Resonant and Non-resonant Inelastic X-ray Scattering (IXS)

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History of IXS

- In which year was the first inelastic X-ray scattering experiment carried out and reported?

1. 1895
2. 1923
3. 1970
4. 1995

Second Series *May, 1923* *Vol. 21, No. 5*

THE

PHYSICAL REVIEW

A QUANTUM THEORY OF THE SCATTERING OF X-RAYS BY LIGHT ELEMENTS

By Arthur H. Compton

Abstract

A quantum theory of the scattering of X-rays and γ-rays by light elements.—The hypothesis is suggested that when an X-ray quantum is scattered it spends all of its energy and momentum upon some particular electron. This electron in turn scatters the ray in some definite direction. The change in momentum of the X-ray quantum due to the change in its direction of propagation results in a recoil of the scattering electron. The energy in the scattered quantum is thus less than the energy in the primary quantum by the kinetic energy of recoil of the scattering electron. The corresponding *increase in the wave-length of the scattered beam* is $\lambda_\theta - \lambda_0 = (2h/mc) \sin^2 \frac{1}{2}\theta = 0.0484 \sin^2 \frac{1}{2}\theta$, where h is the Planck constant, m is the mass of the scattering electron, c is the velocity of light, and θ is the angle between the incident and the scattered ray. Hence the increase is independent of the wave-length. *The distribution of the scattered radiation* is found, by an indirect and not quite rigid method, to be concentrated in the forward direction according to a definite law (Eq. 27).

the secondary. The zero point for the spectrum of both the primary and secondary X-rays was determined by finding the position of the first order lines on both sides of the zero point.

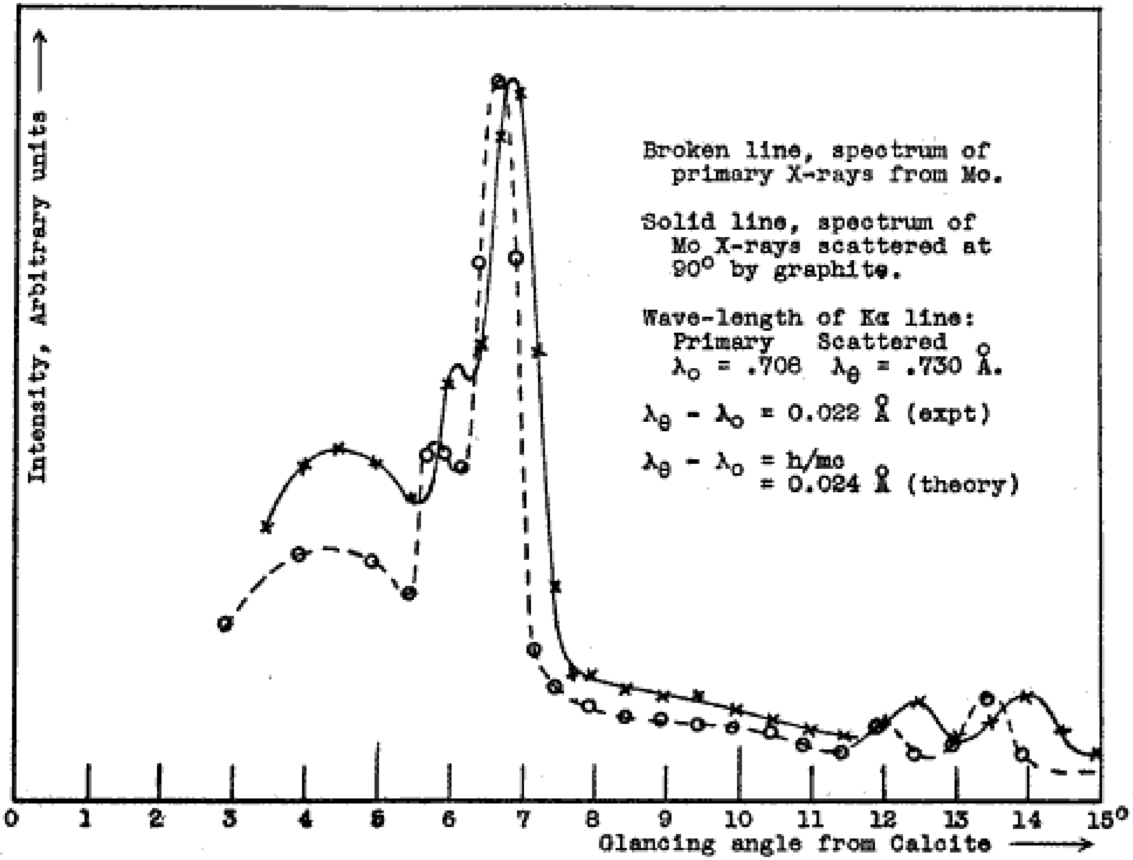


Fig. 4. Spectrum of molybdenum X-rays scattered by graphite, compared with the spectrum of the primary X-rays, showing an increase in wave-length on scattering.

It will be seen that the wave-length of the scattered rays is unquestionably greater than that of the primary rays which excite them.

Inelastic X-ray Scattering

- X-ray spectroscopy usually involves absorption/emission
  - XAS, XES, XMCD, etc.
- IXS (Scattering) is Photon-in, photon-out
- Interaction Hamiltonian between photon and electron (following Blume 1985)

$$\mathscr{H}_{\text{int}} = \frac{e^2}{2mc^2}\sum_j \mathbf{A}(\mathbf{r}_j)^2 - \frac{e\hbar}{2m^2c^2}\frac{e^2}{c^2}\sum_j \mathbf{s}_j \cdot \left[\dot{\mathbf{A}}(\mathbf{r}_j) \times \mathbf{A}(\mathbf{r}_j)\right]$$

$$-\frac{e}{mc}\sum_j \mathbf{A}(\mathbf{r}_j)\cdot\mathbf{P}_j - \frac{e\hbar}{2mc}\sum_j \left(\mathbf{s}_j \cdot \nabla \times \mathbf{A}(\mathbf{r}_j)\right)$$

Ignore for now!

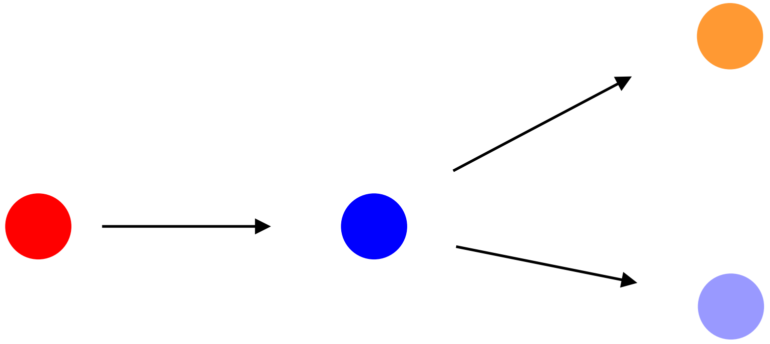
Scattering term

Absorption + Emission=RIXS

$\mathbf{A}(\boldsymbol{r})$ is linear in photon creation and annihilation operators

Inelastic X-ray Scattering

- Inelastic Collision



$\boldsymbol{k}_1, \boldsymbol{k}_2$: Photon Momentum

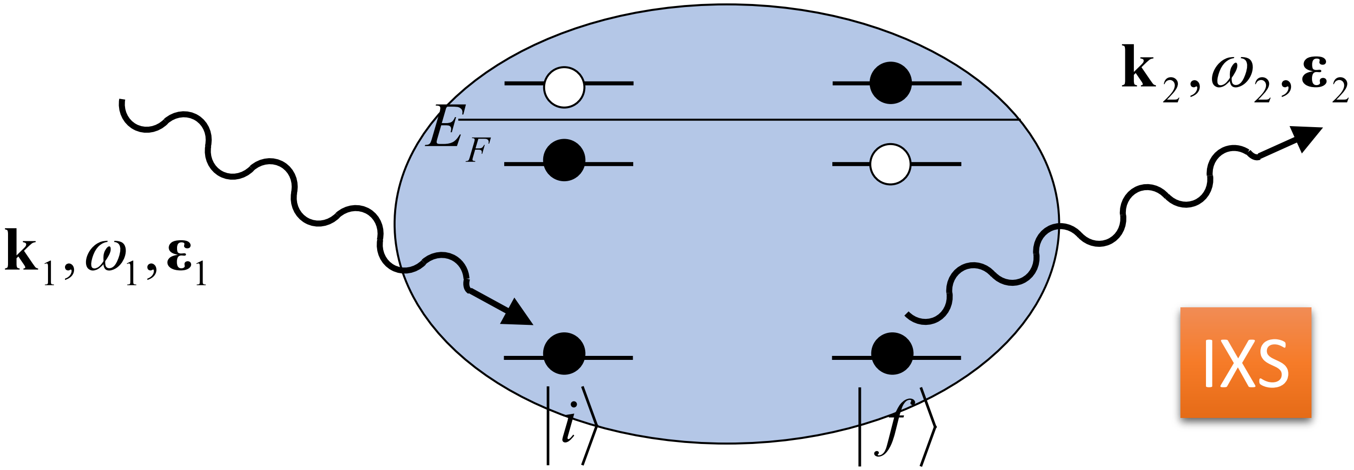
$\boldsymbol{Q} \equiv \boldsymbol{k}_1 - \boldsymbol{k}_2$: Momentum Transfer

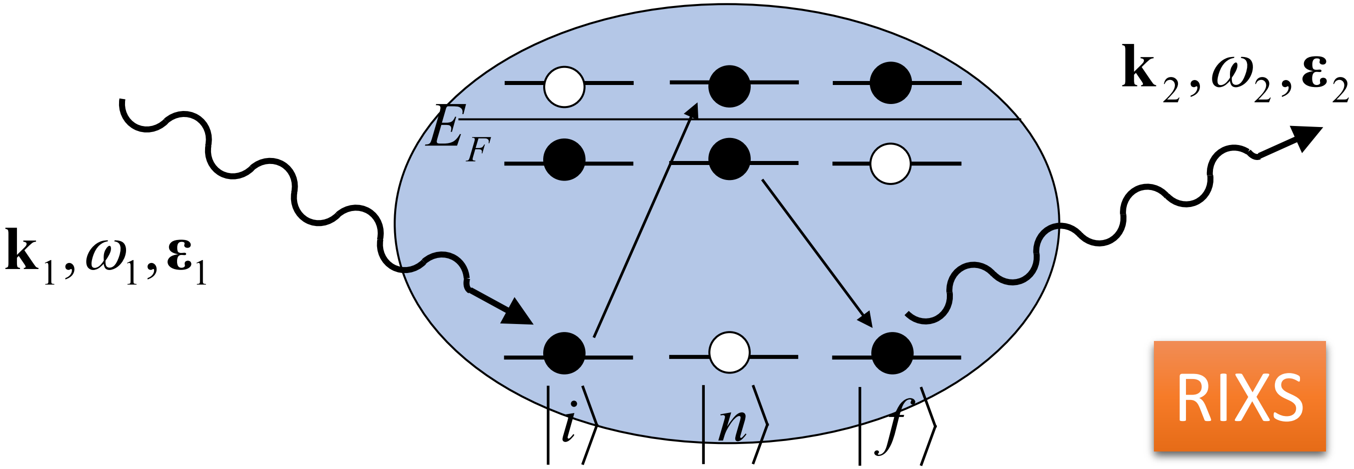
ω_1, ω_2: Photon Energy

$\omega \equiv \omega_1 - \omega_2$: Energy Transfer

$\boldsymbol{\varepsilon}_1, \boldsymbol{\varepsilon}_2$: Photon polarization

- In materials,





Inelastic X-ray Scattering

- Partial differential cross-section (measured)

$$\frac{d\sigma}{d\Omega dE_f} \propto \left|\langle f|\hat{U}|i\rangle\right|^2 S(\boldsymbol{Q},\omega)$$

Matrix Element dependent on interaction with the probing particle

Dynamic Structure Factor
- Intrinsic property of the system

$$S(\boldsymbol{Q},\omega) = \frac{1}{2\pi\hbar}\int G(\boldsymbol{r},t)e^{i(\boldsymbol{Q}\cdot\boldsymbol{r}-\omega t)}d\boldsymbol{r}dt$$

Two-particle correlation function

e.g.
Density correlation fn $\langle n(\boldsymbol{r},t)n(0,0)\rangle$
Spin-spin correlation fn $\langle S(\boldsymbol{r},t)S(0,0)\rangle$

Resonant scattering – quantum mechanical picture

$$W = \frac{2\pi}{\hbar}\left|\langle f|\mathcal{H}_I|i\rangle + \sum_{n=1}^{\infty}\frac{\langle f|\mathcal{H}_I|n\rangle\langle n|\mathcal{H}_I|i\rangle}{\omega_i - E_n - i\Gamma_n}\right|^2 \rho(E_F)$$

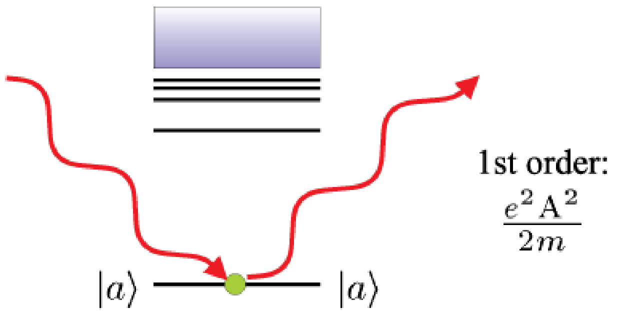
$$\mathcal{H}_I \sim \boldsymbol{A}\cdot\boldsymbol{p} \sim \boldsymbol{\varepsilon}\cdot\boldsymbol{p}\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

Dipole Approximation

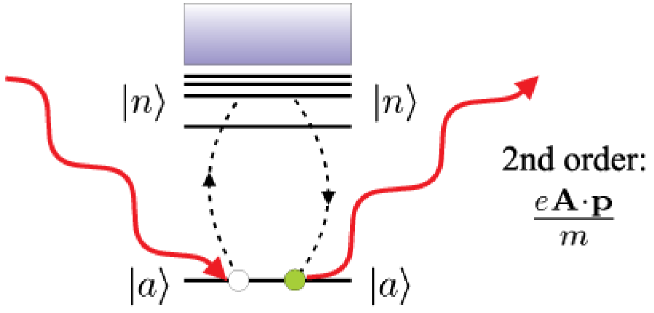
$$\langle n|\boldsymbol{p}|i\rangle \sim \langle n|\boldsymbol{r}|i\rangle$$

$$\langle n|\widehat{\mathcal{D}}|i\rangle$$

(b) Thomson scattering



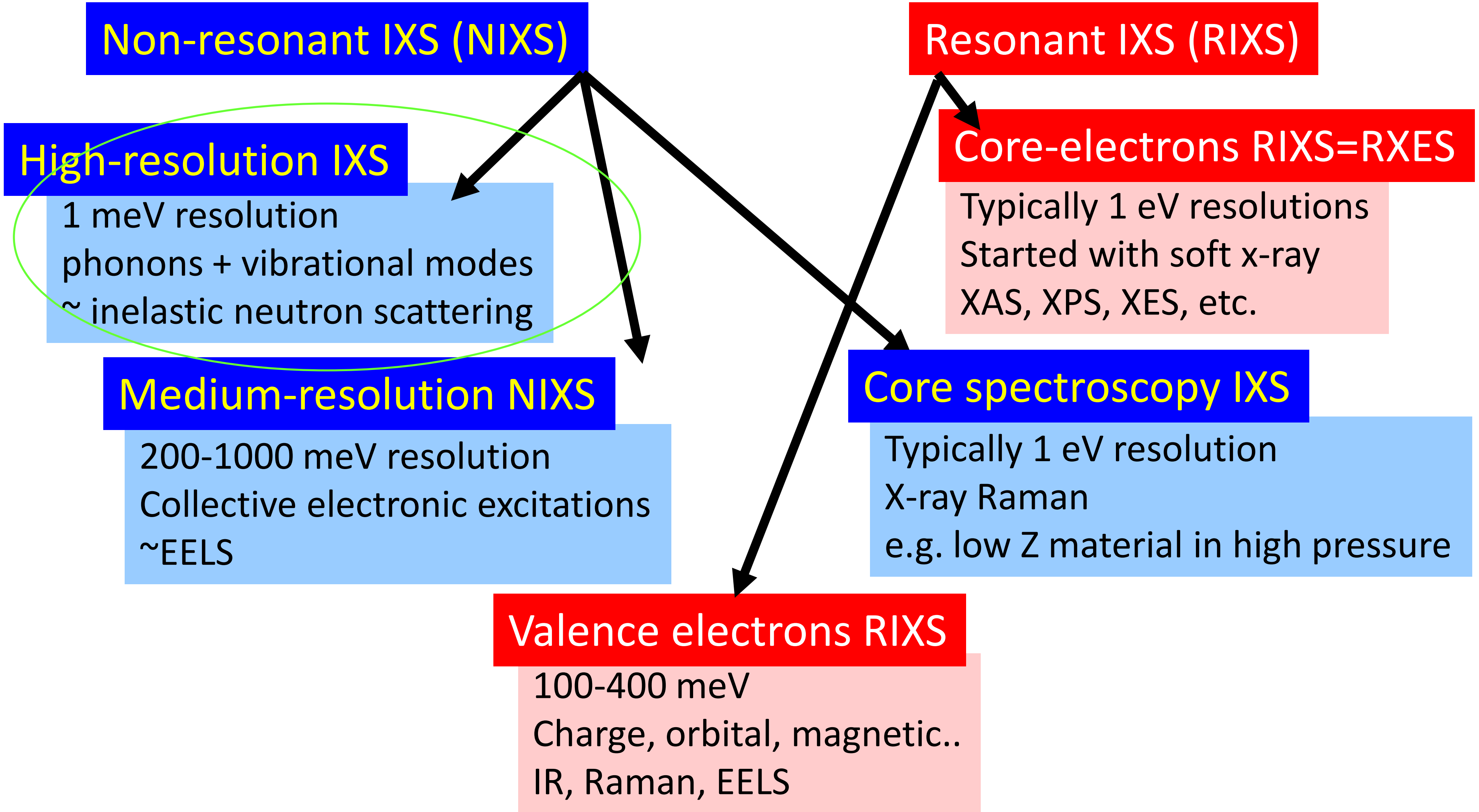
(c) Resonant scattering



Elements of Modern X-ray Physics, Als-Nielsen and McMorrow, *Wiley 2011*

Many flavors of IXS

$$H_{e-\gamma} \propto A^2 + A \bullet p$$



Non-resonant IXS (NIXS)

High-resolution IXS

1 meV resolution
phonons + vibrational modes
~ inelastic neutron scattering

Medium-resolution NIXS

200-1000 meV resolution
Collective electronic excitations
~EELS

Core spectroscopy IXS

Typically 1 eV resolution
X-ray Raman
e.g. low Z material in high pressure

Resonant IXS (RIXS)

Core-electrons RIXS=RXES

Typically 1 eV resolutions
Started with soft x-ray
XAS, XPS, XES, etc.

Valence electrons RIXS

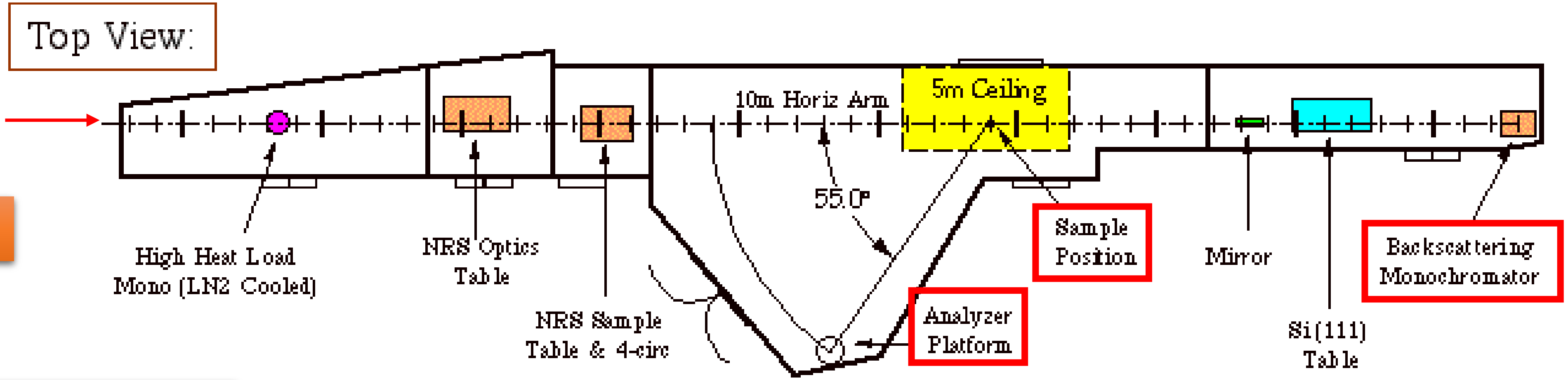
100-400 meV
Charge, orbital, magnetic..
IR, Raman, EELS

Instrumentation – brute force

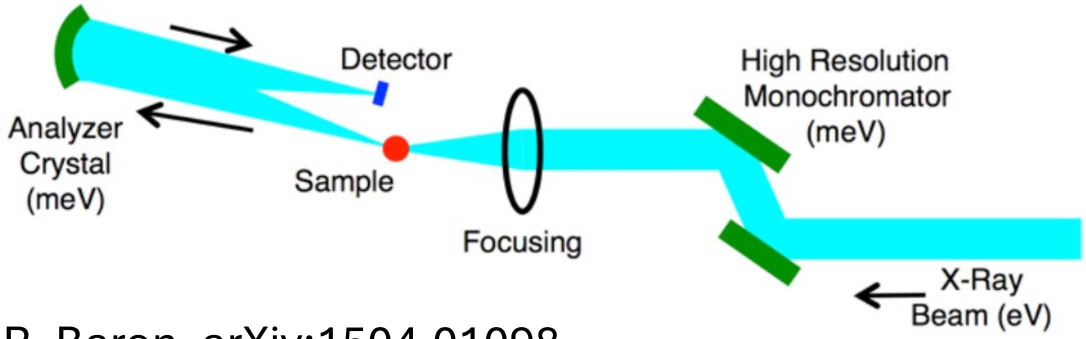
- Technically challenging to obtain meV resolution with 10 keV x-ray
- Equivalent to measuring the length of a football field with the accuracy of 0.1mm

A.Q.R. Baron, *et al*, J. Phys & Chem Solids **61**, (2000) 461.

SPring8 BL35



“Triple-Axis” Spectrometer

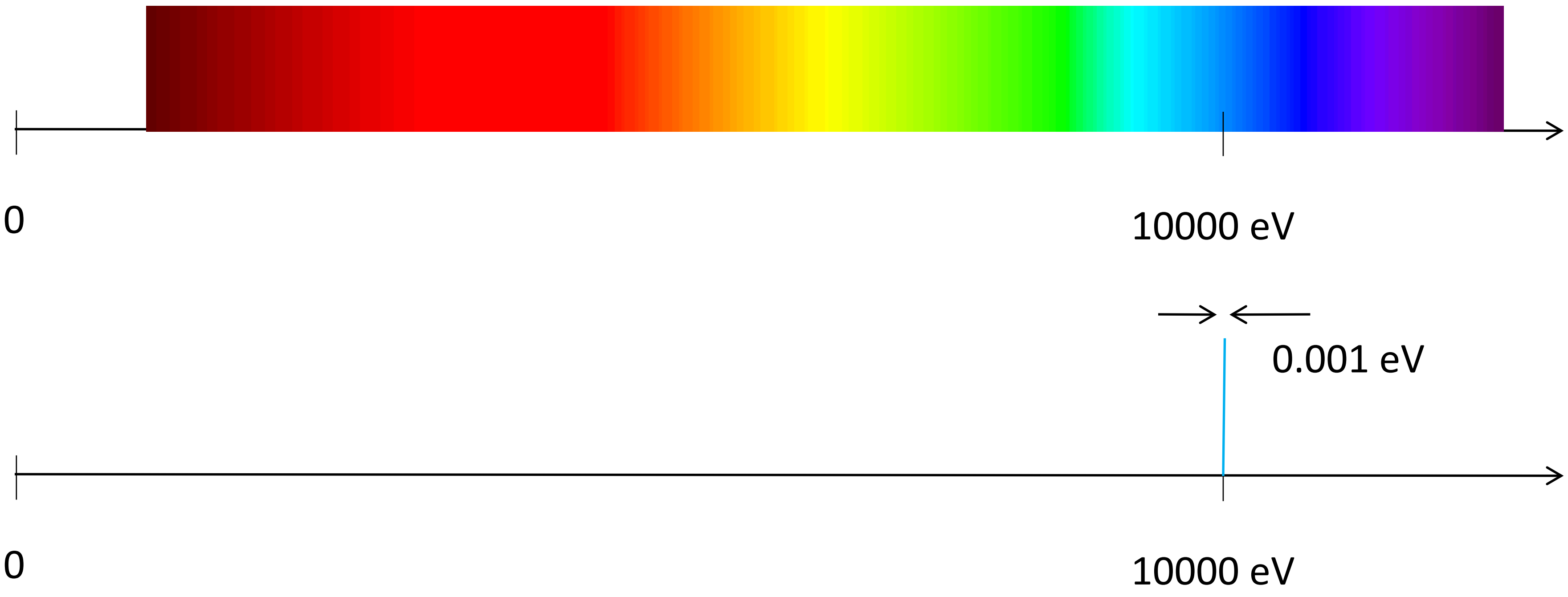


APS 30ID

A. Q. R. Baron, arXiv:1504.01098

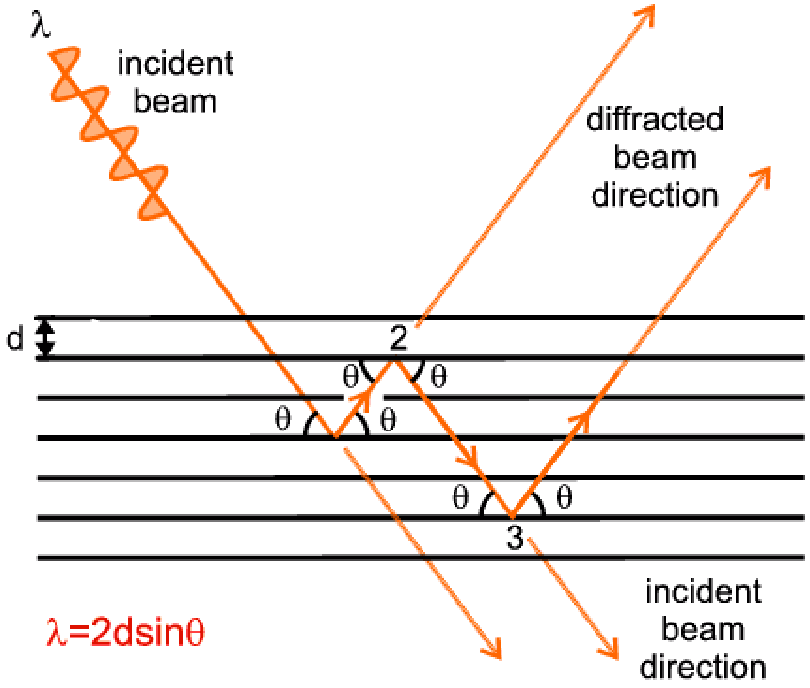
How to get ppm accuracy?

- Start with narrow bandwidth

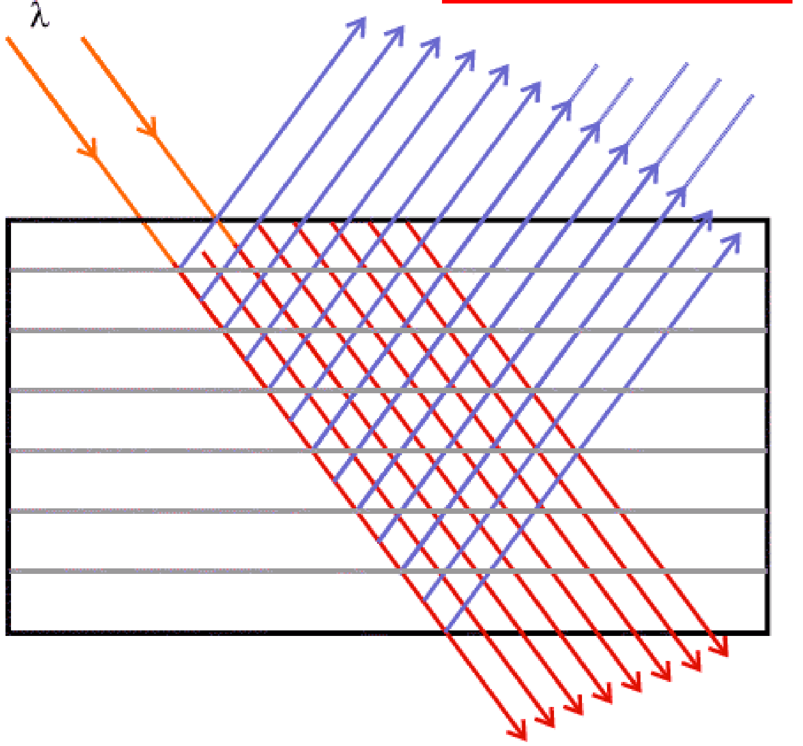


Bragg's law revisited – Dynamic diffraction Theory

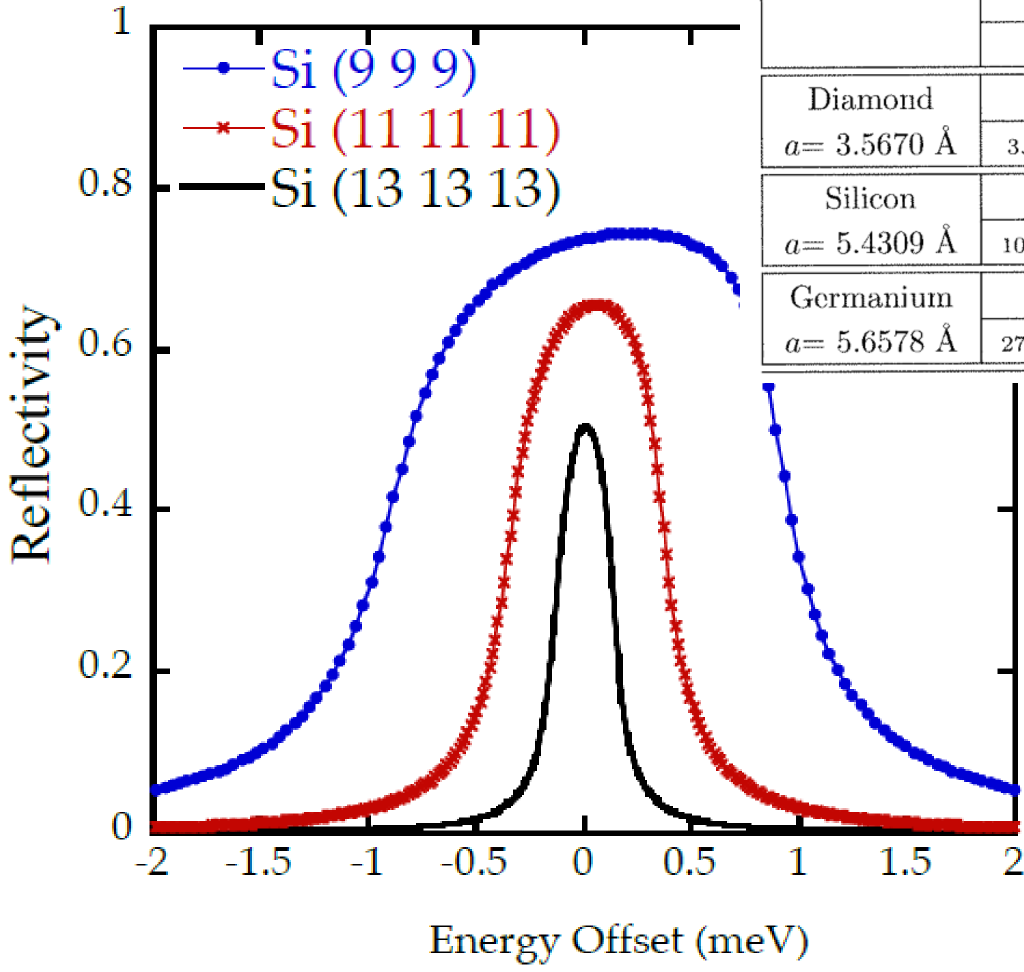
- Only works for perfect crystals
- Finite width of Bragg peaks – Darwin width (1914)

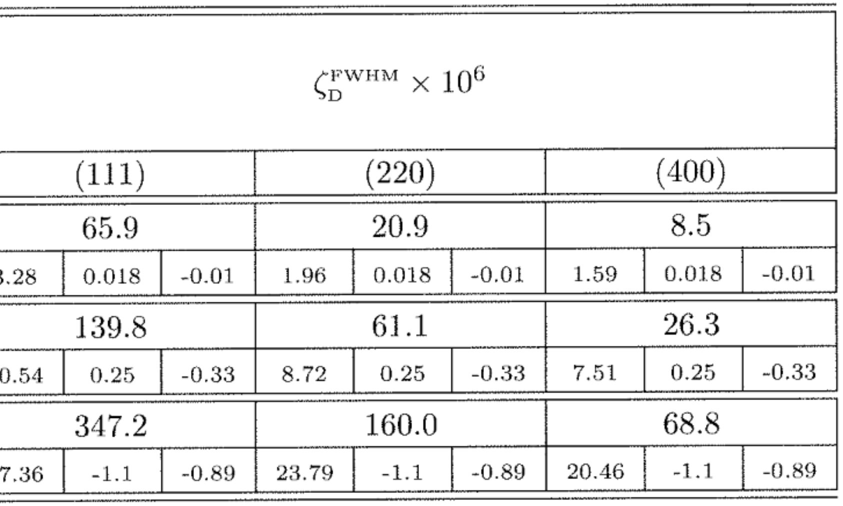


Finite width



Darwin width





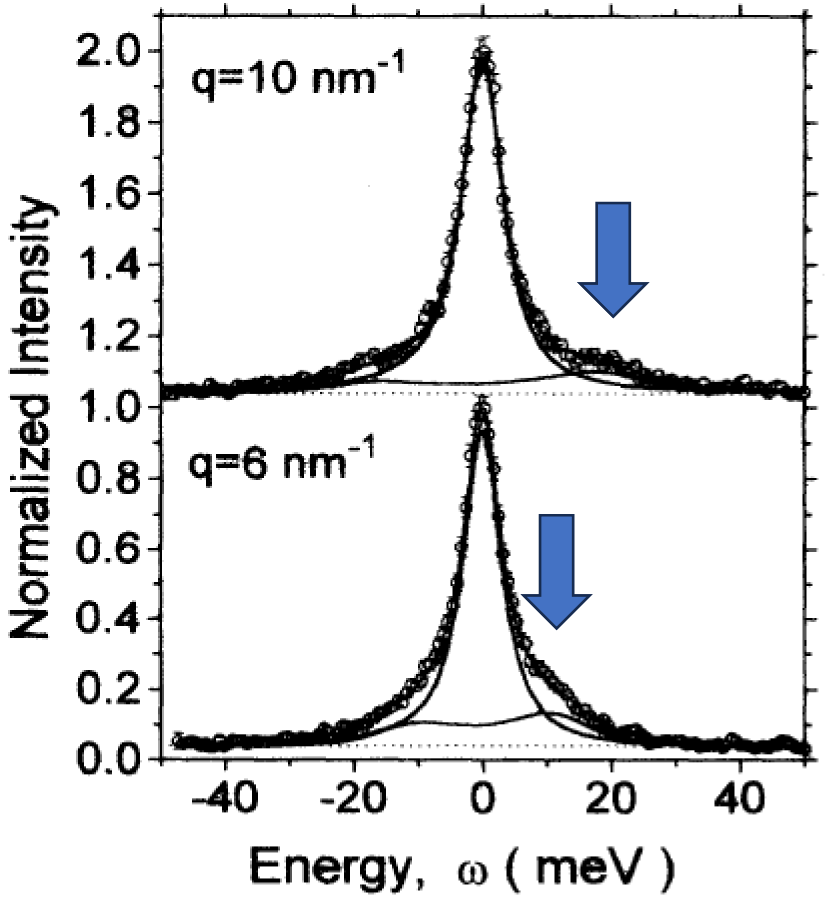
	$\zeta_D^{\mathrm{FWHM}} \times 10^6$								
	(111)			(220)			(400)		
Diamond	65.9			20.9			8.5		
a= 3.5670 Å	3.28	0.018	-0.01	1.96	0.018	-0.01	1.59	0.018	-0.01
Silicon	139.8			61.1			26.3		
a= 5.4309 Å	10.54	0.25	-0.33	8.72	0.25	-0.33	7.51	0.25	-0.33
Germanium	347.2			160.0			68.8		
a= 5.6578 Å	27.36	-1.1	-0.89	23.79	-1.1	-0.89	20.46	-1.1	-0.89

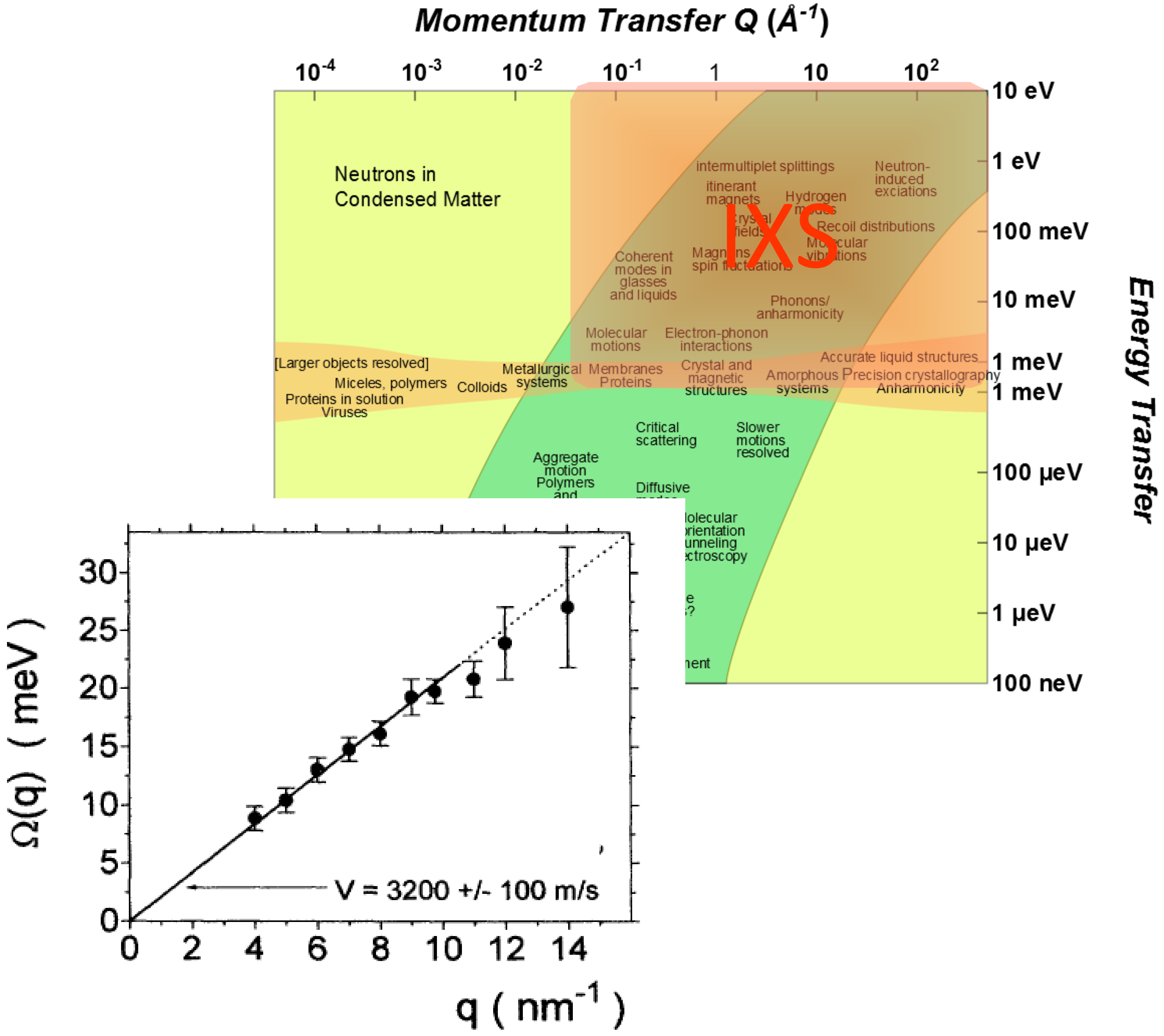
$$\lambda = 2d\sin\theta$$

$$\frac{\delta\lambda}{\lambda} = \delta\theta\cot\theta$$

A. Baron 1504.01098

Fast Sound in Water

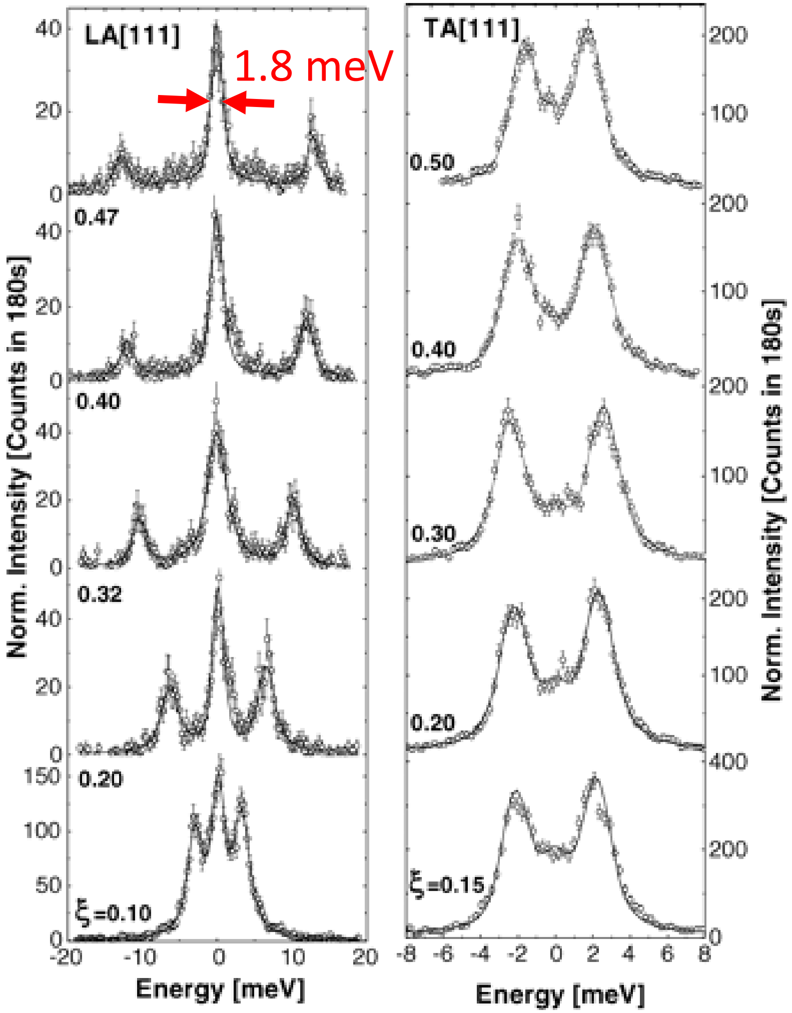


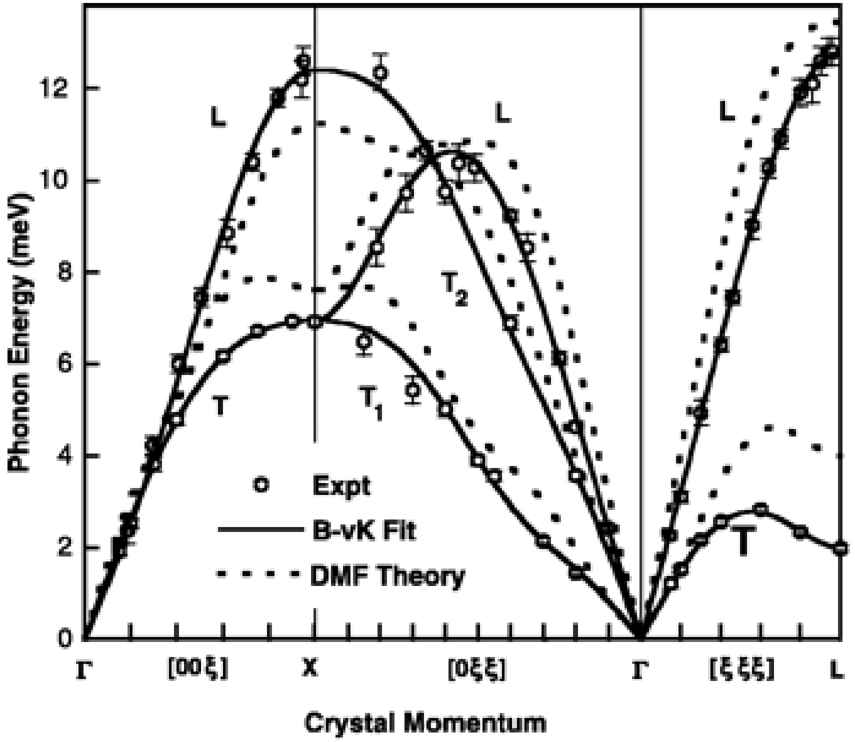


F. Sette et al. Phys. Rev. Lett. 75, 850 (1995)

G. H. Lander and V. J. Emery, Nucl. Instrum. Methods Phys. Res. Sect. B 12, 525 (1985)

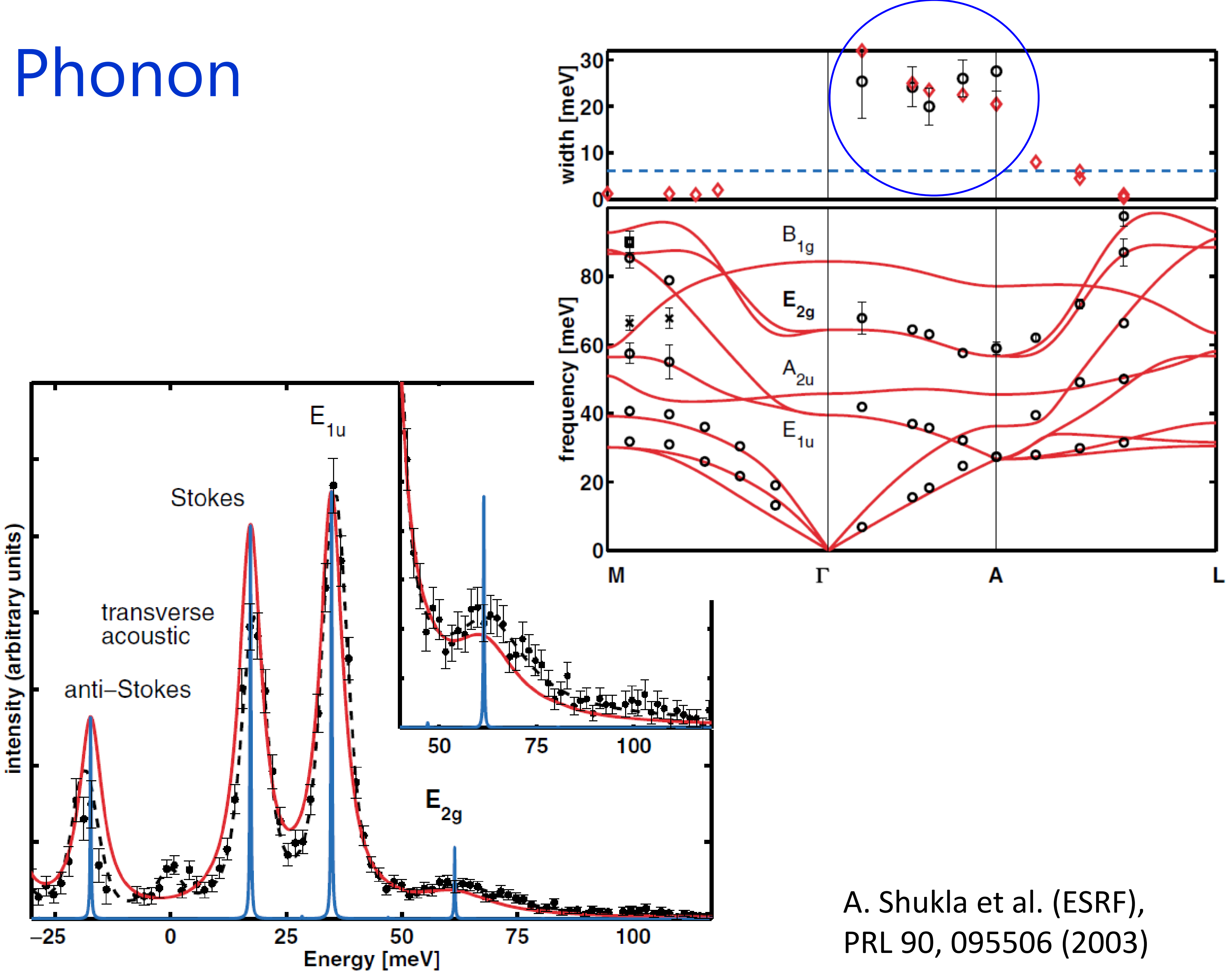
Phonon dispersion


1.8 meV



δ-Pu-Ga, Wong et al. Science 2003

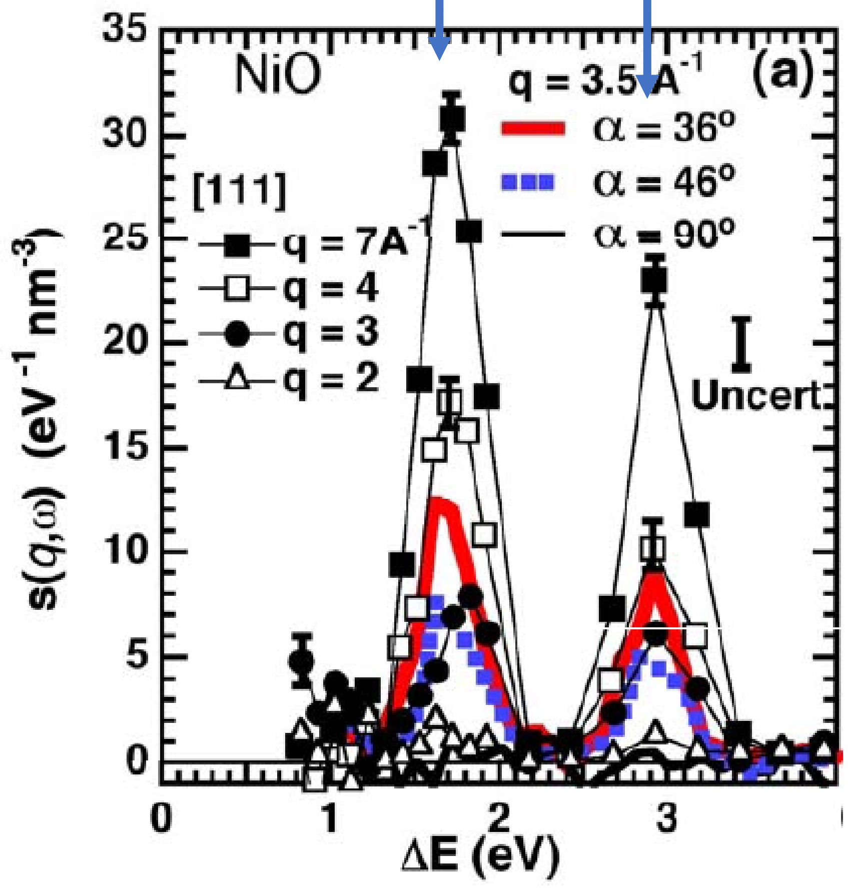
MgB_2 Phonon

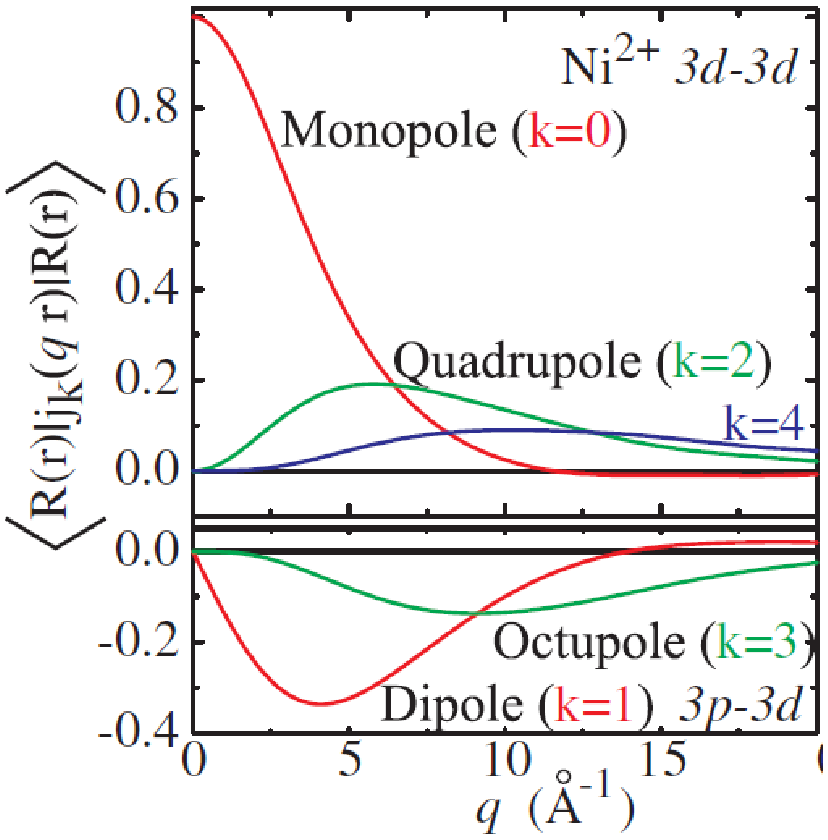


A. Shukla et al. (ESRF),
PRL 90, 095506 (2003)

Non-resonant IXS (NIXS)

d-d transition is forbidden
dipole transition b/c $\Delta L = 0$



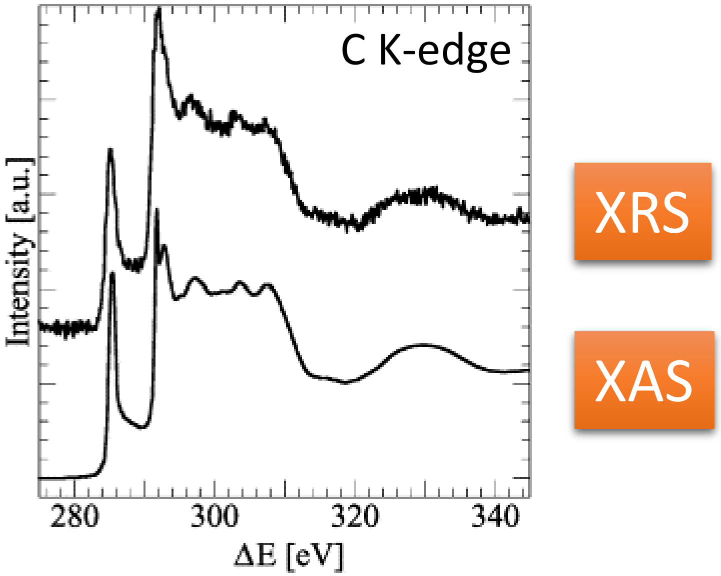


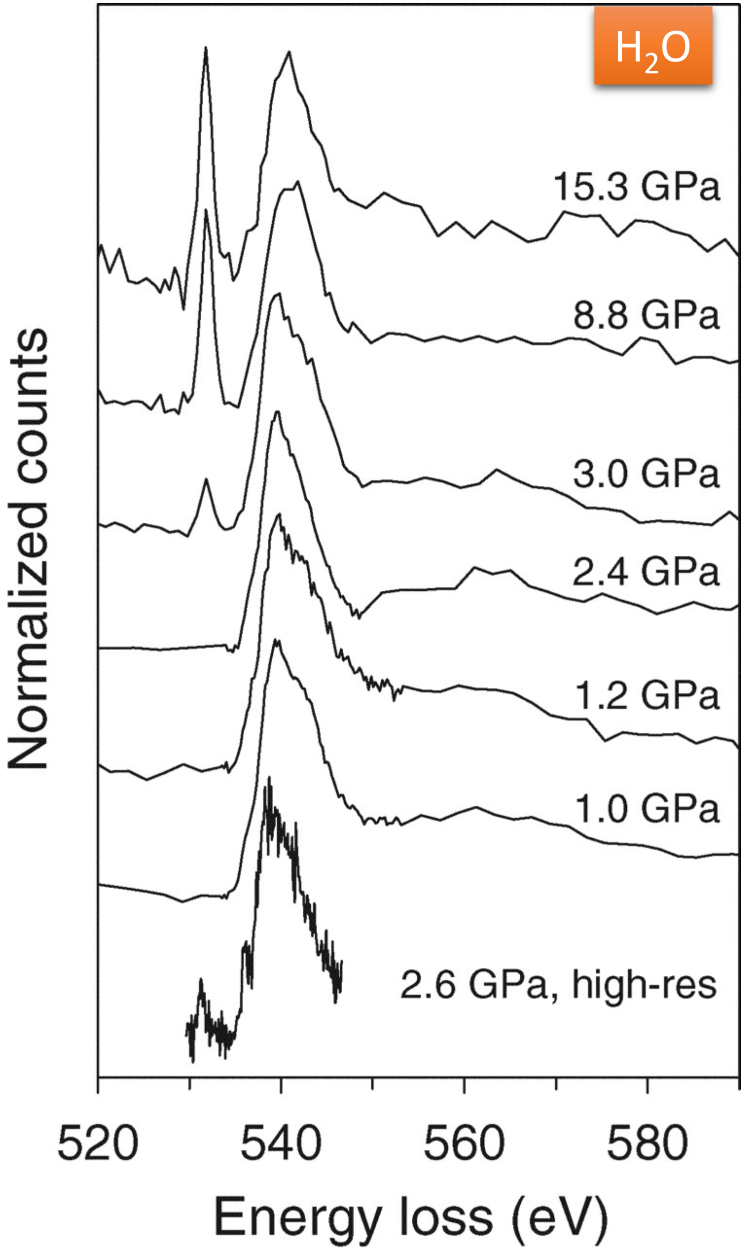
B. Larson et al. PRL 99, 026401 (2007)

M. Haverkort et al. PRL 99, 257401 (2007)

X-ray Raman Scattering

- Misleading/confusing name
- But these days it means





W. L. Mao et al. Science 314, 636 (2006)

RIXS

Why RIXS?

- Electronic excitations are weak
  - E.g. La_2CuO_4 has total (2X57+29+4X16=) 207 electrons per f.u. But only one of these (3d(x^2-y^2)) do anything interesting.
- Resonance can enhance intensity by a lot
- But we still want to measure S(Q,ω)
- (Big) question

$$\left|\sum_{n=1}^{\infty}\frac{\langle f|\widehat{\mathcal{D}}^{\dagger}|n\rangle\langle n|\widehat{\mathcal{D}}|i\rangle}{\omega_i - E_n - i\Gamma_n}\right|^2 \overset{?}{\propto} S(\boldsymbol{Q},\omega)$$

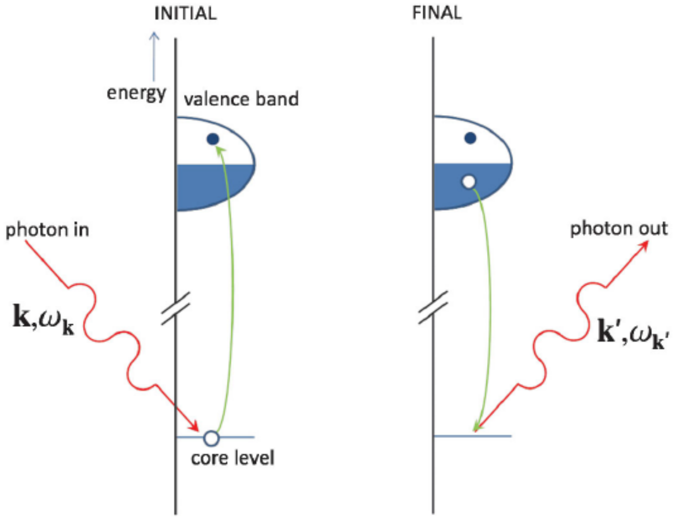
Kramers-Heisenberg formula

- Reviews
  - Kotani and Shin RMP 2001
  - Ament et al. RMP 2011

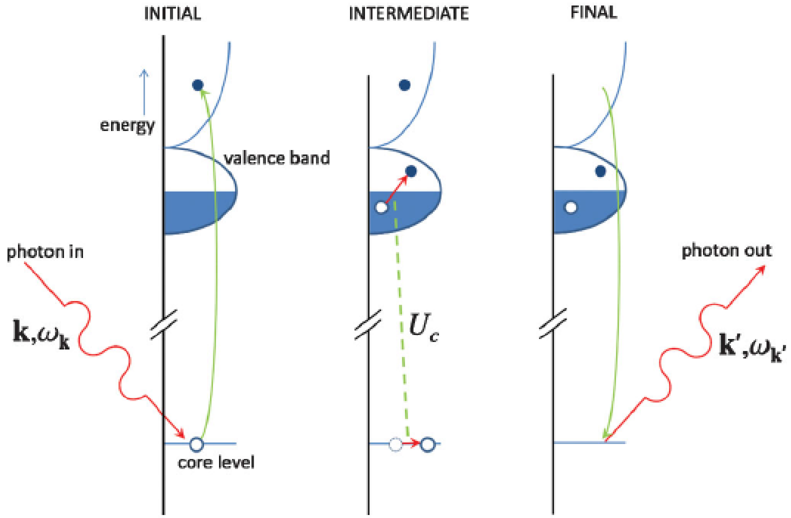
How to calculate RIXS spectrum?

- Exact diagonalization
- Ultrashort Core-hole Lifetime approximation
  - Perturbation expansion of the KH formula
    - van den Brink and van Veenendaal (2005,2006)
  - Correlation functions can be factorized in the case of indirect RIXS

Direct RIXS

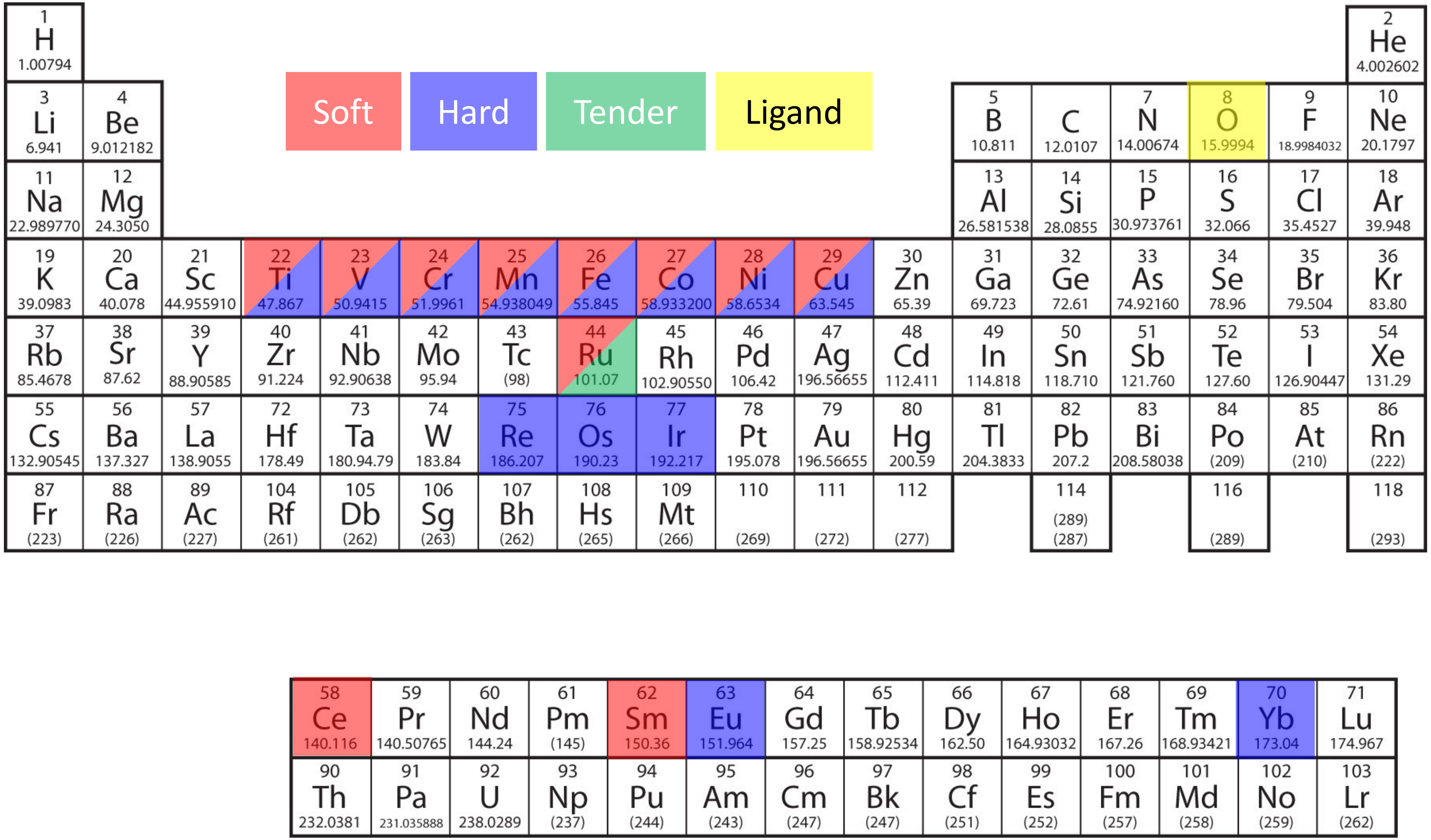


Indirect RIXS



Ament et al. RMP 83, 705 (2011)

Overview (incomplete)



Soft

Hard

Tender

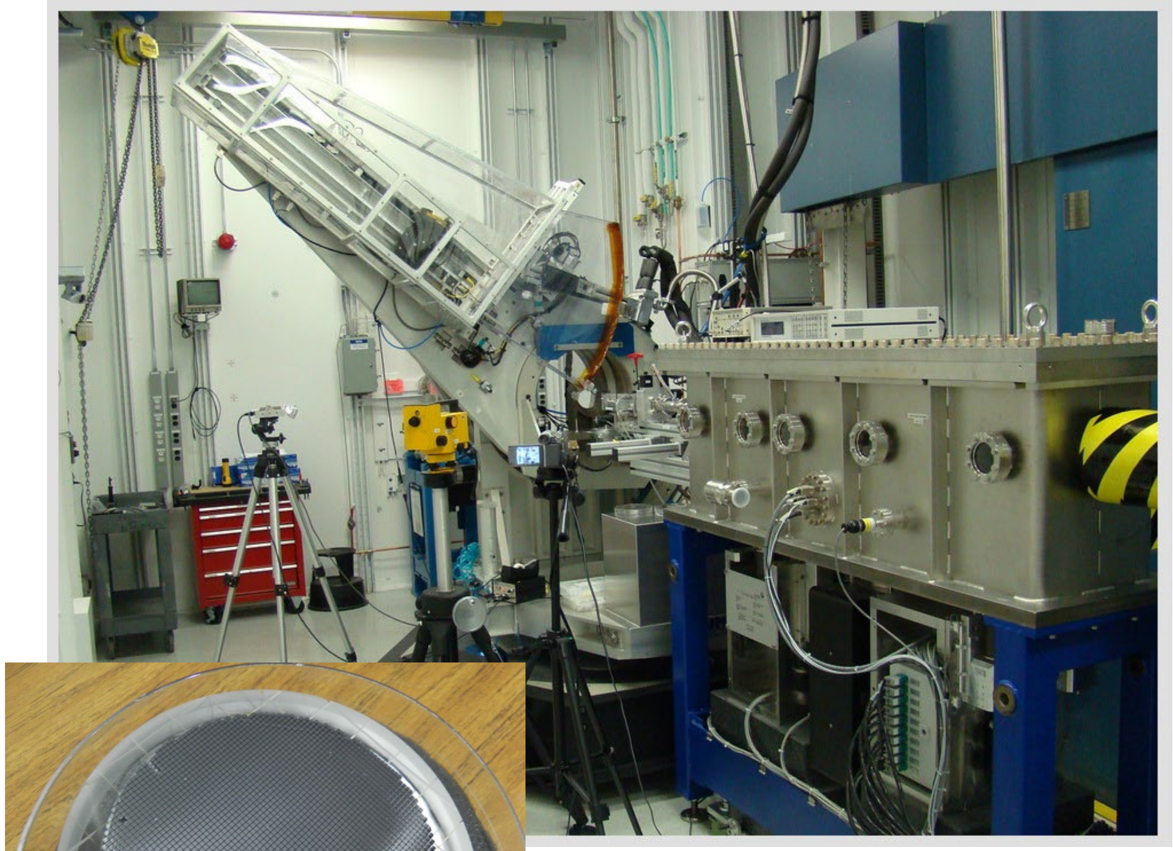
Ligand

1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

RIXS Instrumentation

Beamline 27-ID (MERIX) at APS

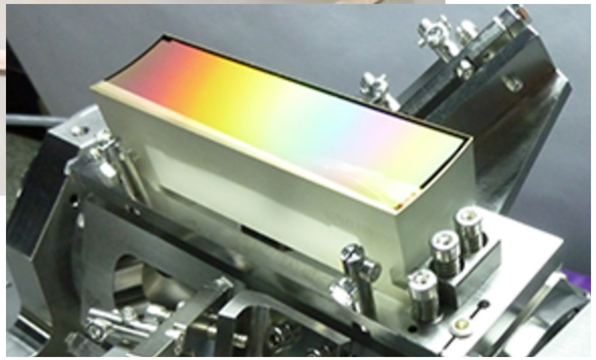



2m spherical diced Si-(844) analyzer

Hard

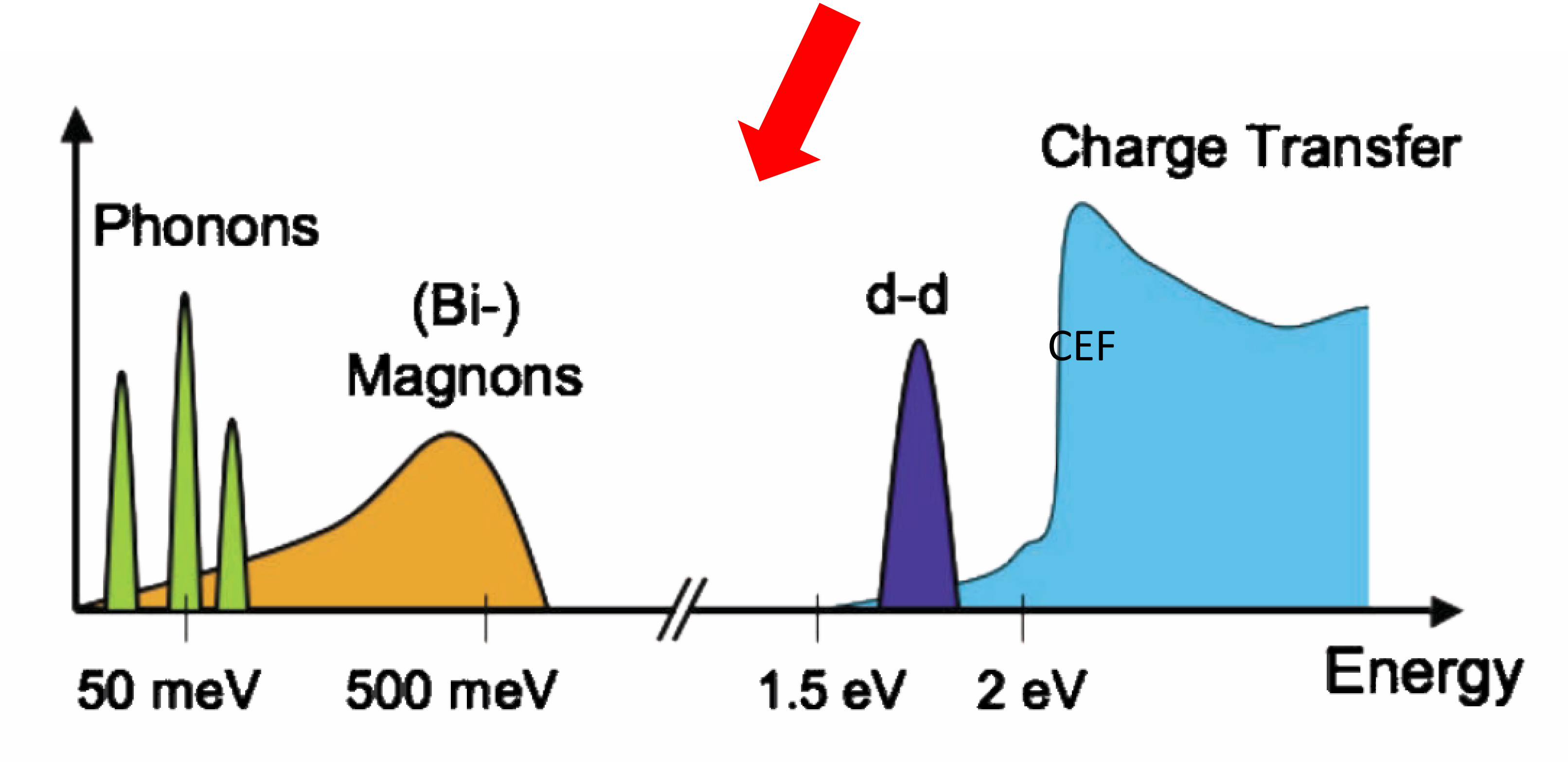

Beamline I21 Diamond Light Source (UK)

Soft


Example of a Diffraction Grating
Image: Horiba

Two types of RIXS

- Core-level RIXS useful for studying electronic structure ➔ RXES
- Valence RIXS – collective excitations (momentum dependence)



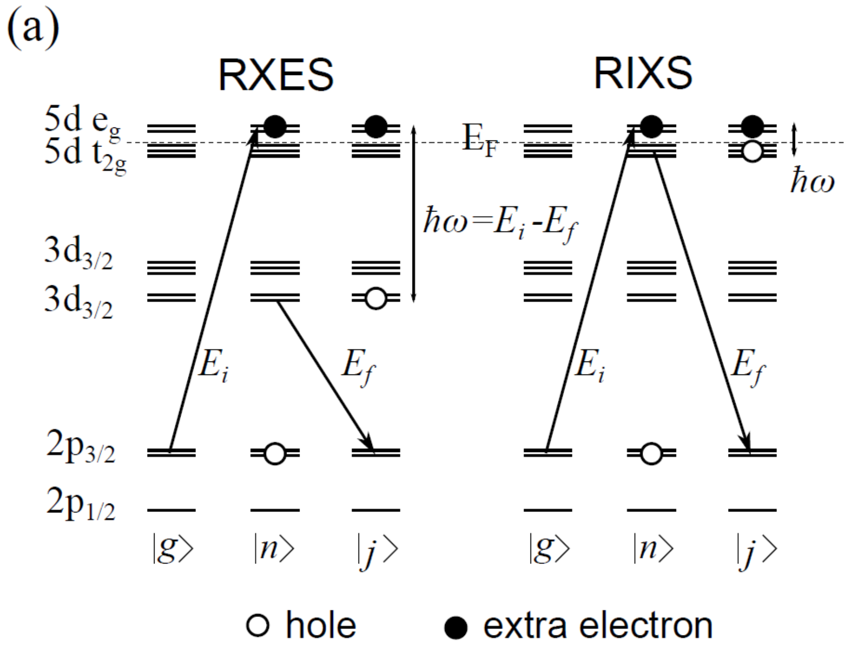
Core-level RIXS

Resonant
X-ray Emission Spectroscopy

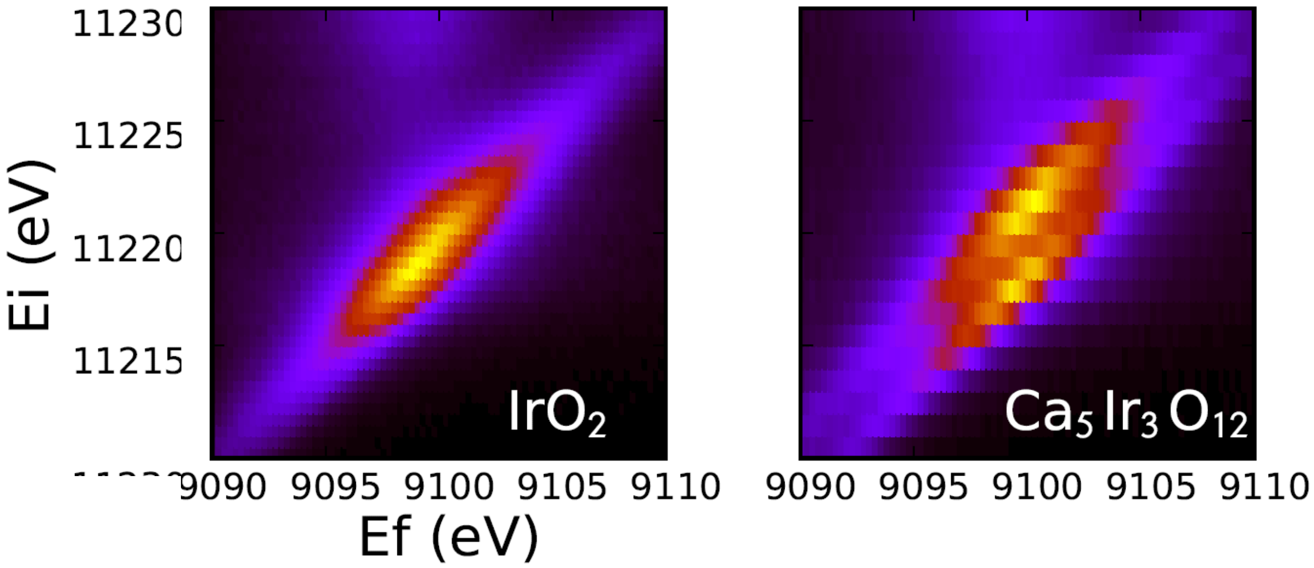
Ament et al. Reviews of Modern Physics 2011

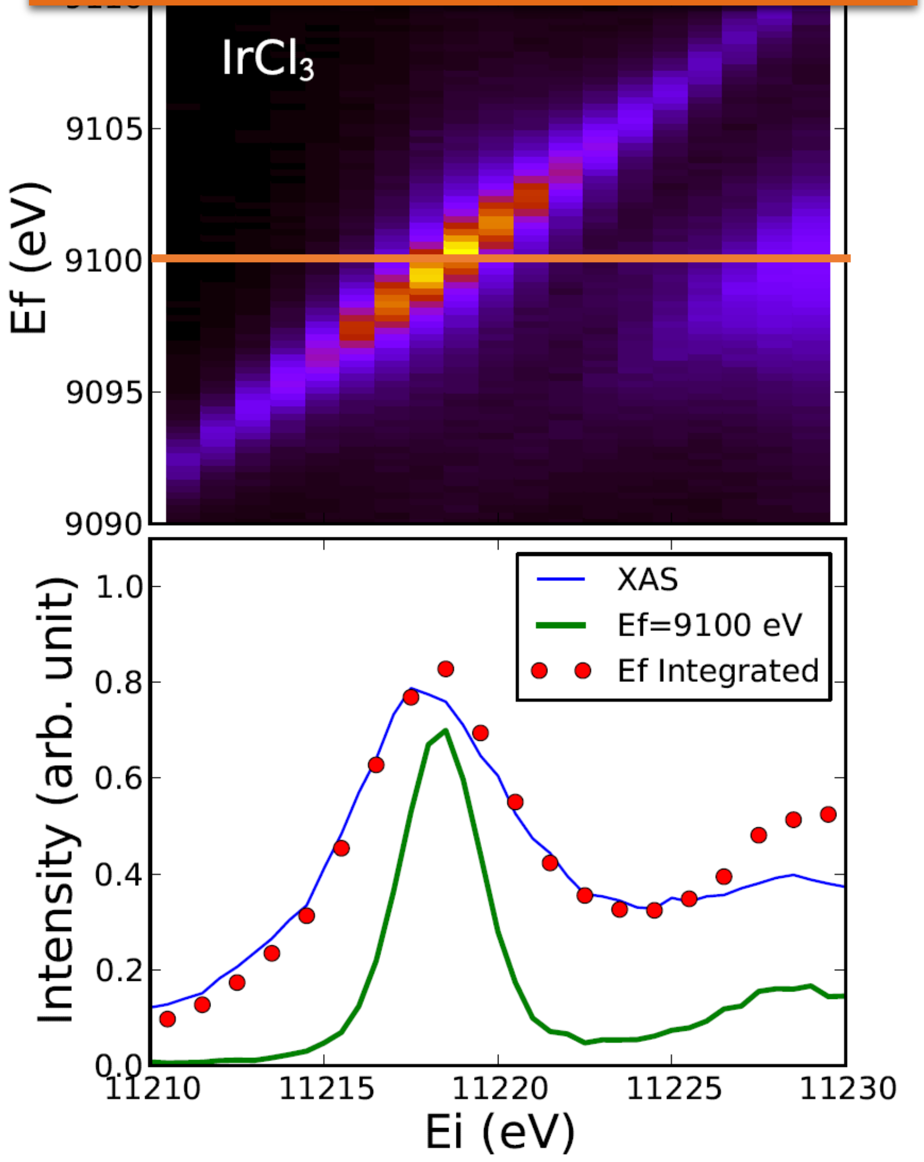
RXES

HERFD (High Energy Resolution Fluorescence Detection)



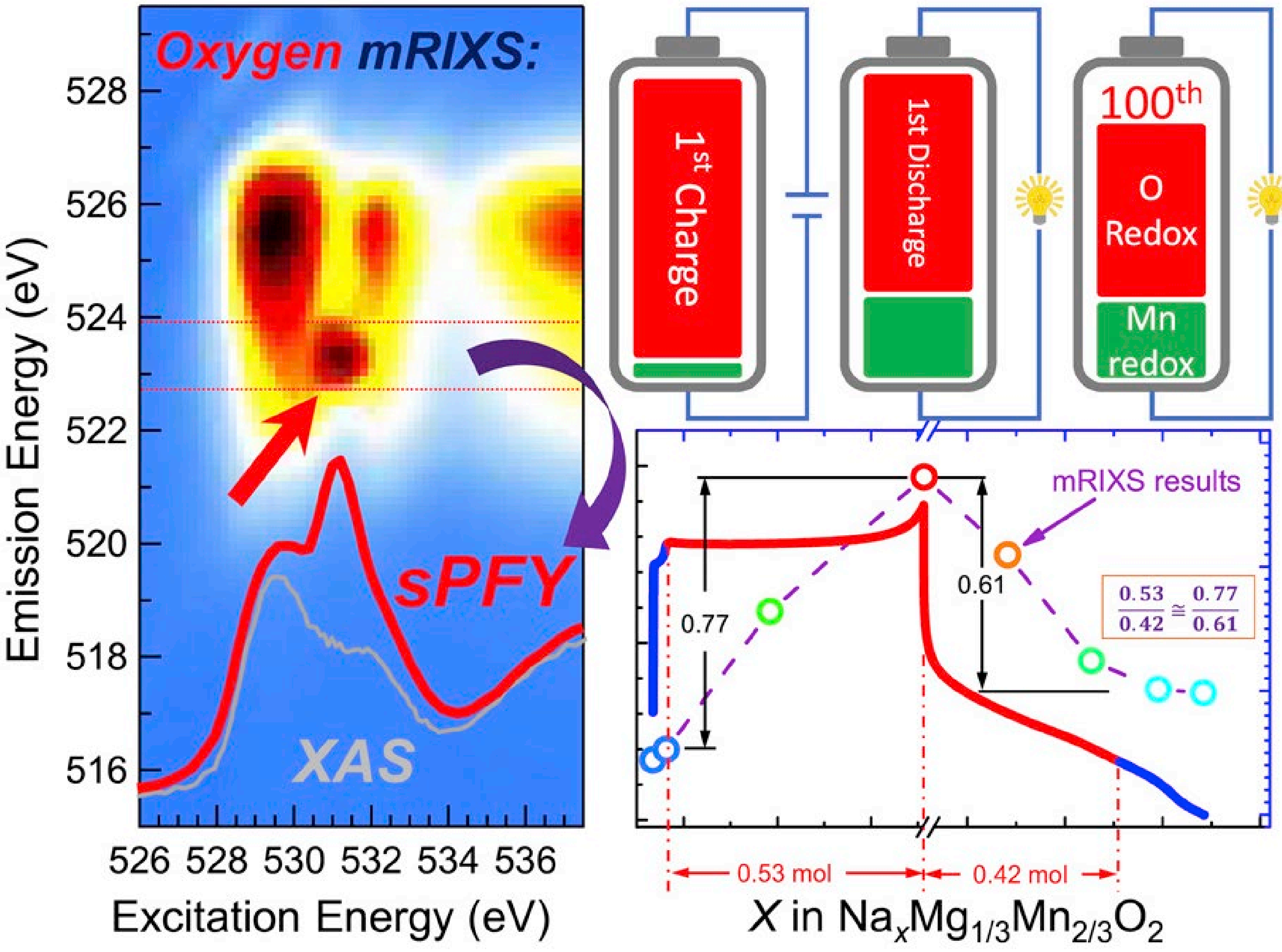
“RIXS map”





arXiv:1805.03612

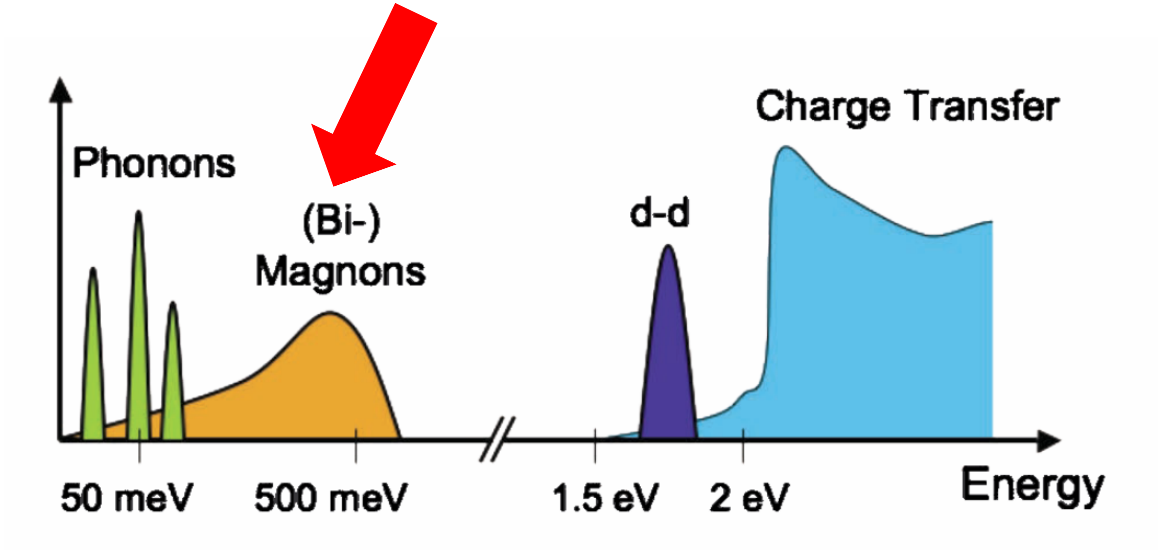
RXES – Very useful for studying complex oxides



K. Dai, W. Yang, et al. Joule, 2019, 3, 518–541

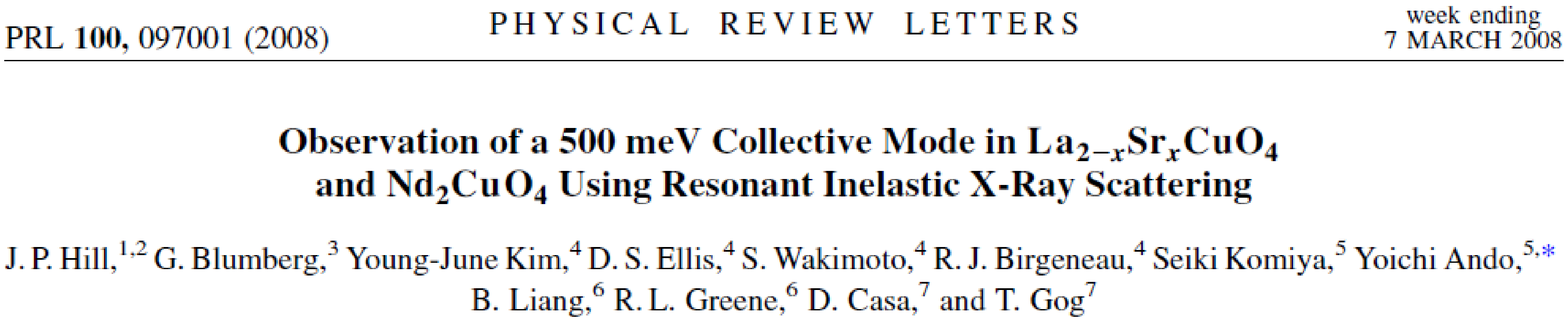
See also J. Wu et al. Dalton Trans., 2020, 49, 13519-13527

Magnons



Ament et al. Reviews of Modern Physics 2011

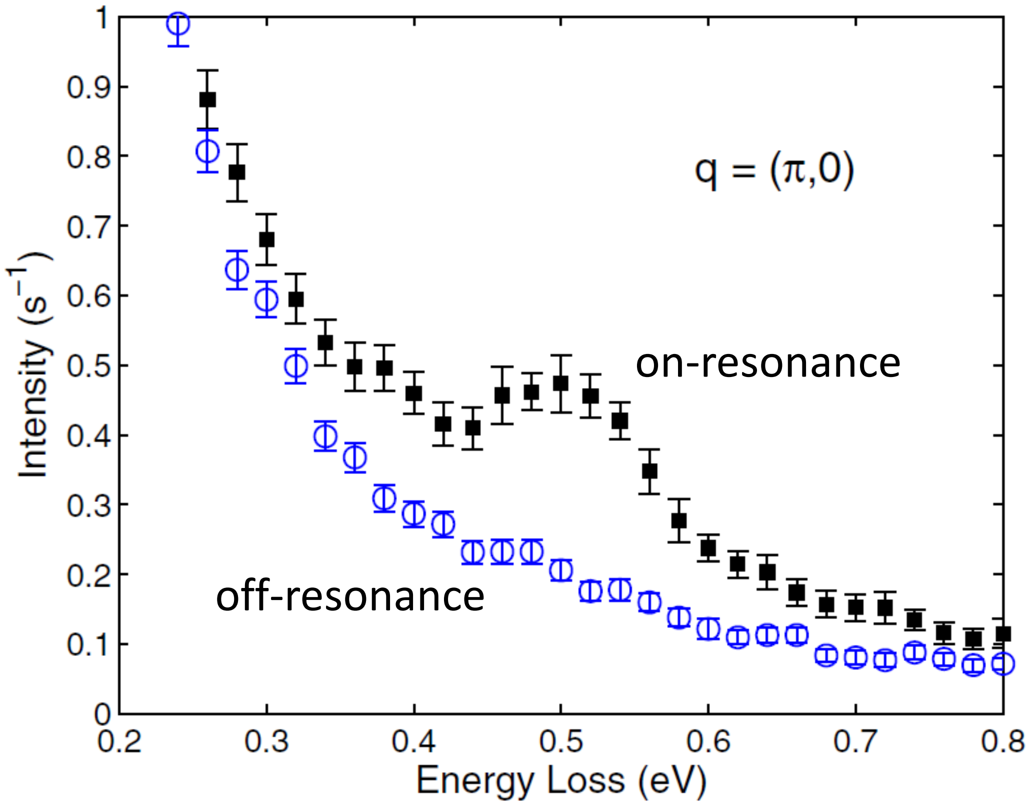
First, Bimagnon



PRL **100,** 097001 (2008) PHYSICAL REVIEW LETTERS week ending 7 MARCH 2008

Observation of a 500 meV Collective Mode in $La_{2-x}Sr_xCuO_4$ and Nd_2CuO_4 Using Resonant Inelastic X-Ray Scattering

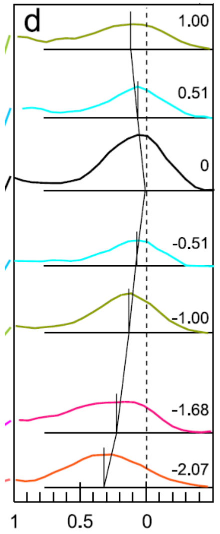
J. P. Hill,[1,2] G. Blumberg,[3] Young-June Kim,[4] D. S. Ellis,[4] S. Wakimoto,[4] R. J. Birgeneau,[4] Seiki Komiya,[5] Yoichi Ando,[5,*]
B. Liang,[6] R. L. Greene,[6] D. Casa,[7] and T. Gog[7]



PRL **102,** 167401 (2009) PHYSICAL REVIEW LETTERS week ending 24 APRIL 2009

Dispersion of Magnetic Excitations in the Cuprate La_2CuO_4 and $CaCuO_2$ Compounds Measured Using Resonant X-Ray Scattering

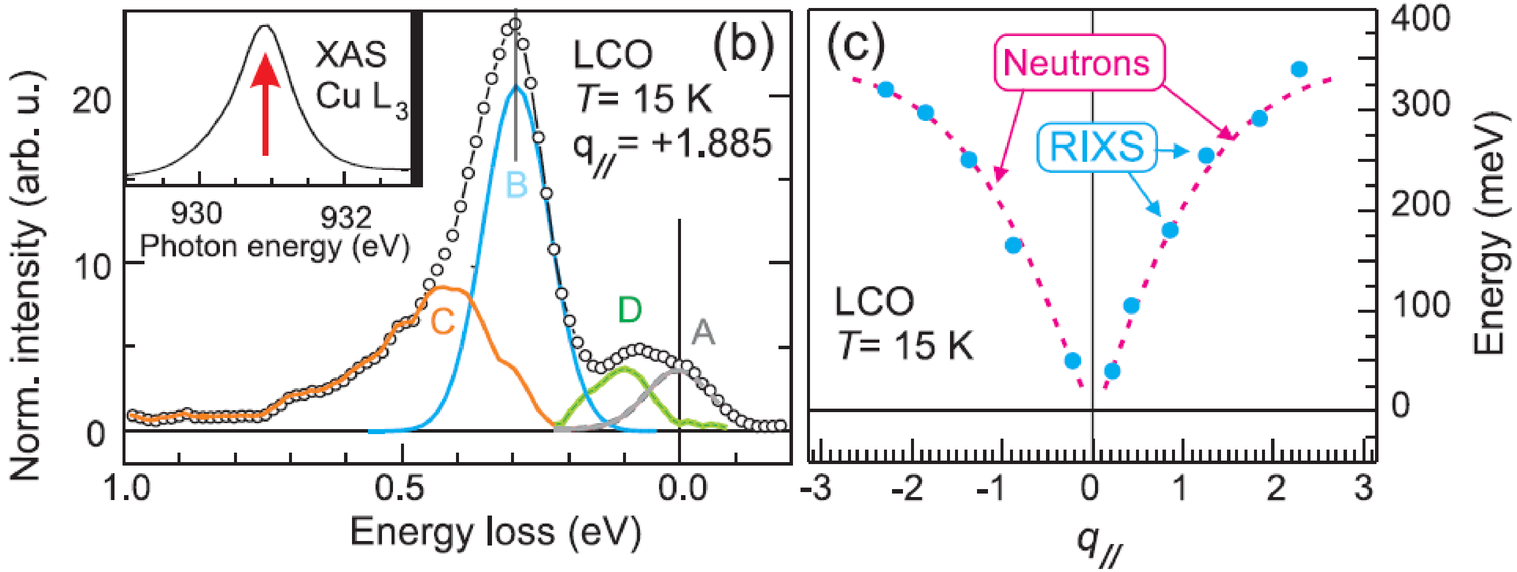
L. Braicovich,[1] L. J. P. Ament,[2] V. Bisogni,[3] F. Forte,[2,4] C. Aruta,[5] G. Balestrino,[6] N. B. Brookes,[3] G. M. De Luca,[5]
P. G. Medaglia,[6] F. Miletto Granozio,[5] M. Radovic,[5] M. Salluzzo,[5] J. van den Brink,[2,7] and G. Ghiringhelli[1]



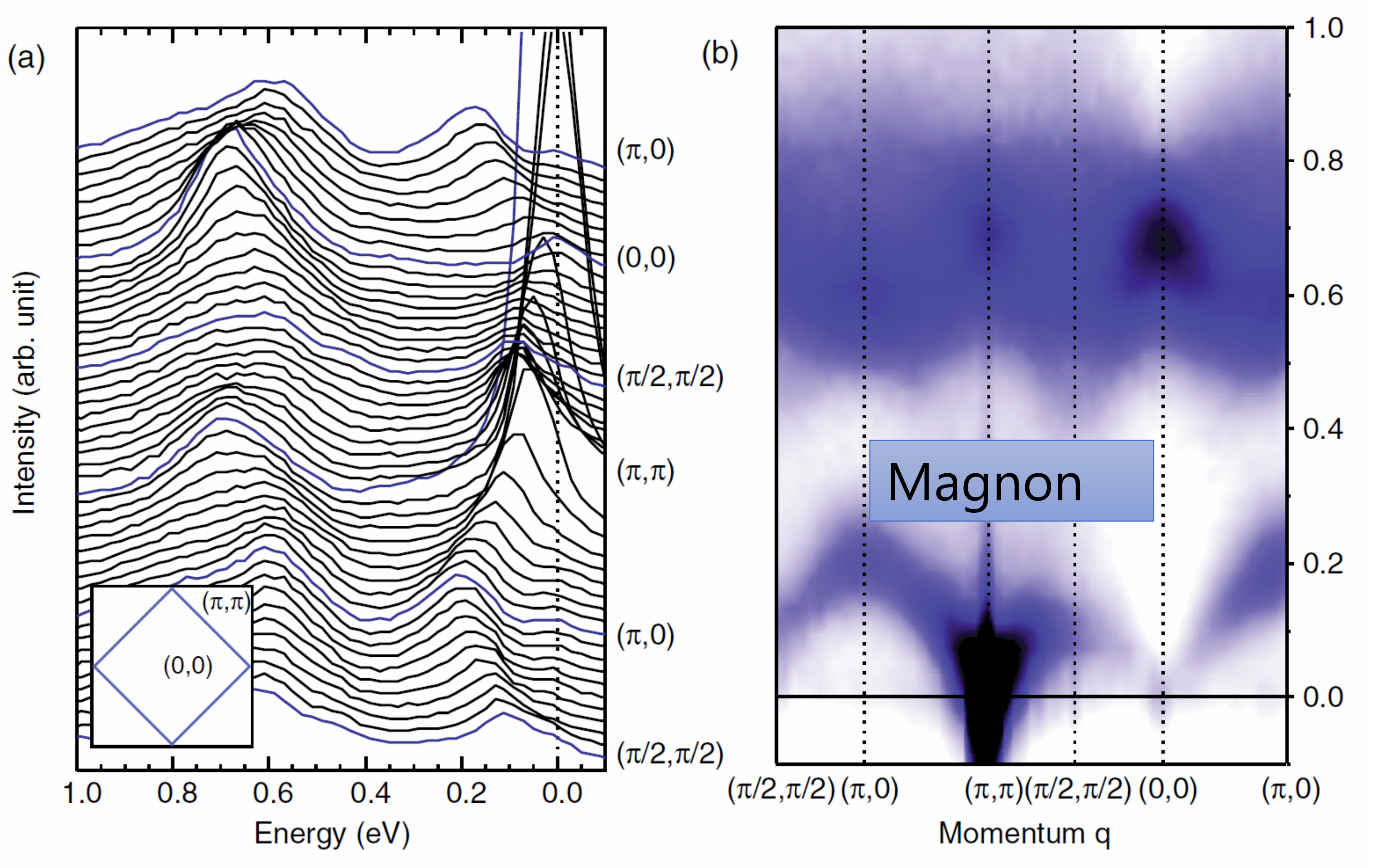
PRL **104,** 077002 (2010) PHYSICAL REVIEW LETTERS week ending 19 FEBRUARY 2010

Magnetic Excitations and Phase Separation in the Underdoped $La_{2-x}Sr_xCuO_4$ Superconductor Measured by Resonant Inelastic X-Ray Scattering

L. Braicovich,[1] J. van den Brink,[2,3,4] V. Bisogni,[5] M. Moretti Sala,[1] L. J. P. Ament,[2,3] N. B. Brookes,[5] G. M. De Luca,[6]
M. Salluzzo,[6] T. Schmitt,[7] V. N. Strocov,[7] and G. Ghiringhelli[1]

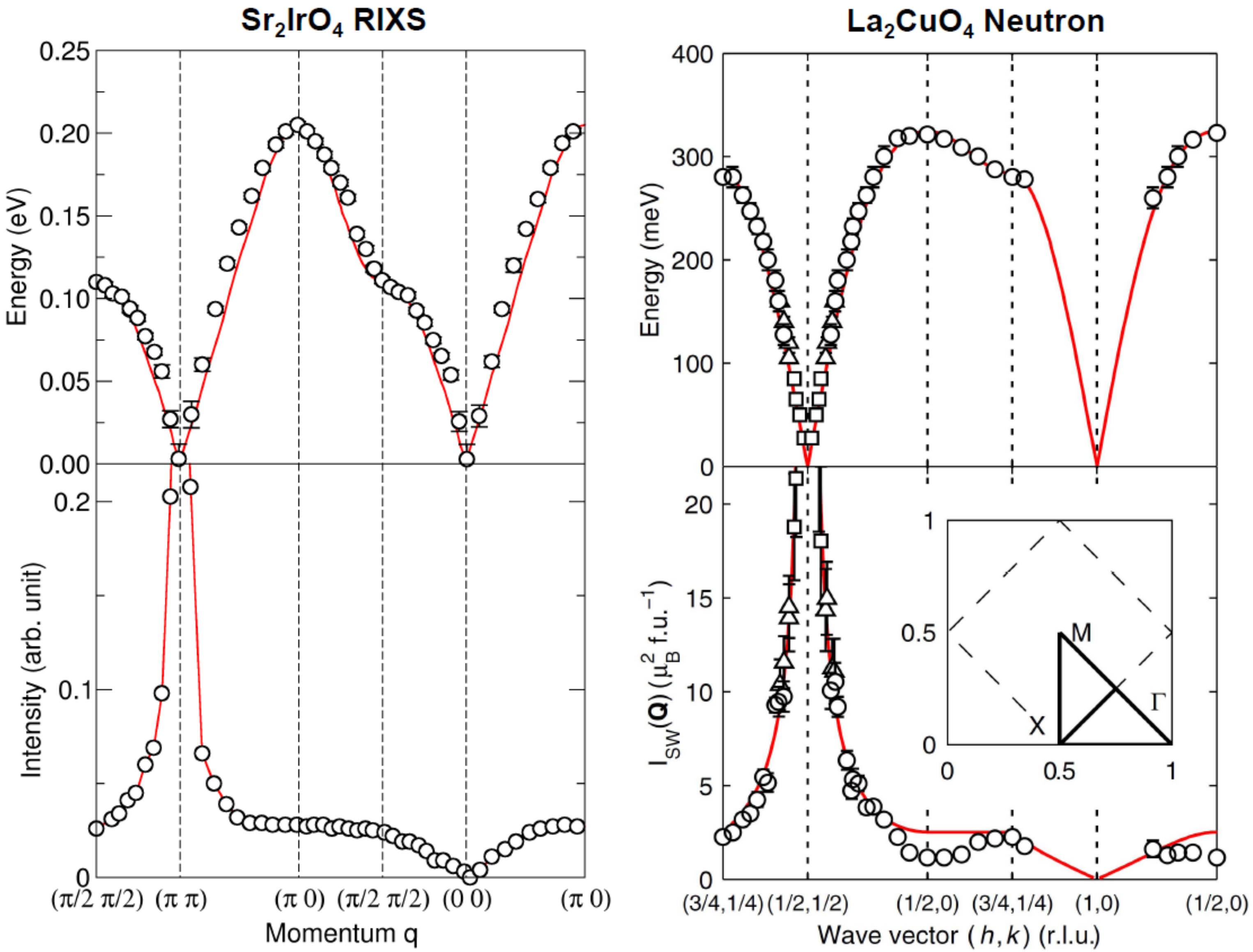


Sr_2IrO_4 – magnons with hard RIXS



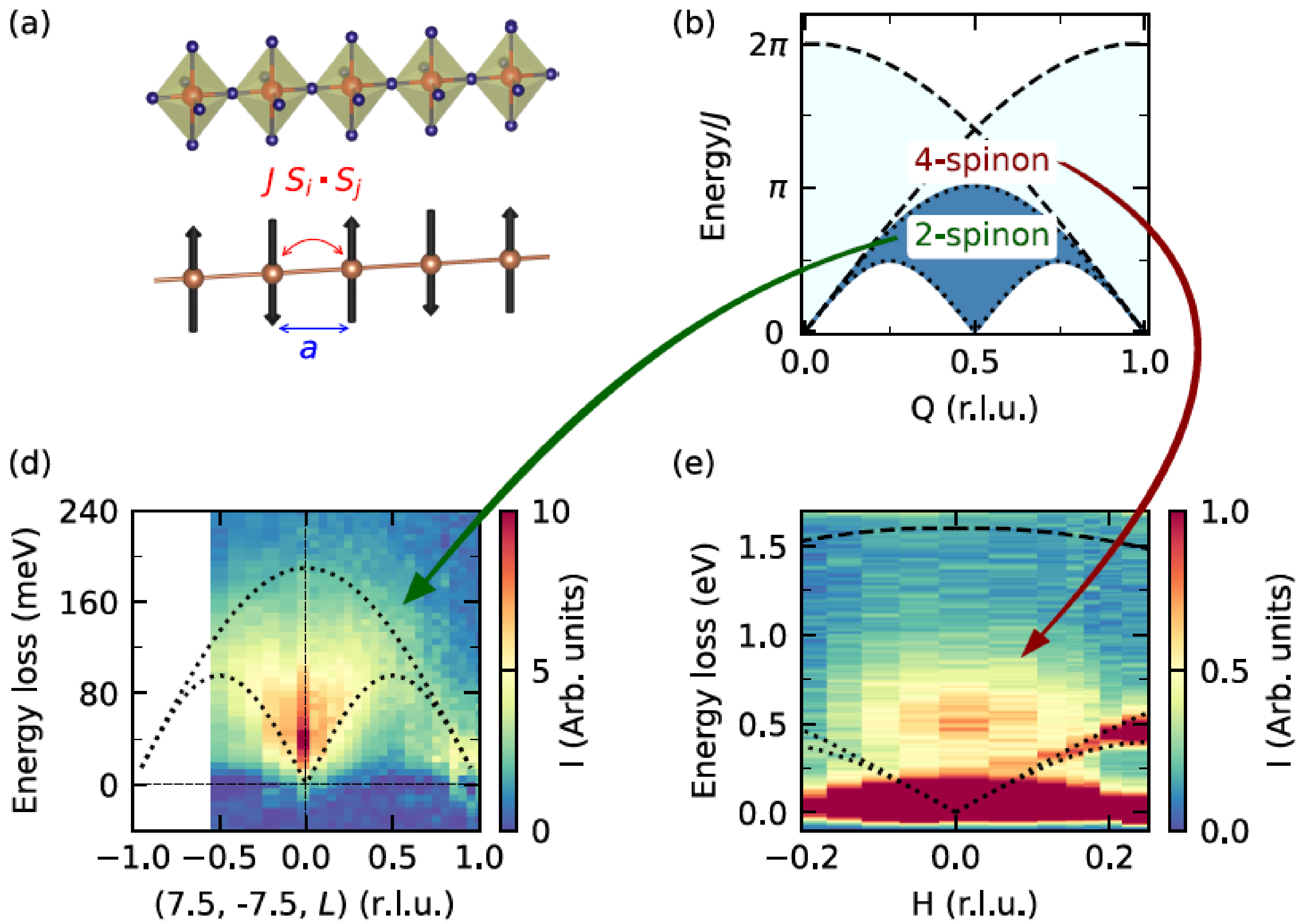
Jungho Kim et al. PRL 108, 177003 (2012)

INS/RIXS Comparison - magnons



YJK et al. Synch. Rad. News 2012

Beyond magnon – spinon



Y. Shen et al. PRL 129, 207201 (2022)

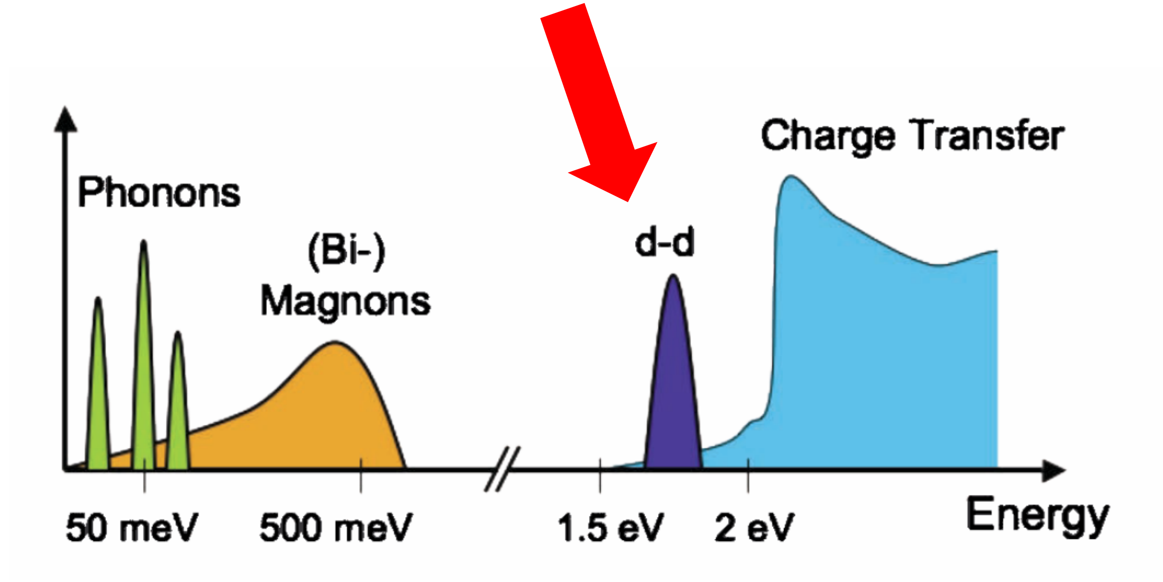
J. Schlappa et al. Nat. Comm. 9, 1 (2018)

Probing particles for elementary excitations

Probes	**Light**	**X-ray**	**Neutron**	**Electron**
Wavelength	500nm	~1 Å	~1 Å	0.01~0.1 Å
$Q(2\pi/\lambda)$	~10^{-3} Å^{-1}	~6 Å^{-1}	~6 Å^{-1}	~60 Å^{-1}
Interaction	Relatively weak	Weak	Very weak	Strong
Primary Interaction	Charge	Charge	Spin Nucleus	Charge
Probing depth	Medium (~μm)	Medium (~μm)	Long (~cm)	Short (~nm)
Multiple scattering	Y	N	N	Y
Particle Energy	1~2 eV	~10 keV	~30 meV	1~100 keV
Energy resolution	Very good	OK (IXS) Limited (RIXS)	Very good	OK (EELS)
Beam size	Small (limited by wavelength)	Very small (down to nm)	Big = Requires large sample	Ultra small

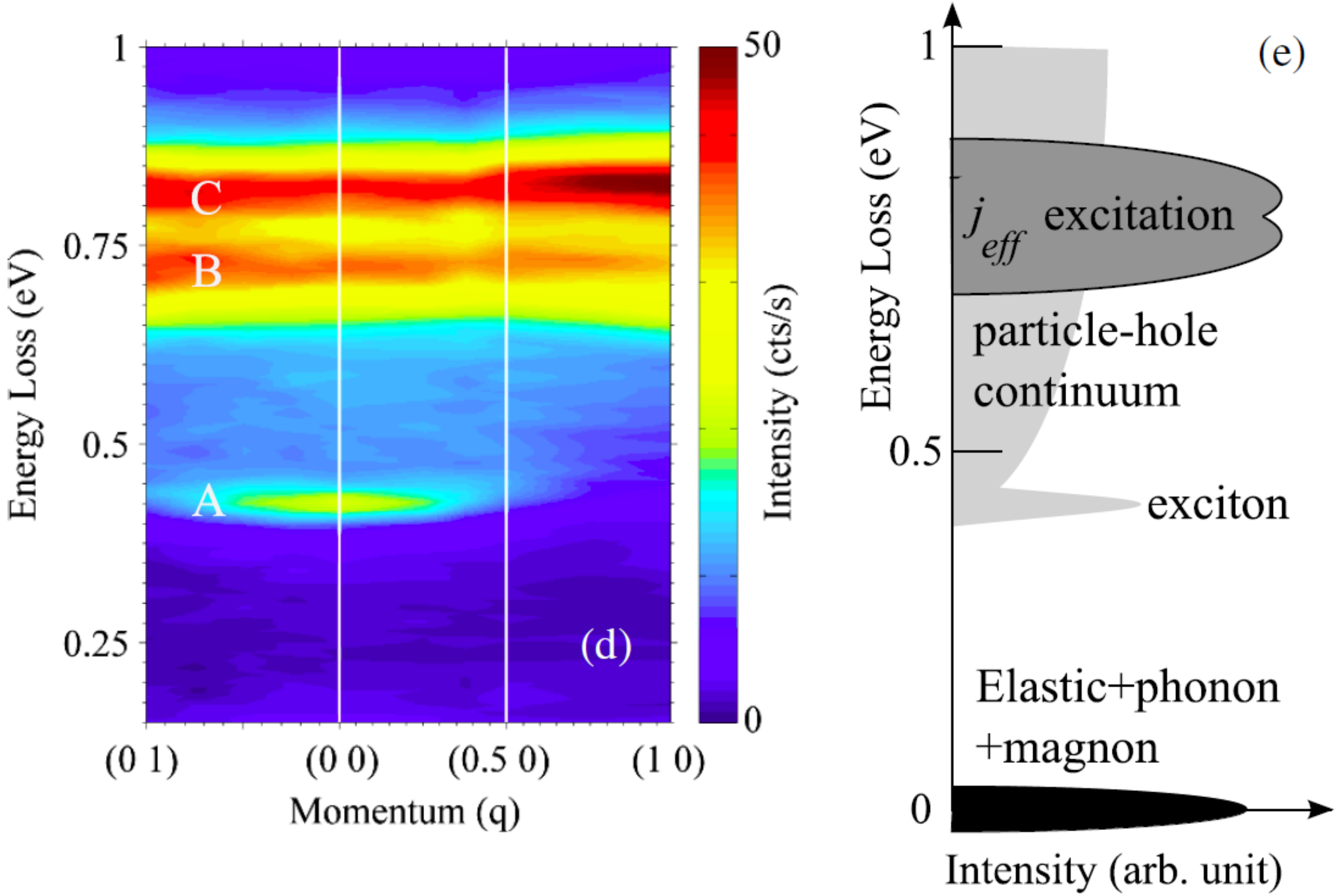
dd
Orbital
Spin-orbit
CEF

Excitations



Ament et al. Reviews of Modern Physics 2011

Momentum dependence



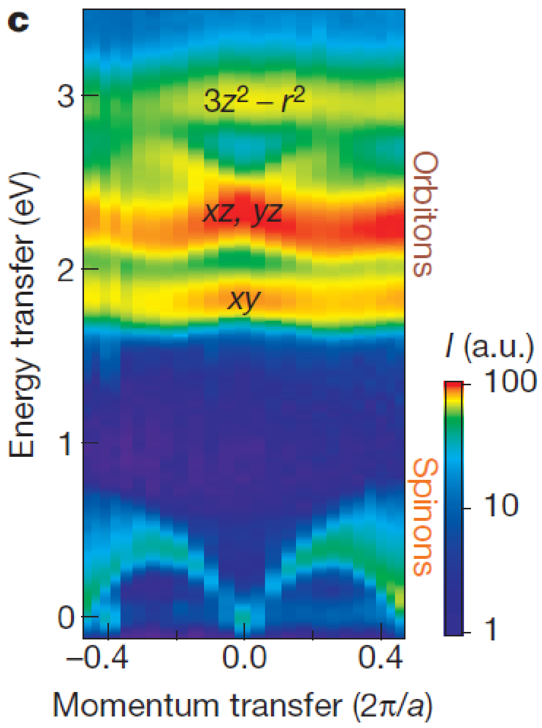
Gretarsson et al. PRL 2013

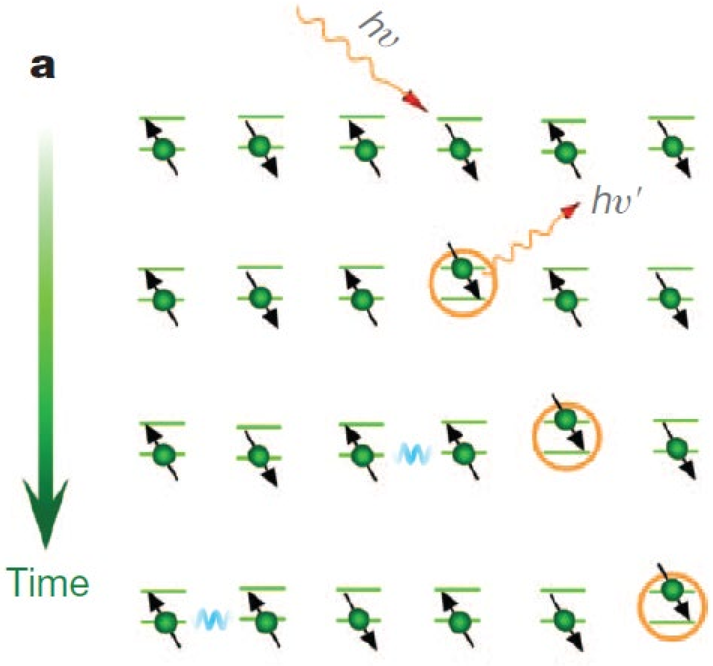
Special Case: spin chain

Nature 482, 82 (2012)

Spin–orbital separation in the quasi-one-dimensional Mott insulator Sr_2CuO_3

J. Schlappa[1,2], K. Wohlfeld[3], K. J. Zhou[1]†, M. Mourigal[4], M. W. Haverkort[5], V. N. Strocov[1], L. Hozoi[3], C. Monney[1], S. Nishimoto[3], S. Singh[6]†, A. Revcolevschi[6], J.-S. Caux[7], L. Patthey[1,8], H. M. Rønnow[4], J. van den Brink[3] & T. Schmitt[1]

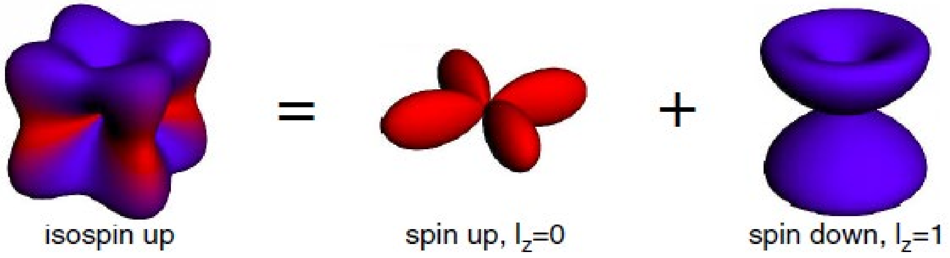


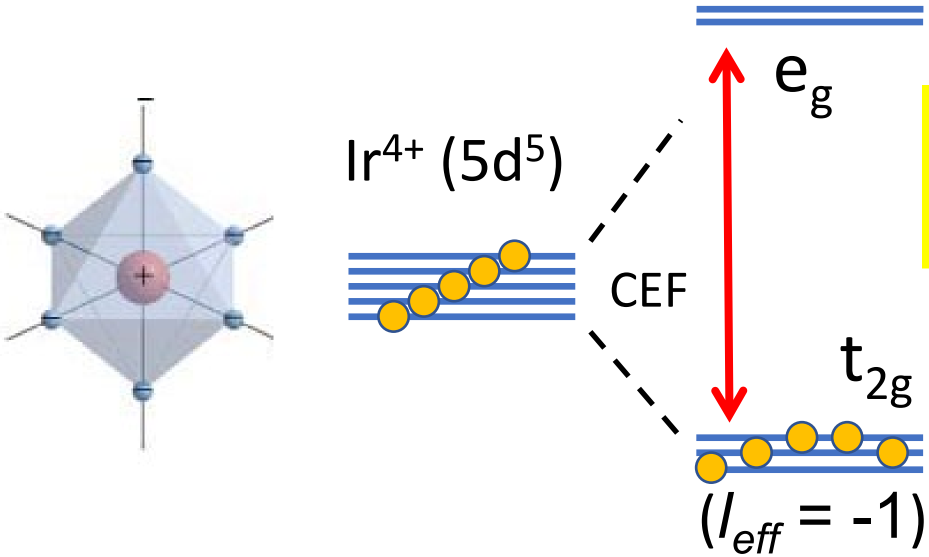


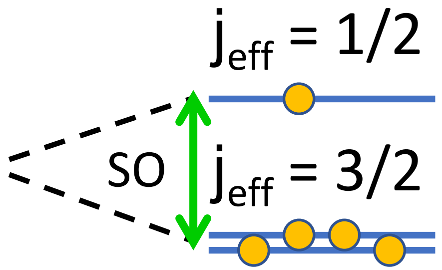
Spin–orbital separation

Special Case II: Strong SOC

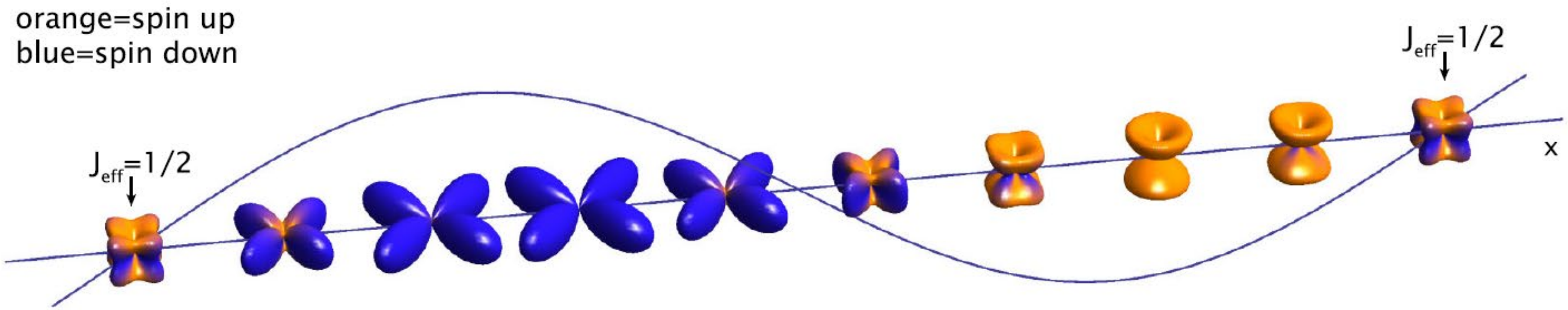
Jackeli and Khaliullin PRL 2009



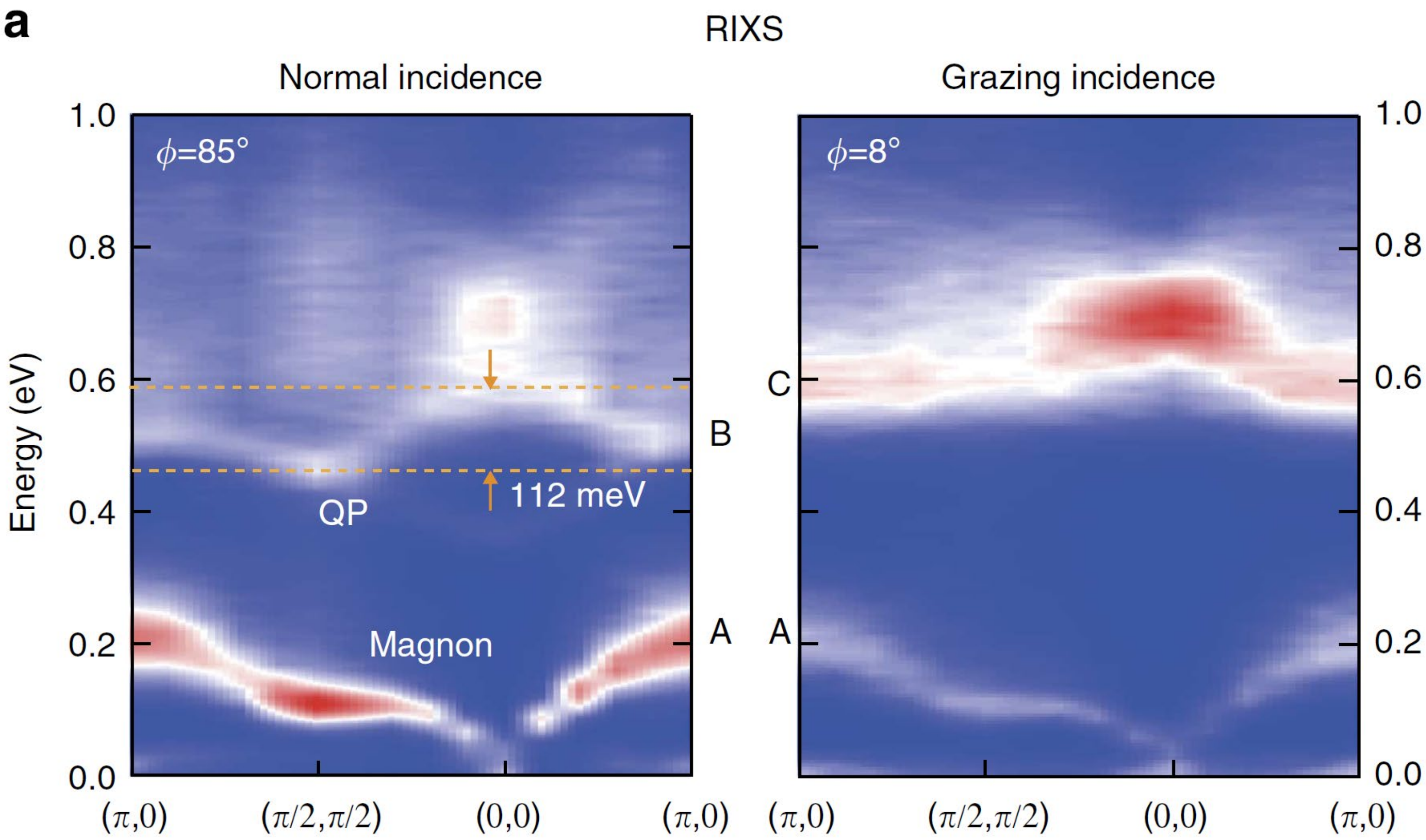




$$\frac{1}{\sqrt{3}}\left|xy,\uparrow\right\rangle+\frac{i}{\sqrt{3}}\left|xz,\downarrow\right\rangle+\frac{i}{\sqrt{3}}\left|yz,\downarrow\right\rangle$$



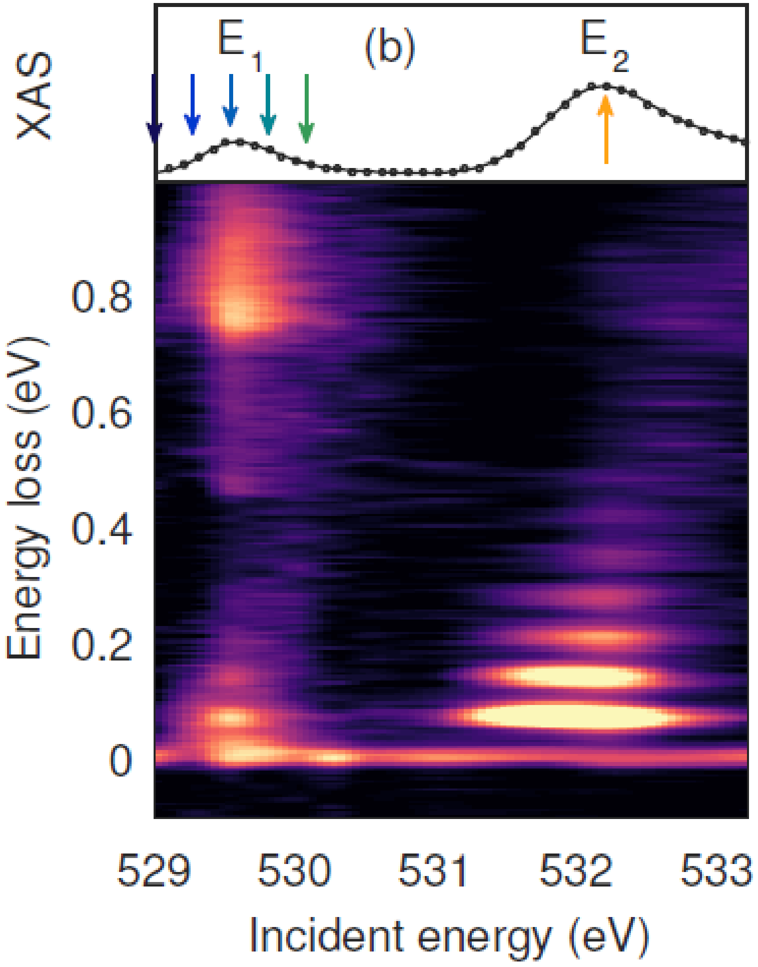
Sr_2IrO_4

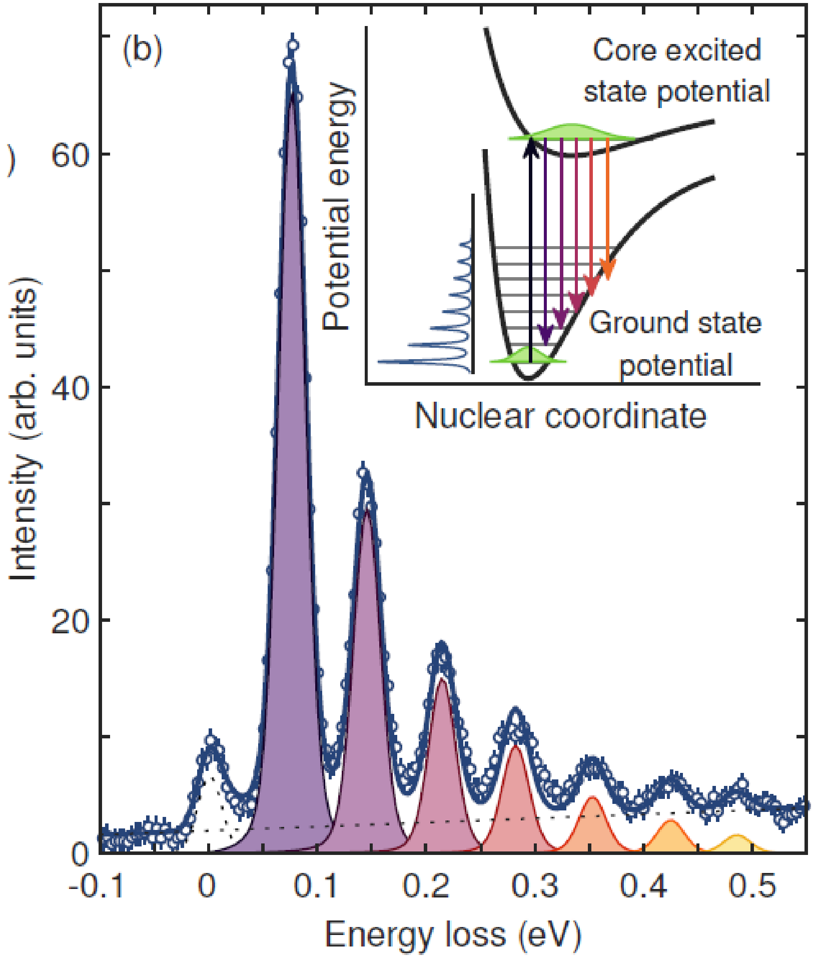


Jungho Kim et al. Nature Communications, 2014

Resonant phonon

Li_2IrO_3

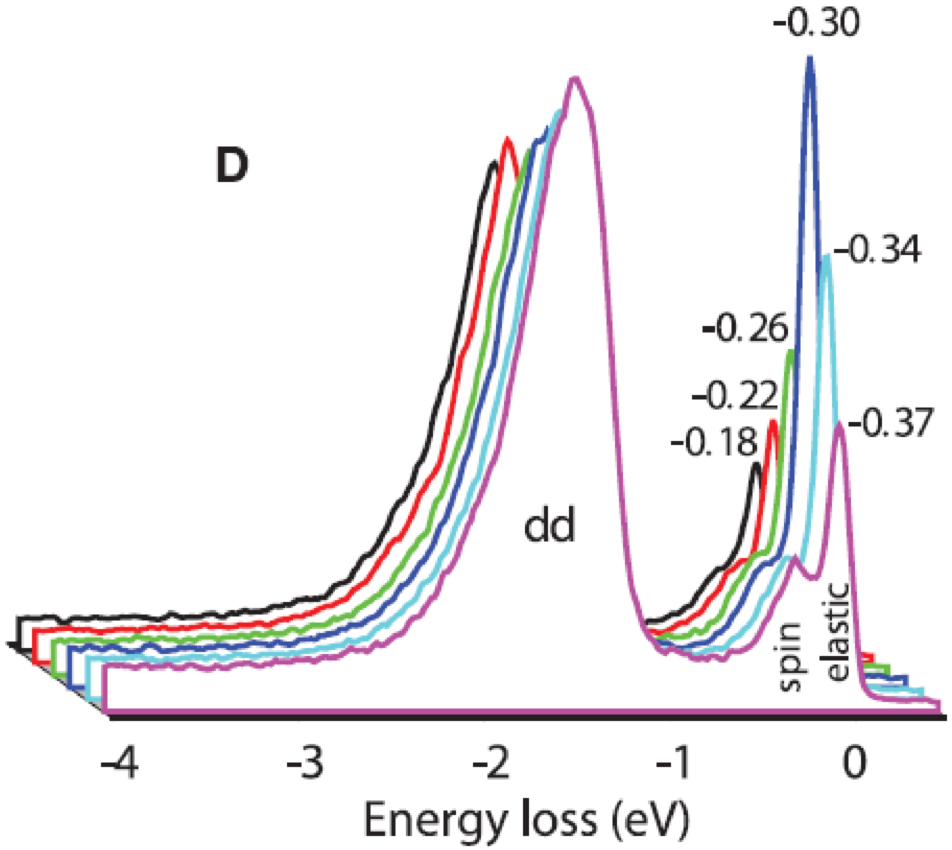


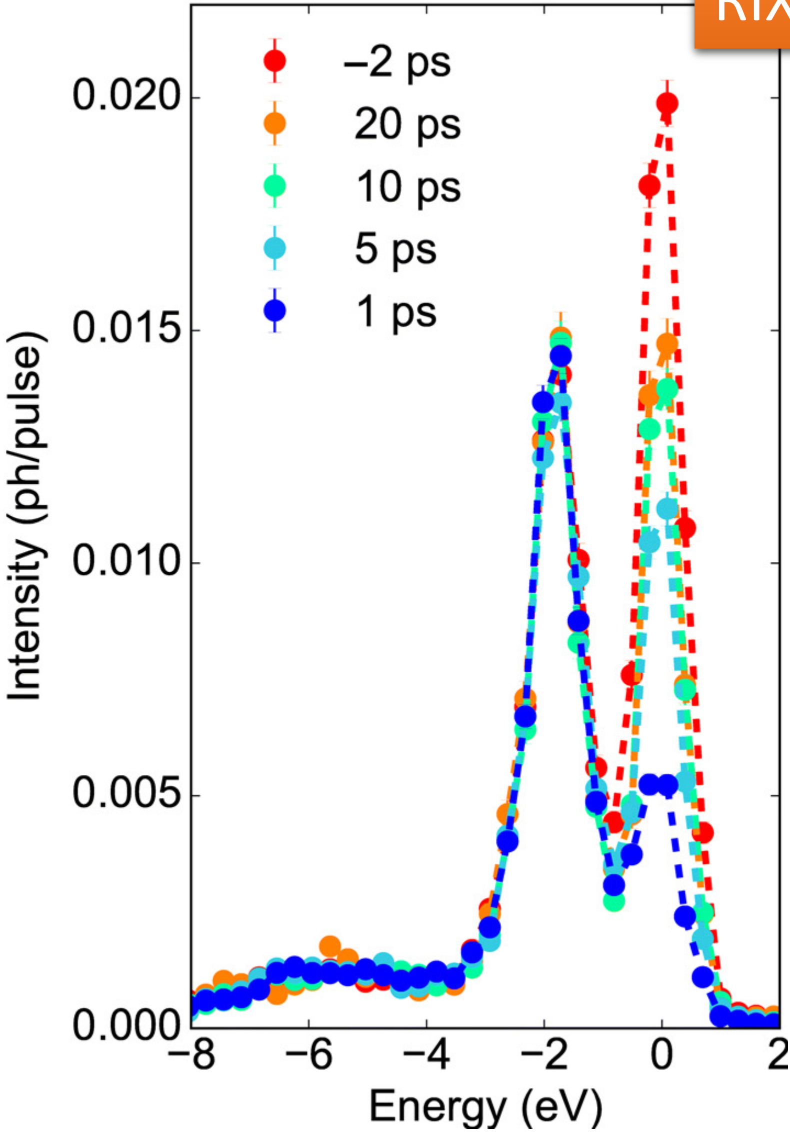


Vale et al. Phys. Rev. B 100, 224303 (2019)

Charge Density Wave in Cuprates

Time-resolved RIXS @ XFEL



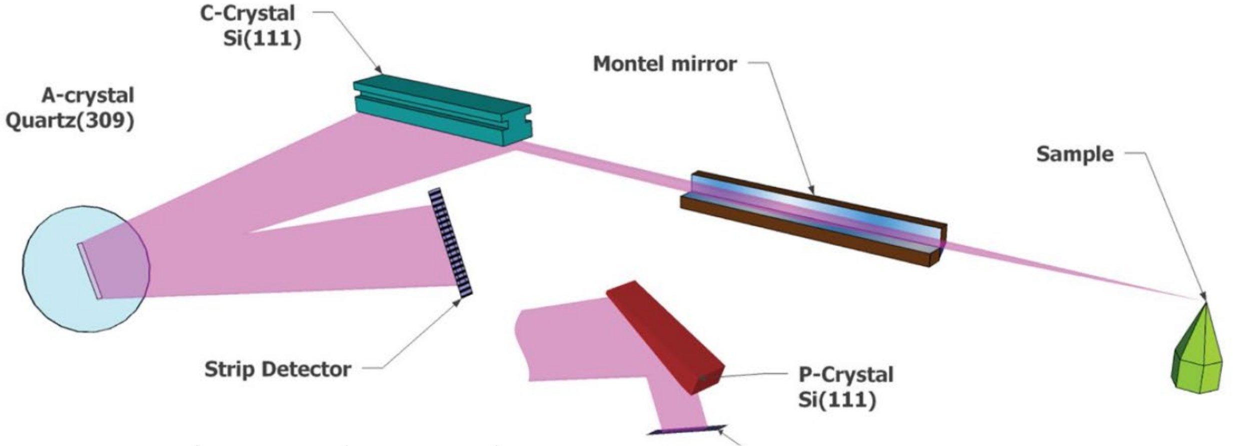


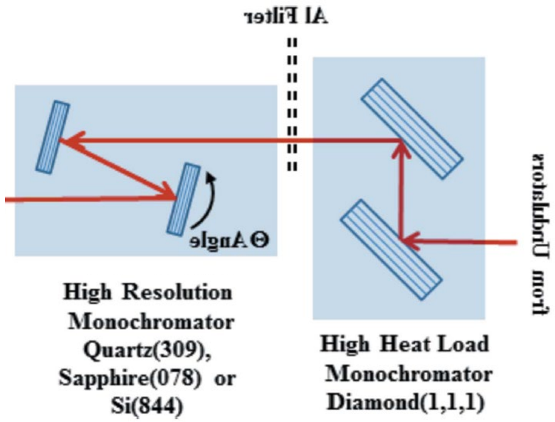
Ghiringhelli et al. Science 337, 821 (2012)

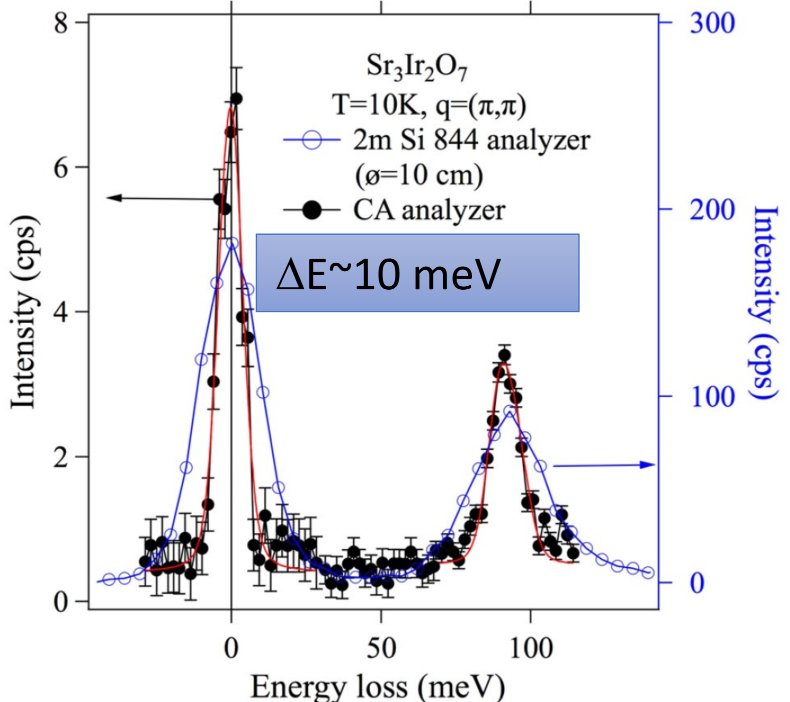
M. Mittrano et al. Science Advances 2019

Future RIXS

Jungho Kim, et al., Sci. Rep. 8, 1958 (2018); Thomas Gog et al. JSR 25, 1030 (2018)

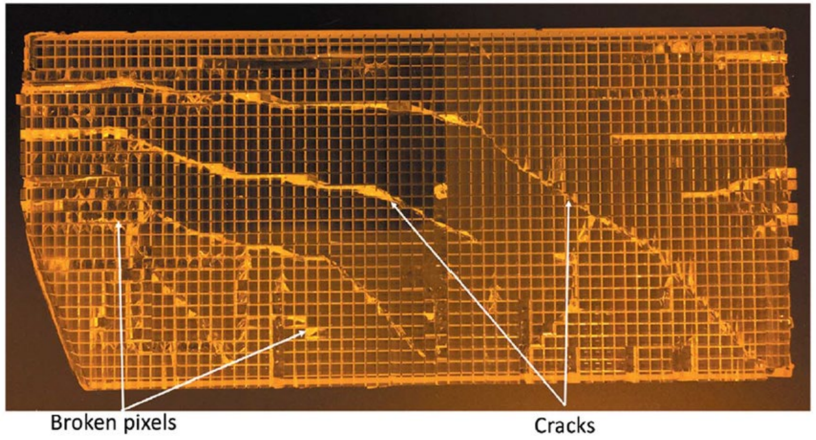






ΔE~10 meV

Diced quartz analyzer



Ayman H. Said et al. JSR 25, 373 (2018).

Summary

- Inelastic X-ray Scattering
  - Workhorse for measuring phonon dispersion relation and other lattice dynamics
  - Useful for studying electronic excitations
    - Crystal field excitations (dd excitations – sensitive to orbital symmetry)
    - X-ray Raman Scattering allows XAS in extreme sample enviroments
- Resonant Inelastic X-ray Scattering
  - RIXS map (RXES) useful for chemical analysis
  - Magnetic Excitations
  - An exciting time for RIXS
- Many materials beyond cuprates are being investigated using RIXS, headed by iridates

NXS Lecture - Young-June Kim:

“Inelastic X-ray Scattering”

https://forms.office.com/g/3JMPrwhuYf