Inelastic x-ray scattering

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Outline

Basics of inelastic x-ray scattering (IXS)

- What is IXS?
- What can be measured and why should you care?
- Cross section and $S(Q, \omega)$

Different material degrees of freedom

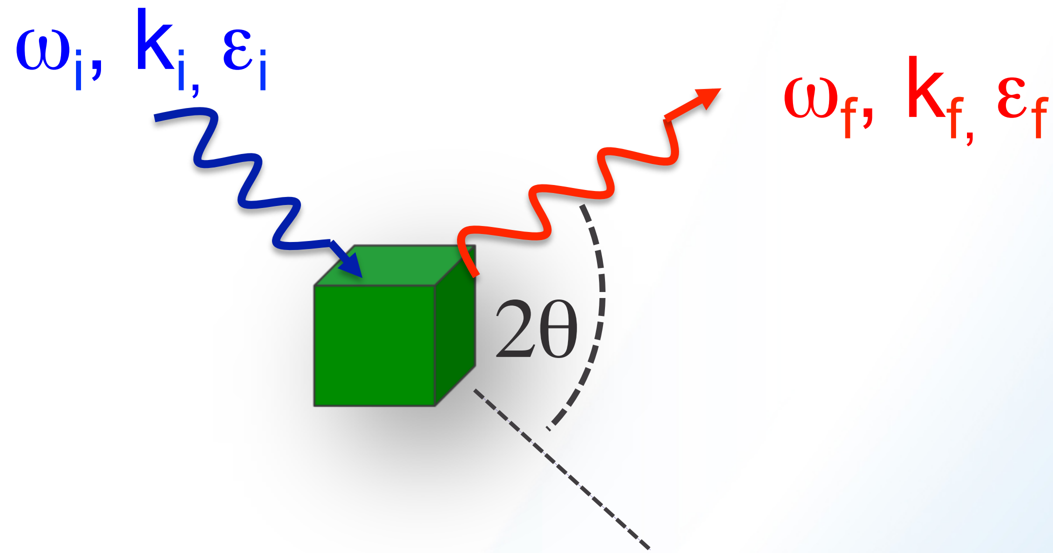
- Lattice
- Spins
- Orbitals
- Charge

Plan for each of these

- Cross section
- Instrument
- Case study
- Advantages/disadvantages of IXS vs. competing methods

BASICS OF INELASTIC SCATTERING

Scattering



Elastic scattering

$$\frac{d\sigma}{d\Omega} \qquad \omega_f = \omega_i$$

Inelastic scattering

$$Q = k_f - k_i \approx \frac{4\pi}{\lambda}\sin(\theta)$$

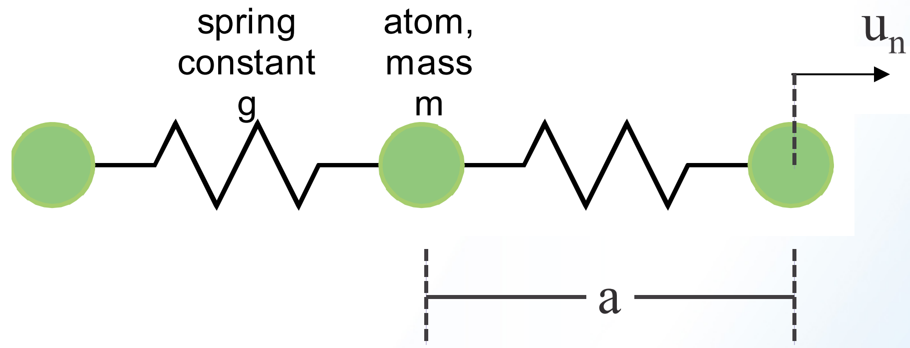
$$\frac{d^2\sigma}{d\Omega d\omega} \qquad \omega_f \neq \omega_i$$

$$\omega = \omega_f - \omega_i$$

For condensed matter need $\lambda \approx a \approx 1$ Å i.e. x-rays!

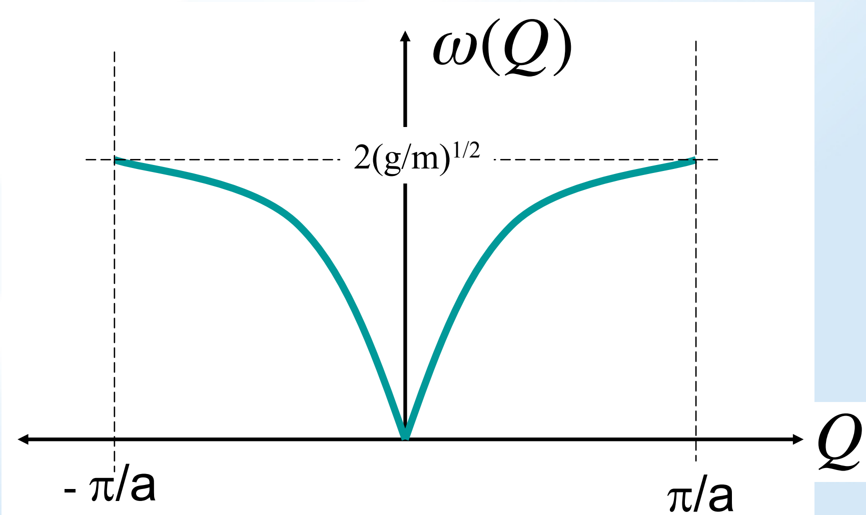
Inelastic scattering – accessing dynamics & Hamiltonian

Inelastic scattering gives excitation spectrum i.e. eigenstates that determine the system's dynamics



Can infer Hamiltonian

$$H = \frac{g}{2}\sum_n (u_n - u_{n+1})^2$$



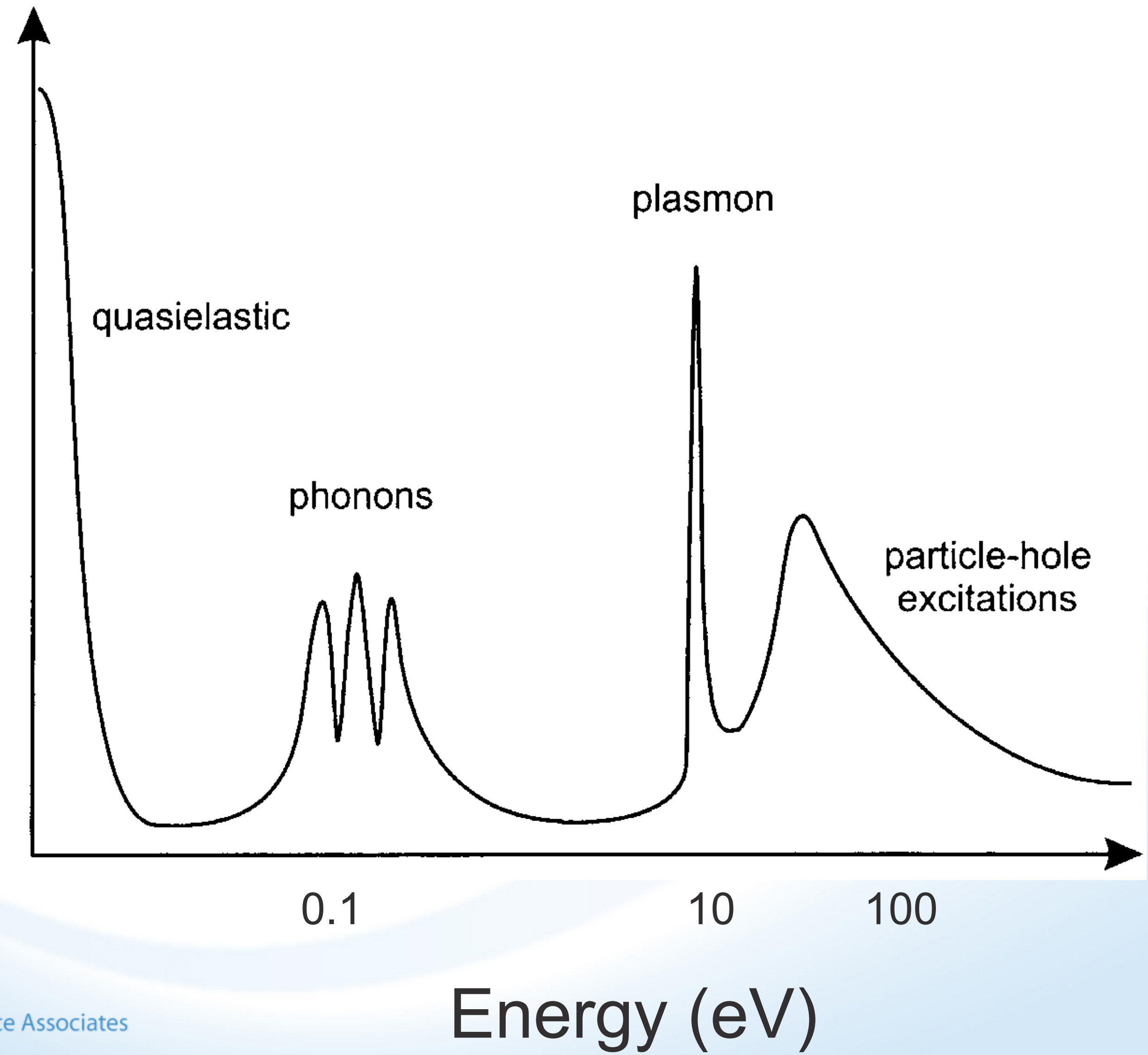
Full description of interactions!

Degrees of freedom & excitations

Degree of freedom	Excitations	Very approximate Energy scale
Lattice	Phonons	0->200 meV
Spin	Magnon, bimagnon, spinon, …	0-500 meV
Orbital	dd-transition or orbiton	~1-5 eV
Charge	Plasmon, charge transfer excitation	~0-100 eV

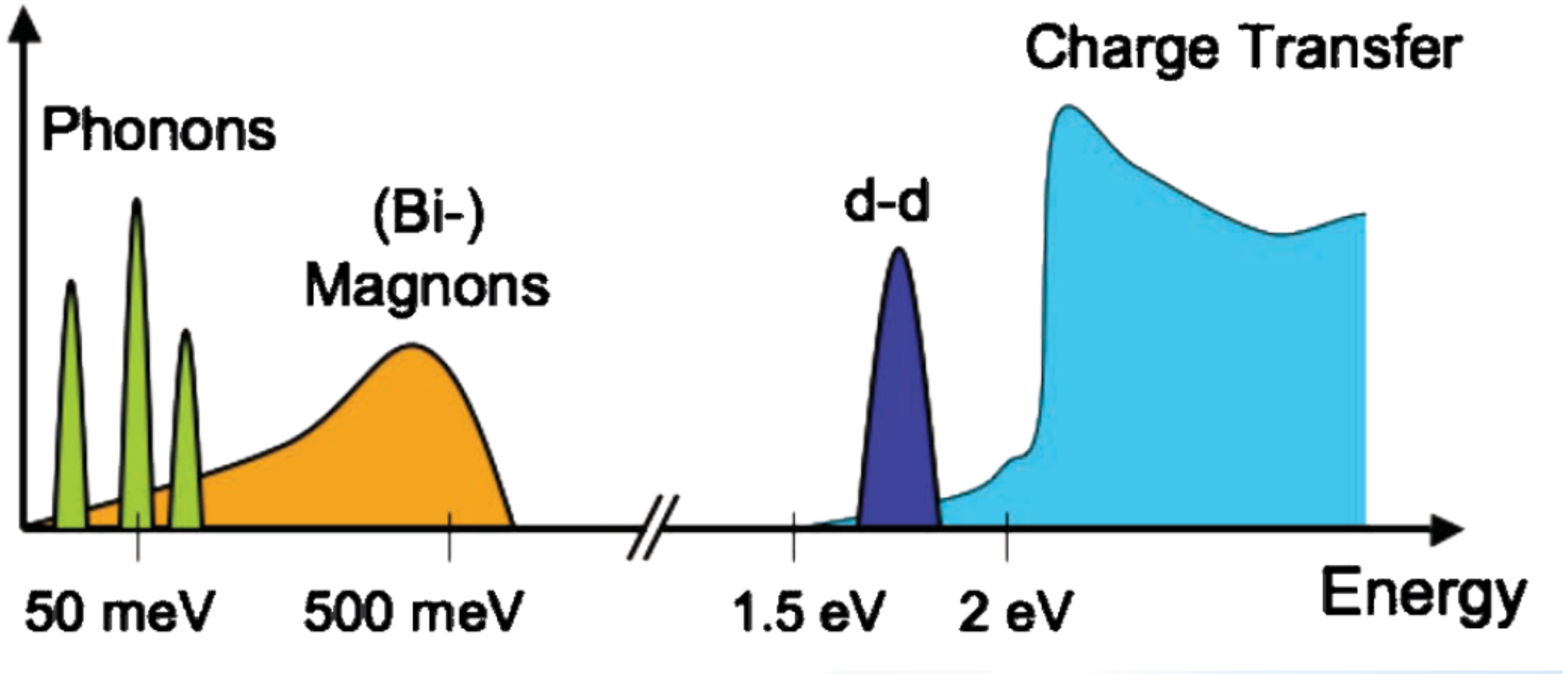
X-rays can access all these excitations!
Very stringent tests for model Hamiltonians related to all these degrees of freedom.

Excitations spectrum of a metal



Excitation spectrum of a strongly correlated material

Mott insulator La_2CuO_4



Word of warning

These excitations cannot be measured in one experiment! Lots of parameters need to be optimized for a particular goal

- Working energy
- Energy resolution / throughput trade off
- Non-resonant or resonant (and which resonance)

IXS is consists of many different sub techniques each with specialized instruments

- Fail to plan – plan to fail!

Kramers–Heisenberg formula

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

1st term   2nd term

Interaction between photon and electrons in a material though H_{int}

Preferable route

$$\left.\frac{d^2\sigma}{d\Omega d\omega}\right)_{res} \approx \underbrace{|P(\omega)|^2}_{\text{Properties of x-rays and core electrons}} \; \underbrace{S(\vec{q},\omega)}_{\text{Properties of valence electrons}} \; ?$$

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

Dynamical structure factor S(Q, ω)

$$S(Q,\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \left\langle \rho(Q,t=0)\rho^{+}(Q,t)\right\rangle$$

$$S(Q,\omega) = \frac{1}{\pi}\frac{\chi''(Q,\omega)}{1-\exp(-\omega/K_B T)}$$

$$\chi(Q,\omega) = \chi'(Q,\omega) + i\chi''(Q,\omega)$$

$$\left.\begin{aligned} P &= \varepsilon_0 \chi E \\ M &= \chi H \end{aligned}\right\}$$

Response of material to a small oscillating field

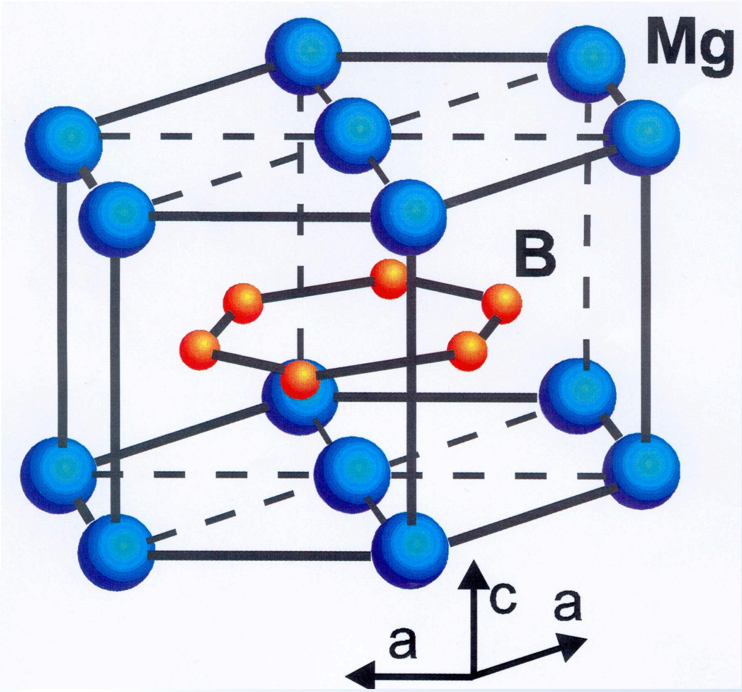
MEASURING THE LATTICE I.E. PHONONS

Case study: MgB_2

Superconductor at 39 K record (at the time) for non-cuprate

Flurry of activity to determine superconducting mechanism

Phonons?



J. Nagamatsu et al., Nature 410, 63-64 (2001)

Back to Kramers–Heisenberg formula

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

1st term 2nd term

$E_i \neq E_n$ 1st term >> 2nd term

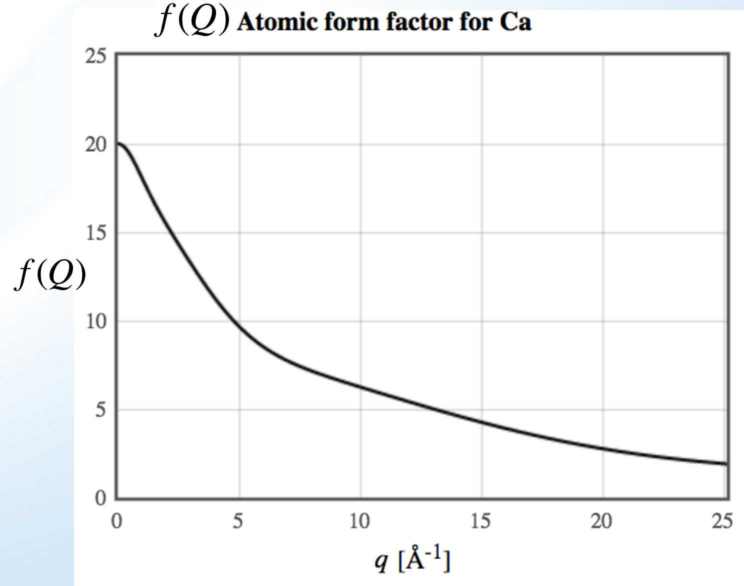
$$H_{\text{int}} = H_{\text{Thomson}} = \frac{1}{2} r_0 \sum_j \mathbf{A}^2(r_j, t)$$

$\mathbf{A}(r_j, t)$ vector potential

Weak interaction

$$\frac{d^2\sigma}{d\Omega d\omega} = \mathrm{r}_0^2 (\varepsilon_i \cdot \varepsilon_f)^2 \frac{k_i}{k_f} \left| f(Q) \right|^2 S(\mathbf{Q}, \omega)$$

for an element



$$S(\mathbf{Q},\omega)=\sum_j\left\langle n(\omega)+\frac{1}{2}\pm\frac{1}{2}\right\rangle\frac{1}{E_j(\mathbf{q})}F_{in}(\mathbf{Q})\delta(\omega\pm E_j(q))$$

$$F_{inj}=\left|\sum M_k^{-1/2}f_k(\mathbf{Q})[e_k^j(\mathbf{q})\cdot\mathbf{Q}]\exp(i\mathbf{Q}\cdot\mathbf{r})\exp(-w_k)\right|^2$$

Which phonons are highest intensity?

General trends for scattering geometry?

Full calculations are required for a full-proof plan!

Instrument concept

Required energy resolution

2 meV / 20 keV = 10^{-7} !

Bragg optics

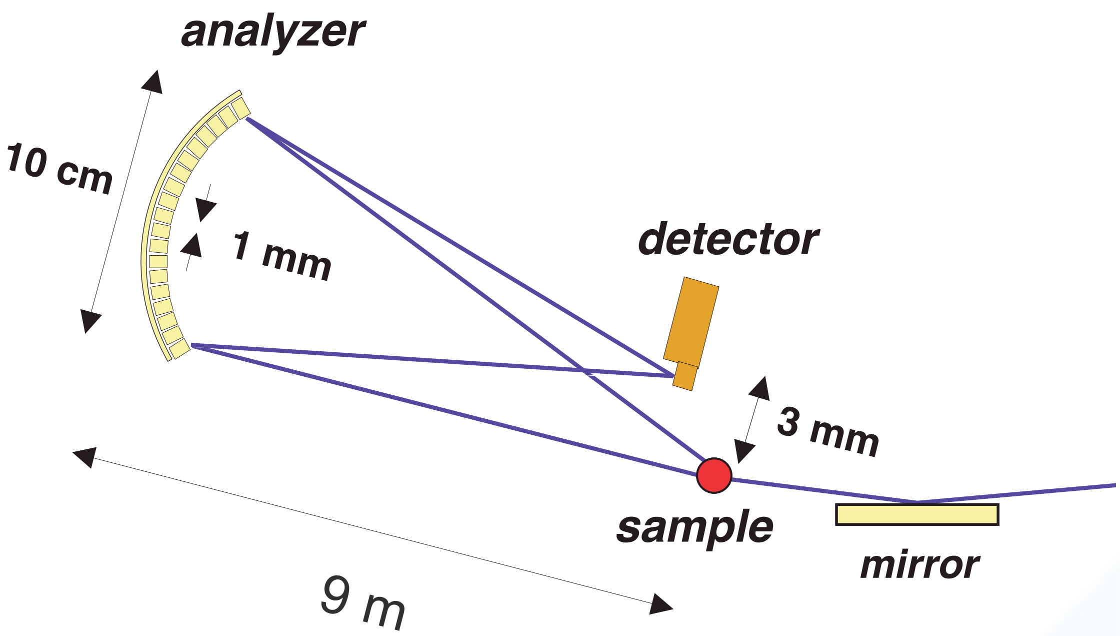
$$\frac{\Delta E}{E} \propto \frac{\Delta d}{d}$$

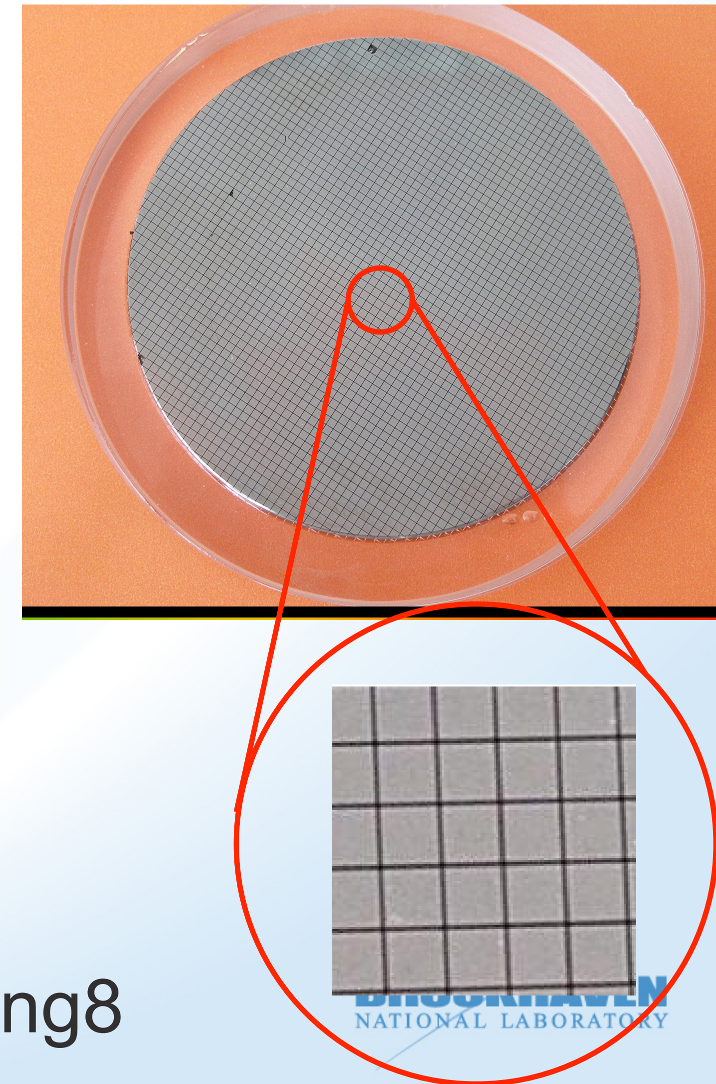
require high energy x-ray ~ 20 keV

$$\lambda = 2d\sin(\Theta_B) \qquad \Delta\theta = \tan(\Theta_B)\frac{\Delta E}{E} \qquad \Theta_B \approx 90^o$$

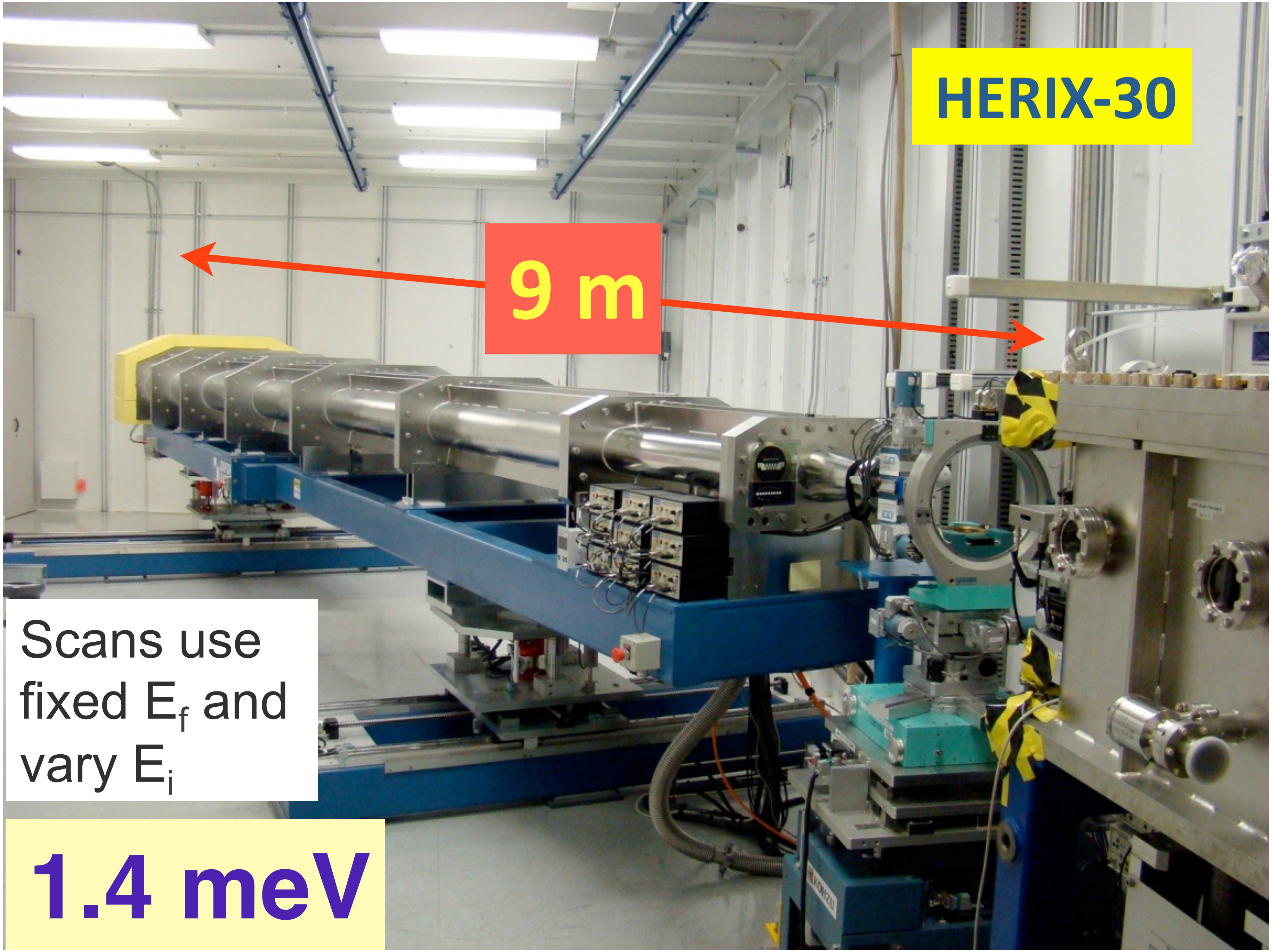
Simplest mono & analyzer based on Si reflections in close-to-back-scattering geometry

An IXS spectrometer for phonons: HERIX, Sector 30, APS





Other instruments: ID28 ESRF,
BL35XU SPring8


HERIX-30
9 m
Scans use fixed E_f and vary E_i
1.4 meV

Phonon spectra

Stokes / Anti-Stokes

Energies match DFT

But broadening of "E_{2g}" mode

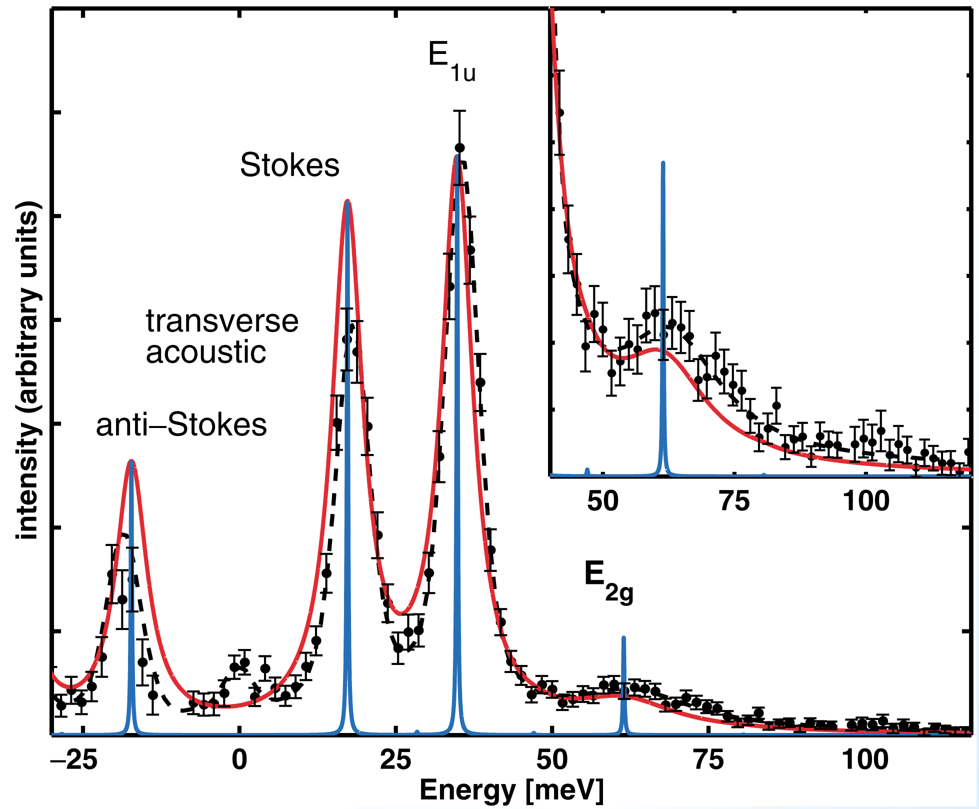


FIG. 1 (color online). Energy loss scan in almost transverse geometry measured at $\mathbf{Q} = (1\ 2\ 0.3)$ corresponding to 0.6 Γ-A. The data, normalized to the incident flux, are shown with the least-squares fit (dashed line) and the *ab initio* spectrum with and without broadening due to experiment and electron phonon coupling (solid lines). The broad peak corresponds to the damped E_{2g} mode and is shown in greater detail in the inset. The peak at zero is due to diffuse scattering.

Shukla et al., PRL 90, 095506 (2003)
Baron et al,. PRL 92, 197004 (2004)

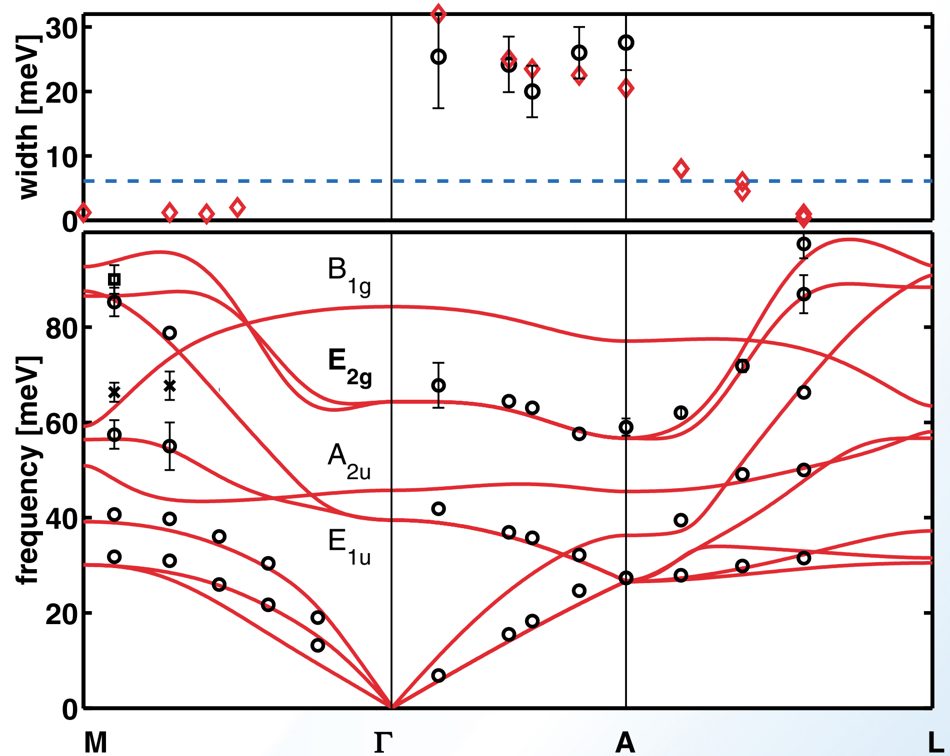
Phonon dispersion

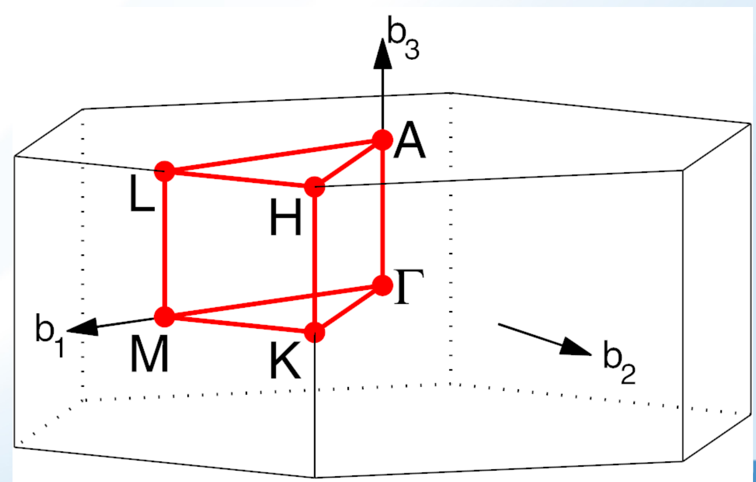
Phonon width contributions

- Disorder ✗
- Anhamonicity ✗
- Electron-phonon coupling ✓

$$\lambda_\nu(q) = \frac{\gamma_\nu(q)}{2\pi N(0)\omega_\nu^2(q)}$$

Compelling verification of e-ph coupling driven SC





Advantage/disadvantages x-ray vs. neutrons for phonons

Use x-rays

- Small samples
- High pressures
- Q, E access
- Need good Q resolution

Use neutrons

- Sub meV energy resolution
- Certain light atoms within compounds – particularly oxygen
- Many more INS spectrometers!

Raman scattering easier and cheaper if Q-resolution is not required!

MEASURING THE SPINS I.E. MAGNETIC EXCITATIONS

Kramers-Heisenberg equation

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

1st term 2nd term

1st term – very low sensitivity to magnetism

Use $E_i=E_n$

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

|n> is state with core hole:

- Increases cross section
- Allows coupling to "forbidden" excitations

Resonant inelastic x-ray scattering (RIXS)

Direct vs indirect RIXS

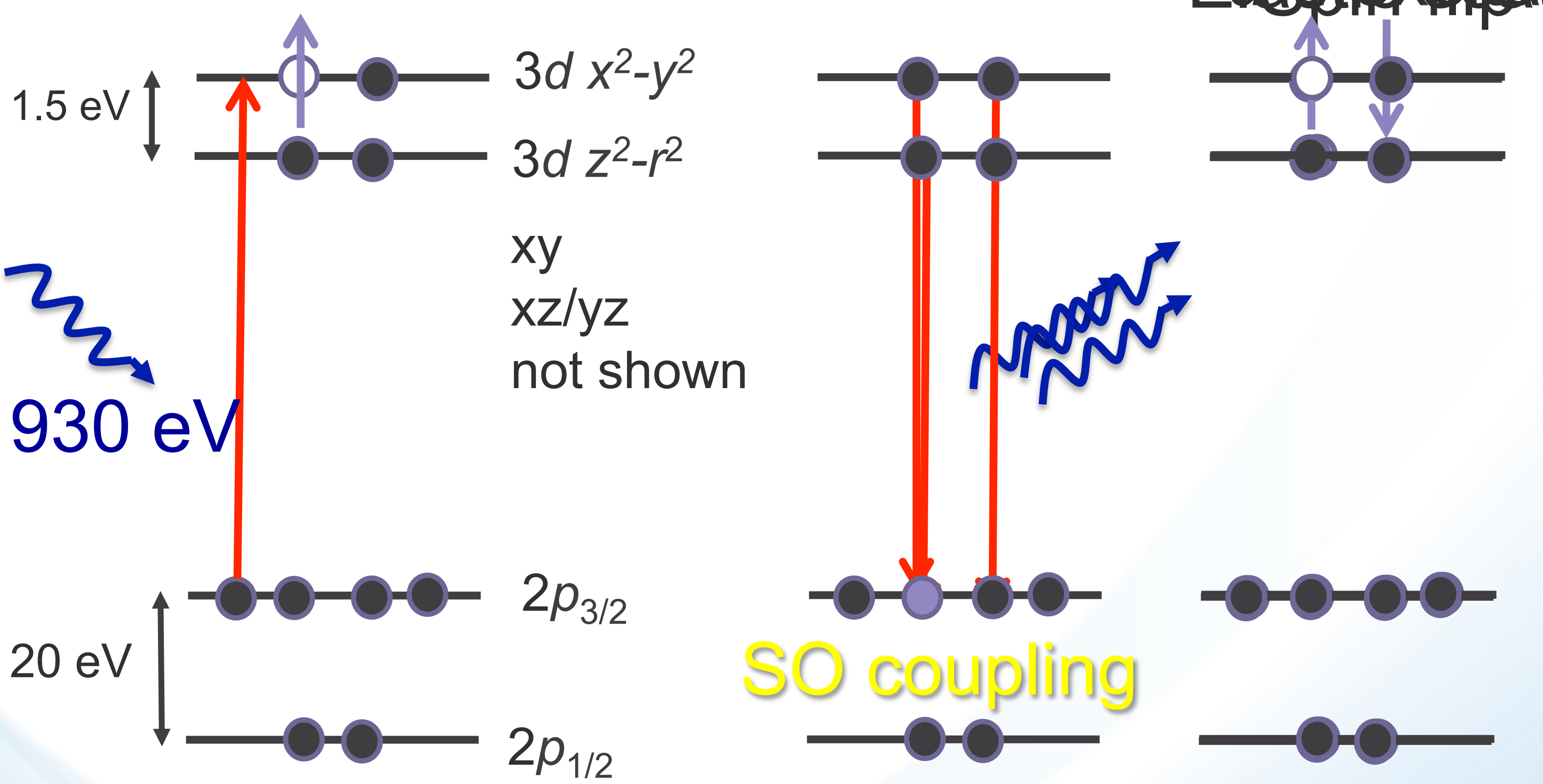
Direct

- Core electron ➔ valance band
- Electron from *different* state fills core hole
- E.g. 2p-3d resonance in $3d^9$ cuprates

Indirect

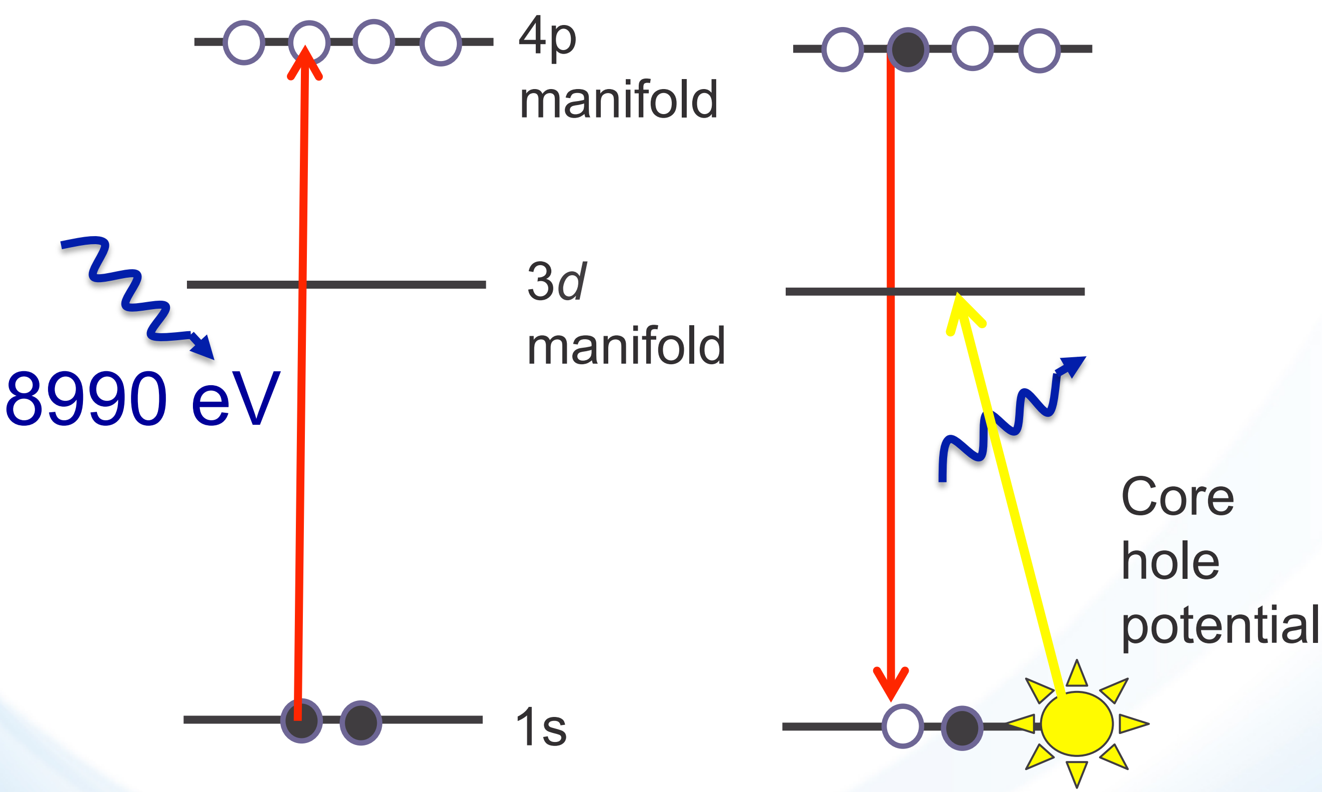
- Core electron ➔ above valance band
- Electron from *same* state fills core hole
- Direct process dominate indirect process when not forbidden
- E.g. 1s-4p resonance in $3d^9$ cuprates

Cu L-edge RIXS in the cuprates



$|i\rangle = 2p_{3/2}^4 3d^9$ $\quad$ $|n\rangle = 2p_{3/2}^3 3d^{10}$ $\quad$ $|f\rangle = 2p_{3/2}^4 3d^9 *$

Cu K-edge RIXS in the cuprates

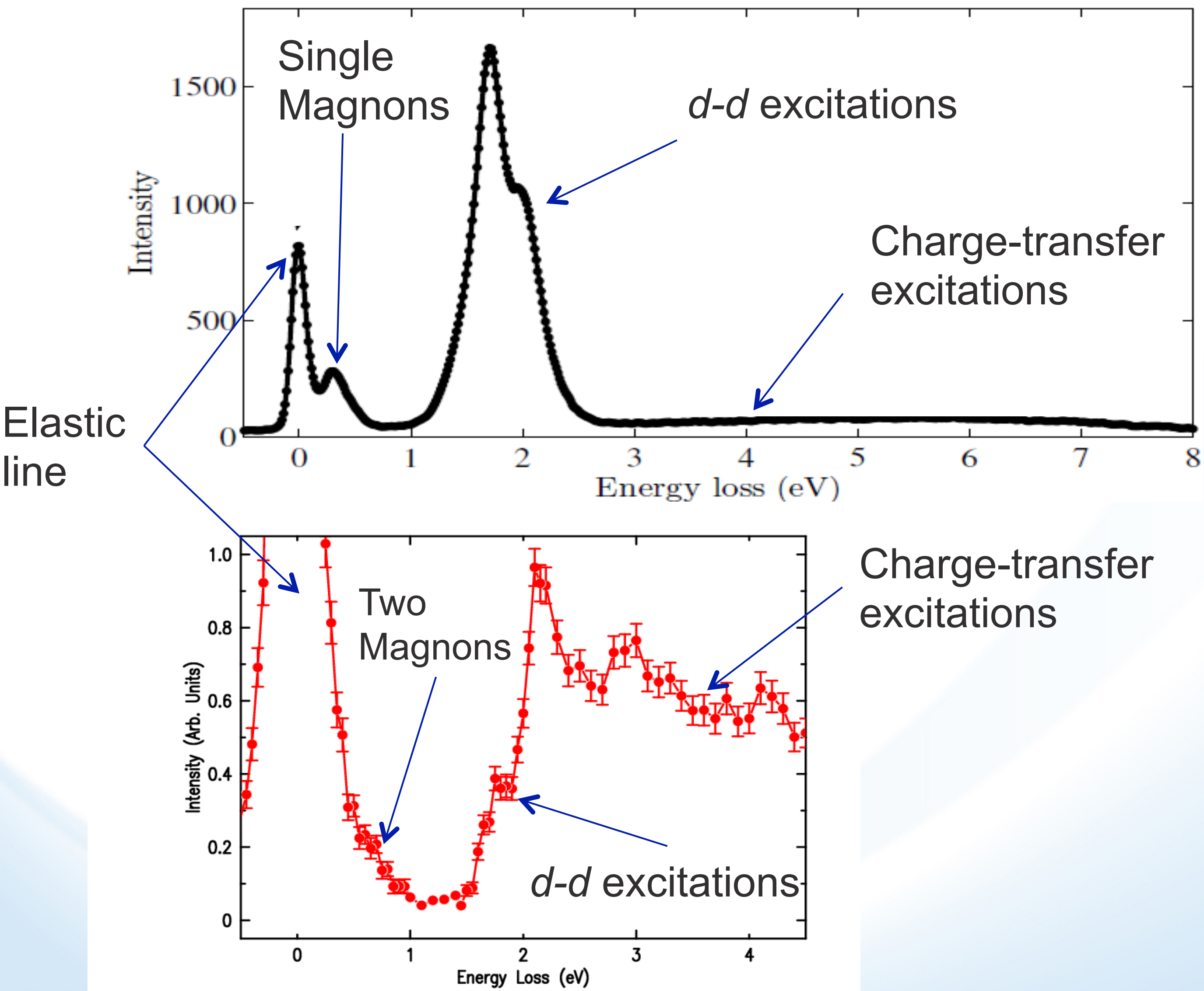


$|i\rangle = 1s^2 3d^9 4p^0$

$|n\rangle = 1s^1 3d^9 4p^1$

$|f\rangle = 1s^2 3d^{9*} 4p^0$

Cu L-edge vs. Cu K-edge: La_2CuO_4



E_i=930 eV

Cu L_3 edge

$2p_{3/2} – 3d$

E_i=8990 eV

Cu K edge

1s – 4p

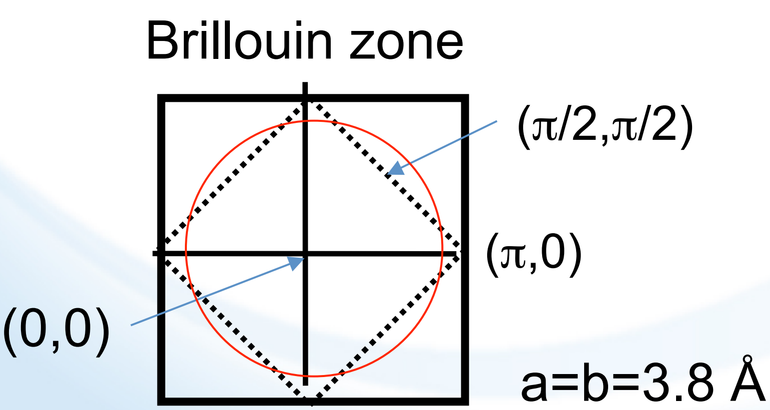
Instrument concept for soft x-rays

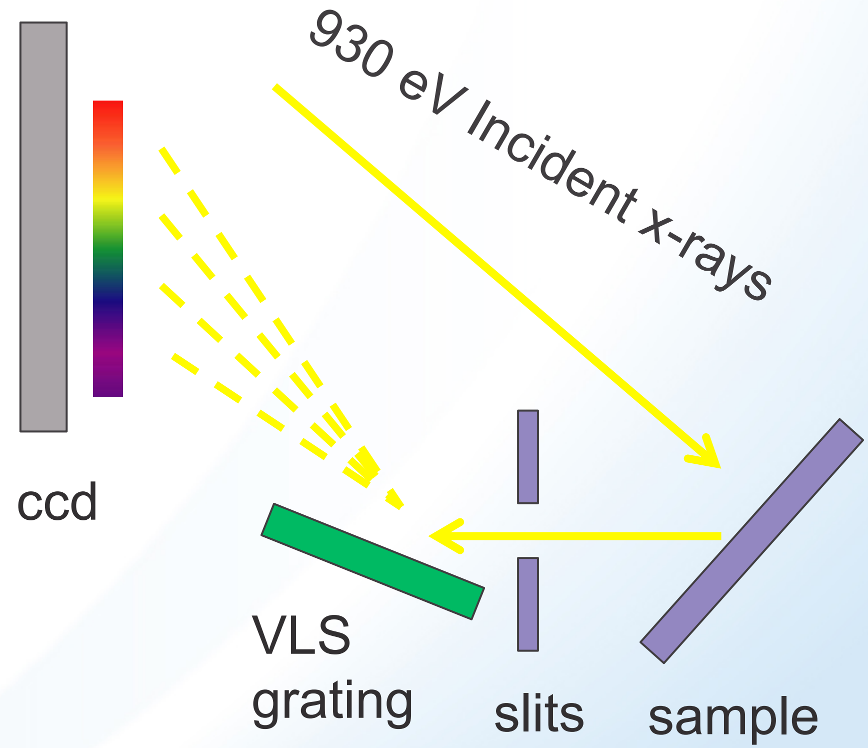
Soft x-rays:

E<2 keV ; λ> 6.2 Å

No suitable Bragg reflections

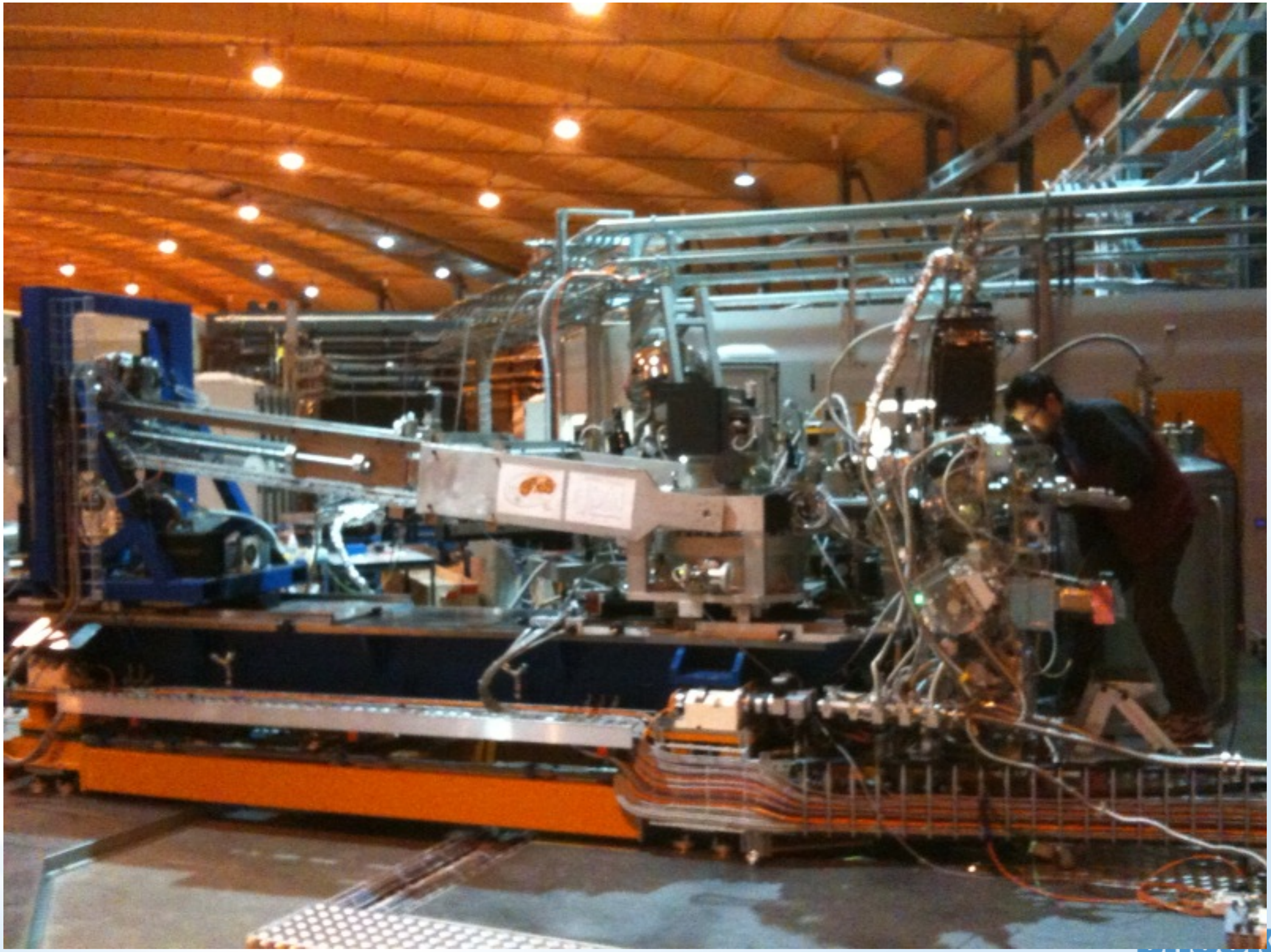
Dispersive elements are gratings



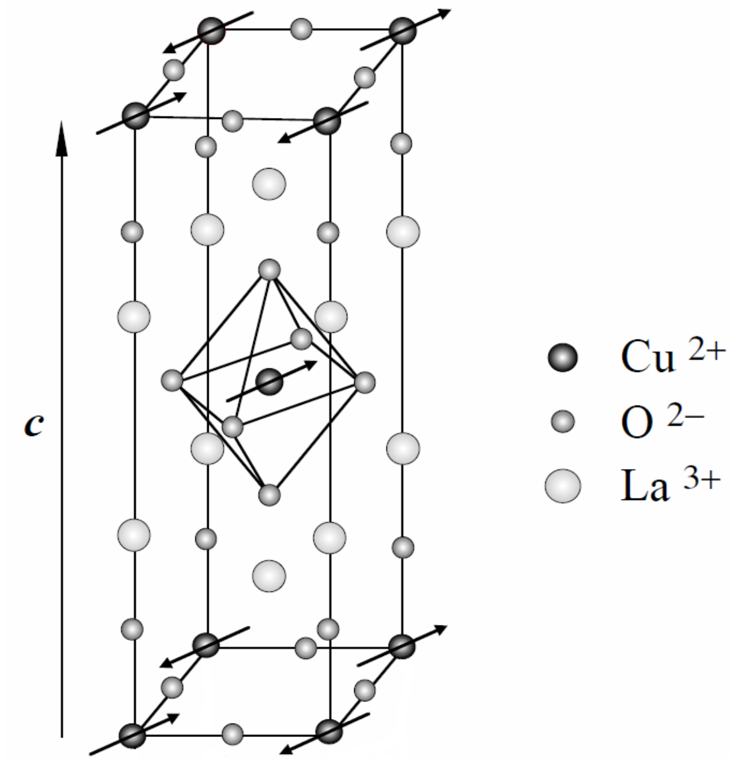


SAXES at SLS

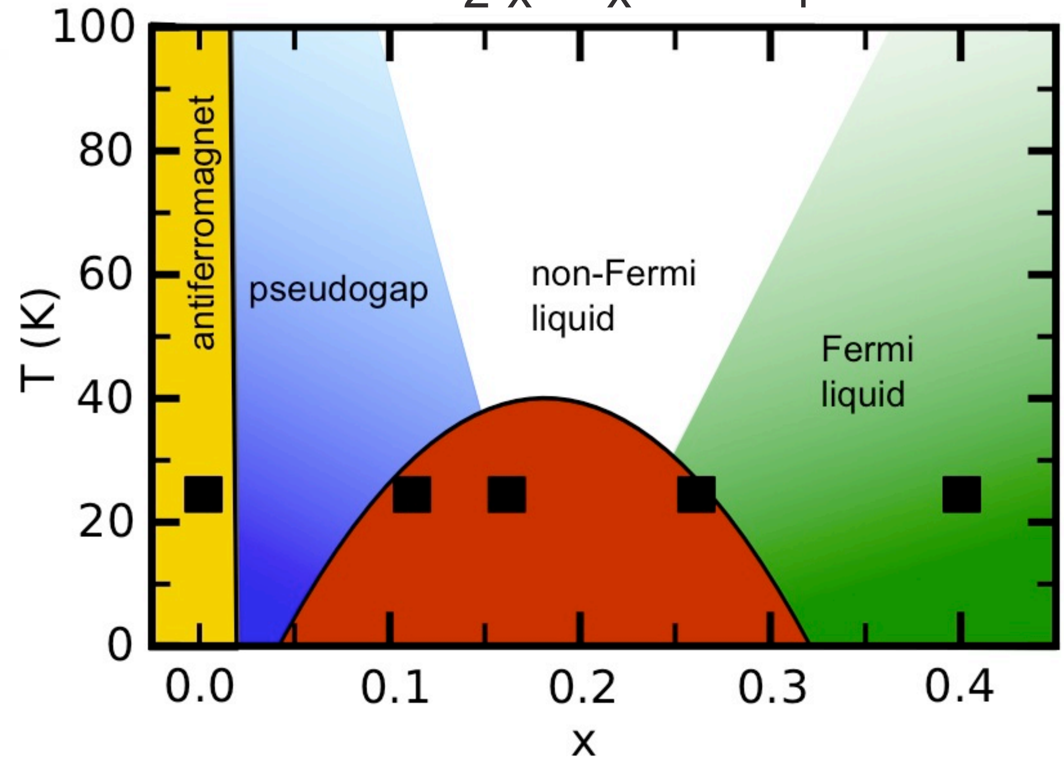
Resolution 130 meV

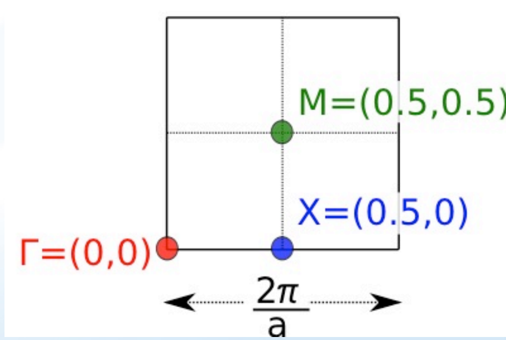


Magnetism in the high temperature superconductors

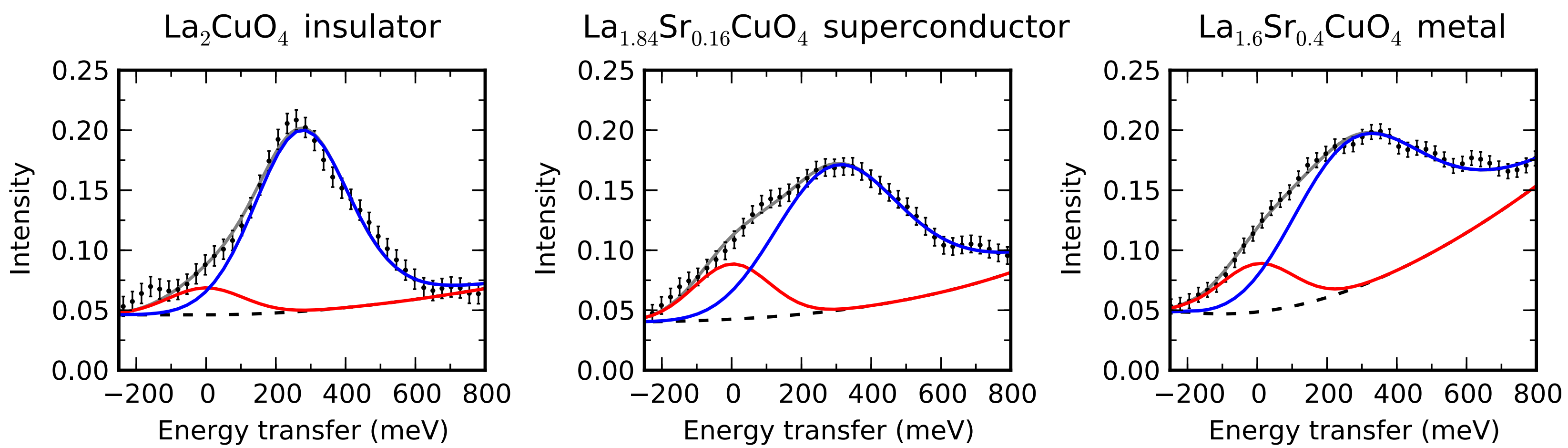


$La_{2-x}Sr_xCuO_4$



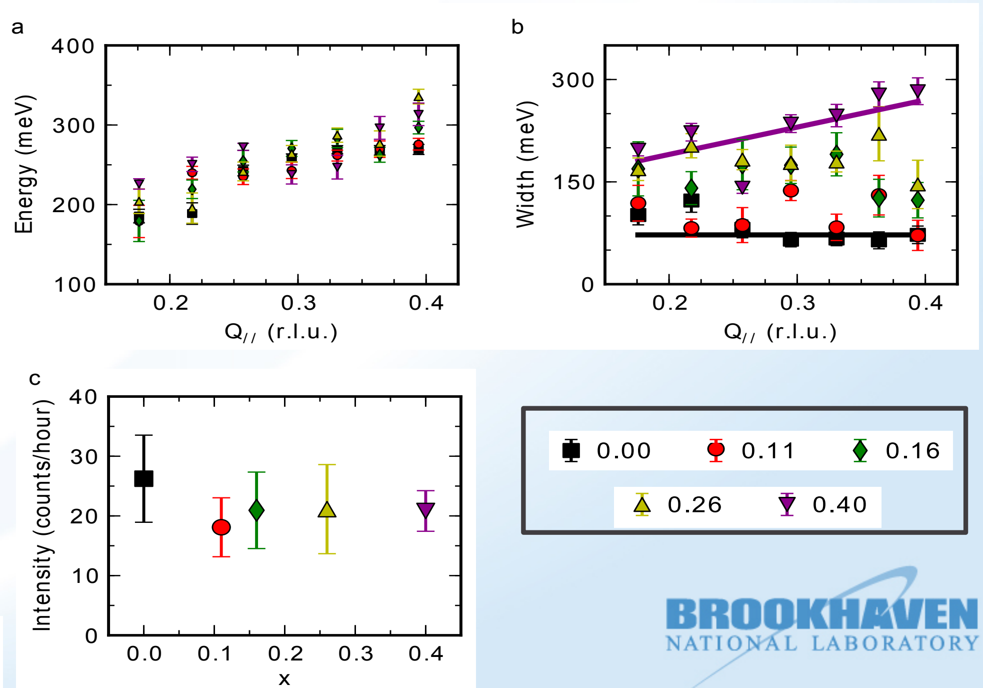


Cu L-edge spectra



Magnetism persists up to x=0.4

This suggests high energy excitations might have marginal role for SC



Dean et al. Nat. Mat. 12, 1019 (2013)

Advantage/disadvantages x-ray vs. neutrons for spin excitations

RIXS has only recently measured spin excitations

- First measurement bimagnons k-edge La_2CuO_4
  Hill et al. PRL (2008)
- First measurement magnons L-edge La_2CuO_4 Braicovich PRL (2010)

Advantages

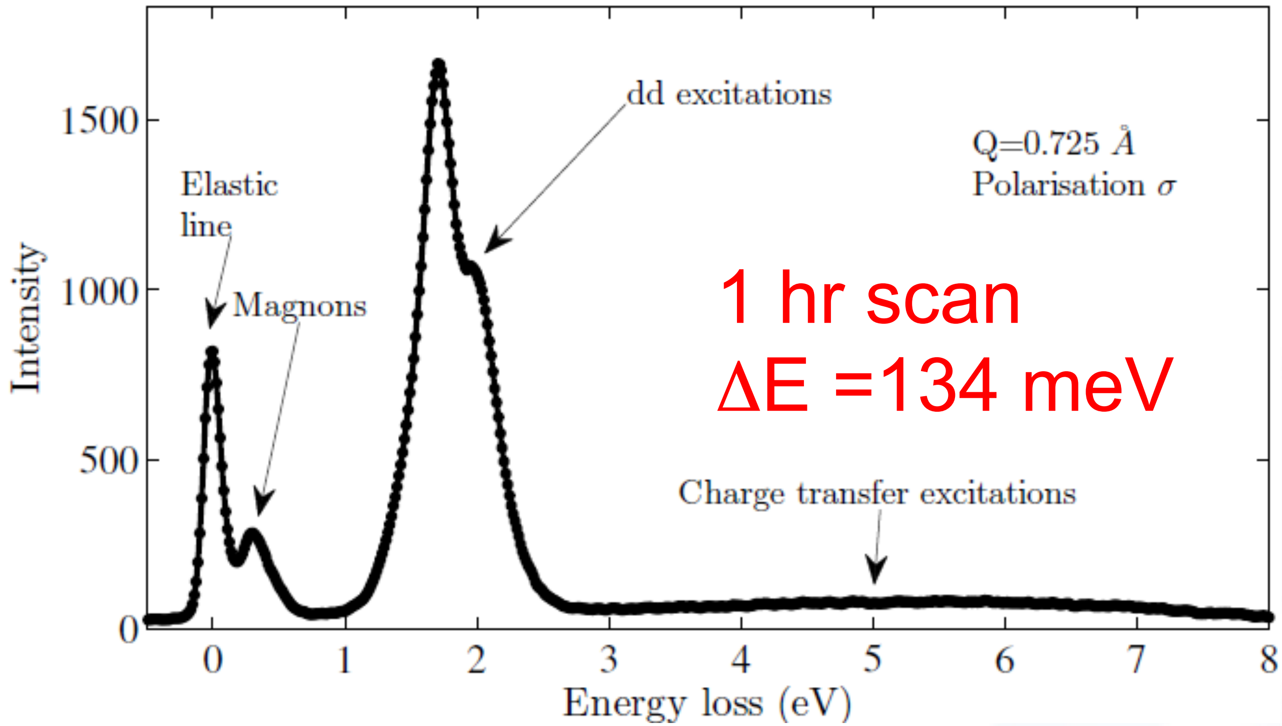
- Small samples
- Relative good count rates
- Good Q resolution
- Good at high E

Disadvantages

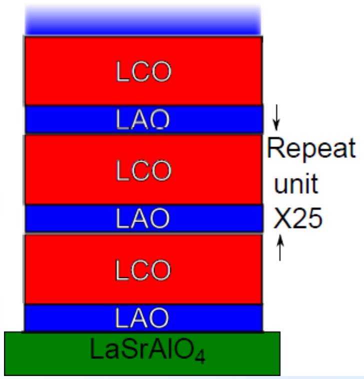
- Poor E resolution
- Upper limit on Q
- Complicated cross-section
- UHV required

M. P. M. Dean, JMMM 15, 3-13 (2015)

Allows measurement of very small samples



MBE
Ivan Bozvic



Inelastic scattering from 25 isolated, single unit cell thick layers of La_2CuO_4

Compare to INS: La_2CuO_4 47.5g of material (Headings *et al.* PRL (2010))
RIXS is a factor of $>10^{11}$ more sensitive!

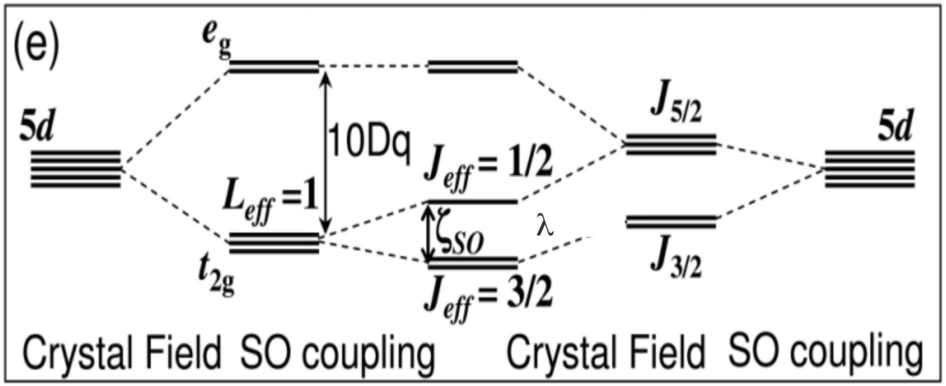
M. P. M. Dean et al. Nature Materials (2012)

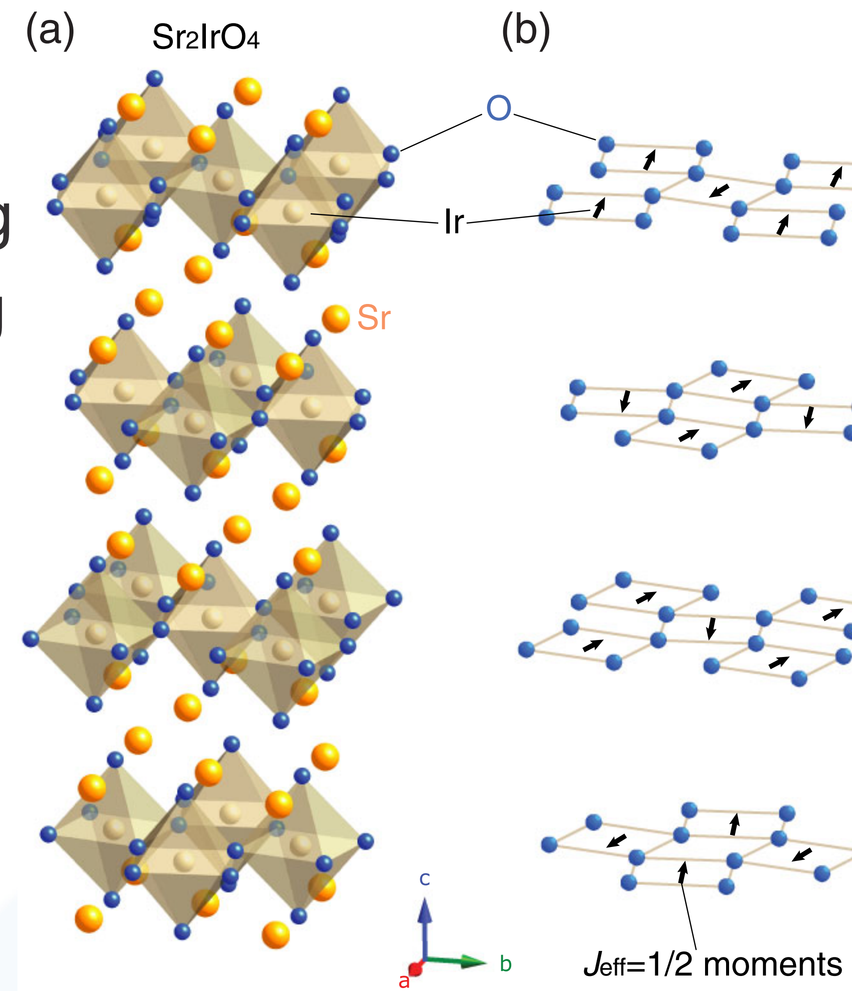
MEASURING ORBITAL EXCITATIONS

Iridates

The combined effect of:

- Strong spin-orbit (SO) coupling
- Octahedra crystal field splitting





Novel type of Mott insulator with J_{eff} (not S) magnetic moments

Kim *et al.*, PRL 101, 076402 (2009)

Orbital transition in L-edge RIXS

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \left| \sum_{|n\rangle} \frac{\langle f \,|\, \hat{D}(\varepsilon) \,|\, n \rangle \langle n \,|\, \hat{D}(\varepsilon) \,|\, i \rangle}{E_i - E_n + \hbar\omega_i + i\Gamma} \right|^2$$

Electric dipole selection rule for optics:

$\Delta l = \pm 1 \quad (\text{not zero})$ $\qquad\qquad \Delta m_l = 0, \pm 1$

L-edge has two dipole operators:

- Direct on-site orbital transition are allowed

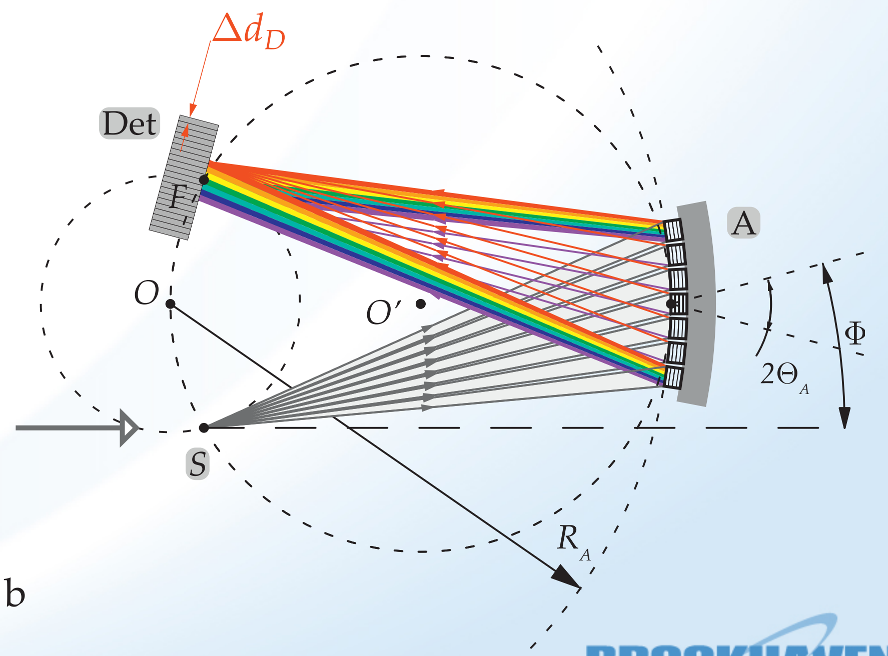
Instrument concept hard x-ray RIXS

For RIXS cannot use arbitrary E_i

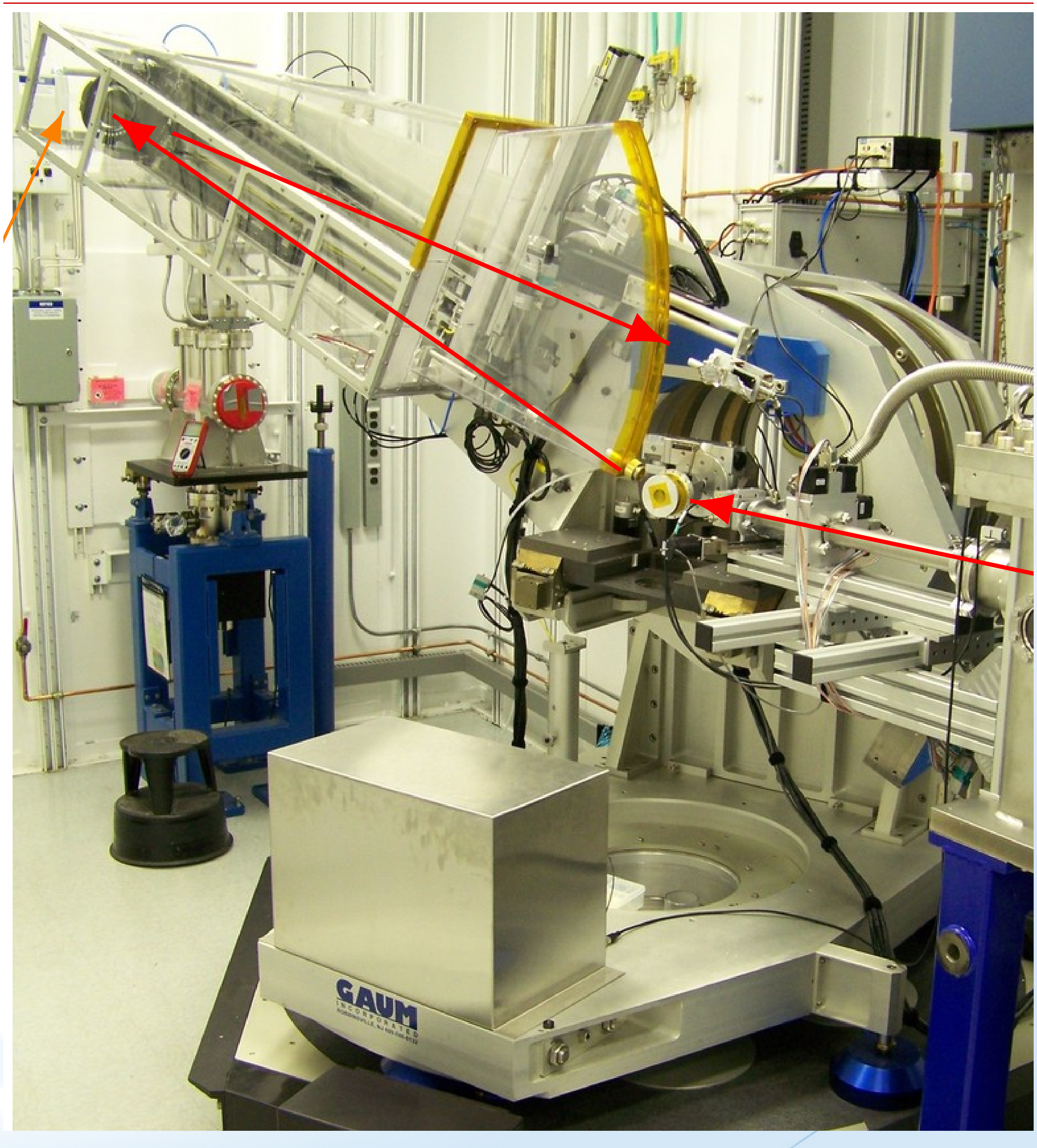
Relax backscattering condition and search for best Bragg reflection $\Theta_B \approx 85^o$

Best energy resolution:

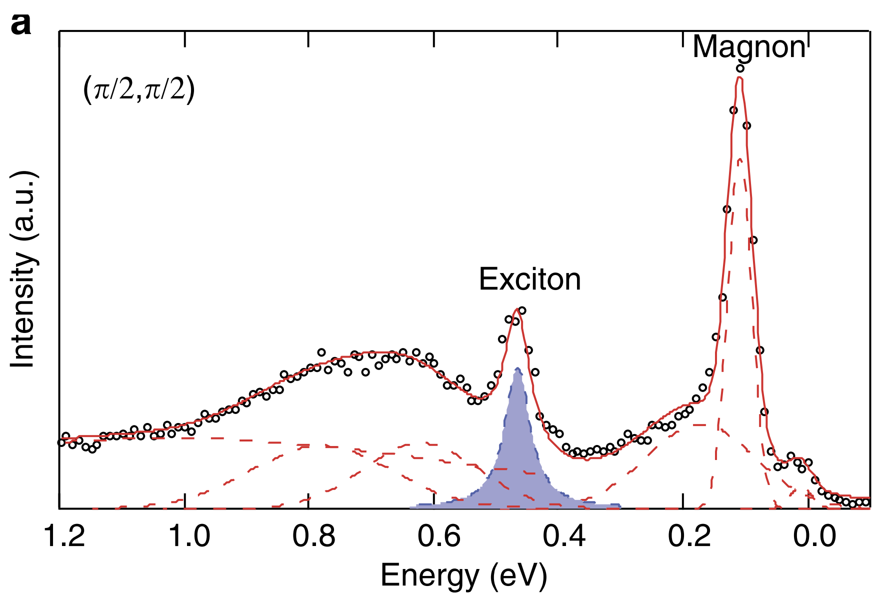
0.04 / 11200 = 4 x 10^{-6}

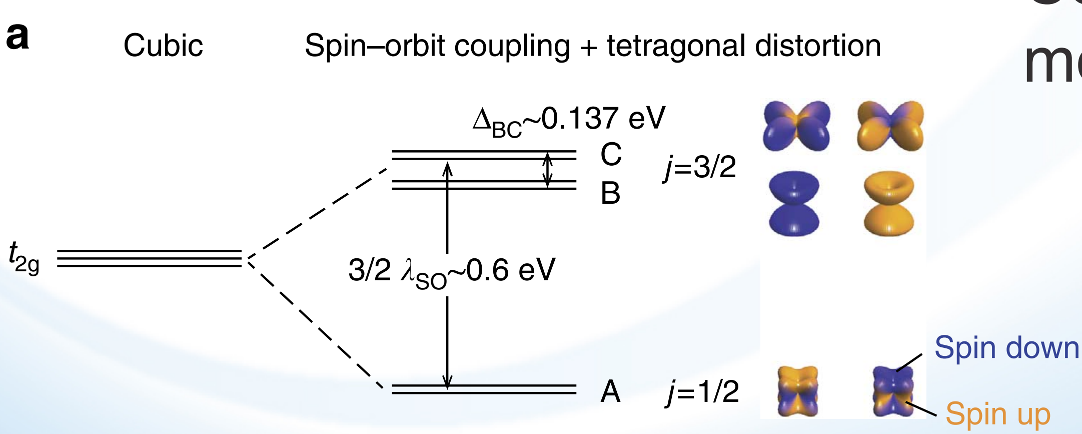


MERIX
Sector 27
APS



Ir L-edge spectrum Sr_2IrO_4





Various excitations in spectrum

- Magnon
- Exciton
- Etc

Consider single site model

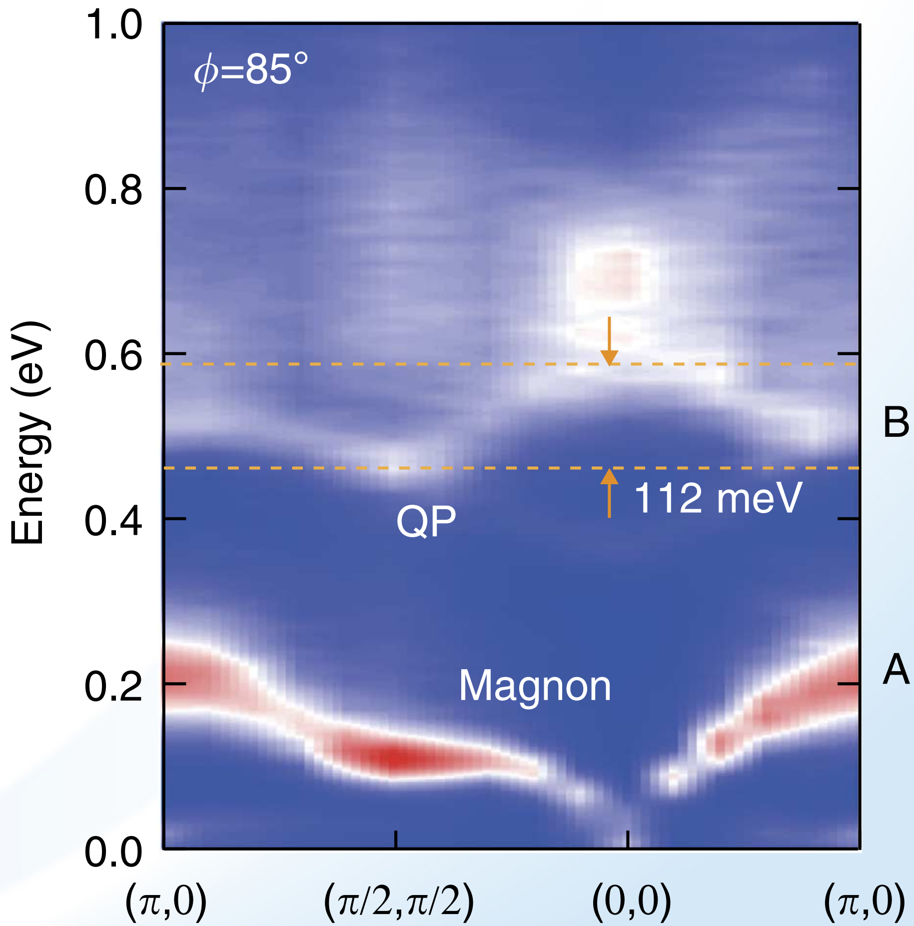
Kim *et al.*, Nat. Comms. 5:4453 (2014)

Q dependence

Dispersive orbital mode

Mode lifetime >> decay rate

Quasi-particle is orbital excitation dressed with magnetic excitations



Kim *et al.*, Nat. Comms. 5:4453 (2014)

Advantages/disadvantages of x-rays for orbital excitations

Raman

- Fast, excellent energy resolution and polarization control
- Not Q-resolved
- Not a simple cross-section

Neutrons

- dd-excitations only *indirectly* allowed
- Challenging to due limited neutron flux at incident energies of several eV

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \left|\langle f \,|\, H_{\text{int}} \,|\, i \rangle\right|^2$$

Non resonant IXS

- At high Q higher order terms in H_{int} beyond dipole are important

MEASURING CHARGE EXCITATIONS

Cross section

Consider density-density correlation function for energy loss 1-100 eV range

$$S(Q,\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \left\langle \rho(Q,t=0)\rho^{+}(Q,t) \right\rangle$$

Excitations are propagating charge modes – plasmons.

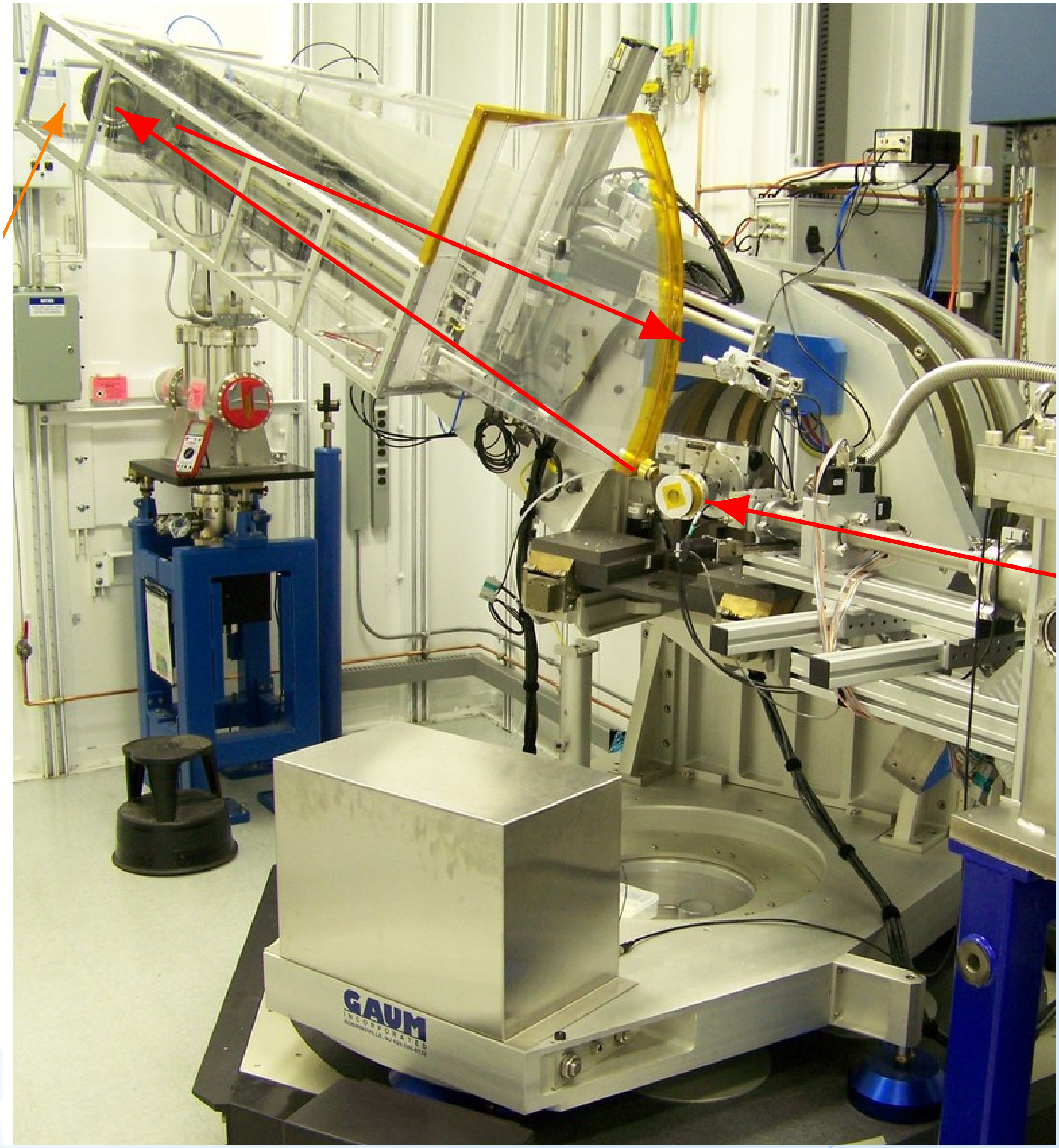
Easiest to measure in materials with low atomic number elements

MERIX Sector 27 APS

Instrument needs:

- Energy range ~0-100 eV

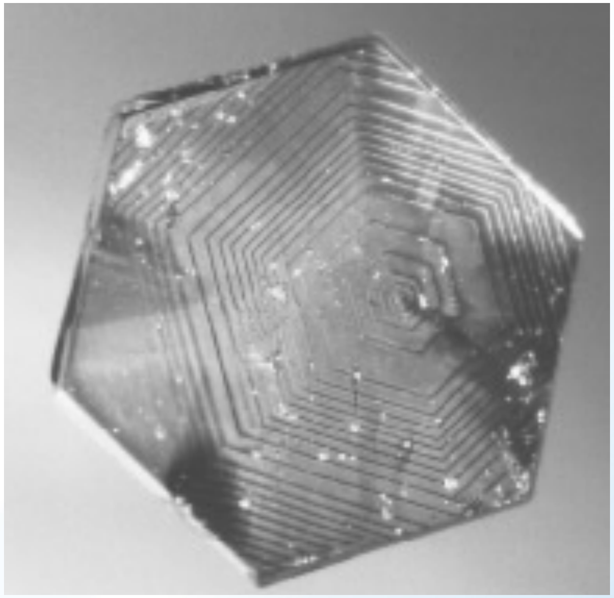
- Energy resolution ~300 meV



Charge response of graphite/ graphene

Dynamical susceptibility linked to dielectric response

$$S(Q,\omega) = \frac{1}{\pi}\frac{1}{1-\exp(-\hbar\omega / k_B T)}\mathrm{Im}\left[-\chi(Q,\omega)\right]$$

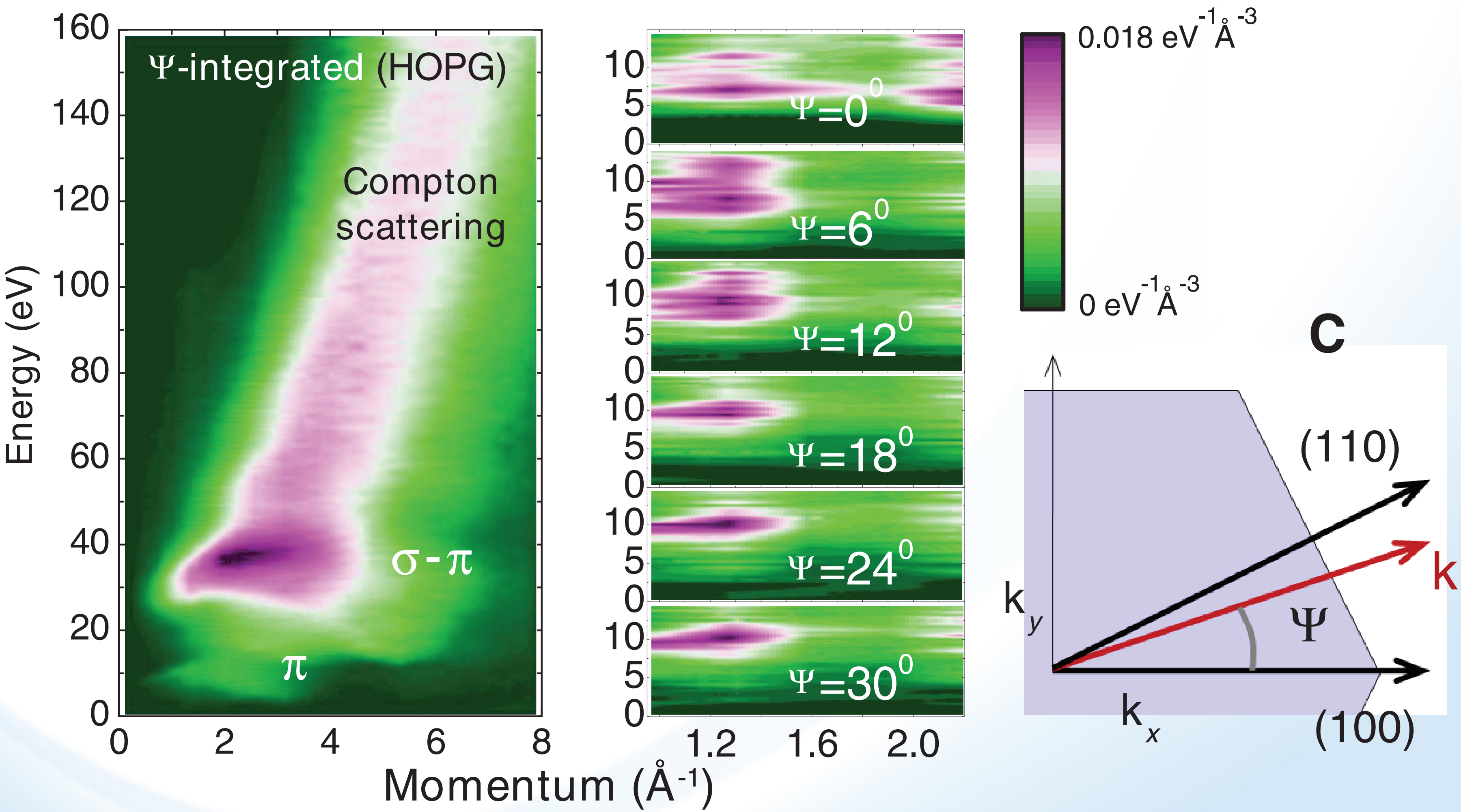


In principle, a full description of charge response:

e.g. charge screening

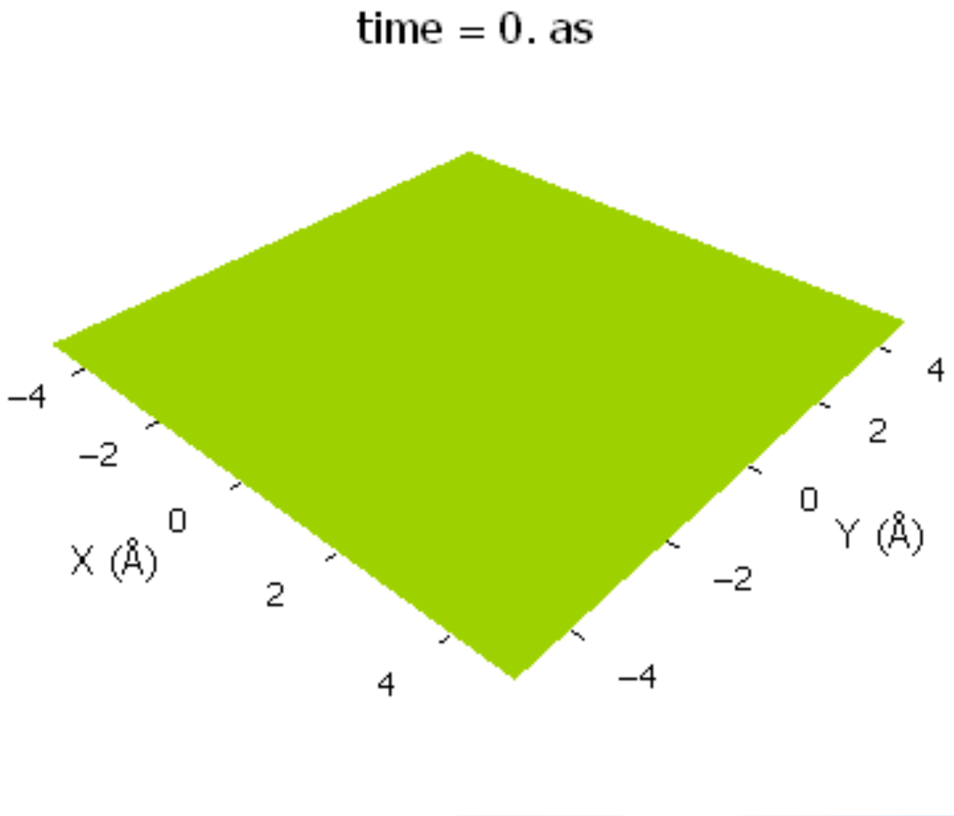
J.P. Reed et al., Science 330, 5 (2010)

Data



J.P. Reed et al., Science 330, 5 (2010)

Electronic screening movie

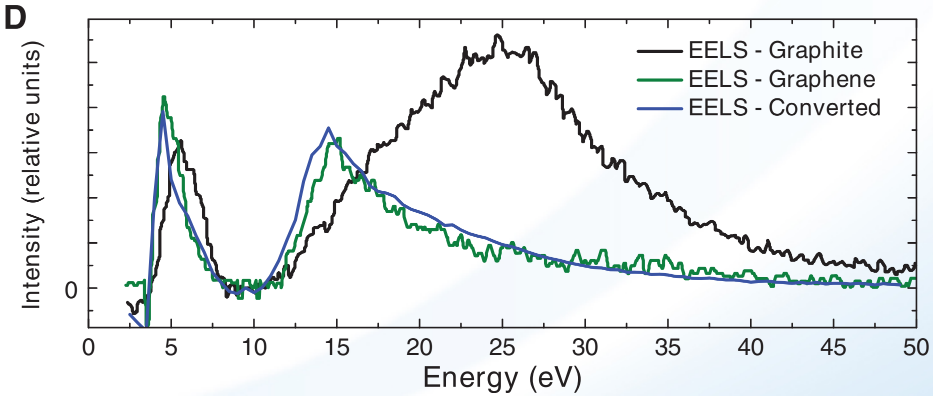


J.P. Reed et al., Science 330, 5 (2010)

Advantages/disadvantages ox x-rays for plasmons

Electron energy loss spectroscopy EELS

- Easier, cheaper
- Better sensitivity to small volumes
- Multiple scattering problems at high Q



More information

RIXS

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

Non resonant IXS and Phonons

- A.Q.R. Baron, arXiv:1504.01098 (2015)
- H. Sinn, J. Phys.: Condens. Matter **13**, 7525–7537 (2001)
- M. d'Astuto and M. Krisch, Collection *SFN* **10**, 487–503 (2010)

IXS and Plasmons (and other topics)

- Electron Dynamics by Inelastic X-Ray Scattering, Winfried Schülke, Oxford (2007)

Inelastic scattering in general (focused on neutrons)

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