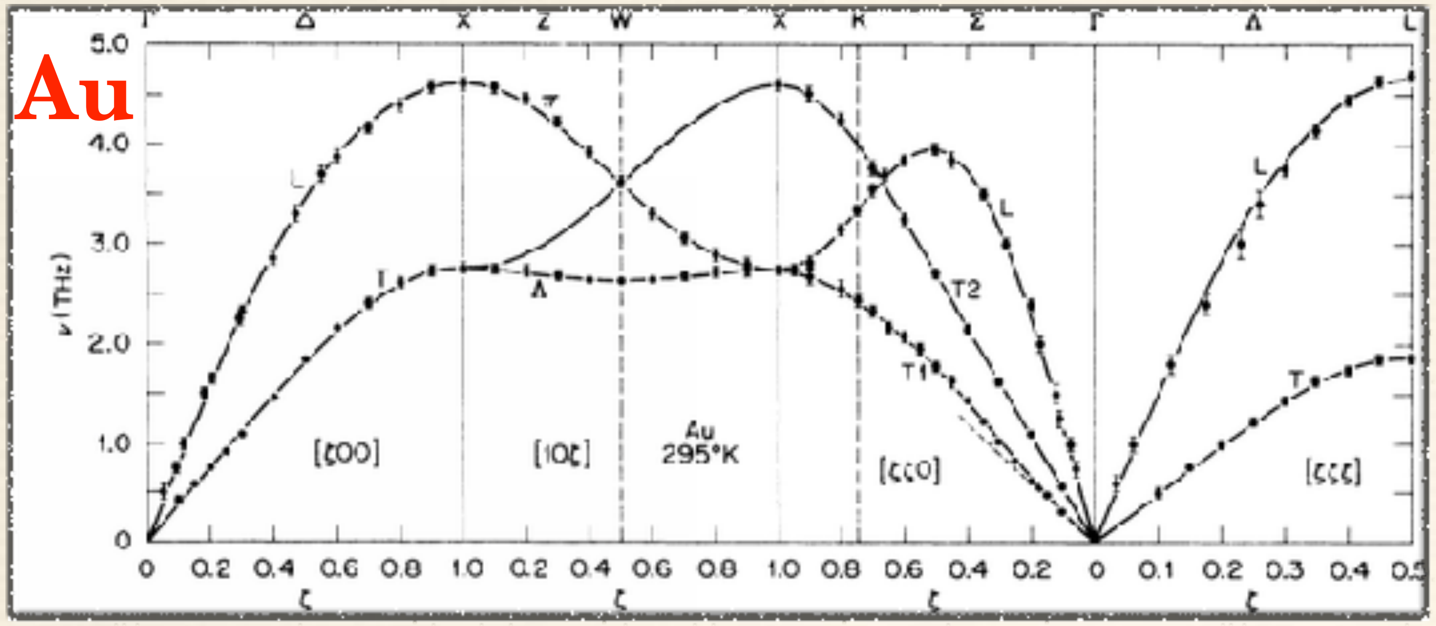
Sensitive to displacement parallel to $\vec{Q}=\vec{G}+\vec{q}$



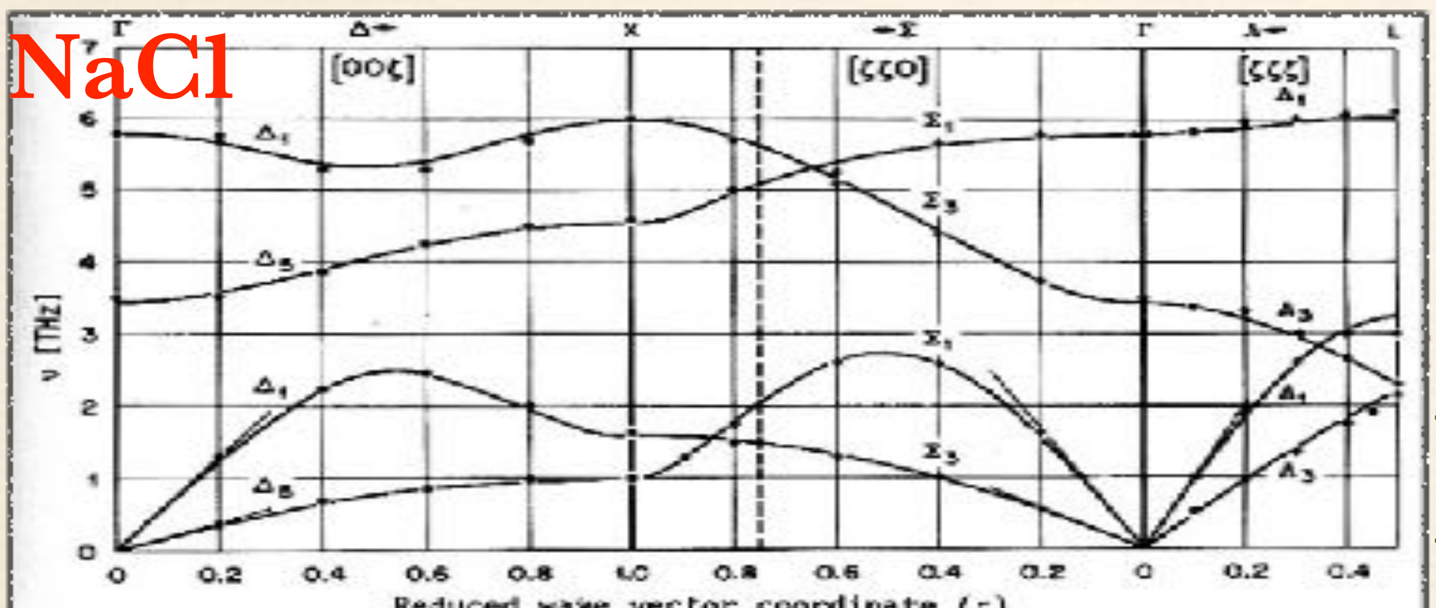


Inelastic Neutron Scattering

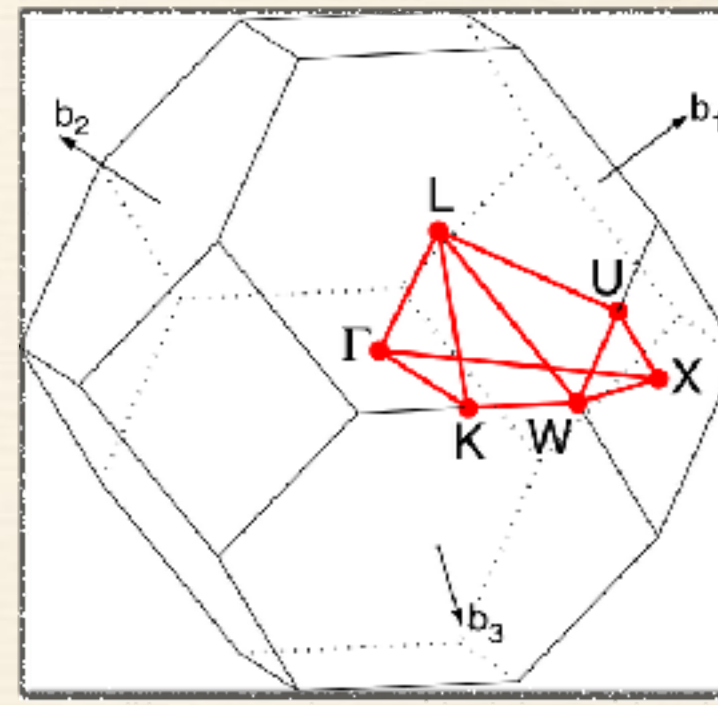
Phonons and polarization factor



PRB 8, 3496 (1973)



PRB 2, 2098 (1970)

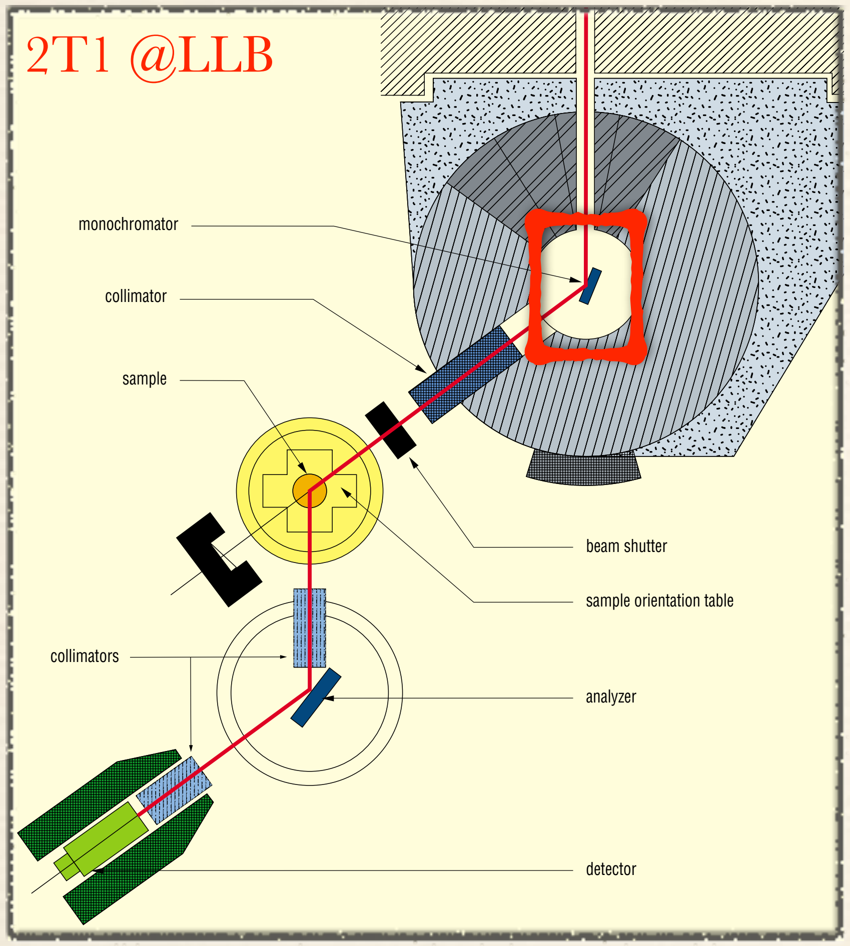


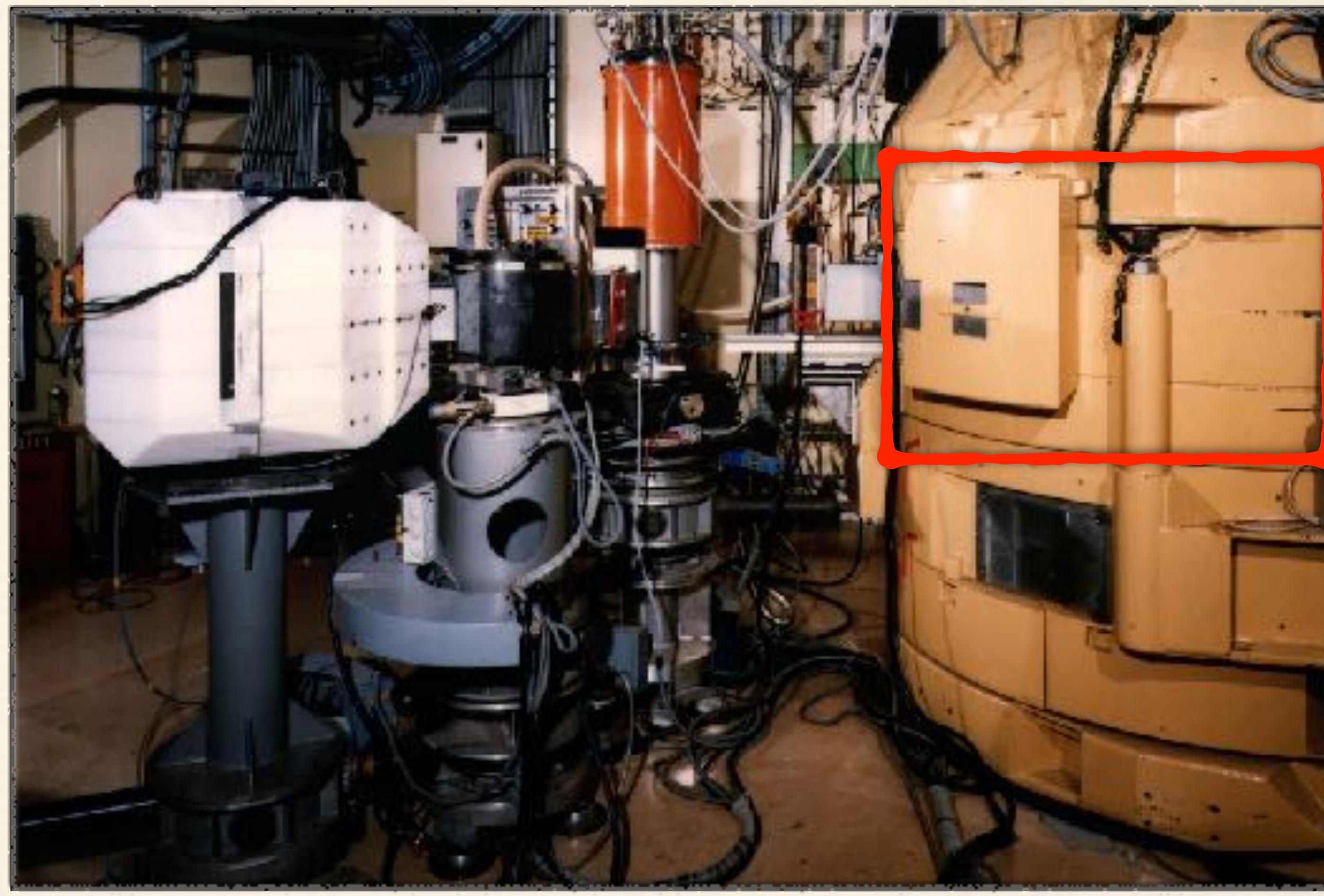
Inelastic Neutron Scattering

Neutron Facilities Worldwide

Inelastic Neutron Scattering

Experimental setup : Triple Axis Spectrometer (TAS)

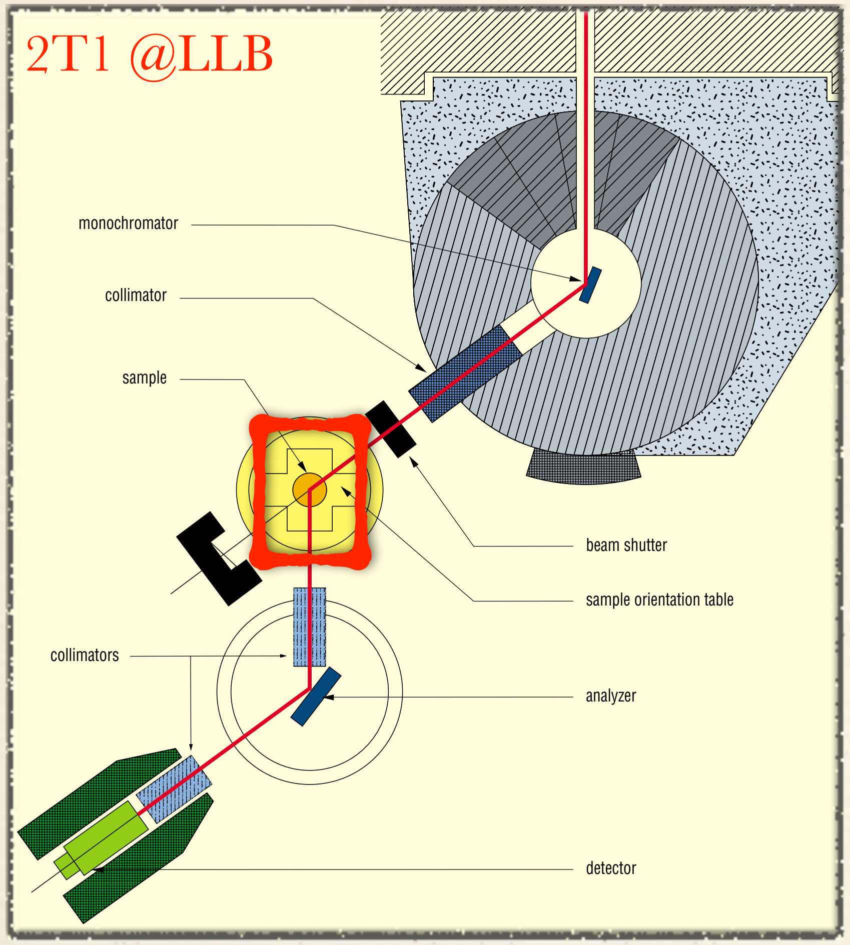


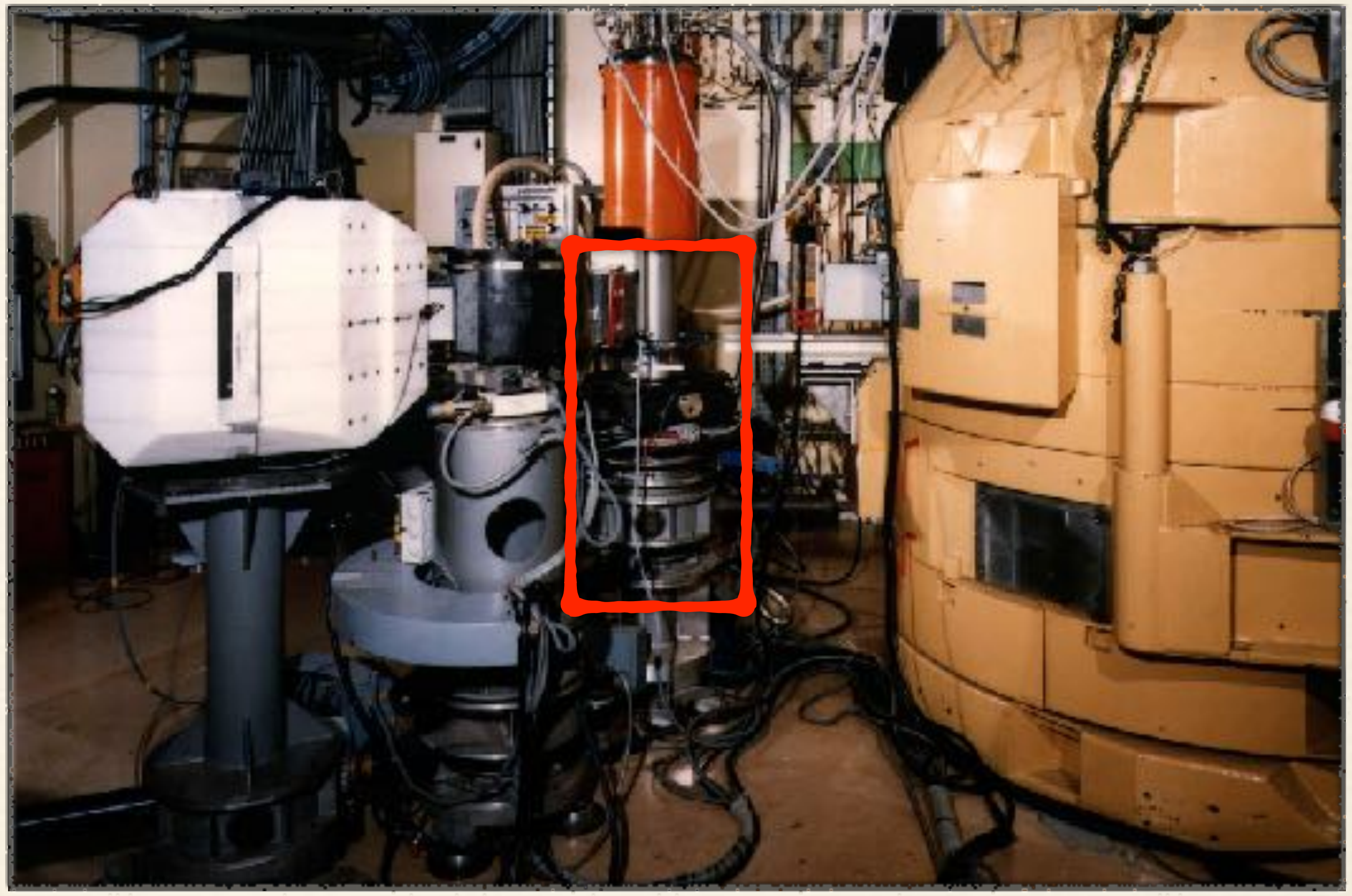


Monochromator (first axis) : Incident energy selection

Inelastic Neutron Scattering

Experimental setup : Triple Axis Spectrometer (TAS)

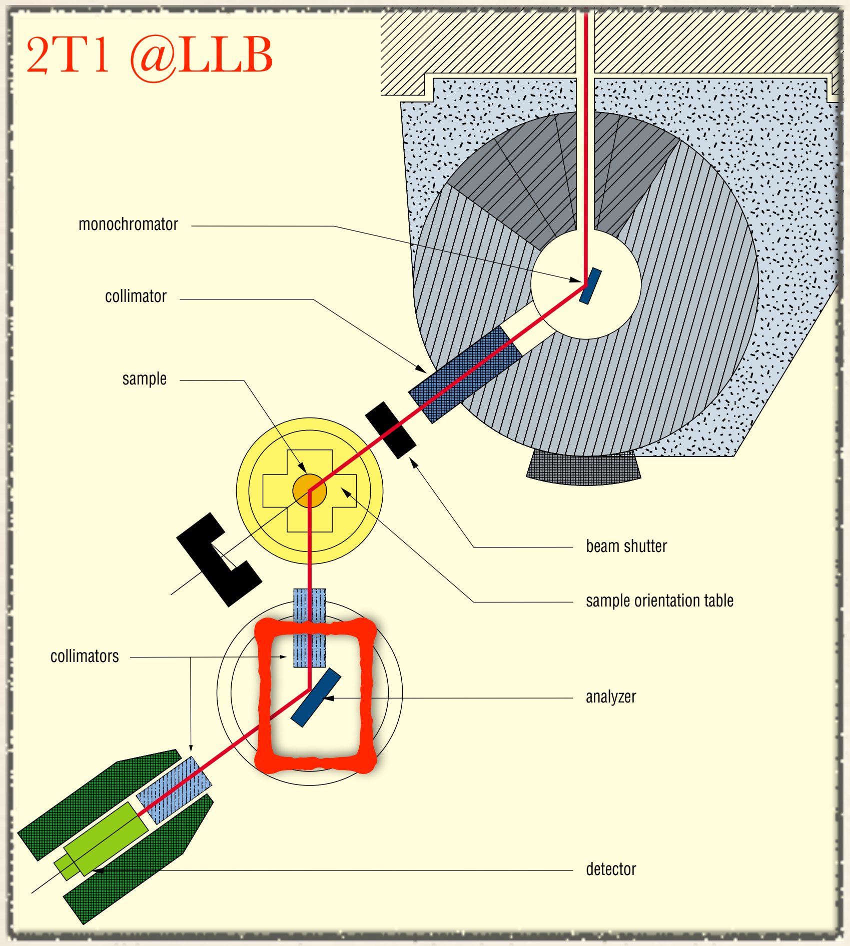


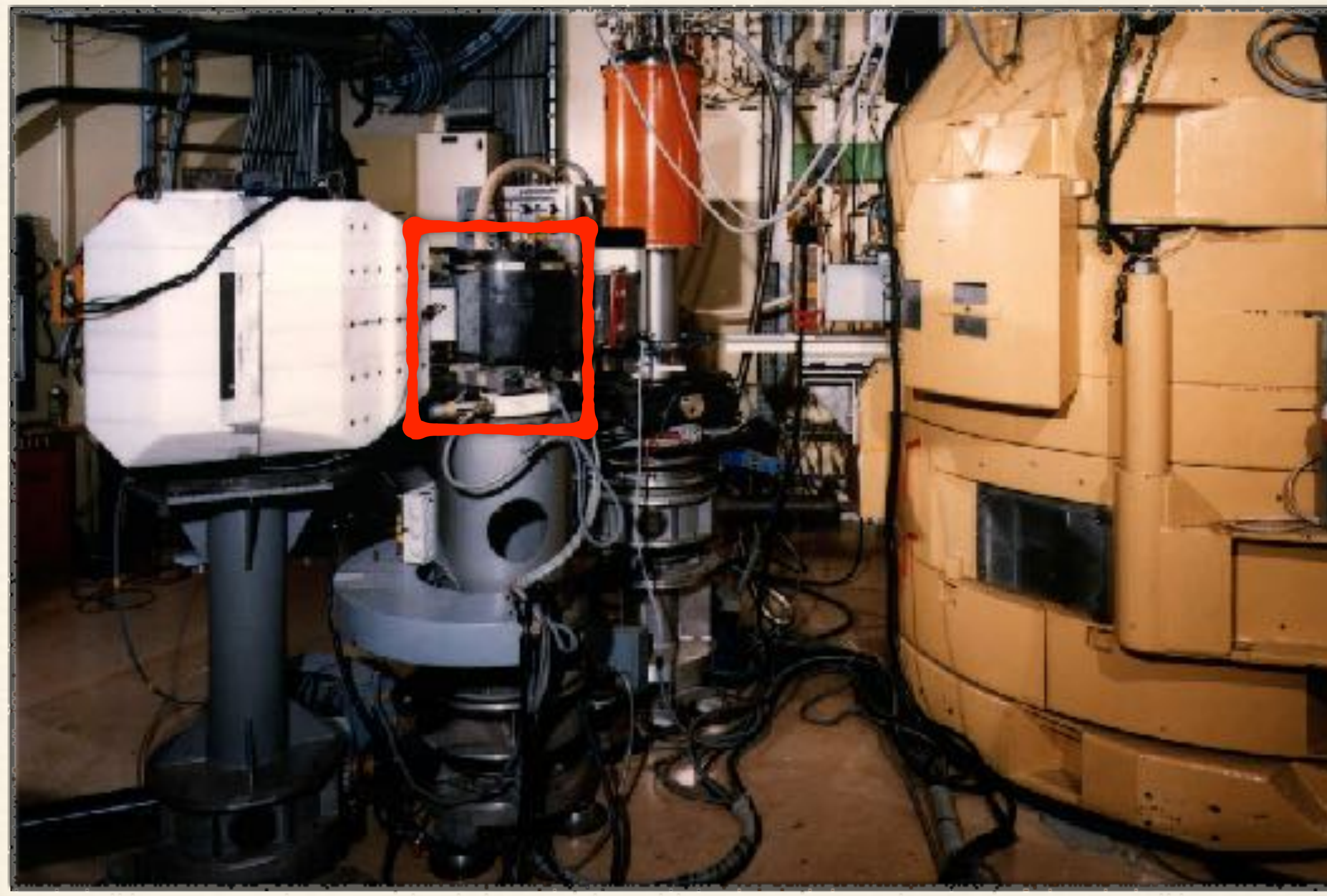


Sample (second axis) : Q selection

Inelastic Neutron Scattering

Experimental setup : Triple Axis Spectrometer (TAS)

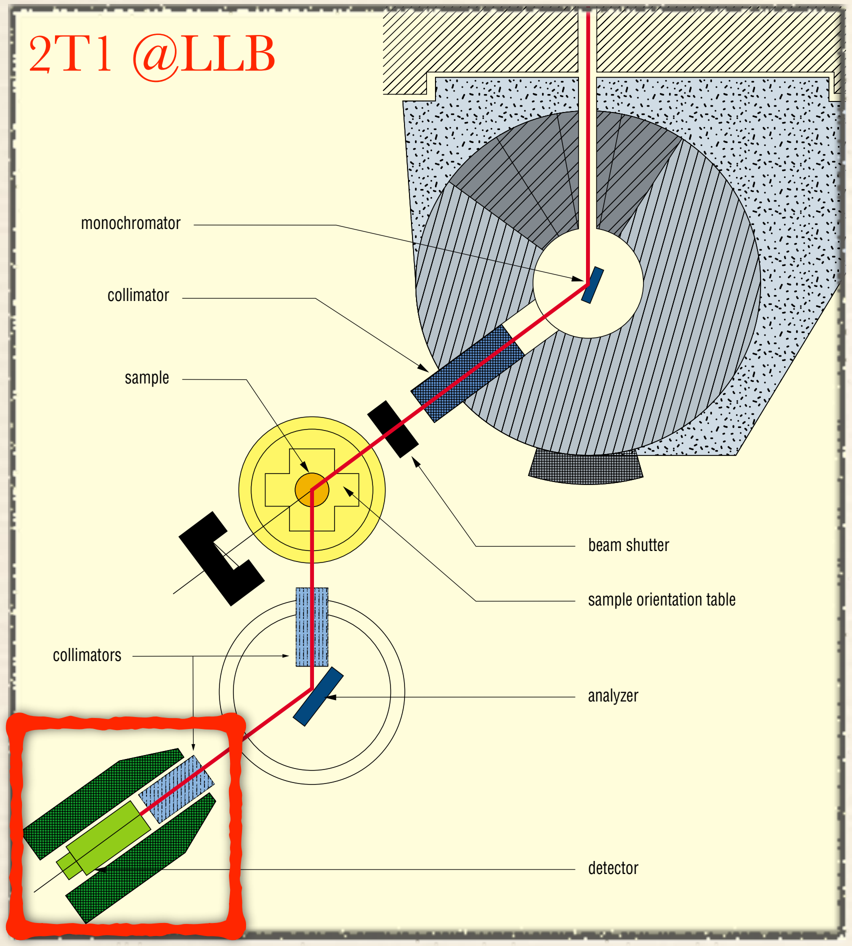


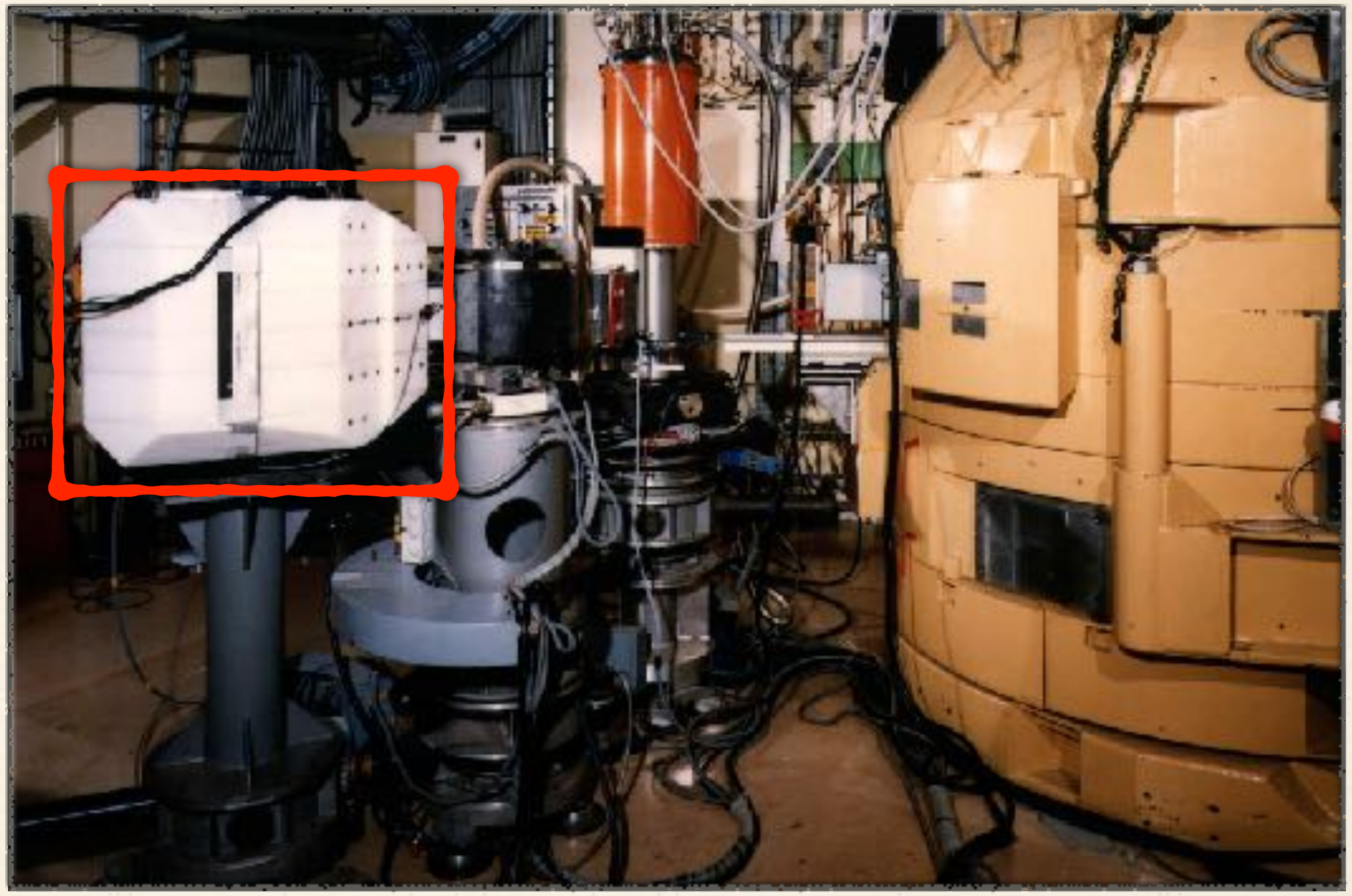


Analyzer (third axis) : Final energy selection

Inelastic Neutron Scattering

Experimental setup : Triple Axis Spectrometer (TAS)

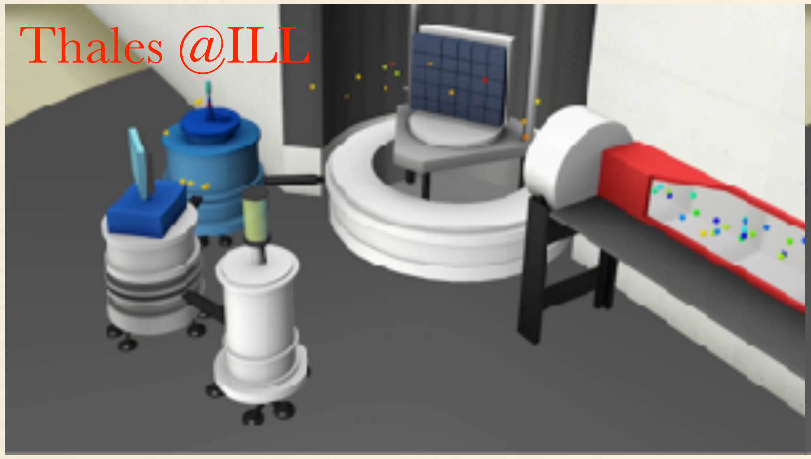




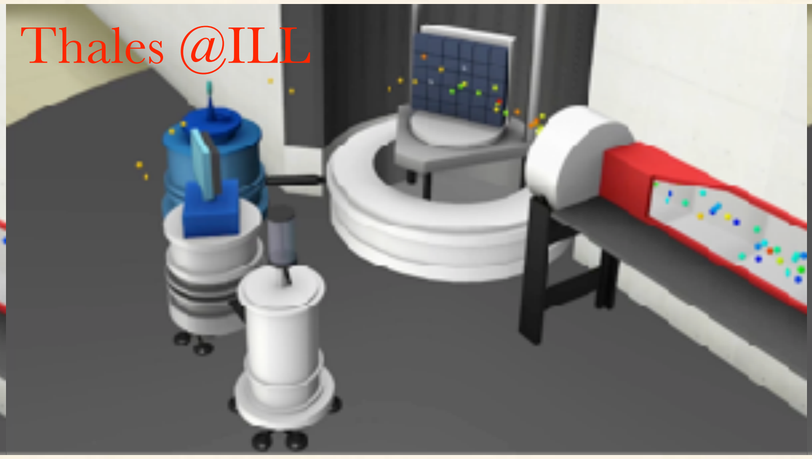
Detector

Inelastic Neutron Scattering

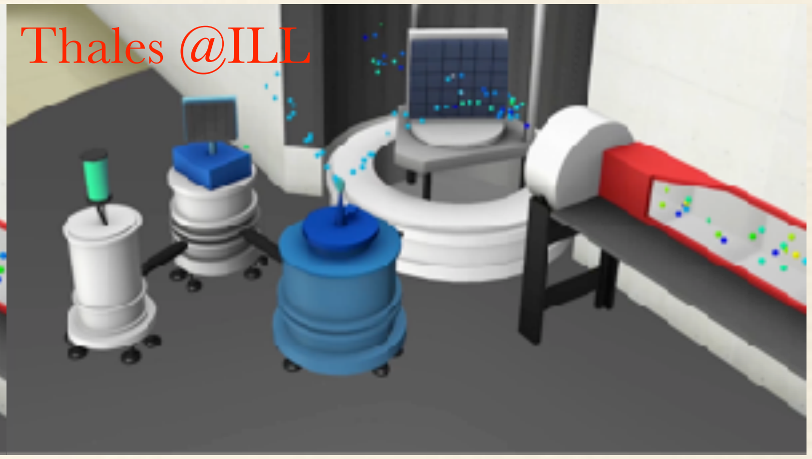
Experimental setup : Triple Axis Spectrometer (TAS)



Elastic



Inelastic

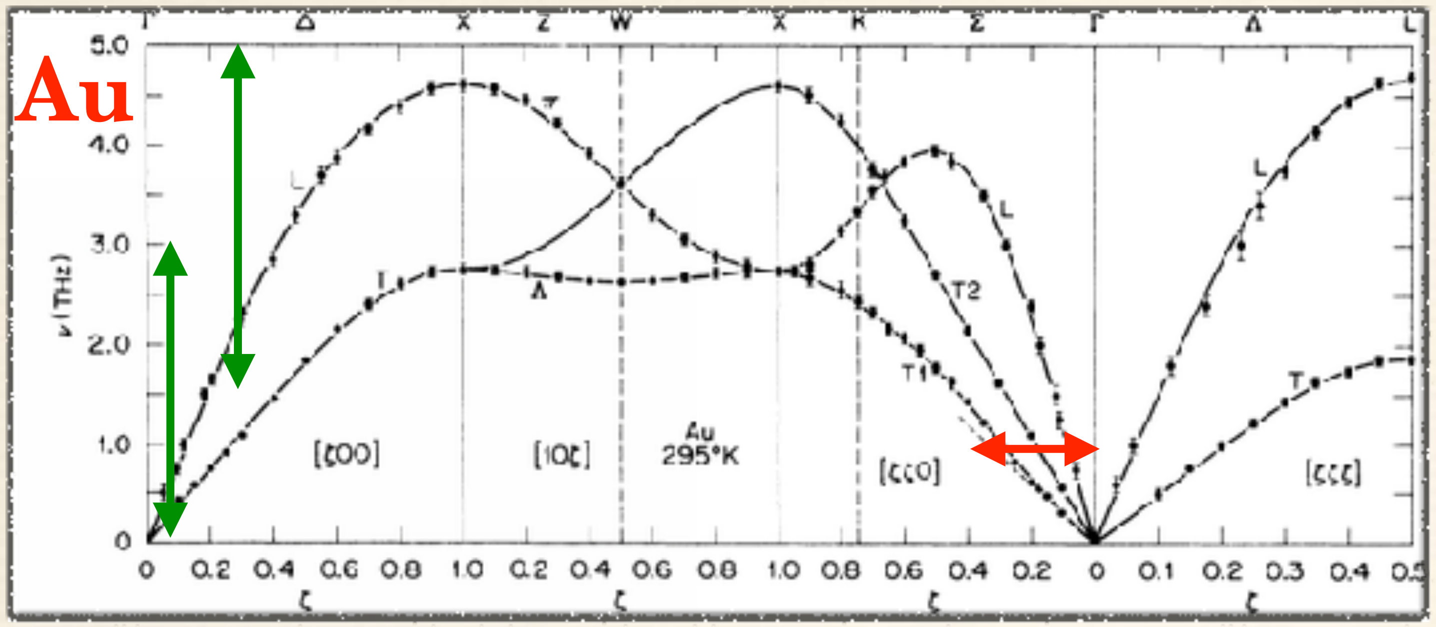


Inelastic

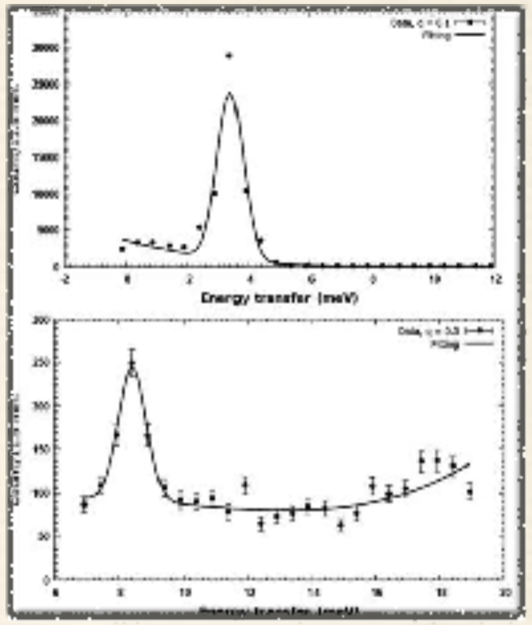
Spectrometer	Incident energy (meV)	Transfered energy (meV)	Resolution (meV)	Q_{max} - Q_{max} (A^{-1})	Resolution (A^{-1})
Cold	2-25	0 - 12	0.05 @1.05A^{-1} 0.2 @1.57A^{-1} 1.2 @2.662A^{-1}	0.01 - 3	0.01
Thermal	10 - 140	0 - 100	0.8 @2.662A^{-1} 3.5 @4.1A^{-1}	0.3 - 10	0.01

Inelastic Neutron Scattering

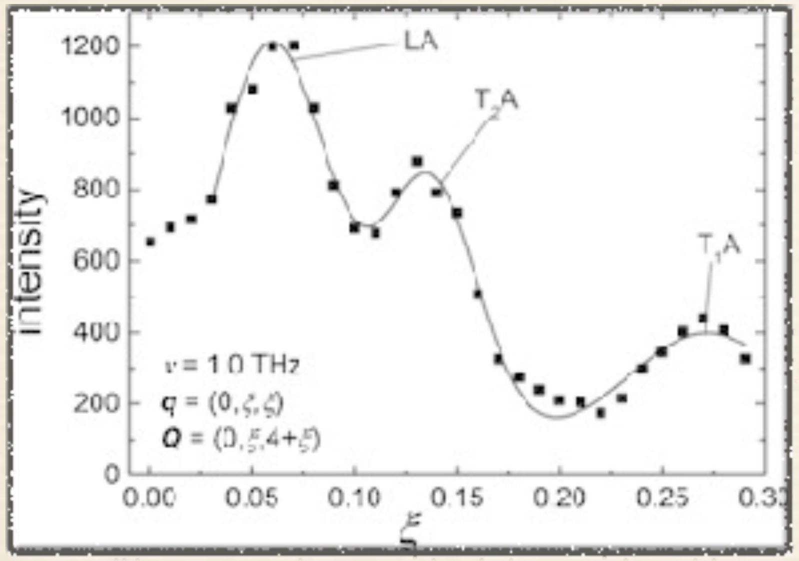
Experimental setup : Triple Axis Spectrometer (TAS)



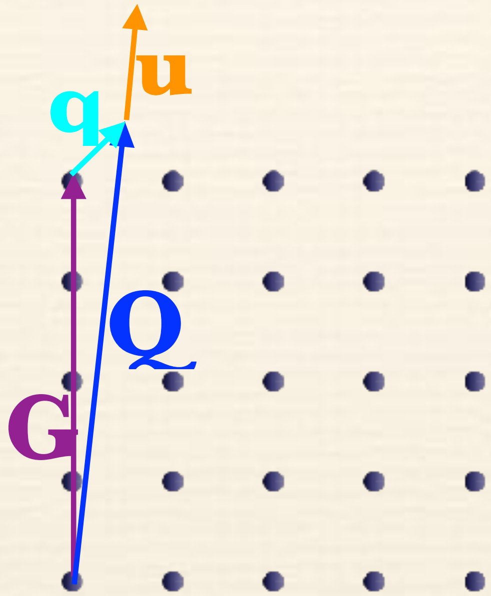
PRB 8, 3496 (1973)

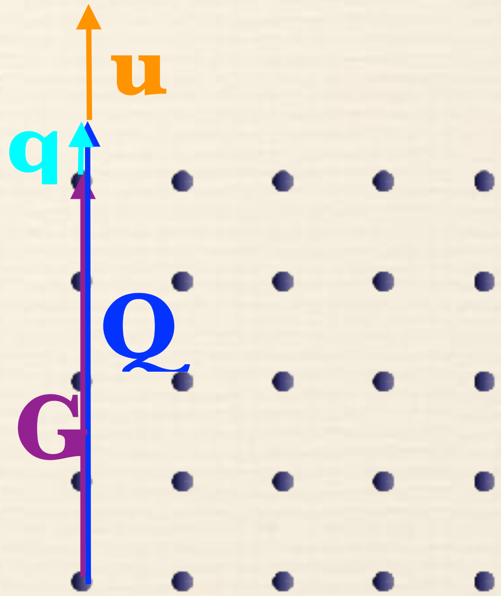


Constant **Q** scan



Constant ω scan

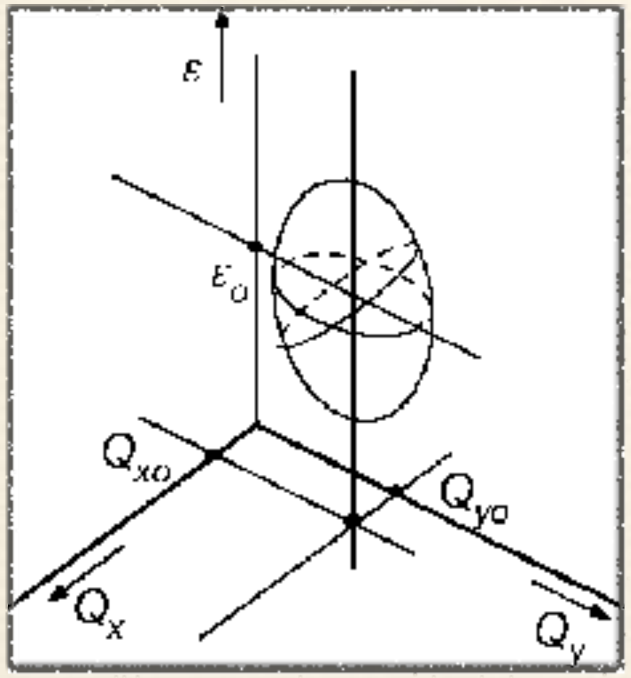


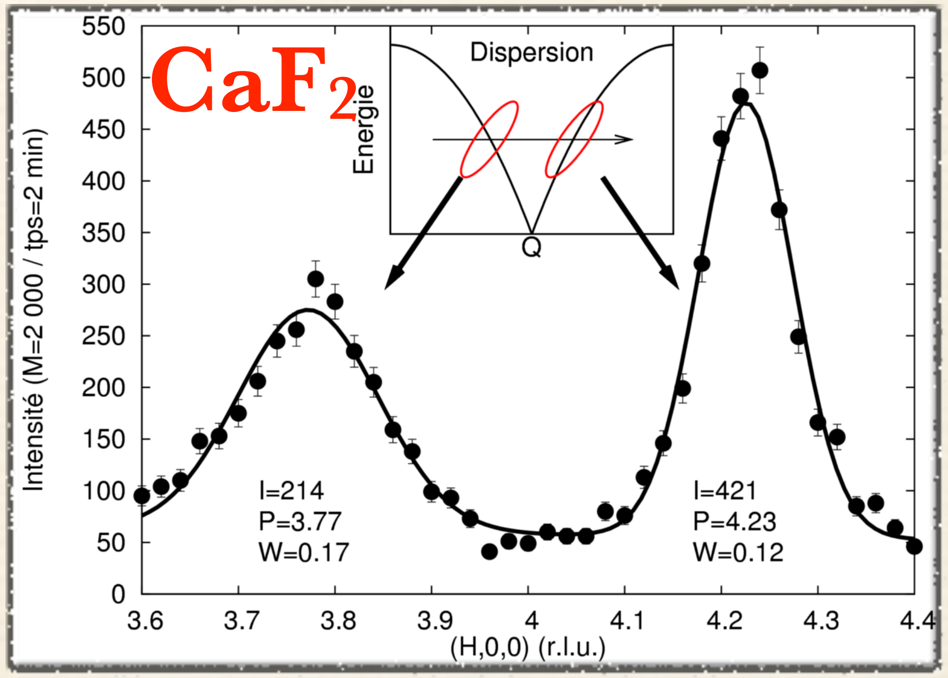


Inelastic Neutron Scattering

Experimental setup : Triple Axis Spectrometer (TAS)

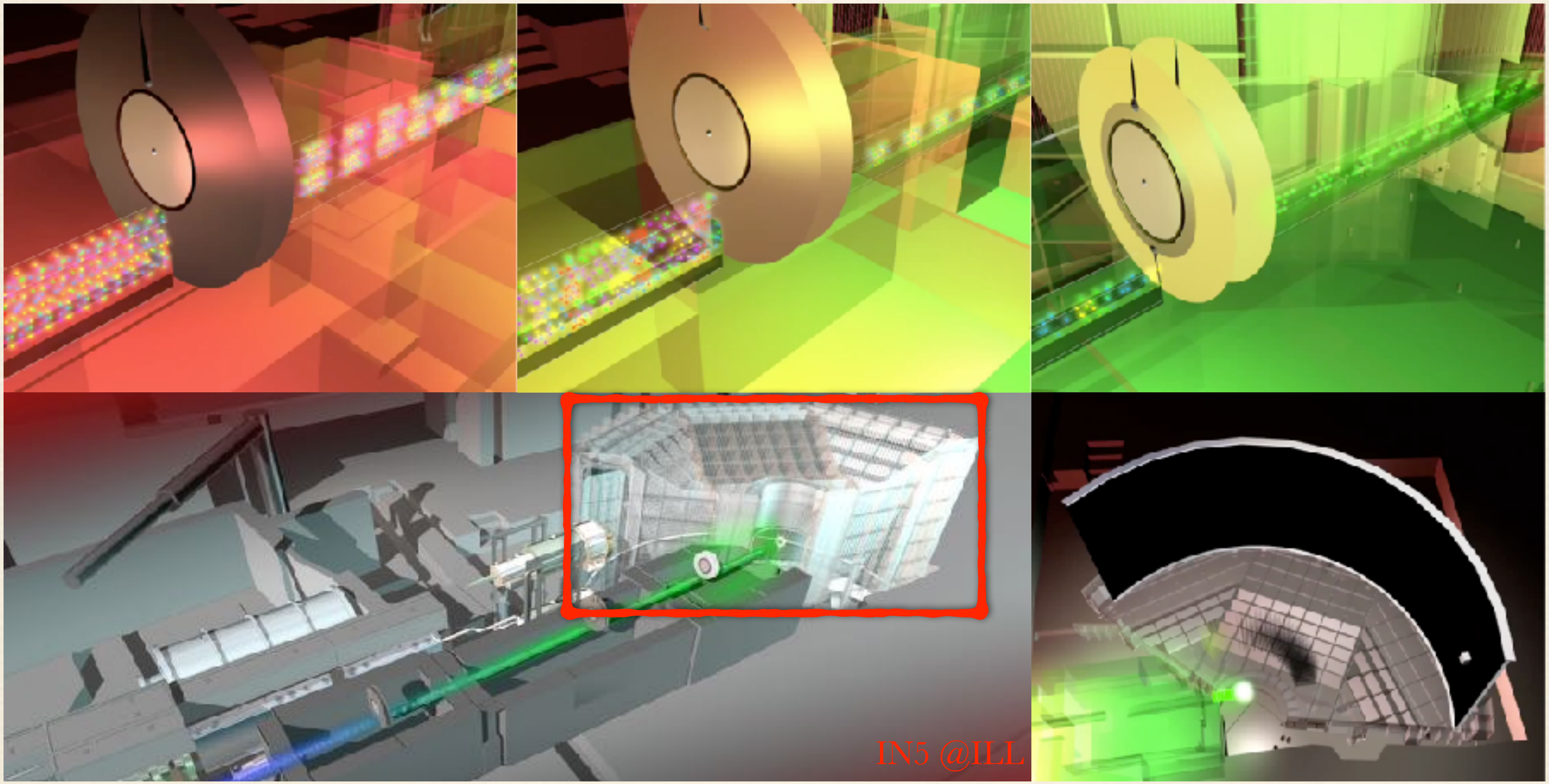
Point-to-point acquisition
Sample orientation, incident and final energy can be selected
Constant **Q** and ω scans
Resolution : 4-dimension ellipsoid, $\delta\omega \propto k_f^3$





Inelastic Neutron Scattering

Experimental setup : Time Of Flight (TOF)



Inelastic Neutron Scattering

Experimental setup : Time Of Flight (TOF)

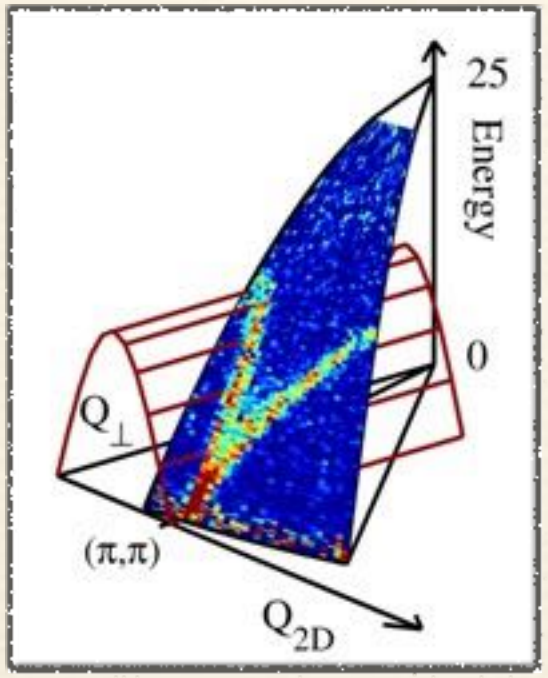
Map acquisition : parabola in (**Q**,ω) space :

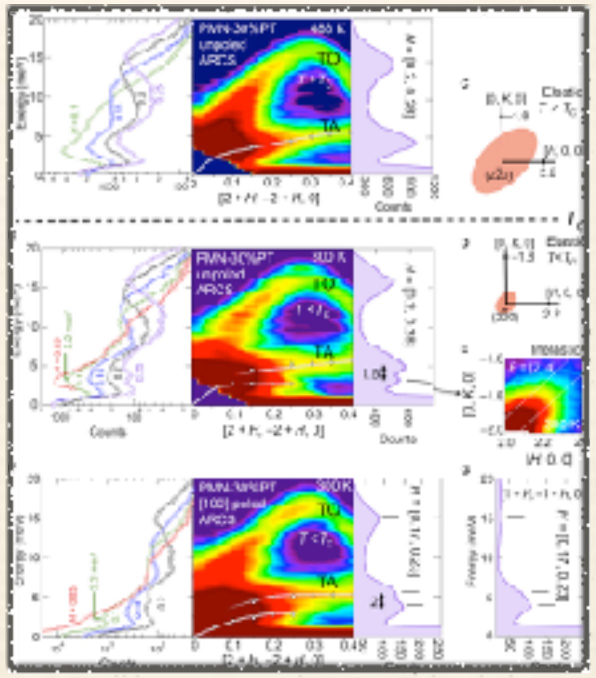
$$\left(\frac{\hbar^2 k_i^2}{2m} - \hbar\omega\right) = \frac{\hbar^2}{2m}\left(Q_\perp^2 + \left(k_I - Q_{//}\right)^2\right)$$

Sample orientation and incident energy can be changed

No constant **Q** and ω scans

Constant **Q** and ω scans : cuts & integration

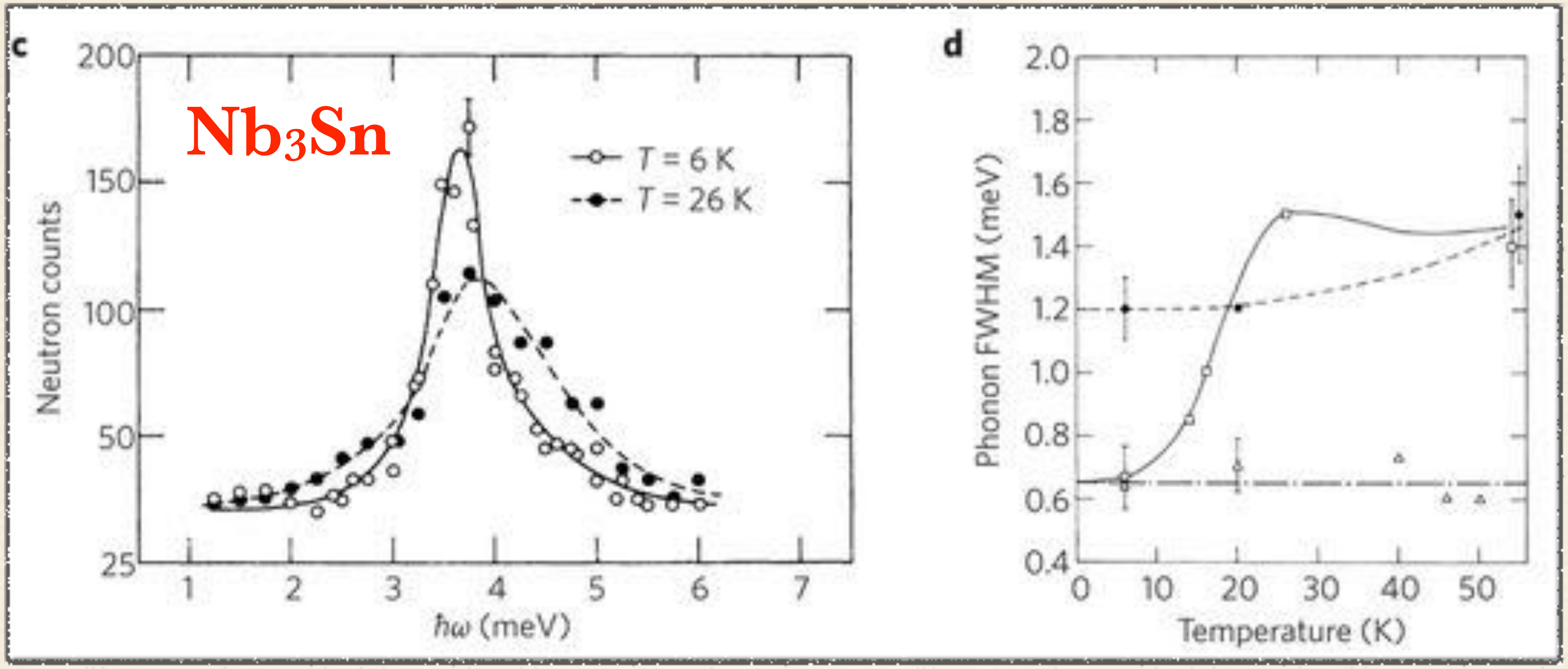




Sci. Adv. 2, 1501814 (2016)

Inelastic Neutron Scattering

Superconductivity



PRB 8,1965 (1973)

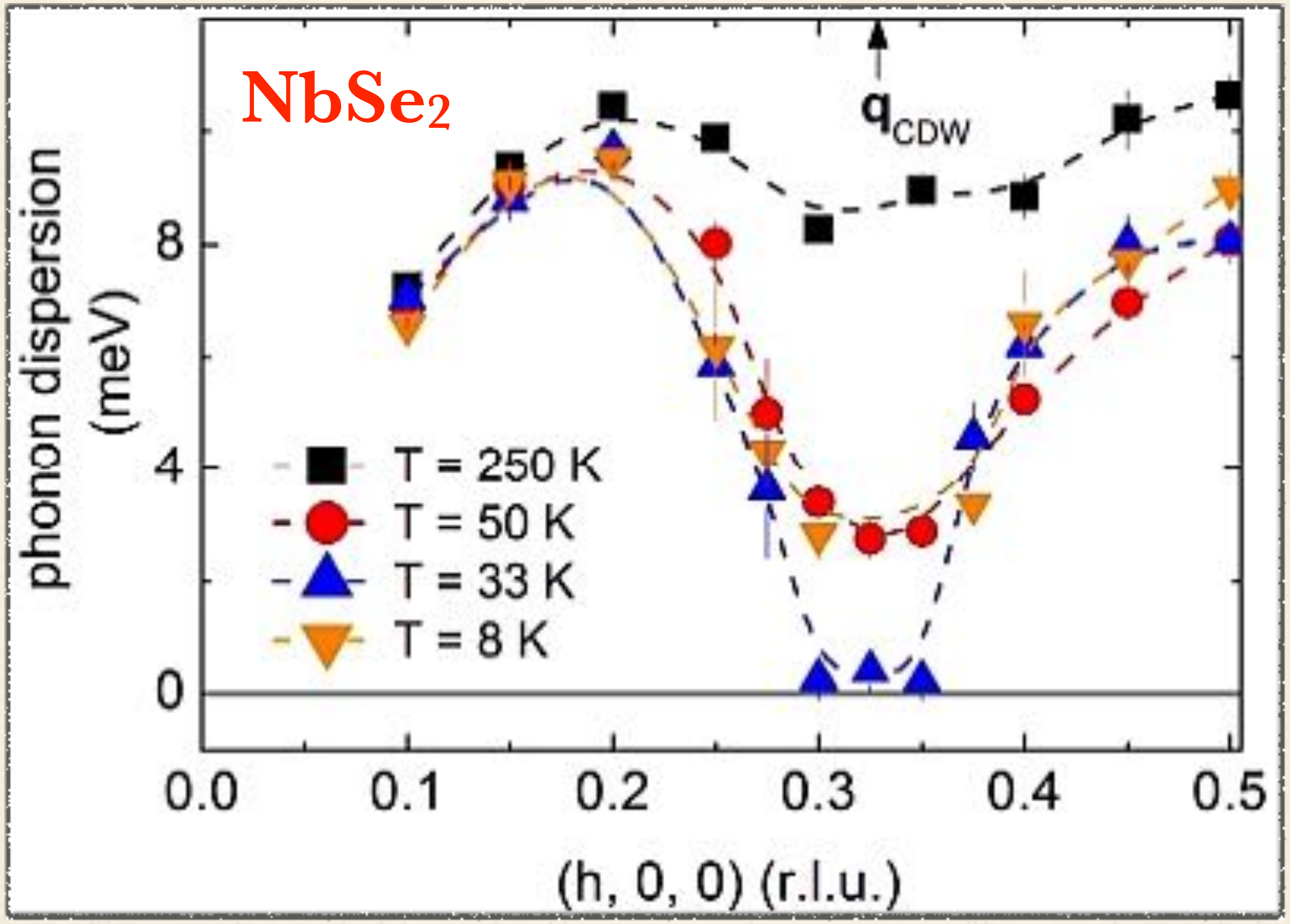
Phonon lifetime increase below T_C

Estimation of the gap (BCS)

$$2\Delta = 4.4 \pm 0.6\ k_B T_C$$

Inelastic Neutron Scattering

Charge Density Wave

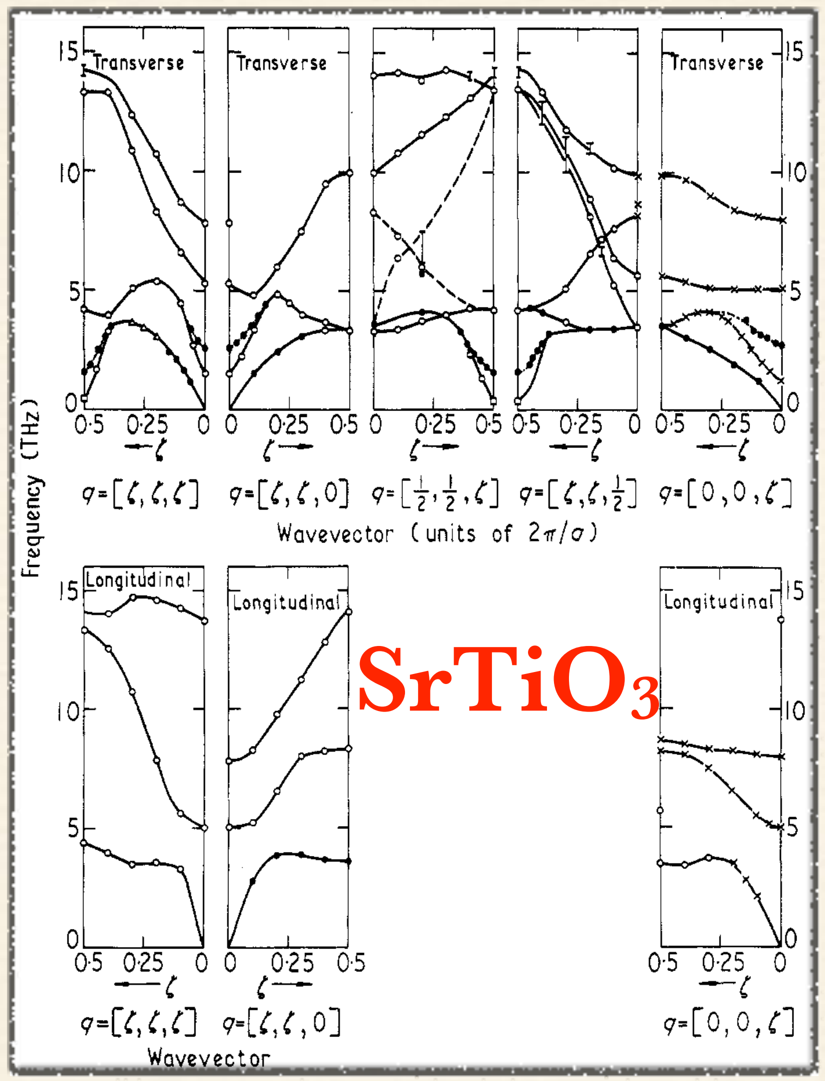


PRL 107, 107403 (2011)

Softening of the phonon at the CDW wavevector

Inelastic Neutron Scattering

Ferroelectricity



J. Phys. C 5, 2711 (1972)

Phonon energy decreases at low temperature
Fingerprint of ferroelectric transition

Inelastic Neutron Scattering

Summary

- Inelastic neutron scattering allows a direct measure of the dispersion relation of acoustic and optical phonons $\omega(\vec{q})$
- Geometrical selection of transverse or longitudinal modes
- Phonon intensity $\sim Q^2$
- This dispersion give access to :
  - Interatomic potential and bonding
  - Phase transition and critical phenomena (soft mode …)
  - Interactions (electron-phonon …)

Inelastic X-ray Scattering

" The photons which constitute a ray of light behave like intelligent human beings: out of all possible curves they always select the one which will take them most quickly to their goal. "

Max Planck
1918 Nobel laureate in Physics

Inelastic X-ray Scattering

Interaction X-ray-electron

Interaction light-electron :

$$\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r}) + \frac{q^2}{m_e c^2}\vec{A}^2$$

m_e : electron mass

Neglecting the second order term :

$$\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r}) = \frac{q}{c}\vec{r}.Ee^{-i\vec{k}.\vec{r}}\vec{\epsilon} = \frac{qE}{c}\vec{r}.\vec{\epsilon}$$

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \frac{k_f}{k_i}\sum_{e_1,e_2} r_e^2\,|\vec{\epsilon}_i.\vec{\epsilon}_f|^2\int_{-\infty}^{+\infty}\langle e^{i\vec{Q}.\vec{r}_{e_1}(0)}e^{-i\vec{Q}.\vec{r}_{e_2}(t)}\rangle e^{-i\omega t}dt$$

$$= \frac{k_f}{k_i}r_e^2\,|\vec{\epsilon}_i.\vec{\epsilon}_f|^2\sum_{a_1,a_2} f_{a_1}(\vec{Q})f_{a_2}(\vec{Q})\int_{-\infty}^{+\infty}\langle e^{i\vec{Q}.\vec{R}_{a_1}(0)}e^{-i\vec{Q}.\vec{R}_{a_2}(t)}\rangle e^{-i\omega t}dt$$

$$= \frac{k_f}{k_i}r_e^2\,|\vec{\epsilon}_i.\vec{\epsilon}_f|^2\,S(\vec{Q},\omega)$$

Inelastic X-ray Scattering

Interaction X-ray-electron

Interaction light-electron :

$$\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r}) + \frac{q^2}{m_e c^2}\vec{A}^2$$

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$$= \frac{k_f}{k_i}r_e^2\,|\vec{\epsilon}_i.\vec{\epsilon}_f|^2\sum_{a_1,a_2} \boxed{f_{a_1}(\vec{Q})} f_{a_2}(\vec{Q})\int_{-\infty}^{+\infty}\langle e^{i\vec{Q}.\vec{R}_{a_1}(0)}e^{-i\vec{Q}.\vec{R}_{a_2}(t)}\rangle e^{-i\omega t}dt$$

$$= \frac{k_f}{k_i}r_e^2\,|\vec{\epsilon}_i.\vec{\epsilon}_f|^2\, S(\vec{Q},\omega)$$

Scattering form factor

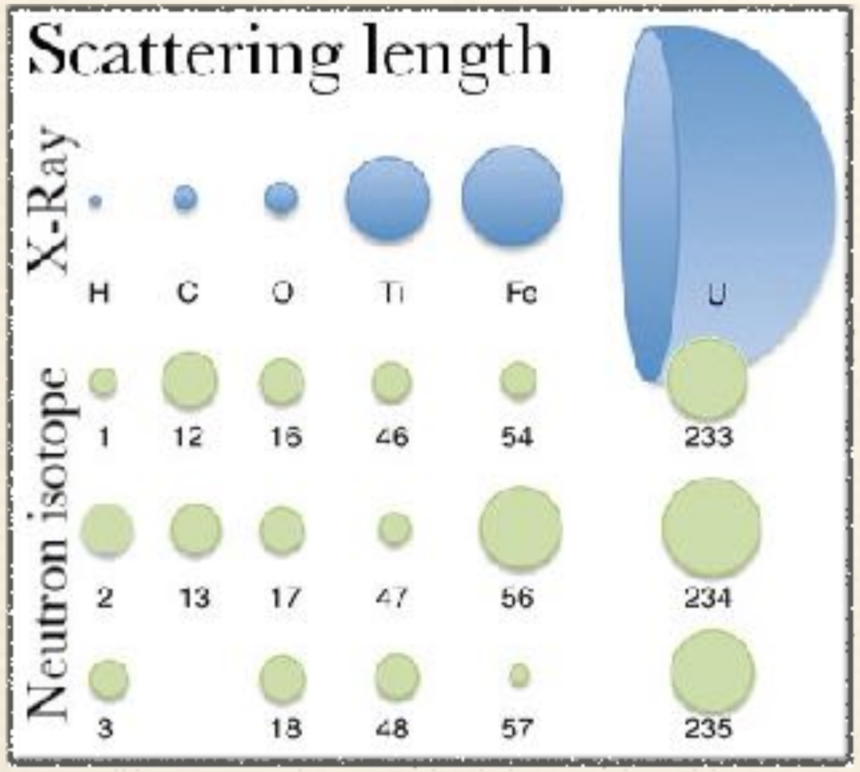
Inelastic X-ray Scattering

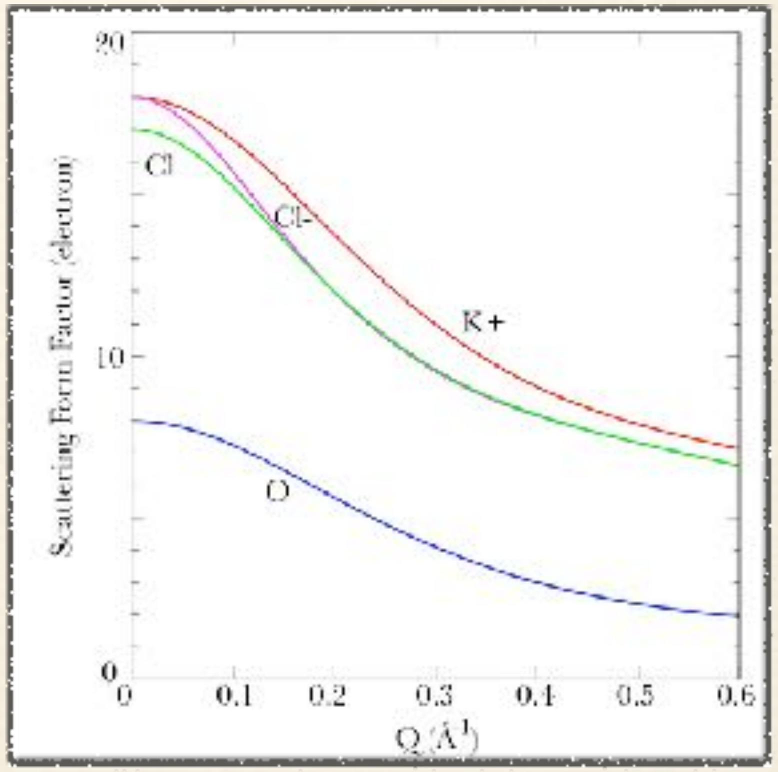
Form factor of an atom

Depends of the electronic density :

$$f(\vec{Q}) = \int \rho(\vec{r}) e^{i\vec{Q}.\vec{r}} d^3\vec{r}$$

$$f(\vec{Q} = \vec{0}) = \mathcal{Z}$$





Inelastic X-ray Scattering

Interaction X-ray-electron

Interaction light-electron :

$$\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r}) + \frac{q^2}{m_e c^2}\vec{A}^2$$

m_e : electron mass

Neglecting the second order term :

$$\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r}) = \frac{q}{c}\vec{r}.Ee^{-i\vec{k}.\vec{r}}\vec{\epsilon} = \frac{qE}{c}\vec{r}.\vec{\epsilon}$$

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \frac{k_f}{k_i}\sum_{e_1,e_2} r_e^2\,|\vec{\epsilon}_i.\vec{\epsilon}_f|^2 \int_{-\infty}^{+\infty}\langle e^{i\vec{Q}.\vec{r}_{e_1}(0)}e^{-i\vec{Q}.\vec{r}_{e_2}(t)}\rangle e^{-i\omega t}dt$$

$$= \frac{k_f}{k_i} r_e^2\,|\vec{\epsilon}_i.\vec{\epsilon}_f|^2 \sum_{a_1,a_2} f_{a_1}(\vec{Q})f_{a_2}(\vec{Q}) \int_{-\infty}^{+\infty}\langle e^{i\vec{Q}.\vec{R}_{a_1}(0)}e^{-i\vec{Q}.\vec{R}_{a_2}(t)}\rangle e^{-i\omega t}dt$$

$$= \frac{k_f}{k_i} r_e^2\,|\vec{\epsilon}_i.\vec{\epsilon}_f|^2\, S(\vec{Q},\omega)$$

Polarization factor

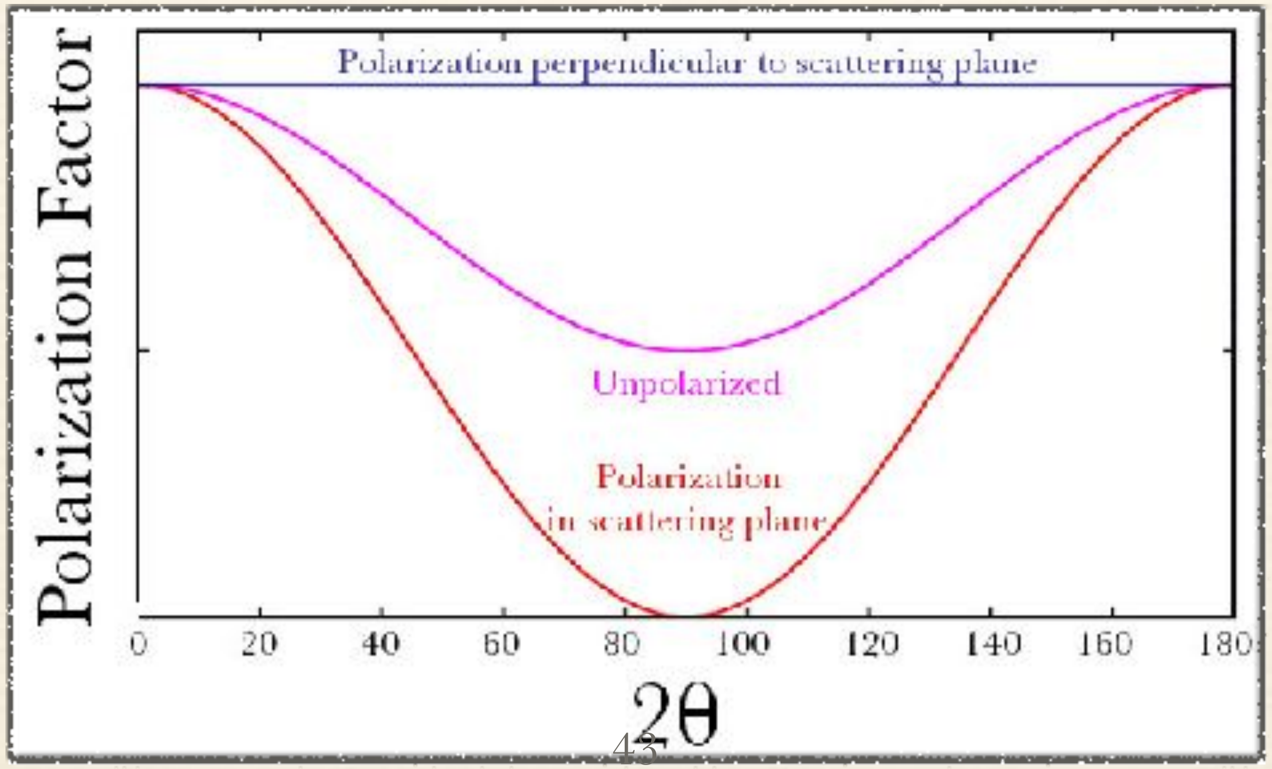
Inelastic X-ray Scattering

Polarization factor

Polarization in scattering plane : $|\vec{\epsilon}_i.\vec{\epsilon}_f|^2 = cos(2\theta)$

Polarization perpendicular to scattering plane : $|\vec{\epsilon}_i.\vec{\epsilon}_f|^2 = 1$

Unpolarized beam : $|\vec{\epsilon}_i.\vec{\epsilon}_f|^2 = \dfrac{1 + cos^2(2\theta)}{2}$



Inelastic X-ray Scattering

Interaction X-ray-cristal

Time-dependent atomic position : $\vec{R}_a(t) = \vec{R}_c + \vec{r}_a + \vec{u}_a(t)$

R_c : cell position, r_a : atom position in the cell

Scattering cross-section :

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \frac{k_f}{k_i} r_e^2 \left|\vec{\epsilon}_i.\vec{\epsilon}_f\right|^2 \sum_{c_1,c_2} e^{i\vec{Q}.(\vec{R}_{a_1}-\vec{R}_{a_2})} \sum_{a_1,a_2} f_{a_1}(\vec{Q}) f_{a_2}(\vec{Q}) e^{i\vec{Q}.(\vec{r}_{a_1}-\vec{r}_{a_2})}$$

$$\times \int_{-\infty}^{+\infty} \langle e^{i\vec{Q}.(\vec{u}_{a_1}(0)-\vec{u}_{a_2}(t))}\rangle e^{-i\omega t} dt$$

Thermodynamic average :

$$\langle e^{i\vec{Q}.(\vec{u}_{a_1}(0)-\vec{u}_{a_2}(t))}\rangle = e^{-W_{a_1}-W_{a_2}} e^{\langle\vec{Q}.(\vec{u}_{a_1}(0)-\vec{u}_{a_2}(t))\rangle}$$

$$= e^{-W_{a_1}-W_{a_2}} \left(1 + \langle\vec{Q}.(\vec{u}_{a_1}(0)-\vec{u}_{a_2}(t))\rangle + \frac{1}{2}\langle\vec{Q}.(\vec{u}_{a_1}(0)-\vec{u}_{a_2}(t))\rangle^2 + ...\right)$$

Elastic Scattering (the term 1)

Inelastic Scattering (the remaining terms)

$W_{a_1} = \frac{1}{2}\langle\left|\vec{Q}.\vec{u}_{a_1}(t)\right|^2\rangle$: Debye-Waller factor

Inelastic X-ray Scattering

Elastic cross-section Phonons

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = N\frac{(2\pi)^3}{v_0} r_e^2 \left|\vec{\epsilon}_i.\vec{\epsilon}_f\right|^2 \sum_{\vec{G}\in RS} \delta(\vec{Q}-\vec{G}) \left|\sum_a f_a(\vec{Q}) e^{-W_a} e^{i\vec{Q}.\vec{r}_a}\right|^2$$

1 phonon term (1st order)

$$+ \frac{k_f}{k_i}\frac{(2\pi)^3}{v_0} r_e^2 \left|\vec{\epsilon}_i.\vec{\epsilon}_f\right|^2 \sum_{\vec{q}\in BZ} \delta(\vec{Q}-\vec{q}-\vec{G}) \sum_p \left|\sum_a \sqrt{\frac{\hbar}{m_a\omega_p(\vec{q})}} f_a(\vec{Q}) e^{-W_a} e^{i\vec{Q}.\vec{r}_a} (\vec{Q}.\vec{\tilde{u}}_{a,p})\right|^2$$

$$\times \left[(1+n_B(\omega_p(\vec{q}),T))\delta(\omega-\omega_p(\vec{q})) + n_B(\omega_p(\vec{q}),T)\delta(\omega+\omega_p(\vec{q}))\right]$$

$$+ \frac{k_f}{k_i}\frac{(2\pi)^3}{v_0} r_e^2 \left|\vec{\epsilon}_i.\vec{\epsilon}_f\right|^2$$

$$\times \sum_{\vec{q},\vec{q'}\in BZ} \delta(\vec{Q}-\vec{q}-\vec{q'}-\vec{G}) \frac{1}{2} \sum_{p,p'} \left|\sum_a \frac{\hbar}{m_a\sqrt{\omega_p(\vec{q})\omega_{p'}(\vec{q'})}} f_a(\vec{Q}) e^{-W_a} e^{i\vec{Q}.\vec{r}_a} (\vec{Q}.\vec{\tilde{u}}_{a,p})(\vec{Q}.\vec{\tilde{u}}_{a,p'})\right|^2$$

$$\times \Big[(1+n_B(\omega_p(\vec{q}),T))(1+n_B(\omega'_p(\vec{q'}),T))\delta(\omega-\omega_p(\vec{q})-\omega_{p'}(\vec{q'}))$$

$$+ 2n_B(\omega_p(\vec{q}),T)(1+n_B(\omega'_p(\vec{q'}),T))\delta(\omega+\omega_p(\vec{q}))-\omega_{p'}(\vec{q'}))$$

$$+ n_B(\omega_p(\vec{q}),T)n_B(\omega'_p(\vec{q'}),T)\delta(\omega+\omega_p(\vec{q}))+\omega_{p'}(\vec{q'}))\Big]$$

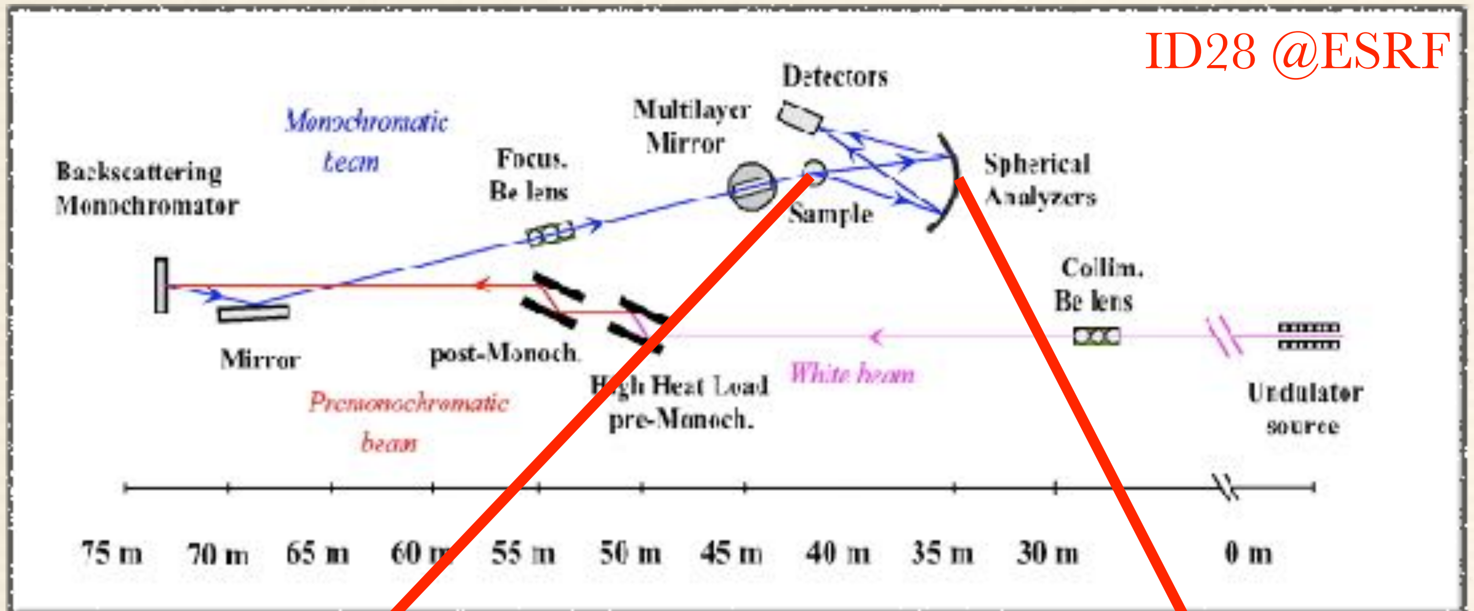
2 phonons term (2nd order)

Inelastic X-ray Scattering

Synchrotron Facilities worldwide

Inelastic X-ray Scattering

Experimental setup

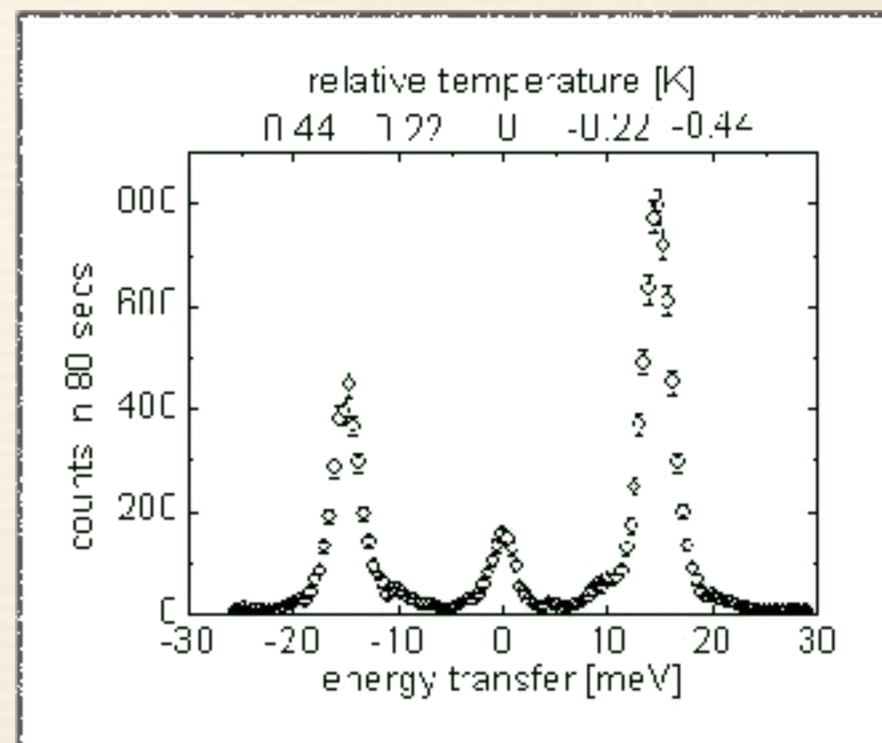


Beam spot : ~100µm

Analyzers Si

$$\frac{\Delta d}{d} = \frac{\Delta E}{E} = 2.58\ 10^{-6} \Delta T$$

$$\delta T \approx 10^{-4} K$$



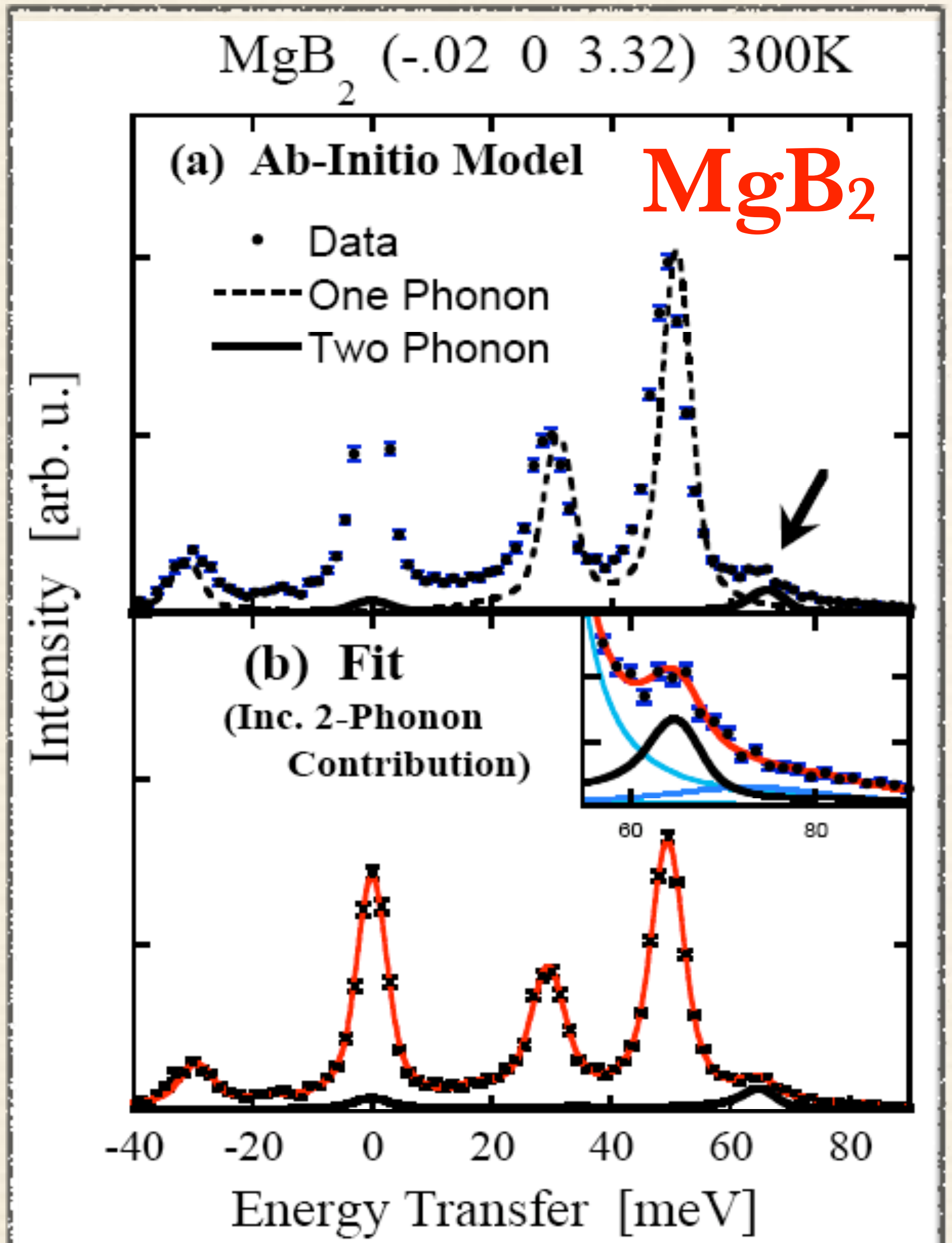
Inelastic X-ray Scattering

Experimental setup

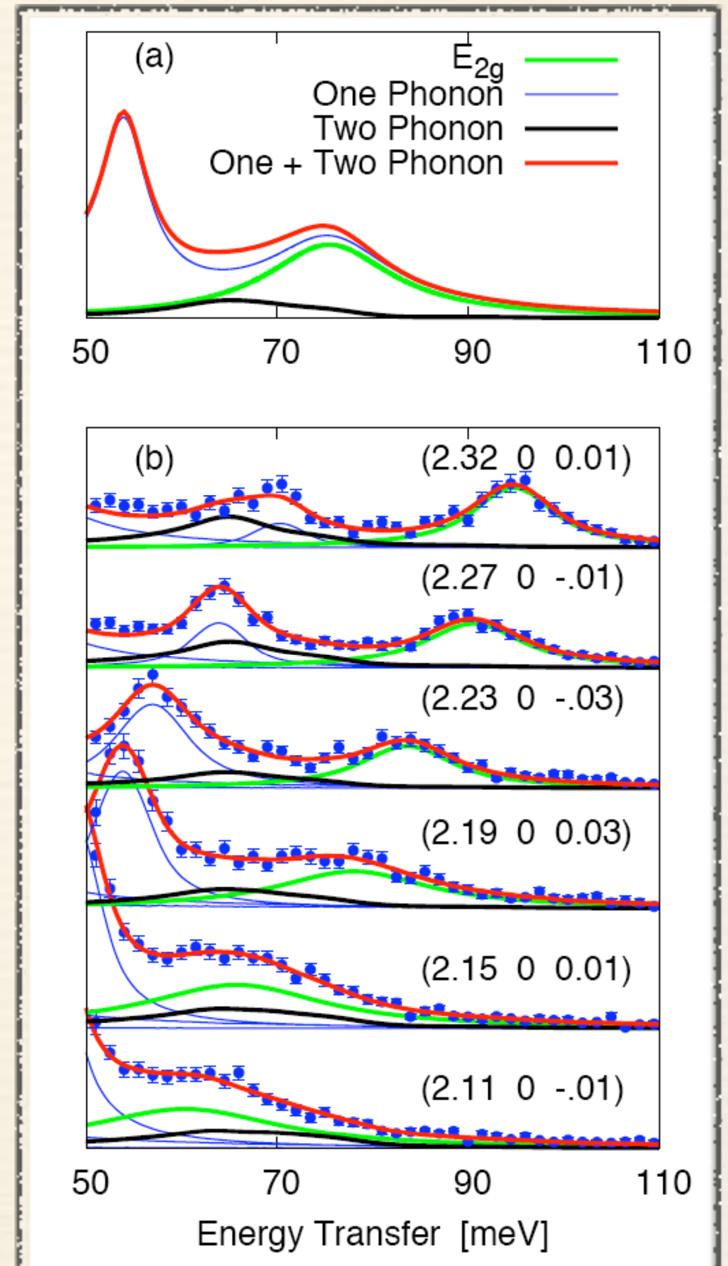
Reflection	Energy (keV)	Resolution (meV)	Q_{max} - Q_{max} (A^{-1})	Resolution (A^{-1})	Flux ($ph.s^{-1}$)
Si(7,7,7)	13.840	7.6 ± .2	0.1 - 6.4	0.02	$1.1\ 10^{11}$
Si(9,9,9)	17.794	3.0 ± .2	0.1 - 8.3	0.027	$2.7\ 10^{10}$
Si(11,11,11)	21.747	1.5 ± .1	0.1 - 10.1	0.034	$6.6\ 10^{9}$
Si(13,13,13)	25.704	1.0 ± .1	0.1 - 12.0	0.040	$1.5\ 10^{9}$

Inelastic X-ray Scattering

Superconductivity

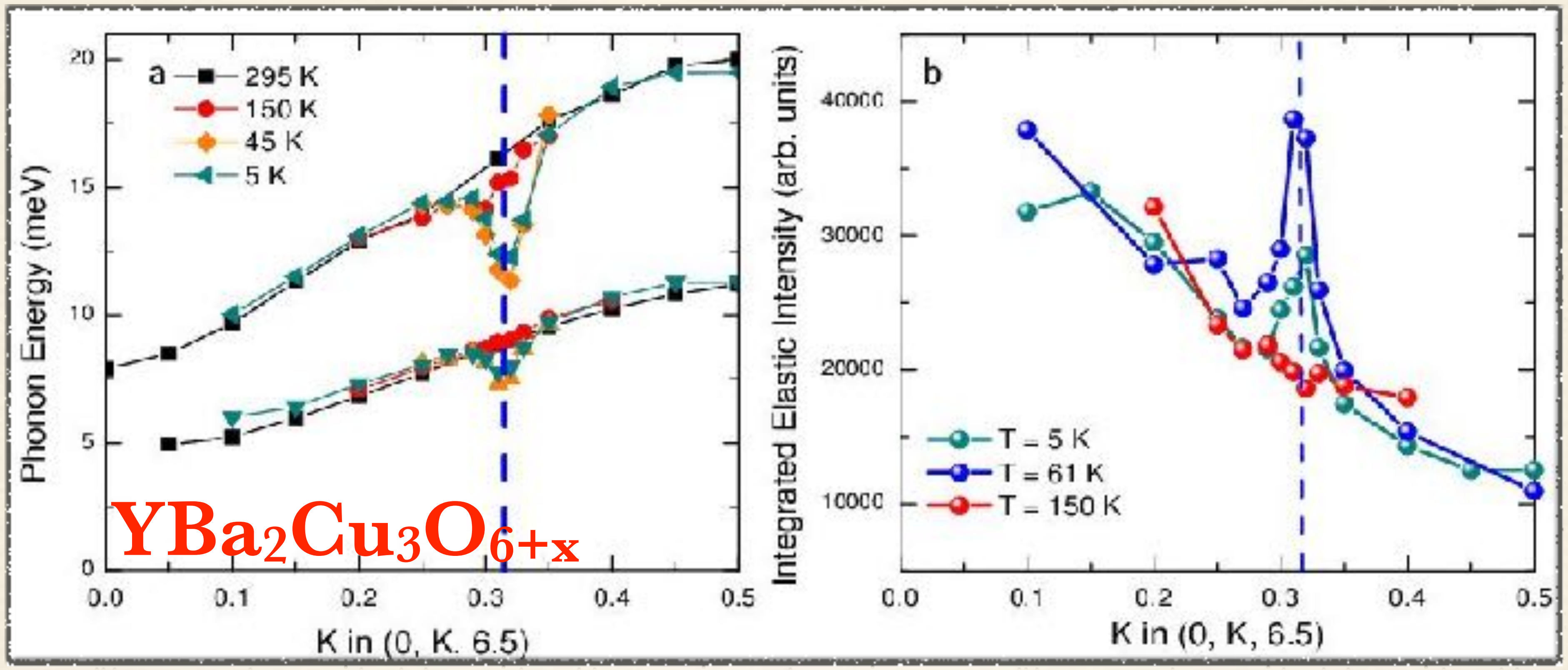


Phys. Rev. B, 75 020505(R) (2007)



Inelastic X-ray Scattering

Charge Density Wave



Nature Physics 10, 52-58 (2014)

Phonon softening at Q_{CDW} : fingerprint of CDW

Inelastic X-ray Scattering

Summary

- Inelastic X-ray scattering allows a direct measure of the dispersion relation of excitations $\omega(\vec{q})$
- Geometrical selection of transverse or longitudinal mode
- Phonon intensity ~Q^2
- This dispersion give access to :
  - Interatomic potential and bonding
  - Phase transition and critical phenomena (soft mode …)
  - Interactions (electron-phonon …)

Inelastic X-ray Scattering

Summary

INS	IXS
Strong ω-**Q** correlation:	No ω-**Q** correlation :
Kinematic limit	No kinematic limitation
No polarization factor	Polarization factor : $\lvert \vec{\epsilon_i}.\vec{\epsilon_f} \rvert^2$
I ~ b^2	I ~ Z^2
Incoherent Scattering	No incoherent Scattering
Bulk measurement	Strong absorption ~ $\lambda^3 Z^4$
Large beam ~ cm	Small beam ~ 100 µm
Resolution down to 0.1 meV	Resolution ~ 1 meV

Raman Spectroscopy

Interaction light-electron

Interaction potential : $\mathcal{V}(\vec{r}) = -\vec{\mu}_{ind}.\vec{E}_f$

$$\vec{\mu}_{ind} = \overline{\overline{\alpha}}.\vec{E}_i = \overline{\overline{\alpha}}_0.\vec{E}_i + \left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} Q.\vec{E}_i$$: induced dipole moment

$Q_p(t) = Q_0 cos(\omega_p t)$: normal phonon p

$\vec{E}_i = E_i cos(\omega_i t)\vec{\epsilon}_i$: incident photon

$$\overline{\overline{\alpha}} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix}$$: polarization tensor

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = k_i k_f^3 r_e^2 \int_{-\infty}^{+\infty} \langle \vec{\epsilon}_f.\overline{\overline{\alpha}}(0).\vec{\epsilon}_i \ \vec{\epsilon}_f.\overline{\overline{\alpha}}(t).\vec{\epsilon}_i \rangle e^{-i\omega t} dt$$

$$= k_i^4 r_e^2 \left|\vec{\epsilon}_i.\overline{\overline{\alpha}}_0.\vec{\epsilon}_i\right|^2$$ **Rayleigh Scattering**

$$+ \frac{k_f}{k_i} r_e^2 \sum_p \int_{-\infty}^{+\infty} \langle \vec{\epsilon}_f. \left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} Q_p(0).\vec{\epsilon}_i \ \vec{\epsilon}_f. \left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} Q_p(t).\vec{\epsilon}_i \rangle e^{-i\omega t} dt$$

Raman Spectroscopy

Sensitive to polarizability variation

$$\vec{\mu}_{ind} = \bar{\bar{\alpha}}_0.\vec{E}_i + \left(\frac{\partial\bar{\bar{\alpha}}}{\partial Q}\right)_{Q=0} Q_p(t).\vec{E}_i$$

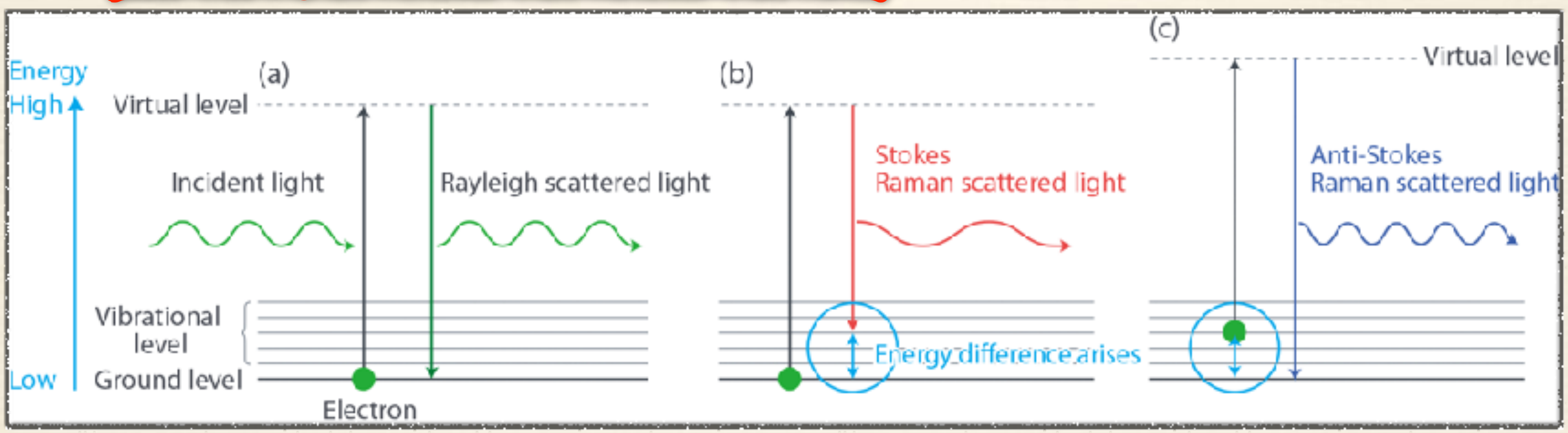
$$\vec{E}_i = E_i cos(\omega_i t)\vec{\epsilon}_i$$

$$Q_p(t) = Q_0 cos(\omega_p t)$$

$$= \bar{\bar{\alpha}}_0.\vec{\epsilon}_i E_i cos(\omega_i t)$$ **Rayleigh Scattering**

$$+ \frac{1}{2}\left(\frac{\partial\bar{\bar{\alpha}}}{\partial Q}\right)_{Q=0} .\vec{\epsilon}_i Q_0 E_i cos((\omega_i + \omega_p)t)$$ **Anti-Stokes Scattering**

$$+ \frac{1}{2}\left(\frac{\partial\bar{\bar{\alpha}}}{\partial Q}\right)_{Q=0} .\vec{\epsilon}_i Q_0 E_i cos((\omega_i - \omega_p)t)$$ **Stokes Scattering**



Raman Spectroscopy

Sensitive to polarizability variation

$$\vec{\mu}_{ind} = \overline{\overline{\alpha}}_0.\vec{E}_i + \left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} Q_p(t).\vec{E}_i$$

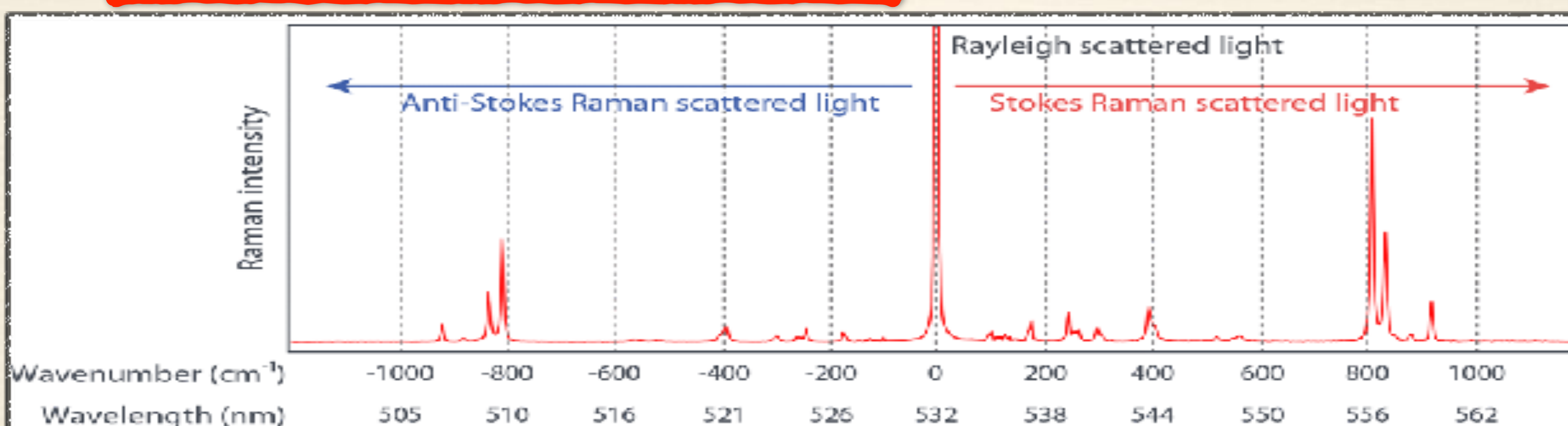
$$\vec{E}_i = E_i cos(\omega_i t)\vec{\epsilon}_i$$

$$Q_p(t) = Q_0 cos(\omega_p t)$$

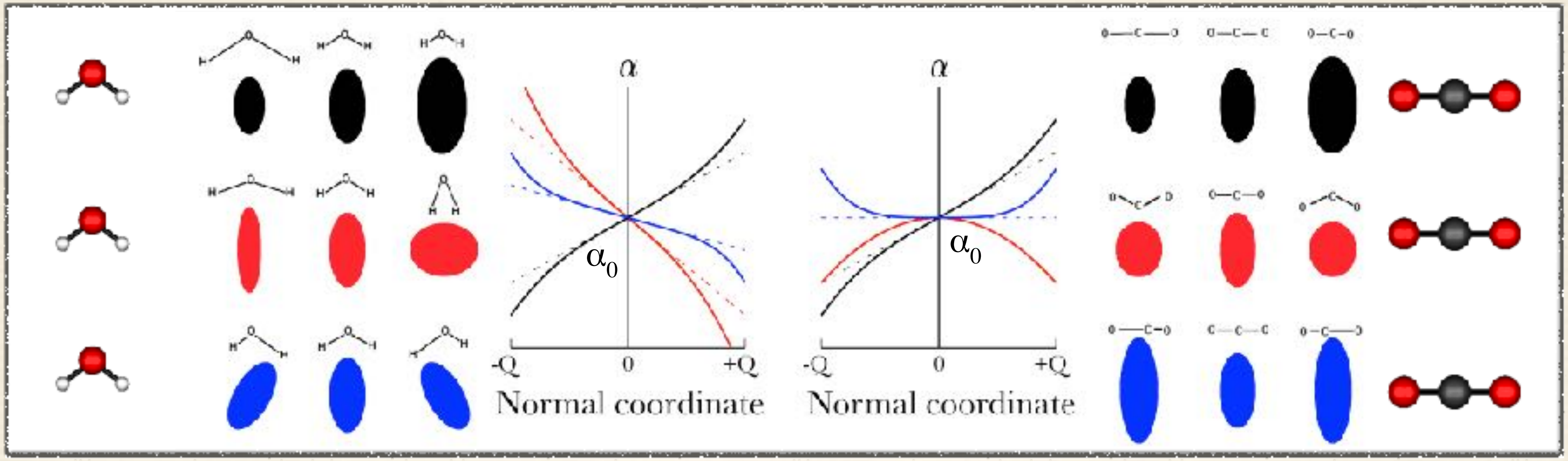
$$= \overline{\overline{\alpha}}_0.\vec{\epsilon}_i E_i cos(\omega_i t)$$ **Rayleigh Scattering**

$$+ \frac{1}{2}\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} .\vec{\epsilon}_i Q_0 E_i cos((\omega_i + \omega_p)t)$$ **Anti-Stokes Scattering**

$$+ \frac{1}{2}\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} .\vec{\epsilon}_i Q_0 E_i cos((\omega_i - \omega_p)t)$$ **Stokes Scattering**



Raman Spectroscopy



3 Raman active modes :

$$\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} \neq 0$$

1 Raman active mode :

$$\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} \neq 0$$

2 Raman inactive modes :

$$\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} = 0$$

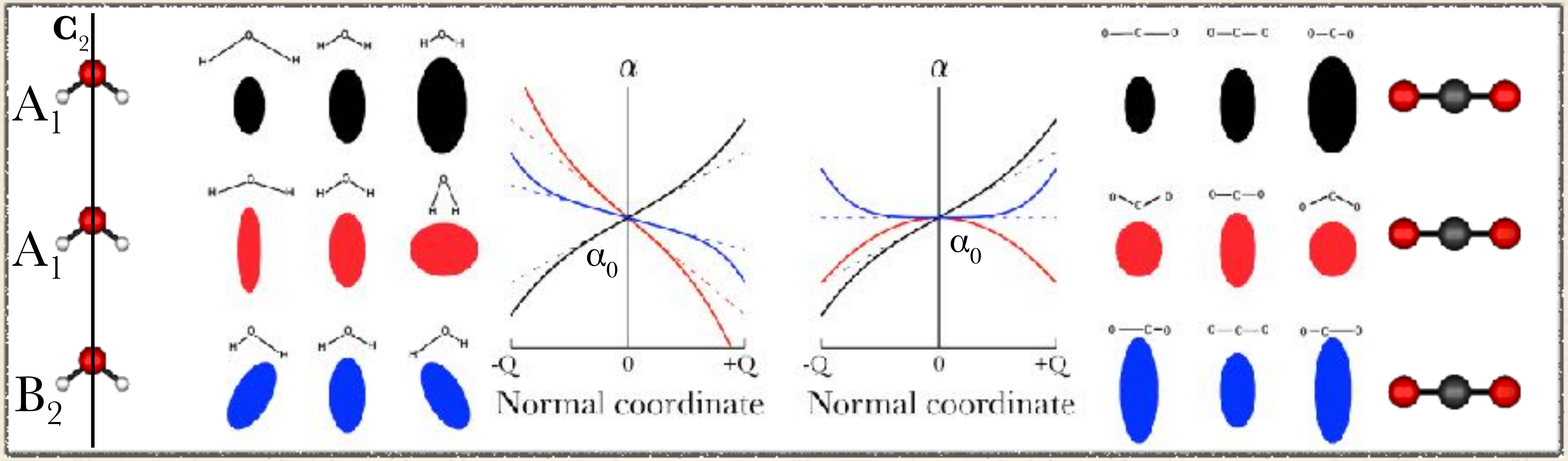
Relation with the mode symmetry !!!

Raman Spectroscopy

Nomenclatura : Mulliken symbols

A	Symmetric with respect to the main axis of symmetry
B	Antisymmetric with respect to the main axis of symmetry
’	Symmetric with respect to a plane of symmetry
’’	Antisymmetric with respect to a plane of symmetry
g	Symmetric with respect to the center of inversion
u	Antisymmetric with respect to the center of inversion
E	Doubly degenerate with respect to the main axis
T (or F)	Triply degenerate with respect to the main axis
G	Fourfold degenerate with respect to the main axis
H	Fivefold degenerate with respect to the main axis
1,2,3…	Symmetric or antisymmetric with respect to a rotation axis

Raman Spectroscopy



3 Raman active modes :

$$\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} \neq 0$$

1 Raman active mode :

$$\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} \neq 0$$

2 Raman inactive modes :

$$\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} = 0$$

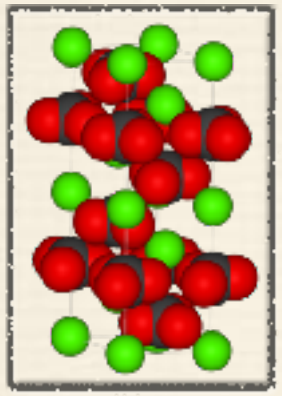
Relation with the mode symmetry !!!

Raman Spectroscopy

Triclinic		Monoclinic		Trigonal (Rhombohedral)		Tetragonal		Hexagonal		Cubic	
C_1	1	C_2	2	C_3	3	C_4	4	C_6	6	T	23
C_i	$\bar{1}$	C_S	m	C_{3i}	$\bar{3}$	S_4	$\bar{4}$	C_{3h}	$\bar{6}$		
		C_{2h}	$2/m$			C_{4h}	$4/m$	C_{6h}	$6/m$	T_h	$m\bar{3}$
		C_{2v}	$mm2$	C_{3v}	$3m$	C_{4v}	$4mm$	C_{6v}	$6mm$		
				D_{3d}	$\bar{3}m$	D_{2d}	$42m$	D_{3h}	$6m2$	T_d	$\bar{4}3m$
		D_2	222	D_3	32	D_4	422	D_6	622	O	432
		D_{2h}	mmm			D_{4h}	$4/mmm$	D_{6h}	$6/mmm$	O_h	$m\bar{3}m$

Symmetry element	Schönflies notation	International (Hermann-Mauguin)
Identity	E	1
Rotation axes	C_n	$n = 1, 2, 3, 4, 6$
Mirror planes	σ	m
⊥ to n-fold axis	σ_h	m, m_z
‖ to n-fold axis	σ_v	m_v,
bisecting ∠(2,2)	σ_d	m_d, m'
Inversion	I	$\bar{1}$
Rotoinversion axes	S_n	$n = \bar{1},\bar{2},\bar{3},\bar{4},\bar{6}$
Translation	t_n	t_n
Screw axes	C_n^k	n_k
Glide planes	σ^g	a, b, c, n, d

Raman Spectroscopy



$CaCO_3$ $R\bar{3}c$(#167)
Ca (6b) : (0,0,0)
C (6a) : (0,0,1/4)
O (18e) : (x,0,1/4)

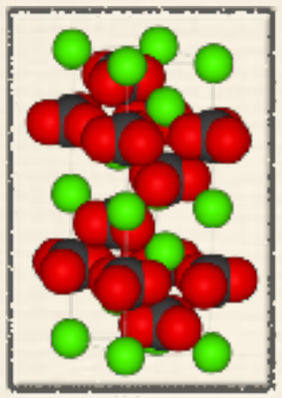
Character Table

D_{3d}(-3m)	#	1	3	2	-1	-3	m_d	functions
Mult.	-	1	2	3	1	2	3	.
A_{1g}	Γ_1^+	1	1	1	1	1	1	x^2+y^2,z^2
A_{2g}	Γ_2^+	1	1	-1	1	1	-1	J_z
E_g	Γ_3^+	2	-1	0	2	-1	0	$(x^2-y^2,xy),(xz,yz),(J_x,J_y)$
A_{1u}	Γ_1^-	1	1	1	-1	-1	-1	.
A_{2u}	Γ_2^-	1	1	-1	-1	-1	1	z
E_u	Γ_3^-	2	-1	0	-2	1	0	(x,y)

5 Raman active modes

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g
18e	1	.	.	.	.	3
6a	.	.	.	.	.	1
6b	.	.	.	.	.	.

Raman Spectroscopy



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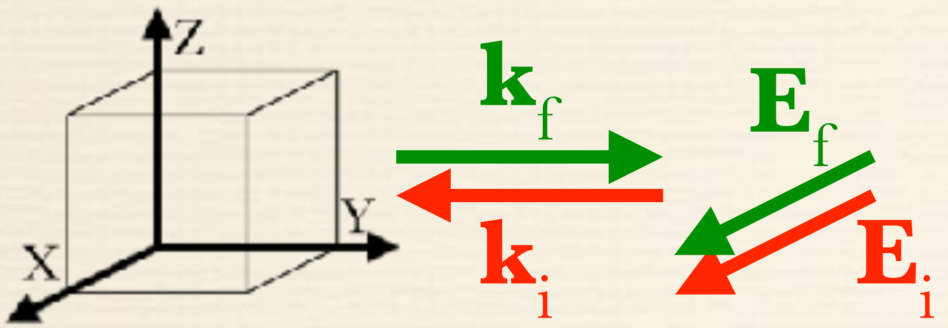
A_{1g}	Γ_1^+	1	1	1	1	1	1	x^2+y^2, z^2
A_{2g}	Γ_2^+	1	1	-1	1	1	-1	J_z
E_g	Γ_3^+	2	-1	0	2	-1	0	$(x^2-y^2, xy), (xz, yz), (J_x, J_y)$
A_{1u}	Γ_1^-	1	1	1	-1	-1	-1	.
A_{2u}	Γ_2^-	1	1	-1	-1	-1	1	z
E_u	Γ_3^-	2	-1	0	-2	1	0	(x,y)

5 Raman active modes
Raman tensors :

A_{1g}			$E_{g,1}$			$E_{g,2}$		
a	.	.	c	.	.	.	-c	-d
.	a	.	.	-c	d	-c	.	.
.	.	b	.	d	.	-d	.	.

Raman Spectroscopy

Back-Scattering Geometry

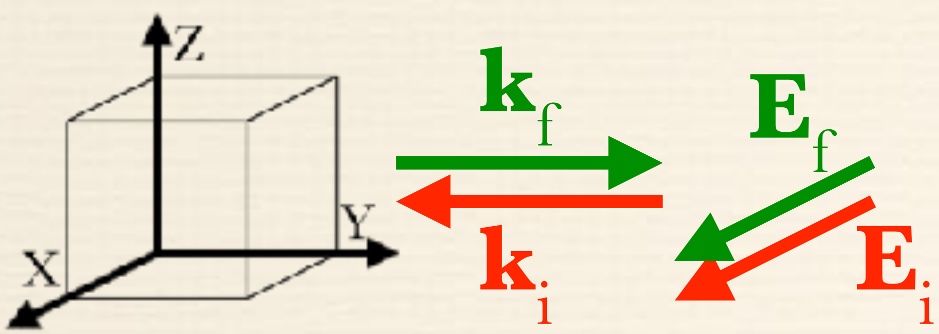


$$\overline{Y}(XX)Y \Rightarrow \alpha_{xx} = a + c$$

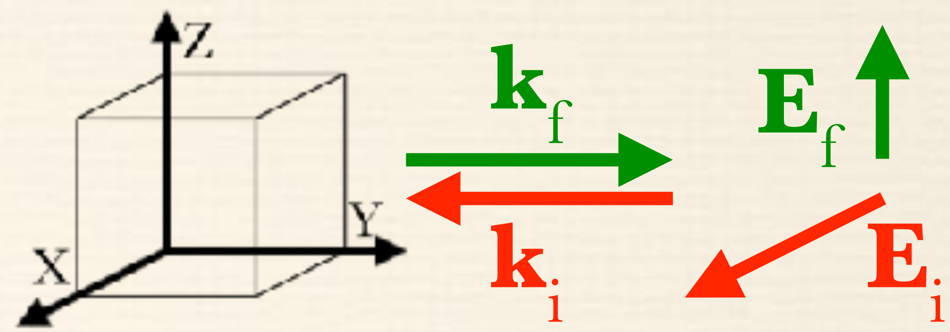
A_{1g}			$E_{g,1}$			$E_{g,2}$		
a	·	·	c	·	·	·	-c	-d
·	a	·	·	-c	d	-c	·	·
·	·	b	·	d	·	-d	·	·

Raman Spectroscopy

Back-Scattering Geometry



$$\overline{Y}(XX)Y \Rightarrow \alpha_{xx} = a + c$$

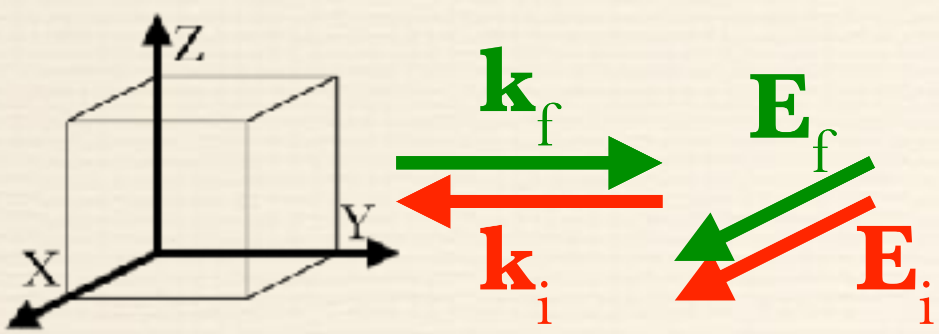


$$\overline{Y}(XZ)Y \Rightarrow \alpha_{xz} = -d$$

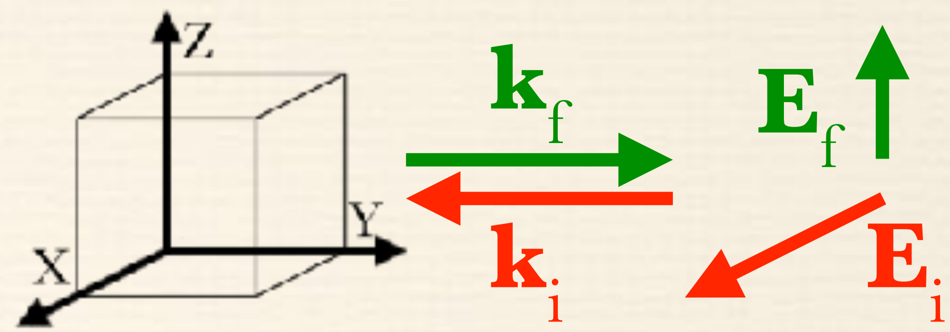
A_{1g}			$E_{g,1}$			$E_{g,2}$		
a	·	·	c	·	·	·	-c	-d
·	a	·	·	-c	d	-c	·	·
·	·	b	·	d	·	-d	·	·

Raman Spectroscopy

Back-Scattering Geometry

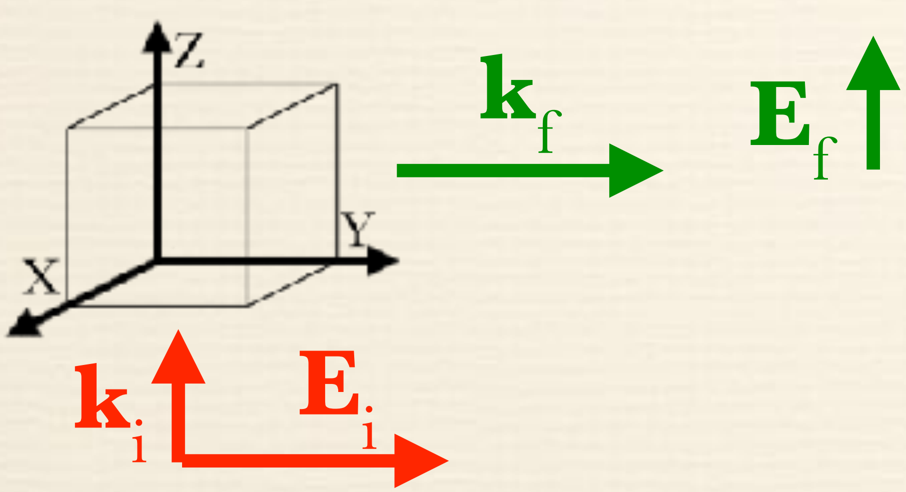


$$\overline{Y}(XX)Y \Rightarrow \alpha_{xx} = a + c$$



$$\overline{Y}(XZ)Y \Rightarrow \alpha_{xz} = -d$$

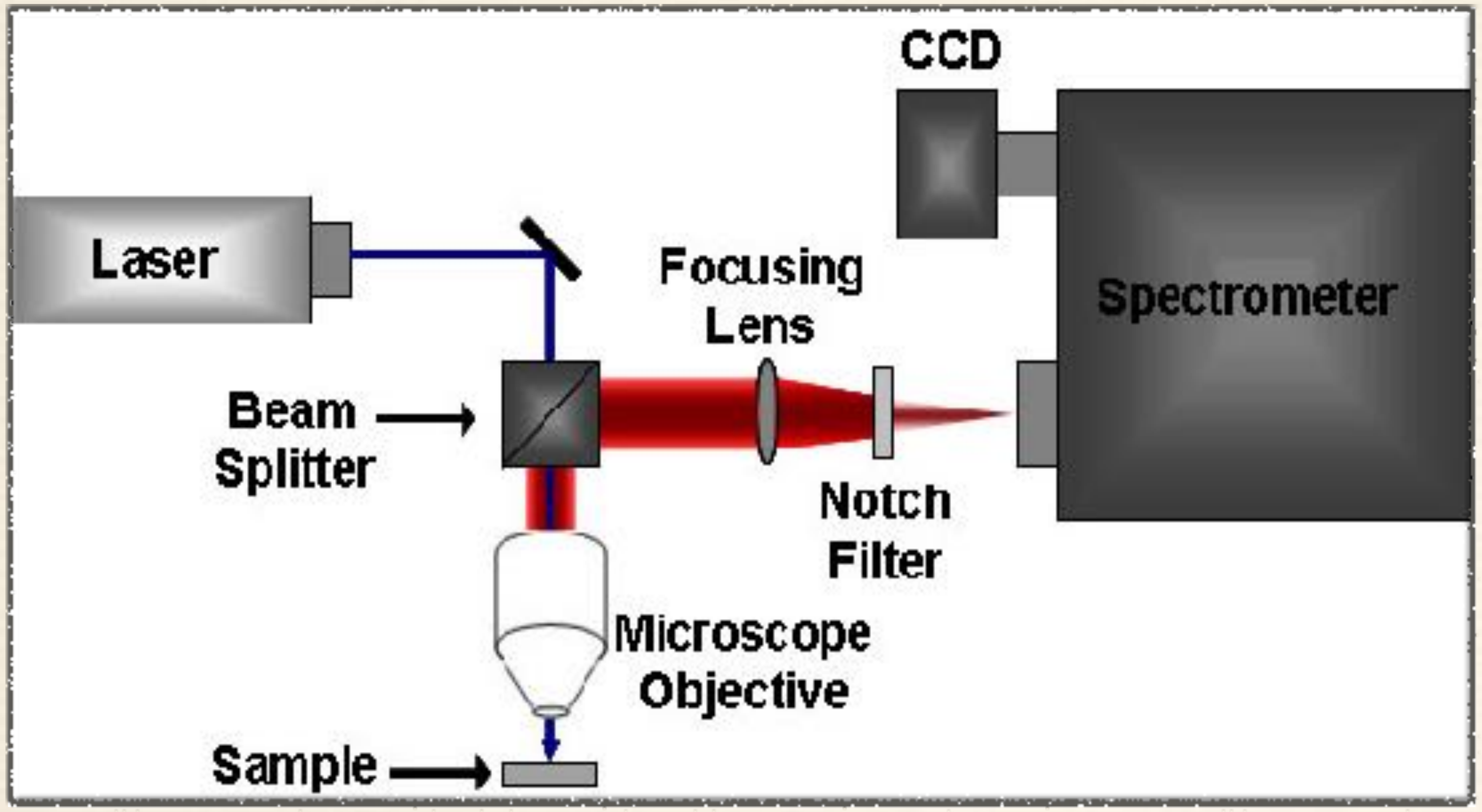
Right Angle Geometry

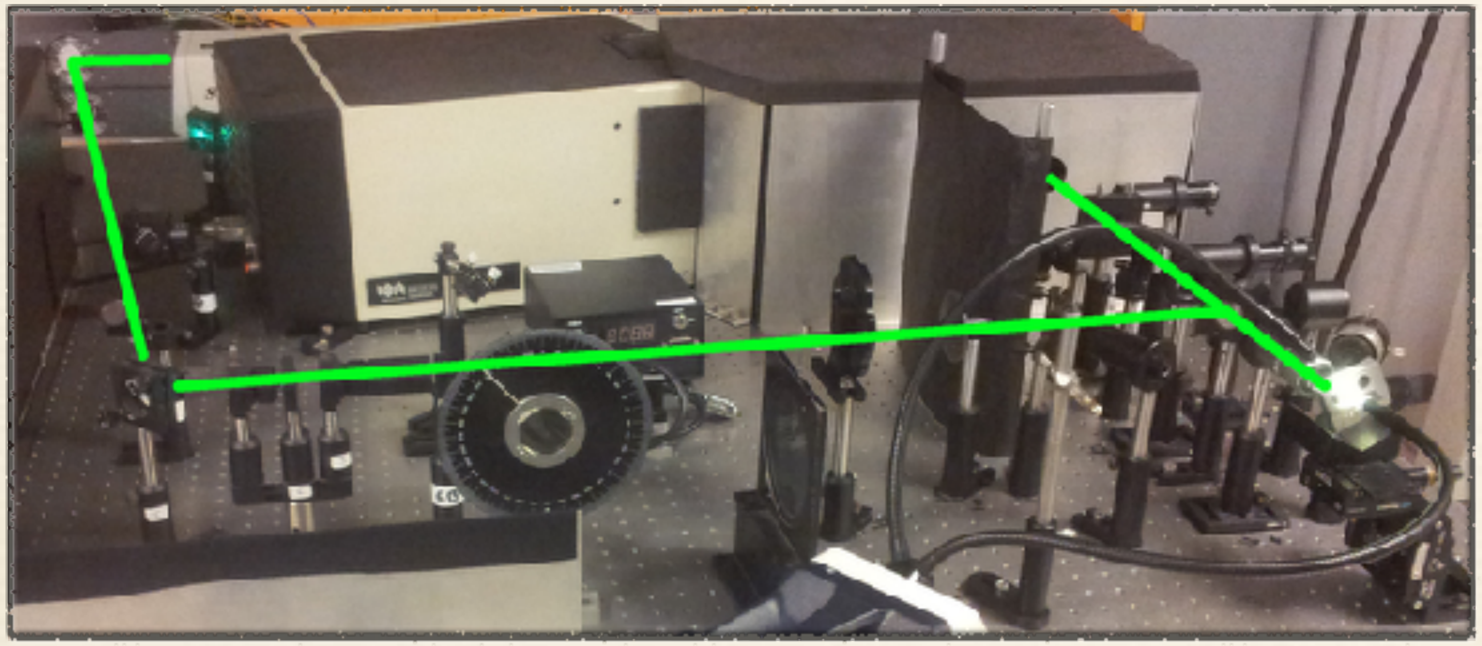


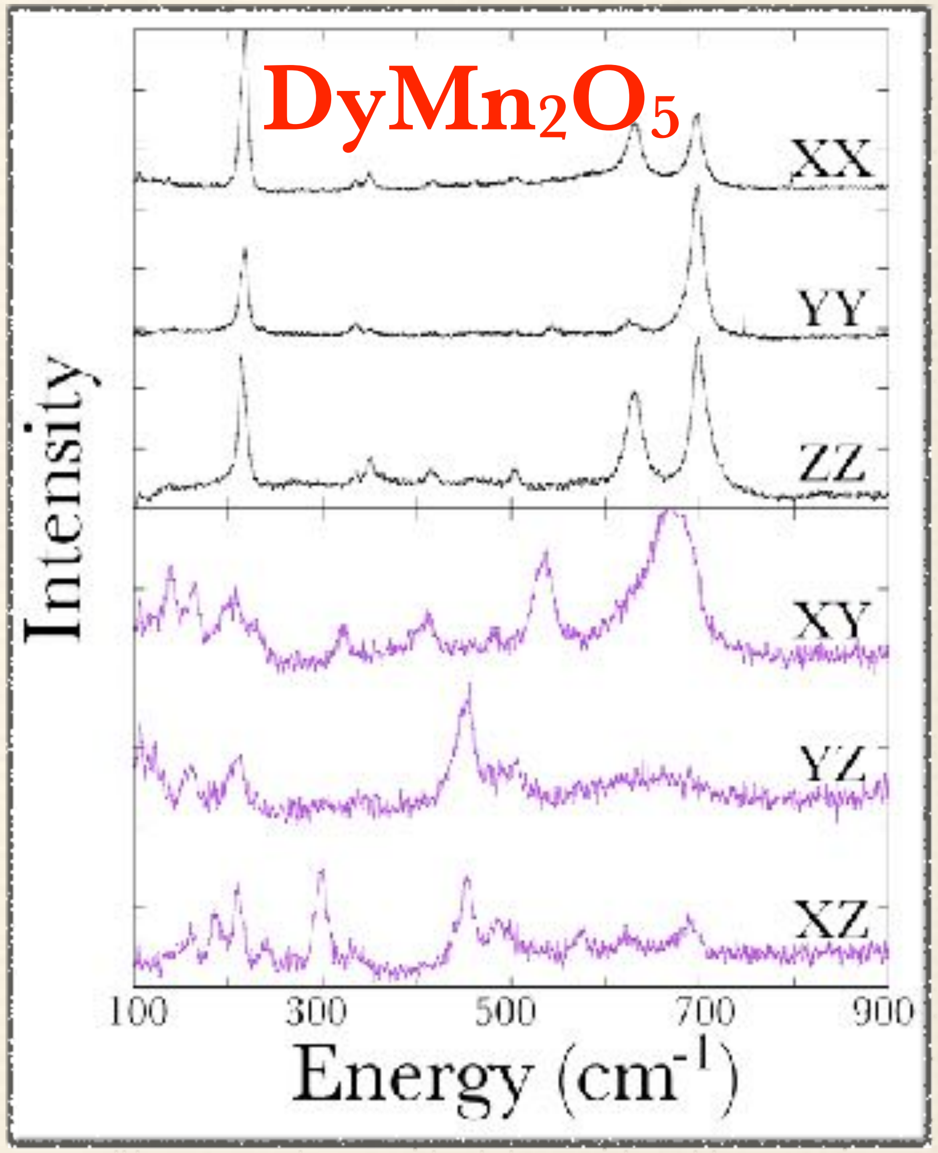
$$Z(YZ)Y \Rightarrow \alpha_{yz} = d$$

A_{1g}			$E_{g,1}$			$E_{g,2}$		
a	·	·	c	·	·	·	-c	-d
·	a	·	·	-c	d	-c	·	·
·	·	b	·	d	·	-d	·	·

Raman Spectroscopy

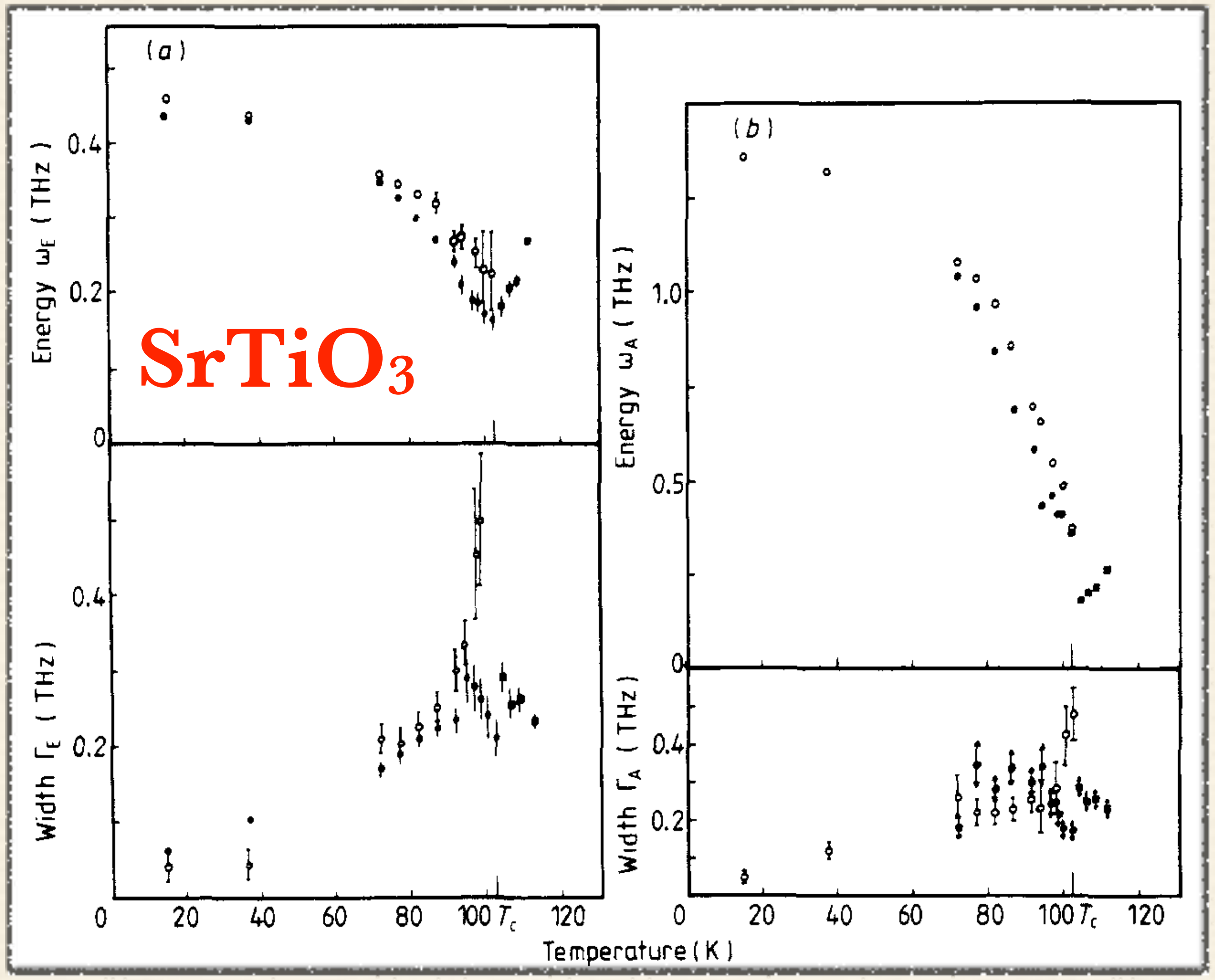






Raman Spectroscopy

Ferroelectricity

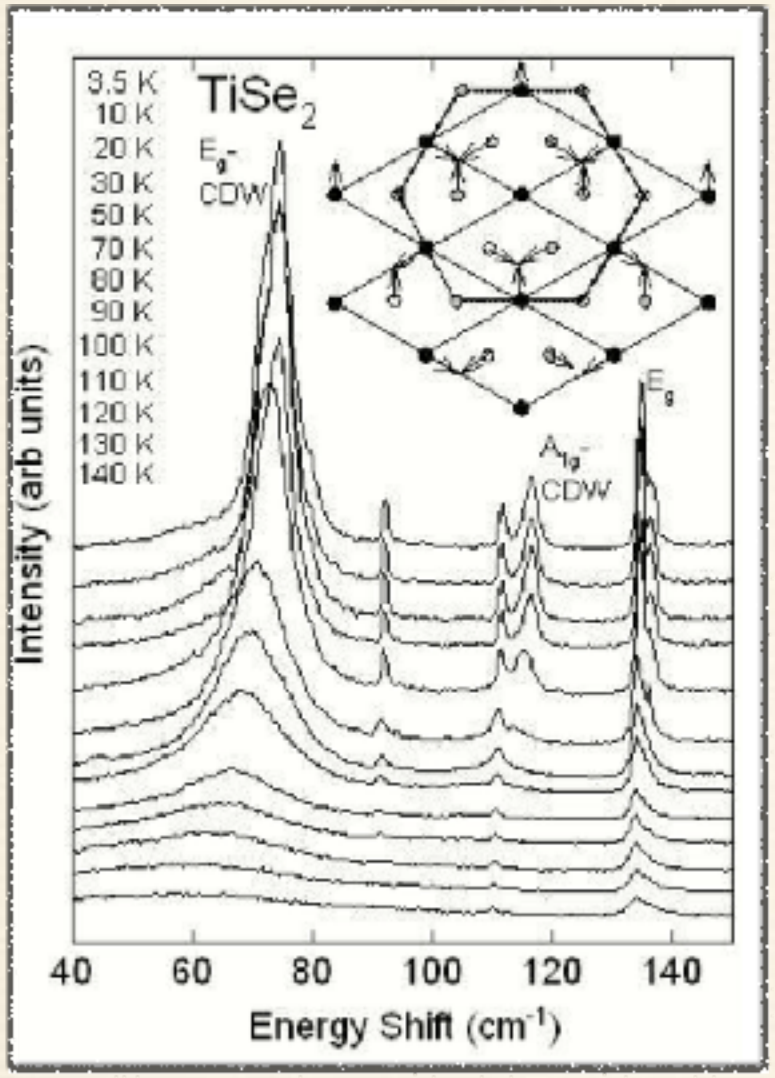


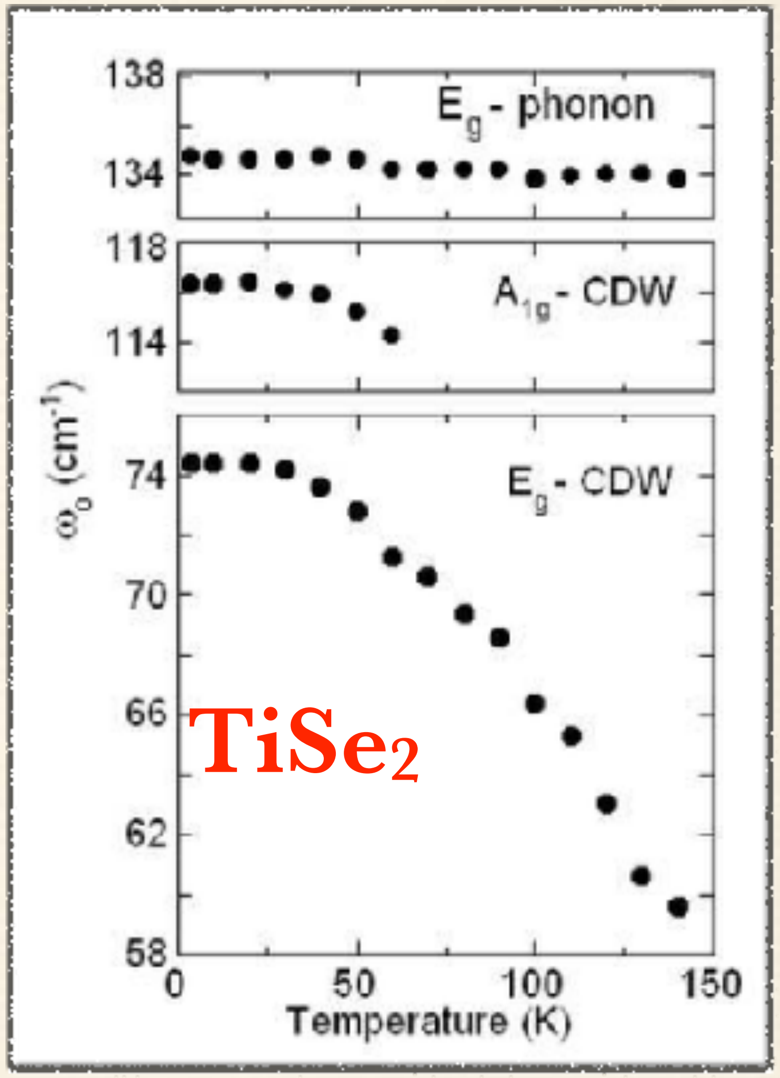
J. Phys. C 16, 841 (1983)

Phonon energy decreases at low temperature
Fingerprint of ferroelectric transition

Raman Spectroscopy

Charge Density Wave





PRL 91, 136402 (2003)

Amplitude mode : zone-boundary (L point) transverse acoustic phonons folded to Q=0 zone center (Γ point) due to CDW

Raman Spectroscopy

Summary

- Sensitive to zone center (**Q**=0) excitations
- Polarization enables mode-symmetry selectivity
- Give access to :
  - Ferroelectric instability
  - CDW fingerprint
  - Translational symmetry breaking
- Overdamped peaks for metals
- Beyond this lecture : Hyper-Raman, Resonant Raman…

1.3 Absorption and Emission Spectroscopy

Infrared Spectroscopy

Interaction light-electron

Interaction potential : $\mathcal{V}(\vec{r}) = -\vec{\mu}_{ind}.\vec{E}_i$

$\vec{\mu}_{ind} = \vec{\mu}_0 + \left(\frac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0} Q_p(\omega_p, t)$: induced dipole moment

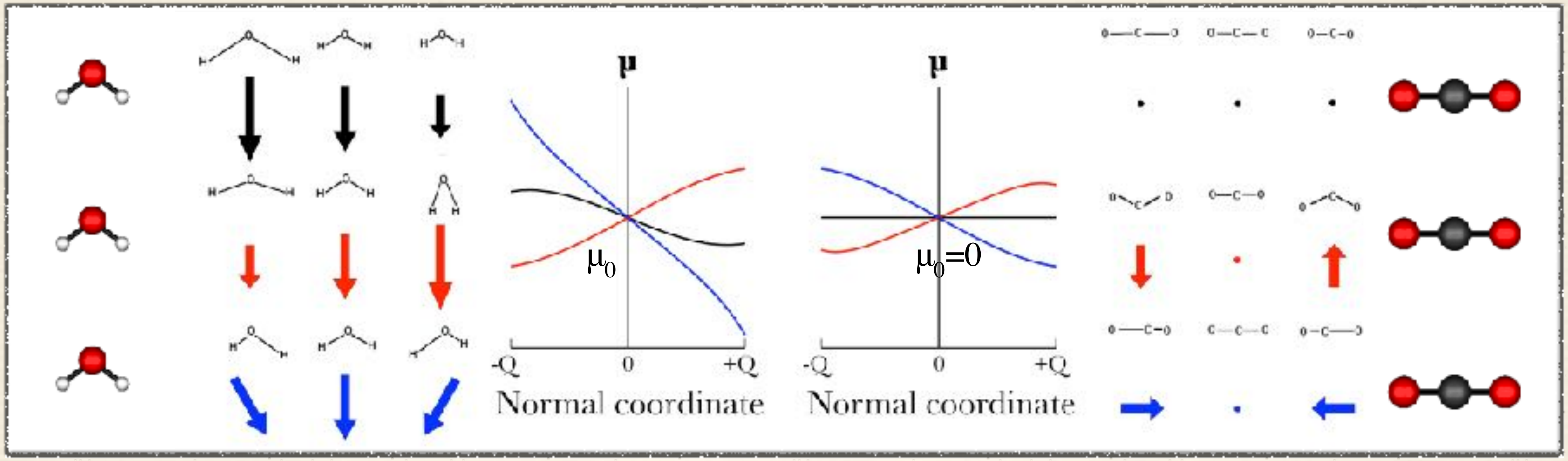
$Q_p(\omega_p, t) = Q_0 cos(\omega_p t)$: normal phonon p

$\vec{E}_i = E_i cos(\omega_i t)\vec{\epsilon}_i$: incident photon

$$\sigma(\omega_i) = \left|\left(\frac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0}\right|^2 \sum_p \int_{-\infty}^{+\infty} \langle Q_p(0) Q_p(t)\rangle e^{-i\omega_i t} dt$$

$$= \left|\left(\frac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0}\right|^2 \sum_p \delta(\omega_i - \omega_p)$$

Infrared Spectroscopy



3 Raman and IR active modes :

$$\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} \neq 0 \qquad \left(\frac{\partial\vec{\mu}}{\partial Q}\right)_{Q=0} \neq 0$$

1 Raman active and IR inactive mode :

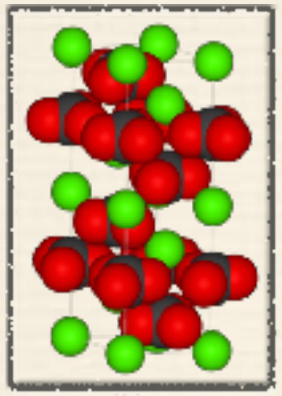
$$\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} \neq 0 \qquad \left(\frac{\partial\vec{\mu}}{\partial Q}\right)_{Q=0} = 0$$

2 Raman inactive and IR active modes :

$$\left(\frac{\partial\overline{\overline{\alpha}}}{\partial Q}\right)_{Q=0} = 0 \qquad \left(\frac{\partial\vec{\mu}}{\partial Q}\right)_{Q=0} \neq 0$$

Relation with the mode symmetry !!!

Infrared Spectroscopy



$CaCO_3$ $R\bar{3}c$(#167)
Ca (6b) : (0,0,0)
C (6a) : (0,0,1/4)
O (18e) : (x,0,1/4)

Character Table

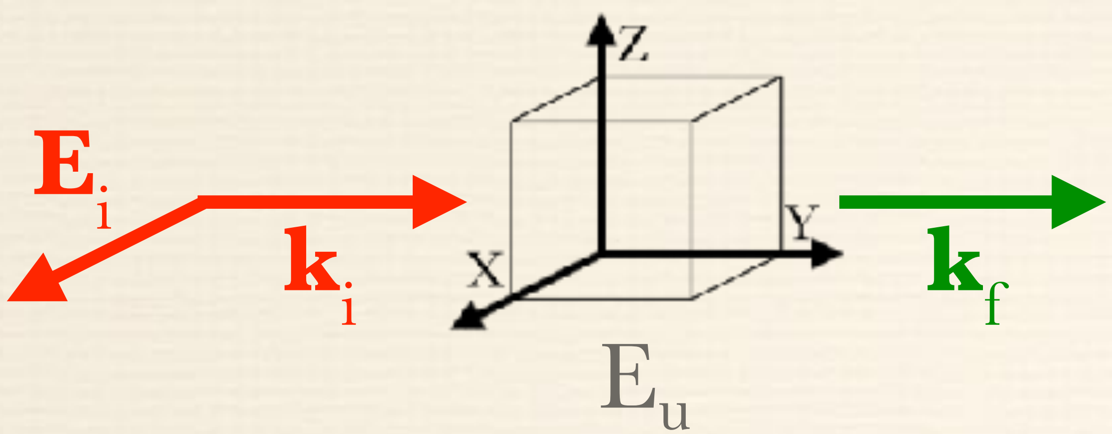
D_{3d}(-3m)	#	1	3	2	-1	-3	m_d	functions
Mult.	-	1	2	3	1	2	3	.
A_{1g}	Γ_1^+	1	1	1	1	1	1	x^2+y^2,z^2
A_{2g}	Γ_2^+	1	1	-1	1	1	-1	J_z
E_g	Γ_3^+	2	-1	0	2	-1	0	$(x^2-y^2,xy),(xz,yz),(J_x,J_y)$
A_{1u}	Γ_1^-	1	1	1	-1	-1	-1	.
A_{2u}	Γ_2^-	1	1	-1	-1	-1	1	z
E_u	Γ_3^-	2	-1	0	-2	1	0	(x,y)

8 IR active modes

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g
18e	.	.	.	2	3	.
6a	.	.	.	1	1	.
6b	.	.	.	1	2	.

Infrared Spectroscopy

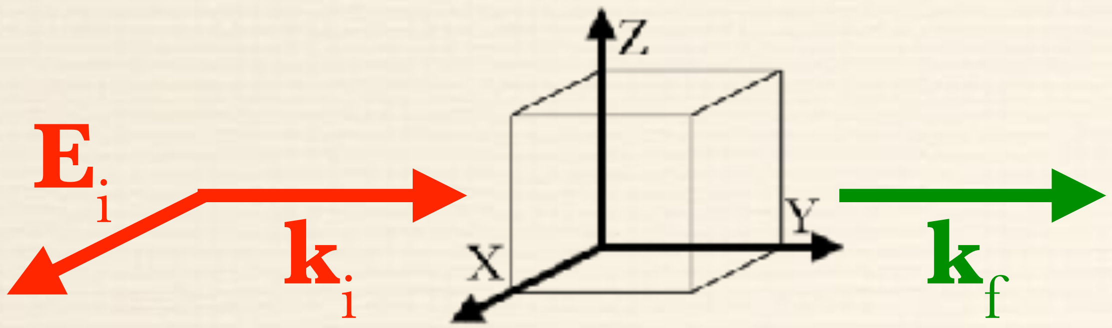
Absorption Geometry



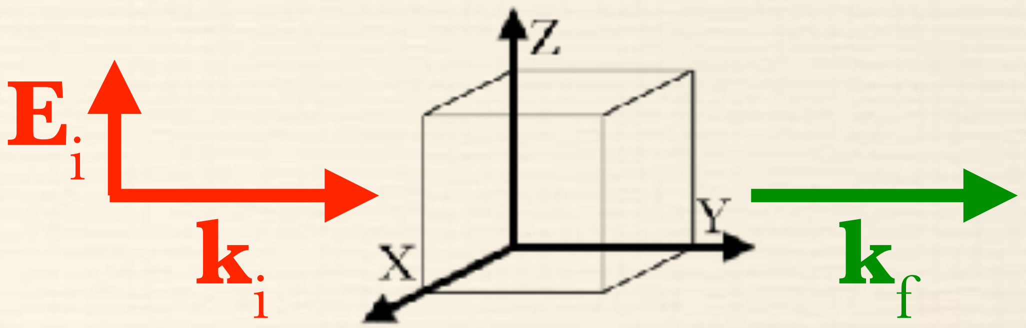
D_{3d}(-3m)	#	1	3	2	-1	-3	m_d	functions
Mult.	-	1	2	3	1	2	3	.
A_{1g}	Γ_1^+	1	1	1	1	1	1	x^2+y^2,z^2
A_{2g}	Γ_2^+	1	1	-1	1	1	-1	J_z
E_g	Γ_3^+	2	-1	0	2	-1	0	$(x^2-y^2,xy),(xz,yz),(J_x,J_y)$
A_{1u}	Γ_1^-	1	1	1	-1	-1	-1	.
A_{2u}	Γ_2^-	1	1	-1	-1	-1	1	z
E_u	Γ_3^-	2	-1	0	-2	1	0	(x,y)

Infrared Spectroscopy

Absorption Geometry

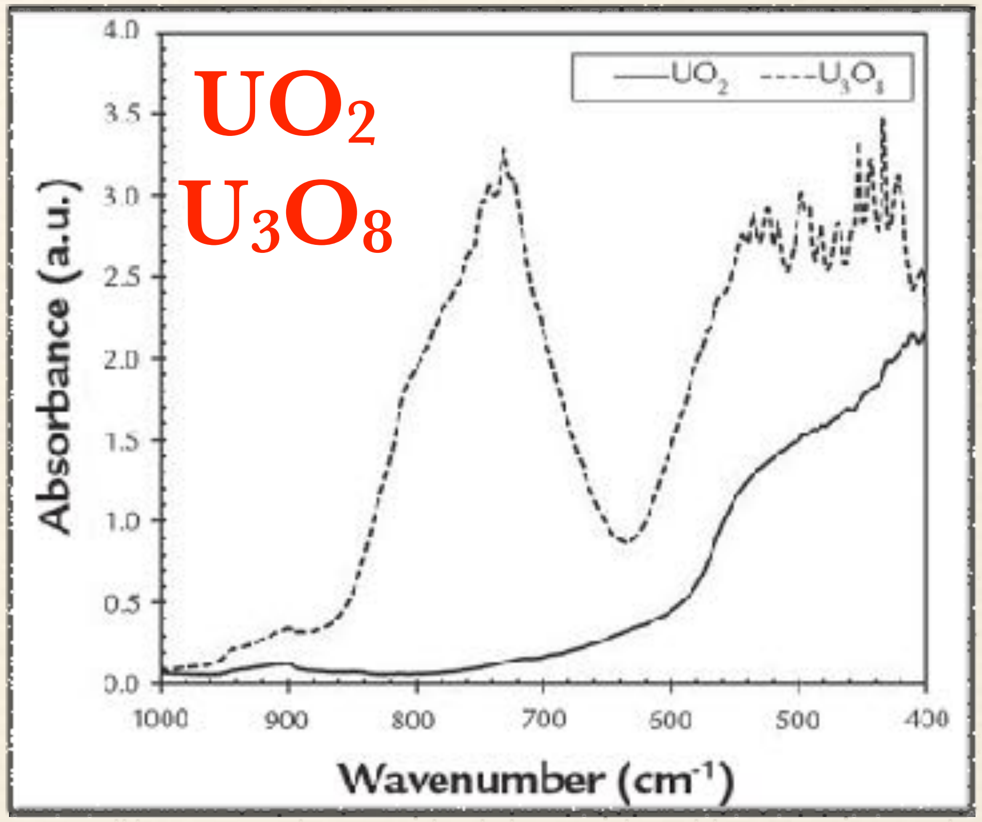


Eu

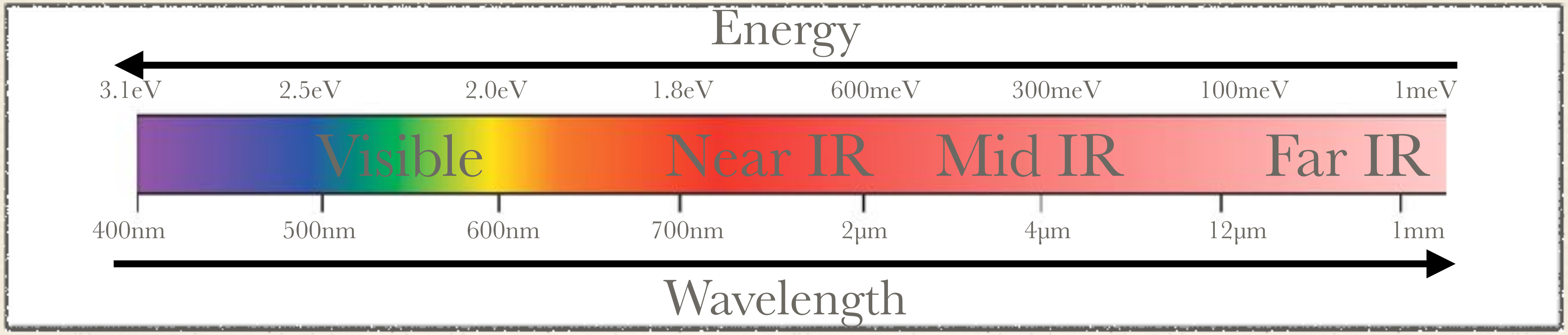


A2u

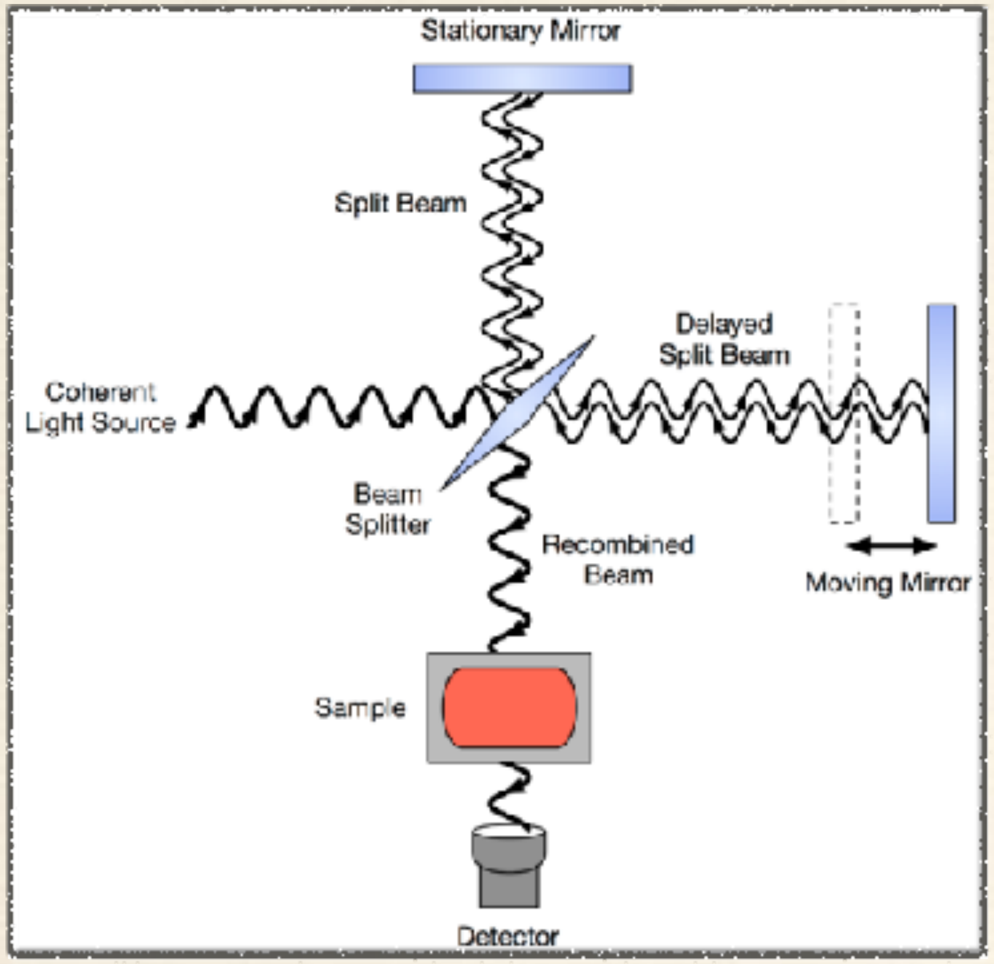
D3d(-3m)	#	1	3	2	-1	-3	md	functions
Mult.	-	1	2	3	1	2	3	·
A_{1g}	Γ_1^+	1	1	1	1	1	1	x^2+y^2, z^2
A_{2g}	Γ_2^+	1	1	-1	1	1	-1	J_z
E_g	Γ_3^+	2	-1	0	2	-1	0	$(x^2-y^2,xy),(xz,yz),(J_x,J_y)$
A_{1u}	Γ_1^-	1	1	1	-1	-1	-1	·
A_{2u}	Γ_2^-	1	1	-1	-1	-1	1	z
E_u	Γ_3^-	2	-1	0	-2	1	0	(x,y)

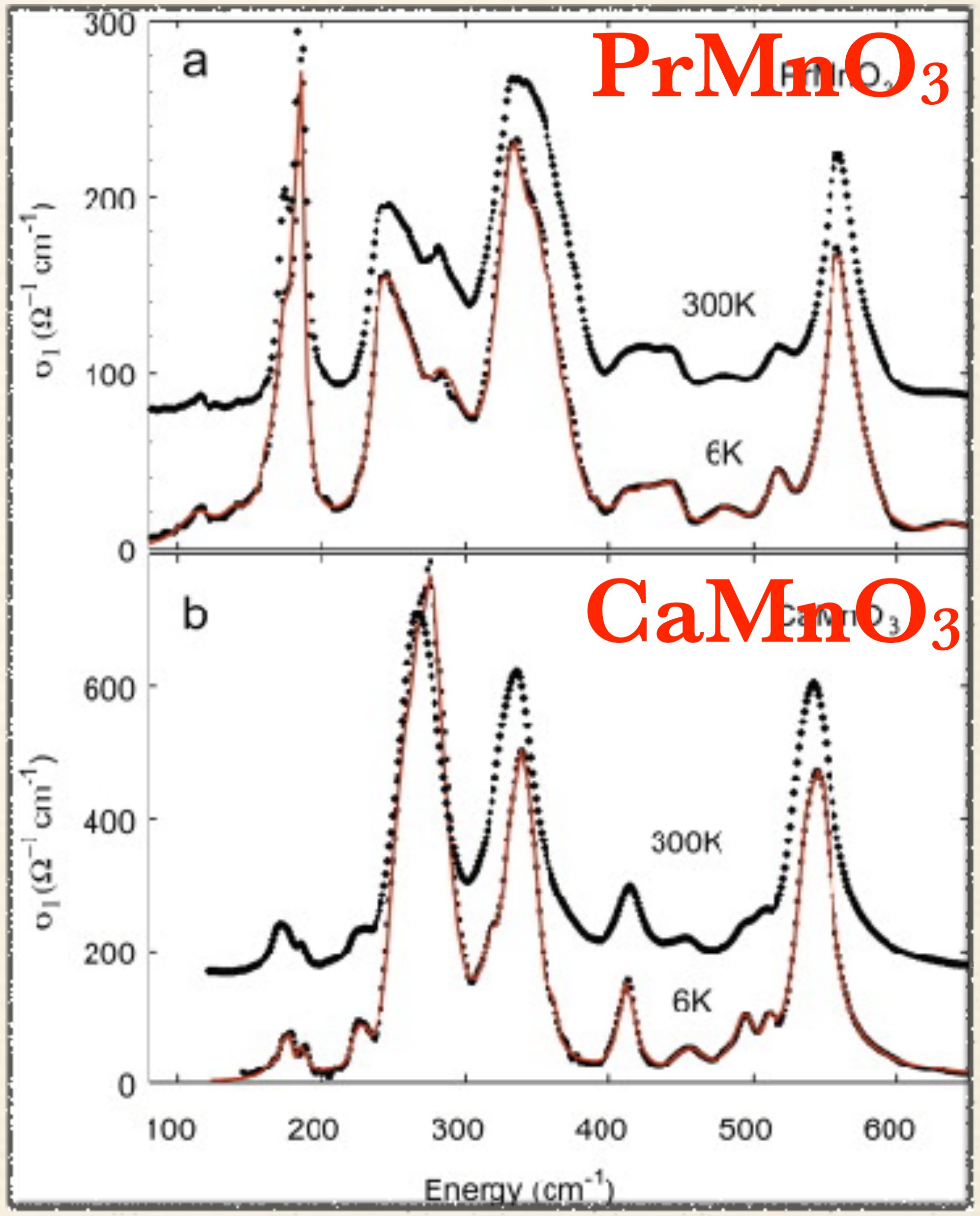


Infrared Spectroscopy



Infrared Spectroscopy





Physica B 405, 45 (2010)

Infrared Spectroscopy

(1) $$n = \sqrt{\epsilon} = n_1 + in_2$$

(2) $$\epsilon = n_1^2 - n_2^2 + i2n_1n_2 = \epsilon_1 + i\frac{4\pi\sigma}{\omega} = \epsilon_1 + i\epsilon_2$$

(3) $$\mathcal{R}(\omega) = \left|\frac{n(\omega)-1}{n(\omega)+1}\right|^2 = \left|r(\omega)e^{i\theta(\omega)}\right|^2 \Rightarrow \quad ln(\mathcal{R}(\omega)) = 2ln(r(\omega))$$

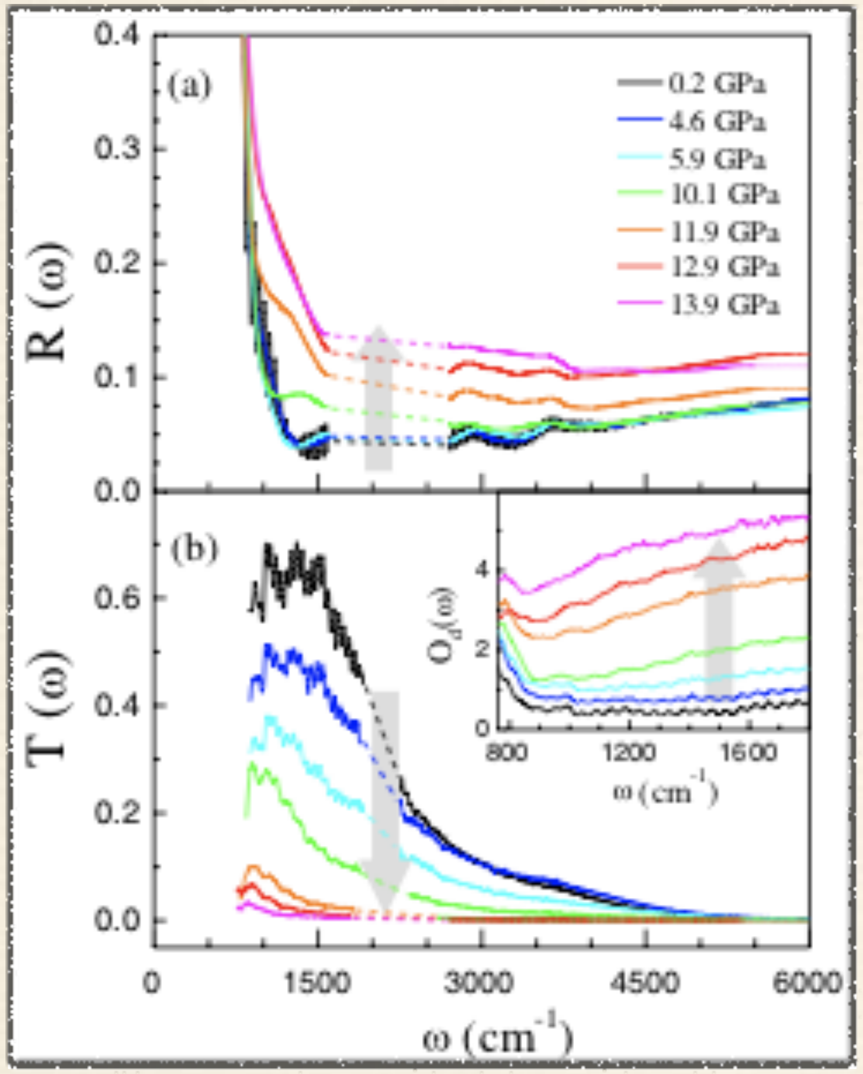
(4) $$r(\omega)e^{i\theta(\omega)} = \frac{n_1(\omega)+in_2(\omega)-1}{n_1(\omega)+in_2(\omega)+1} \Rightarrow \begin{cases} n_1(\omega) = \dfrac{1-r^2(\omega)}{1+r^2(\omega)-2r(\omega)cos(\theta(\omega))} \\ n_2(\omega) = \dfrac{2r(\omega)sin(\theta(\omega))}{1+r^2(\omega)-2r(\omega)cos(\theta(\omega))} \end{cases}$$

(5) Kramers-Krönig $$\Rightarrow \begin{cases} ln(r(\omega)) = \dfrac{2}{\pi}\displaystyle\int_0^\infty \frac{\Omega\theta(\Omega)-\omega\theta(\omega)}{\Omega^2-\omega^2}d\Omega \\ \theta(\omega) = -\dfrac{2\omega}{\pi}\displaystyle\int_0^\infty \frac{ln(r(\Omega))-ln(r(\omega))}{\Omega^2-\omega^2}d\Omega \end{cases}$$

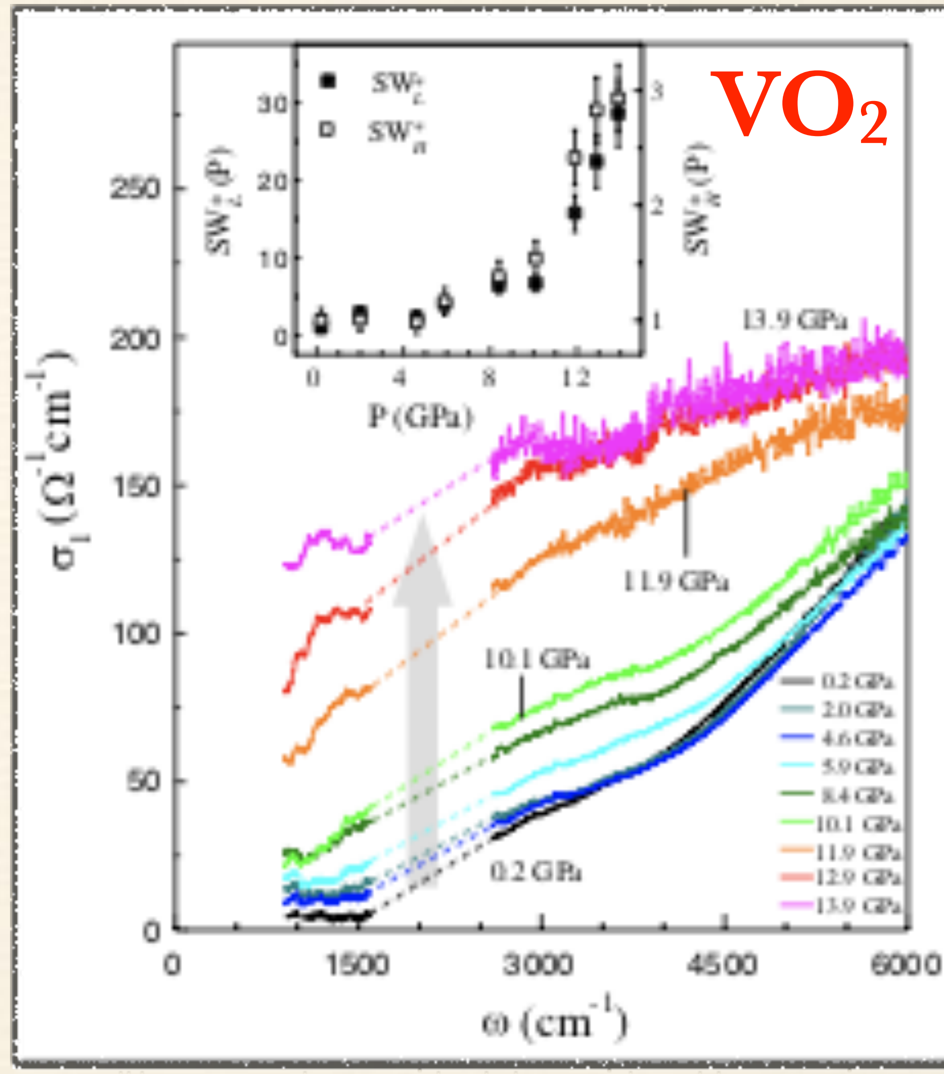
$$\mathcal{R}(\omega) \overset{(3)}{\Rightarrow} ln(r(\omega)) \overset{(5)}{\Rightarrow} [r(\omega),\theta(\omega)] \overset{(4)}{\Rightarrow} [n_1(\omega),n_2(\omega)] \overset{(2)}{\Rightarrow} [\epsilon_1(\omega),\epsilon_2(\omega)]$$

Infrared Spectroscopy

Metal-Insulator Transition



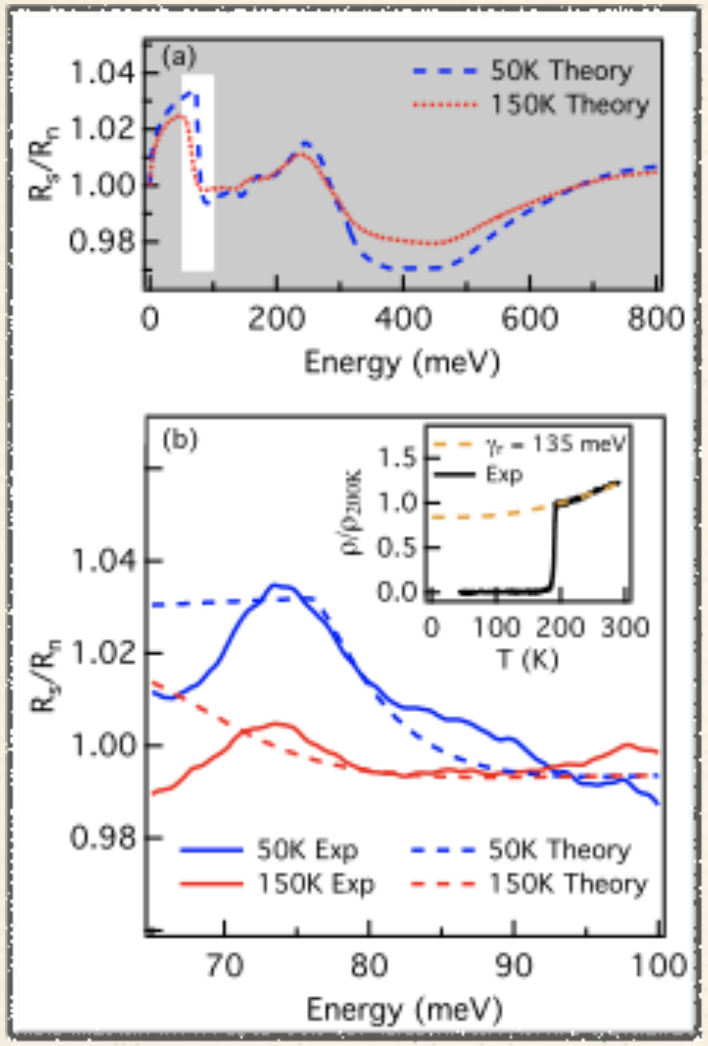
PRL 98, 196406 (2007)



Metallization under pressure

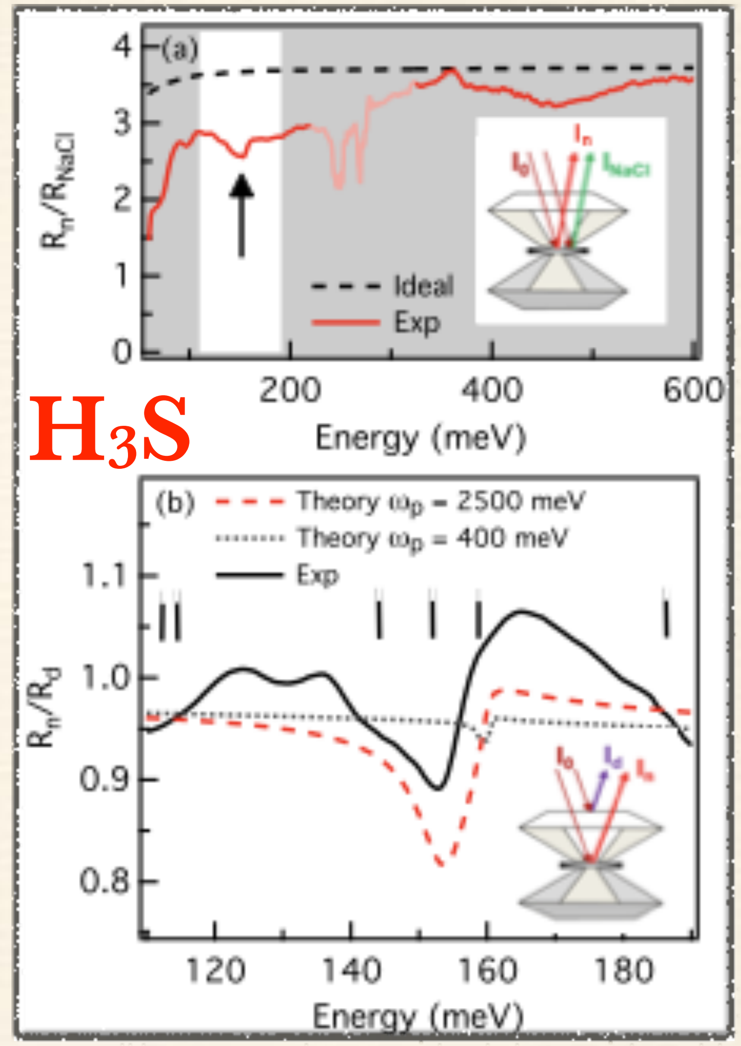
Infrared Spectroscopy

Superconductivity



Nature Physics 13, 859 (2017)

H_3S



Drop of reflectance above the gap

New energy scale for the gap : 73meV

Strong electron-phonon coupling

Infrared Spectroscopy

Summary

- Sensitive to « translational » modes u
- Complementary with Raman for centrosymmetric crystals (g modes : Raman, u modes : IR)
- Polarization dependance of absorption
- Give access to :
  - Gap energy scale
  - Optical phonon modes
  - Optical conductivity, dielectric constant

X-Ray Absorption Spectroscopy

Selection rule

Interaction light-electron :

$$\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r}) + \frac{q^2}{m_e c^2}\vec{A}^2$$

$$\vec{A} = A\vec{\epsilon}e^{-i\vec{k}\vec{r}} = A\vec{\epsilon}(1 - i\vec{k}.\vec{r} + ...)$$

First order in **p**.**A** : dipole operator : $\mathcal{V} \propto \vec{p}.\vec{\epsilon}$

$\Delta L = 1 \qquad \Delta S = 0$

Second order in **p**.**A** : quadrupole operator : $\mathcal{V} \propto -i\left(\vec{p}.\vec{\epsilon}\right)\left(\vec{k}.\vec{r}\right)$

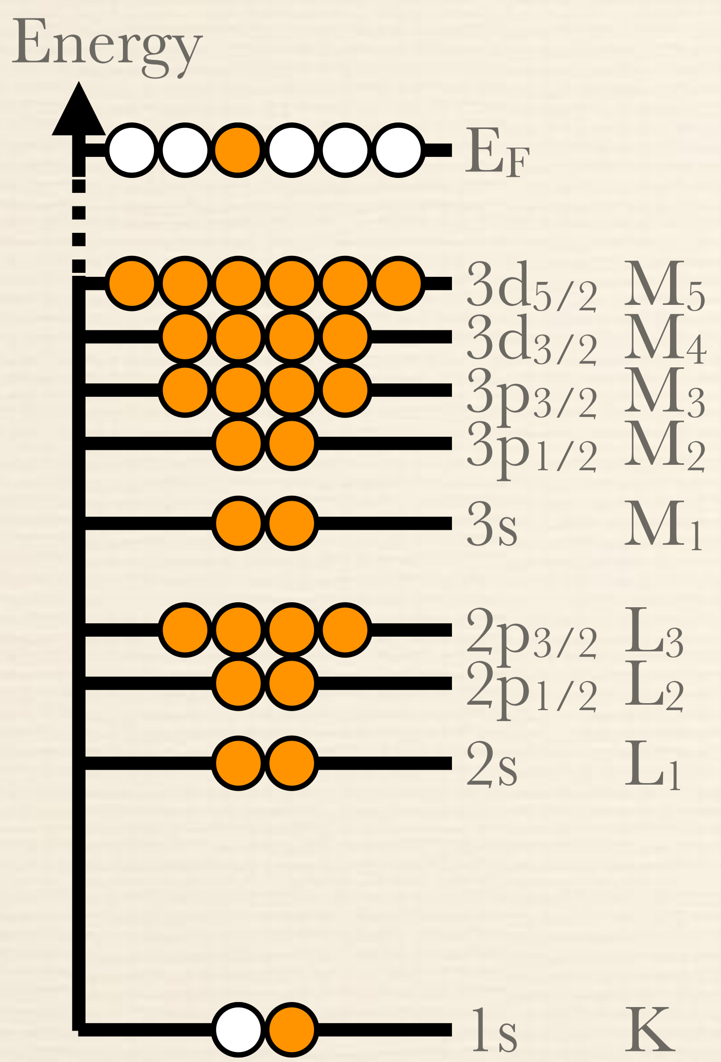
$\Delta L = 0, 2$

Only at high energy (typically more than ~7keV)

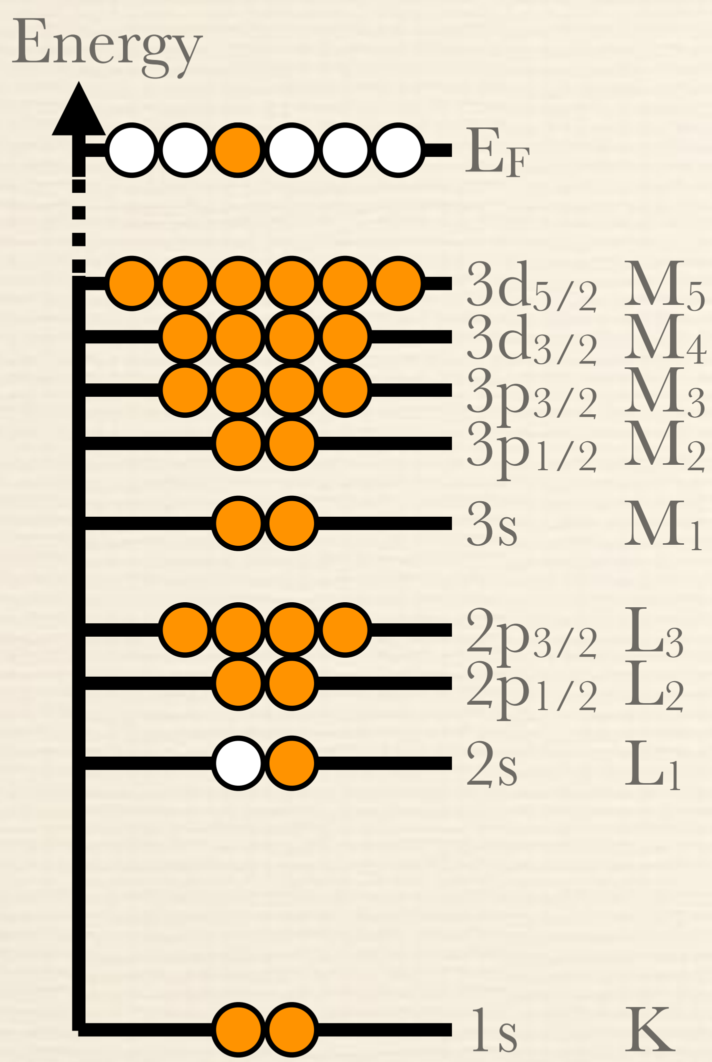
X-Ray Absorption Spectroscopy

Core-hole Spectroscopy

Creation of a 1s core hole : K-edge



X-Ray Absorption Spectroscopy

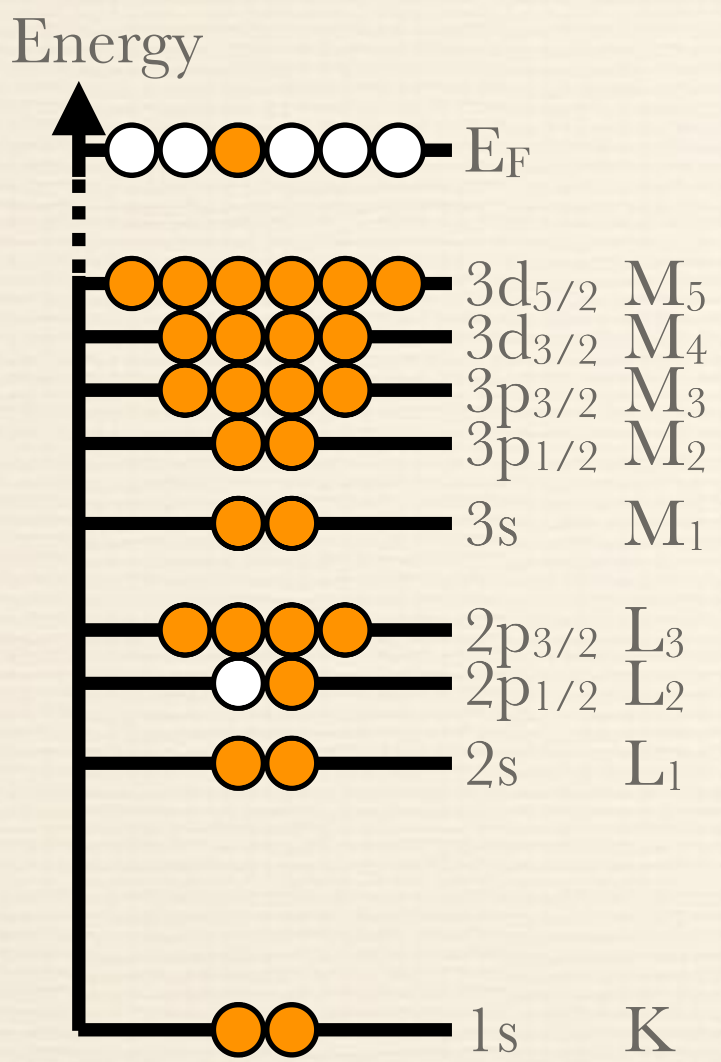


Core-hole Spectroscopy

Creation of a 1s core hole : K-edge
Creation of a 2s core hole : L_1-edge

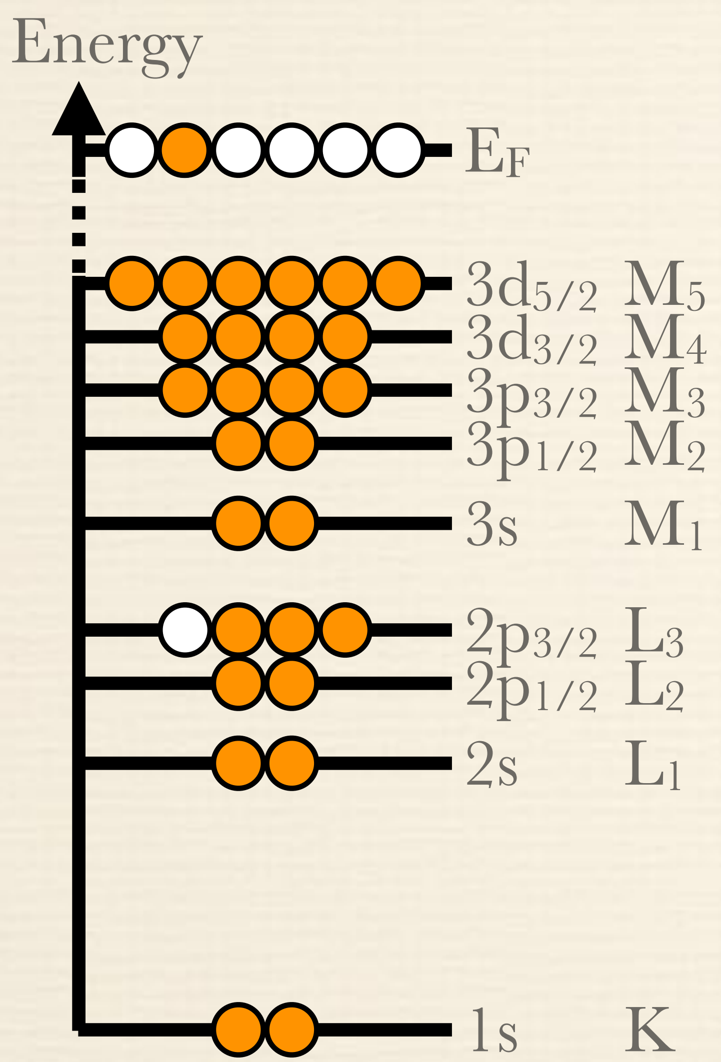
X-Ray Absorption Spectroscopy

Core-hole Spectroscopy



Creation of a 1s core hole : K-edge
Creation of a 2s core hole : L_1-edge
Creation of a $2p_{1/2}$ core hole : L_2-edge

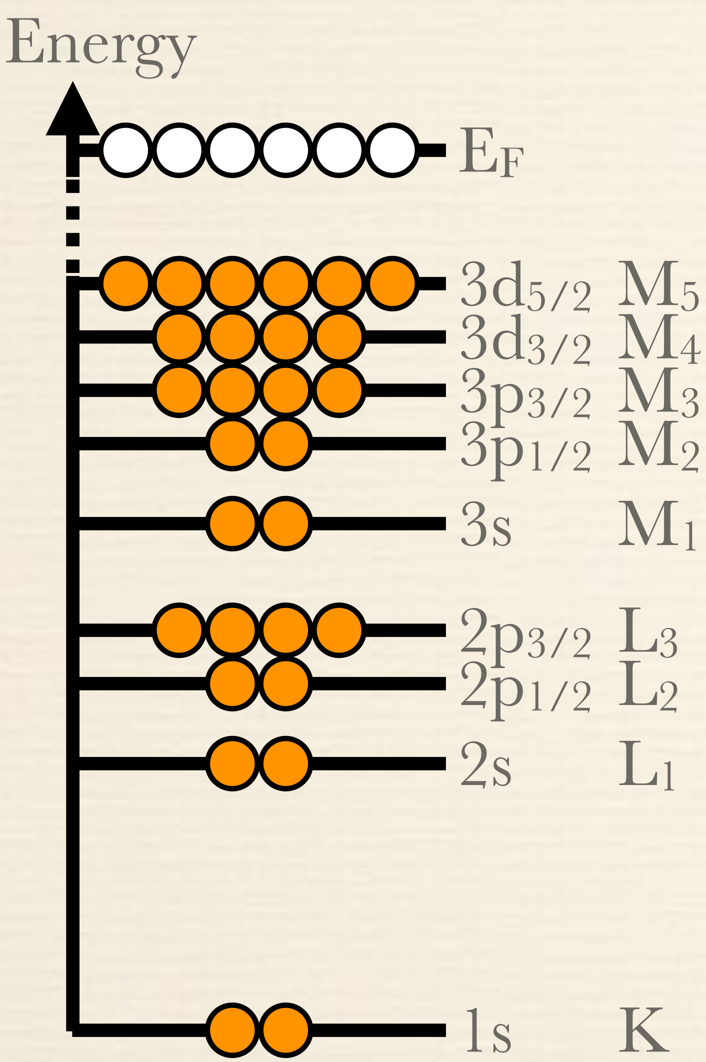
X-Ray Absorption Spectroscopy



Core-hole Spectroscopy

Creation of a 1s core hole : K-edge
Creation of a 2s core hole : L_1-edge
Creation of a $2p_{1/2}$ core hole : L_2-edge
Creation of a $2p_{3/2}$ core hole : L_3-edge

X-Ray Absorption Spectroscopy



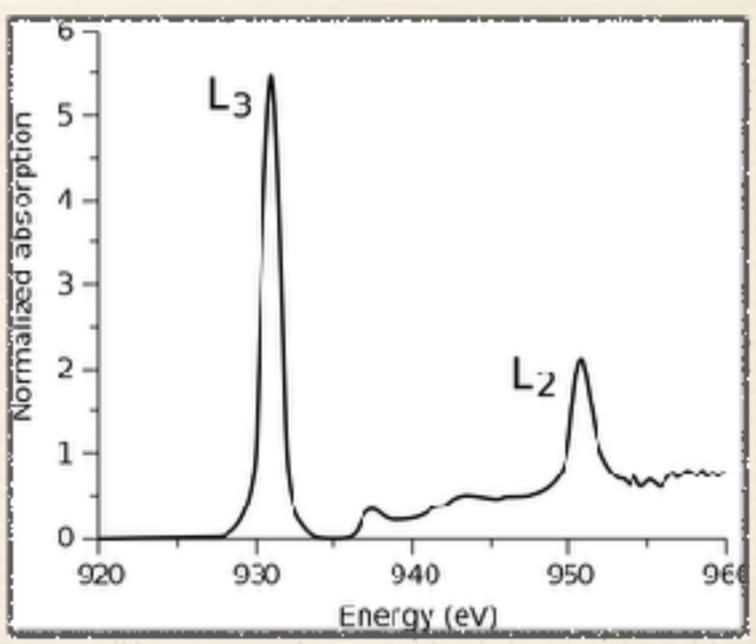
Core-hole Spectroscopy

Creation of a 1s core hole : K-edge
Creation of a 2s core hole : L_1-edge
Creation of a $2p_{1/2}$ core hole : L_2-edge
Creation of a $2p_{3/2}$ core hole : L_3-edge

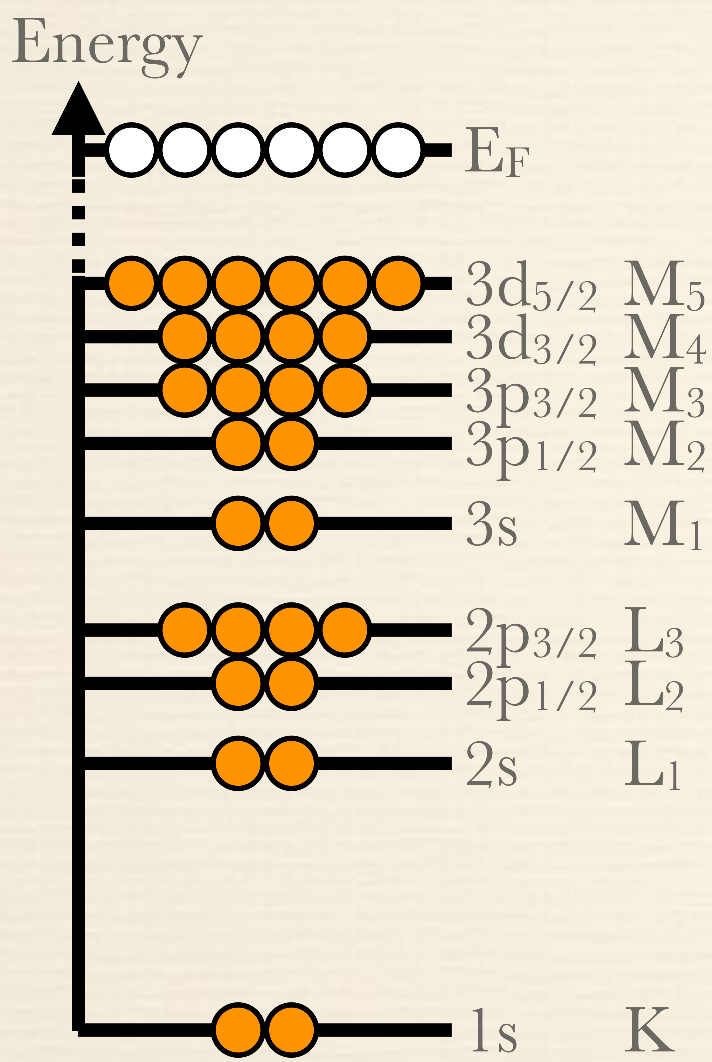
Edges energy is element specific :

Cu K-edge : 8 979 eV

Cu L_1-edge : 1 097 eV
Cu L_2-edge : 952 eV
Cu L_3-edge : 932 eV



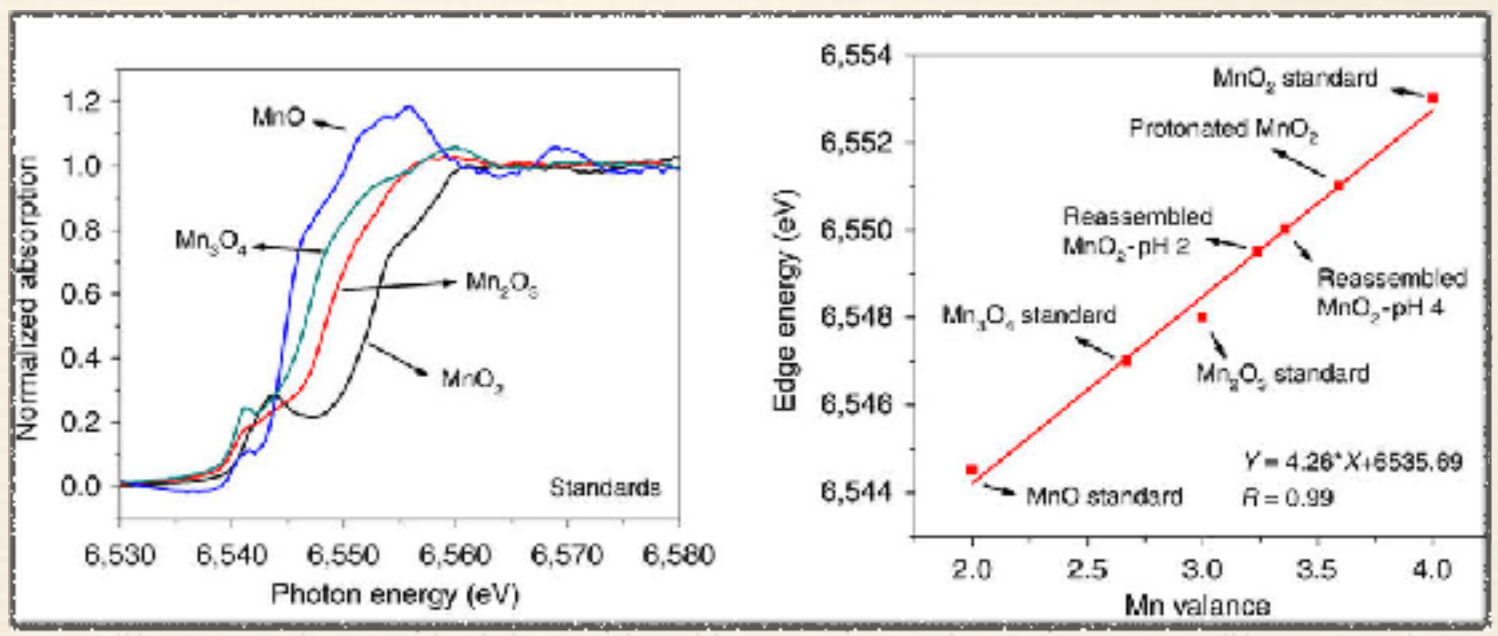
X-Ray Absorption Spectroscopy



Core-hole Spectroscopy

Creation of a 1s core hole : K-edge
Creation of a 2s core hole : L_1-edge
Creation of a $2p_{1/2}$ core hole : L_2-edge
Creation of a $2p_{3/2}$ core hole : L_3-edge

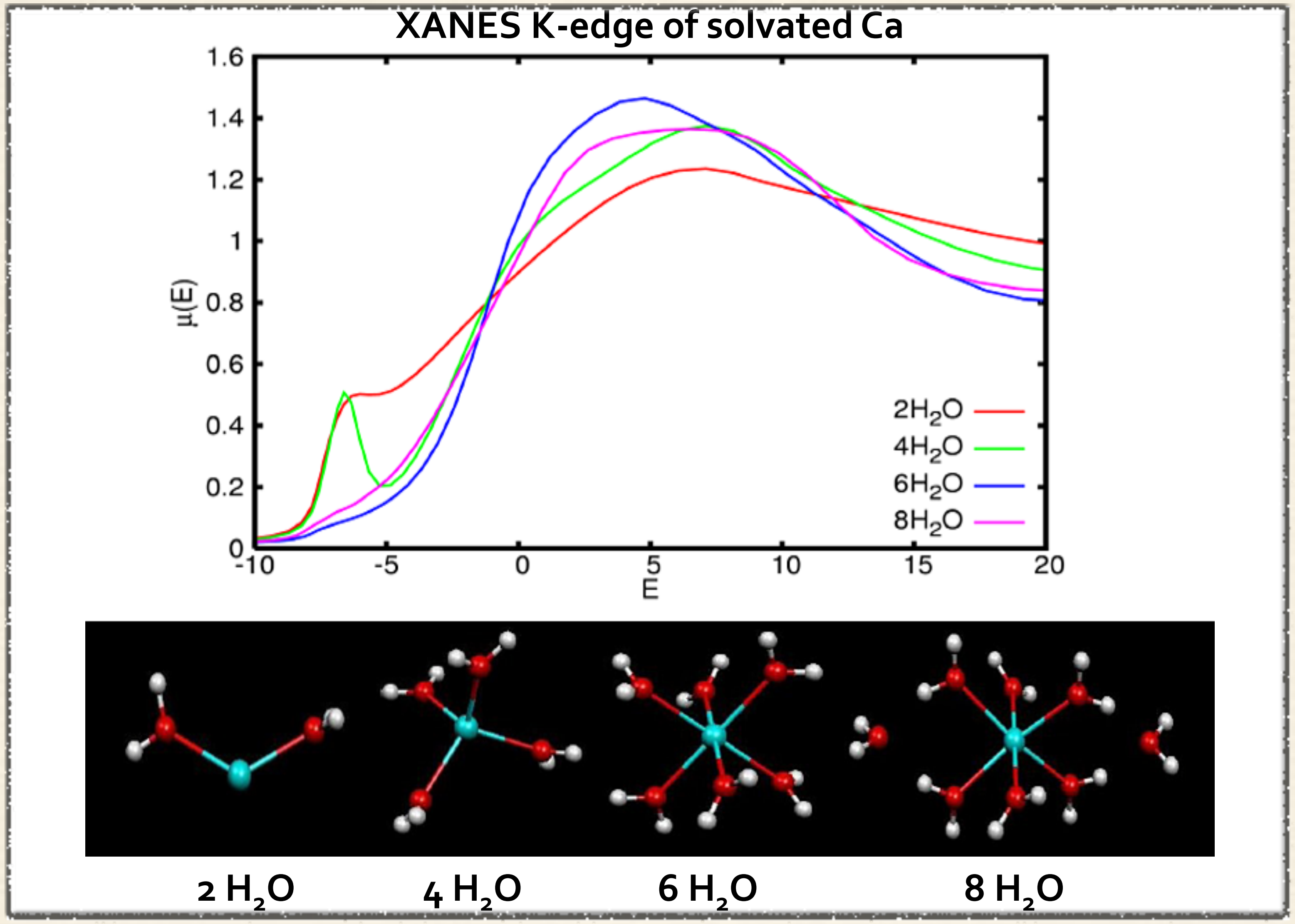
Edges energy is oxydation-state specific :



Nature Com. 8, 14559 (2017)

X-Ray Absorption Spectroscopy

Atom environment

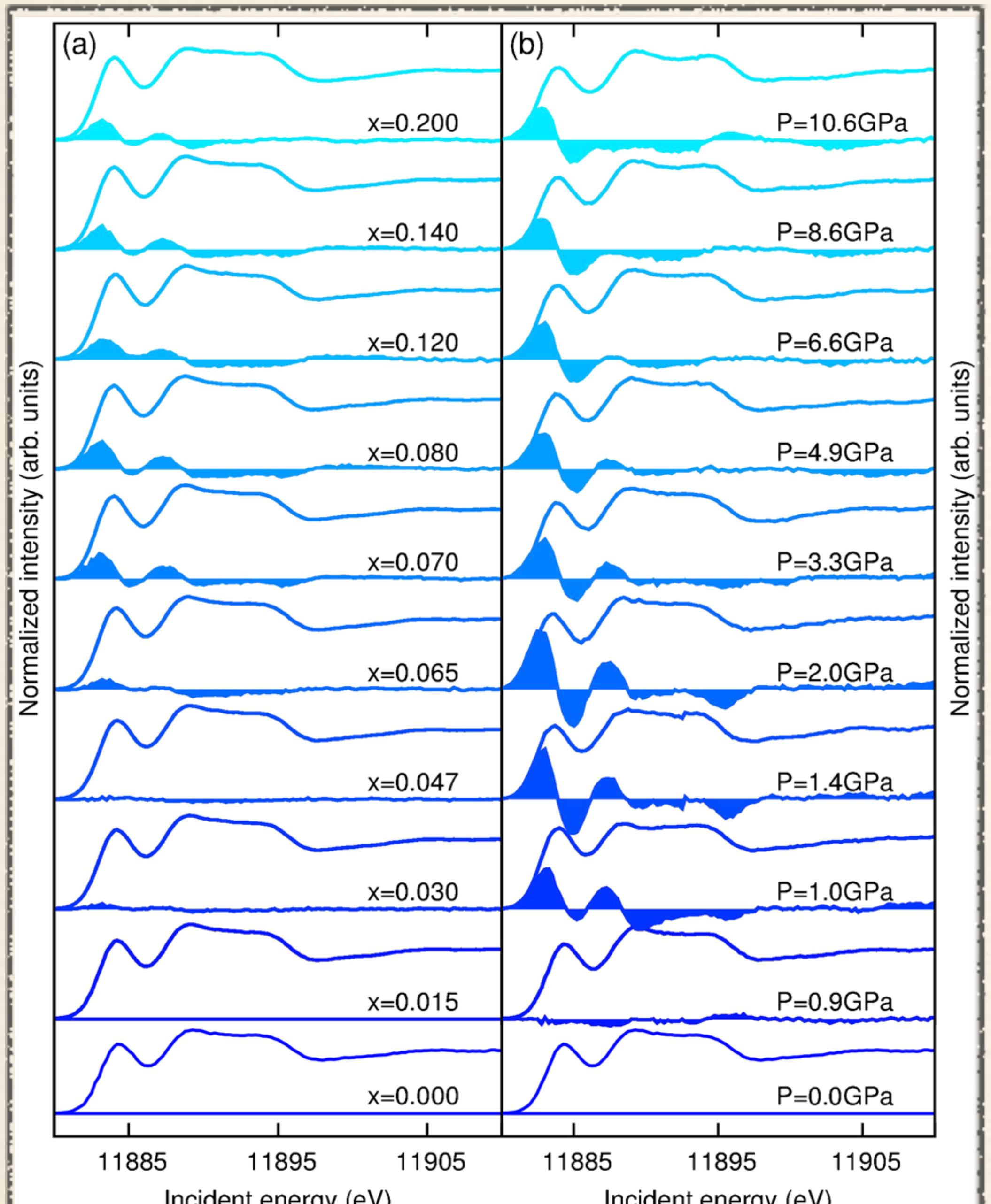


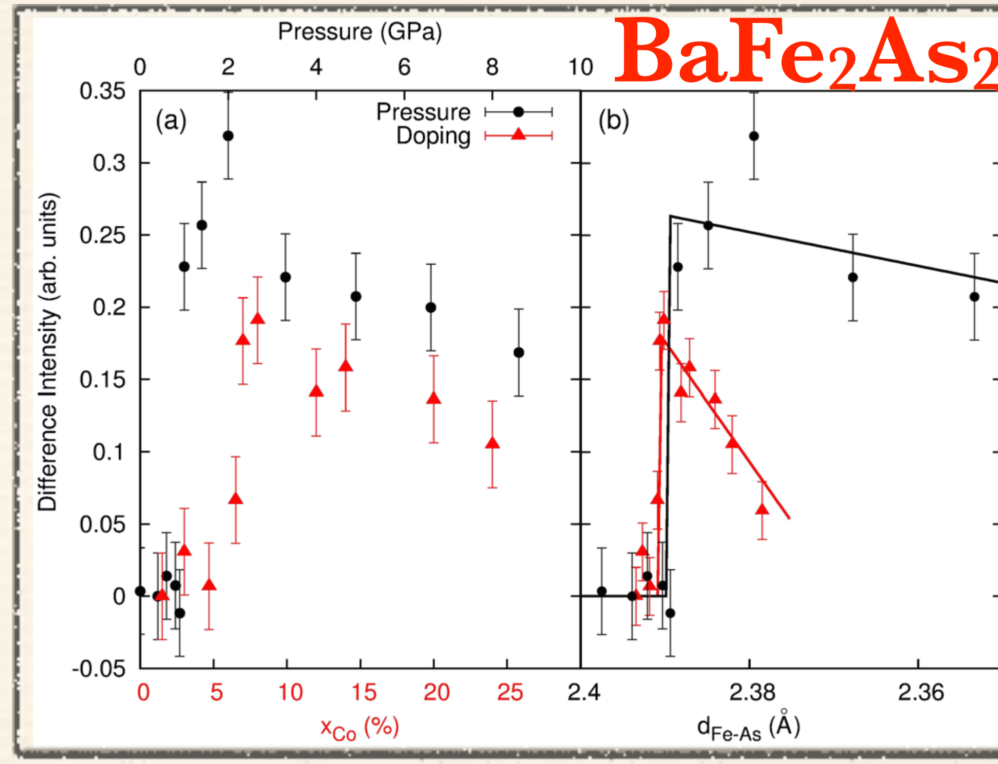
Environment change the spectra shape

Enhancement of pre-edge peak for non centrosymmetric sites

X-Ray Absorption Spectroscopy

Superconductivity





PRL 114, 177001 (2015)

As K-edge. 1s —> 4p

As p orbital involvement in phase transition : ($d_{Fe}+p_{As}$)

X-Ray Absorption Spectroscopy

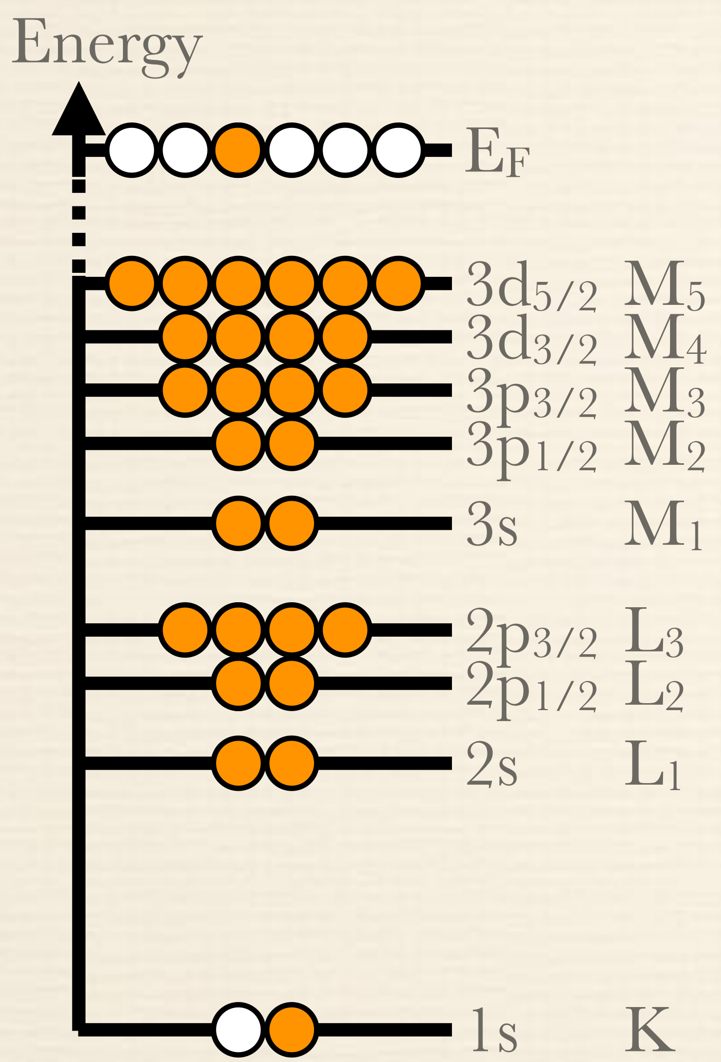
Summary

- Chemical/Element selectivity
- Orbital selectivity (via energy and polarization)
- Give access to :
  - Direct empty DOS for K-edge
  - Information on DOS for L-edge (but more tricky…)
  - Symmetry of the absorbing atom site
- Beyond this lecture : polarization effects, Charge Transfer Multiplet (L-edge)

Resonant Inelastic X-ray Scattering

Emission lines

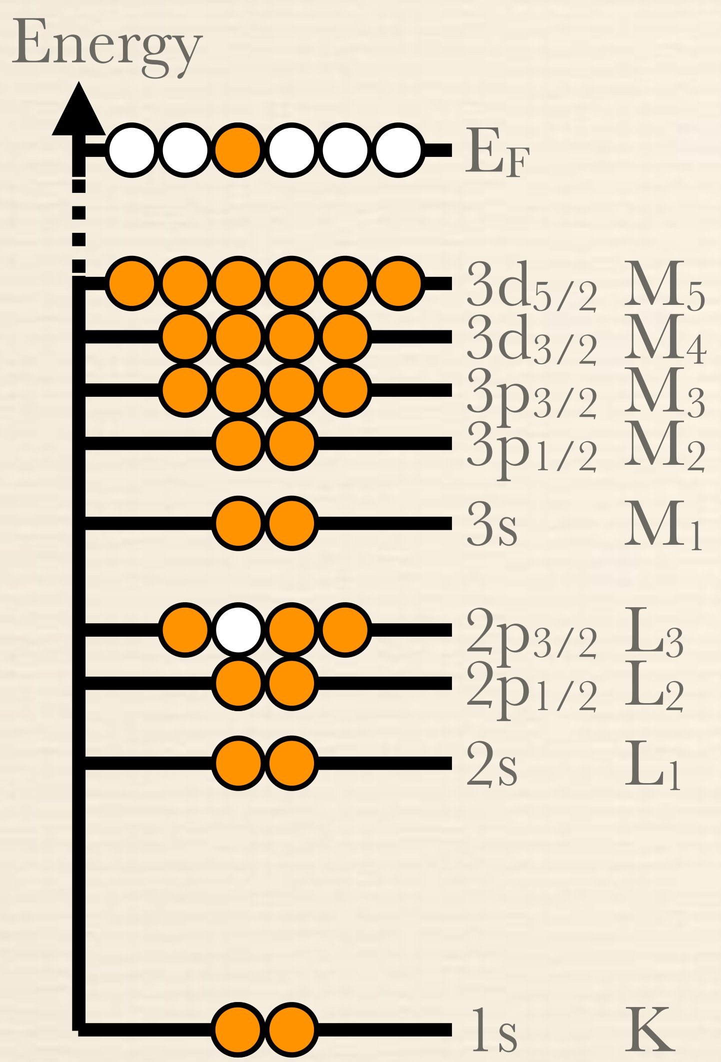
$K_{\alpha 1}$: $2p_{3/2}$ —> 1s



Resonant Inelastic X-ray Scattering

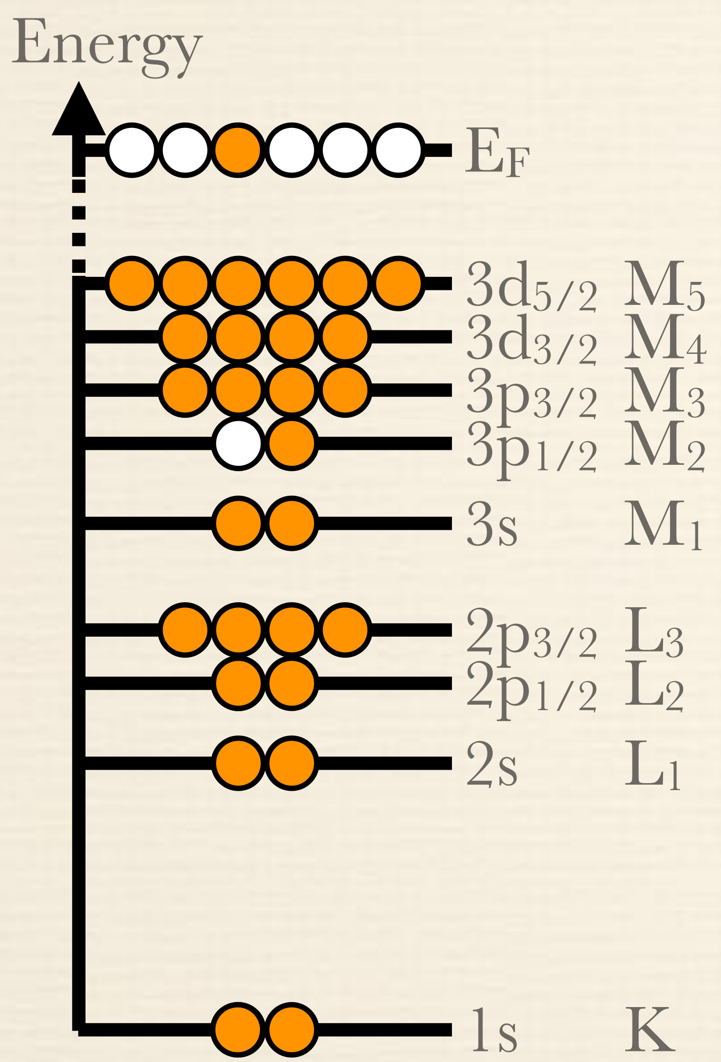
Emission lines

$K_{\alpha 1}$: $2p_{3/2}$ —> 1s



Resonant Inelastic X-ray Scattering

Emission lines



$K_{\alpha 1}$: $2p_{3/2}$ —> 1s

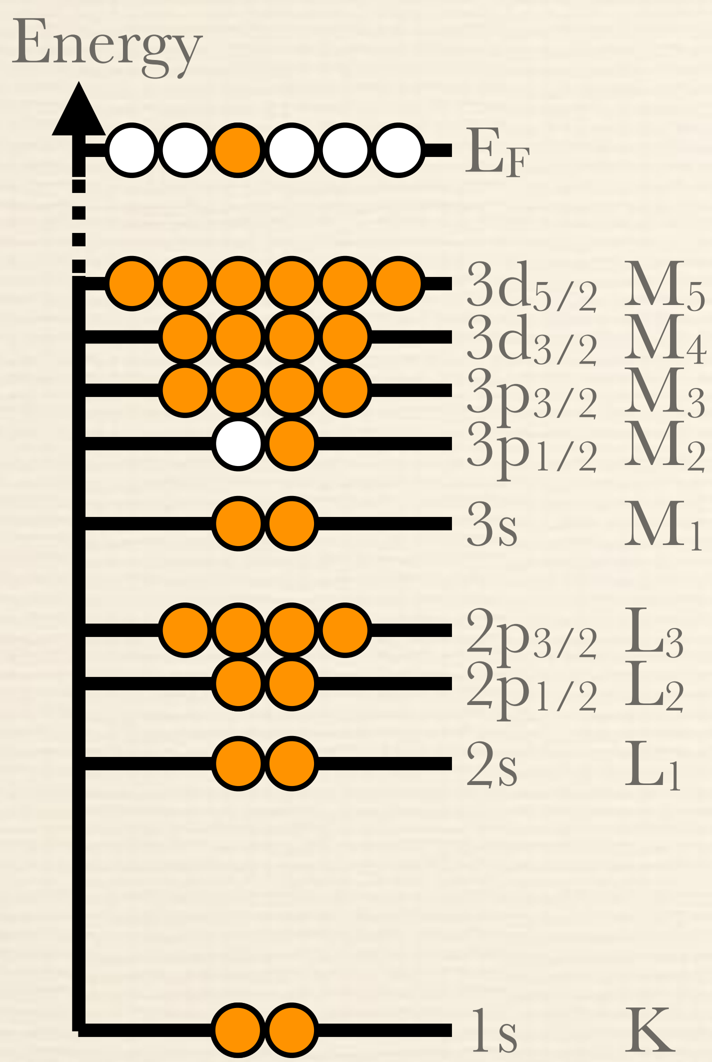
$K_{\alpha 2}$: $2p_{1/2}$ —> 1s

$K_{\beta 1}$: $3p_{3/2}$ —> 1s

$K_{\beta 3}$: $3p_{1/2}$ —> 1s

Resonant Inelastic X-ray Scattering

Emission lines



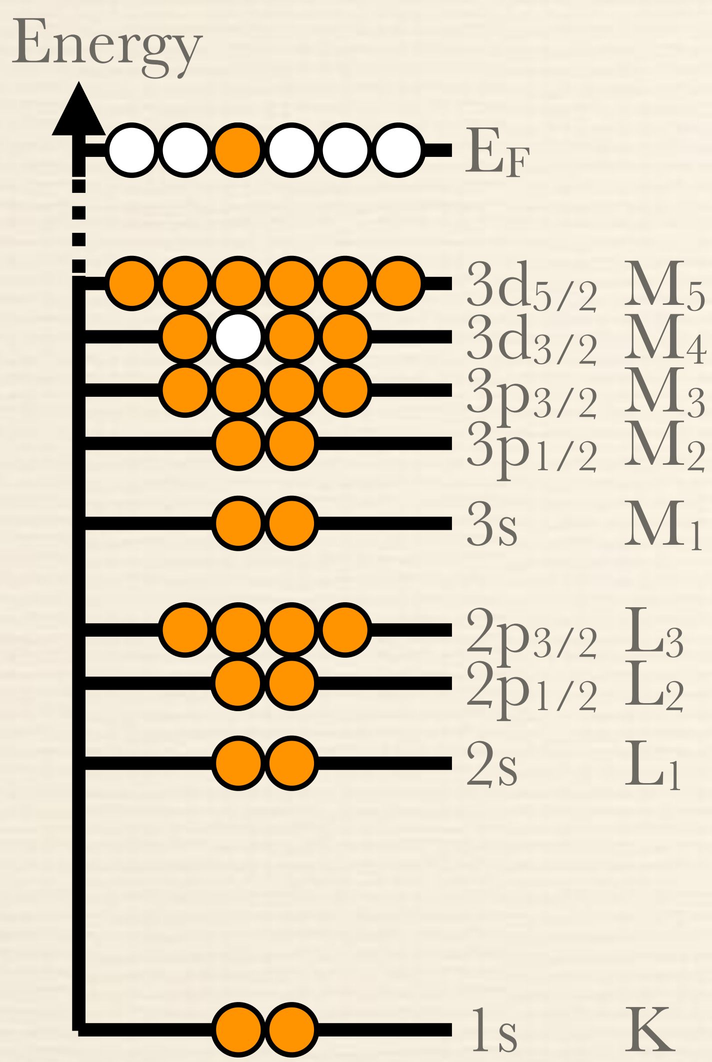
$K_{\alpha 1}$: $2p_{3/2}$ —> 1s
$K_{\alpha 2}$: $2p_{1/2}$ —> 1s
$K_{\beta 1}$: $3p_{3/2}$ —> 1s
$K_{\beta 3}$: $3p_{1/2}$ —> 1s

Emission energy is element specific :

Cu $K_{\alpha 1}$: 8 048 eV
Cu $K_{\alpha 2}$: 8 028 eV

Cu $K_{\beta 1,3}$: 8 905eV

Resonant Inelastic X-ray Scattering



Emission lines

$K_{\alpha1}$: $2p_{3/2}$ —> 1s
$K_{\alpha2}$: $2p_{1/2}$ —> 1s
$K_{\beta1}$: $3p_{3/2}$ —> 1s
$K_{\beta3}$: $3p_{1/2}$ —> 1s

$L_{\alpha1}$: $3d_{5/2}$ —> $2p_{3/2}$
$L_{\alpha2}$: $3d_{3/2}$ —> $2p_{3/2}$
$L_{\beta1}$: $3d_{3/2}$ —> $2p_{1/2}$

Emission energy is element specific :

Cu $K_{\alpha1}$: 8 048 eV
Cu $K_{\alpha2}$: 8 028 eV
Cu $K_{\beta1,3}$: 8 905eV

Cu $L_{\alpha1}$: 929 eV
Cu $L_{\alpha2}$: 929 eV
Cu $L_{\beta1}$: 950 eV

Resonant Inelastic X-ray Scattering

2 photons process

Interaction light-electron :

$$\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r}) + \frac{q^2}{m_e c^2}\vec{A}^2$$

Second order :

XAS : $\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r})$ XES : $\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r})$

Intermediate state :

Intermediate state (no photon)

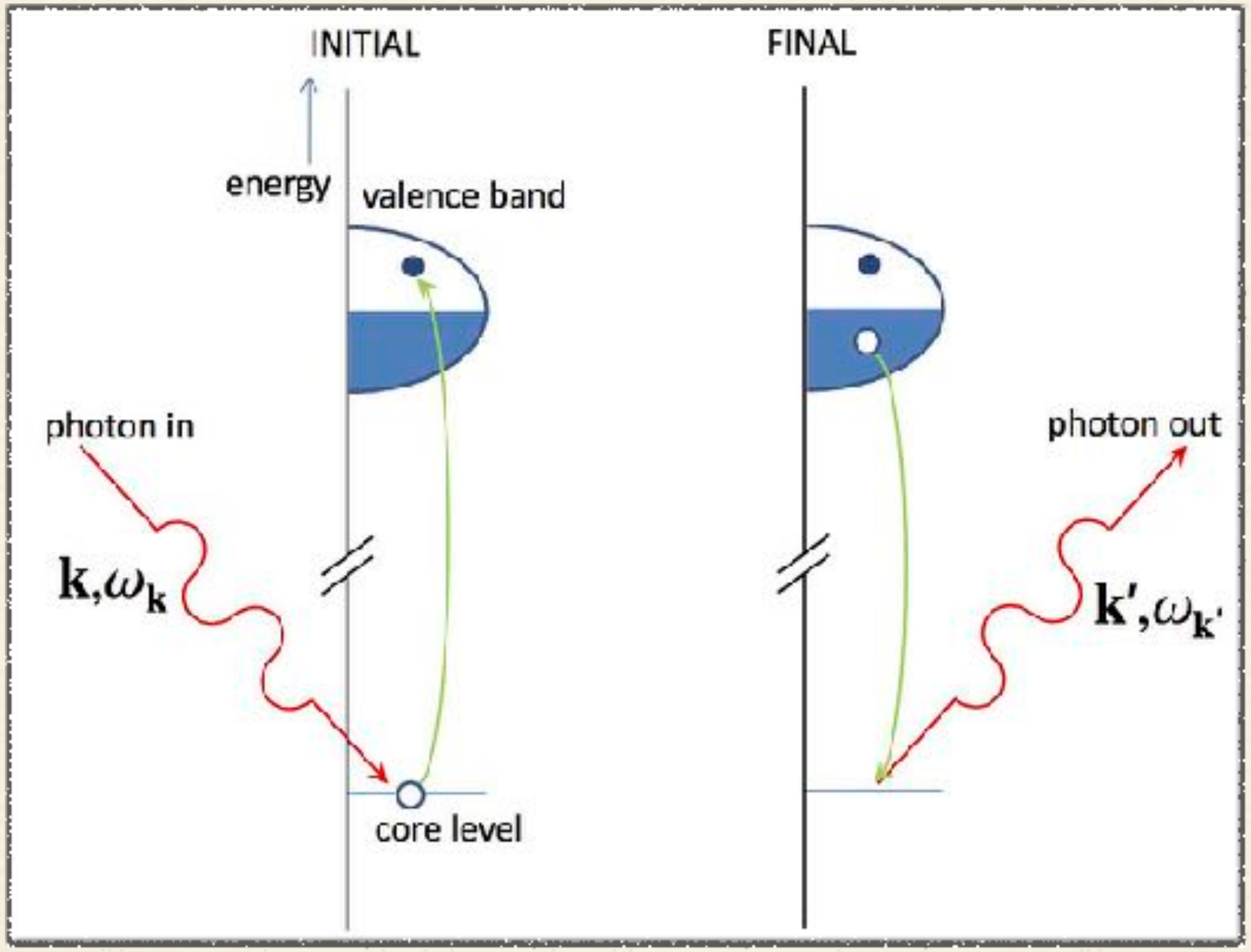
$$\mathcal{V}^{(2)}(\omega) = \left(\frac{q}{m_e c}\right)^2 \sum_n \frac{\langle f|\vec{p}.\vec{A}_f|n\rangle\langle n|\vec{p}.\vec{A}_i|i\rangle}{E_i - E_n + \hbar\omega - i\frac{\Gamma_n}{2}}$$

$$\frac{\partial\sigma}{\partial\Omega_f} = r_0^2 \frac{k_i}{k_f}\left[\vec{\epsilon_i}.\vec{\epsilon_f} + \frac{1}{m}\sum_n \frac{\langle f|\vec{p}.\vec{\epsilon_f}|n\rangle\langle n|\vec{p}.\vec{\epsilon_i}|i\rangle}{E_i - E_n + \hbar\omega - i\frac{\Gamma_n}{2}}\right]^2$$

Dipolar approximation

Resonant Inelastic X-ray Scattering

Direct RIXS

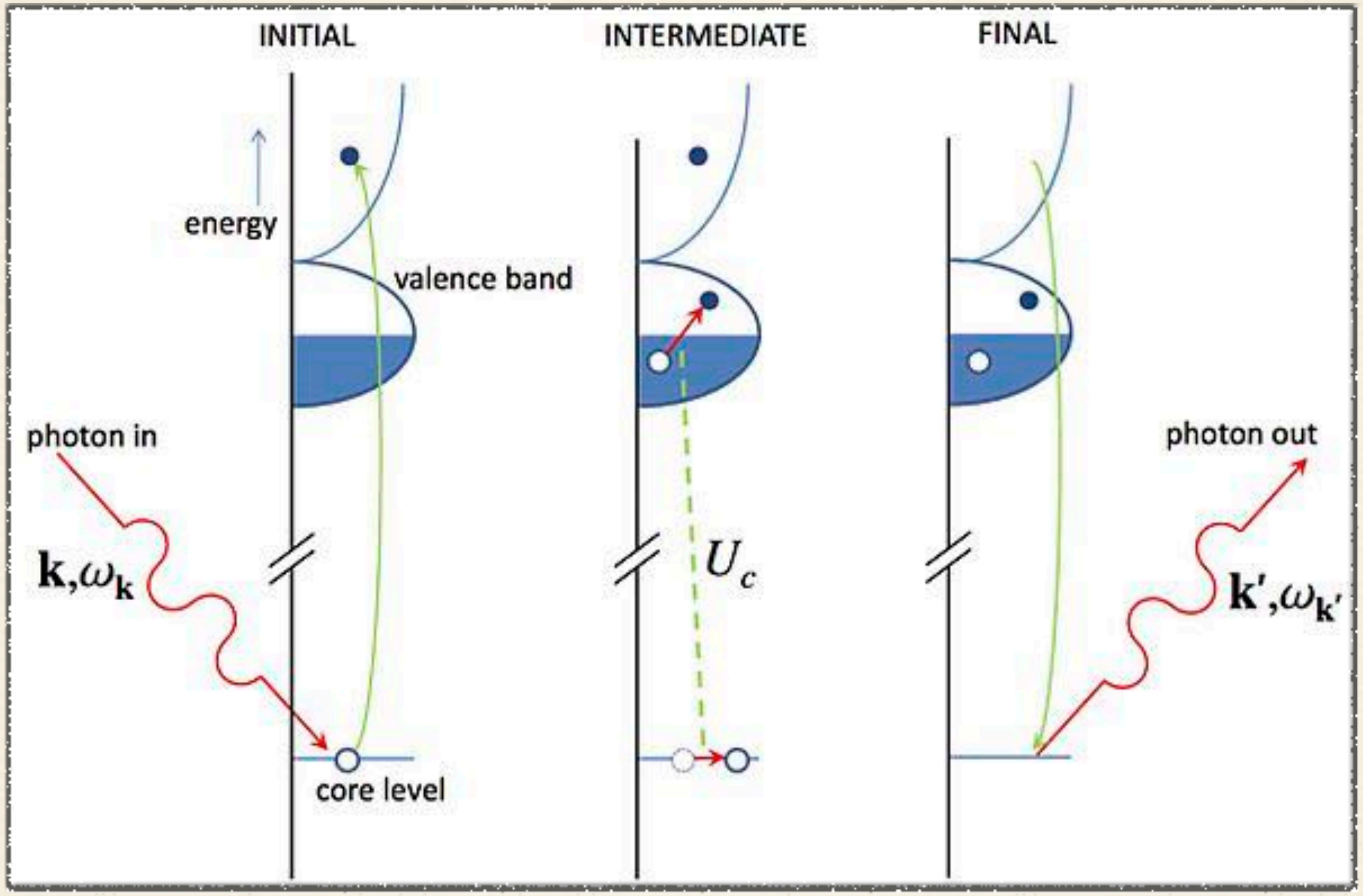


RIXS = XAS + XES

Probes valence and conduction states directly

Resonant Inelastic X-ray Scattering

Indirect RIXS



RIXS = XAS + recombination + XES

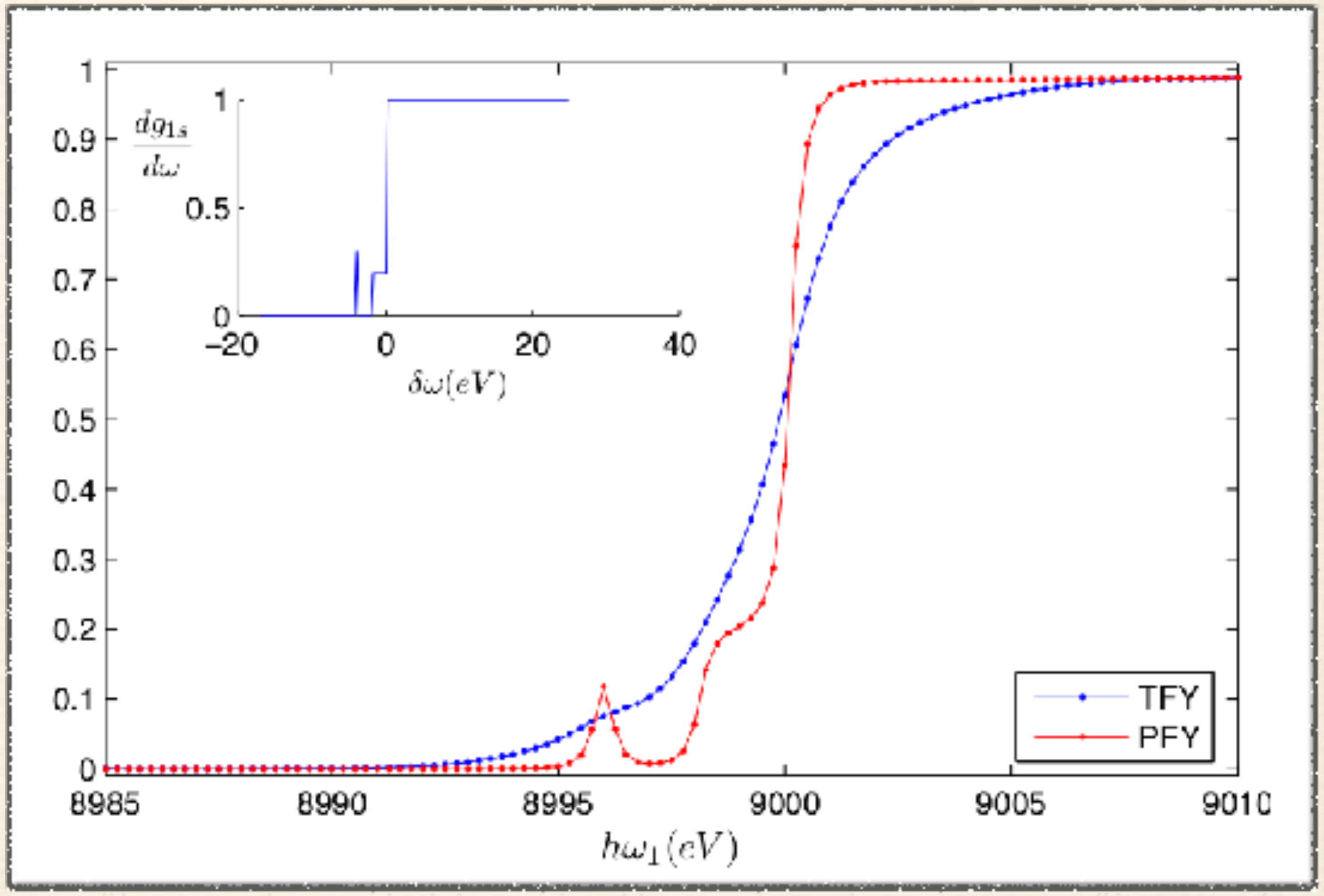
Resonant Inelastic X-ray Scattering

Total and Partial Fluorescence Yield

$$\frac{\partial^2\sigma}{\partial\omega_1\partial\omega_2} = \sum_f \left| \sum_n \frac{\langle f|T_2|n\rangle\langle n|T_1|i\rangle}{E_i - E_n + \hbar\omega_1 - i\frac{\Gamma_n}{2}} \right|^2 \times \frac{\frac{\Gamma_f}{2\pi}}{(E_i - E_f + \hbar\omega_1 - \hbar\omega_2)^2 + \frac{\Gamma_f^2}{4}}$$

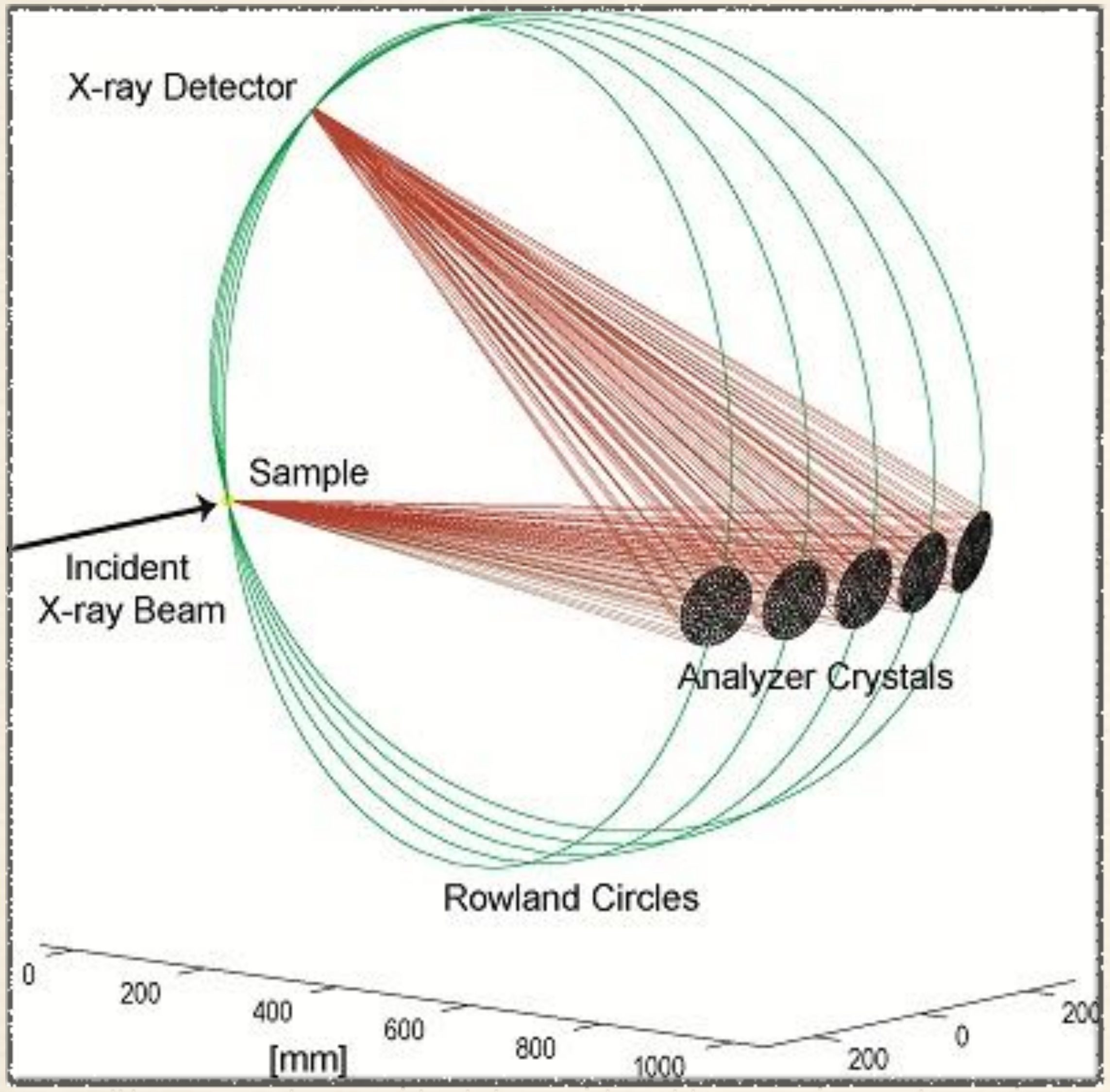
$$\Gamma_{RIXS} = \sqrt{\frac{1}{\Gamma_n^2} + \frac{1}{\Gamma_f^2}}^{\,-1} \approx \Gamma_f$$

$$\Gamma_f << \Gamma_n$$

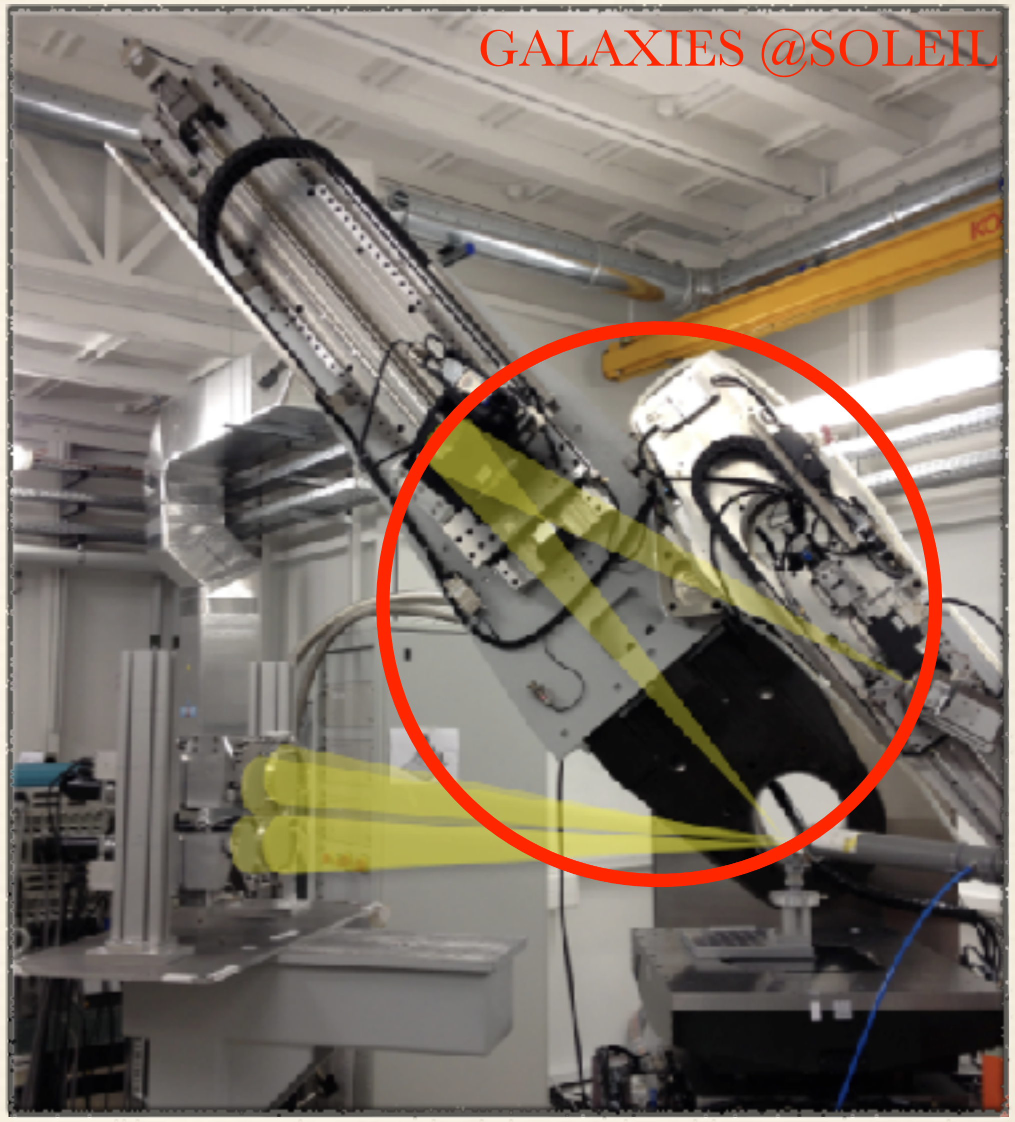


Resonant Inelastic X-ray Scattering

Experimental Setup



Rowland geometry



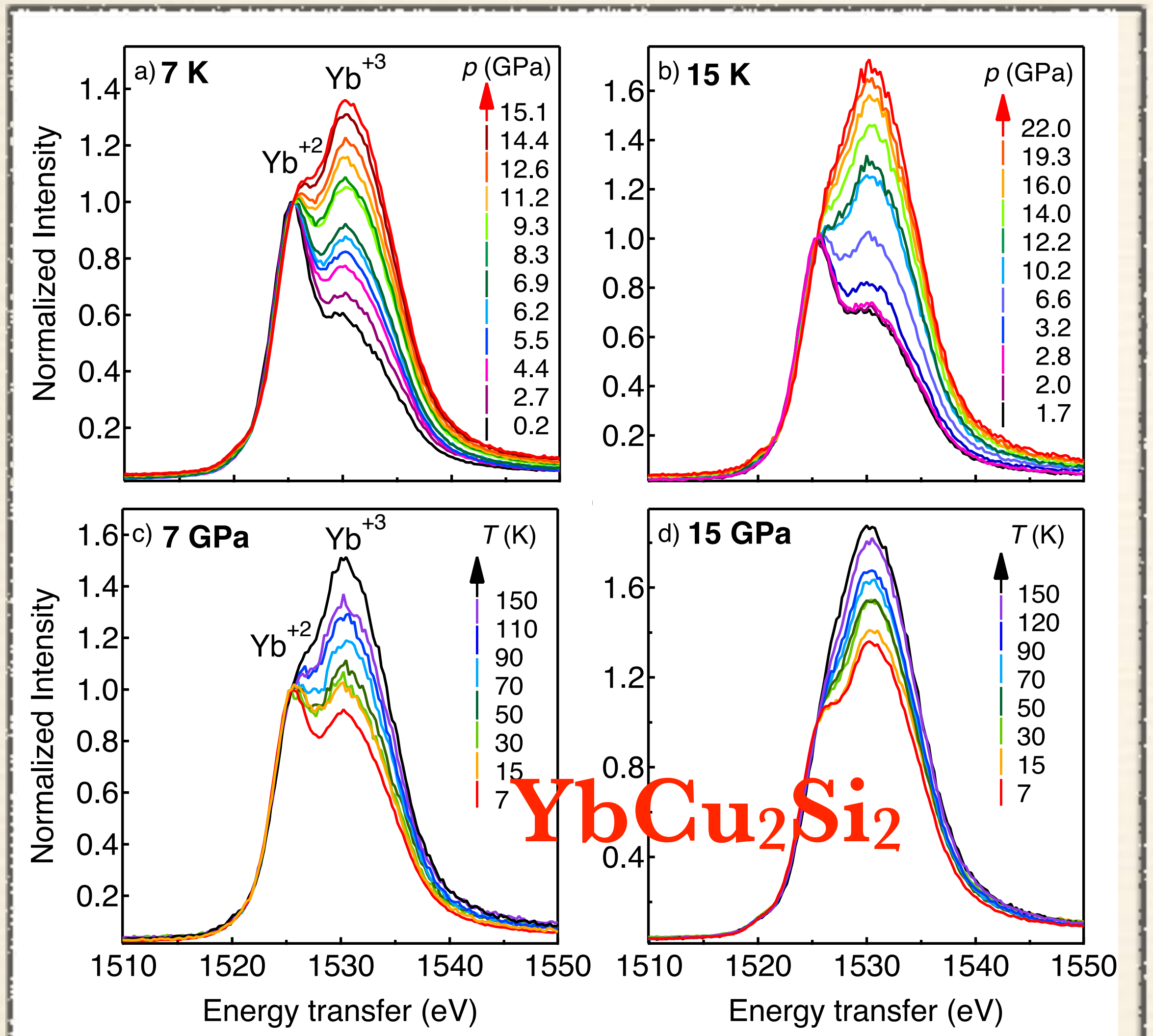
X-ray Diffraction
Probability 0.01

Fluorescence
Probability 0.001

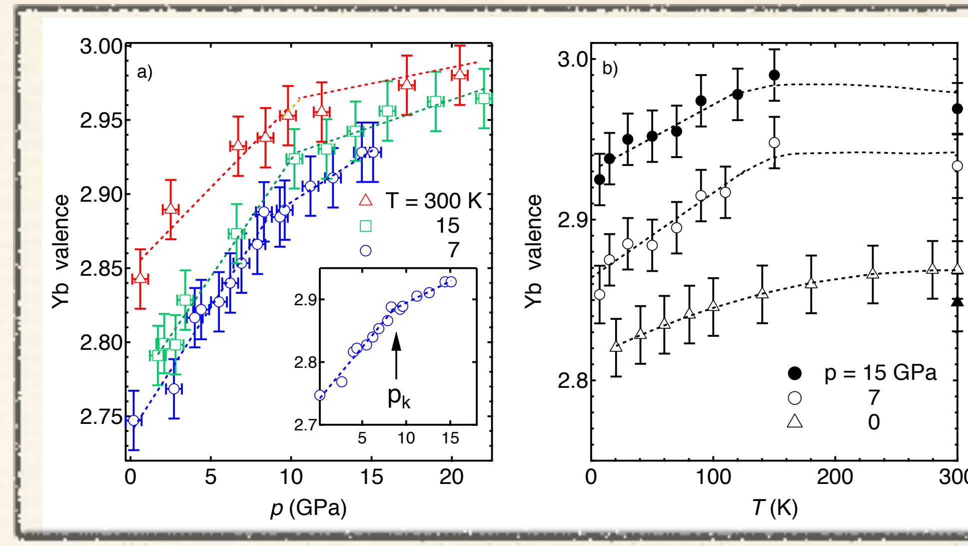
RIXS
Probability 0.00001

Resonant Inelastic X-ray Scattering

Heavy fermion compound



$YbCu_2Si_2$



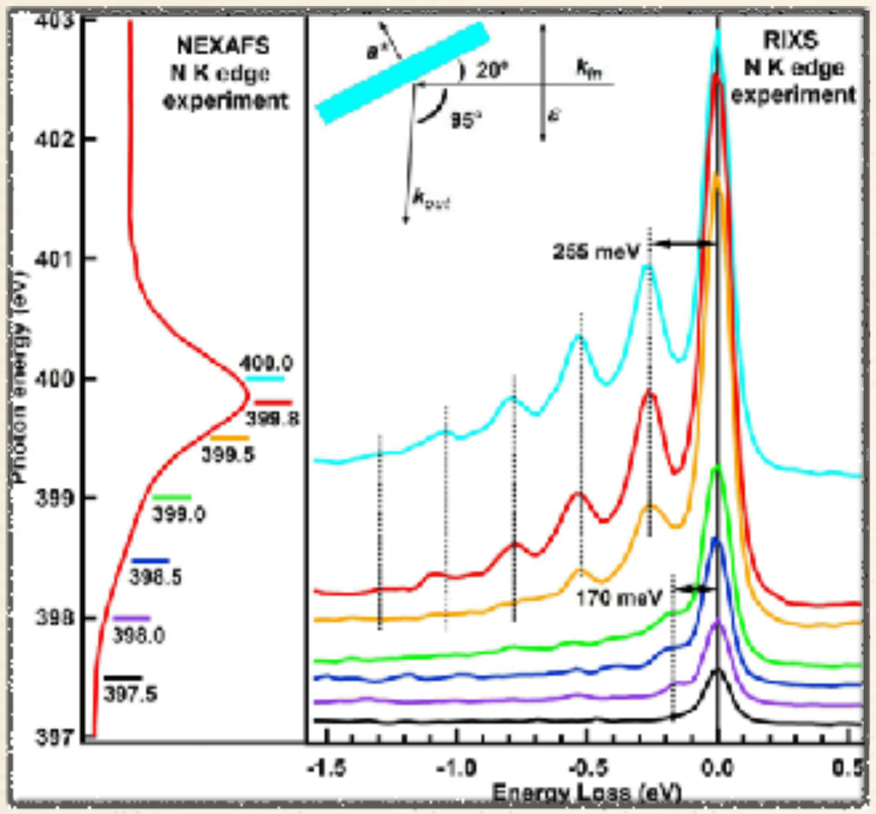
PRB 86, 125104 (2012)

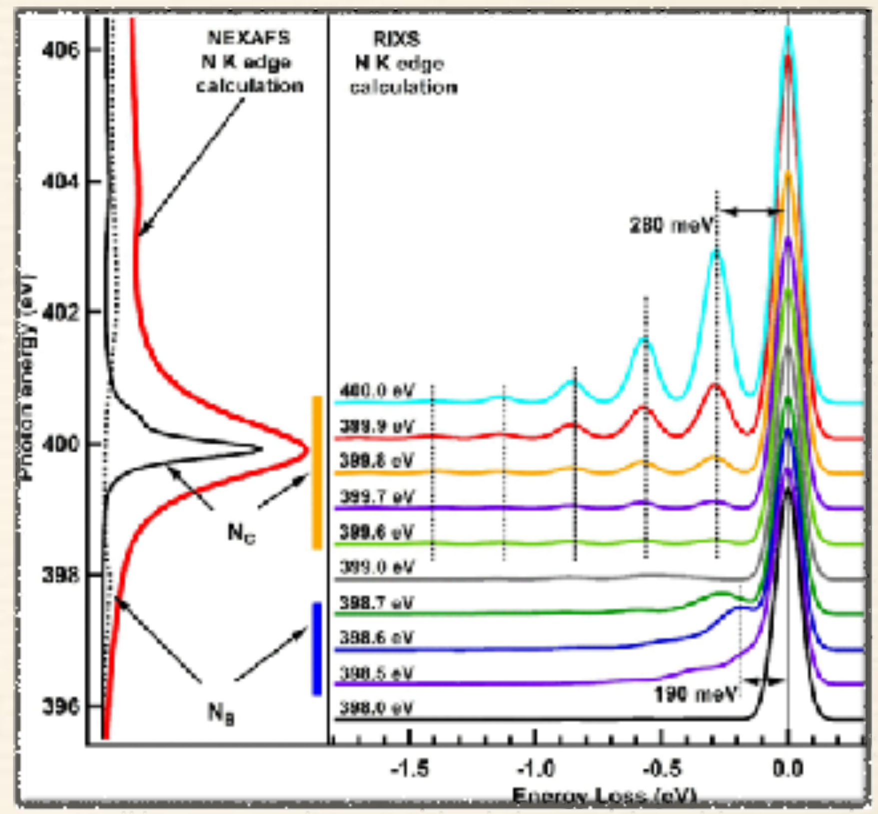
Yb L_3-edge. 2p —> 5d

Valence fluctuations as pairing mechanism ?

Resonant Inelastic X-ray Scattering

Electron-phonon coupling constant





PRB 96, 184303 (2017)

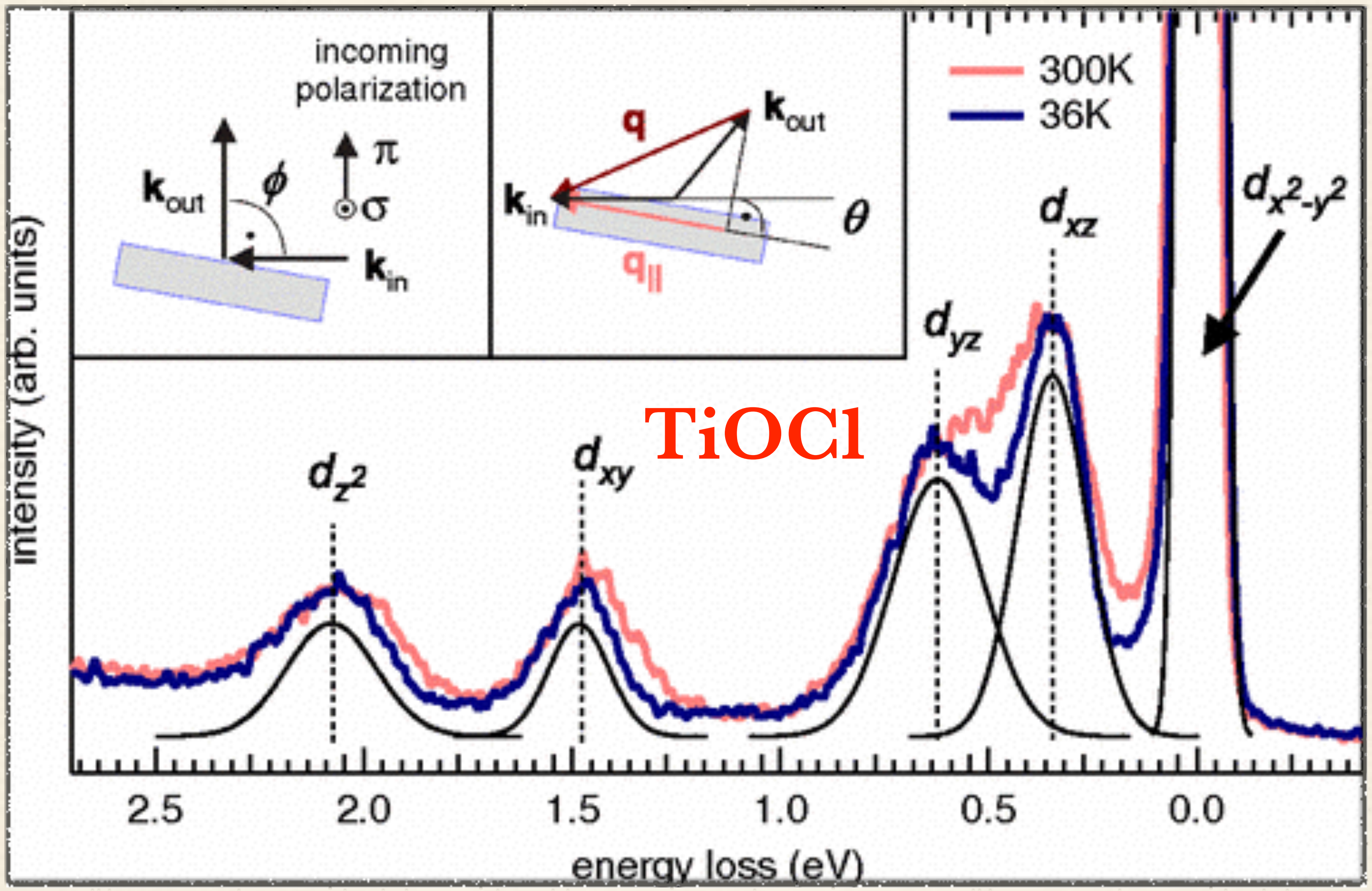
Mode	CN stretching	CN sliding	CN bending
a	1	2	3
crystal [26]	k-ET-Cu		
σ	2100-2140	508-515	195-225
$\hbar\omega$	260-265	63-64	24-28
cluster	$Cu_2(CN)_5H_4$	*calculations*	
σ (6%)	2258	510	200
$\hbar\omega$ (6%)	280	64	25
S (6%)	0.334	0.608	0.235
g (9%)	230	71	17
λ (35%)	0.076	0.032	0.004

Sensitivity to phonons through electron : several harmonics

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

Resonant Inelastic X-ray Scattering

dd excitations



PRL 107, 107402 (2017)

Crystal Field of Ti (3d[1]) L3-edge (450eV)

Resonant Inelastic X-ray Scattering

Summary

- Chemical/Element selectivity
- Orbital selectivity (Incident and Final Energy, Polarization)
- Small sample size required ($< 1mm^2$)
- Gives access to:
  - electron-phonon coupling
  - valence state and fluctuations
  - dd excitations
- Beyond this lecture : Polarization effects, Multipolar extension, Interference terms…

End of part I

(but part II is coming…)

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Université Paris-Sud, Orsay