Resonant Inelastic X-ray Scattering (RIXS): Introduction and Applications

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Credits for some slides to V. Bisogni, S. Fan, C. Mazzoli, I. Jarrige, C. Occhialini

Outline:

- Some view of light matter interaction
- X-ray Sources
- Specifics of Resonant Inelastic X-Ray Scattering
- Examples of RIXS studies

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- **Some view of light matter interaction**
- X-ray Sources
- Specifics of Resonant Inelastic X-Ray Scattering
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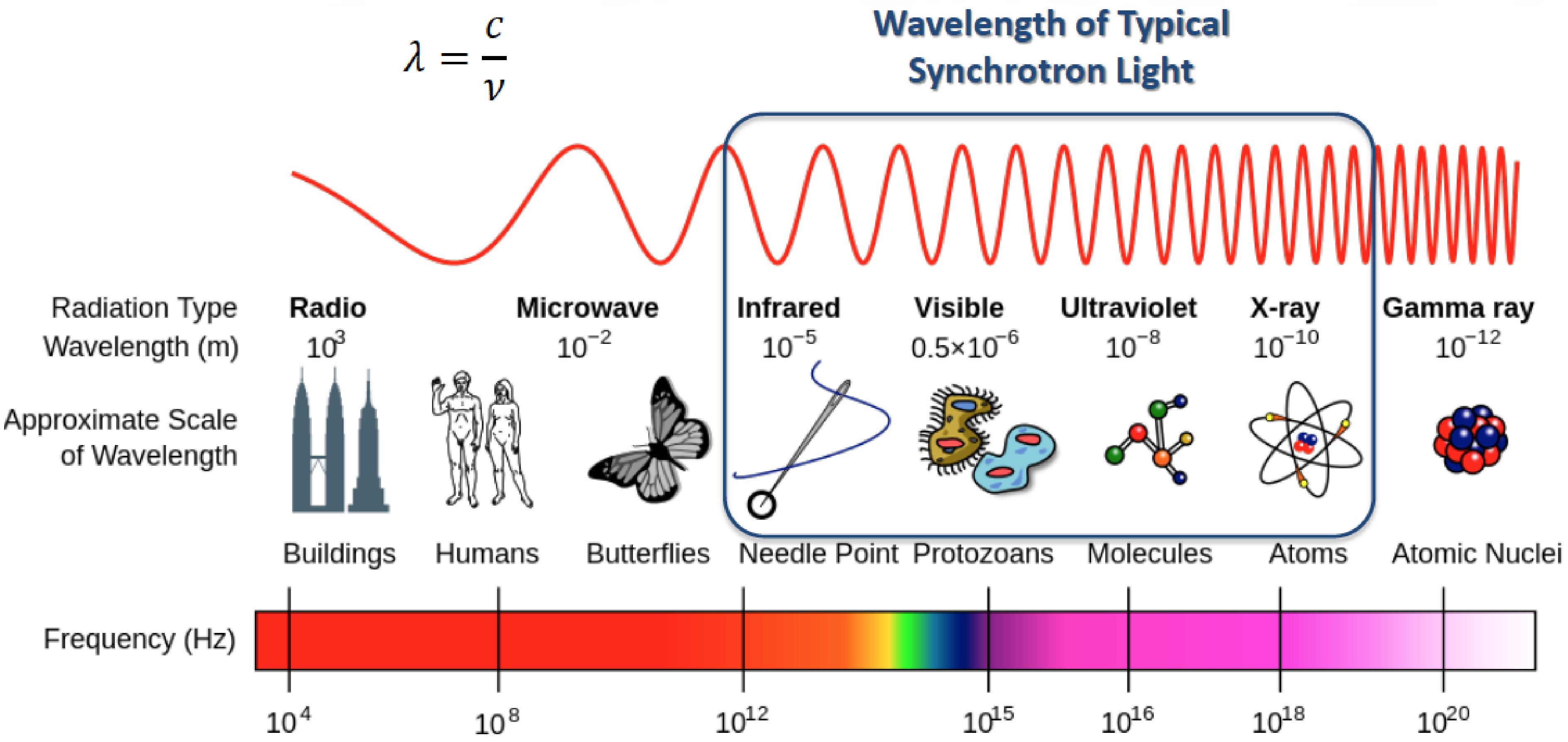
Light and matter

$$\lambda = \frac{c}{\nu}$$



Courtesy of Q. Shen

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Light-matter interaction

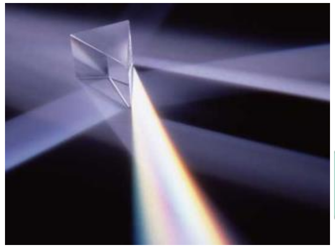
Visible regime (λ ~ 0.5 μm, E ~ 1 eV)

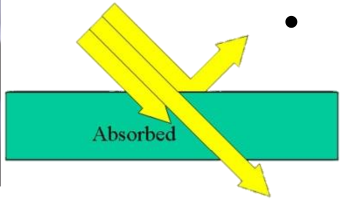
X-rays regime (0.5 nm, 1 keV)

Phenomena:

Visible regime:

- Absorption
- Refraction
- Reflection
- (Diffusion, …)





X-rays regime:

- Absorption
- Scattering

} Particle-wave dualism

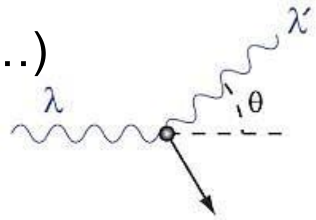
Energy point of view:

Visible regime:

- Elastic
  (Rayleigh, …)
- Inelastic
  (Brillouin, Raman, …)

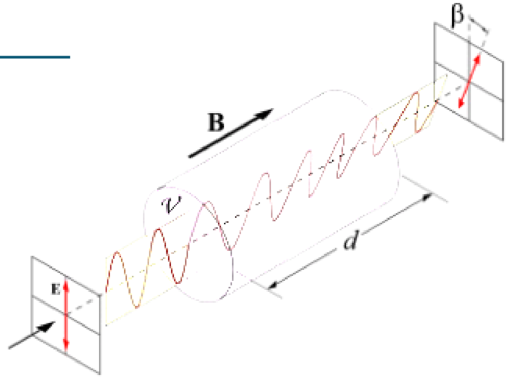
X-rays regime:

- Elastic
  (XRD, diffusion, …)
- Inelastic
  (Compton, IXS, …)



Polarization:

- Faraday rotation



- Excitation
  (thermal, ionization, photoemission, …)

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Light-matter interaction - regimes

n= c / v

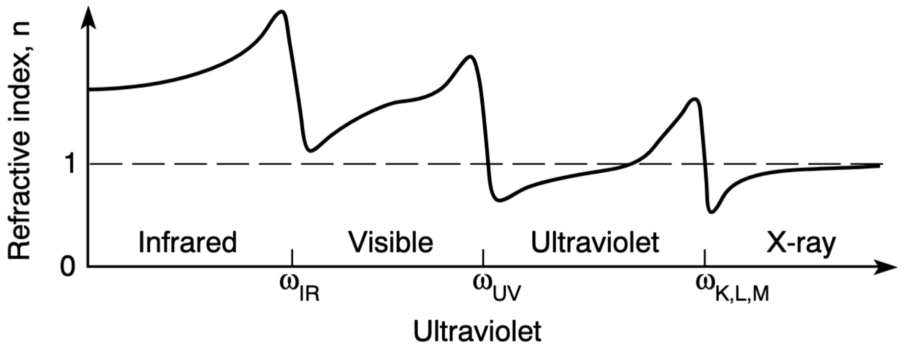

FIGURE 3.1. A sketch of refractive index showing the strong variations near IR, UV, and x-ray resonances (ω_s), and the general tendency toward unity for very short wavelengths where the frequencies are higher than all atomic resonances. Only the real part of the refractive index is shown here.

Wavelength light give different *n* regimes
n in X-ray is below 1!

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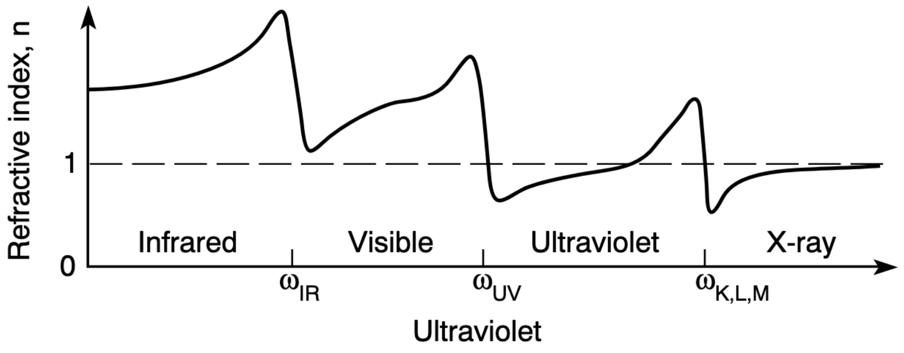
Attwood & Sakdinawat, "Soft x-rays and extreme UV radiation"

Light-matter interaction - regimes

n= c / v



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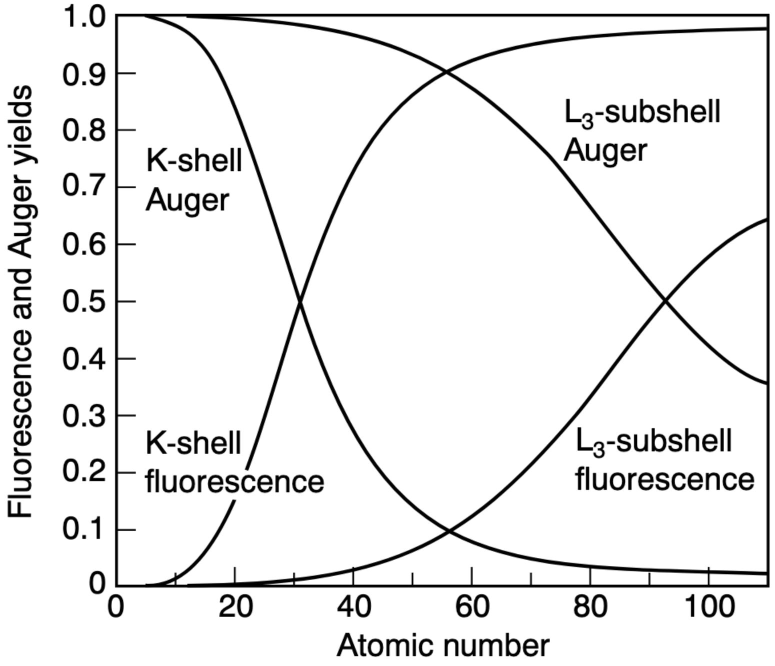

Wavelength light give different *n* regimes
n in X-ray is below 1!
Not confined to refractive index but decay processes also (photon or electrons)

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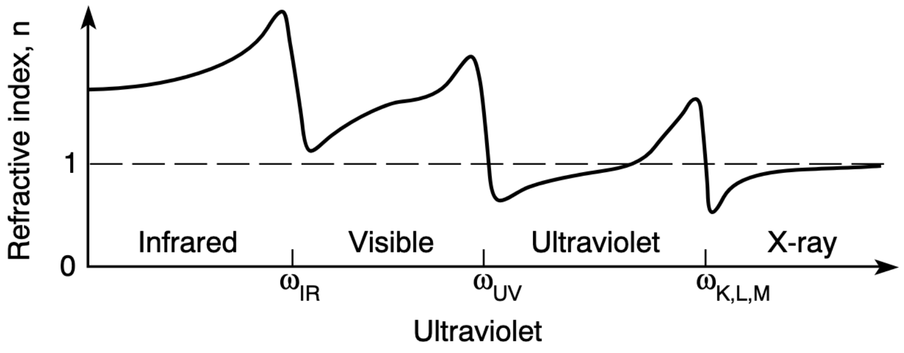
Attwood & Sakdinawat, "Soft x-rays and extreme UV radiation"

Light-matter interaction - regimes

n= c / v



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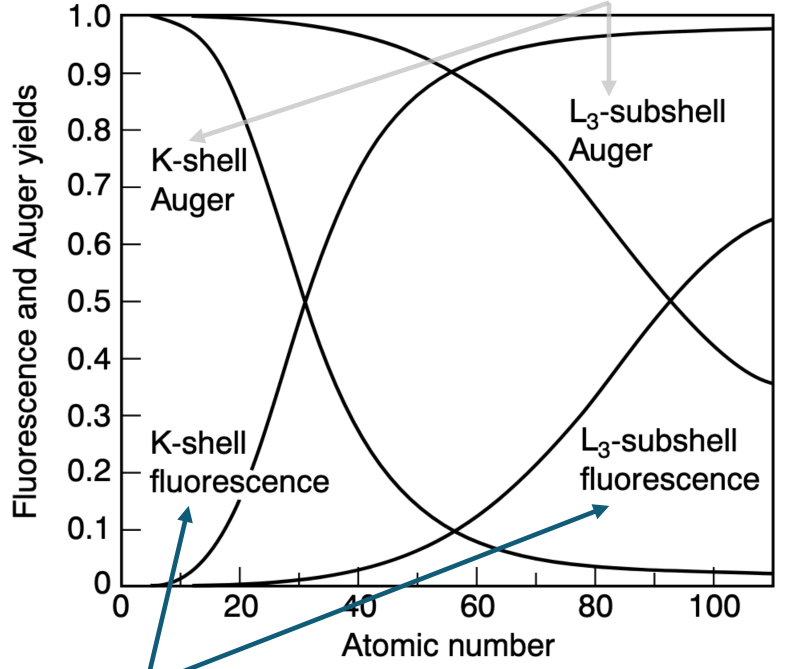
Photon-in
Electron-out



Photon-in
Photon out

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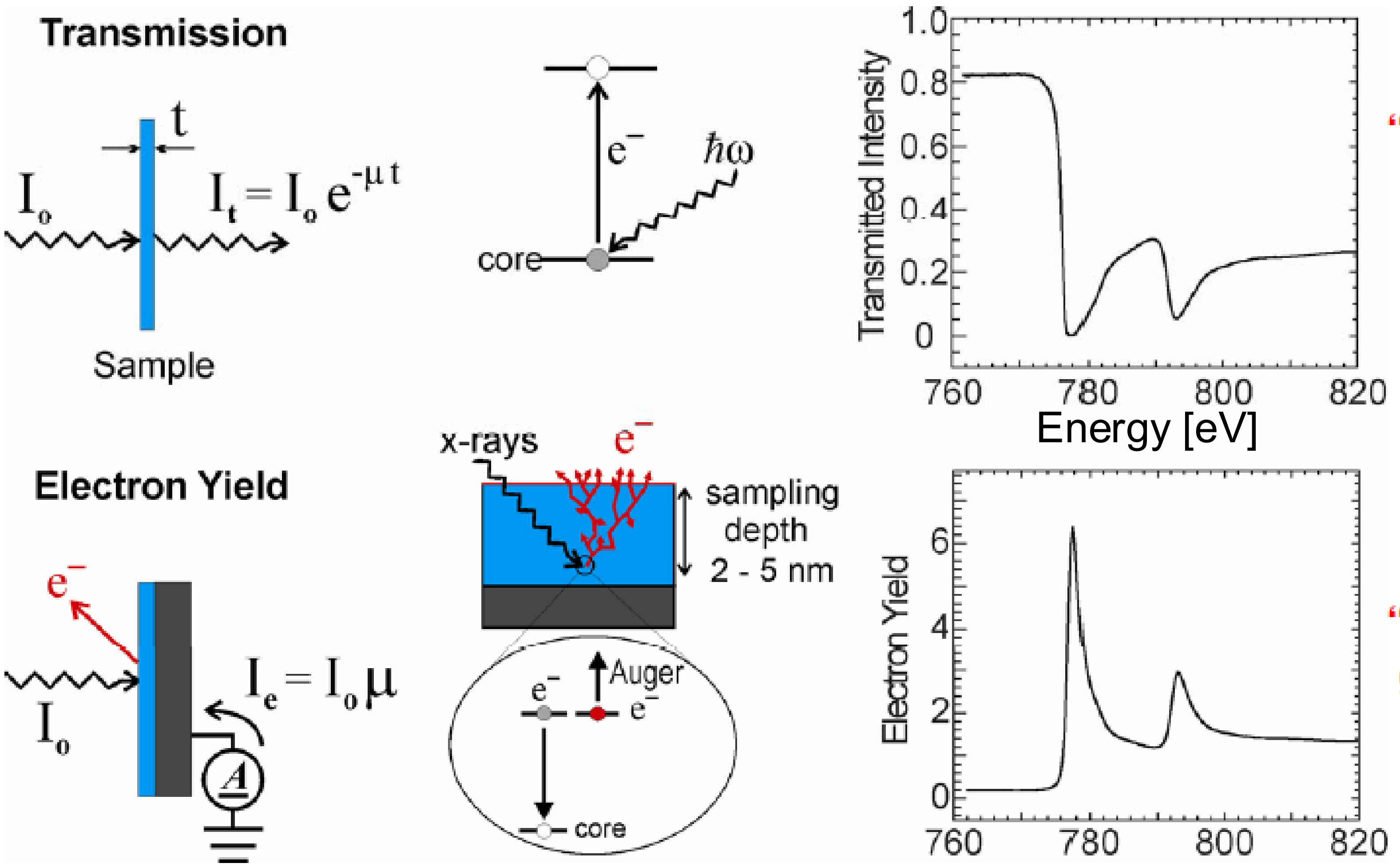
Attwood & Sakdinawat, "Soft x-rays and extreme UV radiation"

The basic X-ray experiment: absorption



"Photons lost"

"Electrons generated"

from J. Stohr lectures, SLAC

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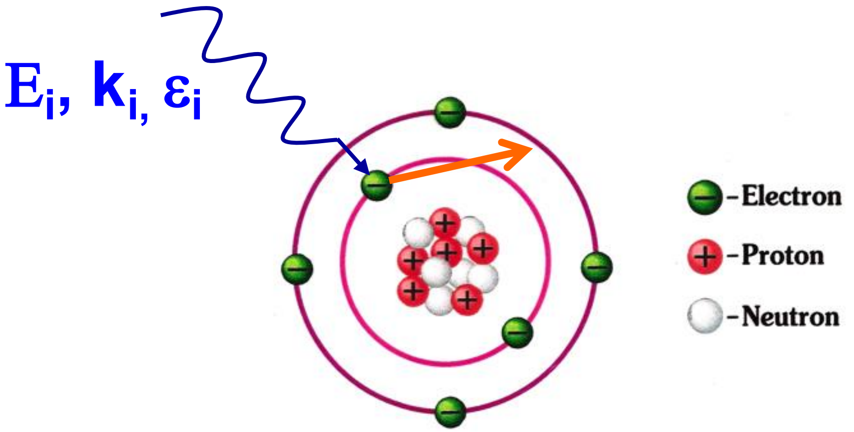
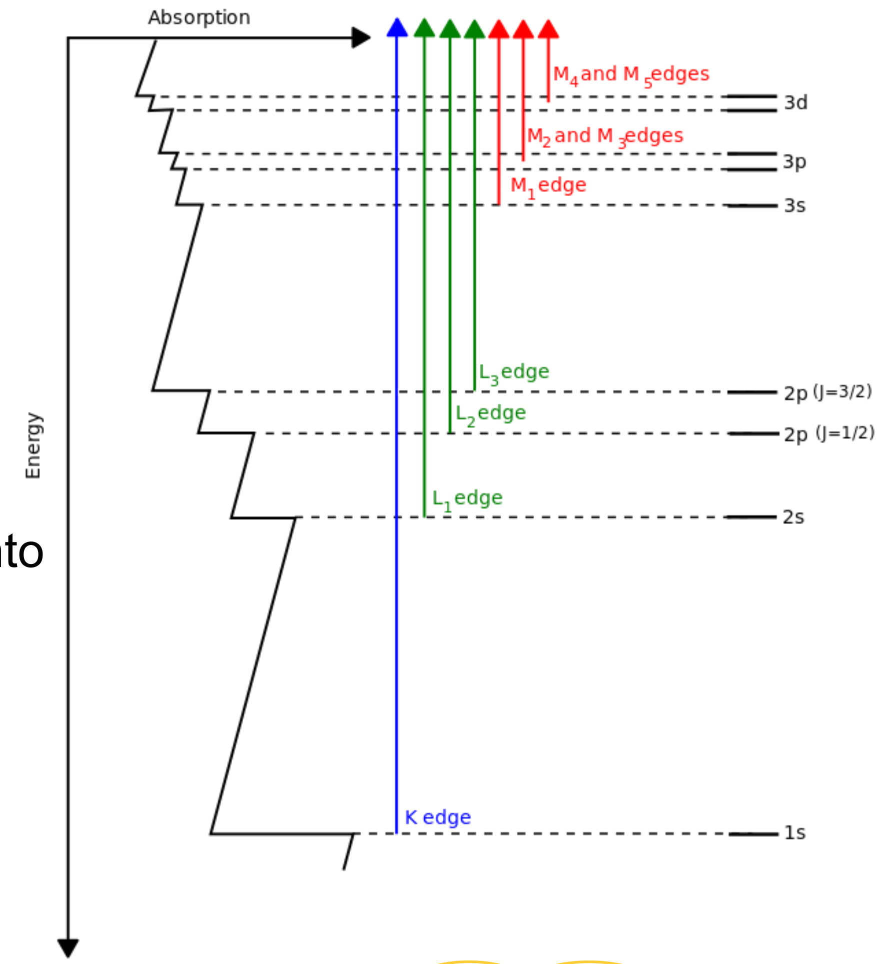
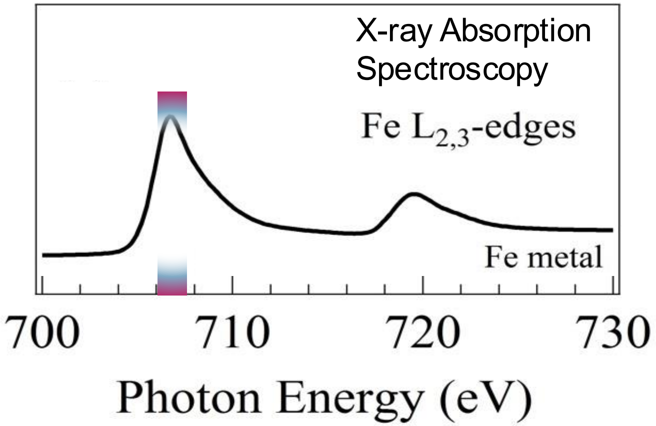
Absorption in steps

Resonance Effect



- E_i is tuned to a specific "**edge**" or transition, promoting a core electron into the outer shell / valance band → this process is called X-ray Absorption
- The absorption edges are usually sharp in Energy → E_i **needs to be tunable and monochromatic**
- The x-ray attenuation length is < 100 nm → **small sample volume**





Example:
Fe L_3 edge ($2p_{3/2}$ → 3d transition) in Iron metal corresponds to ~708 eV

Resonance guarantees **site** and **chemical** selectivity

X-ray absorption edges

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†					
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†					
25 Mn	6539	769.1†	649.9†	638.7†	82.3†	47.2†	47.2†					
26 Fe	7112	844.6†	719.9†	706.8†	91.3†	52.7†	52.7†					
27 Co	7709	925.1†	793.2†	778.1†	101.0†	58.9†	59.9†					
28 Ni	8333	1008.6†	870.0†	852.7†	110.8†	68.0†	66.2†					
29 Cu	8979	1096.7†	952.3†	932.7	122.5†	77.3†	75.1†					
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*			
31 Ga	10367	1299.0*b	1143.2†	1116.4†	159.5†	103.5†	100.0†	18.7†	18.7†			
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b	180.1*	124.9*	120.8*	29.8	29.2			
33 As	11867	1527.0*b	1359.1*b	1323.6*b	204.7*	146.2*	141.2*	41.7*	41.7*			
34 Se	12658	1652.0*b	1474.3*b	1433.9*b	229.6*	166.5*	160.7*	55.5*	54.6*			
35 Br	13474	1782*	1596*	1550*	257*	189*	182*	70*	69*			
36 Kr	14326	1921	1730.9*	1678.4*	292.8*	222.2*	214.4	95.0*	93.8*	27.5*	14.1*	14.1*
37 Rb	15200	2065	1864	1804	326.7*	248.7*	239.1*	113.0*	112*	30.5*	16.3*	15.3 *
38 Sr	16105	2216	2007	1940	358.7†	280.3†	270.0†	136.0†	134.2†	38.9†	21.3	20.1†
39 Y	17038	2373	2156	2080	392.0*b	310.6*	298.8*	157.7†	155.8†	43.8*	24.4*	23.1*
40 Zr	17998	2532	2307	2223	430.3†	343.5†	329.8†	181.1†	178.8†	50.6†	28.5†	27.1†
41 Nb	18986	2698	2465	2371	466.6†	376.1†	360.6†	205.0†	202.3†	56.4†	32.6†	30.8†
42 Mo	20000	2866	2625	2520	506.3†	411.6†	394.0†	231.1†	227.9†	63.2†	37.6†	35.5†
43 Tc	21044	3043	2793	2677	544*	447.6	417.7	257.6	253.9*	69.5*	42.3*	39.9*
44 Ru	22117	3224	2967	2838	586.1*	483.5†	461.4†	284.2†	280.0†	75.0†	46.3†	43.2†
45 Rh	23220	3412	3146	3004	628.1†	521.3†	496.5†	311.9†	307.2†	81.4*b	50.5†	47.3†
46 Pd	24350	3604	3330	3173	671.6†	559.9†	532.3†	340.5†	335.2†	87.1*b	55.7†a	50.9†
47 Ag	25514	3806	3524	3351	719.0†	603.8†	573.0†	374.0†	368.3	97.0†	63.7†	58.3†

The strongest, not the only ones..
(not even in the energy range shown)

t:
https://xdb.lbl.gov
(https://xdb.lbl.gov/Section1/Table_1-1a.htm)

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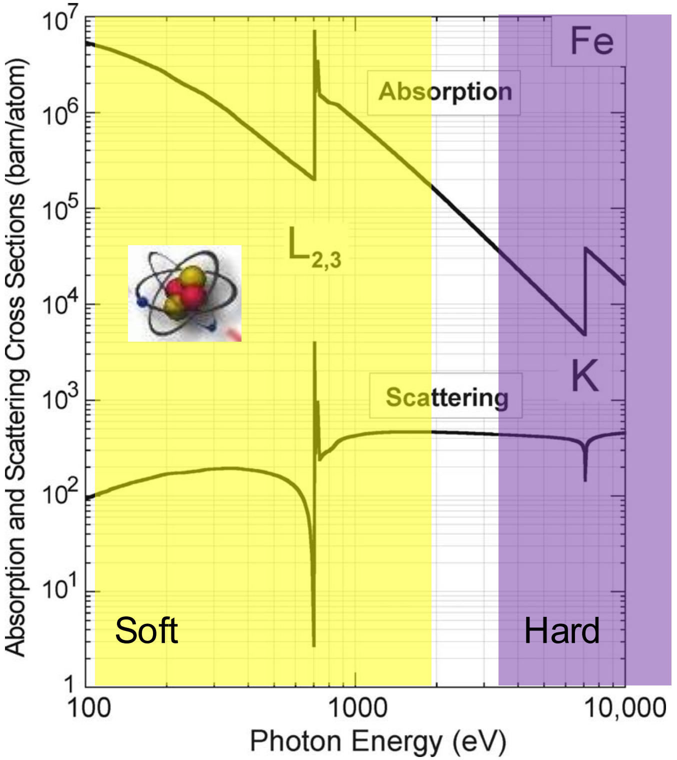
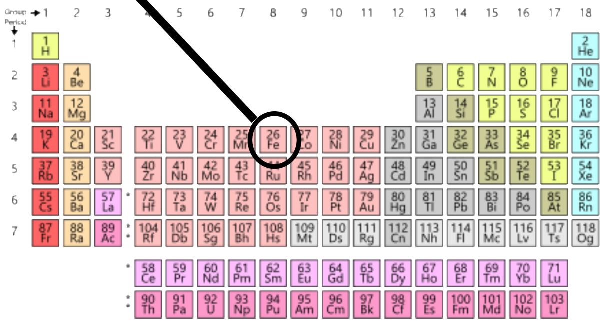
X-ray refraction index





"Control" of impinging energy gives **Chemical specificity**
(& **increased sensitivity** to faint **electronic signals)**

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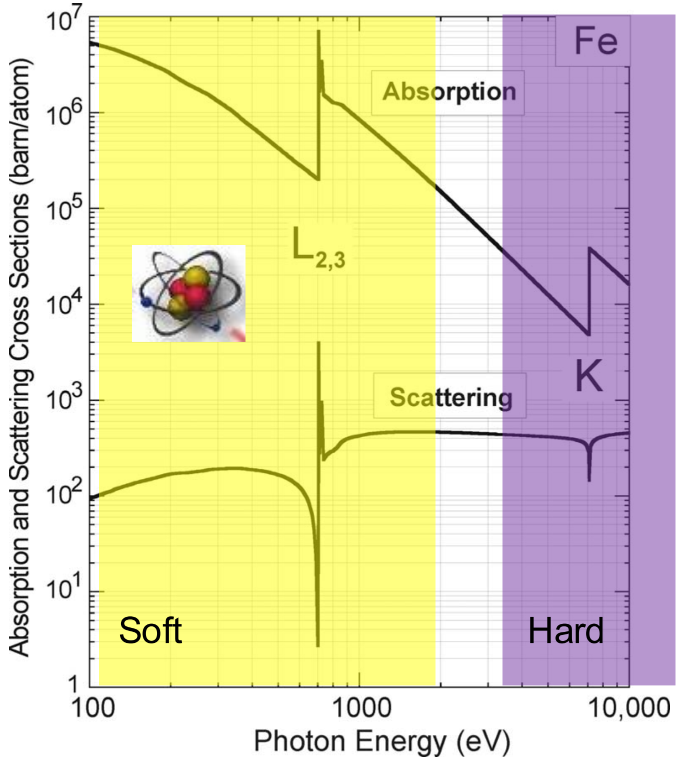
Attwood & Sakdinawat, "Soft x-rays and extreme UV radiation"

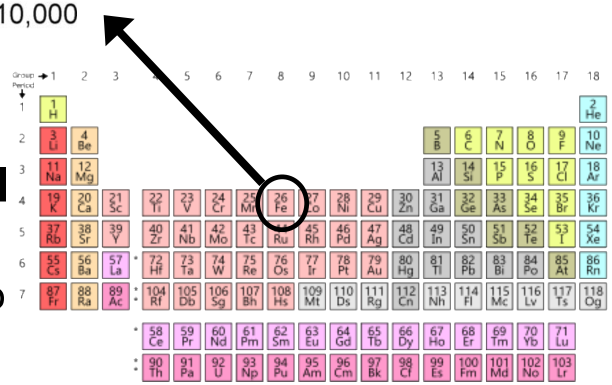
X-ray refraction index



$$\tilde{n} = 1 - \delta + i\beta = 1 - \frac{r_o \lambda^2}{2\pi} N_{at}(f_1 - i f_2),$$

Atomic scattering factors

Macro – micro
-scopic link
(optical theorem, KK)



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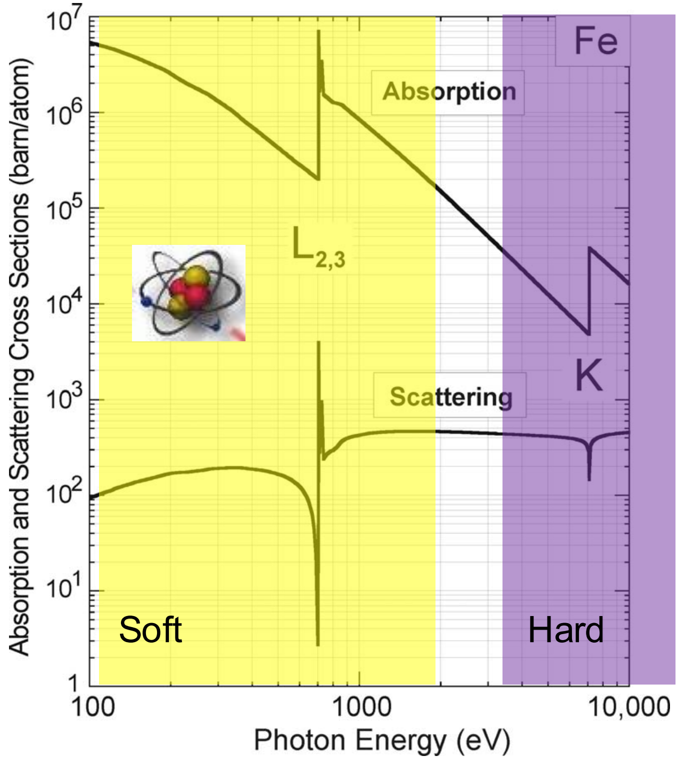

Dispersion / scattering   absorption

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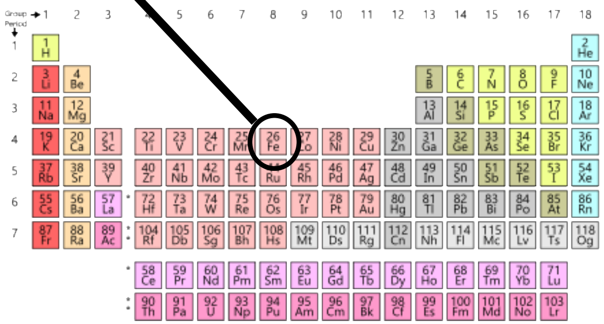

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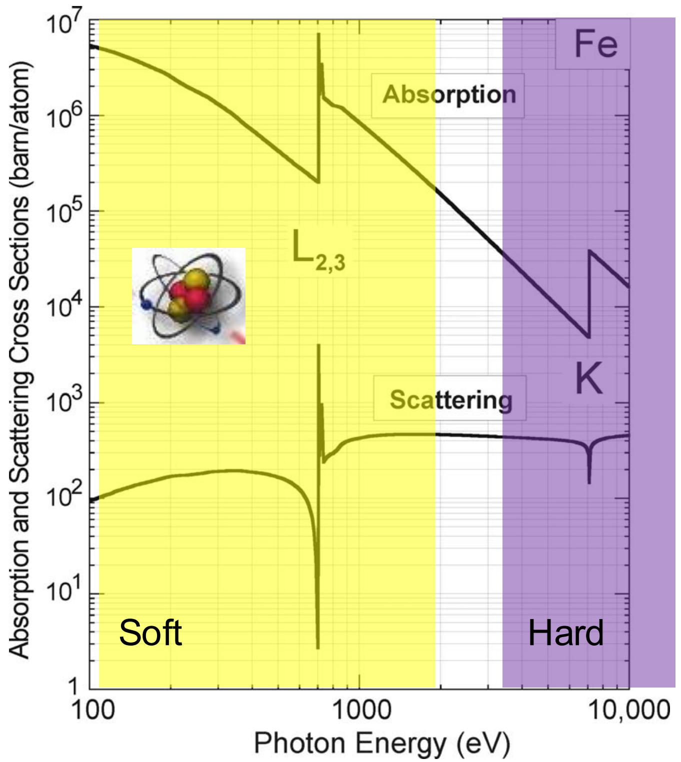
X-ray refraction index



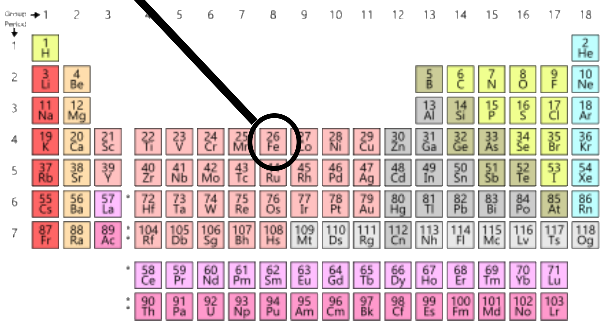
Dispersion / scattering absorption

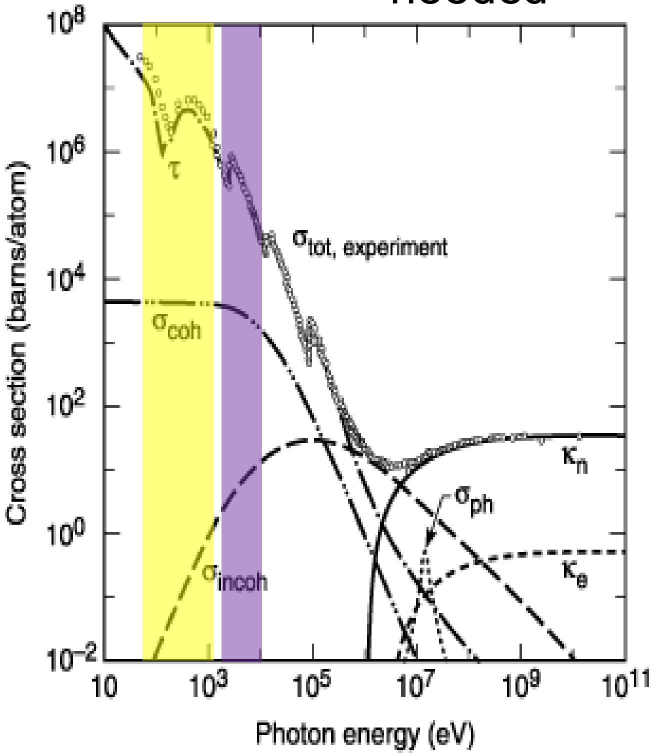
$$\tilde{n} = 1 - \delta + i\beta = 1 - \frac{r_o \lambda^2}{2\pi} N_{at}(f_1 - if_2),$$

Atomic scattering factors

Photon hungry
high brilliance needed

Macro – micro-scopic link
(optical theorem, KK)





"Control" of impinging energy gives **Chemical specificity**
(& **increased sensitivity** to faint **electronic signals)**

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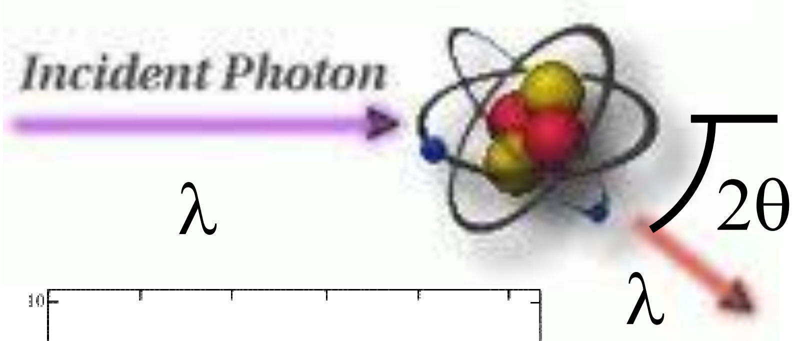
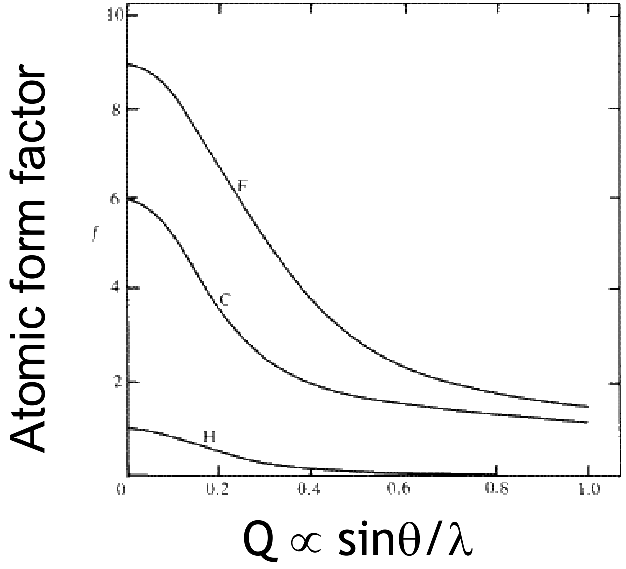
Elastic x-ray scattering ("free" e$^-$)

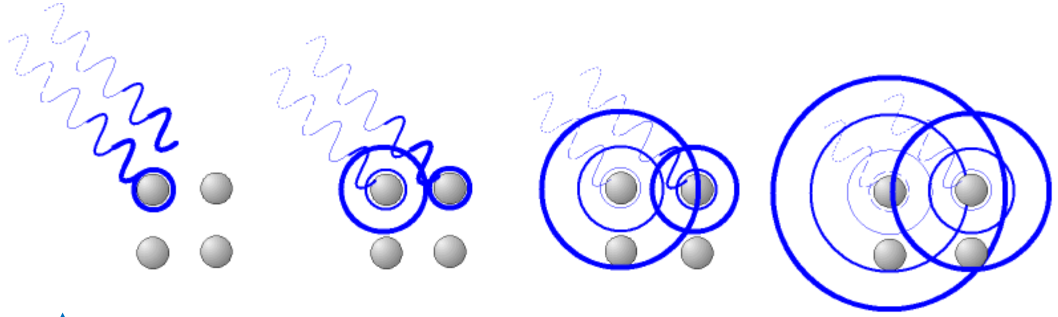
From various e$^-$ in one atom..

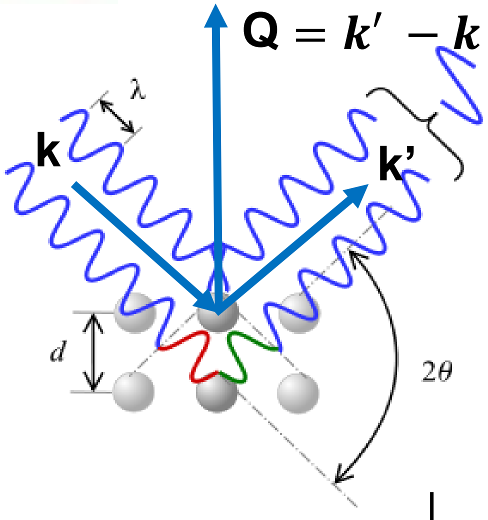


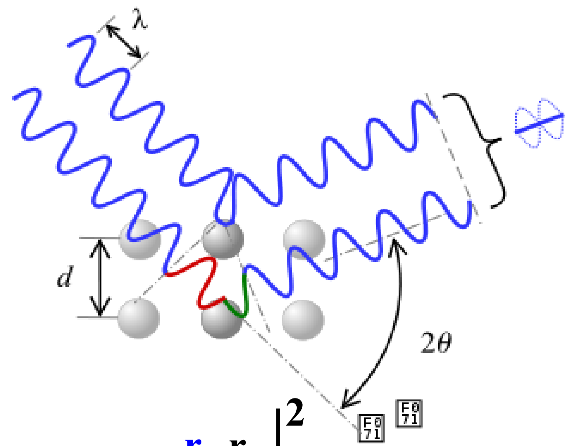


$$f(\mathbf{Q}) = \int \rho(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d^3\mathbf{r},$$

… to several atoms together







$$I_{scattered} \propto \left| \sum_{n(atoms)} f_{n0} \cdot e^{i\vec{Q}.\vec{R}_n} \right|^2$$

Diffraction, Bragg's law, polarization

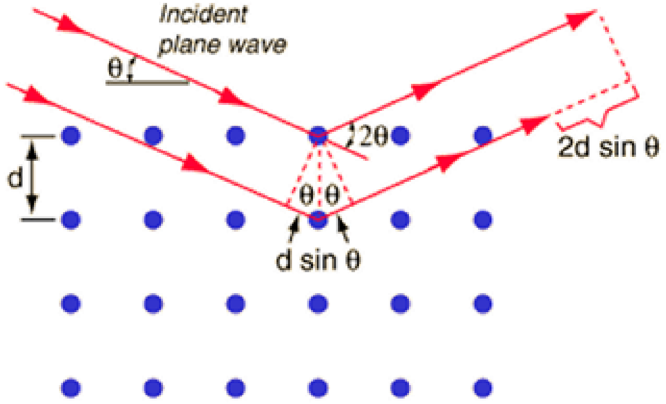
Laue notation

$$\frac{d\sigma}{d\Omega} = r_0^2 \left| \sum_n e^{i\mathbf{Q}\cdot\mathbf{R}_n} f(\mathbf{Q}) \right|^2$$

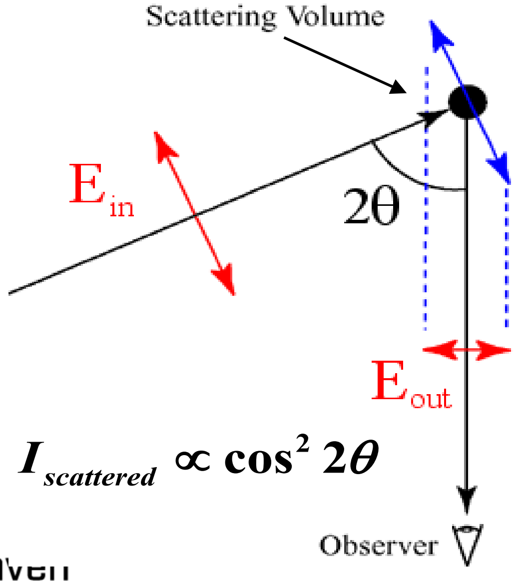
Space Fourier transform

Bragg's law

$$\lambda \cdot n = 2 \cdot d_{hkl} \cdot \sin\theta$$



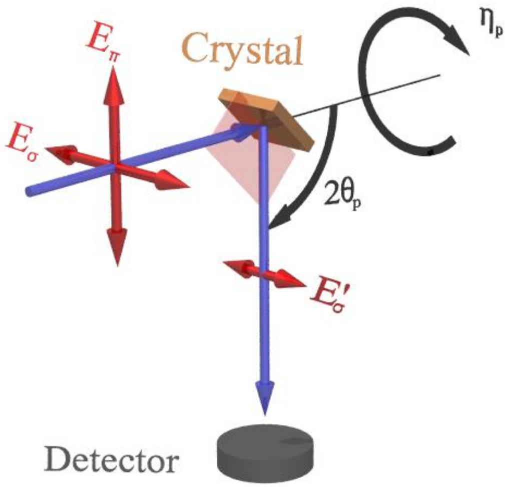
Thomson scattering



$$I_{scattered} \propto \cos^2 2\theta$$

$$\varepsilon'' \cdot \varepsilon' = \begin{pmatrix} \varepsilon''_\sigma \\ \varepsilon''_\pi \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & \cos(2\theta_p) \end{pmatrix} \begin{pmatrix} \varepsilon'_\sigma \\ \varepsilon'_\pi \end{pmatrix}$$

Jones notation



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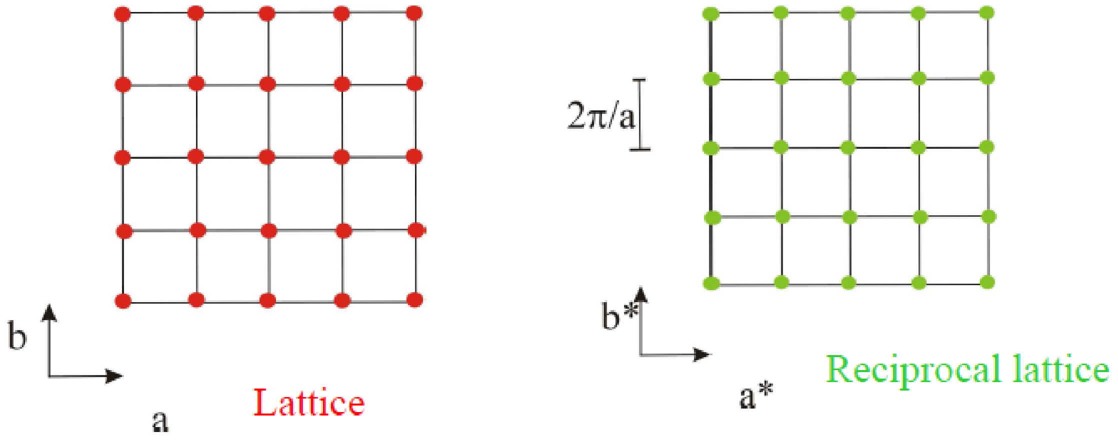
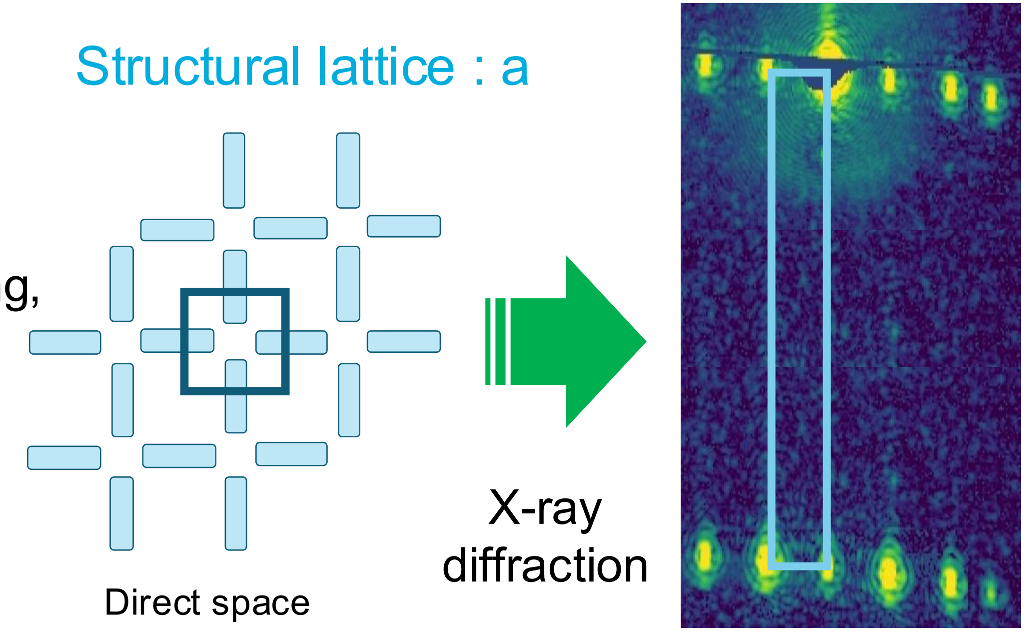
Direct and reciprocal lattice

$$\frac{d\sigma}{d\Omega} = r_0^2 \left| \sum_n e^{i\mathbf{Q}\cdot\mathbf{R}_n} \; f(\mathbf{Q}) \right|^2$$



Direct space structural information
from Q dependence
in the RL (where diffraction naturally lives)



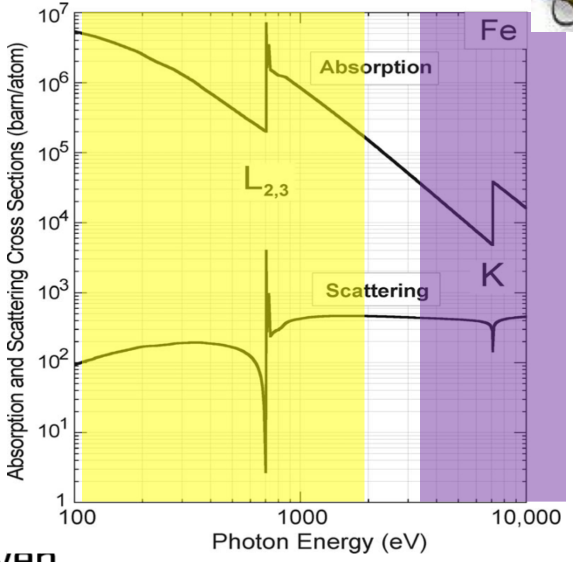
<u>Conventions</u> (science, engineering, chemistry/crystallography -> FT):
k = 2π/λ (or 1/λ) wave vector
$\boldsymbol{Q} = \boldsymbol{k}' - \boldsymbol{k}$ (or $\boldsymbol{k} - \boldsymbol{k}'$)
a* = 2π/a (or 1/a)

Spectroscopy + scattering = RXS

Photon in – photon out process,
site coherent (scattering)
intersite coherent (diffraction)

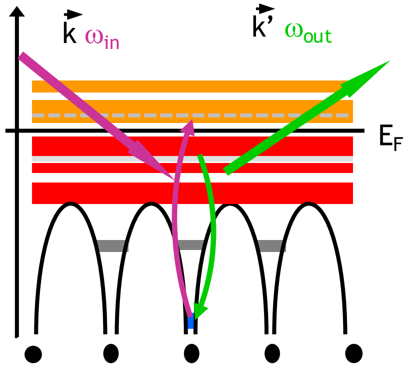
$$I(\boldsymbol{Q}) \propto \left| \sum_{j=1}^{N} f_j(\vec{\varepsilon},\vec{\varepsilon}',\vec{k},\vec{k}')\, e^{\,i\boldsymbol{Q}\cdot\boldsymbol{r}_j} \right|^2 \sim N^2$$

Atomic scattering factor
(resonant, tensorial)



Second order perturbation theory
(Kramers – Heisenberg)

$$f_j(\vec{\varepsilon},\vec{\varepsilon}',\vec{k},\vec{k}') \propto \int_{E_F}^{\infty} \frac{\langle fin|\tilde{O}^{+}(\vec{\varepsilon}',\vec{k}')|exc\rangle\langle exc|\tilde{O}(\vec{\varepsilon},\vec{k})|gr\rangle}{E_{exc}-E_{gr}-\hbar\omega_k+i\Gamma}\, dE$$



Targeting specific electrons,
but all contributions mixed:

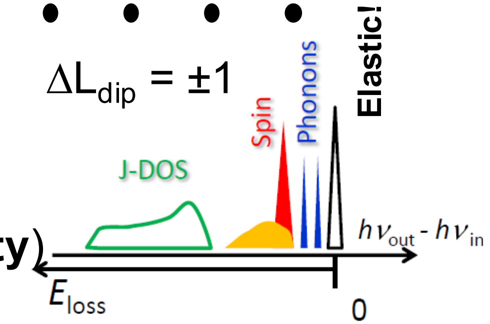
- elastic + inelastic
- symmetry of process

$\Delta L_{dip} = \pm 1$

Elastic if:

$$\langle fin| = \langle gr|,\ \omega_{in} = \omega_{out}$$

(diffraction via Bragg;
new reflection cond. & intensity)



Attwood & Sakdinawat, "Soft x-rays and extreme UV radiation"

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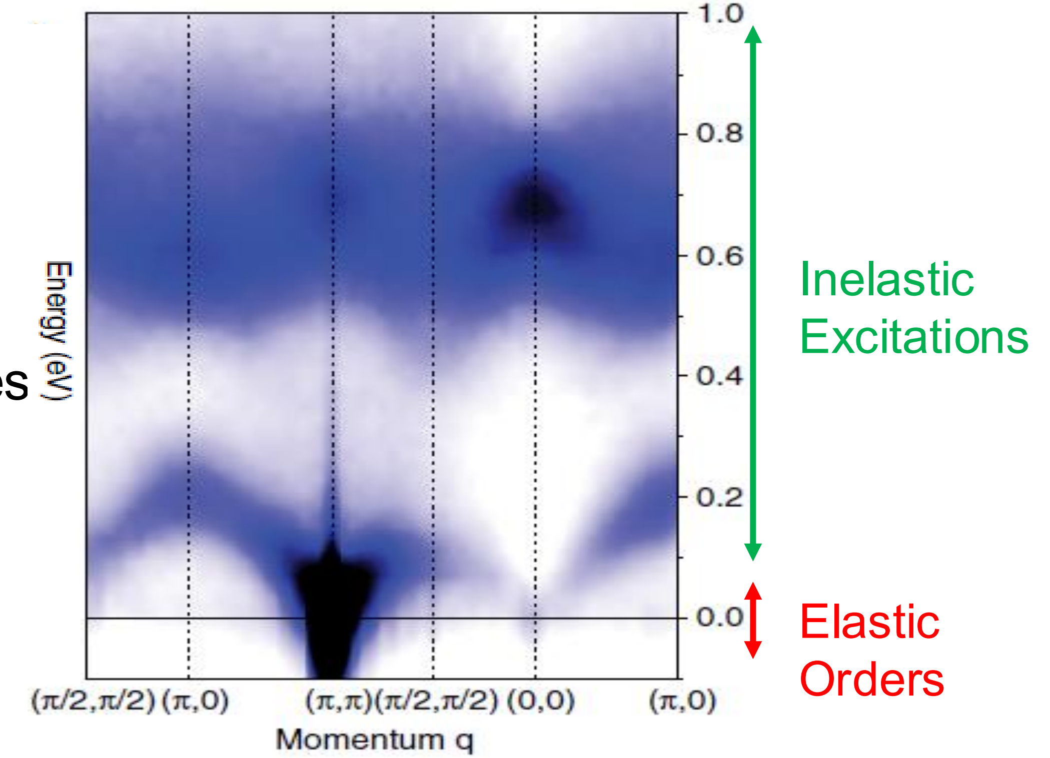
What does it mean all of this for us Condensed Matter Physicists?

RXS: absorption + scattering (elastic and inelastic)

- Electromagnetic field (photons) as a probe for e$^-$ states of the matter ($\mathbf{A}_{\text{radiation}} \leftrightarrow \mathbf{E}, \mathbf{B}_{\text{atomic charges}}$)
- Chemical selectivity (absorption$\rightarrow$ site selective)

- 3D e$^-$ distributions (due to atomic scattering factor, in
- diffraction condition, site contrast due to structure
- factor)
- Bosonic excitations
  - spin, charge, orbital (absorption relaxes selection rules
  - dispersion relations (exchange of E and Q)
- Scattering + Spectroscopy + Diffraction



to fulfill Bragg's law:

<u>l ~ atomic spacing « keV</u> (hard regime: K 3d, L 4f, M 5f; soft regime: $L_{2,3}$ 3d)

S. Di Matteo et al., Phys. Rev. B **72** (2005) 144406
C. Detlefs et al., Eur. Phys. J. ST 208 (2012) 359
L. J. P. Ament et al., Rev. Mod. Phys. 83 (2011) 705
Kim et al, Phys. Rev. Lett. 108, 177003 (2012)

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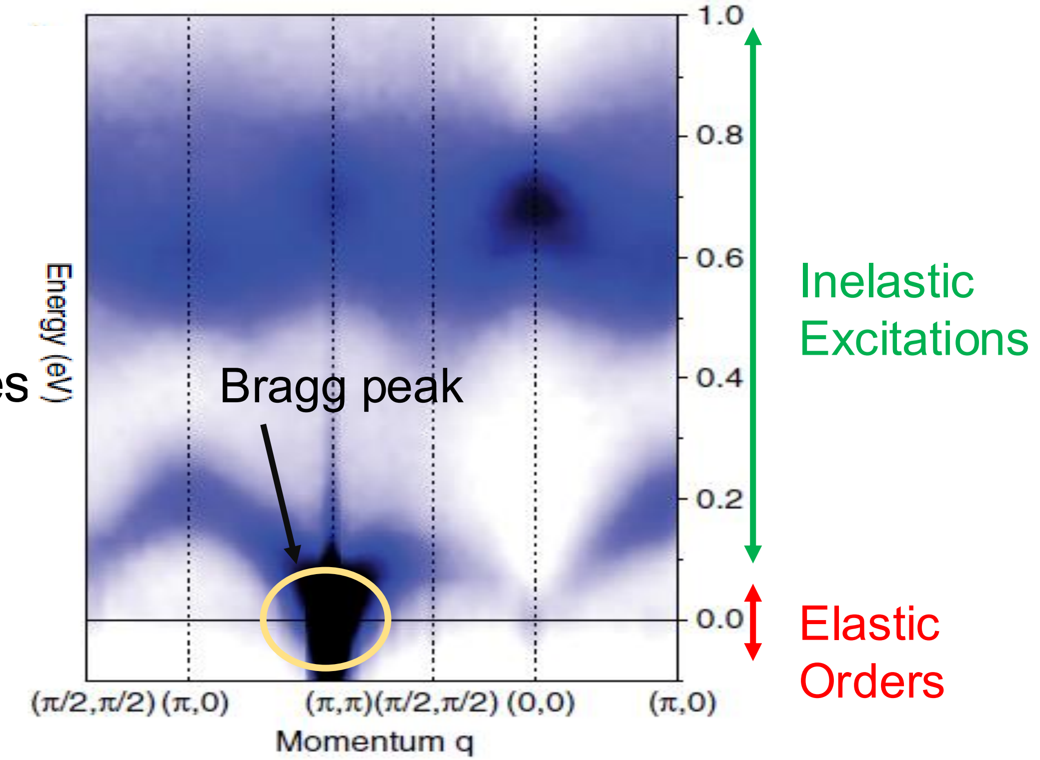
- Bosonic excitations
  - spin, charge, orbital (absorption relaxes selection rules)
  - dispersion relations (exchange of E and Q)
- Scattering + Spectroscopy + Diffraction



to fulfill Bragg's law:
<u>l ~ atomic spacing « keV</u> (hard regime: K 3d, L 4f, M 5f; soft regime: $L_{2,3}$ 3d)

S. Di Matteo et al., Phys. Rev. B **72** (2005) 144406
C. Detlefs et al., Eur. Phys. J. ST 208 (2012) 359
L. J. P. Ament et al., Rev. Mod. Phys. 83 (2011) 705
Kim et al, Phys. Rev. Lett. 108, 177003 (2012)

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Outline:

- Some view of light matter interaction
- **X-ray Sources**
- Specifics of Resonant Inelastic X-Ray Scattering
- Examples of RIXS studies

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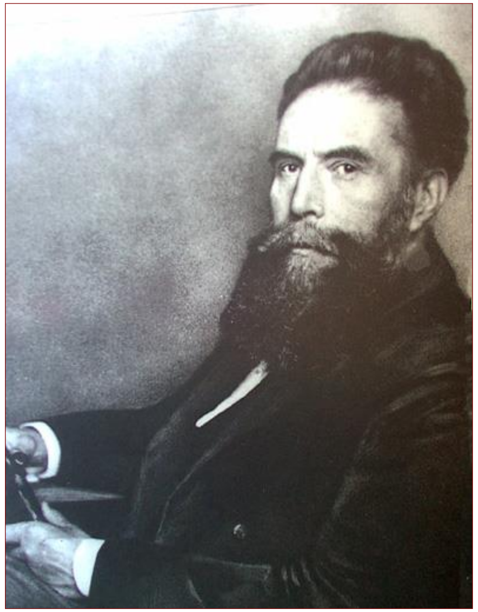
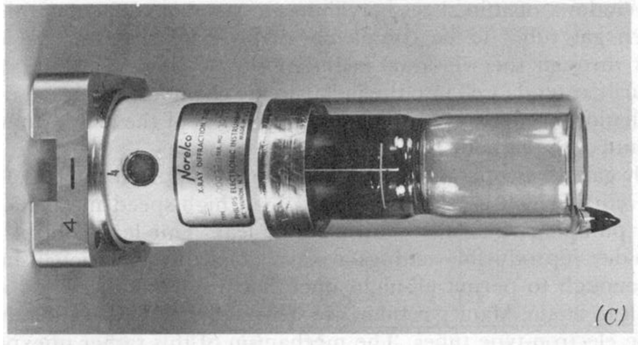
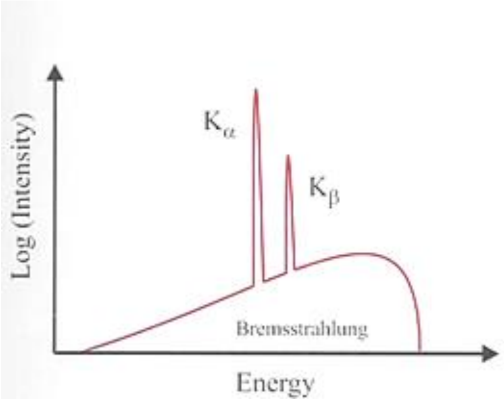
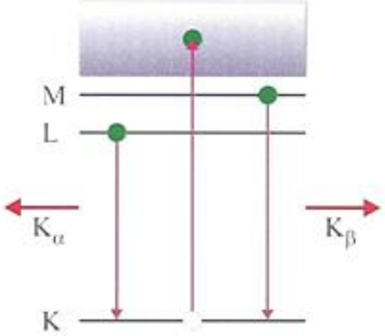
X-ray technology: the early days

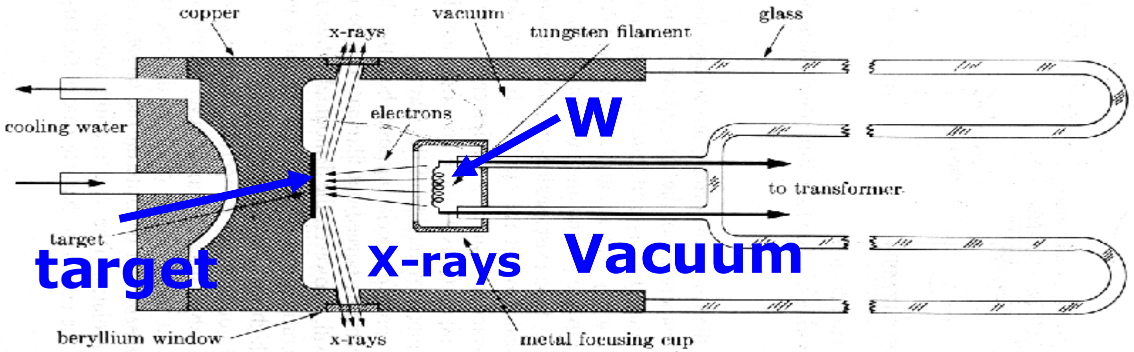


W.C. Röntgen
1895







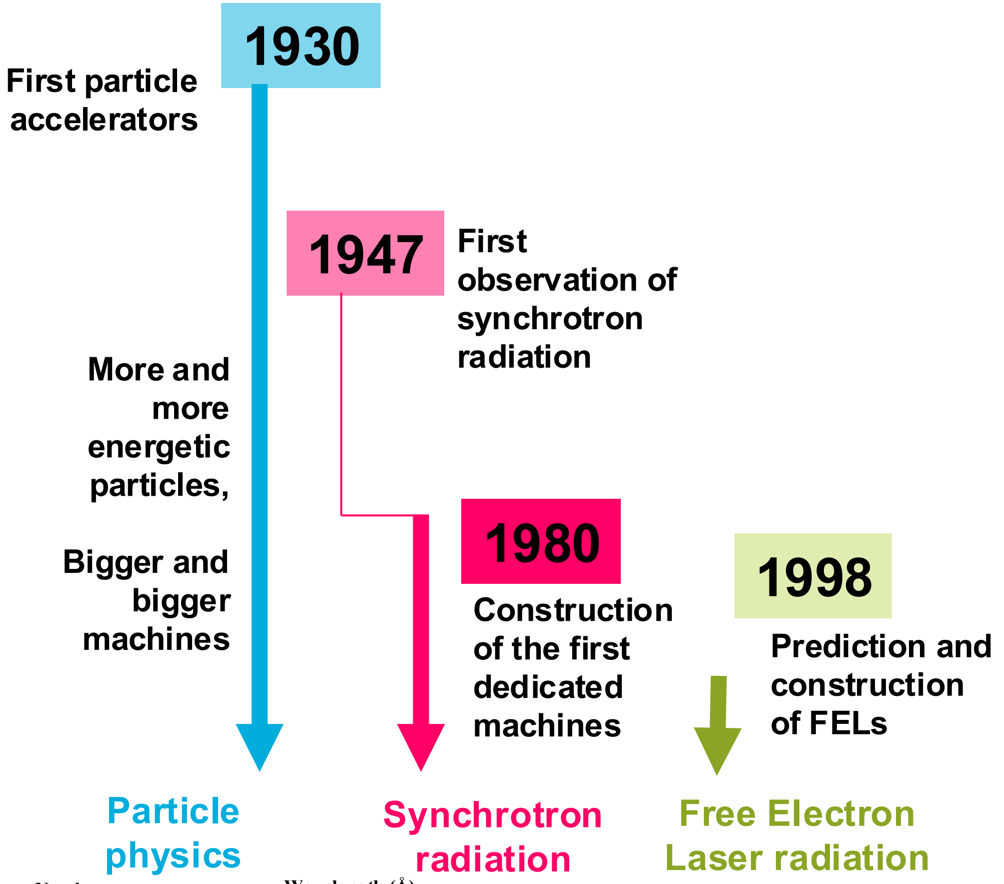


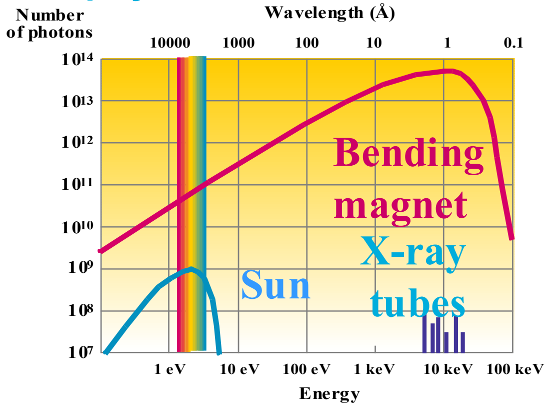
The advent of synchrotrons

EVOLUTION

1947
First observation of synchrotron radiation at General Electric (USA)

- Energy tuning
- Brilliance
- Polarization
- Stability
- Coherence
- Intrinsic time structure (pulsed source)





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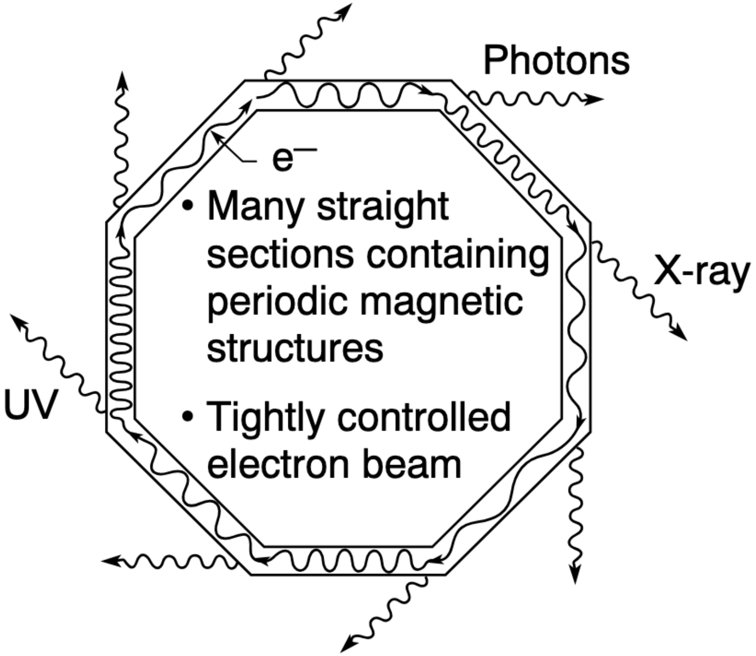
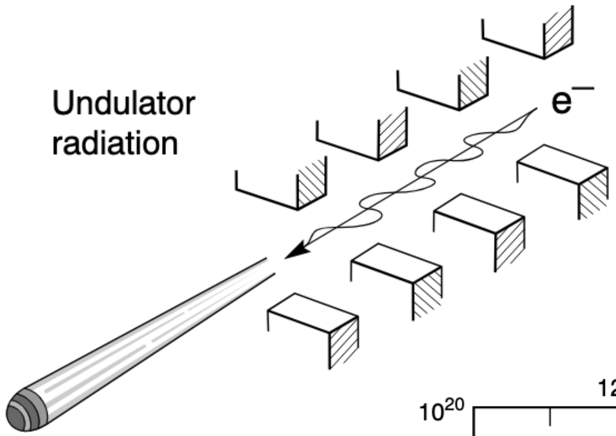
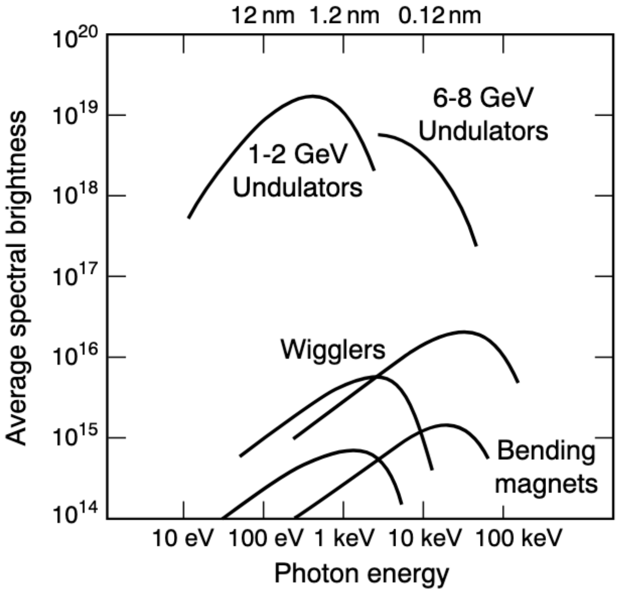
Synchrotrons - sources

Bremsstrahlung







Bending Magnet:

$$\hbar\omega_c = \frac{3e\hbar B\gamma^2}{2m} \quad (5.7)$$

Wiggler:

$$\hbar\omega_c = \frac{3e\hbar B\gamma^2}{2m}$$

$$n_c = \frac{3K}{4}\left(1 + \frac{K^2}{2}\right)$$

$$P_T = \frac{\pi e K^2 \gamma^2 I N}{3\epsilon_0 \lambda_u}$$

Undulator:

$$\lambda = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right) \quad (5.28)$$

$$K = \frac{eB_0\lambda_u}{2\pi mc} \quad (5.18)$$

$$\theta_{cen} = \frac{1}{\gamma^* \sqrt{N}} \quad (5.15)$$

$$\left.\frac{\Delta\lambda}{\lambda}\right|_{cen} = \frac{1}{N} \quad (5.14)$$

$$\bar{P}_{cen} = \frac{\pi e \gamma^2 I}{\epsilon_0 \lambda_u} \frac{K^2}{\left(1 + \frac{K^2}{2}\right)^2} f(K) \quad (5.41)$$

Electrons in storage ring and insertion devices
Straight sections
- undulators
- wigglers

NSLS-II, BNL
Aerial view

Attwood & Sakdinawat, “Soft x-rays and extreme UV radiation”

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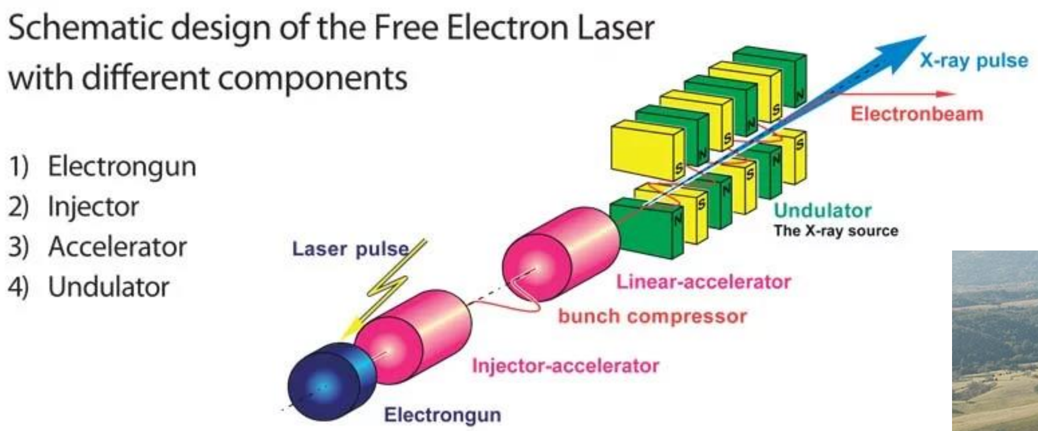
Free Electron Lasers (FEL)



https://www.psi.ch/en/swissfel/how-it-works

New type of source
Pulsed vs ”continuous”
Linear vs circular

Different kind of experiment
Pulsed source with very short pulses (at-fs)
Time resolved pump and probe schemes
High peak power

LCLS-II, Stanford, Aerial view

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Outline:

- Some view of light matter interaction
- X-ray Sources
- **Specifics of Resonant Inelastic X-Ray Scattering**
- Examples of RIXS studies

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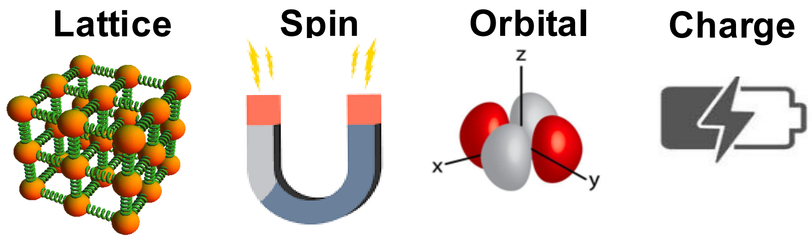
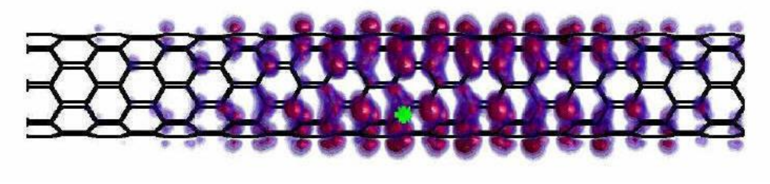
Elementary excitations in solids

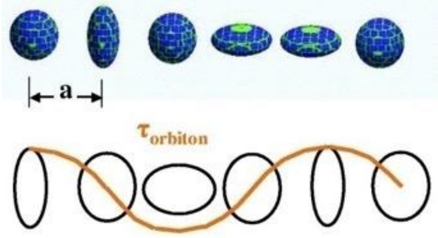


Energy

- ❑ 1 - 100 eV:
  Plasmon
  Exciton
  Charge (e^- - h^+) excitations

Exciton in carbon nanotube

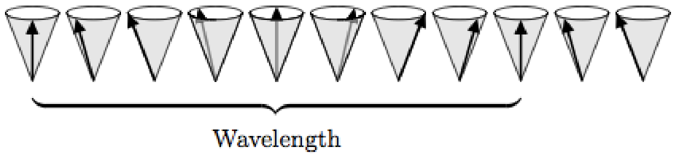




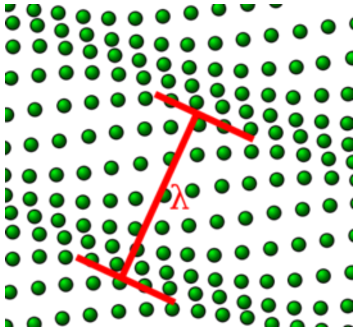
Collective modes of orbital waves

- ❑ 0.1 - 2 eV:
  Orbital excitations
  Orbiton (collective)

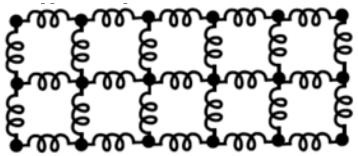
- ❑ 0 - 0.3 eV:
  Magnon

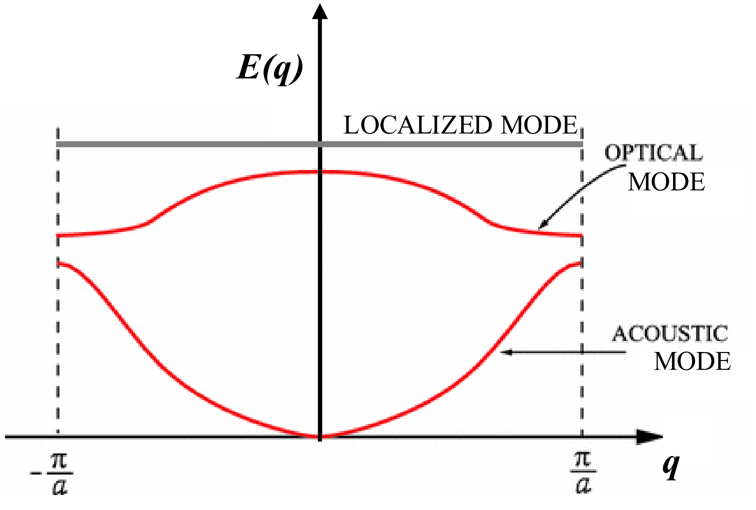


- ❑ 0 – 0.1 eV:
  Phonon



Collective modes of lattice





Measuring the dispersion relation $E(q)$ of elementary excitations provides **information about the relevant electronic interactions** at play in the system

Electronic Properties

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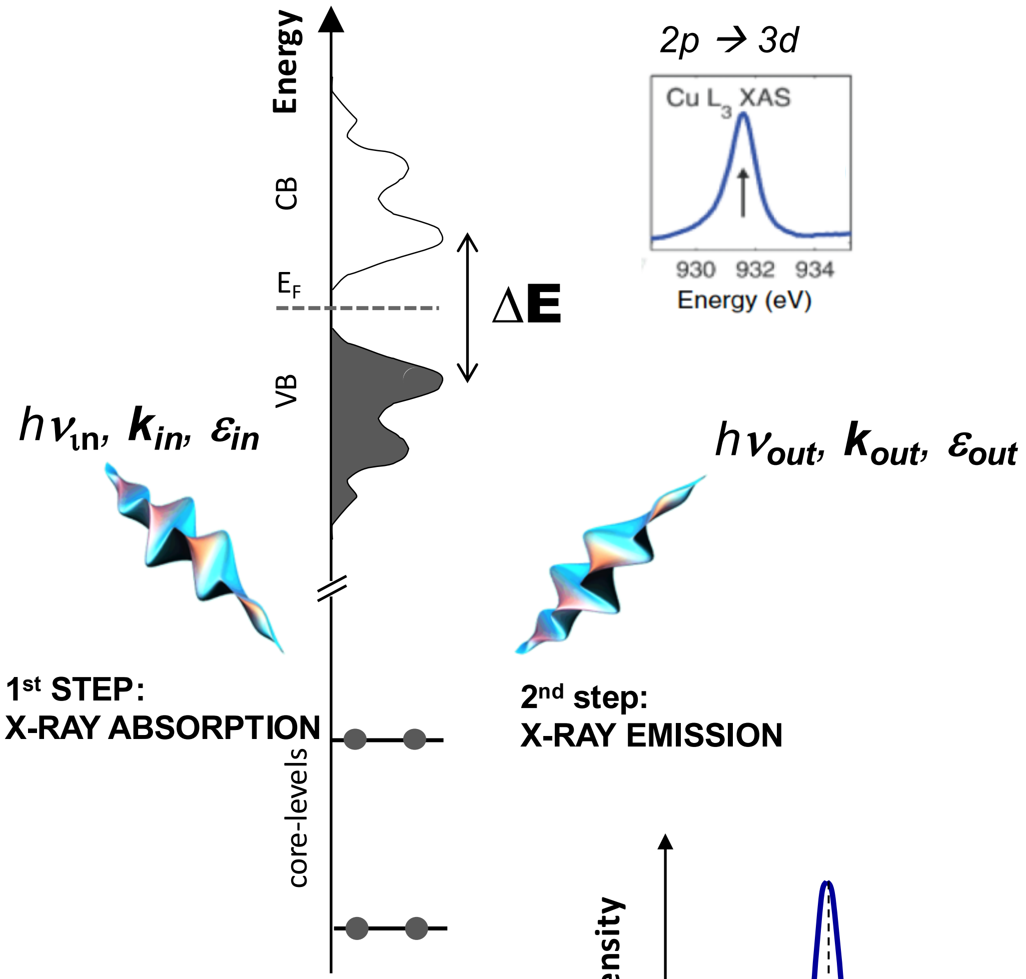
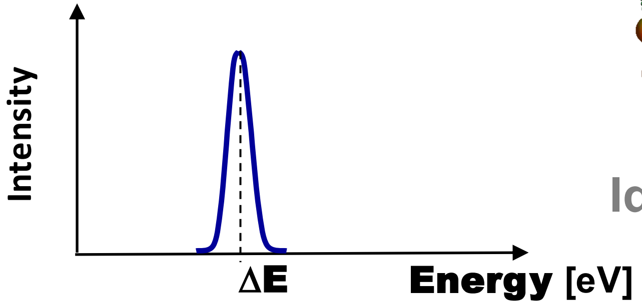
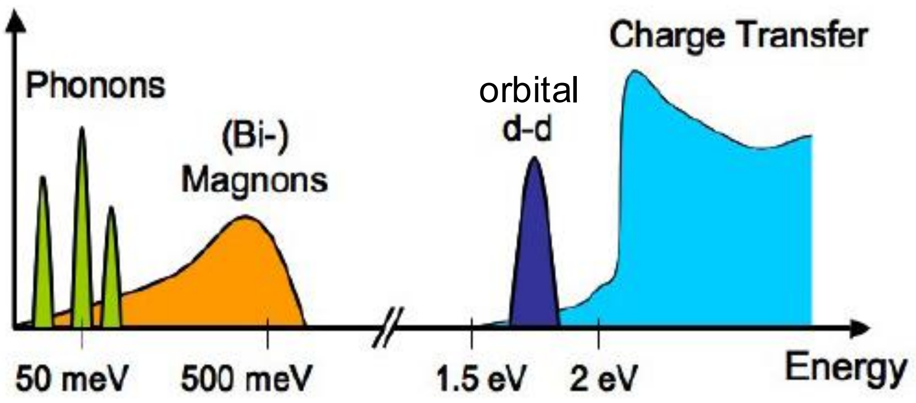
RIXS: X-ray Scattering + Inelastic + Resonant

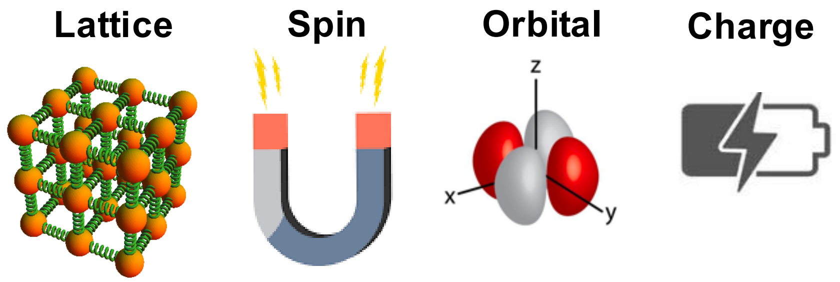




Schematic of a RIXS Spectrum



RIXS sensitive to all electron degrees of freedom



Ideal to study electronic properties!

A. Kotani and S. Shin, *Rev. Mod. Phys.* 73, 203 (2001)
L.J.P. Ament et al., *Rev. Mod. Phys.* 83,705 (2011)
P.M. Platzman, E.D. Isaac, PRB 57,11107 (1997)

Overview:

- List of Techniques sensitive to Excitations:

	Energy resolution	Momentum resolution	Bulk Probe	Spatial resolution	Sample Mass Requirement	Sensitivity to e⁻ degrees of freedom
Resonant Inelastic X-ray Scattering (RIXS)						
Light Scattering (Raman, IR, Brillouin)						
Inelastic Neutron Scattering (INS)						
Electron Energy Loss Spectroscopy (EELS)						
Scanning Tunneling Microscopy (STM)						
NMR, μSR, ESR						

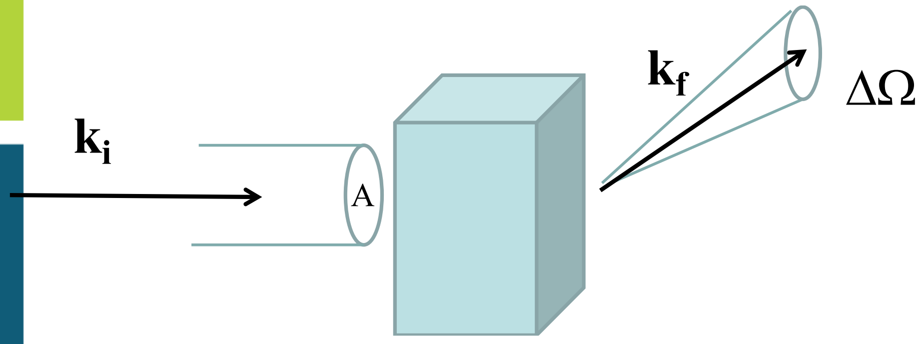
EXCELLENT

GOOD

MEDIOCRE

POOR

RIXS response or cross-section



$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{n_s}{j_i \Delta\Omega \Delta E}$$

\# of scattered photons n_s per solid angle $\Delta\Omega$, per energy bandwidth of scattered particle ΔE, normalized by the incoming flux j_i

RIXS cross-section = Kramers-Heisenberg Equation

1st term   2nd term

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \left| \langle f | \cancel{H}_{\text{int}} | i \rangle + \sum_{|n\rangle} \frac{\langle f | H_{\text{int}} | n \rangle \langle n | H_{\text{int}} | i \rangle}{E_i - E_n + \hbar\omega_i + i\Gamma} \right|^2$$

|i>=initial, ground state
|n>=intermediate, excited
|f>=final (excited or not)

J. App. Phys. 57, 3615 (1985)

$$H_{\text{int}} = \text{Dipole operator}$$

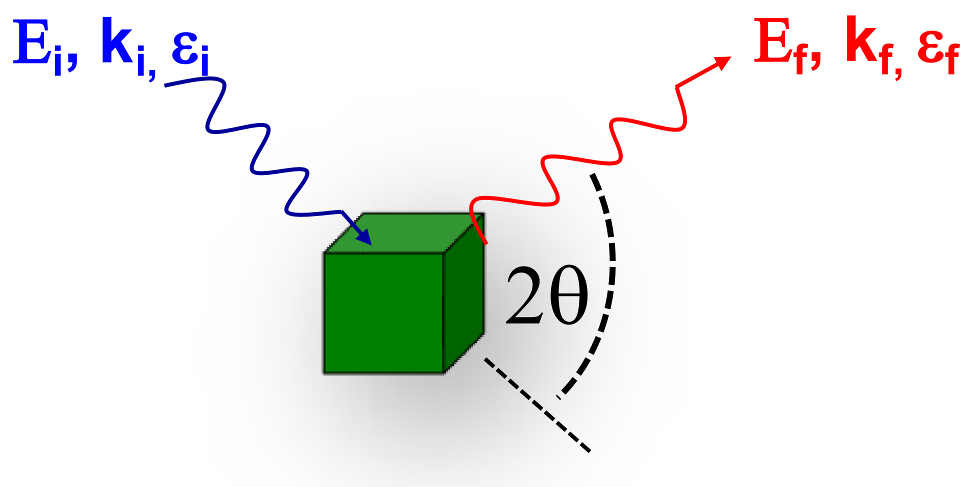
Under resonance conditions:

$\hbar\omega_i \sim E_i - E_n$ → **2nd term** >> 1st term (non-resonant)

- enhancement of the cross-section
- enables coupling to forbidden non-dipolar excitations (intra-band *d-d* orbital excitations, magnetic excitations)

RIXS in steps

X-ray Scattering



Photon *in* – Photon *out* technique

$E_f = E_i$ **Elastic Scattering ($\Delta E=0$)**

$E_f \neq E_i$ **Inelastic Scattering**

$\Delta E = E_f - E_i$ **Energy loss**

X-ray photon:

- Energy $E = h\nu$ → **Soft X-rays 0.2 – 2 keV**
  Hard X-ray 2 – 20 keV
- Wavevector $k = 2\pi/\lambda$
- Polarization ε

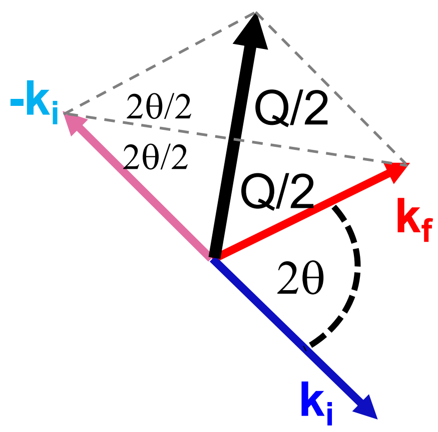
To study crystals, λ H *a* H 3 Å is needed
➔ Photon Energy E **(keV) ~ 12.4/λ(Å)** i.e. **X-rays**!

If $\Delta E \ll E_i$ → $|k_i| \sim |k_f|$

Momentum Transfer:

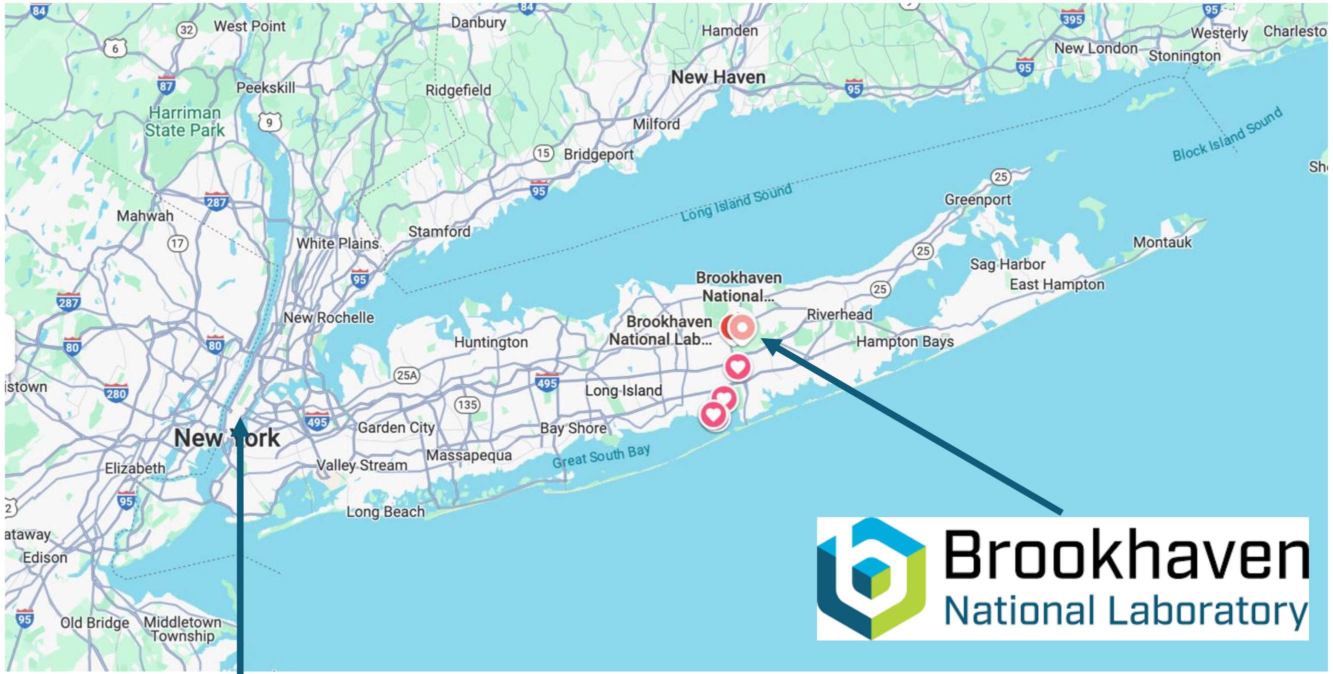
$$Q = k_f - k_i$$
$$= 2 \times |k_i| \times \sin(2\theta/2)$$
$$= (4\pi/\lambda) \times \sin(2\theta/2)$$

Scattering Triangle



RIXS – NSLS-II and BNL

Electron storage ring



Manhattan

Our endstation / lab

Google map

NSLS-II, BNL, Upton, NY
Aerial view

Brookhaven National Laboratory

RIXS: instrument concept for Soft X-rays

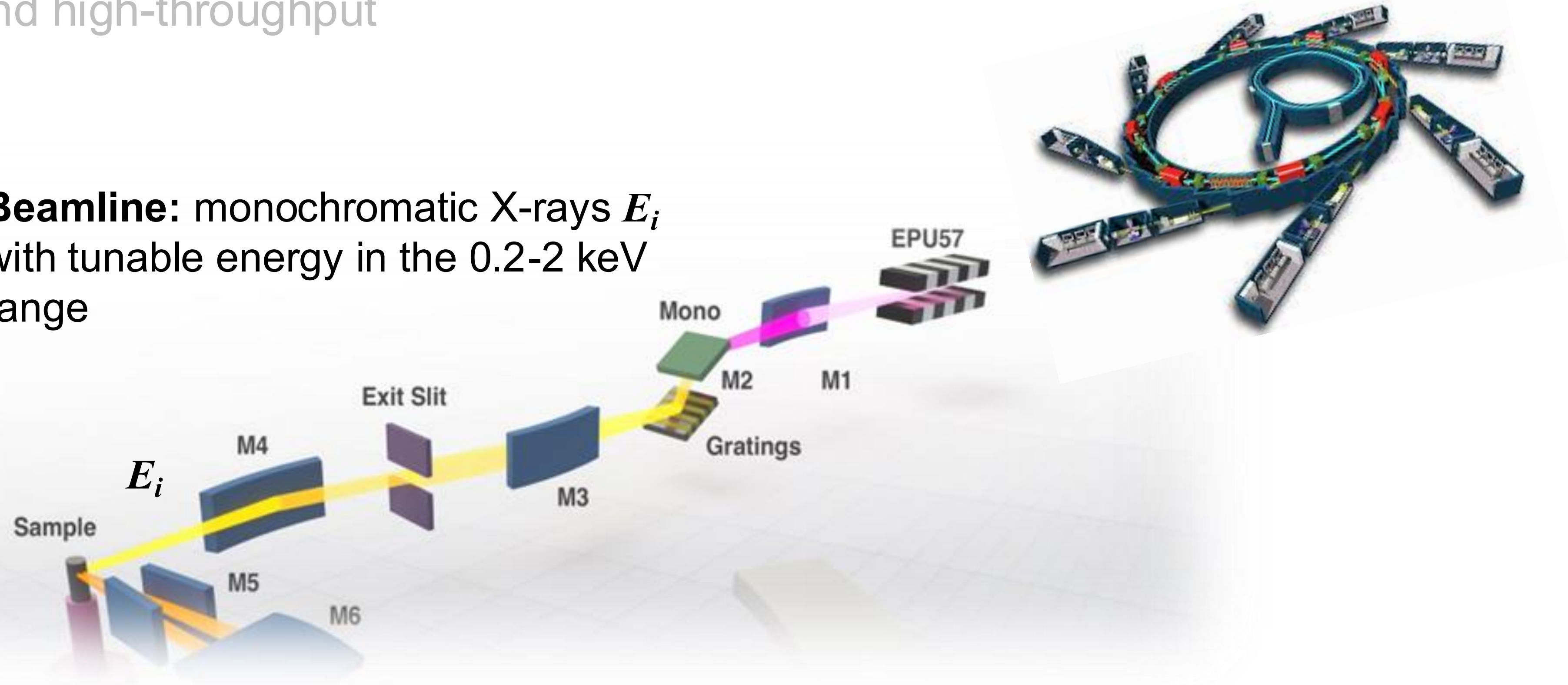
Requirements

1) resonance → monochromatic and tunable E_i
2) RIXS cross section intrinsically low → high photon flux for E_i and high-throughput instrument

➔ **Special X-ray Source !**

Synchrotron: bright, high photon flux X-ray source

Beamline: monochromatic X-rays E_i with tunable energy in the 0.2-2 keV range



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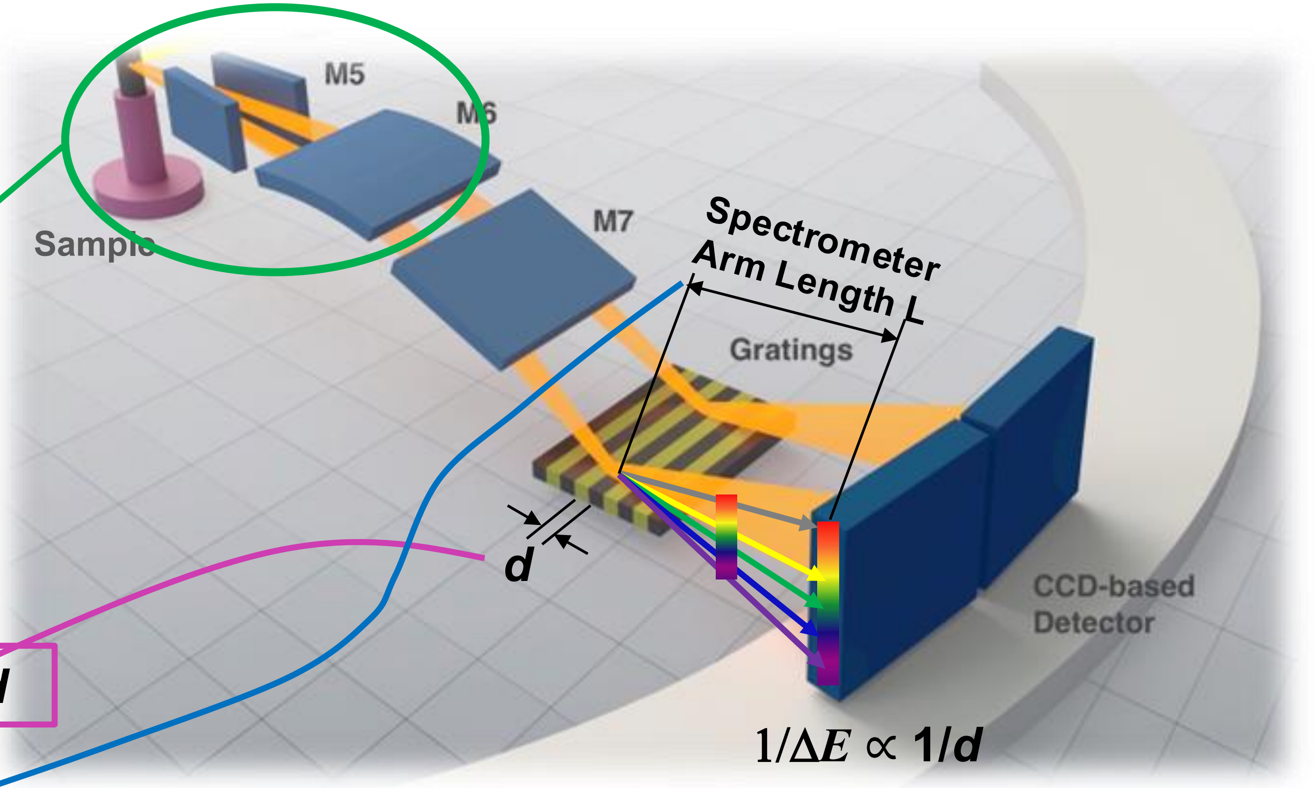
RIXS: instrument concept for Soft X-rays

Requirements

2) RIXS cross section intrinsically low → high photon flux for E_i and high-throughput instrument
3) distinguish overlapping excitations → high resolving power $R = 1/\Delta E$ to resolve E_f with high precision

→ **Special-design for RIXS Spectrometer !**



Collective Optics to increase the "collected solid angle" $\Delta\Omega$ → increase spectrometer throughput

Grating: dispersive optical element for Soft X-rays → separates in energy the scattered X-rays

Smaller grating line separation ***d*** → increase ***R*** ∝ **1/*d***

Longer Spectrometer Arm ***L*** → increase ***R*** ∝ ***L***

$1/\Delta E \propto 1/d$

$1/\Delta E \propto L$

→ **Long Spectrometer Arm design enables RIXS with high resolving power!**

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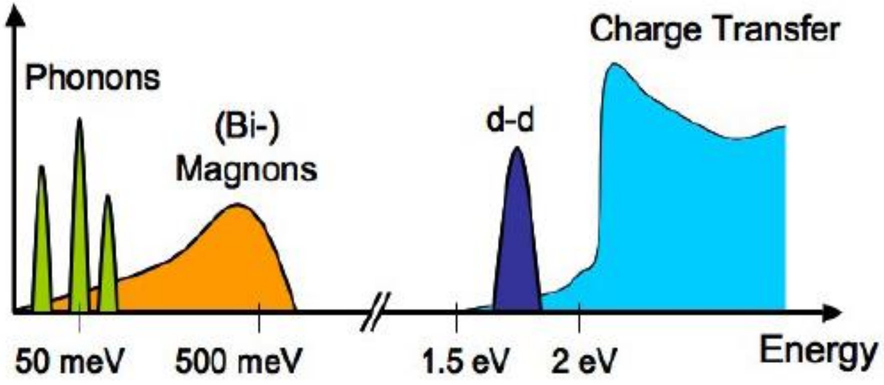
RIXS in a nutshell

Summary

- **Inelastic:** create excitations sensitive to all electron degrees of freedom → ideal for studying electronic properties in novel materials
- **Momentum Transfer Q** → measure E(q) dispersion relation
- **Resonant** → cross-section enhancement, **site** and **chemical** selectivity, small sample volume needed



L.J.P. Ament et al., *Rev. Mod. Phys*. 83,705 (2011)

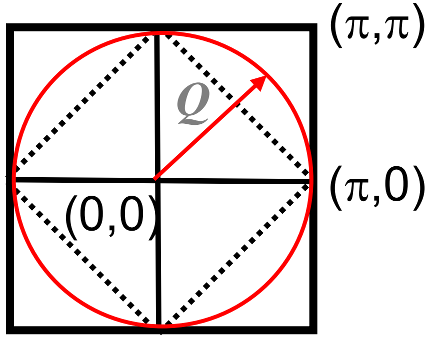
Requirements

1) resonance → monochromatic and tunable E_i
2) RIXS cross section intrinsically low → high photon flux for E_i and high-throughput instrument
3) distinguish overlapping excitations → high resolving power $R = 1/\Delta E$ to resolve E_f with high precision

Limitations

1) Intrinsic limitation in Q
2) Poor energy resolution ΔE compared to INS
3) complicated cross-section

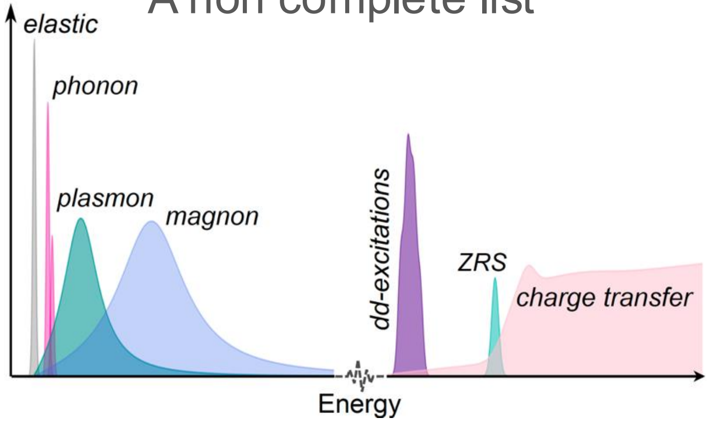
Brillouin Zone



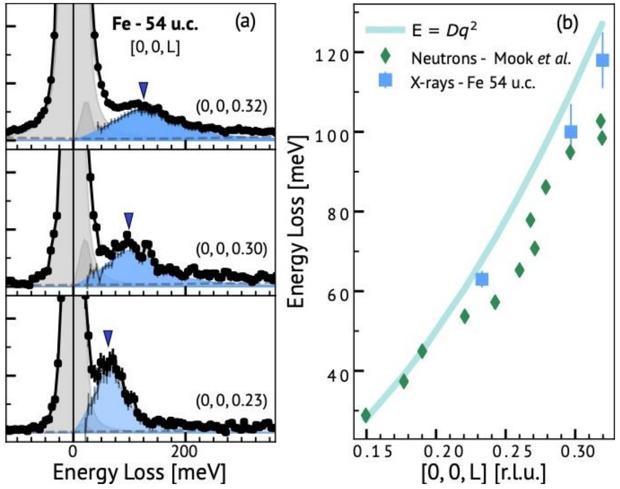
a=b=3.8 Å
E=930eV 2θ=150°

RIXS & excitations

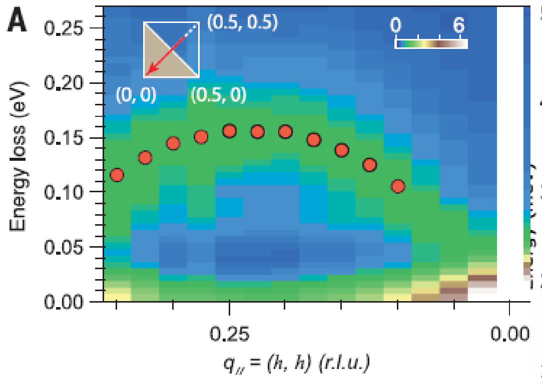
A non complete list



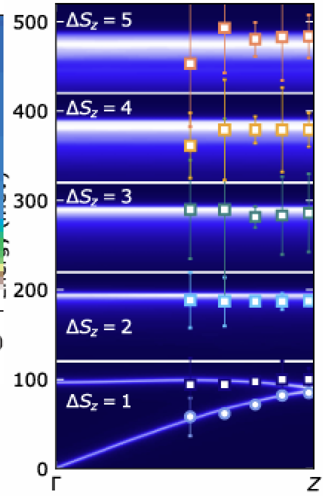
Spin excitations



J. Pelliciari et al. **Nat. Mater.** 20, 188 (2021).



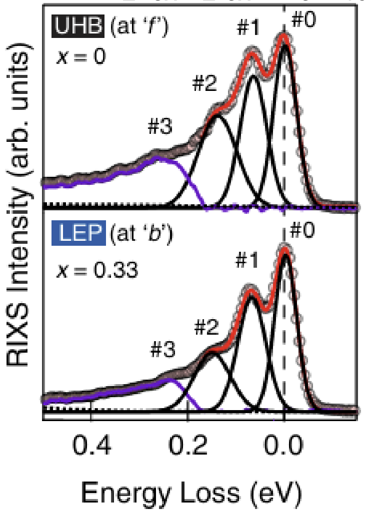
H. Lu et al. **Science.** 373, 213 (2021).



J. Li et al. **Phys. Rev. X.** 13, 011012 (2023).

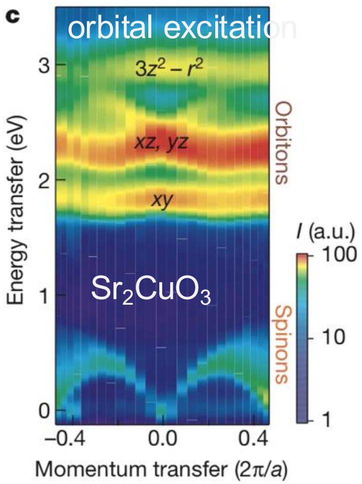
Phonons

$Ca_{2+5x}Y_{2-5x}Cu_5O_{10}$



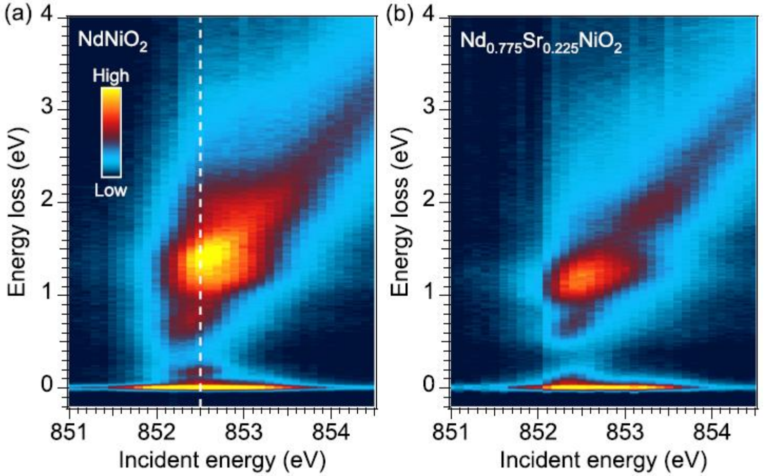
W.S. Lee et al., **PRL** 110, 265502 (2013); S. Johnston et al., **Nat. Comm.** 10563 (2016).

Spinon - orbiton



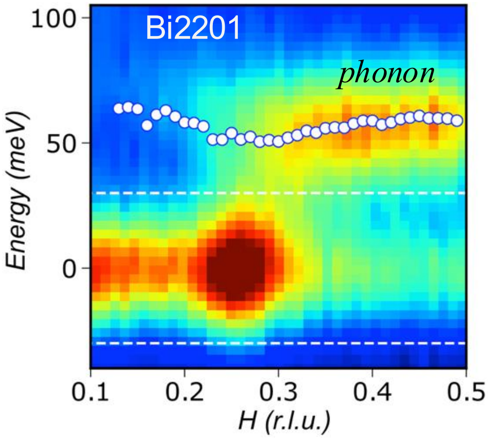
J. Schlappa et al., **Nature** 485, 82 (2012).

Crystal-field excitations



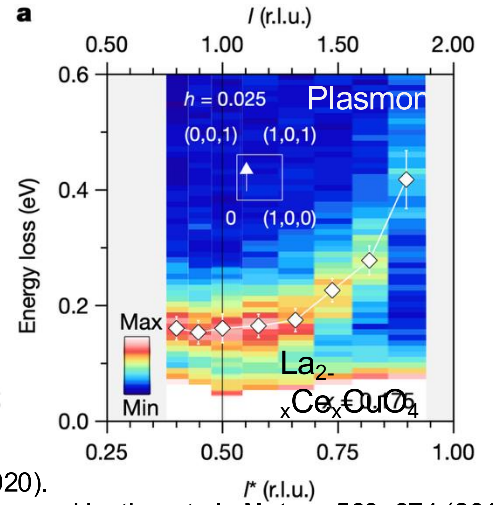
M. Rossi et al., **Phys. Rev. B** 104, L220505 (2021).

Charge order



J. Li et al., **PNAS** 117, 16219 (2020).

Plasmon



Hepting et al., **Nature** 563, 374 (201

Outline:

- Some view of light matter interaction
- X-ray Sources
- Specifics of Resonant Inelastic X-Ray Scattering
- **Examples of RIXS studies**
  - Novel superconductors – Fan et al, Phys. Rev. Lett. 133, 206501
  - Experiments on thin magnets – Pelliciari et al, Nat. Mat. 20, 188
  - Excitons – Occhialini et al, Phys. Rev. X 14, 031007

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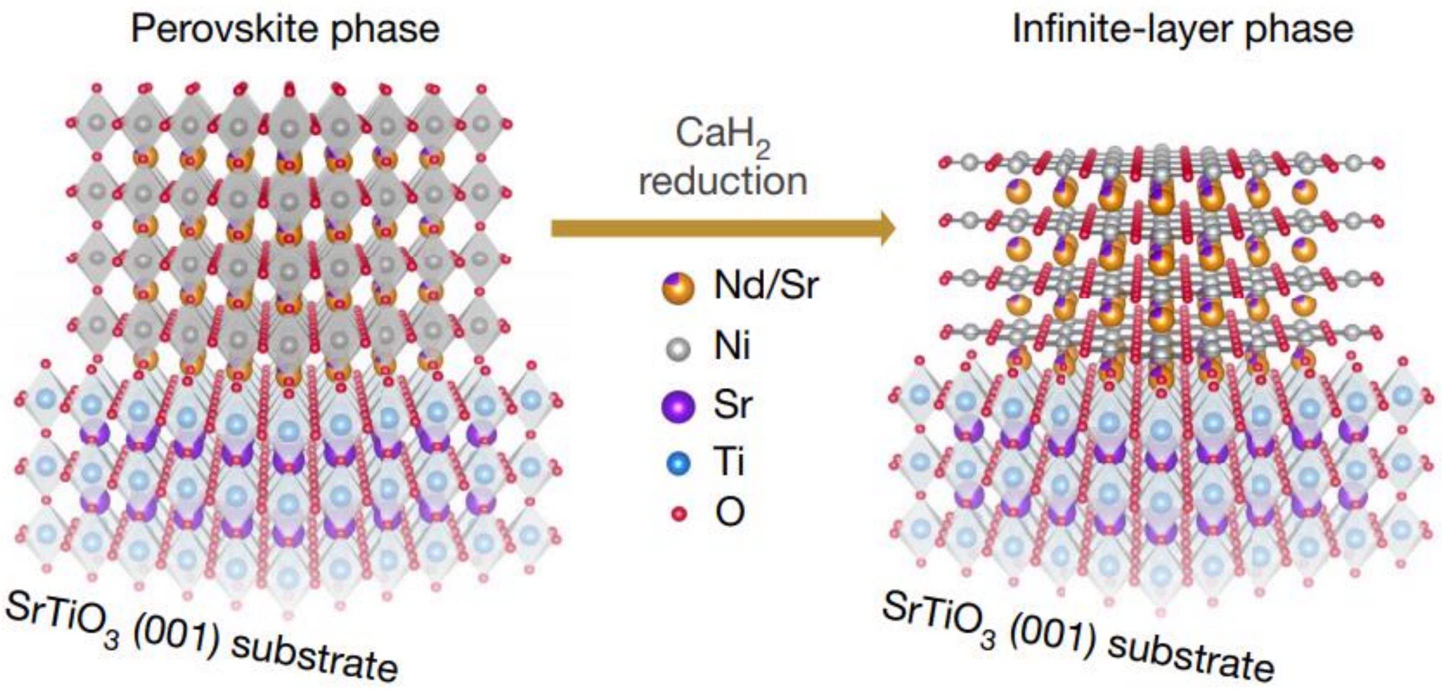
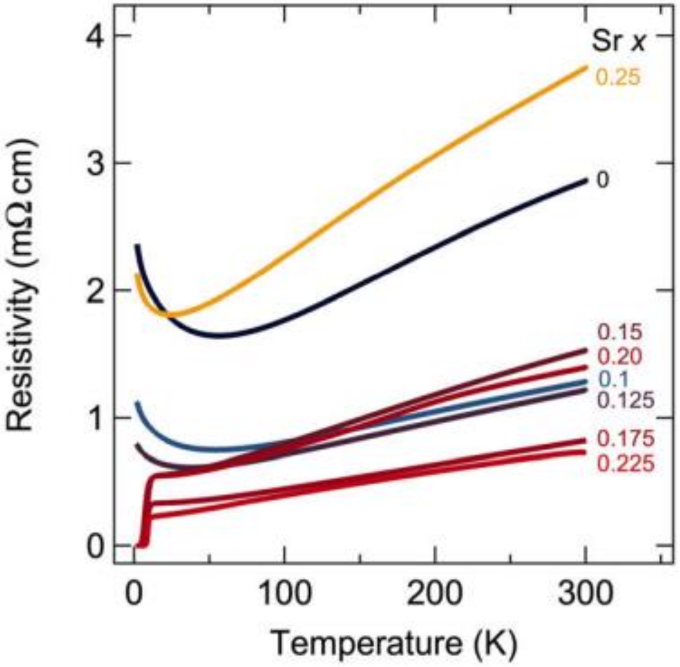
Nickelates -- Intro





- Developed from $RNiO_3$ by CaH_2 Reduction
- Superconducting at 20% hole/ Sr doping
- T_C ~ 15 K
- An STO capping layer can be added

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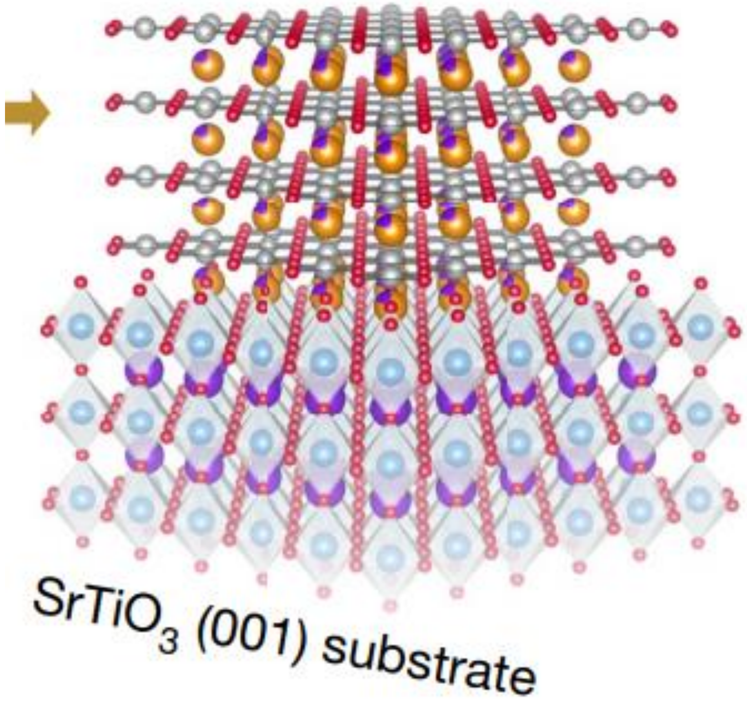
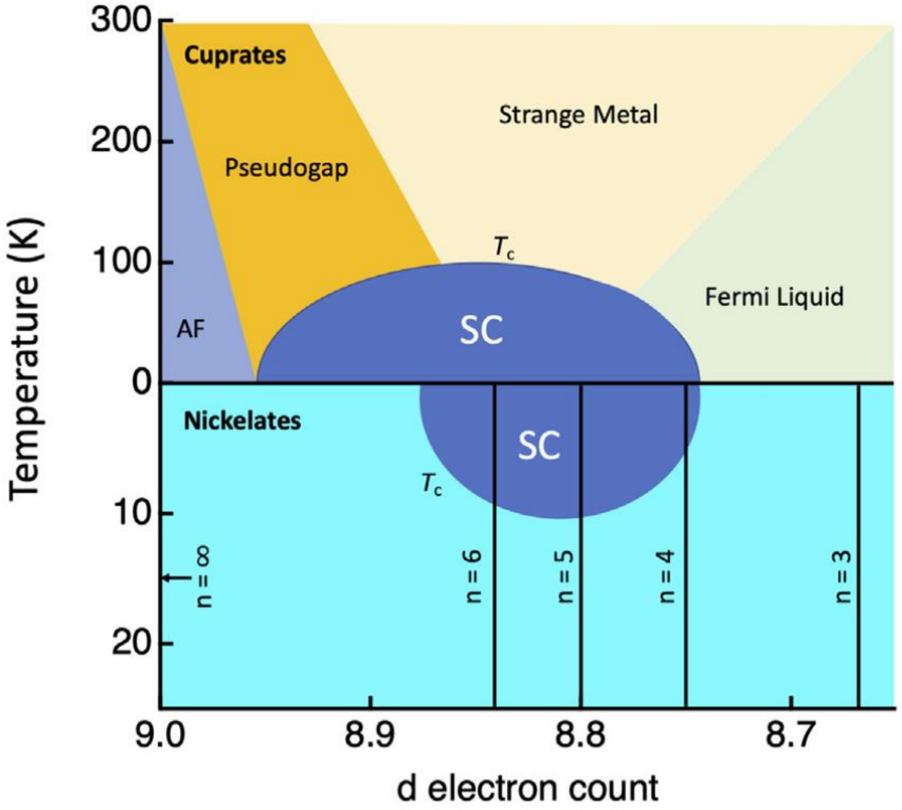
D. Li et al. Nature. 572, 2019.
D. Li et al. Phys. Rev. Lett. 125, 2020.

Nickelates -- Intro





- Layered structure
- d^9 electronic configuration
- Likely unconventional SC with typical dome shaped phase diagram
- Only thin films are superconducting
- STO capping layer can be added

D. Li et al. Nature. 572, 2019.
D. Li et al. Phys. Rev. Lett. 125, 2020.
J. Mitchell, Frontiers in Physics
https://doi.org/10.3389/fphy.2021.813483

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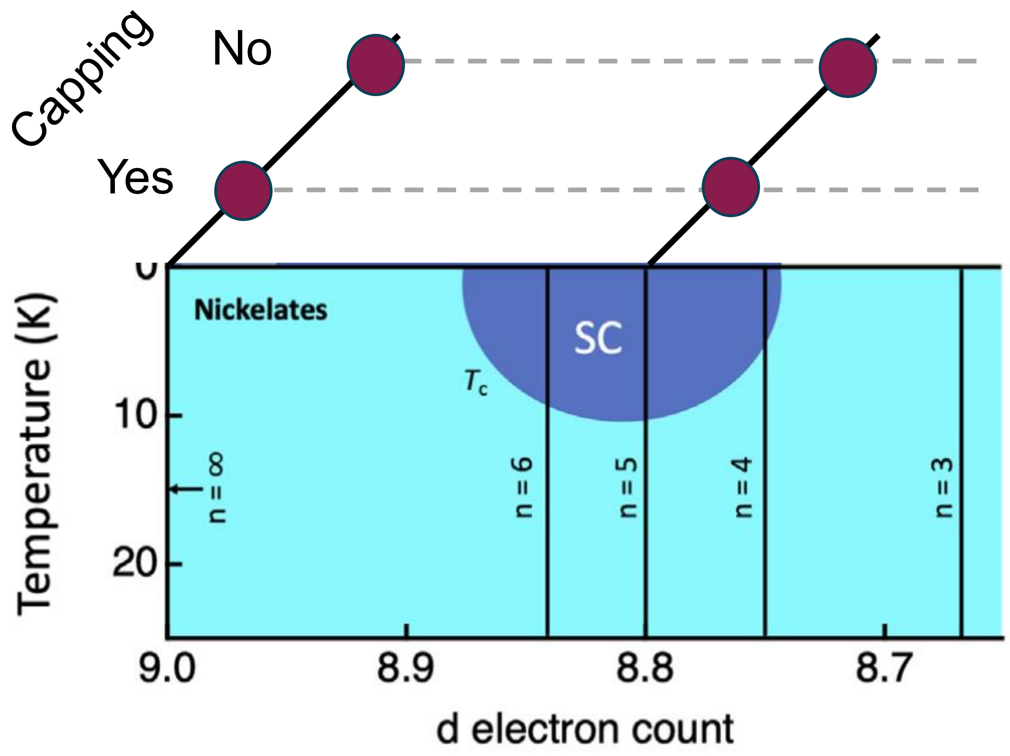
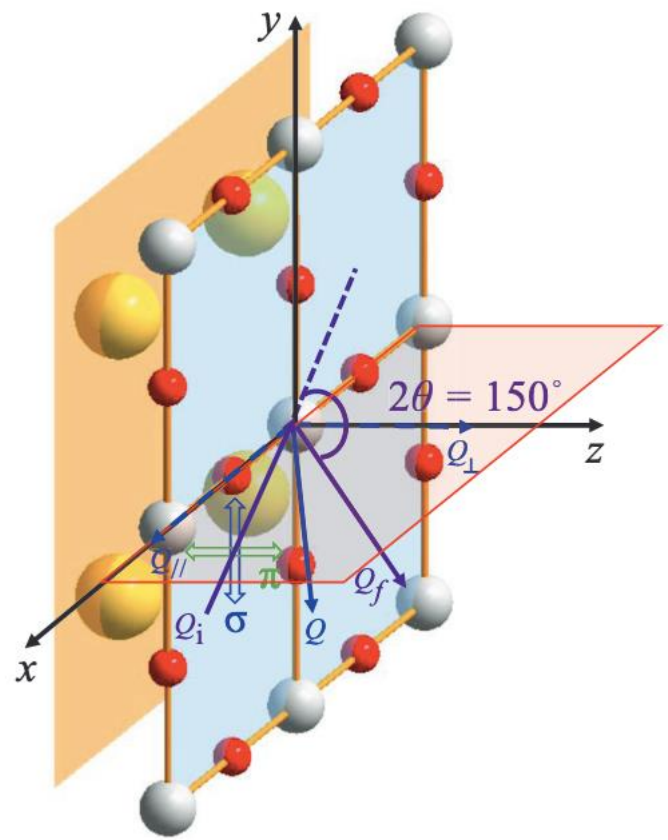
Samples & Experimental conditions

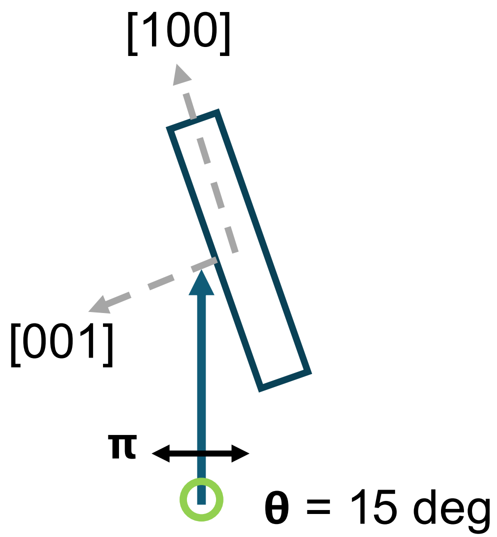


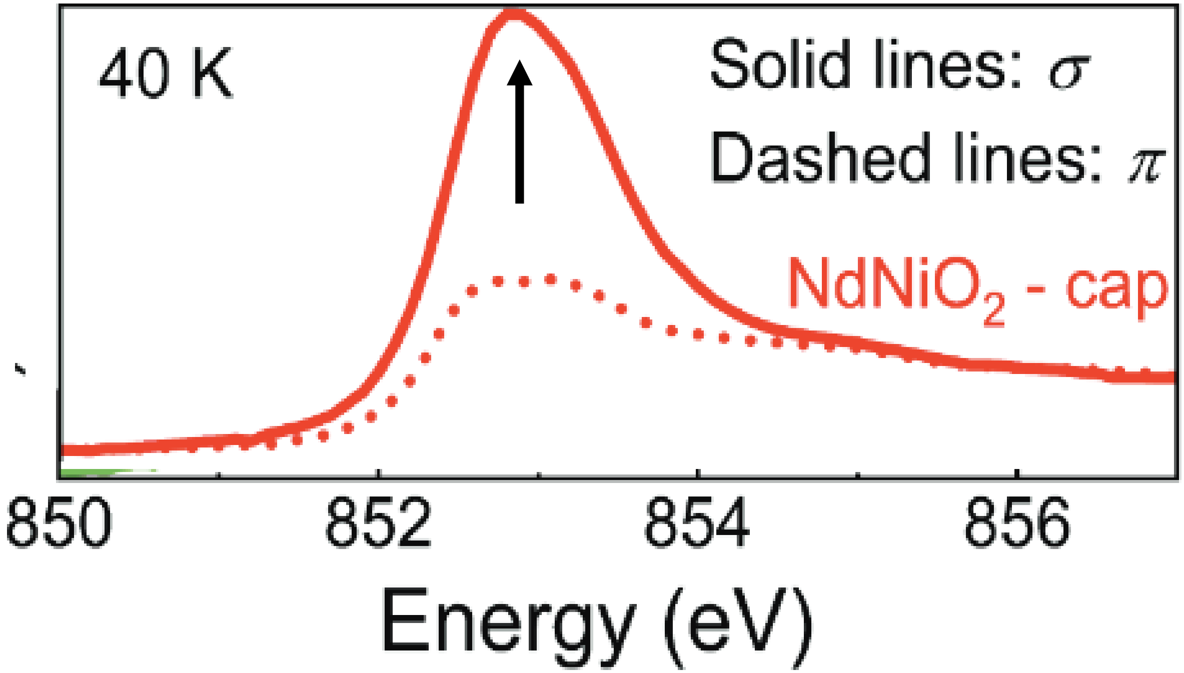


- Thickness ~10nm
- Temperature 30 K
- 2theta = 150deg, grazing incidence geometry
- Resolution 35 meV

J. Mitchell, Frontiers in Physics https://doi.org/10.3389/fphy.2021.813483

Nickelates – XAS response





Strong linear dichroism indicate a Ni-d^9 electronic configuration
Ground state -> hole with x^2-y^2 symmetry

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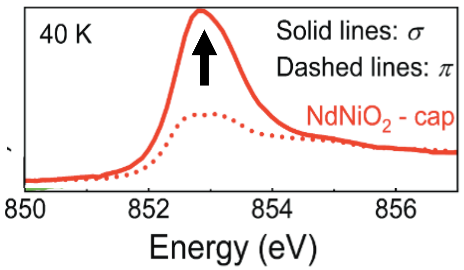
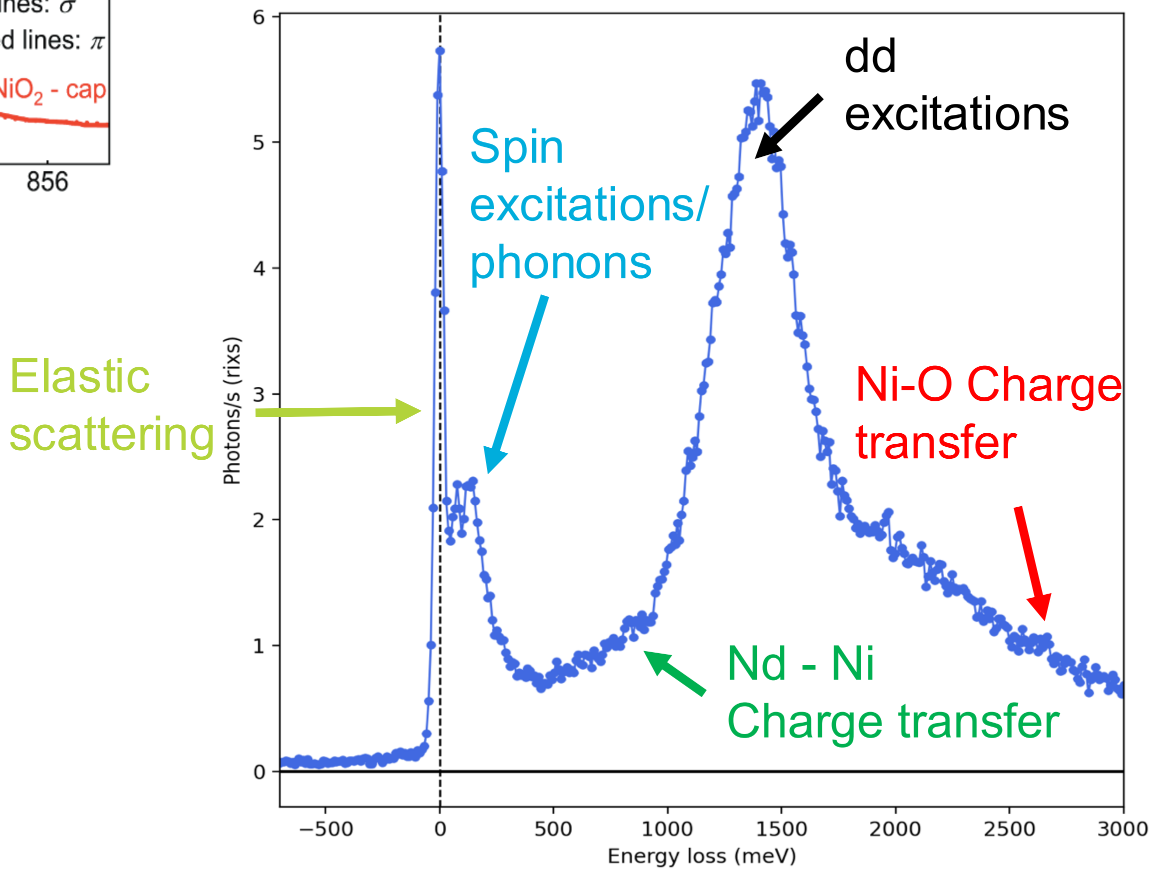
Nickelates – RIXS response





Broad perspective of the spin/charge/orbital elementary excitations

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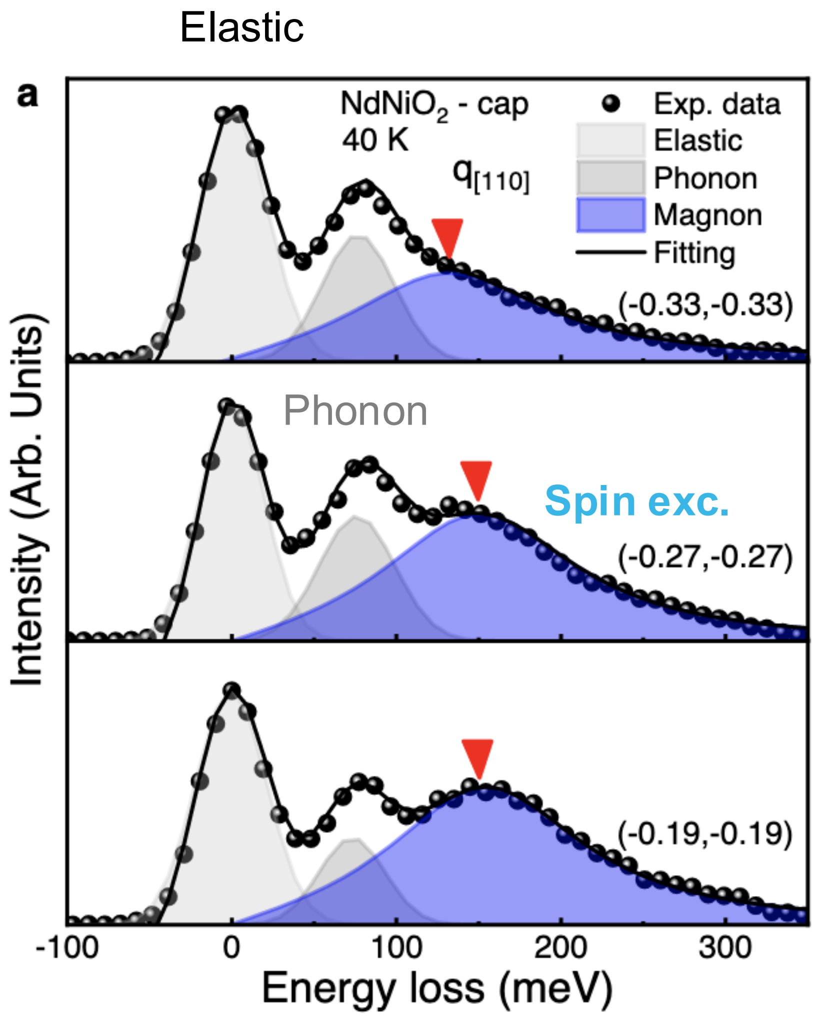
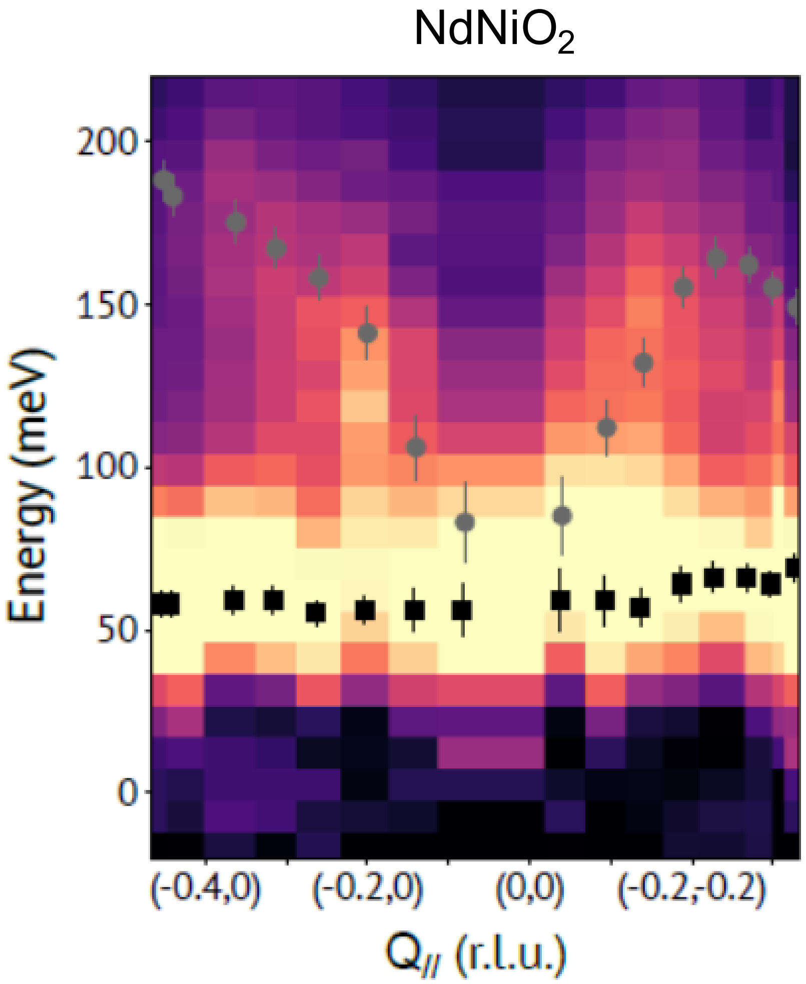
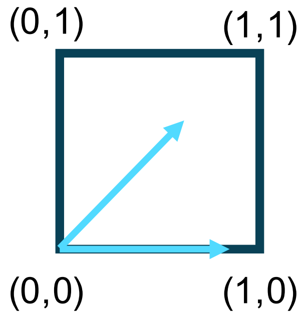
Nickelates – Low Energy excitations







Spin Excitations

Phonon

- Presence of phonons and spin excitations in $NdNiO_2$
- Dispersive spin excitations

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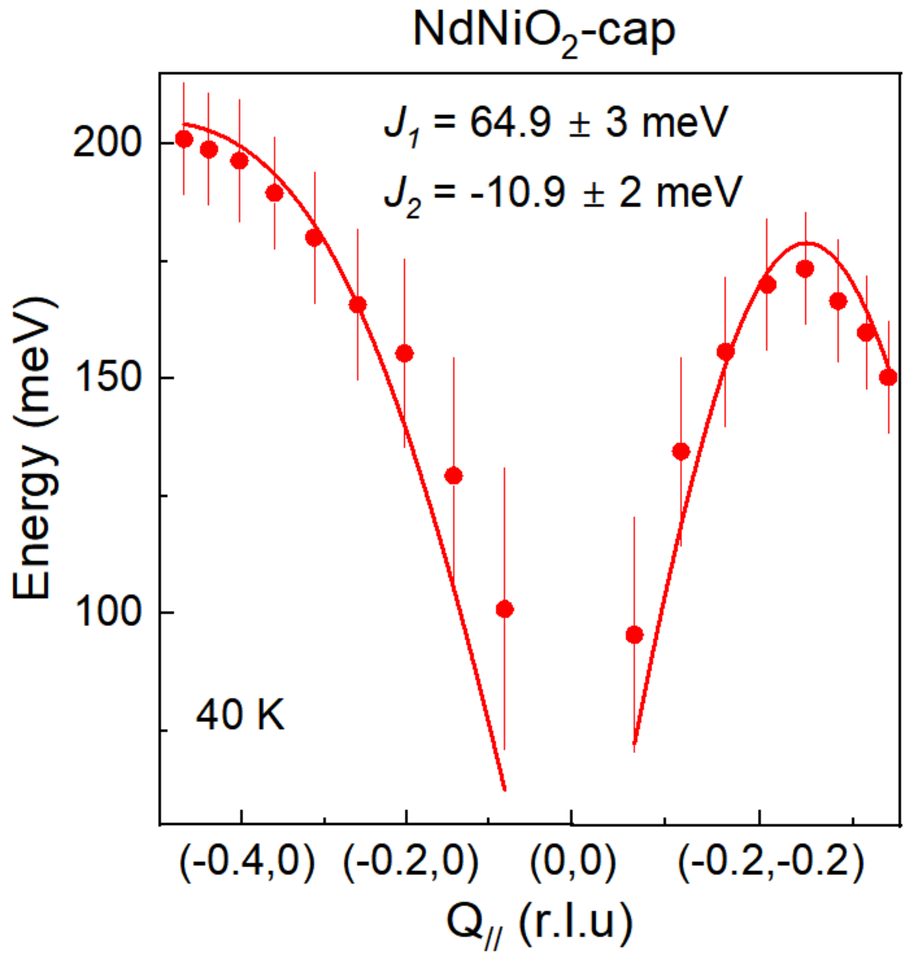
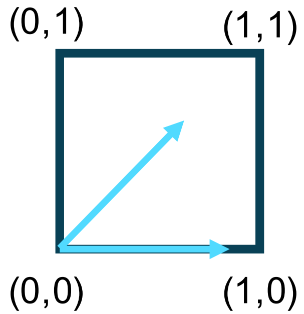
Capping effect – Low Energy excitations





$$H = J_1 \sum_{\langle ij \rangle} S_i \cdot S_j + J_2 \sum_{\langle ii' \rangle} S_i \cdot S_{i'}$$

Dispersion of spin excitations fit with J_1-J_2 Heisenberg model

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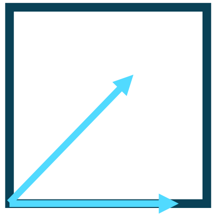
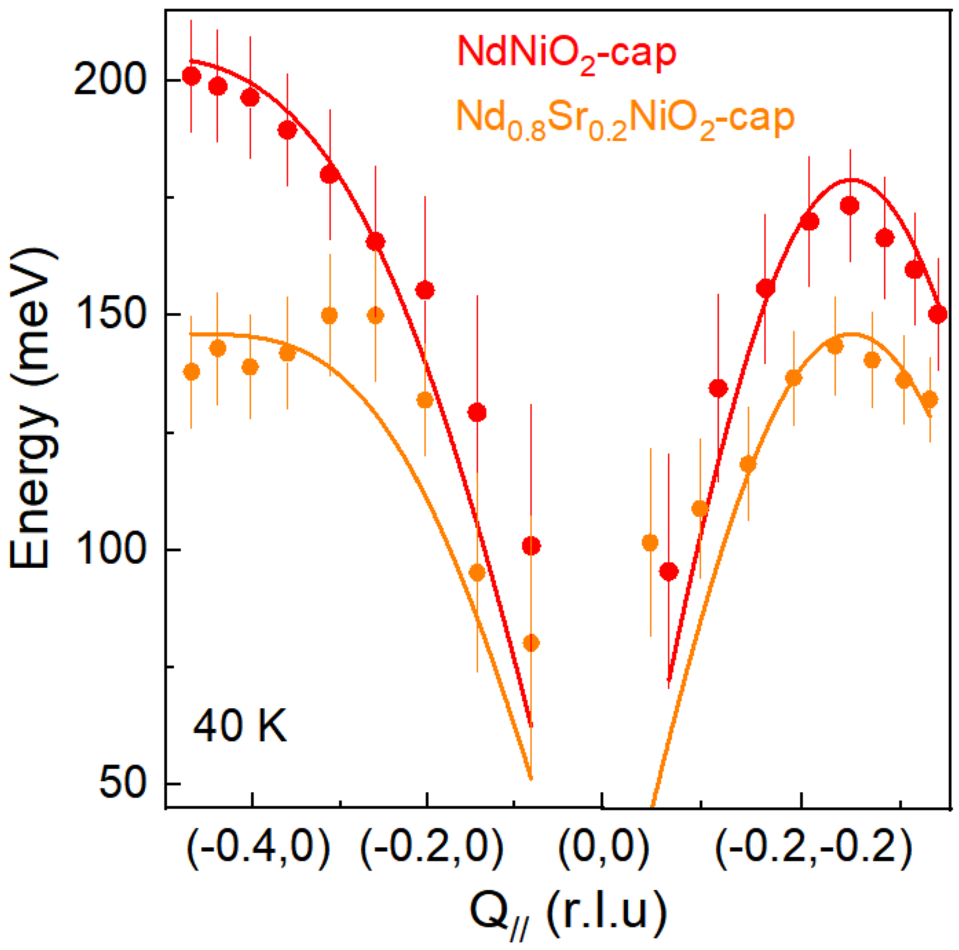
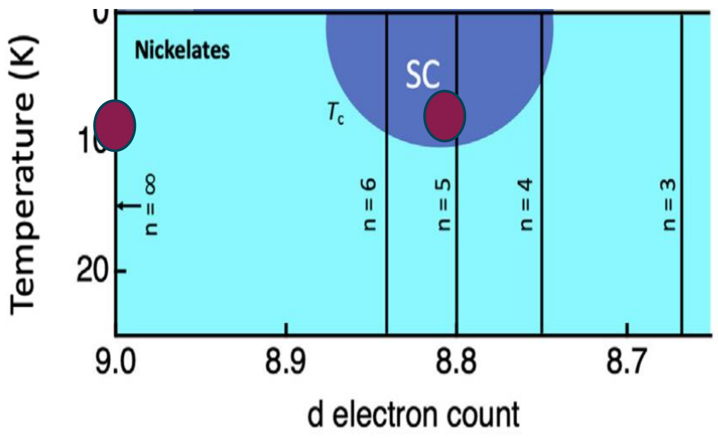
Doping effect – Low Energy excitations



Capped (NNO)
J_1= 64.9 meV;
J_2 = -10.9 meV

Capped (NSNO)
J_1= 62 meV;
J_2 = 0 meV





- Doping consistently softens the spin excitations
- Magnetic dilution effect explain the doping dependence

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Conclusions

Intrinsic effects

- Spin excitations are intrinsic of 112 nickelates (regardless of capping)
- No CDW in parent infinite layer nickelates
- Doping effect of spin excitations

Interfacial effects

- STO Capping slightly affects spin excitations and Nd/Ni charge transfer
- DFT calculations show STO capping (apolar interface) affects the Nd/Ni hybridization
- Consequence of this is an increase of magnetism (more calculations underway)

More at Fan et al, Phys. Rev. Lett. 133, 206501

Conclusions in general

X-rays

- **Elastic and Inelastic scattering fundamental to study materials**
- **Sensitivity to electronic orders**
- **Sensitivity to excitations**

Large scale facilities

- **New instrumentation leads to better understanding**
- **Collaboration using multiple techniques to deeply understand the physics**

More at Fan et al, Phys. Rev. Lett. 133, 206501

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Outline:

- Some view of light matter interaction
- X-ray Sources
- Specifics of Resonant Inelastic X-Ray Scattering
- **Examples of RIXS studies**
  - Novel superconductors – Fan et al, Phys. Rev. Lett. 133, 206501
  - Experiments on thin magnets – Pelliciari et al, Nat. Mat. 20, 188
  - Excitons – Occhialini et al, Phys. Rev. X 14, 031007

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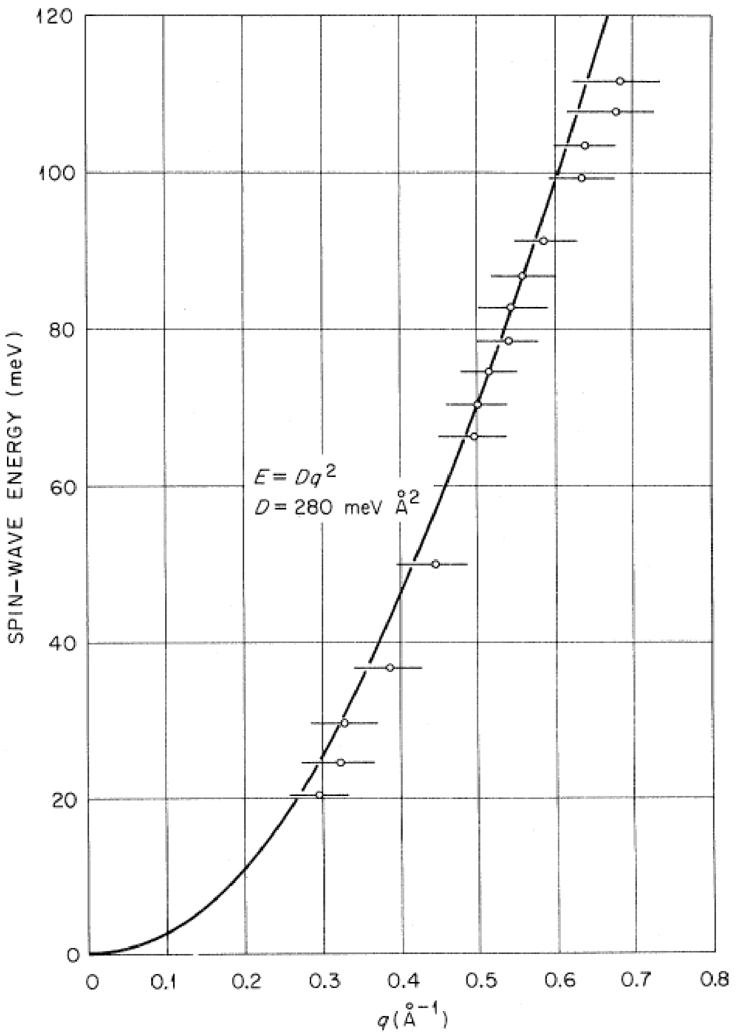
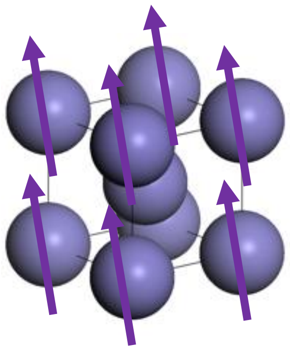
Spin-waves in Fe



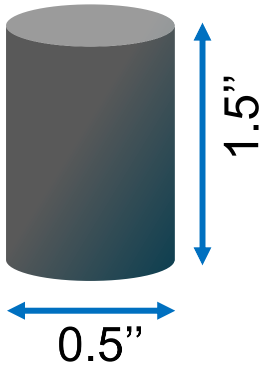
PRL **179**, 417 (1969)

- Fe metal is one of the simplest, known ferromagnet

Iron Metal:



Fe crystal



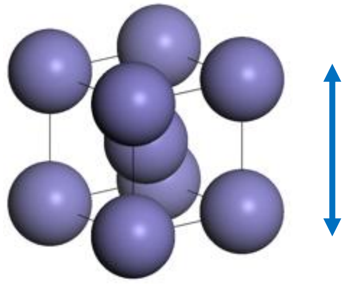
- Spin-wave in Fe metal were measured ~ 50 years ago in single crystal by INS (inelastic neutron scattering)

- Spin-wave dispersion relation E(q) reveals the typical behaviour for ferromagnet at small q:

$$E(q) = Dq^2 \propto q^2$$

Spin-waves in Fe studied with RIXS

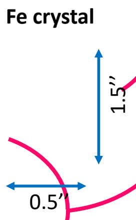
- Fe thin films grown by Molecular Beam Epitaxy (Yale University) on MgO substrate
- Film thicknesses: 105 unit cell (u. c.), 54 u.c., 29 u.c., 17 u.c., 6 u.c. and 3 u.c.

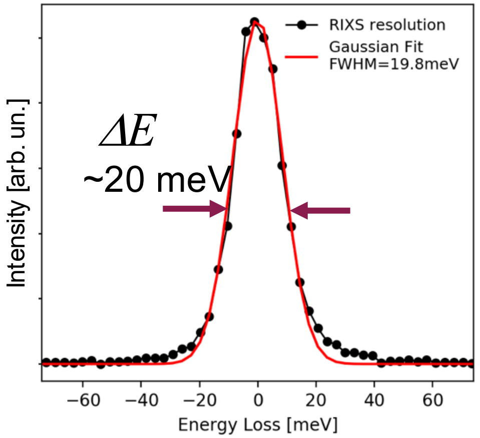


ently 30 nm, 16 nm, 9 nm, 5 nm, 2 nm, **1 nm!**

High-sensitivity of RIXS at Fe L_3 edge + few tens of nm penetration depth +high resolving power to investigate the low-energy spin-waves in ultrathin samples

Up to 37 million times thinner than the sample used in INS study!!





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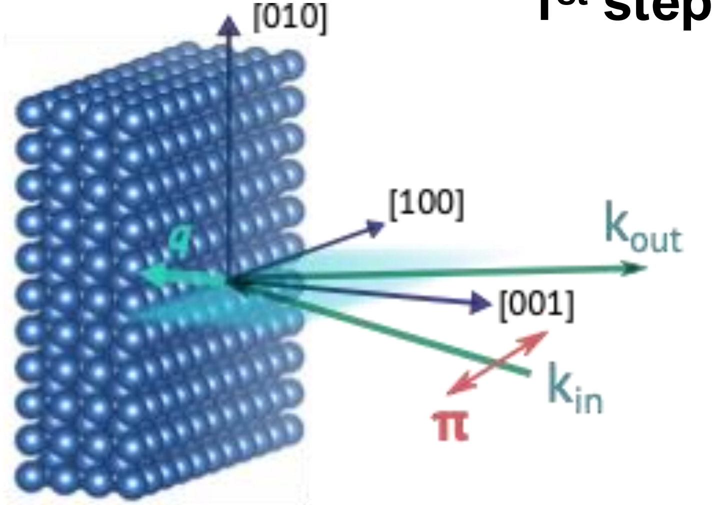
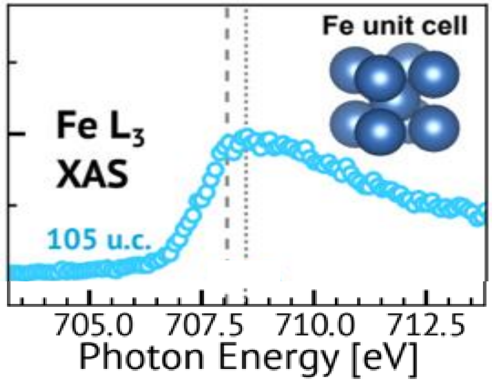
Spin-waves in Fe studied with RIXS

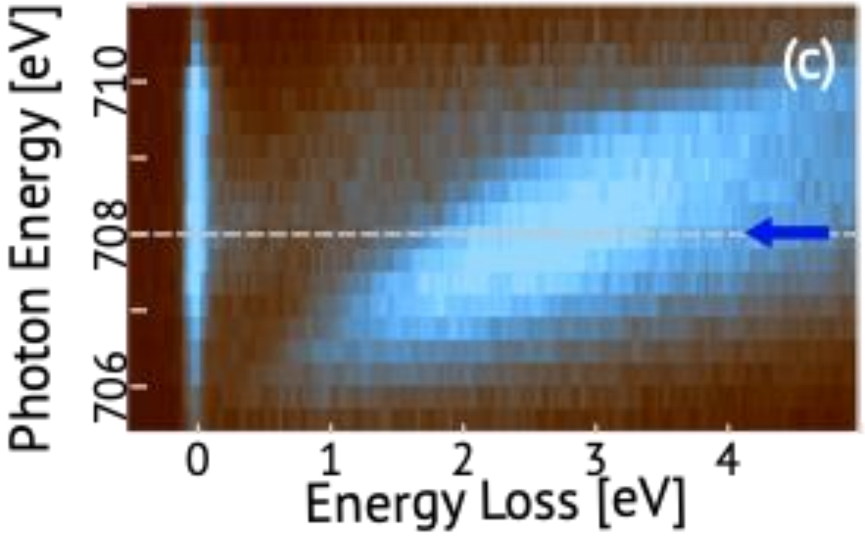


1st step: RIXS on Fe thick films 105 u.c. → check sensitivity and feasibility of the proposed approach

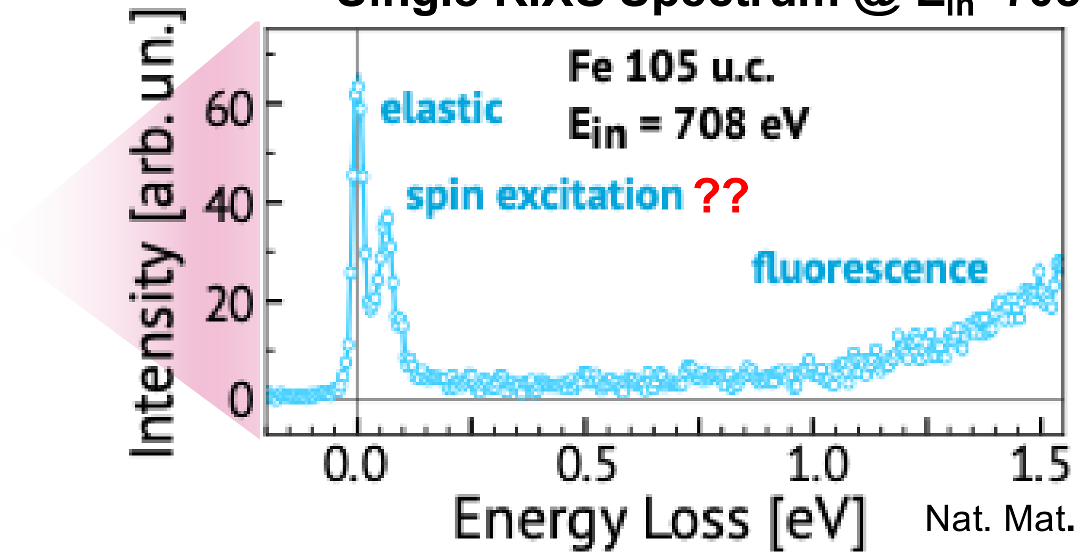


X-ray Absorption Spectrum: identify the resonance and energy range for $\boldsymbol{E_{in}}$

RIXS across the Fe L_3 edge

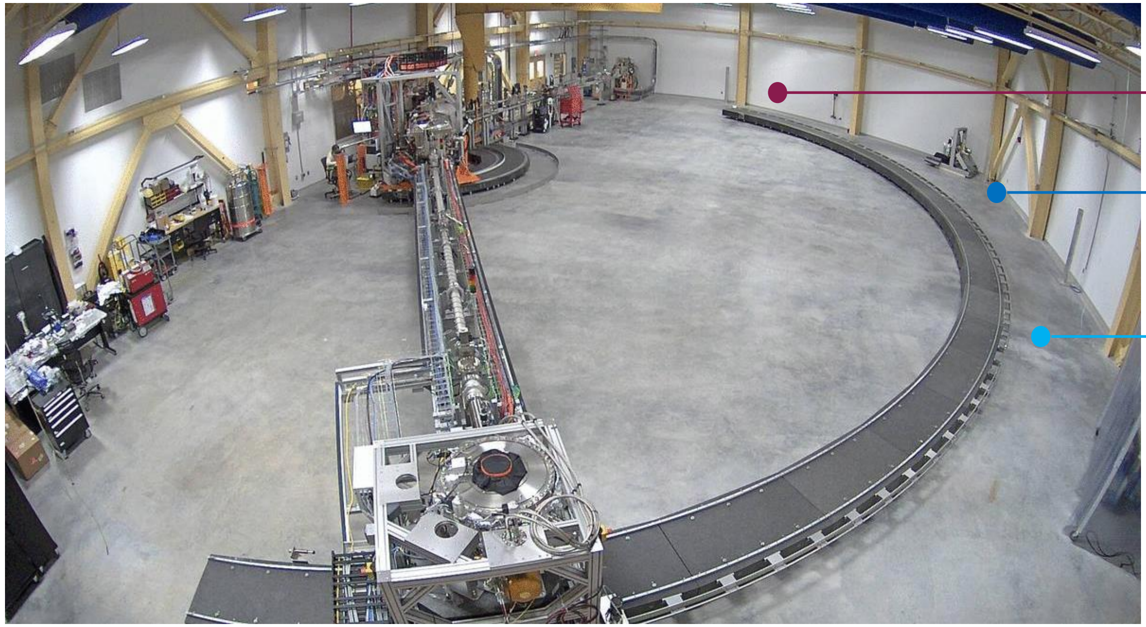


Single RIXS Spectrum @ E_{in}=708 eV

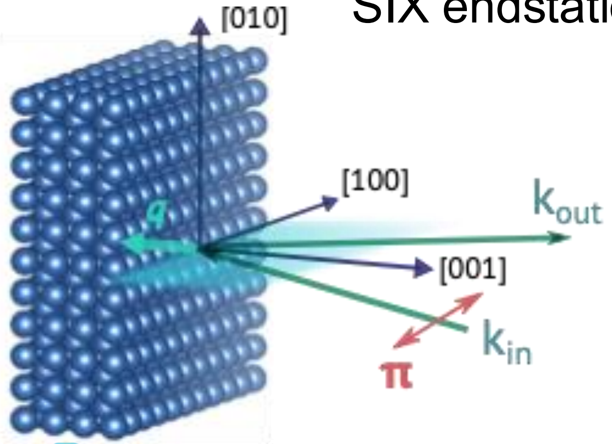


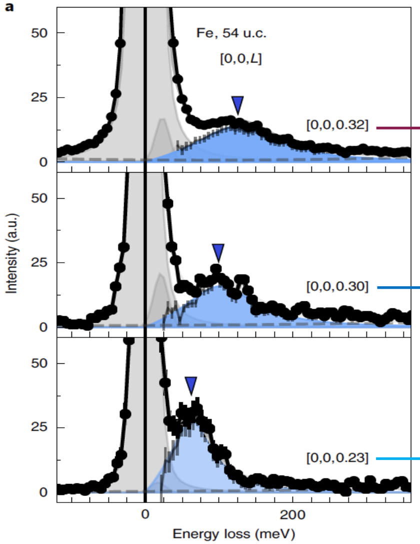
Nat. Mat. 20, 188 (2021)

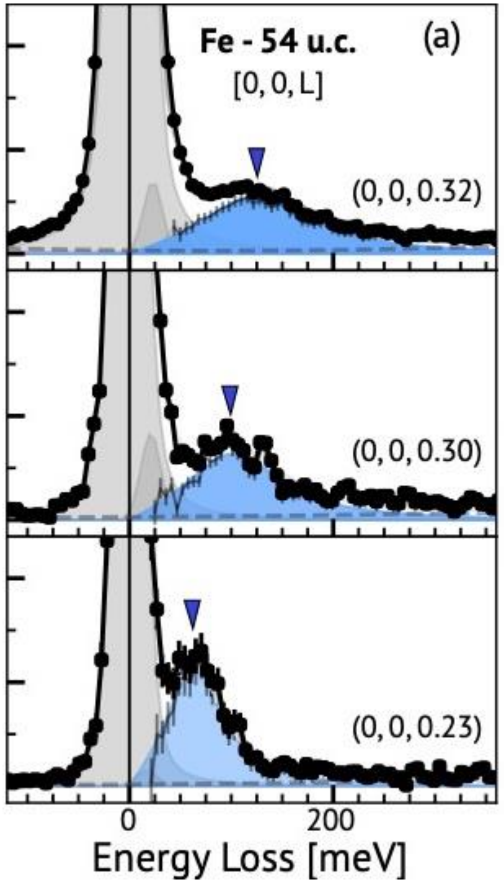
Spin-waves in Fe studied with RIXS

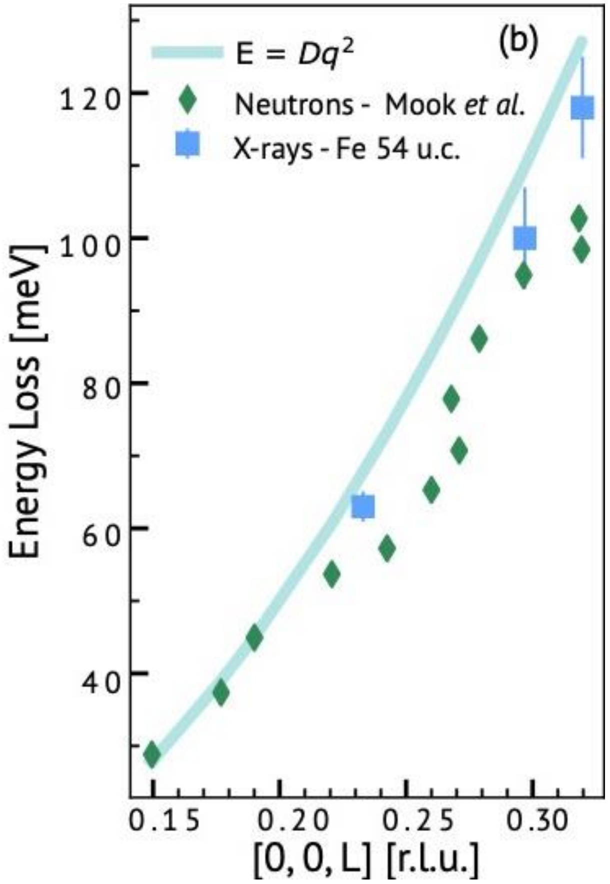


SIX endstation









Mook et al., PRB 7, 336 (1973)

- q - momentum dependence study to evaluate E(q)
- E(q) compatible with INS and $\propto q^2$

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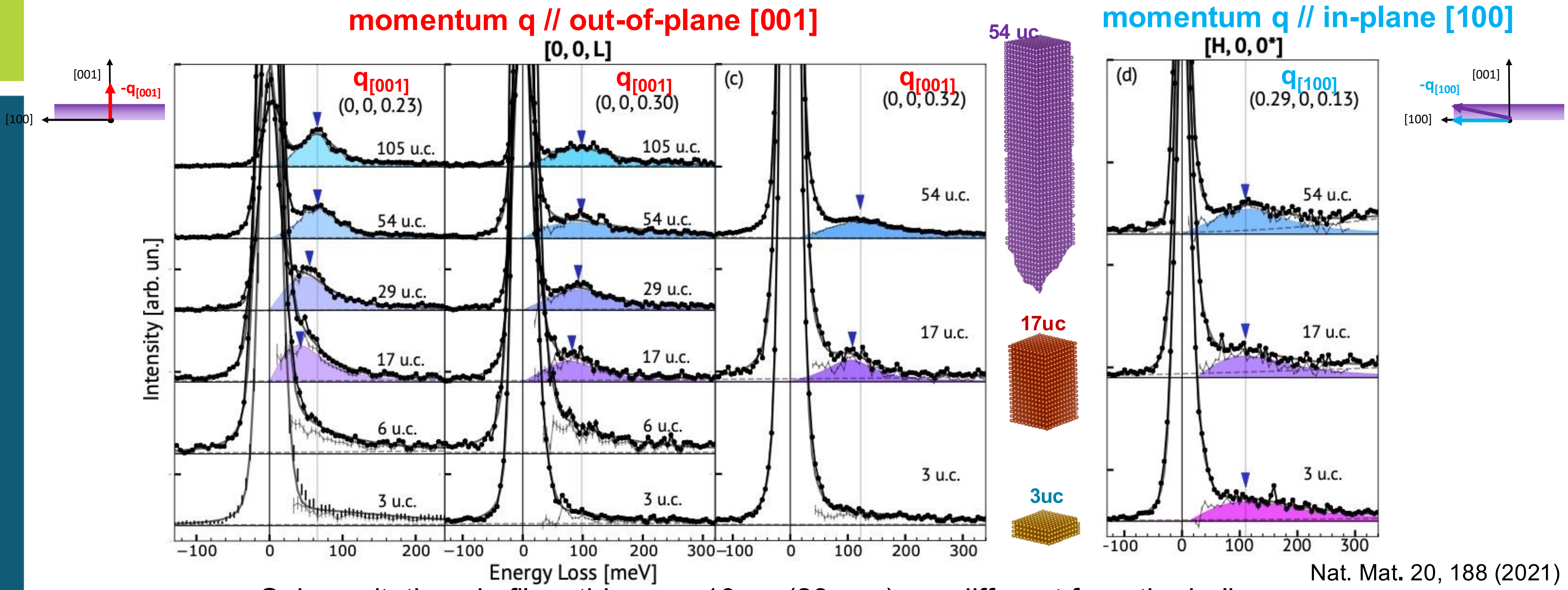
Spin-waves in Fe studied with RIXS: versus thickness



Nat. Mat. 20, 188 (2021)

- Spin excitations in films thinner < 10nm (29 u.c.) are different from the bulk
- Softening of the spin excitations along the [001] direction
- No change along the [100] direction

→ **Anisotropic** evolution between **[001]** and **[100]**

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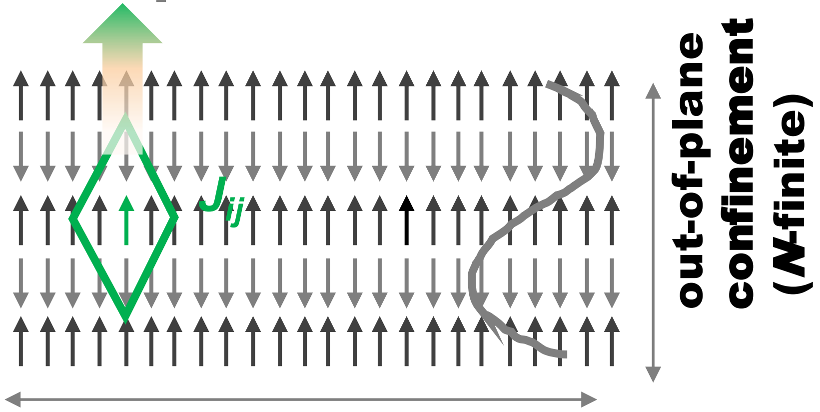
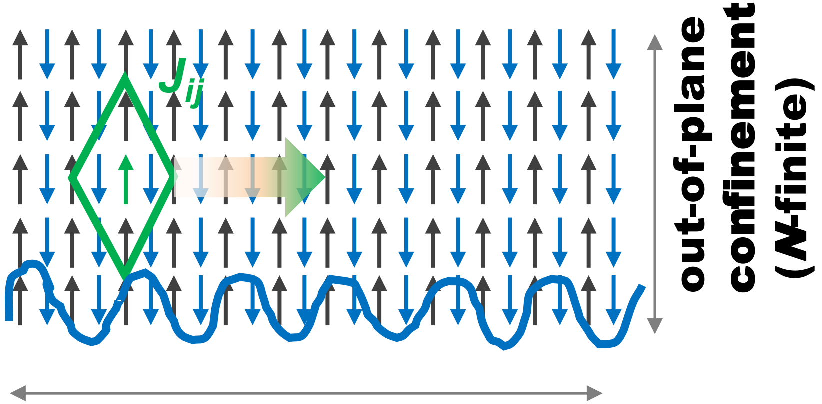
Tuning spin excitations in magnetic films by confinement

Out-of-plane mode at Zone Boundary



In-plane mode at Zone Boundary

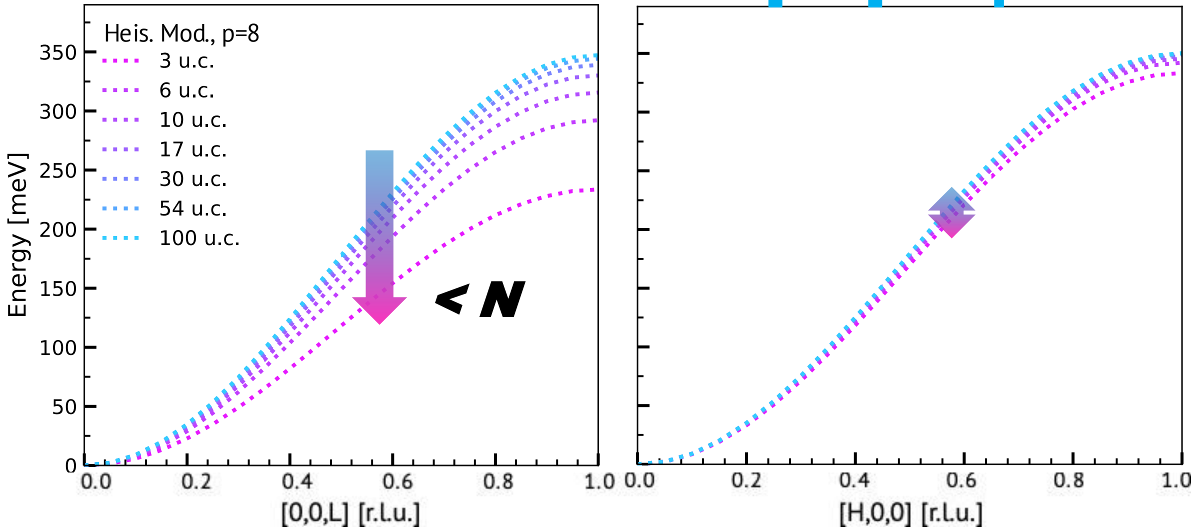


- **Heisenberg model** with an effective J_{ij} interaction to account for itinerant electron behaviour

$$\mathcal{H} = -\sum_{ij} J_{ij}\hat{S}_i \cdot \hat{S}_j \quad \textbf{with} \quad J_{ij} = J_0\left(\frac{a}{R_{ij}}\right)^p, \quad p=8$$

- Consider a finite number of layer ***N*** to simulate the confinement effect
- Anisotropic evolution of ***E(q) vs N*** between **out-of-plane** and **in-plane**

[001] – out of plane **[100] – in plane**



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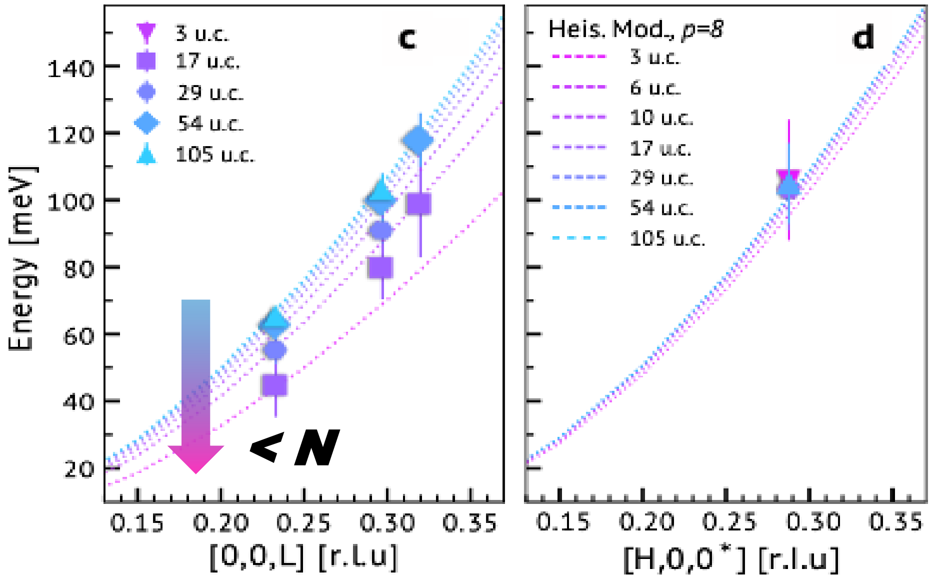
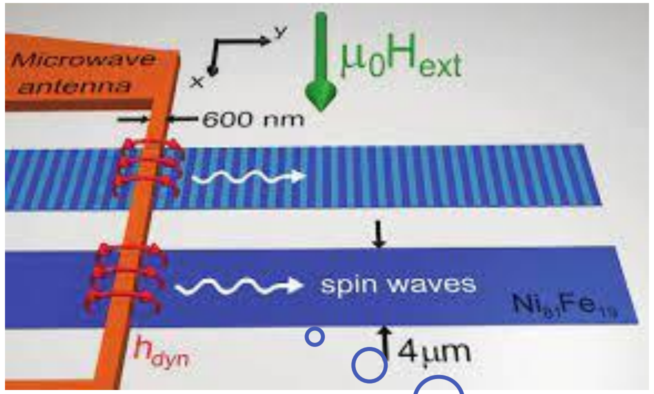
Tuning spin excitations in magnetic films by confinement



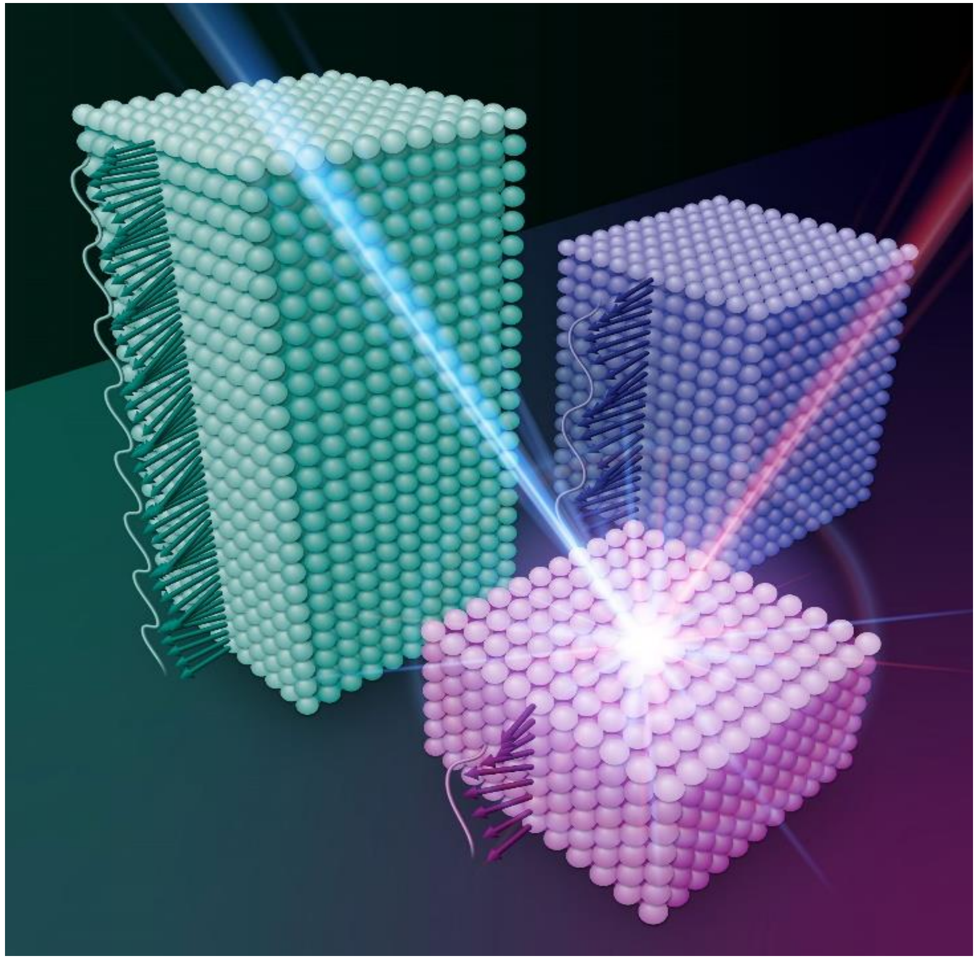
- The **geometrical confinement** causes the softening of the spin spin excitations // [001] while leaves them unchanged // [100]
- Tunability of **E(q) vs film thickness N** can be used to gain control of spin excitations energy in magnetic films for future devices.



Thickness of magnetic medium can be optimized to match the frequency/energy transmitted by the antenna

Summary

- RIXS results from thick (~ 30 nm) film are consistent with INS data measured on bulky single crystal (~40 mm)
- Thanks to high resolving power and high sensitivity of RIXS, spin-excitations could be detected in 1nm thin sample for the first time
- In Fe films with thickness N < 10nm, the spin-excitations present clear changes w.r.t. the bulk
- Anisotropic evolution of the spin dispersion $E(q)$ between [001] and [100]: softening along [001] for < N and invariance along [100]
- This result is understood as the effect of geometrical confinement due to the reduction of Fe-layers
- Film thickness can be used as a knob to manipulate $E(q)$ and optimize magnetic materials for future devices



Nat. Mat. 20, 188 (2021)

Outline:

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- Novel superconductors – Fan et al, Phys. Rev. Lett. 133, 206501
- Experiments on thin magnets – Pelliciari et al, Nat. Mat. 20, 188
- Excitons – Occhialini et al, Phys. Rev. X 14, 031007

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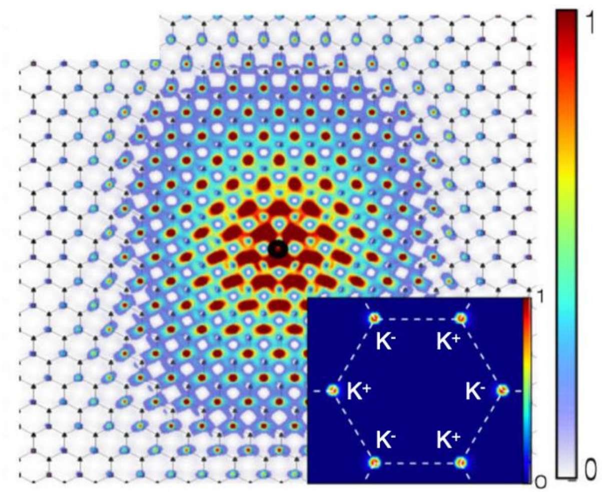
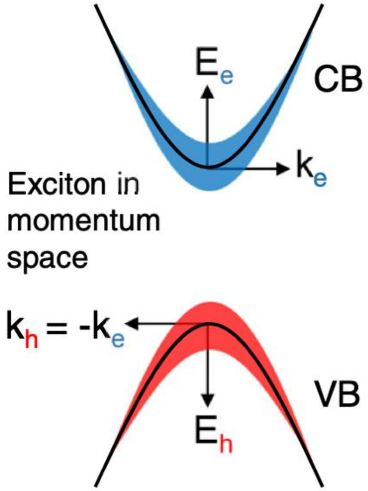
Excitons in 2D materlals: Wannier vs. Frenkel

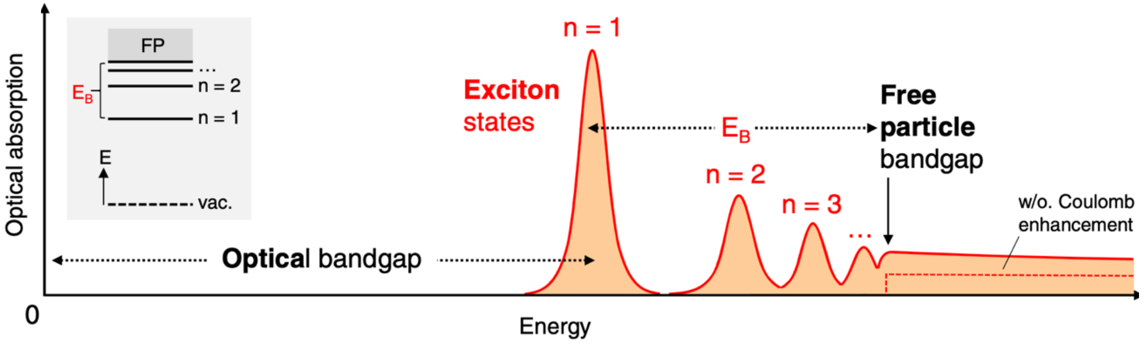
Extended Wannier excitons (e.g. TMDs)



exciton wavefunction

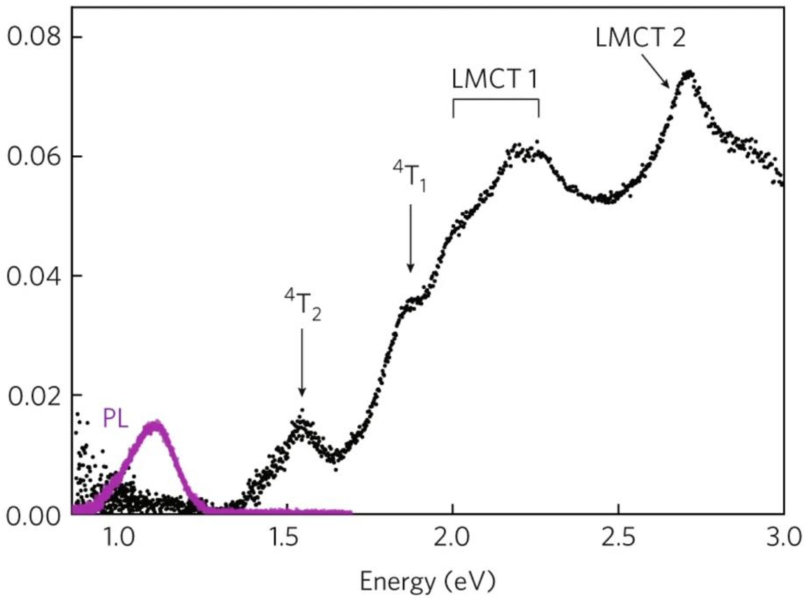


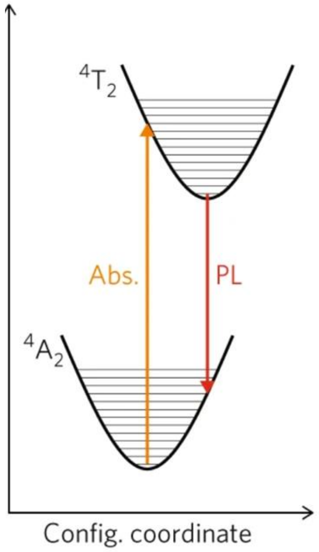
band contribution



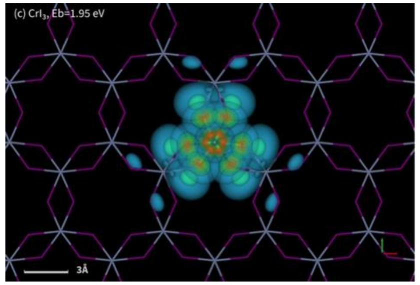
Rev. Mod. Phys. **90**, 021001 (2018)

Localized (Frenkel) 'excitons' (e.g. CrI3)

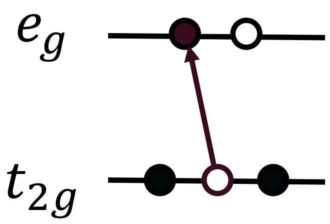




Localized to TM site



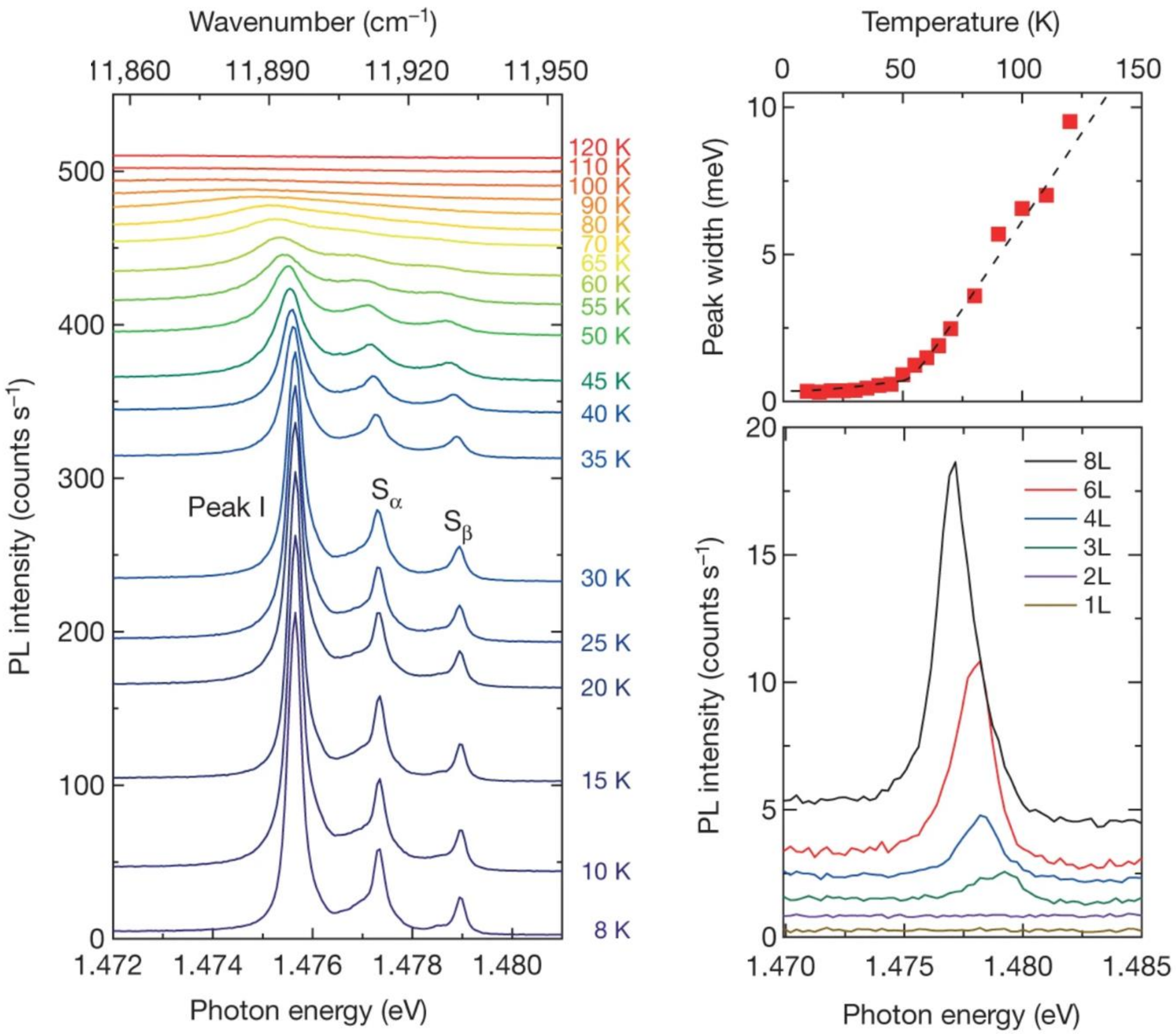
dd or ligand-field transitions



npj 2D Mat. **6**, 33 (2022)
Nat. Phys. **14**, 277 (2018)

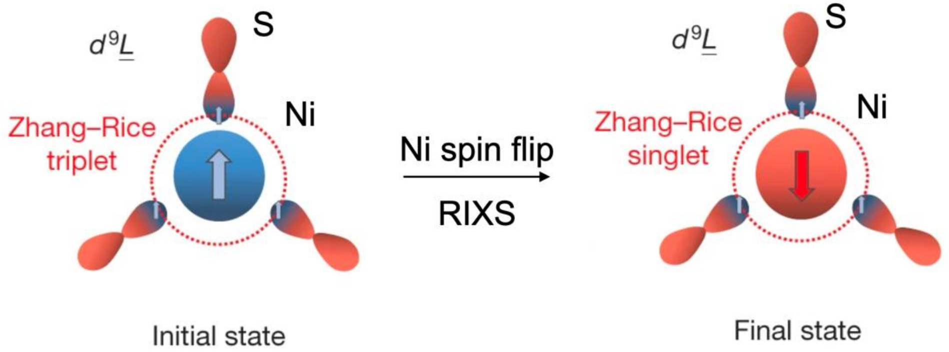
Sharp optical excitations in van der Waals magnet $NiPS_3$

Sharp excitons below T_N ~ 155 K in $NiPS_3$



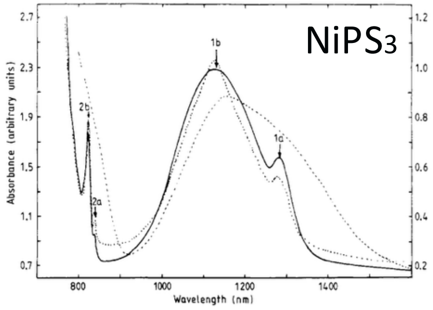
Nature **583**, 785-789 (2020)

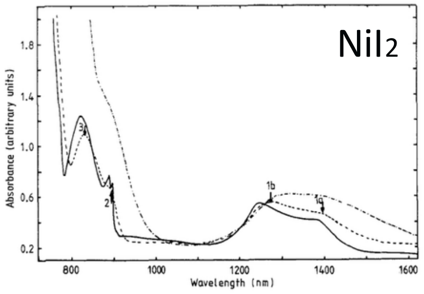
Interpretation: Zhang-Rice analog Frenkel-type exciton with large Ni-S charge transfer contribution



versus…

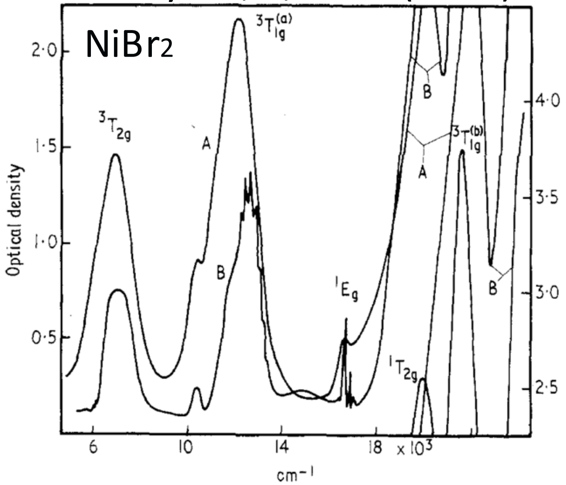
J. Phys. C, **19**, 7329 (1986)





Ligand field spectra of Ni^{2+} systems

J. Phys. C, **5**, 1253 (1972)



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Importance of sharp excitons for magnetic control and detection

Dual importance of ‘magnetic excitons’

(1) magnetic characterization of vdW magnets

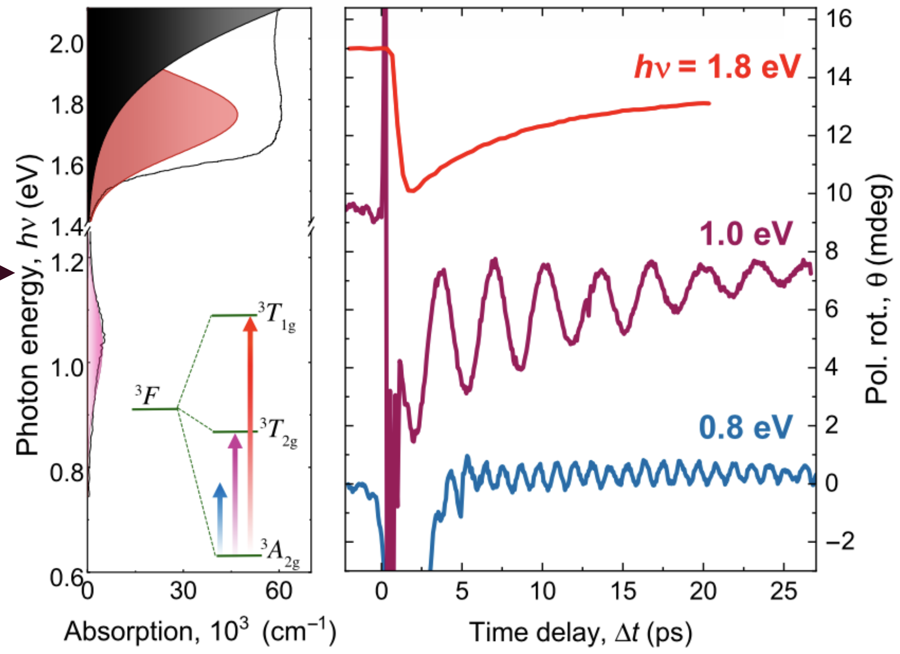
Nat. Mat. **20**, 964-970 (2021). Nat. Nano **16**, 655-660 (2021).

Adv. Mat. **35**, 2207585 (2023).

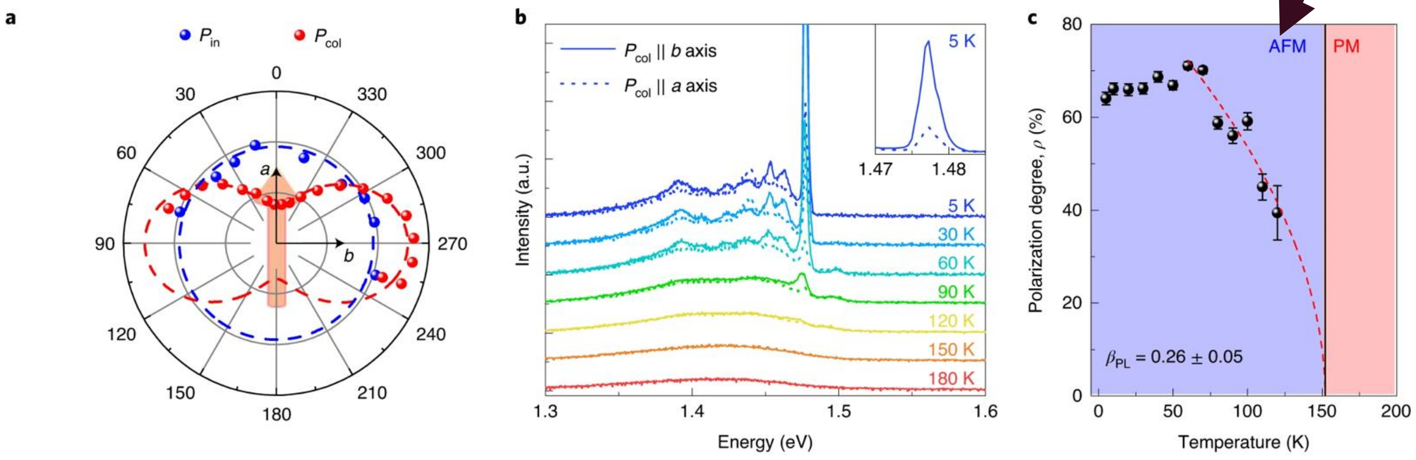
(2) photo-induced magnetic effects

Nat. Comm. **12**, 4837 (2021). Nat. Nano. **17**, 1060-1064 (2022).

Nat. Comm. **13**, 98 (2022). Sci. Adv. **7**, eabf3096 (2021).



Sci. Adv. **7**, eabf3096 (2021).



linear polarized PL emission for detecting magnetic order/ local spin degree of freedom to few-layer limit

driving below gap ligand field transitions for selective excitation of coherent magnons

Nat. Mat. **20**, 964-970 (2021).

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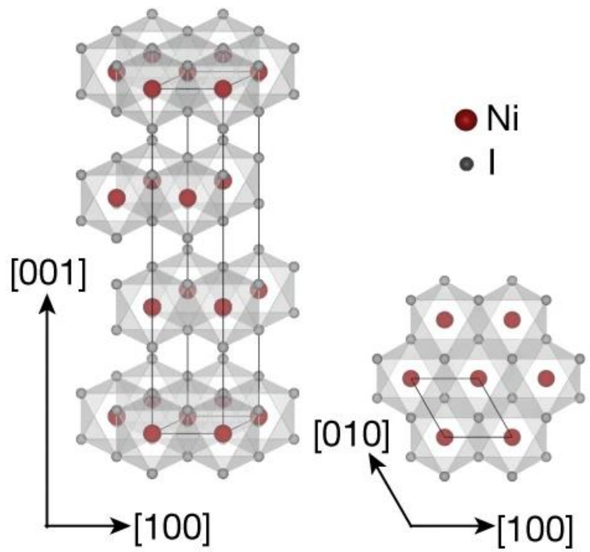
Nickel dihalides - isostructural tuning of charge transfer



Outstanding Questions

Goal 1: Effect of ligand holes and microscopic origin

Goal 2: Effect of magnetic order

Goal 3: Intersite coupling mechanisms or properties beyond localized transitions

isostructural Nickel dihalides

isovalent Ni^{2+}

charge transfer insulators

T_N ~ 55K ← $NiCl_2$

T_N ~ 45K ← $NiBr_2$

T_N ~ 75K ← NiI_2

ionic ↕ covalent

↓ decrease CT gap (Δ)

increase hybridization/ covalency

increase self-doped ligand holes

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C.A. Occhialini*, Y. Tseng* Phys. Rev. X 14, 031007 (2024)

Ingredients of Charge Transfer Multiplet Theory

Ni^{2+} ion ($3d^8$)

Electronic correlations
(e.g. Hund's exchange)

$3d^8$

$O(3)$

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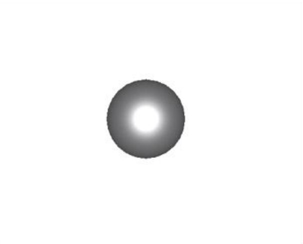
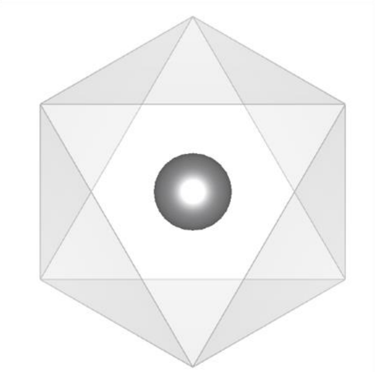
Ingredients of Charge Transfer Multiplet Theory

Ni^{2+} ion ($3d^8$)

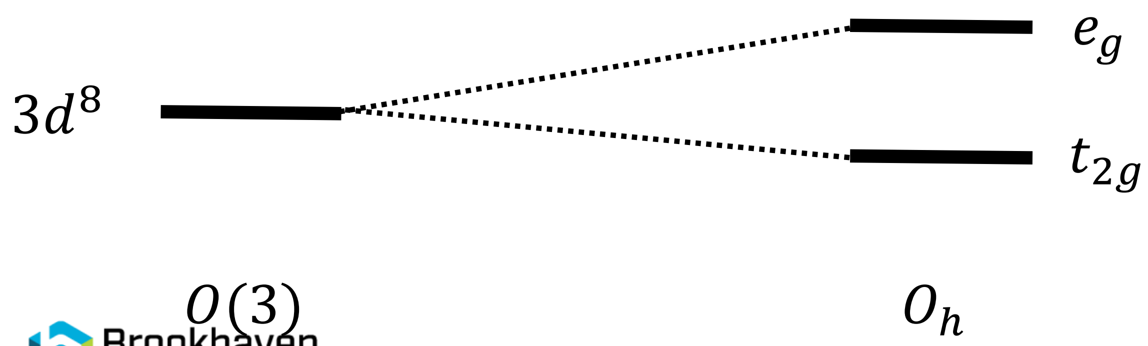


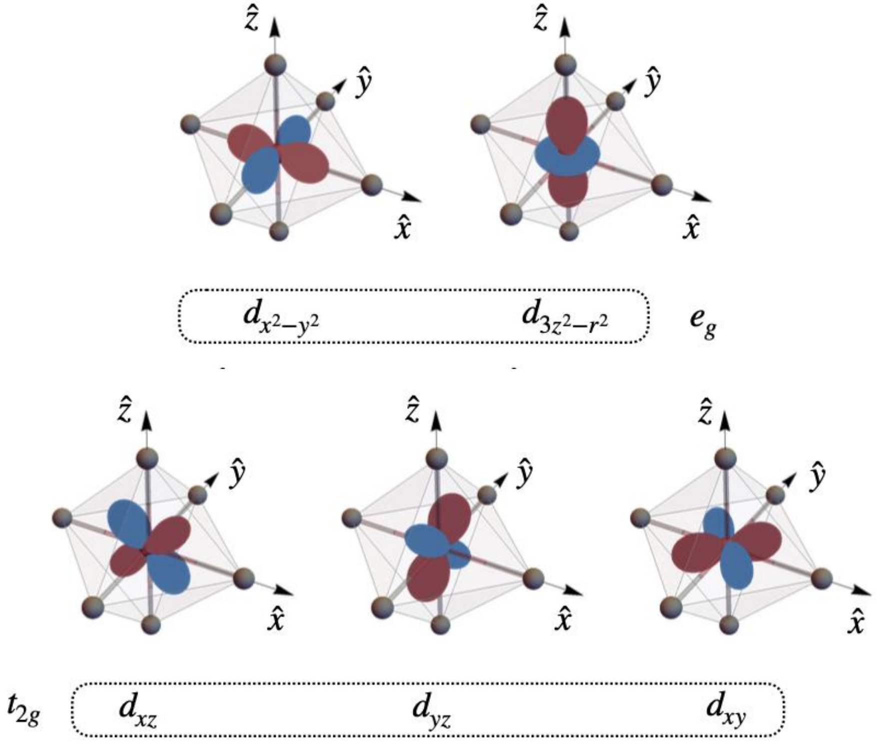
Electronic correlations
(e.g. Hund's exchange)

O_h crystal field



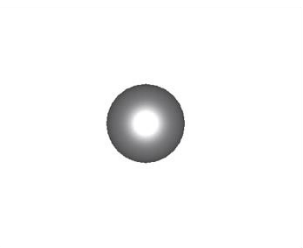
3d orbital degeneracy breaking





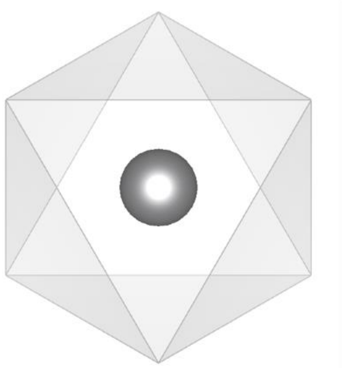
Ingredients of Charge Transfer Multiplet Theory

Ni^{2+} ion ($3d^8$)



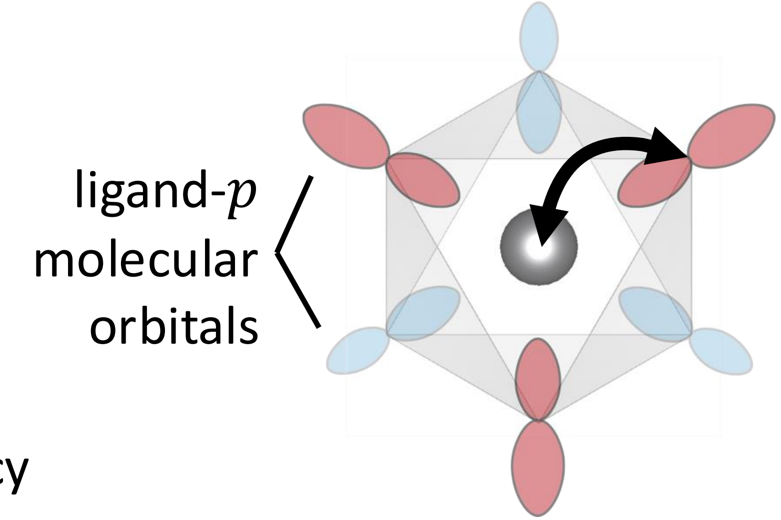
Electronic correlations
(e.g. Hund's exchange)

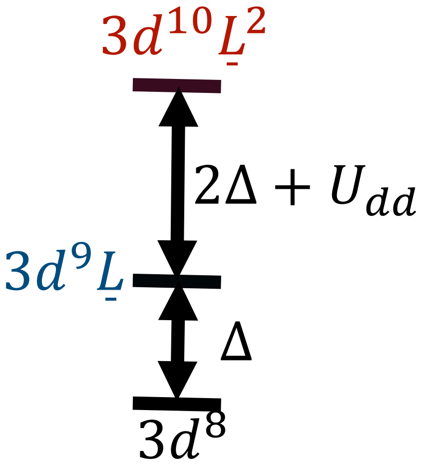
O_h crystal field



$3d$ orbital degeneracy
breaking

Ligand-Metal Charge Transfer

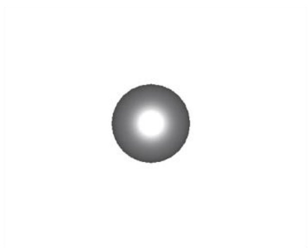




Charge-Transfer Configs.

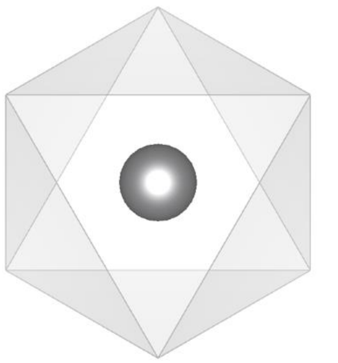
Ingredients of Charge Transfer Multiplet Theory

Ni^{2+} ion ($3d^8$)



Electronic correlations (e.g. Hund's exchange)

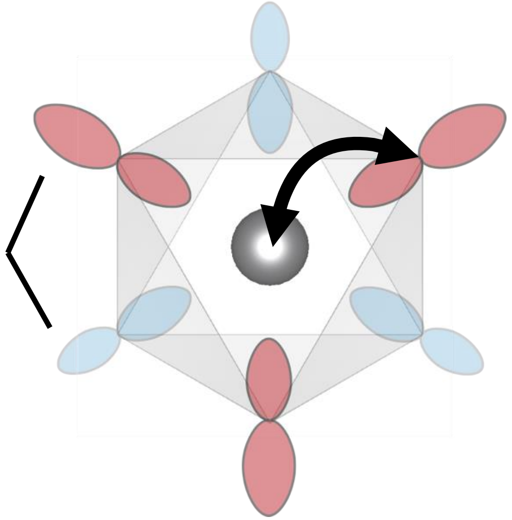
O_h crystal field

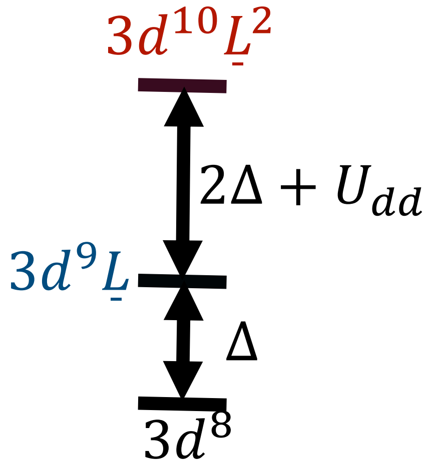


$3d$ orbital degeneracy breaking

Ligand-Metal Charge Transfer

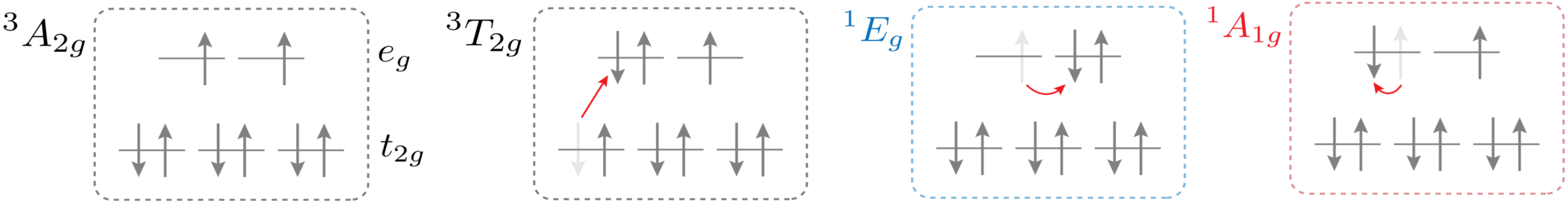
ligand-p molecular orbitals





Charge-Transfer Configs.

dd Excitations (Multiplets) of O_h Coordinated Ni^{2+}

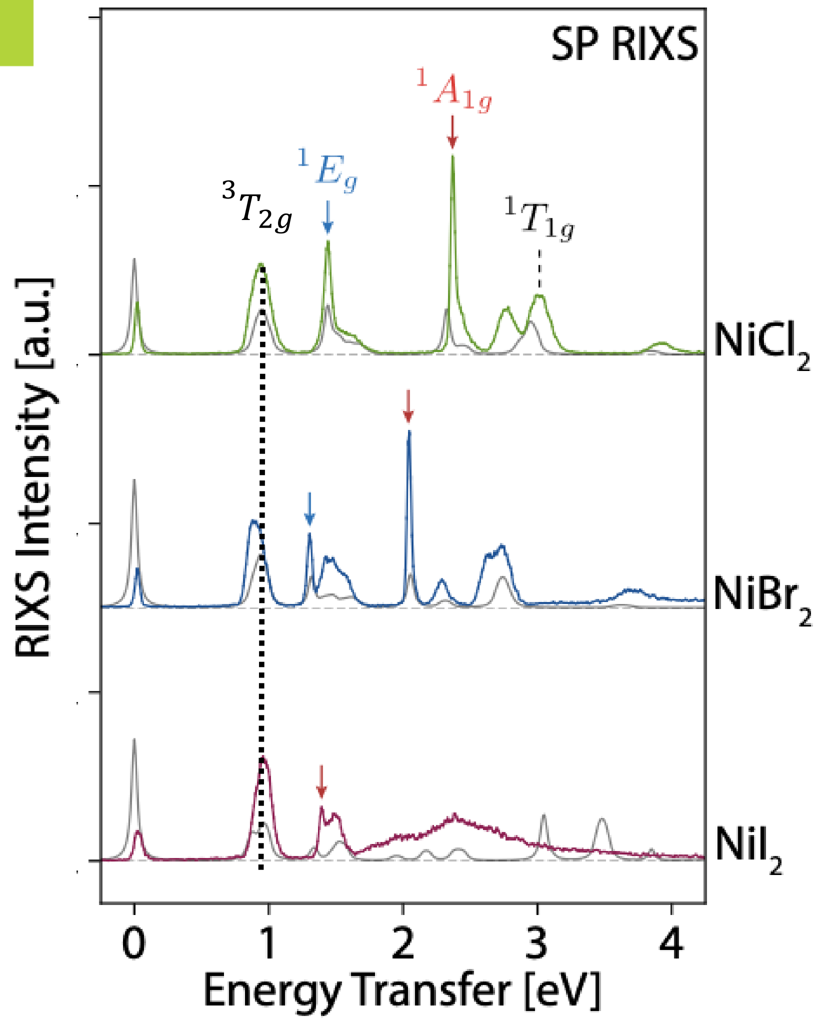


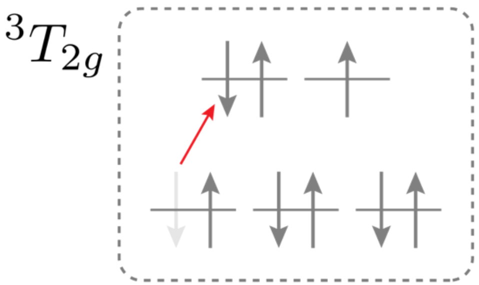
Ground State

Crystal Field Exc. ($\Delta S = 0$)

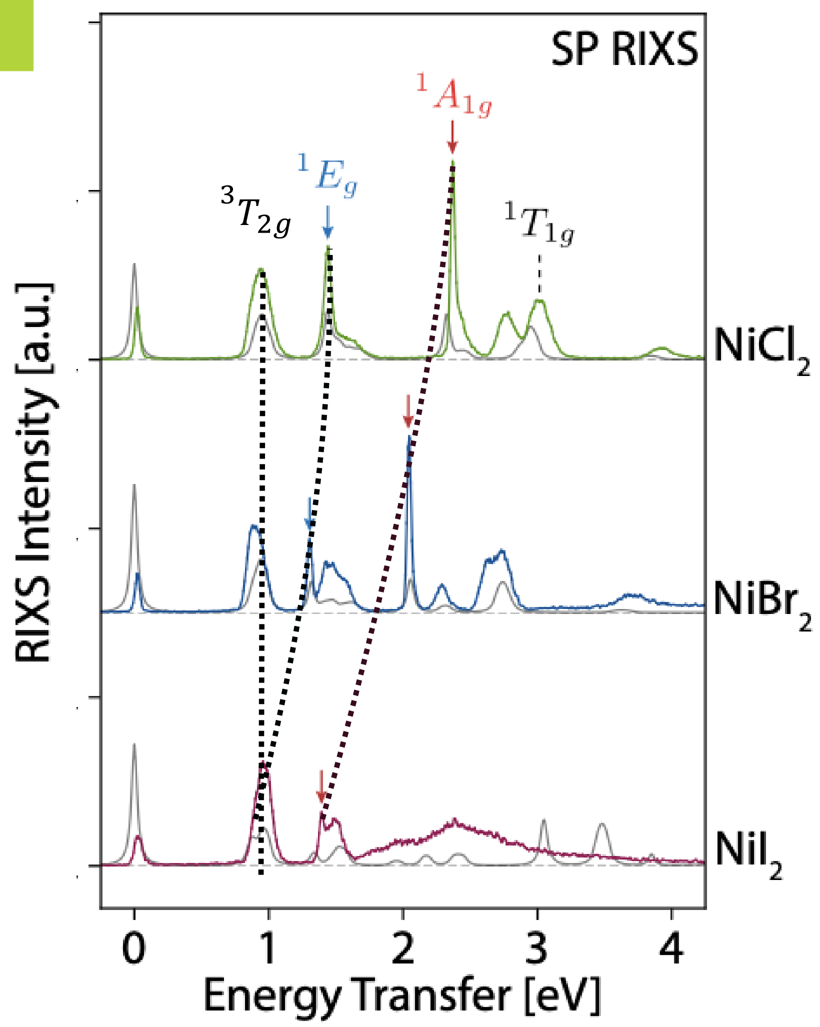
Intra-Configurational $\Delta S = 1$

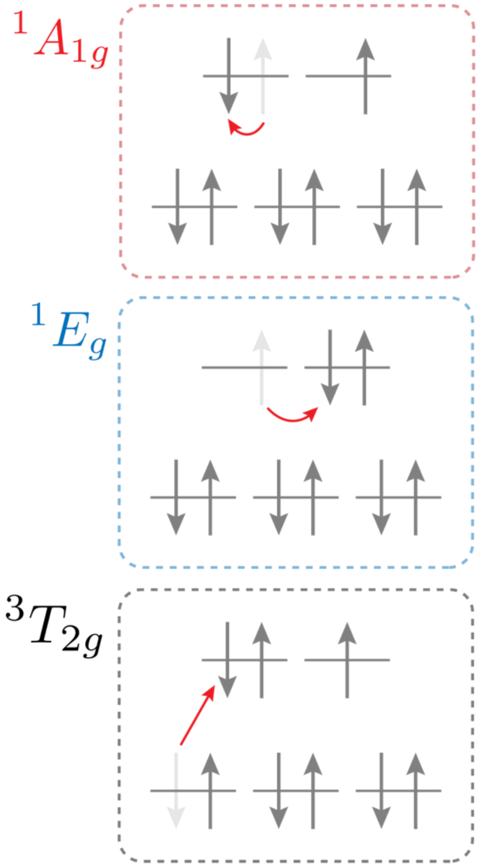
Ligand-dependence of excitation spectra





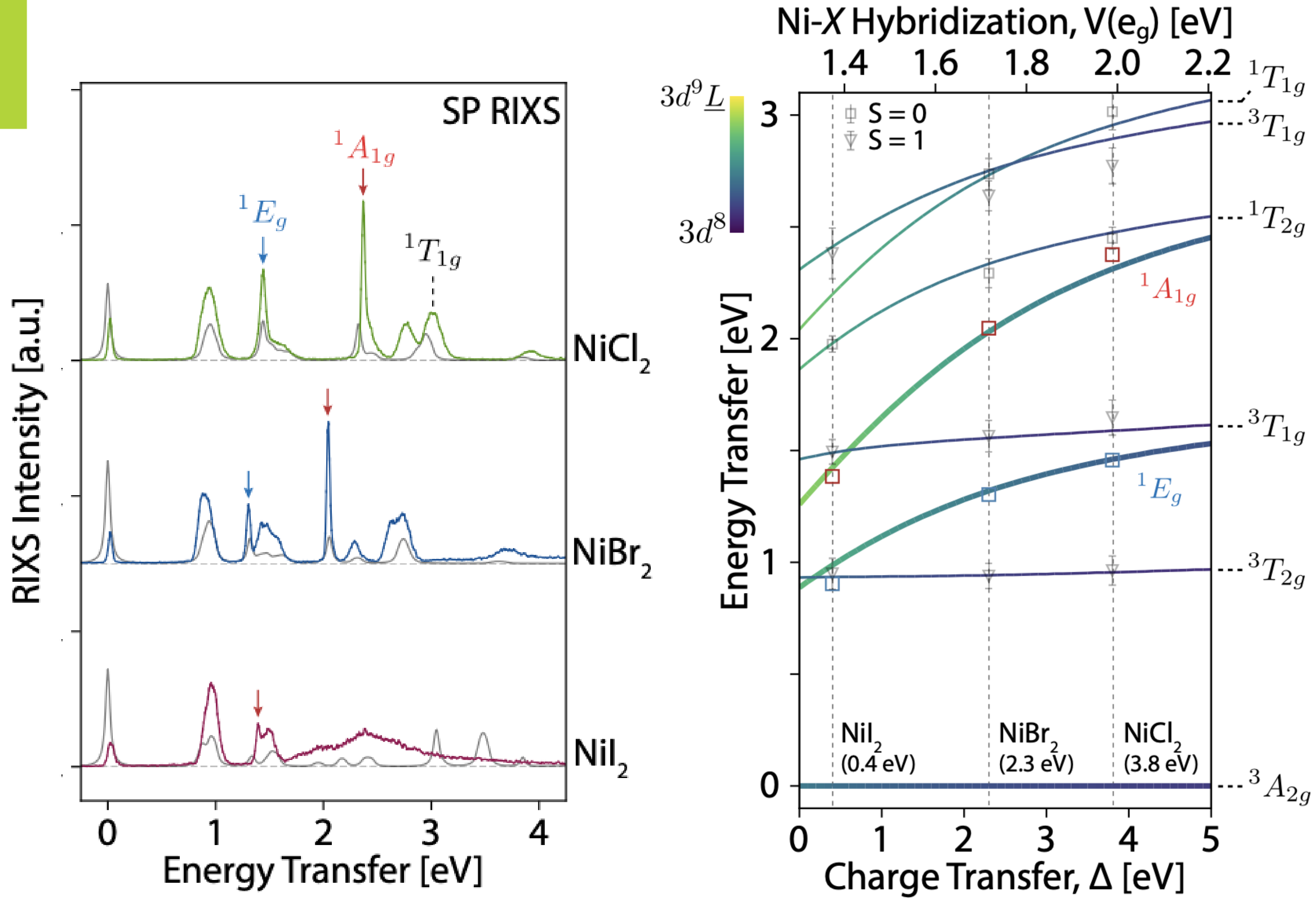
Ligand-dependence of excitation spectra





Sharp excitations observed in all samples with near resolution-limited linewidth

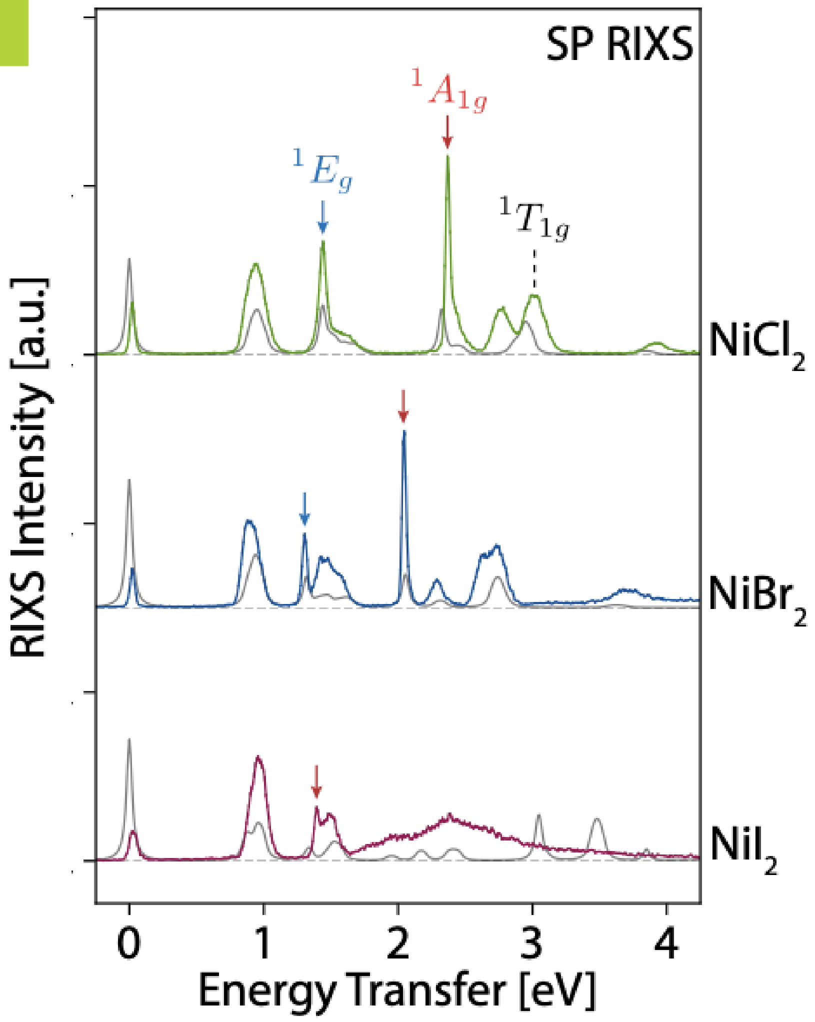
Ligand-dependence of excitation spectra

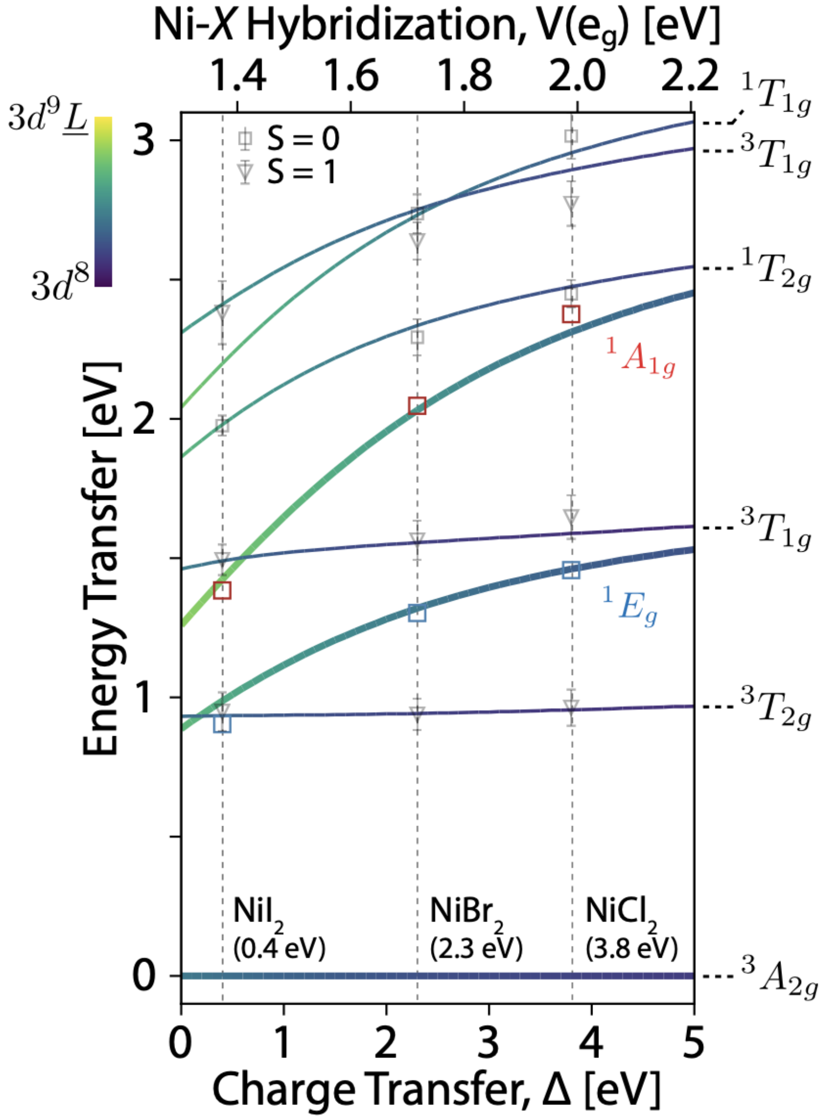


Sharp excitations observed in all samples with near resolution-limited linewidth

Assignment: spin-forbidden ($\Delta S = 1$) intra-configurational multiplets of octahedral Ni^{2+} (universal origin)

Ligand-dependence of excitation spectra





Sharp excitations observed in all samples with near resolution-limited linewidth

Assignment: spin-forbidden ($\Delta S = 1$) intra-configurational multiplets of octahedral Ni^{2+} (universal origin)

Energy scale: Ni Hund's exchange

Effect of Ni-X charge transfer
~ Coulomb interaction screening
~ "Nephelauxetic effect"

Explains ligand dependence and sharp linewidths

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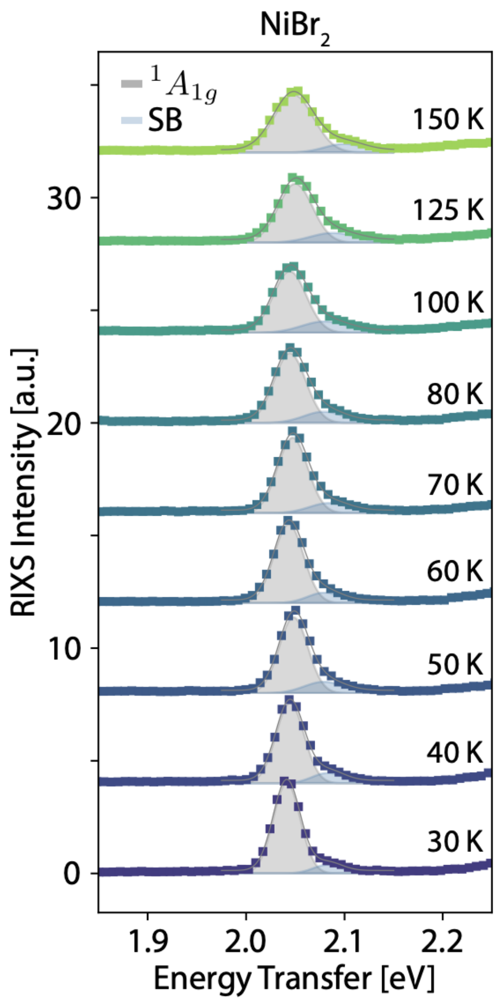
Temperature and momentum dependence of $^{1}A_{1g}$ *states in NiBr₂*

Temperature Dependence



$T_N \sim 45$ K

independent of magnetic order

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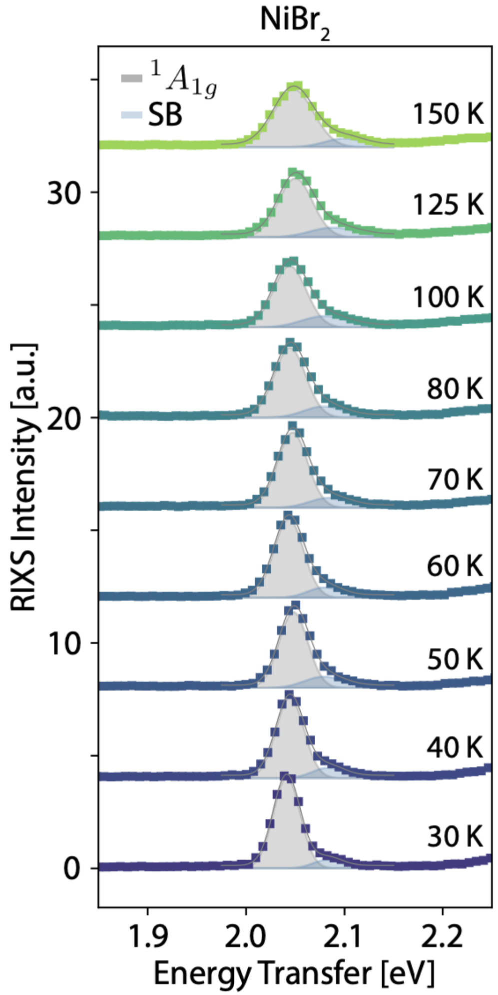
Temperature and momentum dependence of $^1A_{1g}$ states in $NiBr_2$

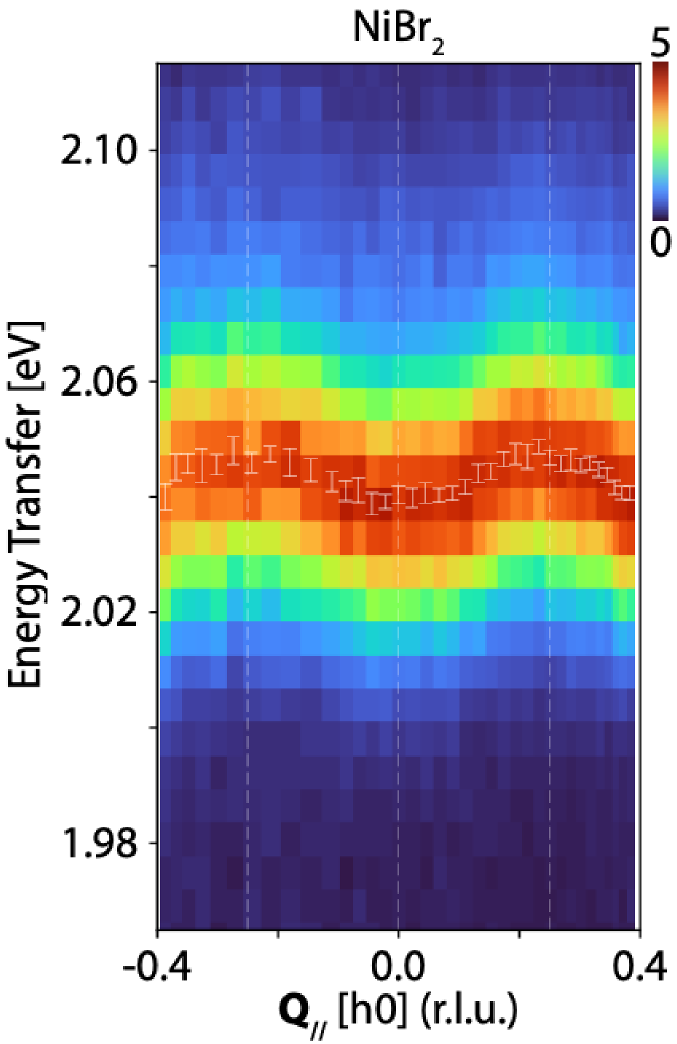
Temperature Dependence

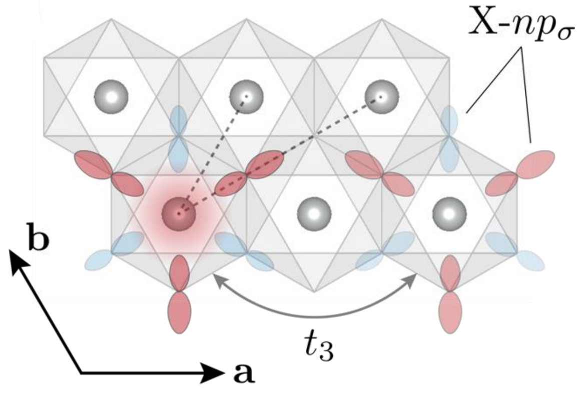


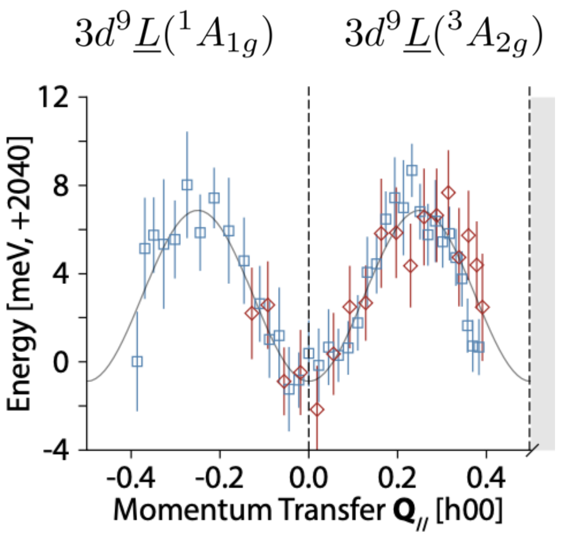
$T_N \sim 45$ K

independent of magnetic order

Momentum Dispersion

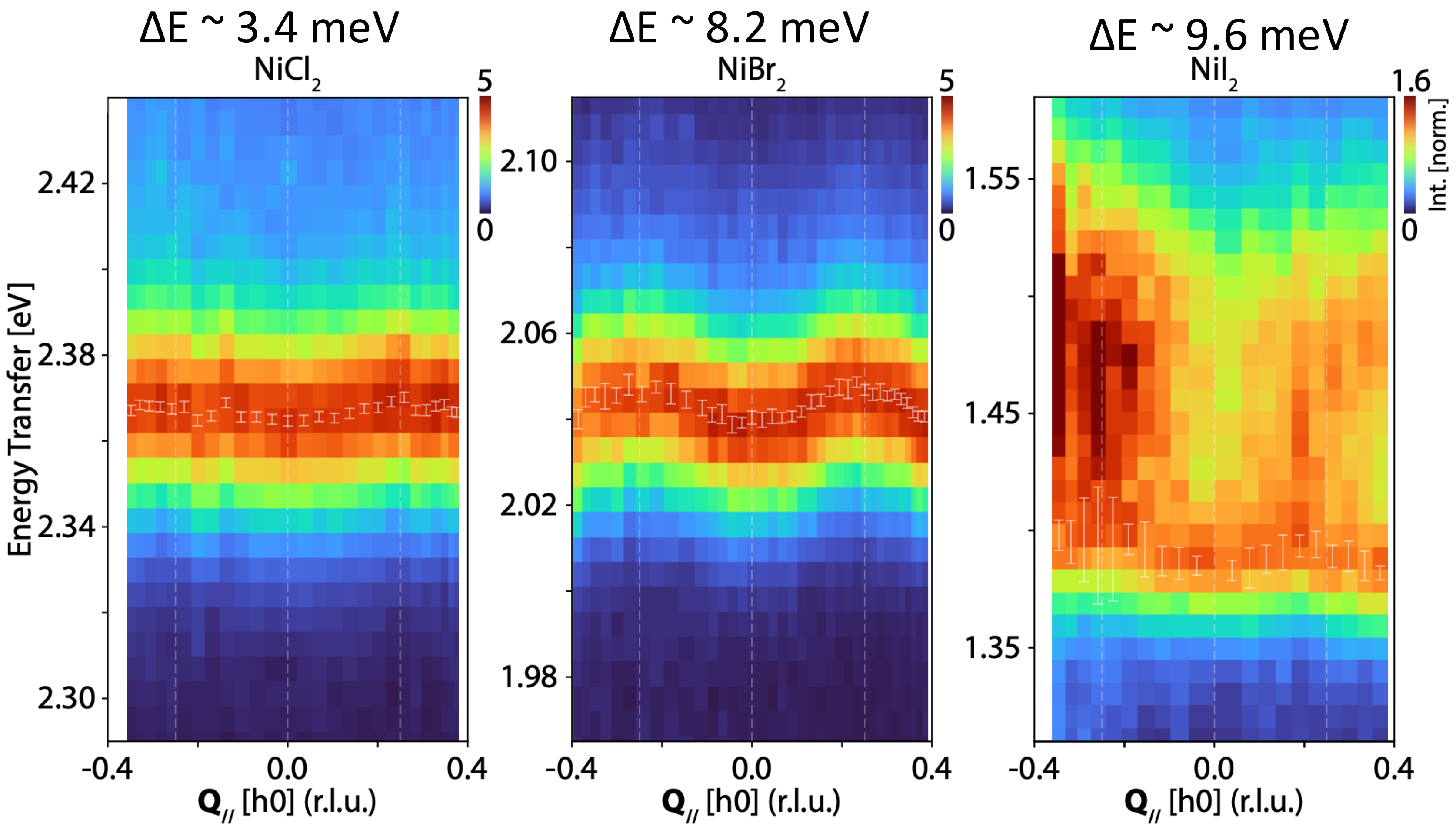






Momentum-dependence of $^{1}A_{1g}$ *states versus ligand*

X =Cl decrease Δ/increase bandwidth X =I



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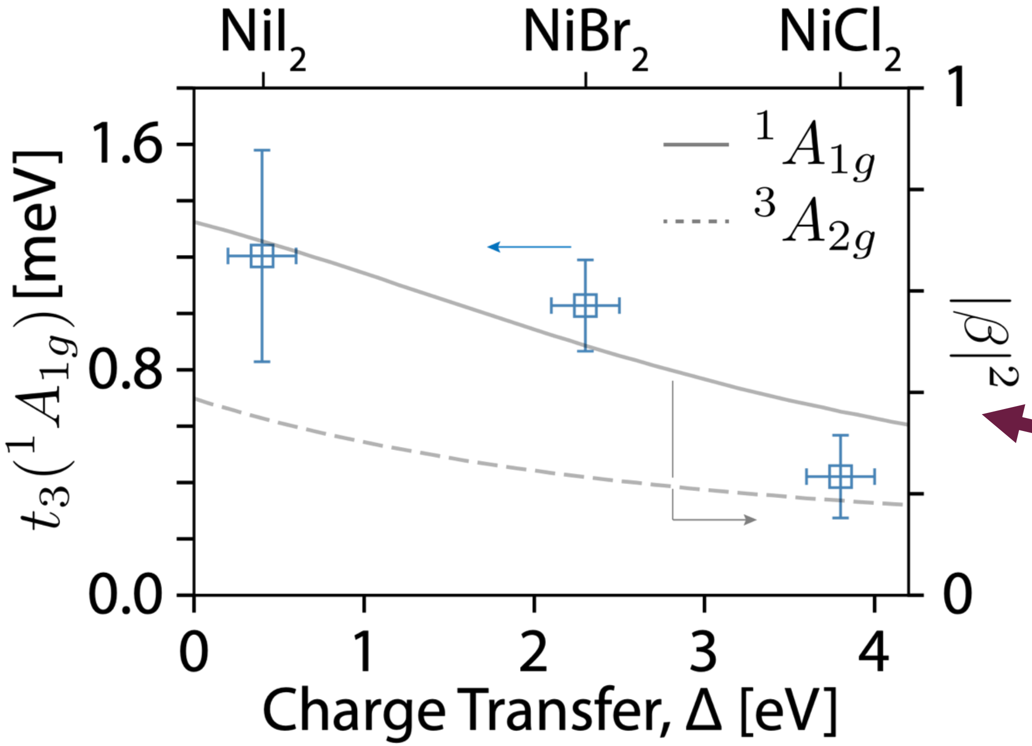
Charge-transfer tuned exciton delocalization



Delocalization tuned by charge transfer

energy and metal-ligand covalency

from CTM calculations of level diagram…

$$\Psi \rightarrow \alpha|3d^8(\psi)\rangle + \beta|3d^9\underline{L}(\psi)\rangle$$

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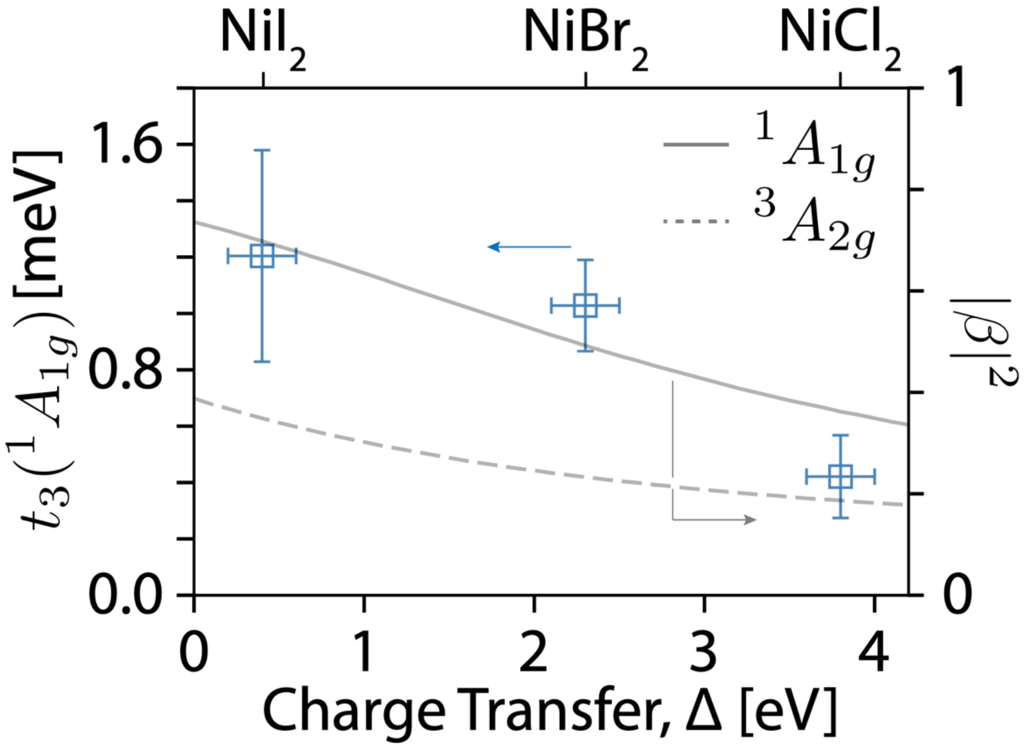
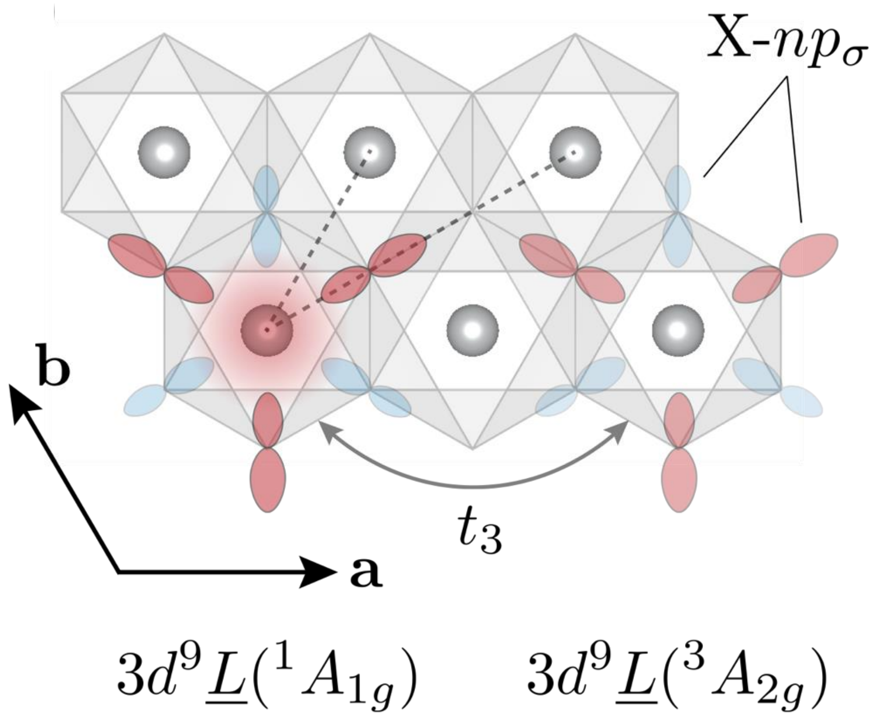
Charge-transfer tuned exciton delocalization



Delocalization tuned by charge transfer energy and metal-ligand covalency



Third nearest neighbor delocalization pathway mediated by self-doped molecular orbitals

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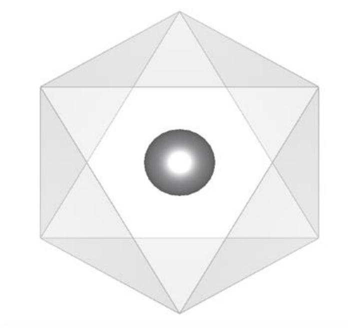
Summary: Effects of charge transfer on localized multiplet excitations

Degree of Locality

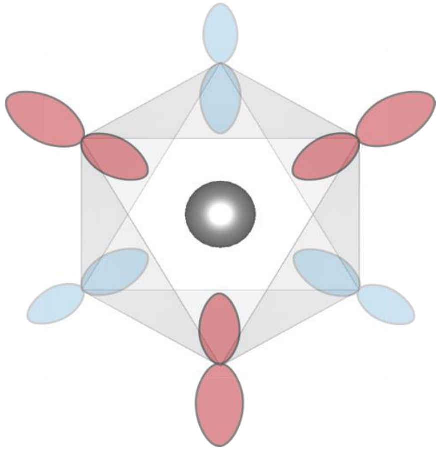
Local ⟷ Itinerant

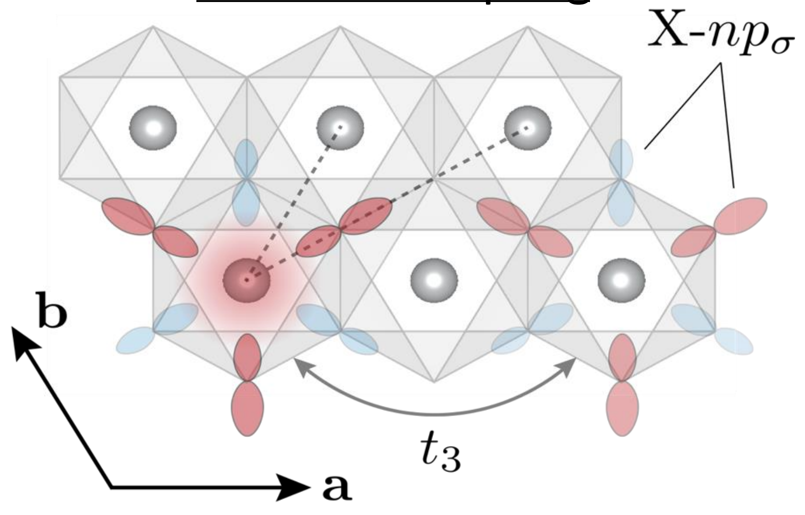
<u>Crystal field multiplets</u> | <u>Charge transfer</u> | <u>Intersite coupling</u>



3d orbital degeneracy breaking

ligand-*p* molecular orbitals

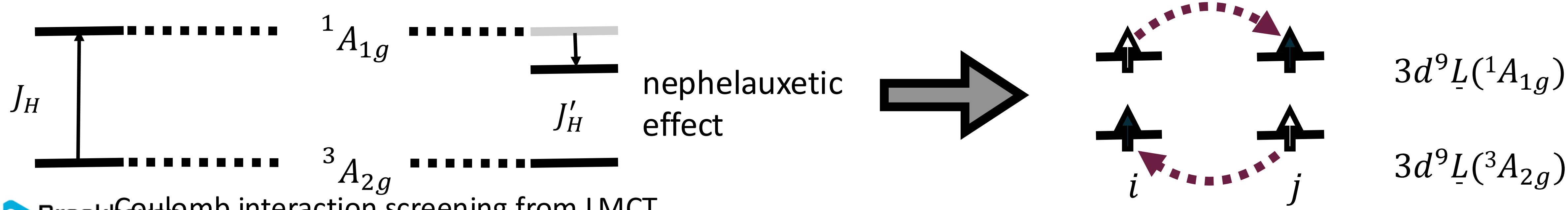




Metal-centered multiplets

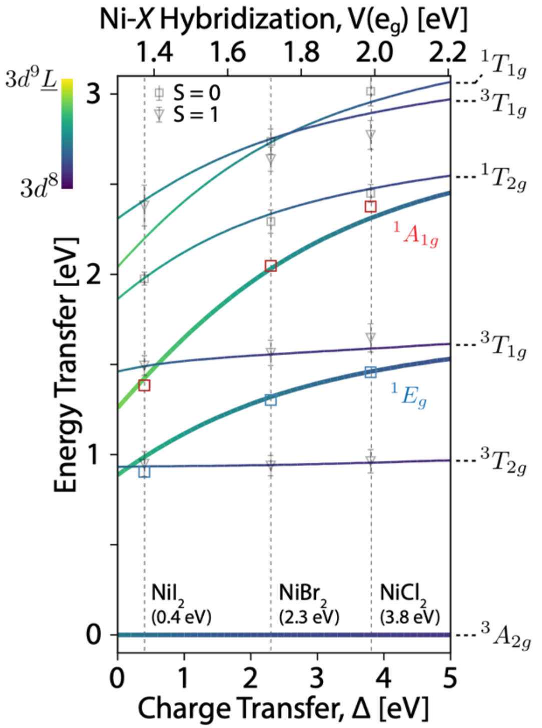
$3d^9\underline{L}$ mixing

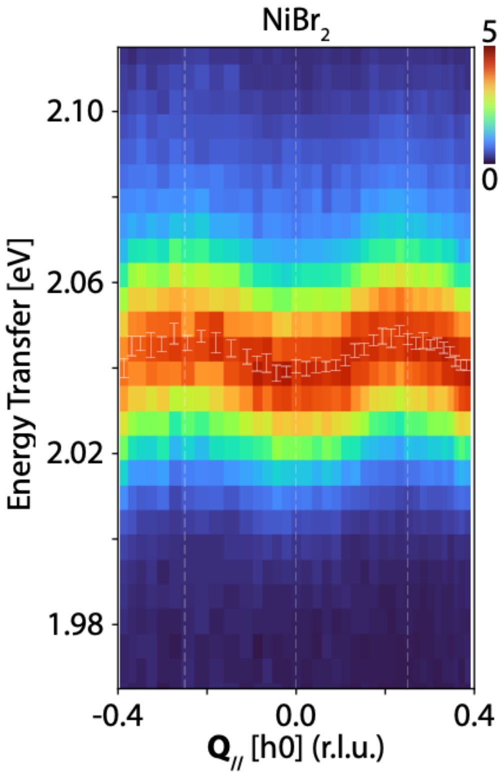
'excited-state' ligand-mediated superexchange



Coulomb interaction screening from LMCT

Summary and Outlook

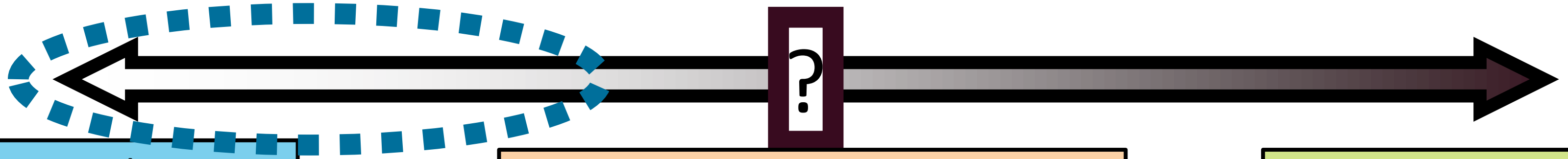




Tuning and brightening of spin forbidden excitons

- Chemical tuning to establish origin of excitons
- Control energy/locality of excitons with charge transfer
- ‘Excited-state superexchange’ and **q**-resolved picture for non-local properties of Frenkel-type excitons
- Towards probing/controlling magnetism with photons

Description of excitons in correlated systems



Ligand field theory

Wannier excitons,
Band structure + BSE

Local spin/orbital degrees of freedom
Strong correlations

Increased oscillator strength
Exciton dispersion
Coupling to – long range order

Band degrees of freedom
(Valley, spin)
‘weak’ correlations

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