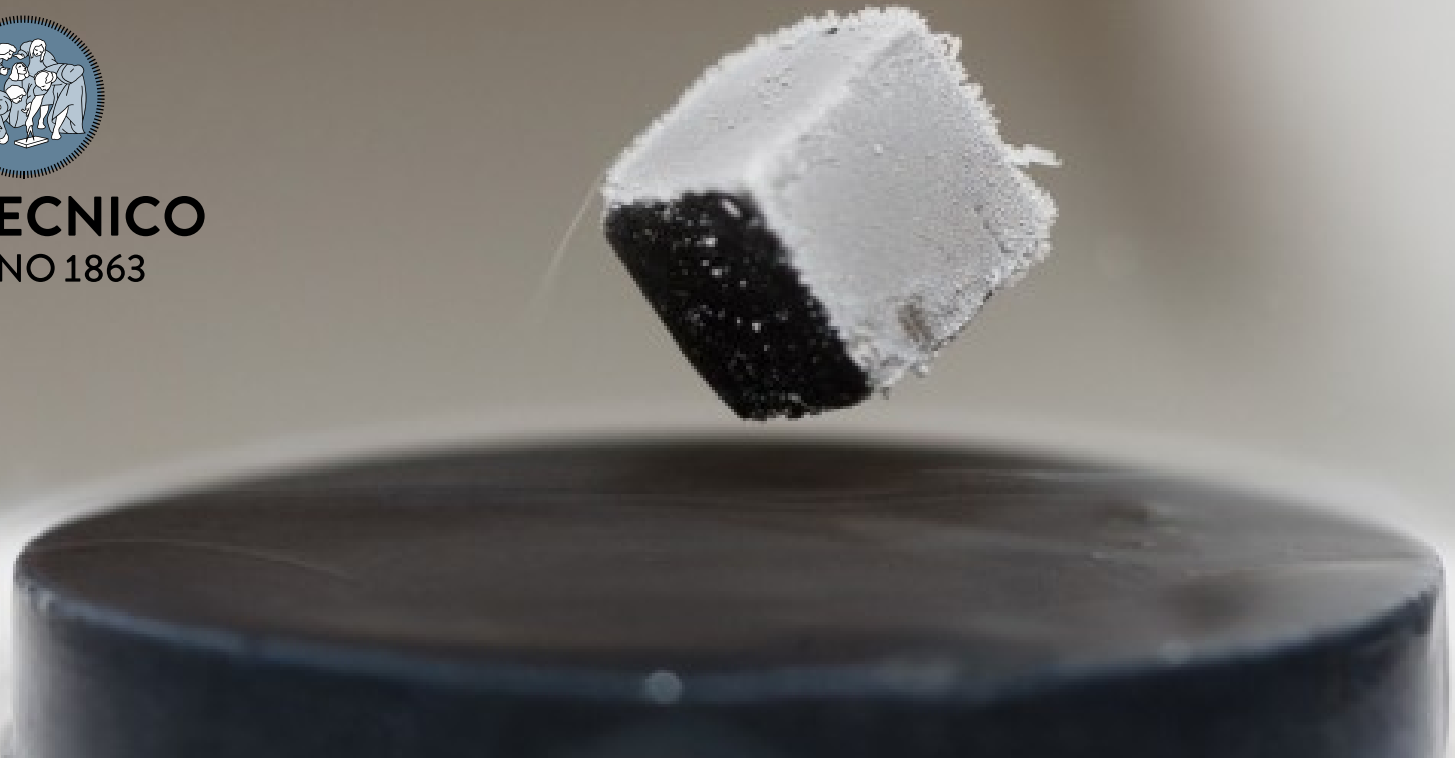




POLITECNICO
MILANO 1863



X-ray vision of High Temperature Superconductivity

Giacomo Ghiringhelli

Dipartimento di Fisica – Politecnico di Milano – Italy

Colloquium di Dottorato

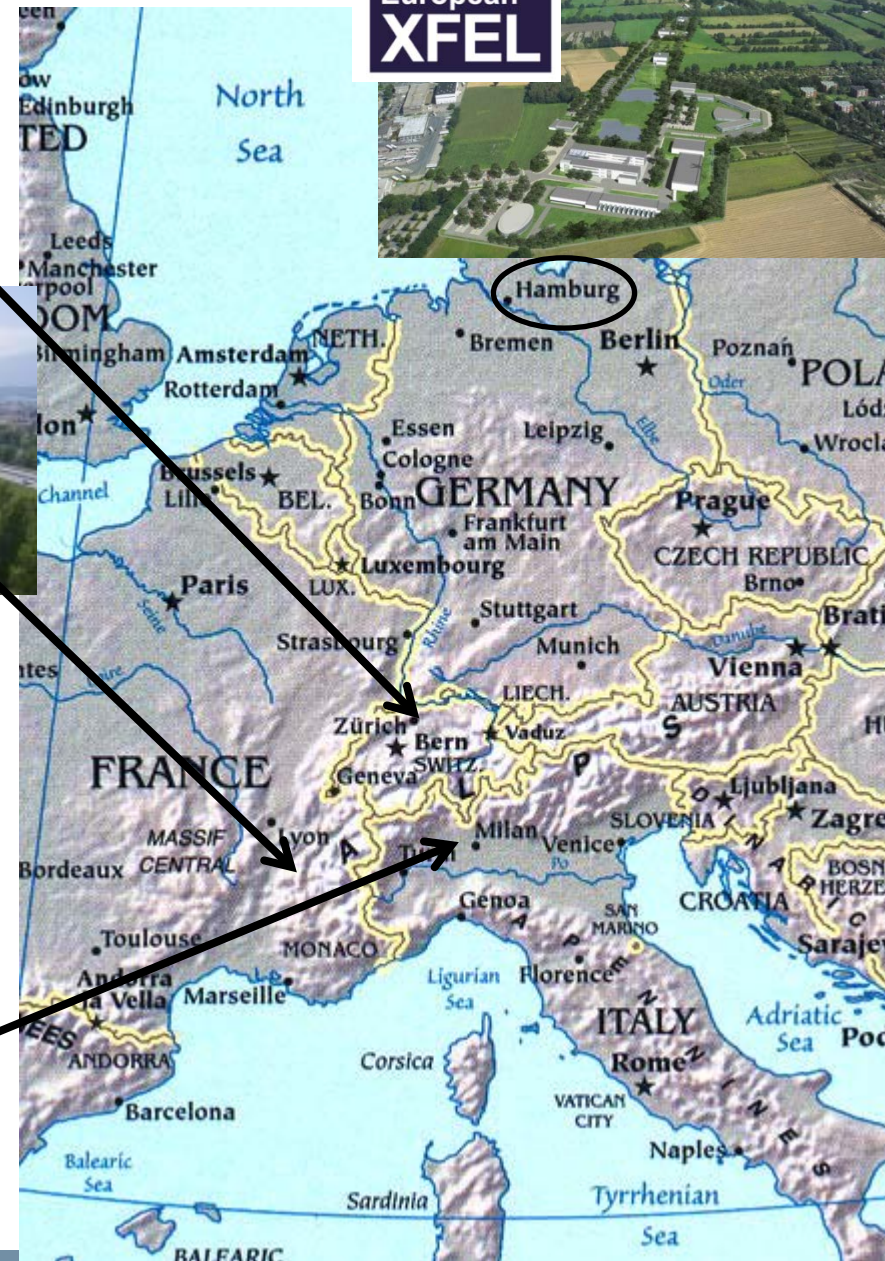
Università di Pavia, Dipartimento di Fisica - 11 Maggio 2017



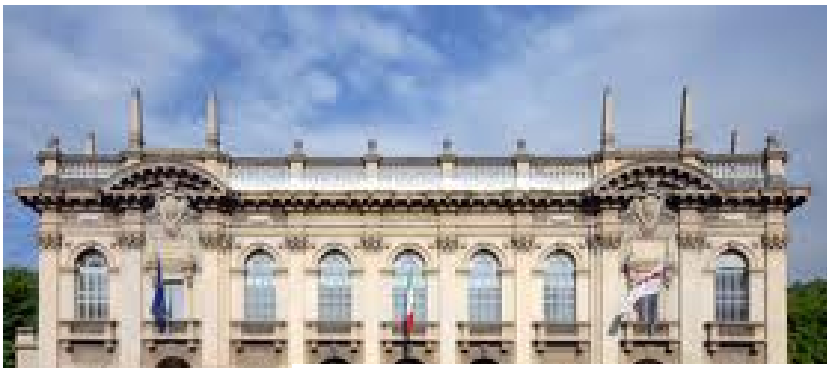


PAUL SCHERRER INSTITUT
PSI
SWISS LIGHT SOURCE
SLS

European
XFEL




ESRF



**POLITECNICO
MILANO 1863**

POLITECNICO MILANO 1863

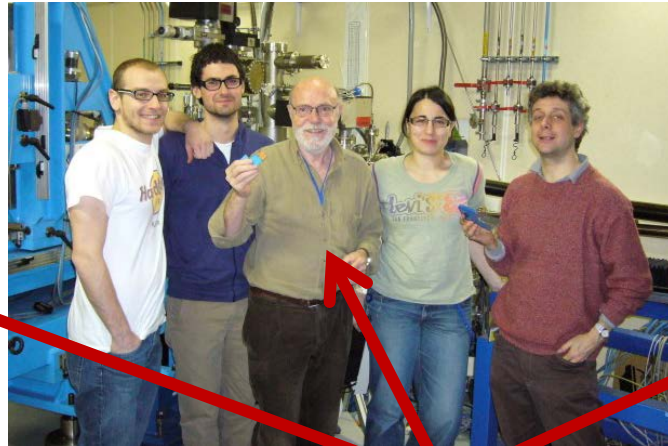


Soft x-rays, spectra and Lucio

1994 - 2000: ID12B

2001 - 2013: ID08

2015: ID32



Lucio Braicovich

2006 - 2011: ADDRESS @ SLS



INFM



POLITECNICO
MILANO 1863



ESRF



PAUL SCHERRER INSTITUT
PSI

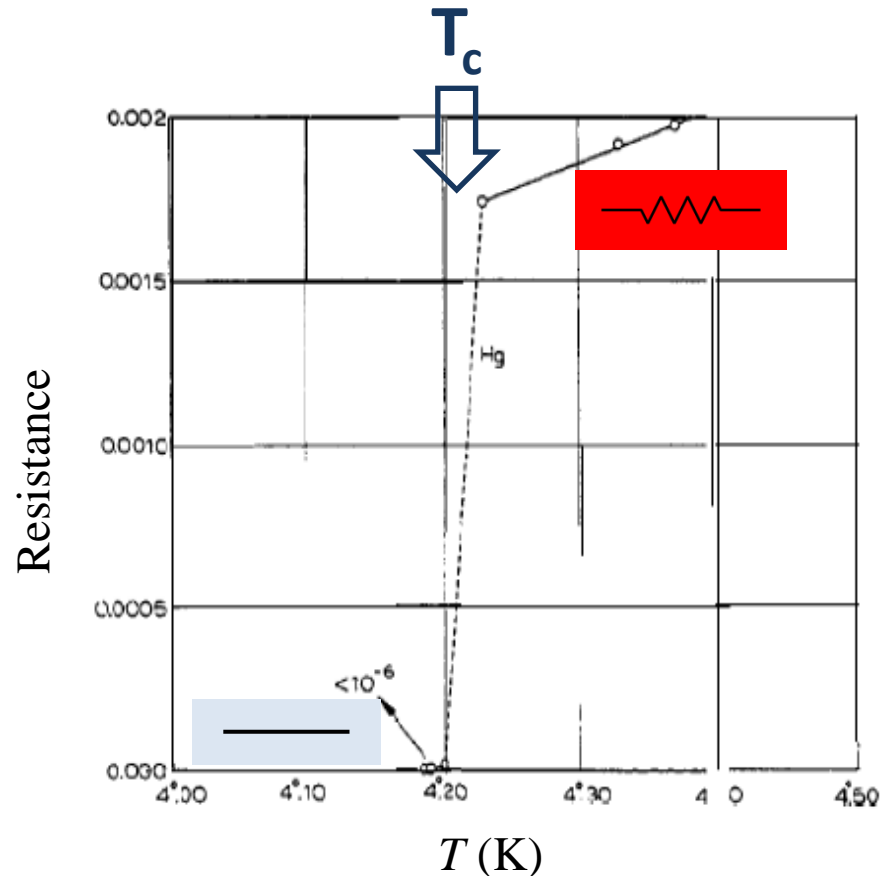
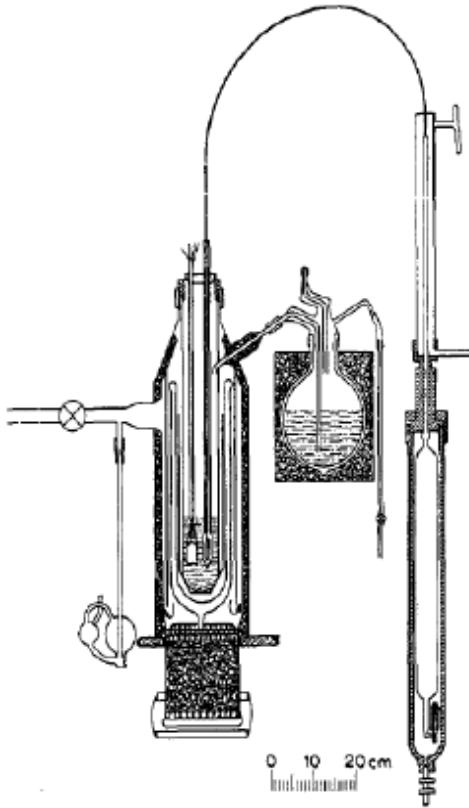


Superconductivity

Discovered in 1911 in mercury

Electric **resistivity** is **ZERO**
below a critical temperature

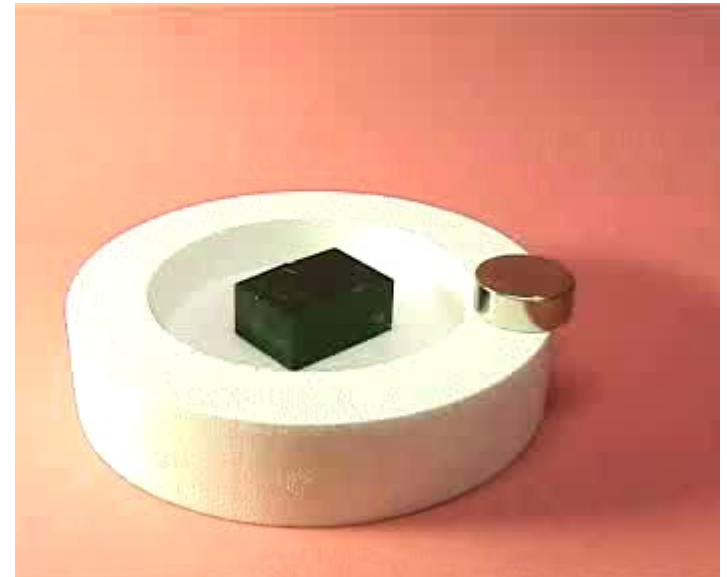
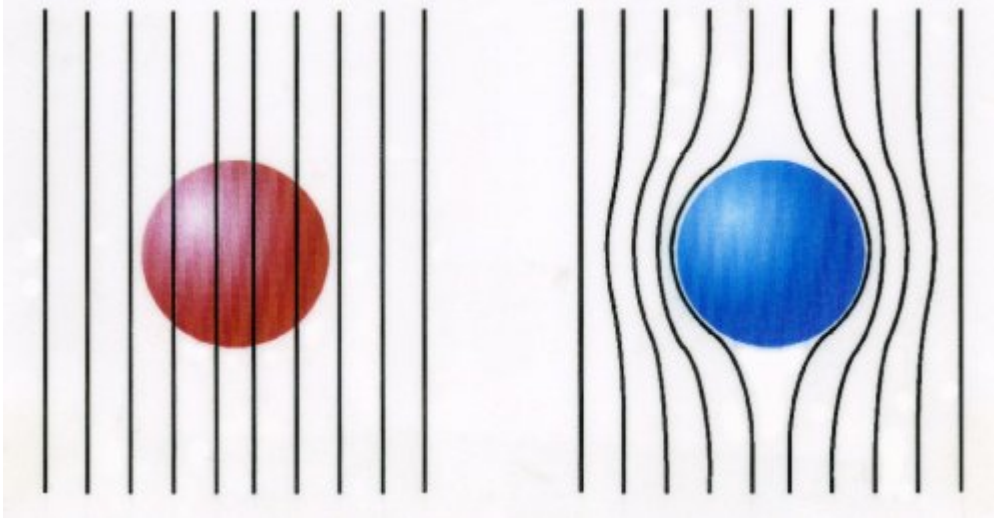
Very low T



Perfect diamagnetism

Not only a perfect **conductor**, but also a perfect “**anti-magnet**”:
Meissner effect

A superconductor repels magnetic fields



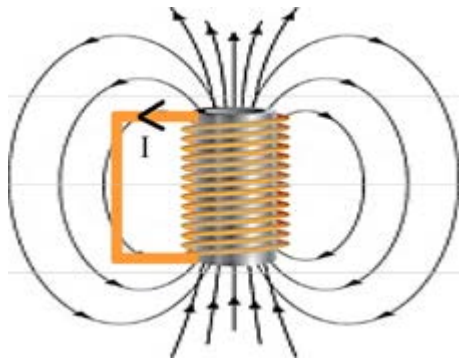
How can we use SC?



**Transport and storage
of electric power:**
no waste of energy

Limitations

- Low T
- Critical current



High magnetic fields:
no need to dissipate
heat from the coils of
electromagnets

- Critical current
- Critical field
- Low T

SC technology today

Despite the difficulty due to **cryogenics**, **superconducting wires** have been developed for special applications and are currently used in commercial **medical devices** and advanced **scientific instrumentation**.



LHe



Nb alloys



MRI



High field magnets
Particle accelerators
SQUID magnetometers

Low temperatures

For **75 years** the search for materials with higher T_c has been quite frustrating

KNOWN SUPERCONDUCTIVE ELEMENTS

■ BLUE = AT AMBIENT PRESSURE
■ GREEN = ONLY UNDER HIGH PRESSURE

1	H																	He						
2	Li	Be																	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar									Kr							
4	K	Ca	Sc	Ti	Y	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
6	Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
7																		112	113					
8																		114	115					
9																		116	117					
10																		118	119					
11																		120	121					
12																		122	123					
13																		124	125					
14																		126	127					
15																		128	129					
16																		130	131					
17																		132	133					
18																		134	135					
19																		136	137					
20																		138	139					
21																		140	141					
22																		142	143					
23																		144	145					
24																		146	147					
25																		148	149					
26																		150	151					
27																		152	153					
28																		154	155					
29																		156	157					
30																		158	159					
31																		160	161					
32																		162	163					
33																		164	165					
34																		166	167					
35																		168	169					
36																		170	171					
37																		172	173					
38																		174	175					
39																		176	177					
40																		178	179					
41																		180	181					
42																		182	183					
43																		184	185					
44																		186	187					
45																		188	189					
46																		190	191					
47																		192	193					
48																		194	195					
49																		196	197					
50																		198	199					
51																		200	201					
52																		202	203					
53																		204	205					
54																		206	207					
55																		208	209					
56																		210	211					
57																		212	213					
58																		214	215					
59																		216	217					
60																		218	219					
61																		220	221					
62																		222	223					
63																		224	225					
64																		226	227					
65																		228	229					
66																		230	231					
67																		232	233					
68																		234	235					
69																		236	237					
70																		238	239					
71																		240	241					
72																		242	243					
73																		244	245					
74																		246	247					
75																		248	249					
76																		250	251					
77																		252	253					
78																		254	255					
79																		256	257					
80																		258	259					
81																		260	261					
82																		262	263					
83																		264	265					
84																		266	267					
85																		268	269					
86																		270	271					
87																		272	273					
88																		274	275					
89																		276	277					
90																		278	279					
91																		280	281					
92																		282	283					
93																		284	285					
94																		286	287					
95																		288	289					
96																		290	291					
97																		292	293					
98																		294	295					
99																		296	297					
100																		298	299					
101																		300	301					
102																		302	303					
103																		304	305					
104																		306	307					
105																		308	309					
106																		310	311					
107																		312	313					
108																		314	315					
109																		316	317					
110																		318	319					
111																		320	321					
112																		322	323					
113																		324	325					
114																		326	327					
115																		328	329					
116																		330	331					
117																		332	333					
118																		334	335					
119																		336	337					
120																		338	339					
121																		340	341					
122																		342	343					
123																		344	345					
124																		346	347					
125																		348	349					
126																		350	351					
127																		352	353					
128																		354	355					
129																		356	357					
130																		358	359					
131																		360	361					
132																		362	363					
133																		364	365					
134																		366	367					
135																		368	369					
136																		370	371					
137																		372	373					
138																		374	375					
139																		376	377					
140																		378	379					
141																		380	381					
142																		382	383					
143																		384	385					
144																		386	387					
145																		388	389					
146																		390	391					
147																		392	393					
148																		394	395					
149																		396	397					
150																		398	399					
151																		400	401					
152																		402	403					
153																		404	405					
154																		406	407					
155																		408	409					
156																		410	411					
157																		412	413					
158																		414	415					
159																		416	417					
160																		418	419					
161																		420	421					
162																		422	423					
163																		424	425					
164																		426	427					
165																		428	429					
166																		430	431					
167																		432	433					
168																		434	435					
169																		436	437					
170																		438	439					
171																		440	441					
172																		442	443					
173																		444	445					
174																		446	447					
175																		448	449					
176																		450	451					
177																		452	453					
178																		454	455					
179																		456	457					
180																		458	459					
181																		460	461					
182																		462	463					
183																		464	465					
184																		466	467					
185																		468	469					
186																		470	471					
187																		472	473					
188																		474	475					
189																		476	477					
190																		478	479					
191																		480	481					
192																		482	483					
193																		484	485					
194																		486	487					
195																		488	489					
196																		490	491					
197																		492	493					
198																		494	495					
199																		496	497					
200																		498	499					
201																		500	501					
202																		502	503					
203																		504	505					
204																		506	507					
205																		508	509					
206																		510	511					
207																		512	513					
208																		514	515					
209																		516	517					
210																		518	519					
211																		520	521					
212																		522	523					
213																		524	525					
214																		526	527					
215																		528	529					
216																		530	531					
217																		532	533					
218																		534	535					
219																		536	537					
220																		538	539					
221																		540	541					
222																		542	543					
223																		544	545					
224																		546	547					
225																		548	549					
226																		550	551					
227																		552	553					
228																		554	555					
229																		556	557					
230																		558	559					
231																		560	561					
232																		562	563					
233																		564	565					
234																		566	567					
235																		568	569					
236																		570	571					
237																		572	573					
238																		574	575					
239																		576	577					
240																		578	579					
241																		580	581					
242																		582	583					
243																		584	585					
244																		586	587					
245																		588	589					
246																		590	591					
247																		592	593					
248																		594	595					
249																		596	597					
250																		598	599					
251																		600	601					
252																		602	603					
253																		604	605					
254																		606	607					
255																		608	609					
256																		610	611					
257																		612	613					
258																		614	615					
259																		616	617					
260																		618	619					
261																		620	621					
262																		622	623					
263																		624	625					
264																		626	627					
265																		628	629					
266																		630	631					
267																		632	633					
268																		634	635					
269																		636	637					
270																		638	639					
271																		640	641					
272																		642	643					
273																		644	645					
274																		646	647					
275																		648	649					
276																		650	651					
277																		652	653					
278																		654	655					

High T_c superconductors (HTS)



J. Georg Bednorz

K. Alex Müller

Bednorz & Müller

Discovery: Jan. 1986
 Publication: April 1986



Nobel 1987

Z. Phys. B - Condensed Matter 64, 189-193 (1986)

*Reproduction of fax to Joe Eck
 001 785 263 016*

Possible High T_c Superconductivity in the Ba - La - Cu - O System

J.G. Bednorz and K.A. Müller
 IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

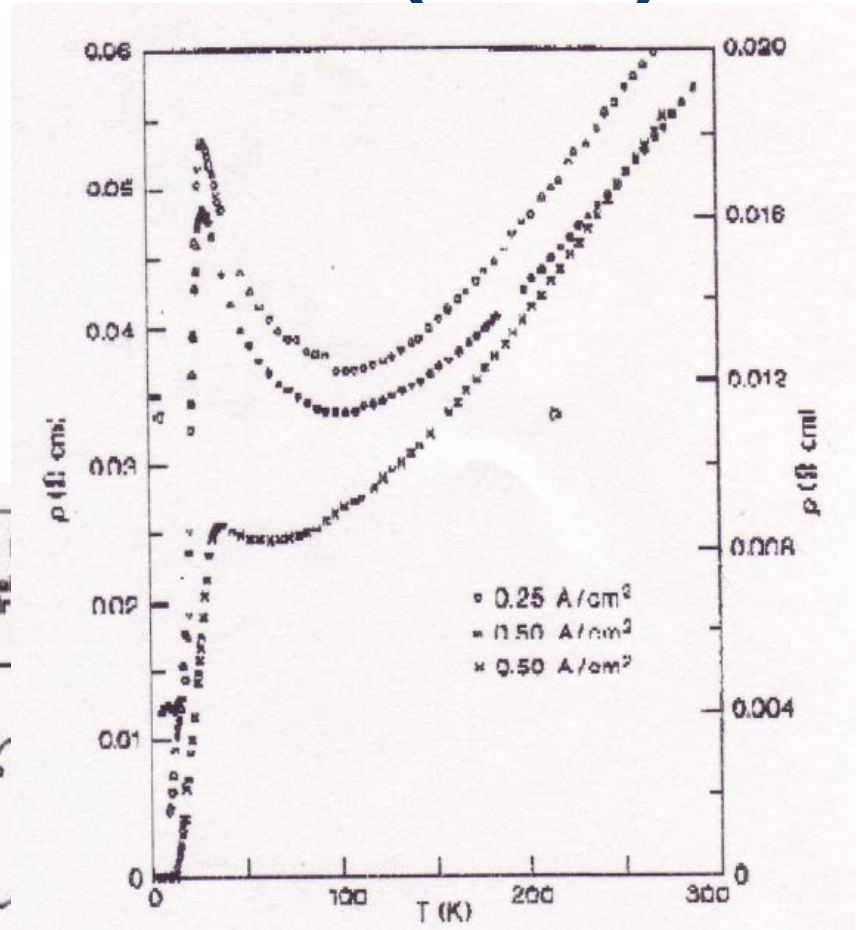


Fig. 1. Temperature dependence of resistivity in $Ba_xLa_{5-x}Cu_5O_{5(3-x)}$ for samples with $x(Ba)=1$ (upper curves, left scale) and $x(Ba)=0.75$ (lower curve, right scale). The first two cases also show the influence of current density

A new cult is born during the Woodstock of Physics (1987)

American Physical Society, March Meeting, New York, 1987

On 18 March, more than a thousand physicists jammed the outer lobbies of the ballrooms at the New York Hilton as they waited for more than an hour for the doors to open 45 minutes before the 7:30 pm panel discussion on high- T_c oxides. A brief, two-line announcement about the panel discussion had been made in the program for the annual March meeting of The American Physical Society, held in New York on 16–20 March. Of the 3080 contributed abstracts in the program for the meeting, there was only one—from IBM Yorktown Heights and Zurich—on superconductivity in Ba-La-Cu-O. But because of the growing interest in these oxides by the middle of December, Neil Ashcroft (Cornell University), then chairman of the Division of Condensed Matter Physics of the APS, told us, an effort was made to announce the panel discussion in the program even though it had already been closed.

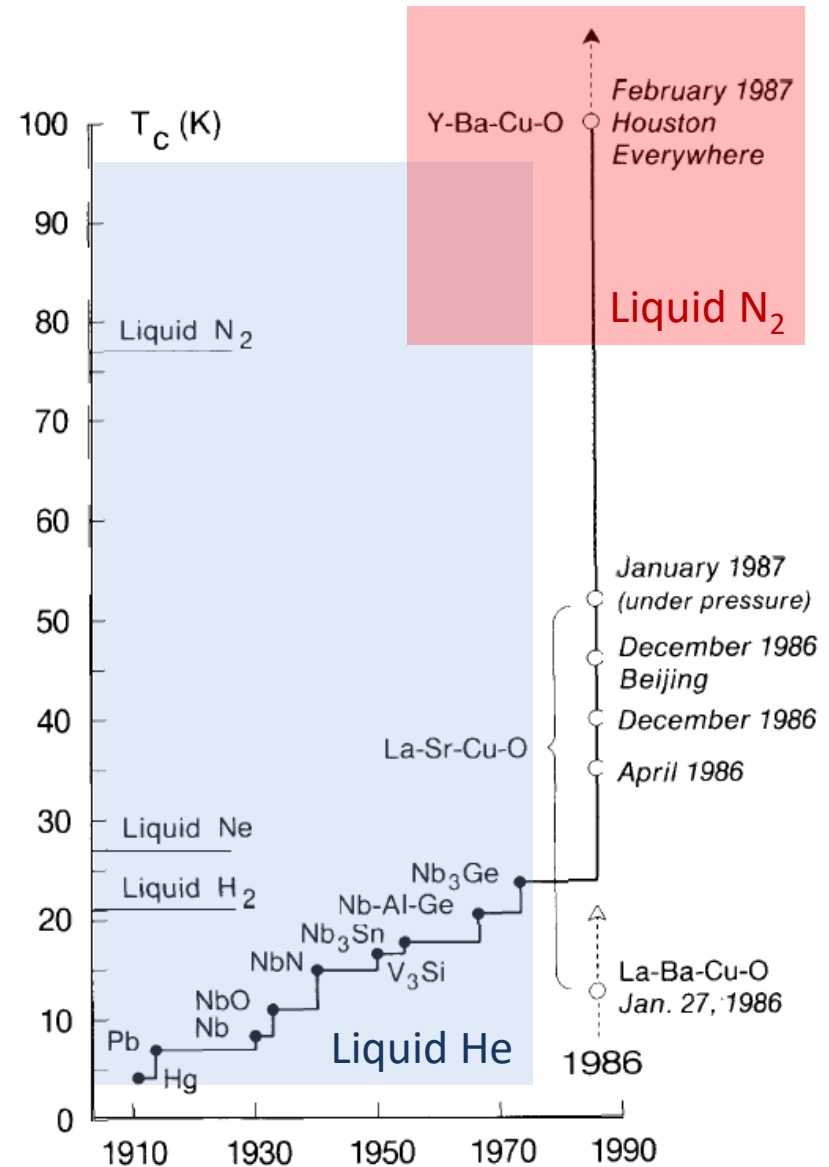
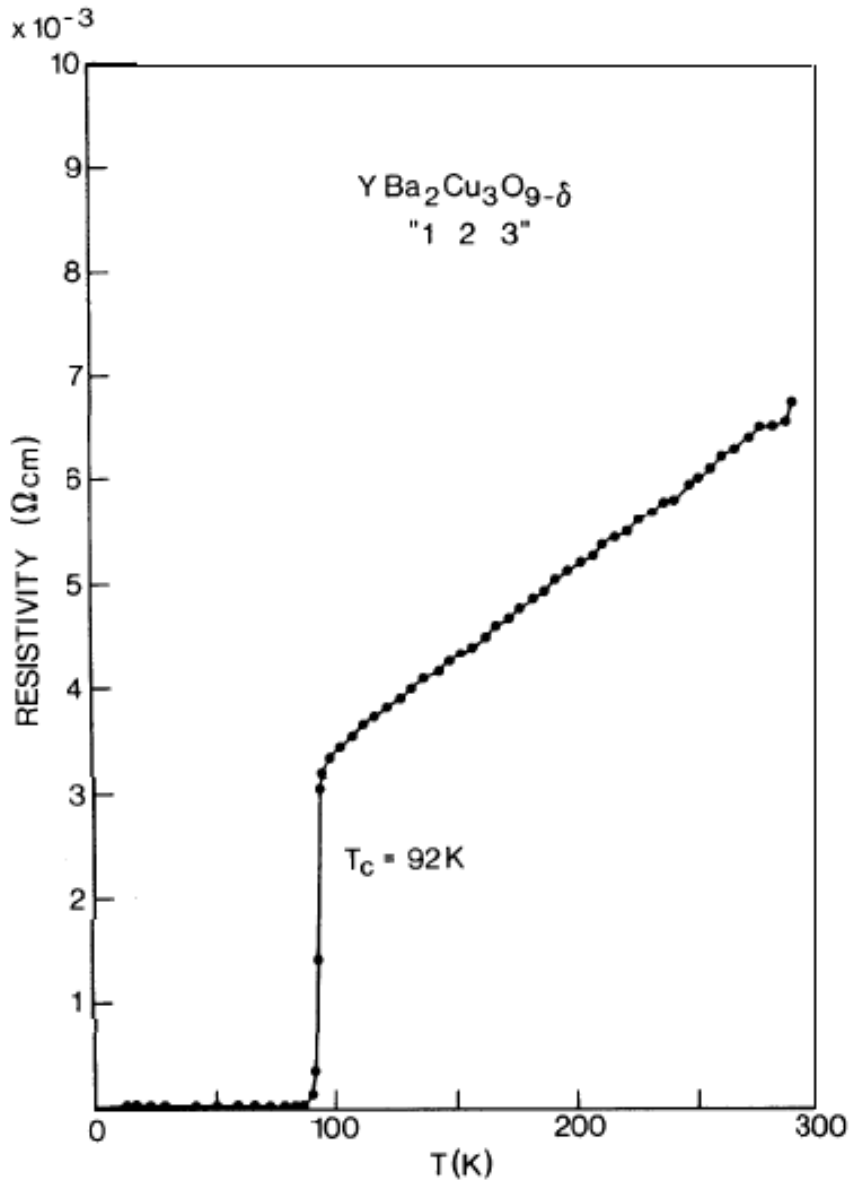
There was a thunderous applause when Ashcroft, after introducing the members of the first panel—Müller, Shoji Tanaka (University of Tokyo), Paul C. W. Chu (University of Houston), Zhongxian Zhao (Institute of Physics, Academia Sinica, Beijing) and Bertram Batlogg (AT&T Bell Laboratories)—concluded his opening remarks with “These are some of the men, ladies and gentlemen, who set this engine running.” The 1140 seats in the Rendezvous Trianon Ballroom had been filled in just a few minutes after the doors opened. Several hundred physicists stood patiently in the side aisles for several hours to listen to a series of five-minute presentations; many more

watched the proceedings on monitors placed in the lobbies. According to Ashcroft, more than a hundred physicists were still present when he closed the session at a quarter after three. Many remained until 6 am, when the hotel staff reclaimed the rooms.

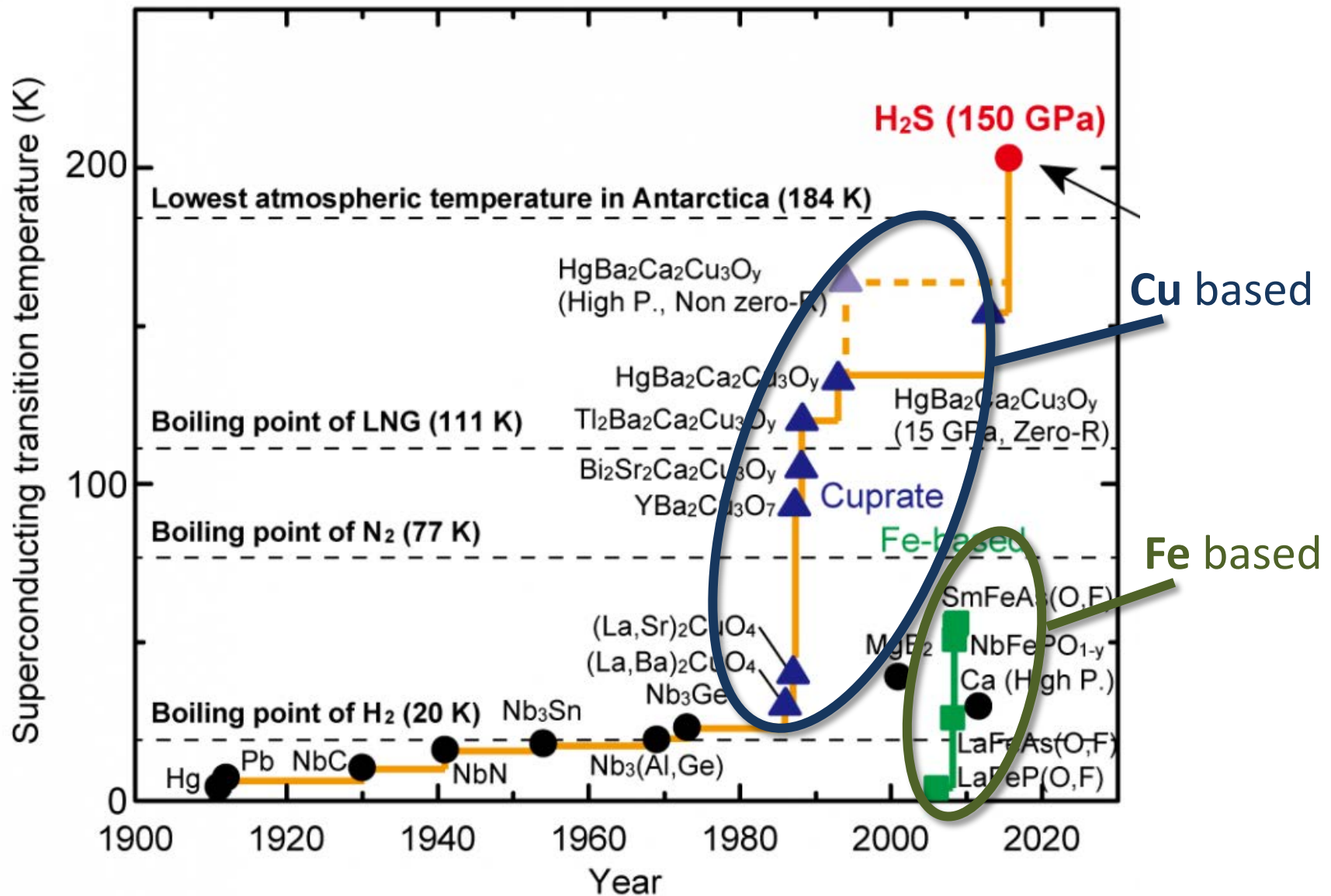
“A Woodstock for physics” is how Michael Schluter (AT&T Bell Laboratories) described the session at a press conference the following day. Indeed, the repeated requests that Ashcroft, APS vice-president James Krumhansl and APS headquarters staff had to make, requesting their colleagues to please clear the center aisle or the hotel security staff would not let the session begin, were easy reminders of the scene at a rock concert. But the analogy to Woodstock may apply at a deeper level as well: As leaders of research teams hurriedly discussed their evidence for superconductivity above 90 K—a phenomenon unheard of until a month earlier—one could have felt as if one were a part of a ceremonial gathering organized to affirm a new cult. Of

The **arXiv** was invented to keep track of discoveries on **HTS**: normal editorial procedures were too slow to guarantee priority claims

YBCO: T_c above 77 K



Where are we with T_c 30 years later?

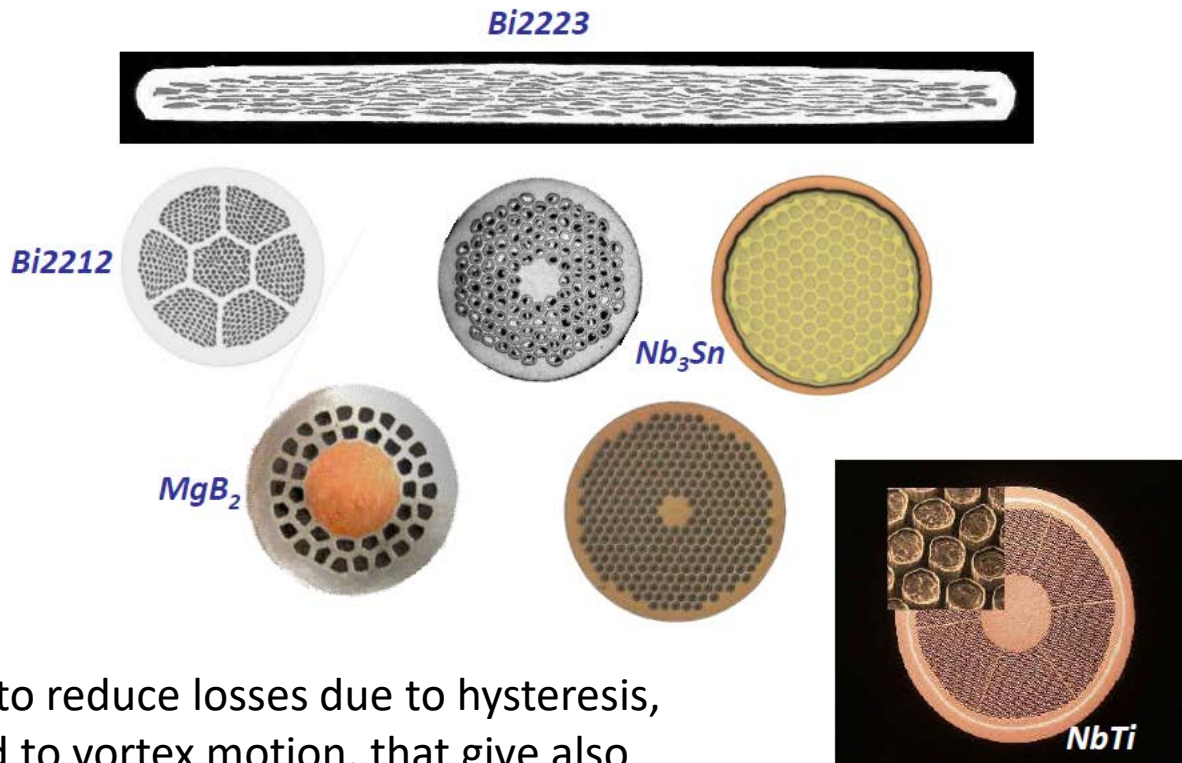


New hope from Cu based HTS

Higher T_c : above Liquid N_2 , cryogenics is cheaper and simpler

Higher critical field: stronger electromagnets (potentially up to 40T)

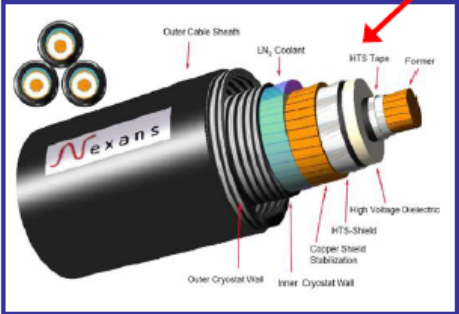
Higher critical current, provided we learn how to make good (multifilament) wires



Multifilament: to reduce losses due to hysteresis, which is related to vortex motion, that give also energy losses

Future applications with HTS?

Power distribution, generation and storage



*superconducting cables
fault current limiters*

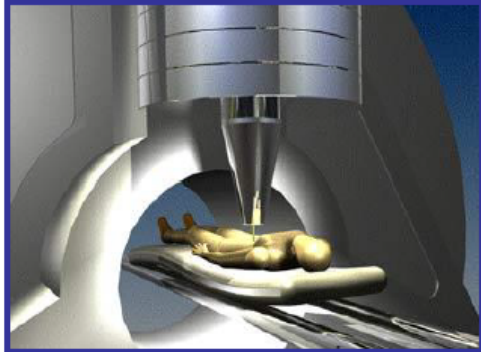


20% from renewable sources by 2020

$$E = \frac{1}{2} \frac{B^2}{\mu}$$

*energy density of the
magnetic field*

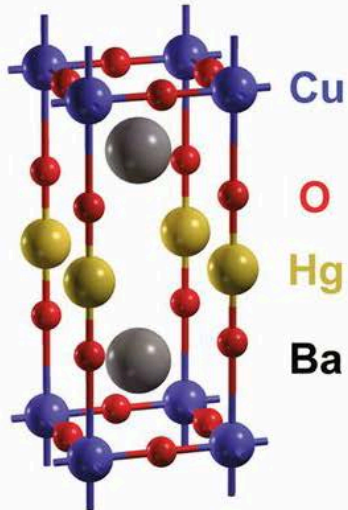
*New medical applications:
Compact accelerators for
hadron therapy*



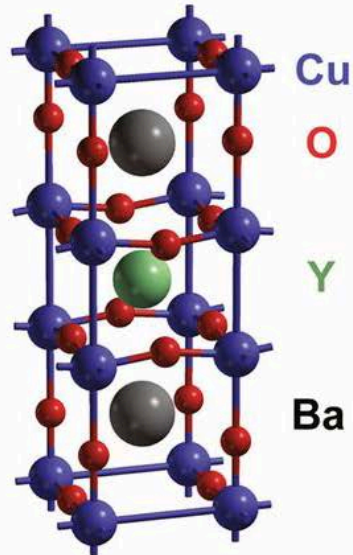
A big step to get there...

Cuprates: structure

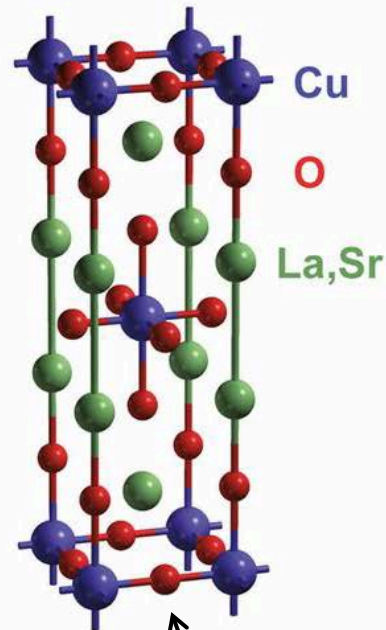
$\text{HgBa}_2\text{CuO}_{4+\delta}$
(Hg1201)



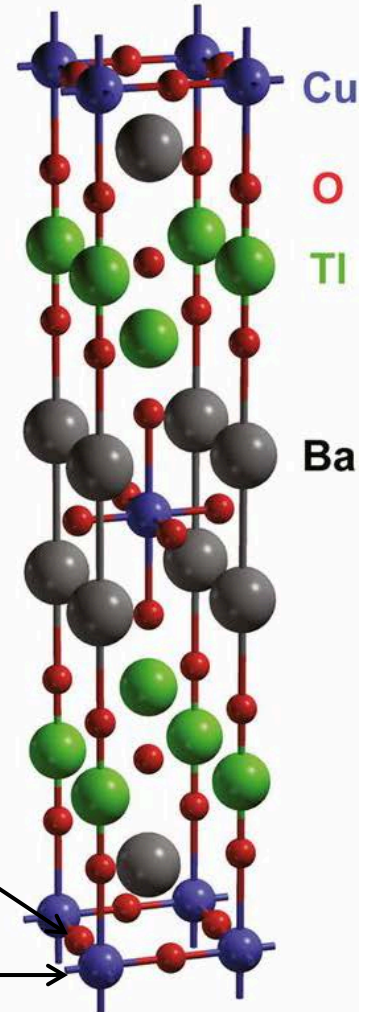
$\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$
(YBCO)



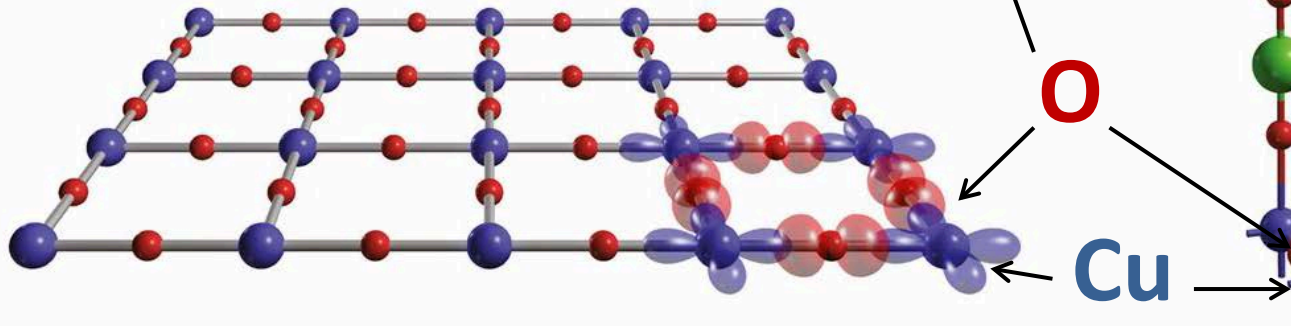
$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$
(LSCO)



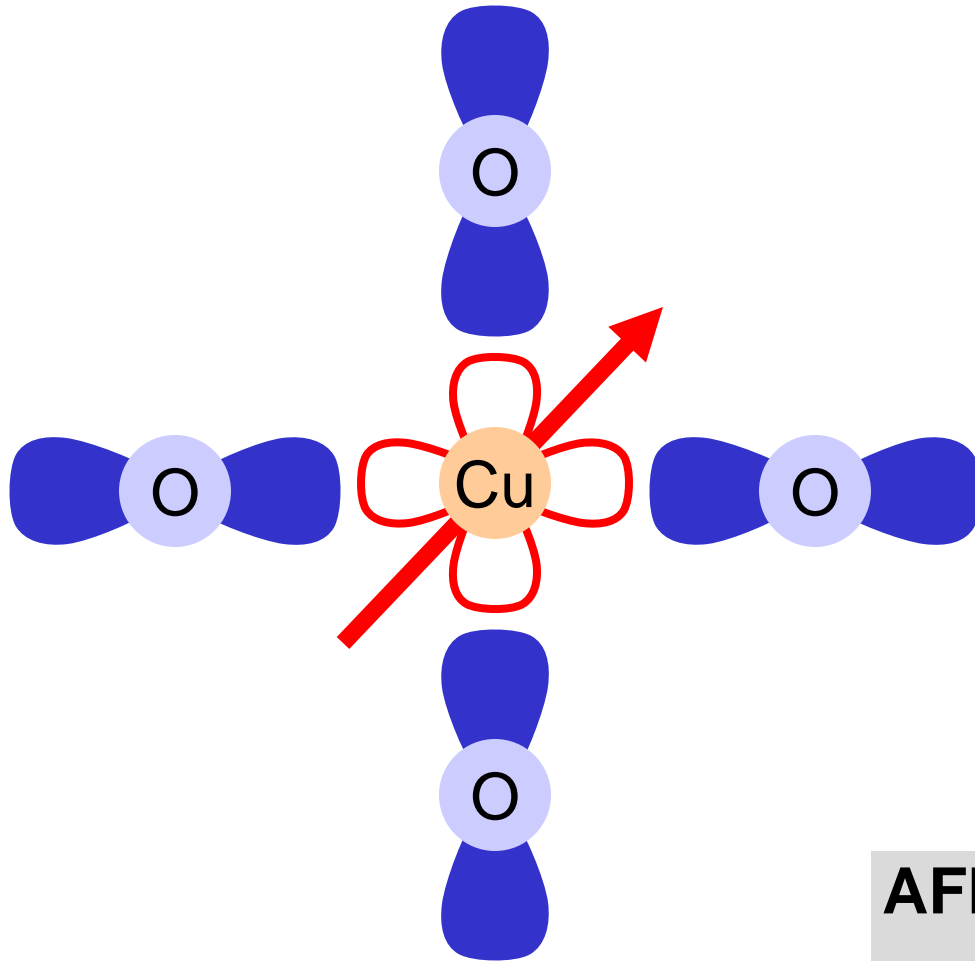
$\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$
(TI2201)



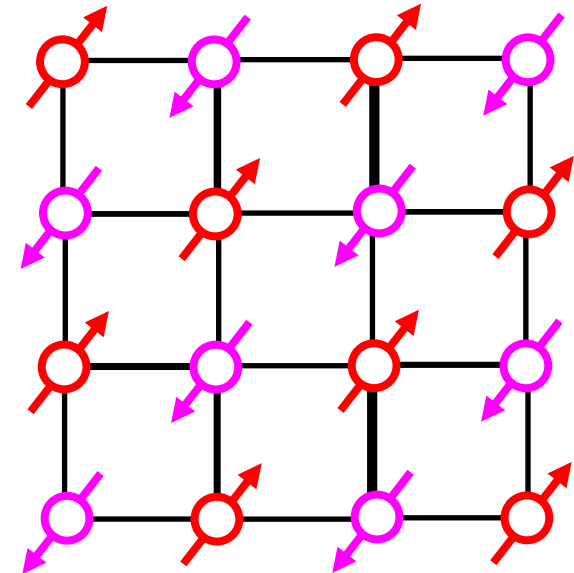
CuO_2 planes



AntiFerroMagnetic order in CuO_2 planes

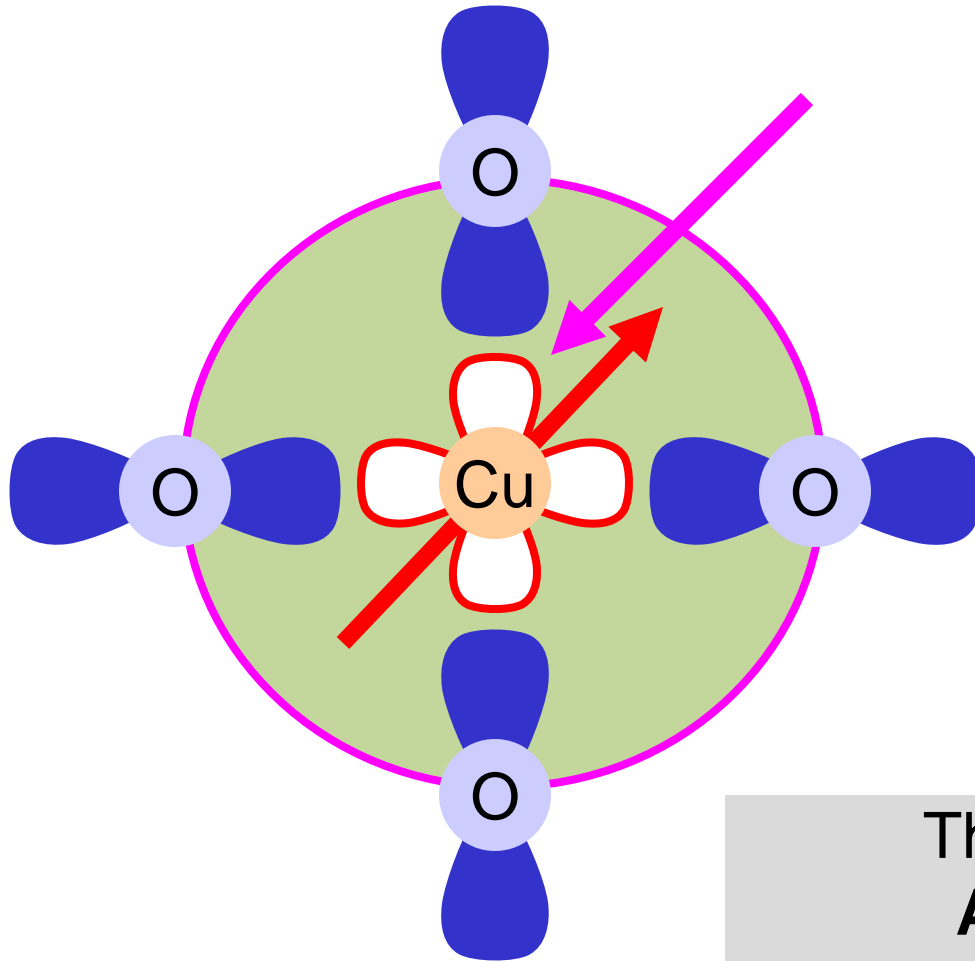


Cu^{2+} , $3d^9$

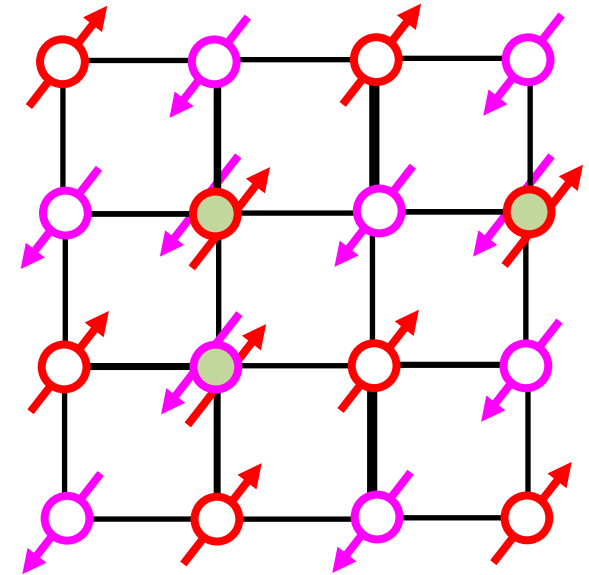


AFM order in the CuO_2 planes
INSULATOR

Doping of planes: holes

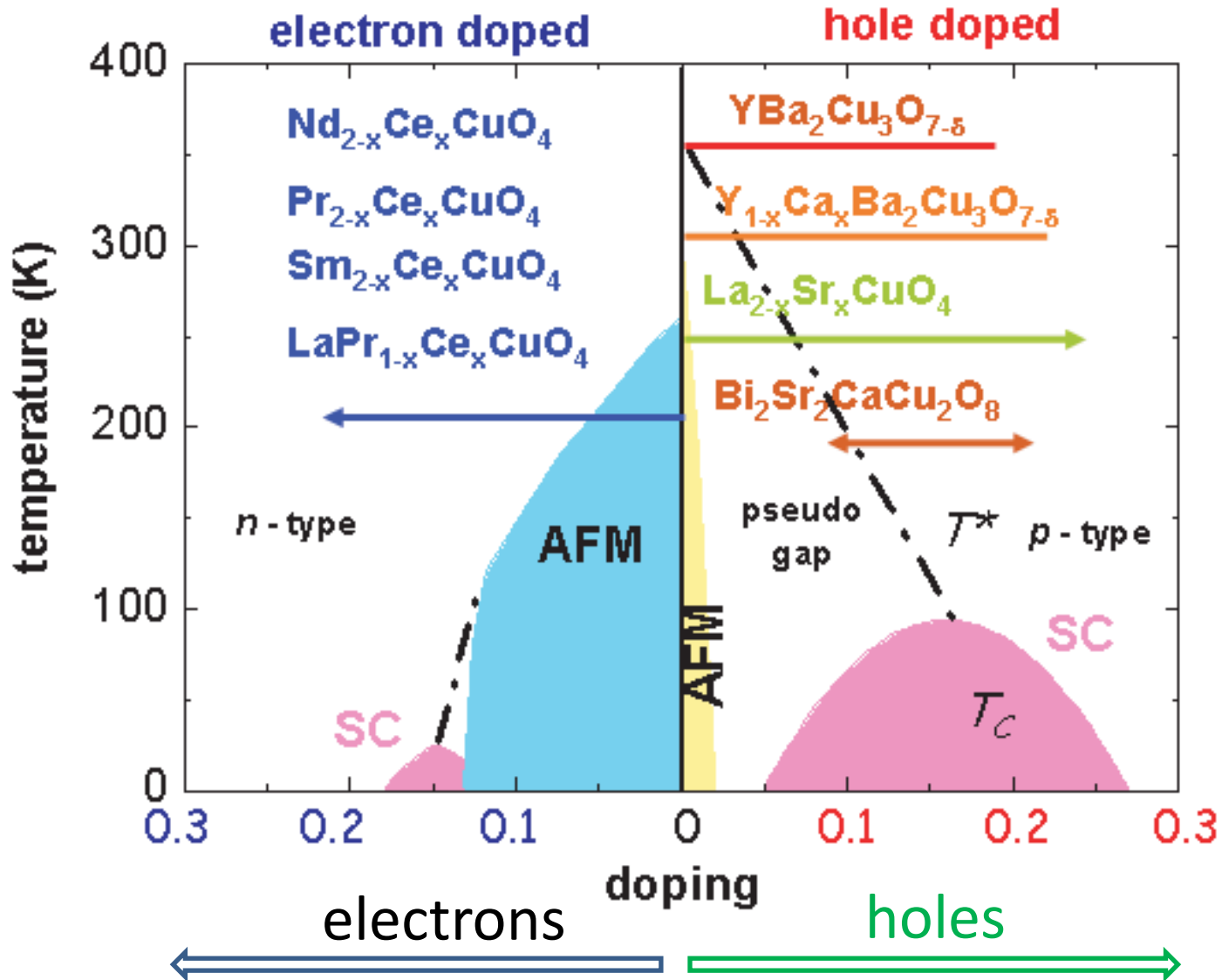


$\text{Cu}^{2+}, 3d^9$

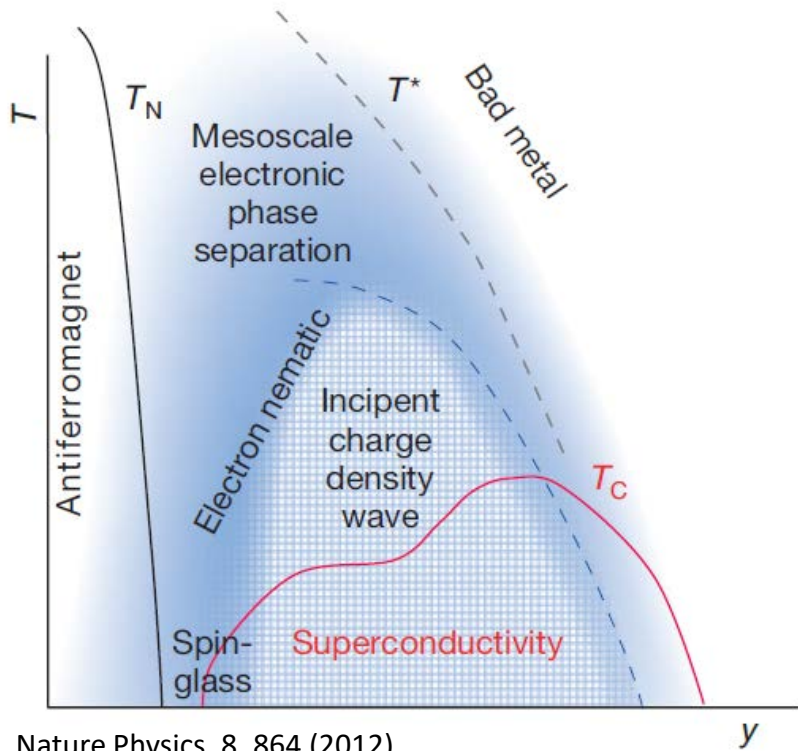


The perfect (long range)
AFM order is broken
Superconductivity becomes possible

Phase diagram

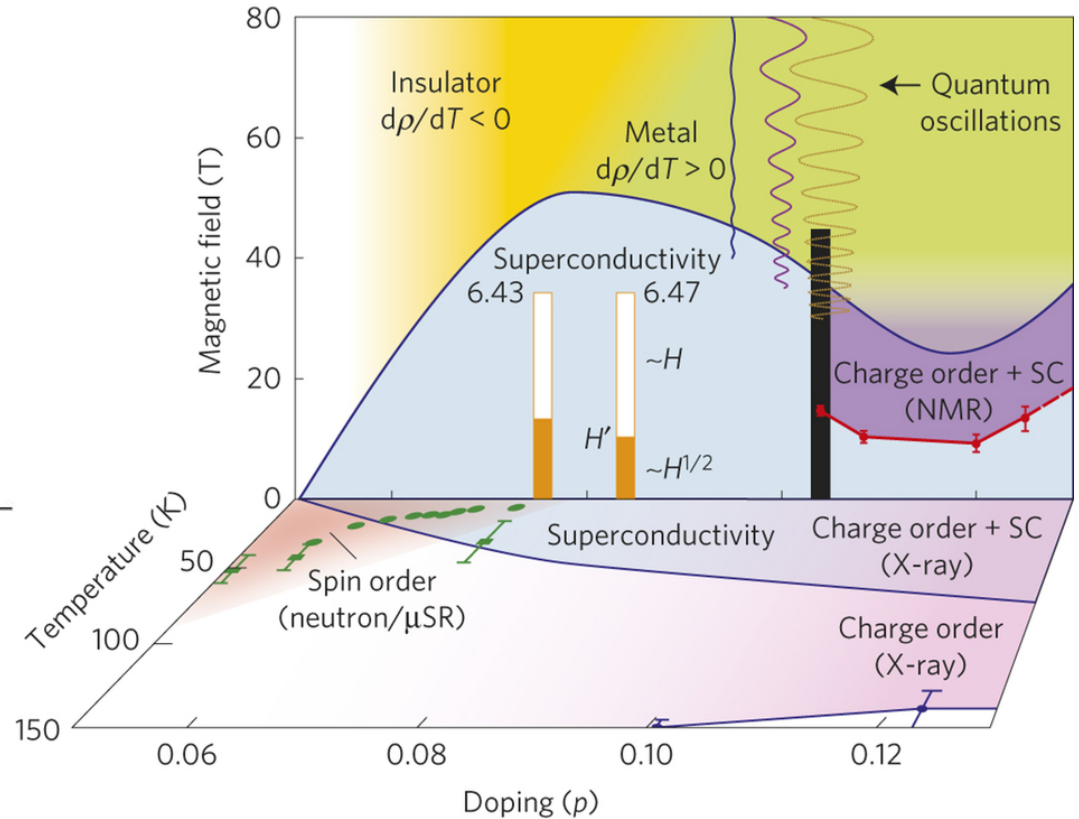


Extreme Complexity



Nature Physics, 8, 864 (2012)

All experimental techniques have been used to unveil the secrets of cuprates, but in most cases results have added complexity rather than clarity



Nature Physics 12, 47 (2016)

What is special in HTS?

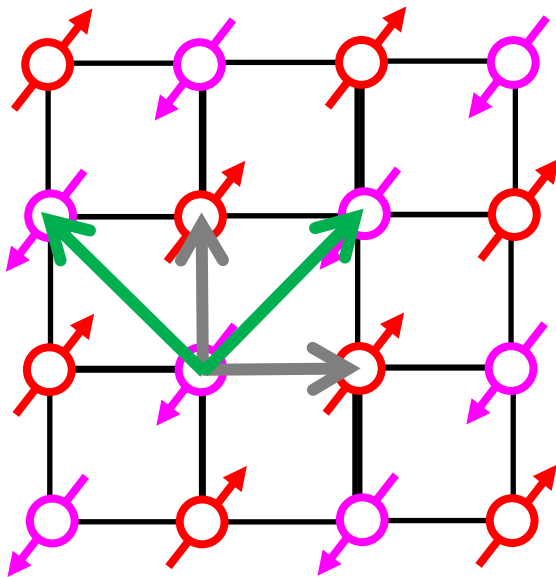
The common property is in the **CuO₂ planes**, ie the system is considered **quasi 2D**.

Thus all properties are referred to the squared **2D reciprocal lattice**.

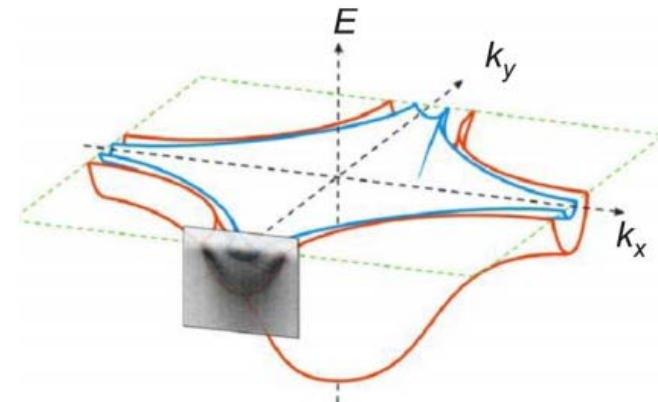
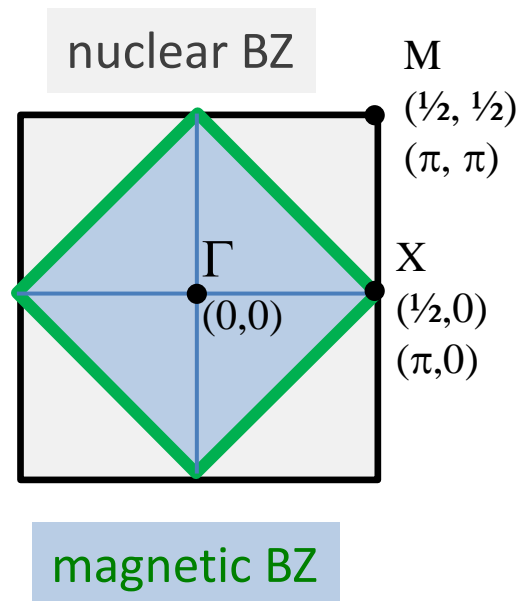
For example:

The electronic band structure as determined by Angle Resolved PhotoElectron Spectroscopy (**ARPES**)

Quasi 2D STRUCTURE



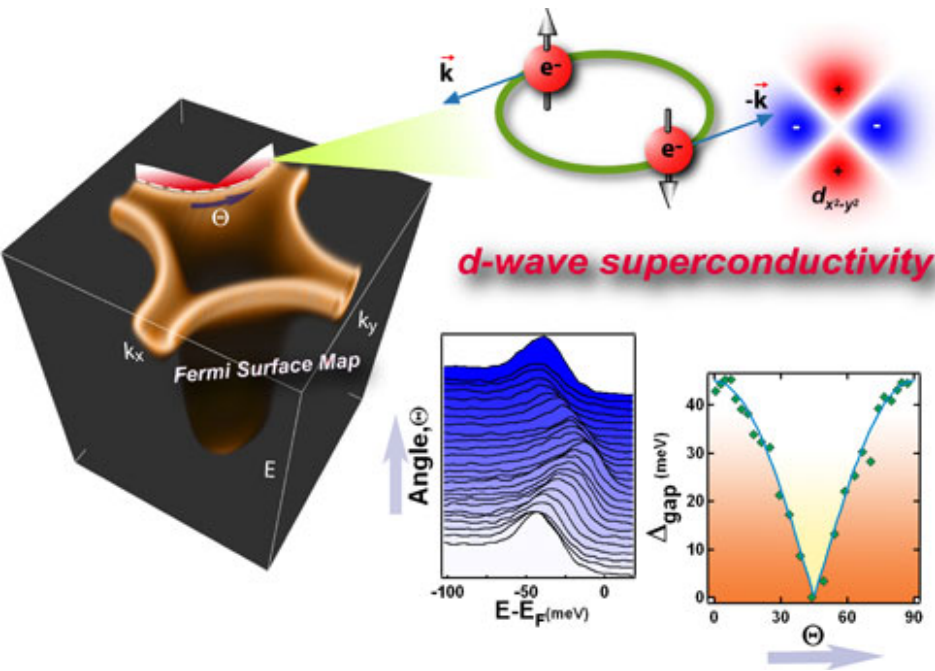
RECIPROCAL SPACE



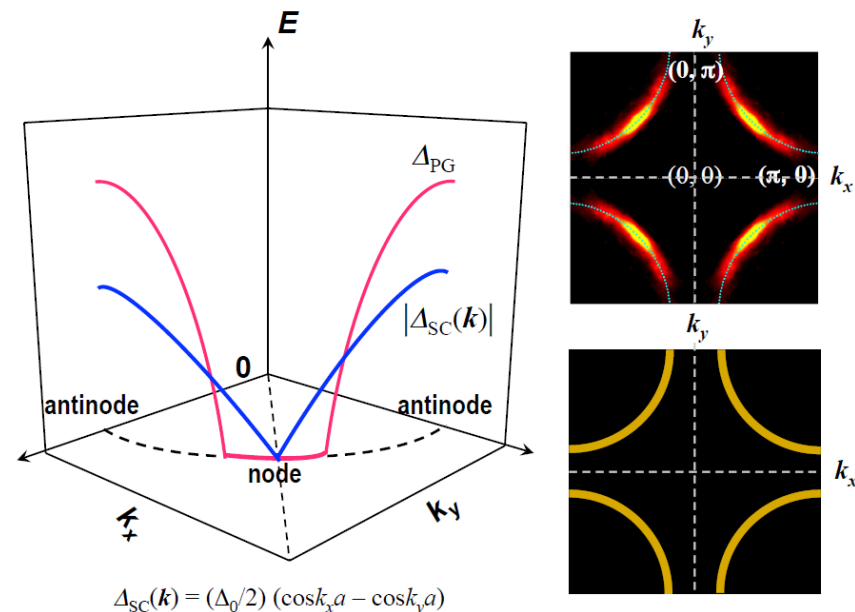
The Superconducting gap...

By ARPES we can determine the **Fermi surface shape** and the **SC gap**.
The **gap** is not constant along the Fermi surface, but has **x^2-y^2 symmetry**

But ARPES cannot tell us
what is the **glue** of
Cooper pairs



...and Pseudo-Gap



Enter X-ray spectroscopy!

XAS: ground state **orbital symmetry**

XMCD: **weak ferromagnetism** and proximity effect

Spin-Resolved XPS: **spin character** of doped sites

RIXS: **crystal field** splitting

RIXS: spin excitations (**magnons**)

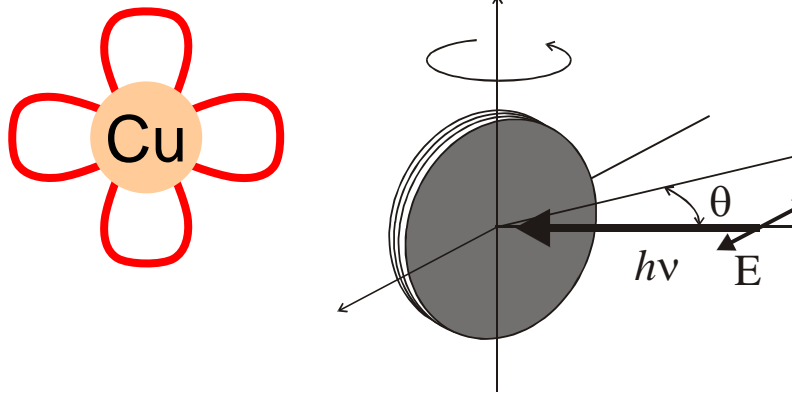
R(I)XS: **charge density waves**

IXS: **phonon** dispersion

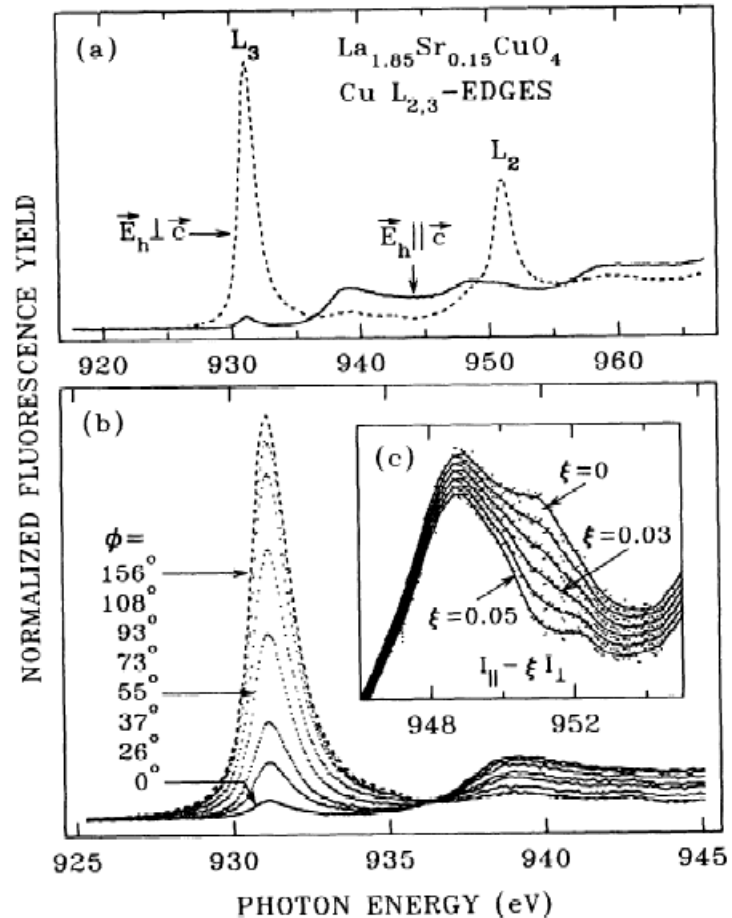
RIXS: **electron-phonon coupling**

XAS: 3d hole symmetry

Linear dichroism of Cu $L_{2,3}$ XAS was used to probe the symmetry of the empty Cu 3d orbital

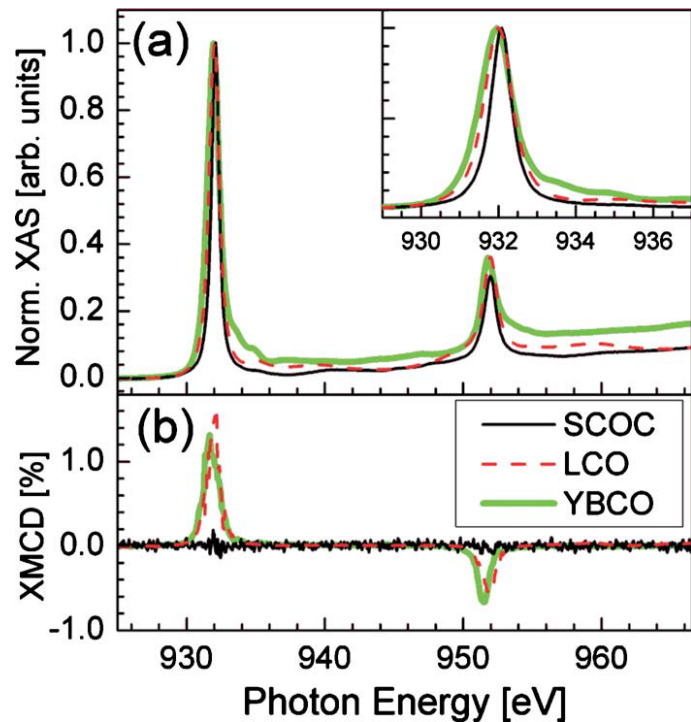


Result: the hole in Cu^{2+} has 100% x^2-y^2 symmetry

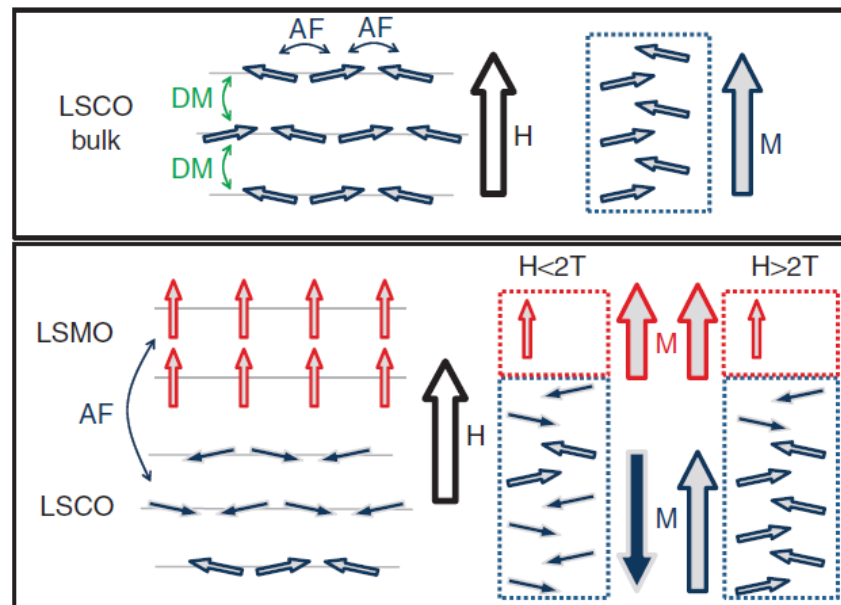
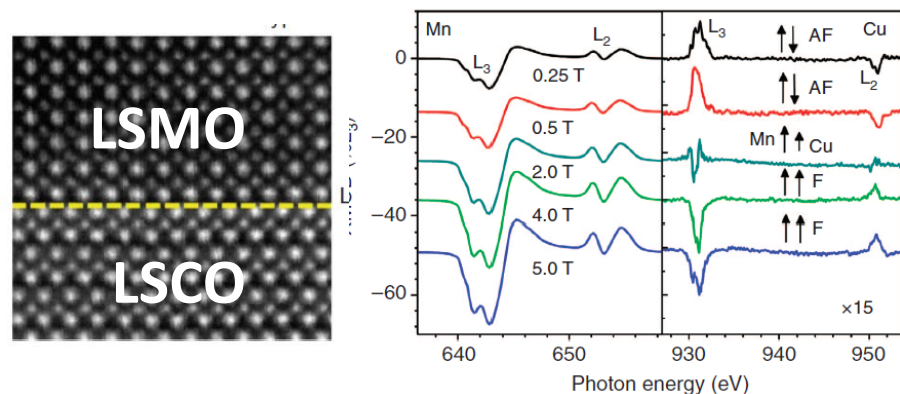


XMCD: weak ferromagnetism and proximity effect

The spin moments are **not perfectly in-plane**: they are tilted by few degrees and a strong external field can orient their out-of-plane component and we can detect it with XMCD

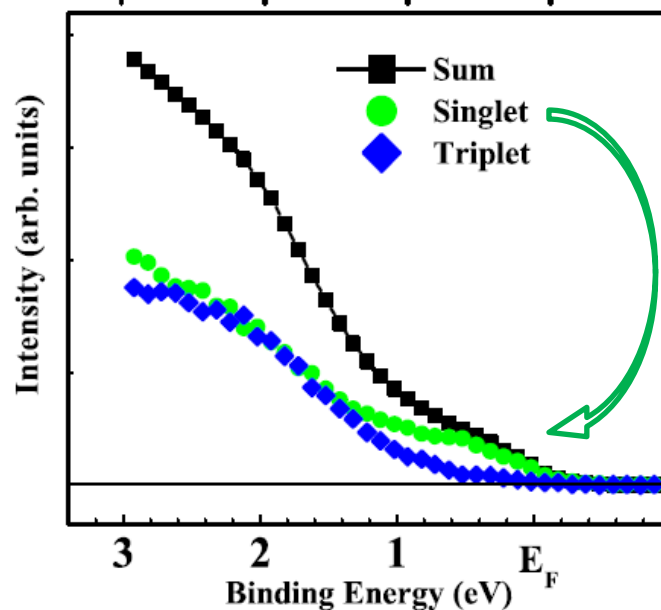
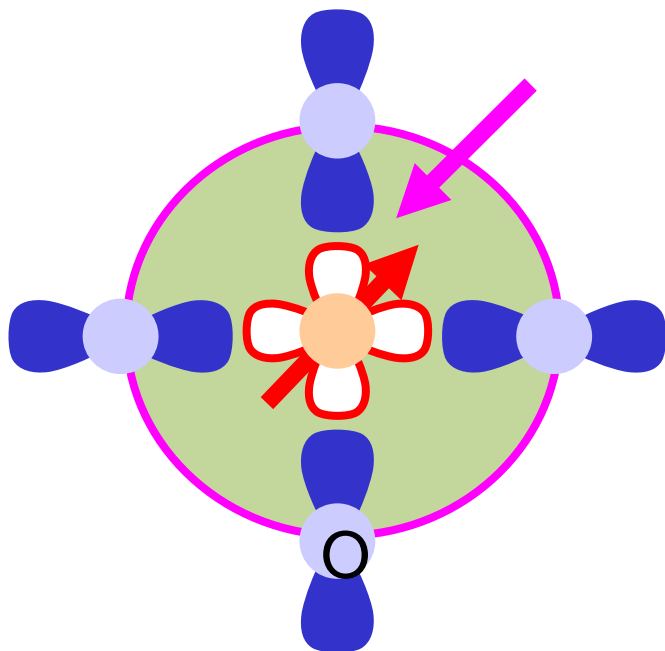


A ferromagnetic oxide can act similarly (proximity effect)



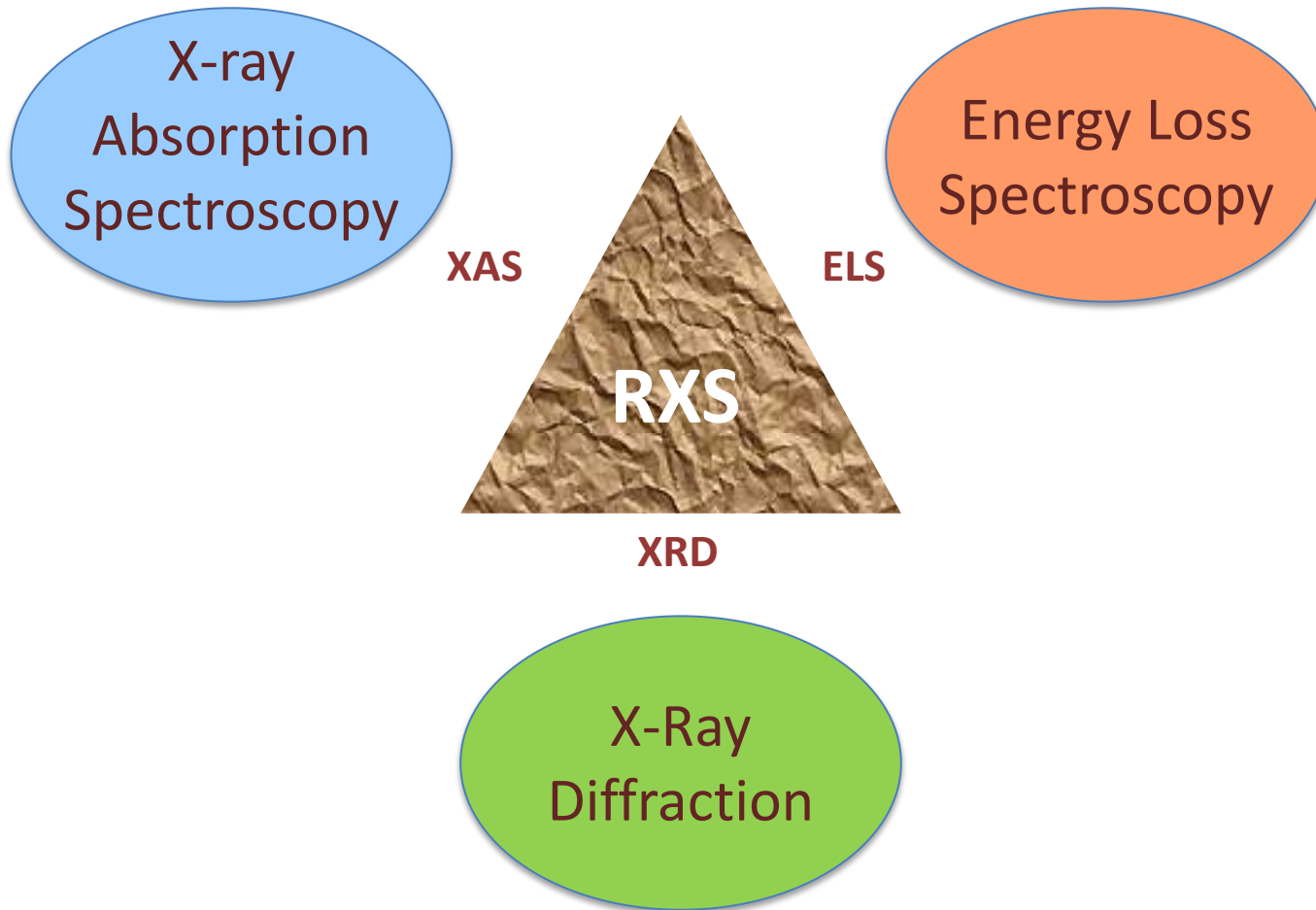
Spin-Resolved XPS: Zhang-Rice singlets

How are the spins aligned when two holes sit at the same Cu site? Theory predict **antiparallel** configuration (Zhang-Rice singlet) A smart combination of **resonant photoemission** made with **circularly polarized photons** and by detecting the **spin polarization** of photoelectrons has **confirmed it**.

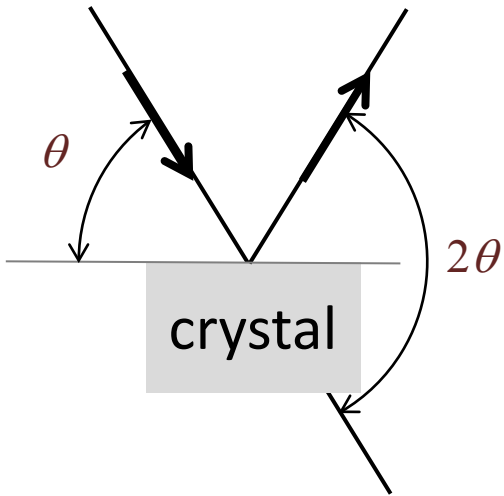


N.B. Brookes, GG et al, PRL 87 237003 (2001); PRL 115, 027002 (2015)

Introduction to Resonant X-ray Scattering



From XRD to X-ray Scattering

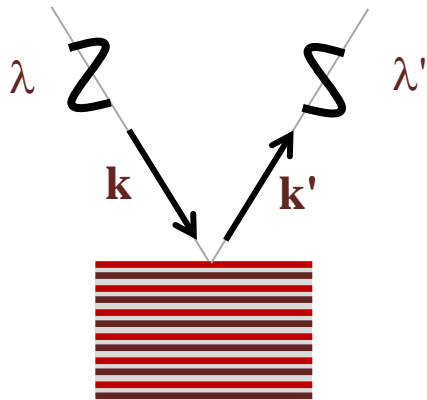
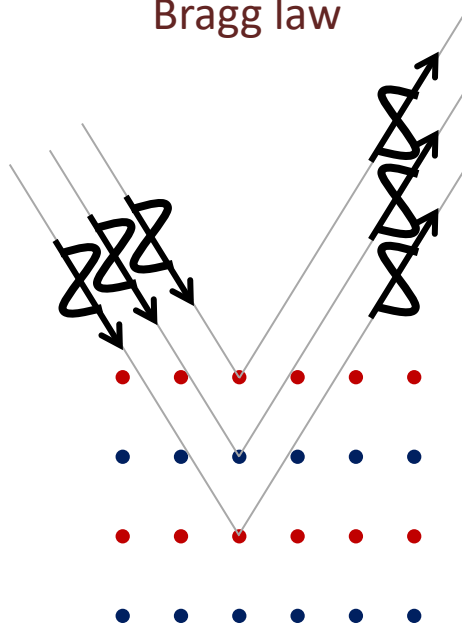


X-Ray Diffraction

$$|\mathbf{k}'| = |\mathbf{k}|$$

$$\lambda = \lambda'$$

Real space Bragg law

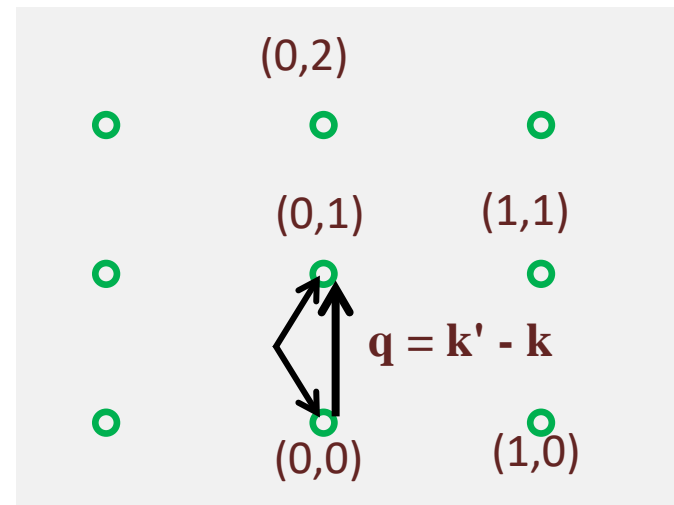


X-Ray Scattering

~~$$|\mathbf{k}'| = |\mathbf{k}|$$~~
~~$$\lambda = \lambda'$$~~

~~$$\mathbf{q} = \mathbf{G}$$~~

Reciprocal lattice $\mathbf{q} = \mathbf{G}$

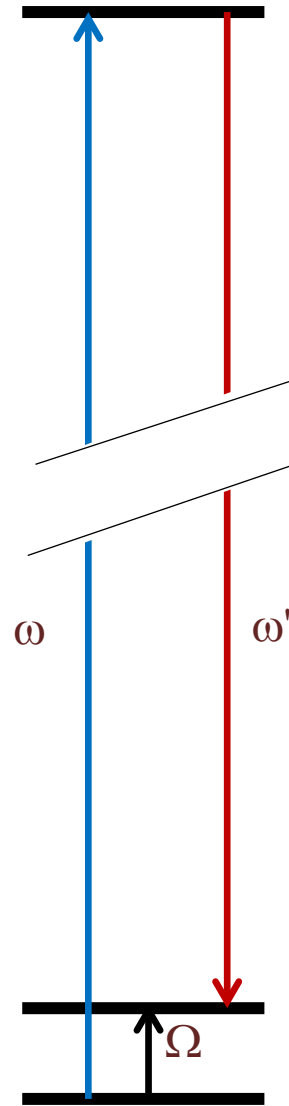
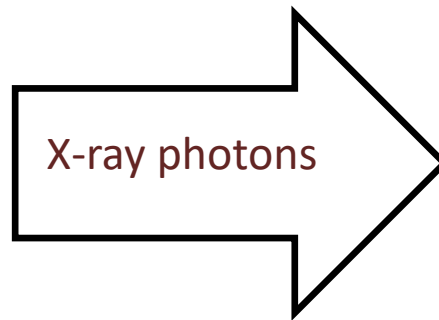
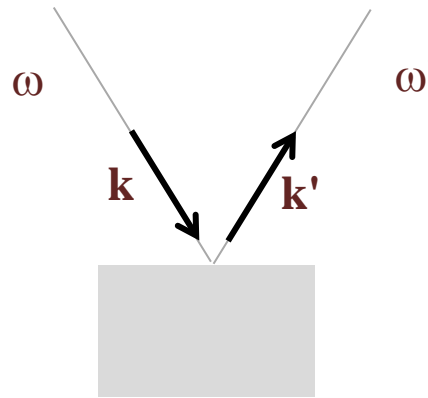
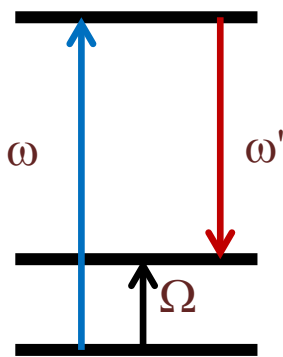


ELS: from Raman to Inelastic X-ray Scattering

Energy Loss Spectroscopy

Raman light scattering

$$k \approx 0, q \approx 0, \Omega = \omega - \omega'$$



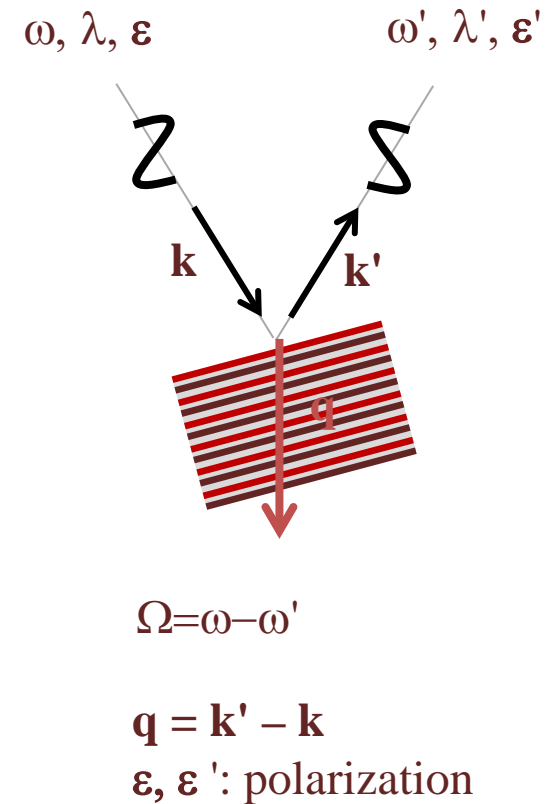
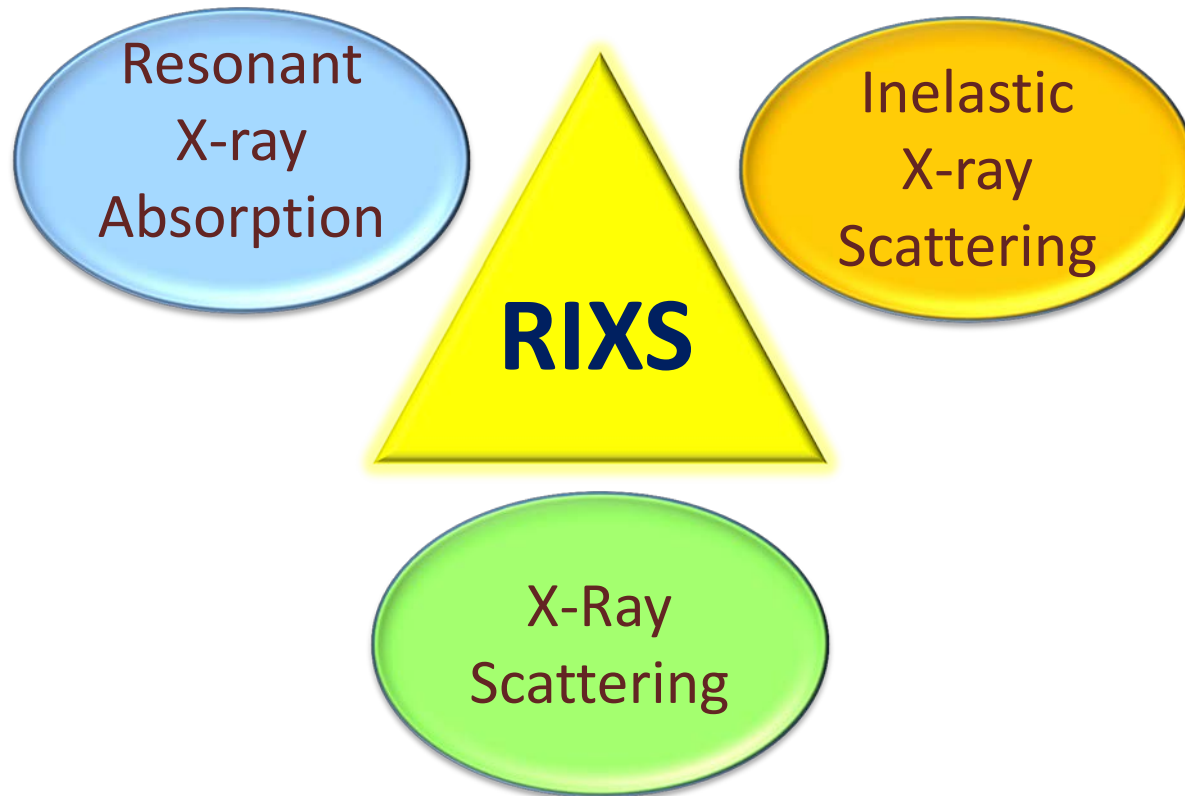
Inelastic X-ray Scattering

$$\Omega = \omega - \omega'$$

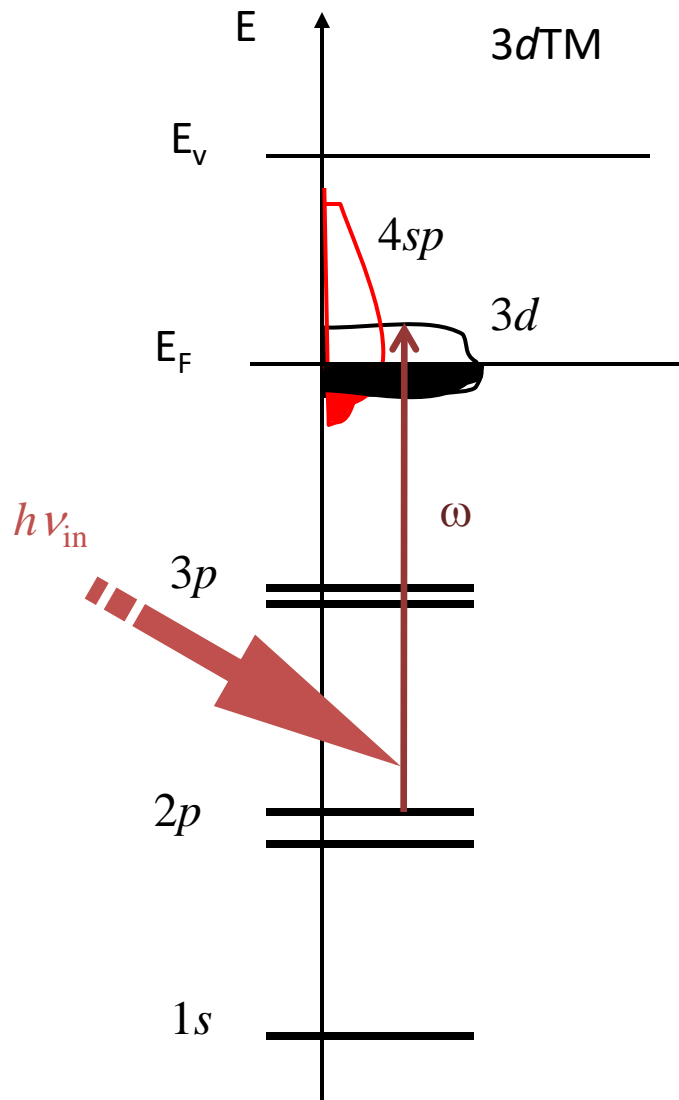
$$\mathbf{q} = \mathbf{k}' - \mathbf{k}$$

RIXS

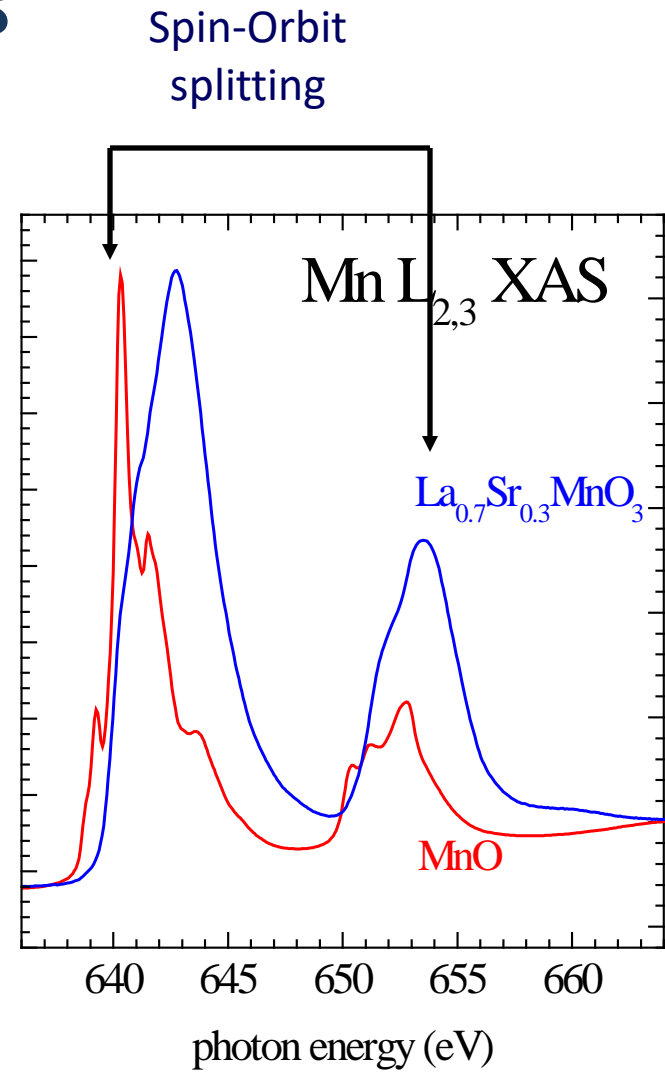
Resonant Inelastic X-ray Scattering



Why soft x-rays for 3d transition metals

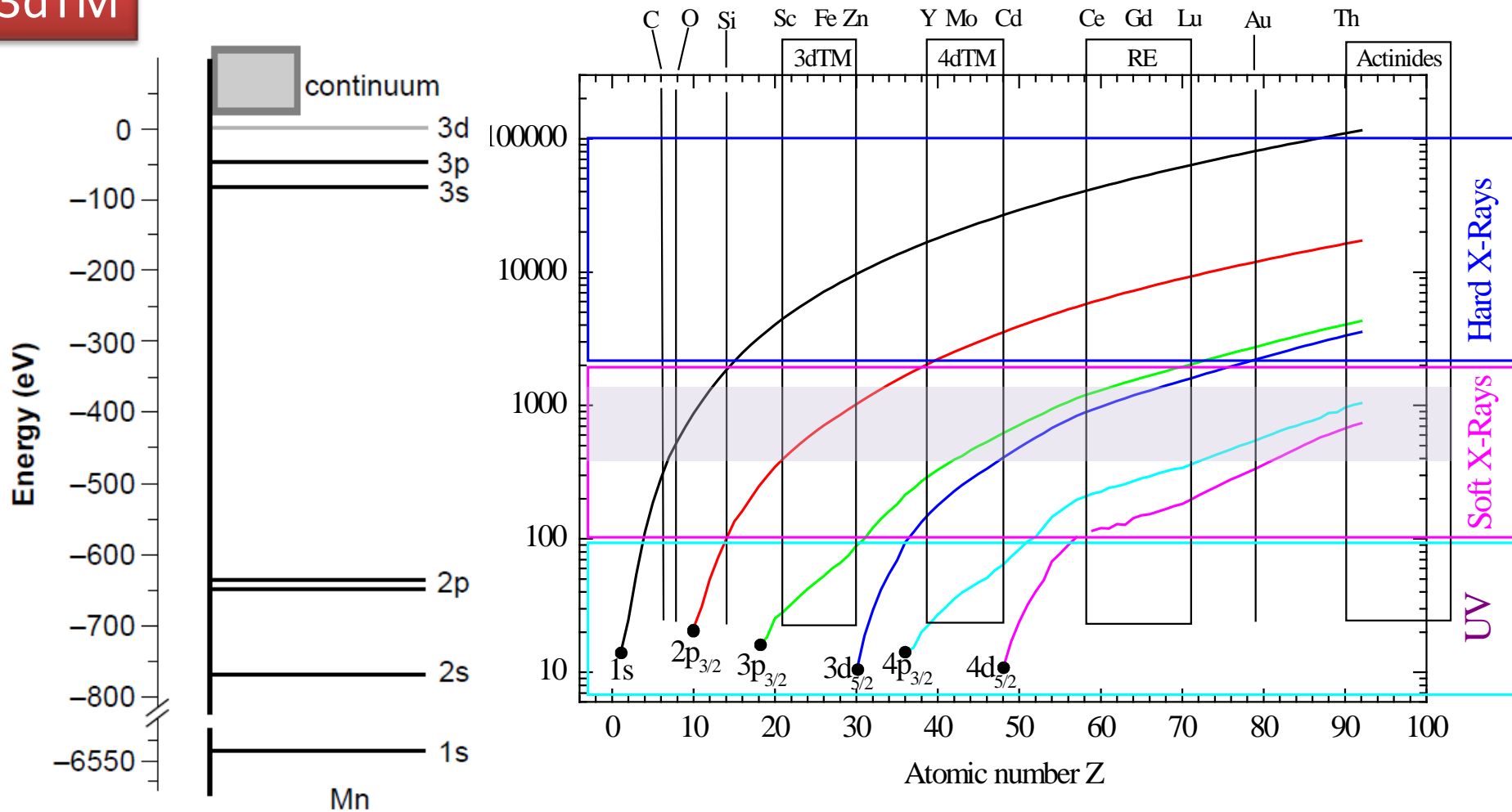


metals

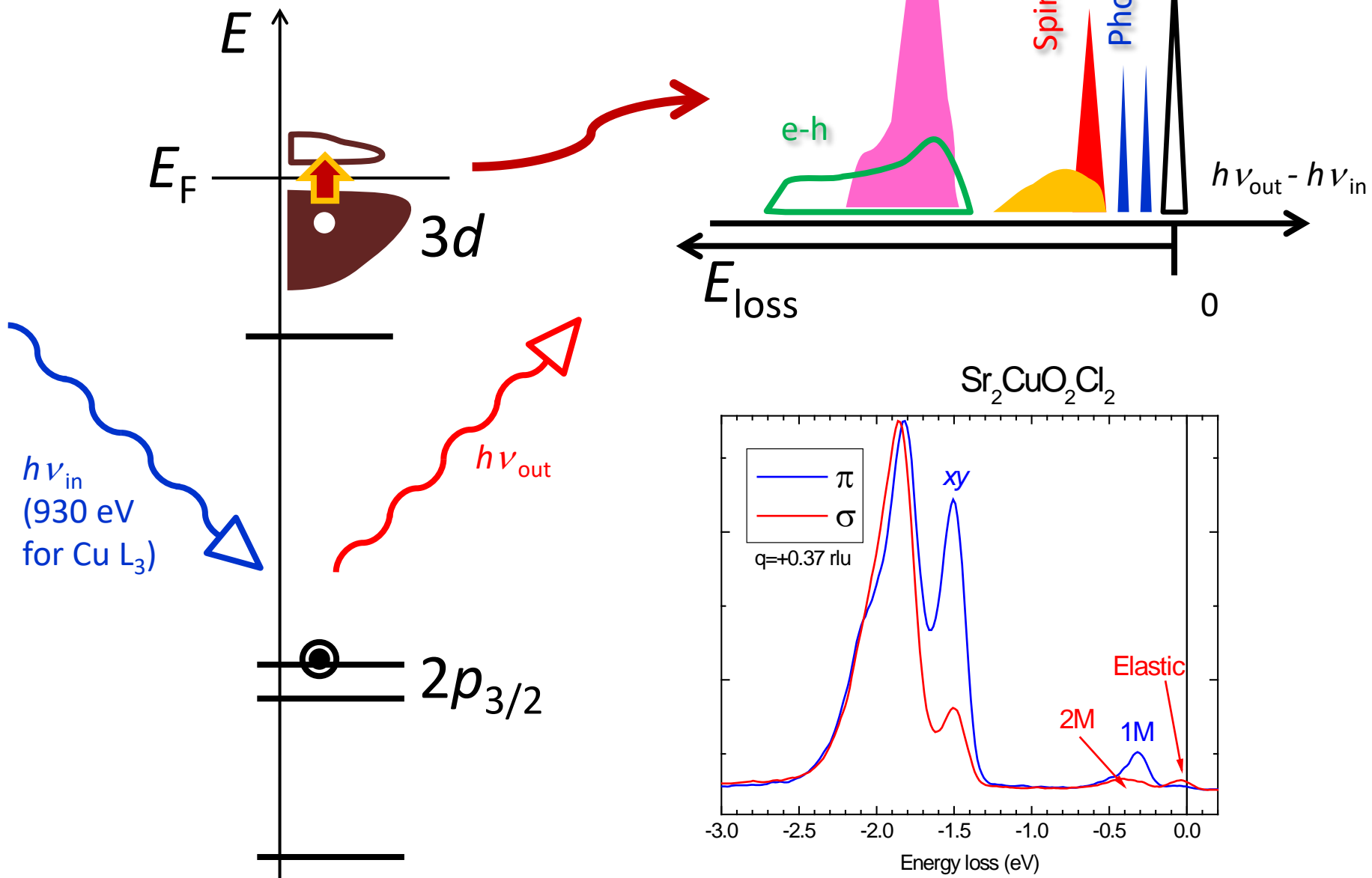


Core level binding energies and edges

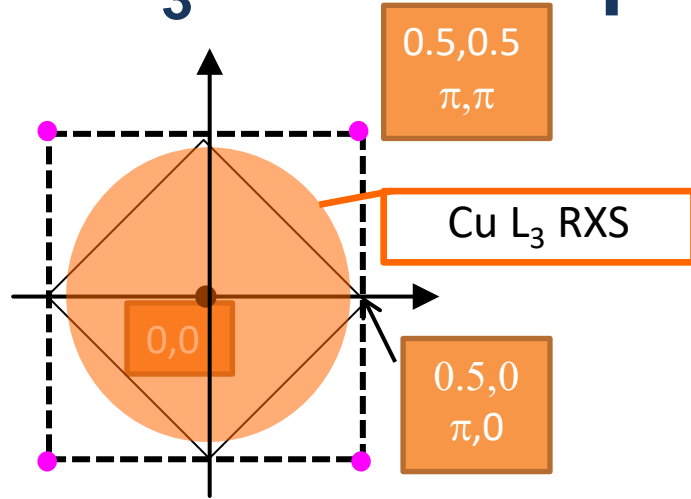
3dTM



Cu L₃ RIXS



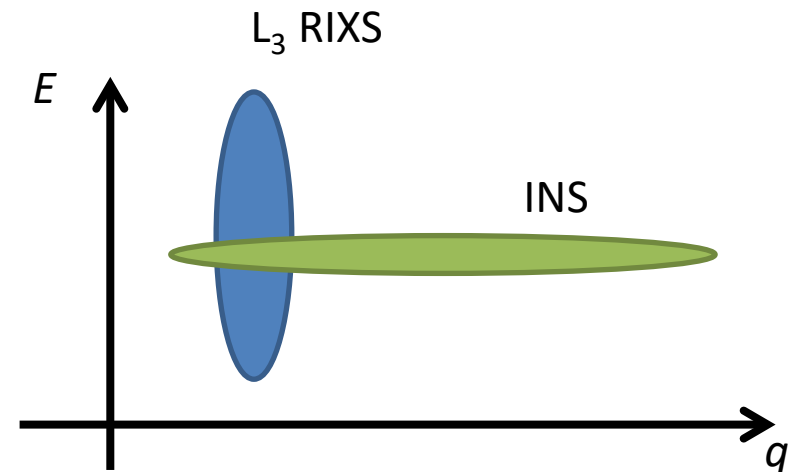
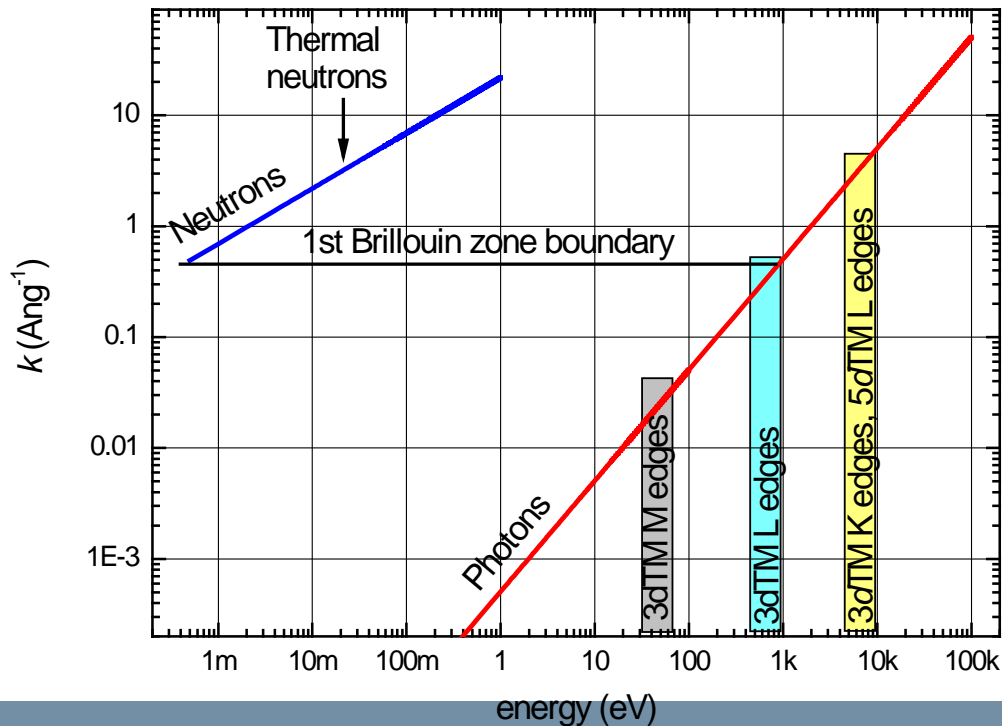
Cu L₃ RIXS: Experimental conditions



Wavevector of particles used in inelastic scattering

Cu L₃ resonance:

- $E_0 = 930$ eV
- $q_{\max} = 0.86$ Ang⁻¹
- confined inside a region around Γ
- 2p core hole: spin-orbit interaction
- **E resolution: 20-50 meV**
- q resolution: 0.005 rlu
- $\frac{1}{2}$ - 1 hour per spectrum

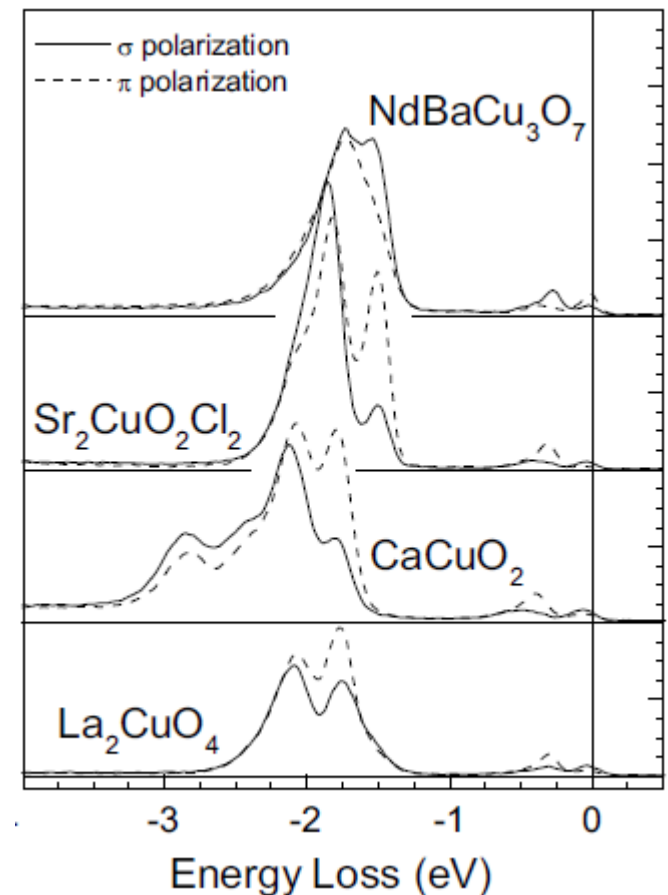
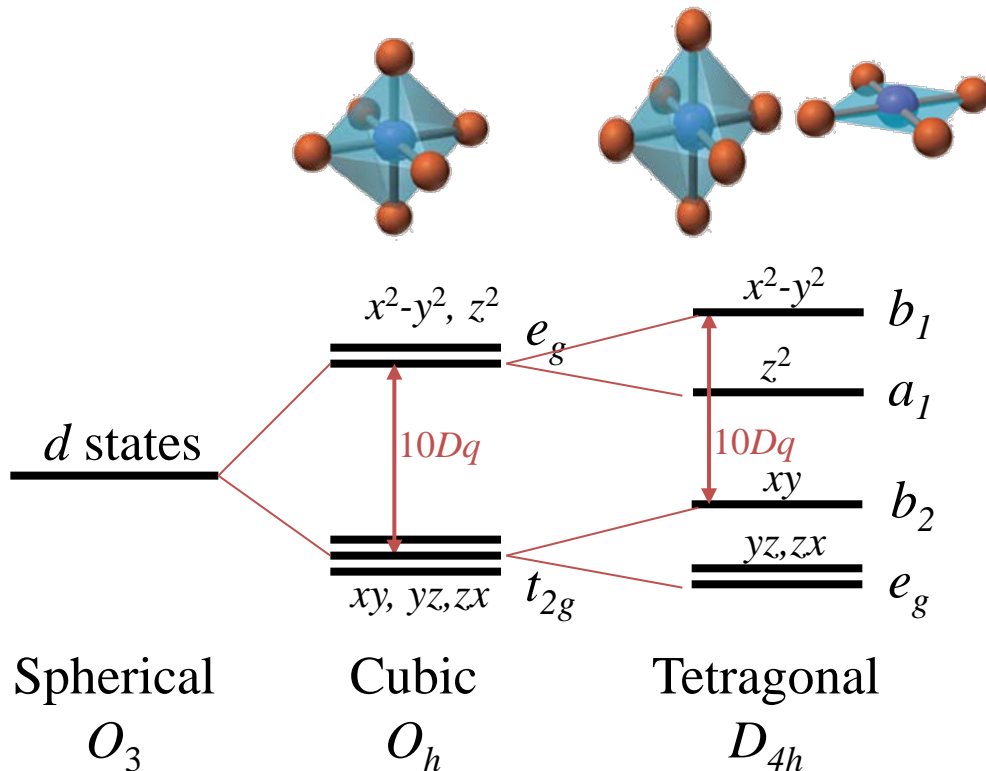


RIXS: crystal field

How much are the 3d orbitals separated in energy in the cuprates (crystal field splitting)?

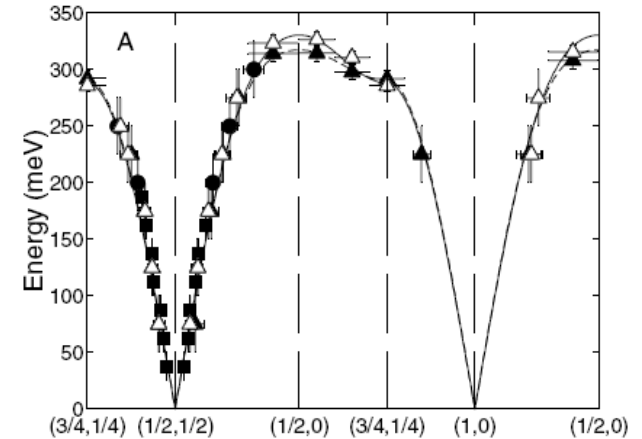
What is the relation to the coordination and atomic distances?

RIXS has determined these values.



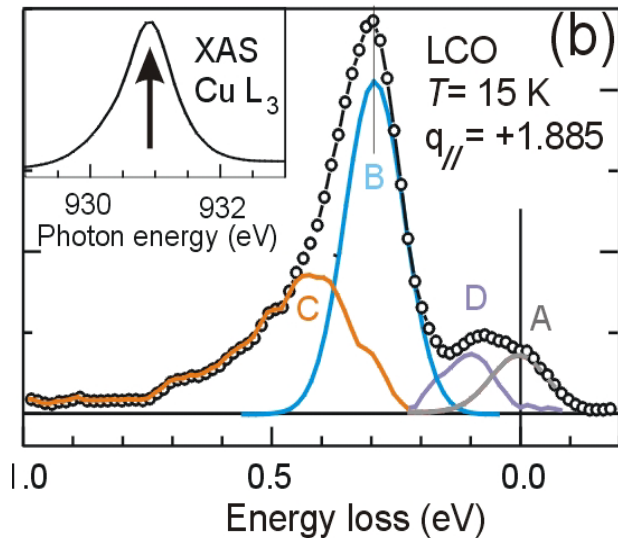
RIXS: spin excitations

RIXS can measure the **dispersion of magnons**. The energy of spin excitations tells us how strong the **exchange interaction** between Cu moments is, ie how stable the **antiferromagnetic order**.

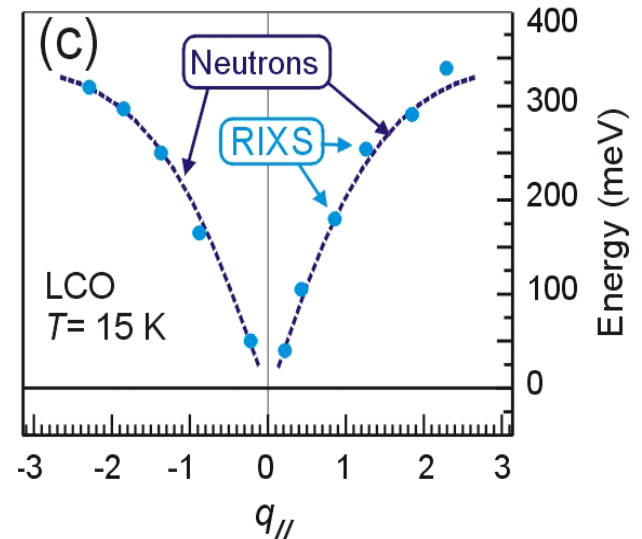


R. Coldea et al, Phys. Rev. Lett. **86**, 5377 (2001).

Until 2010 only neutrons could do that, with limitations due to tiny x-sections



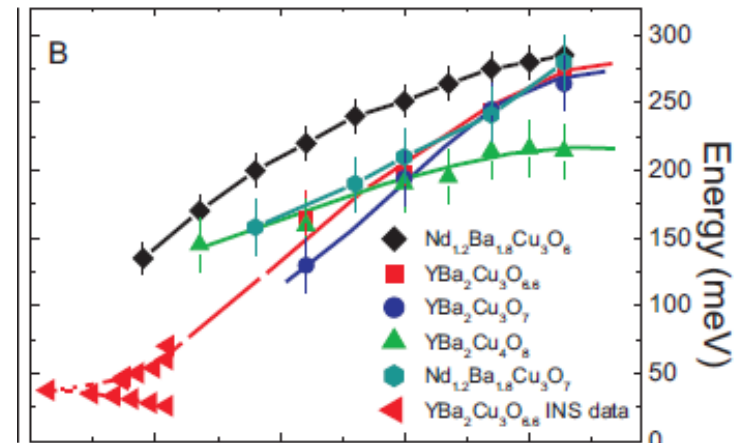
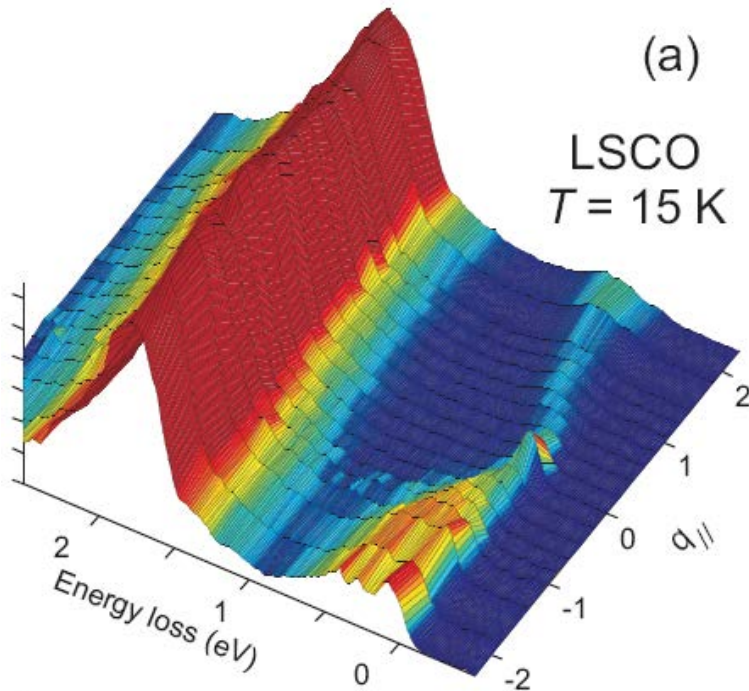
High resolution is necessary



L. Braicovich, J. van den Brink, M. Moretti Sala, GG et al PRL **104** 077002 (2010)

RIXS: paramagnons

Interestingly RIXS has demonstrated that antiferromagnetism remains very strong even in doped, superconducting cuprates.



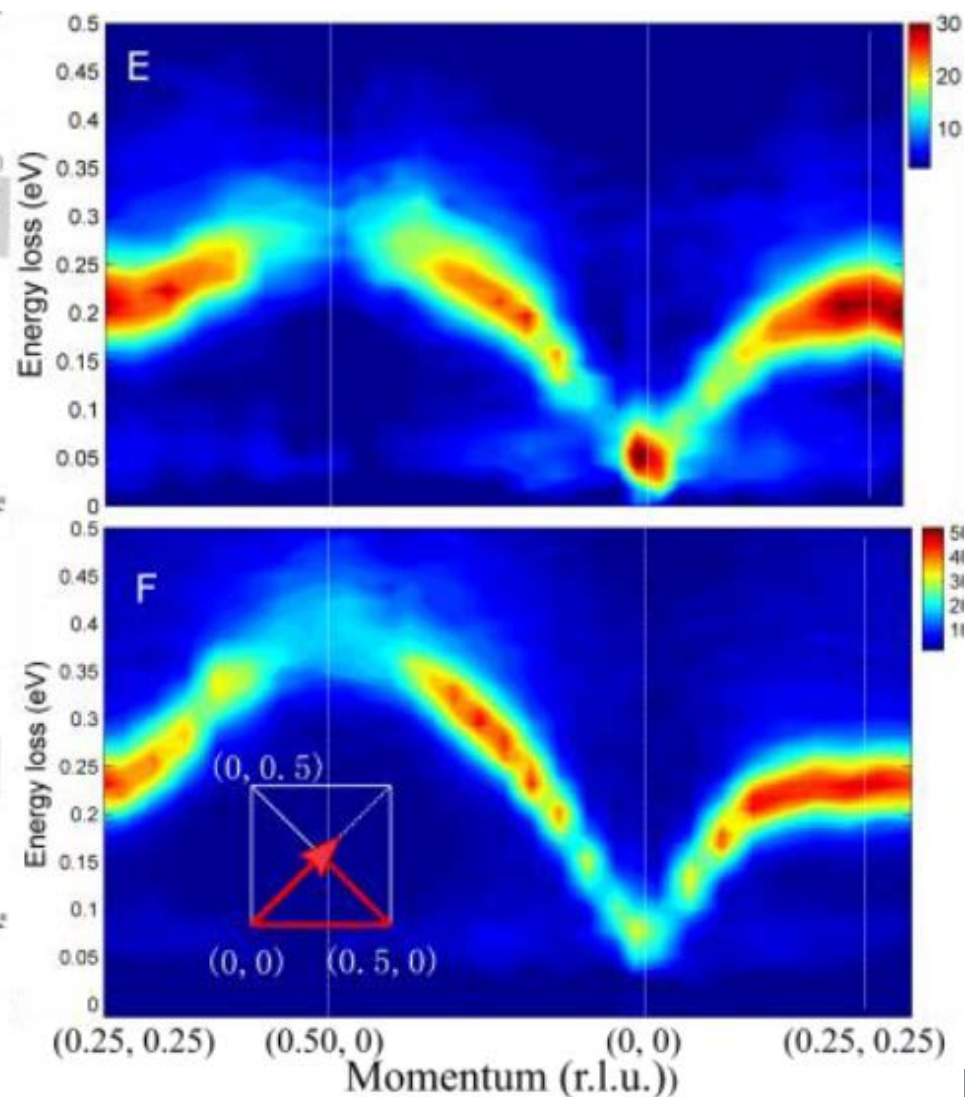
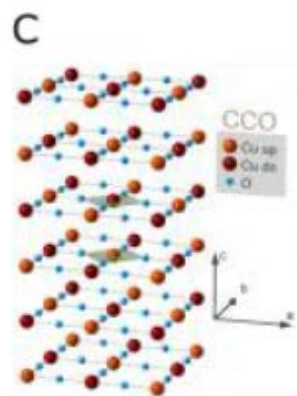
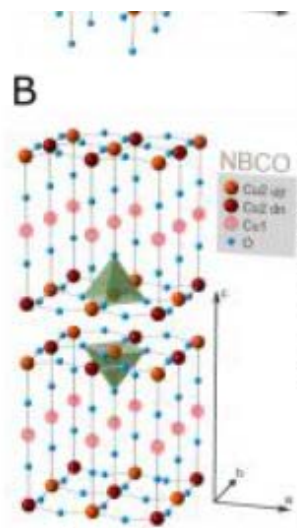
This observation makes **spin fluctuations** the best candidate for **Cooper pairing!**

L. Braicovich, J. van den Brink, M. Moretti Sala, GG et al PRL **104** 077002 (2010)

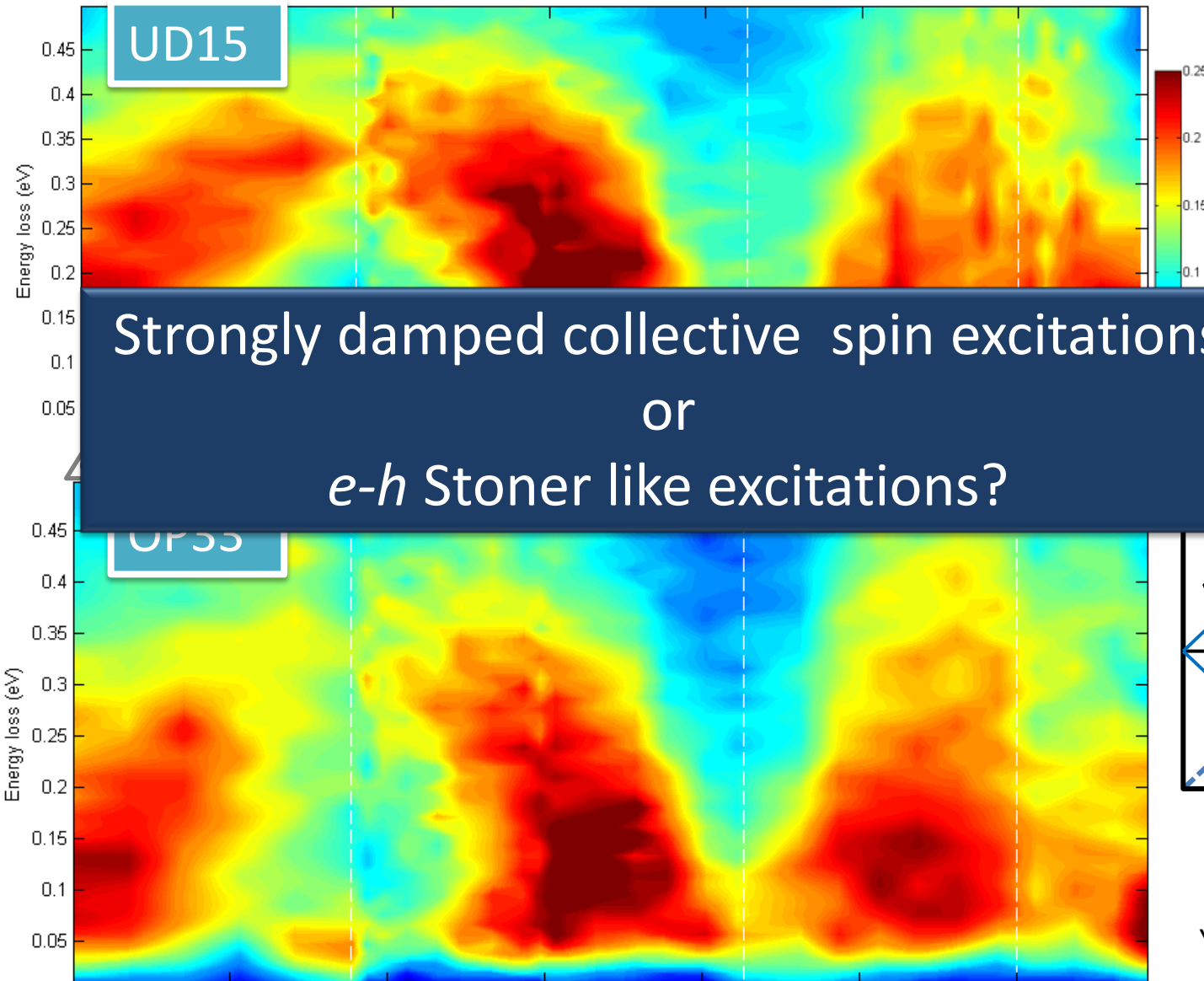
M. Le Tacon, GG, B. Keimer et al, Nat. Phys. **7**, 725 (2011)

ERIXS at ESRF: full maps of magnons

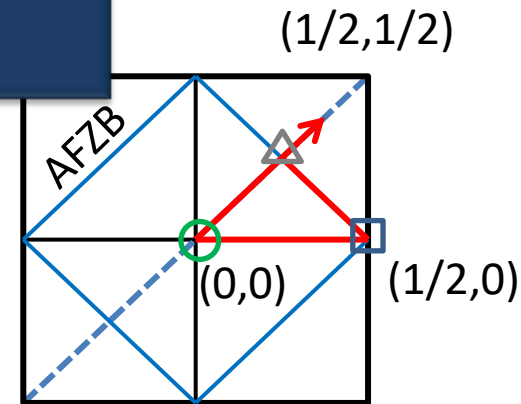
The detailed maps of spin excitations reveal why **different families of cuprates** have **different max T_c**



Paramagnons in Bi2201



Inelastic part

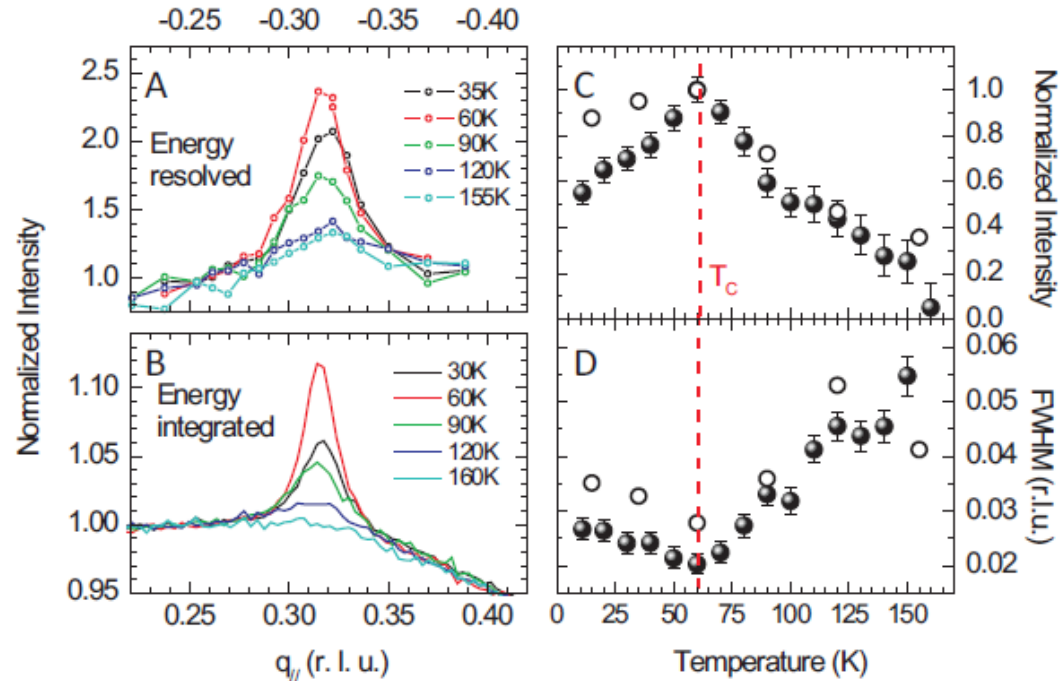
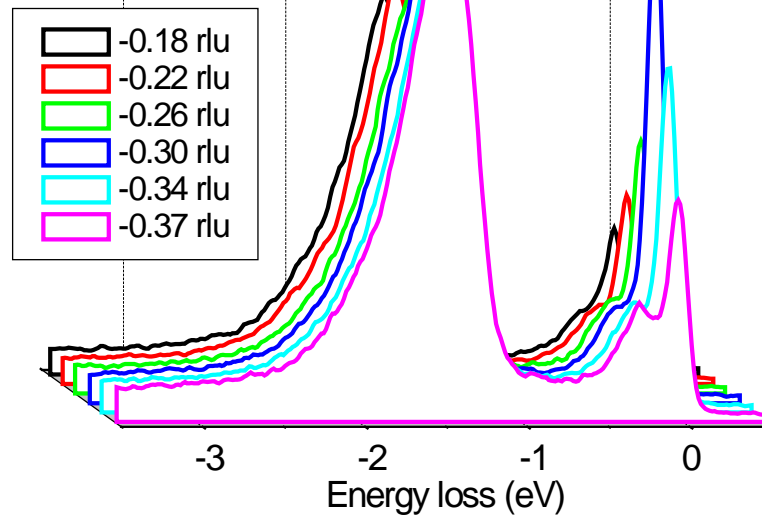


YY. Peng, GG et al, unpublished

R(I)XS: charge density waves

RIXS was used to **discover CDW in YBCO**. Within a few months, CDW were observed, with RIXS and other techniques, in many other cuprates

NBCO $T_c=65K$
V pol, $T=15K$

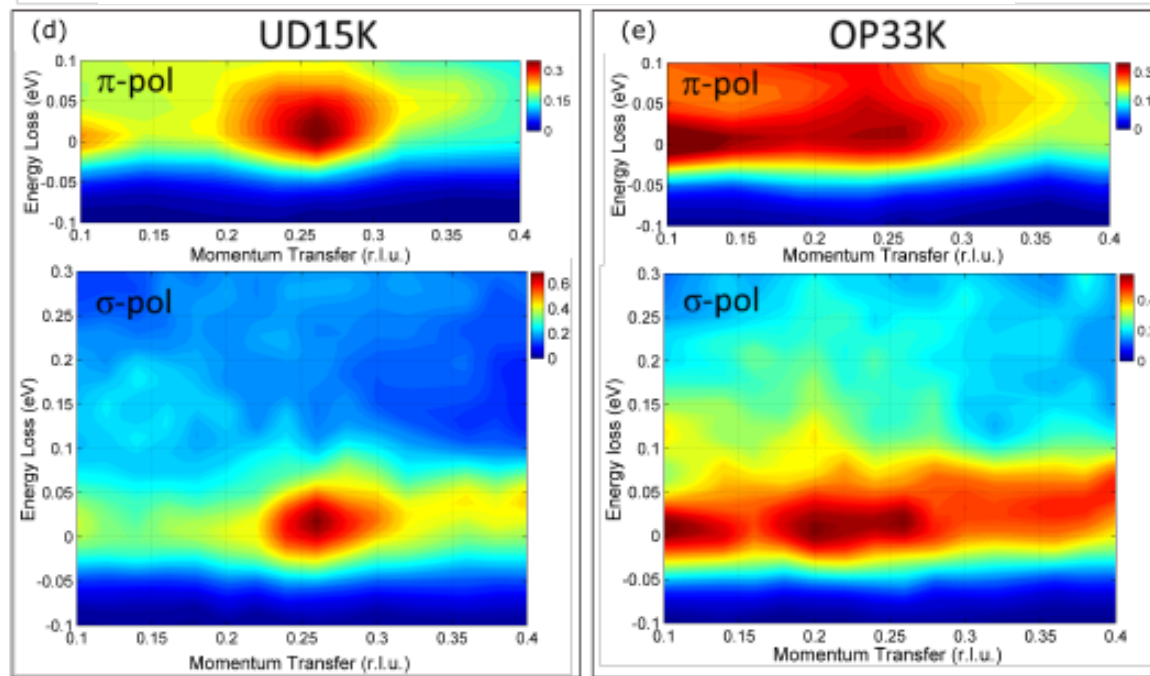
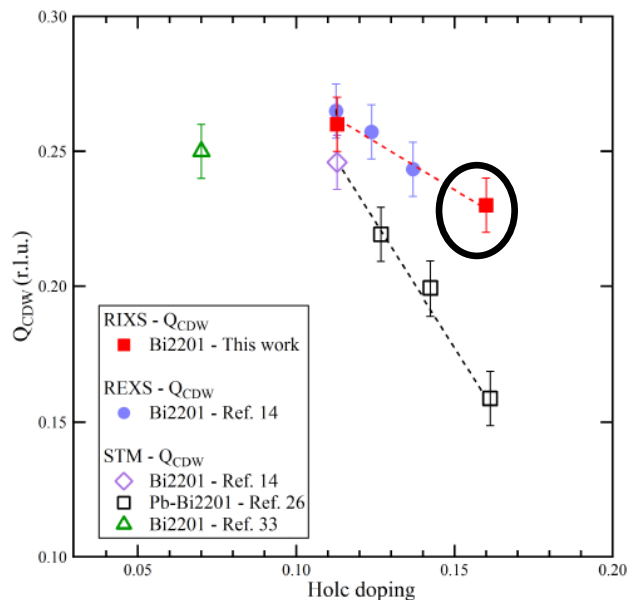
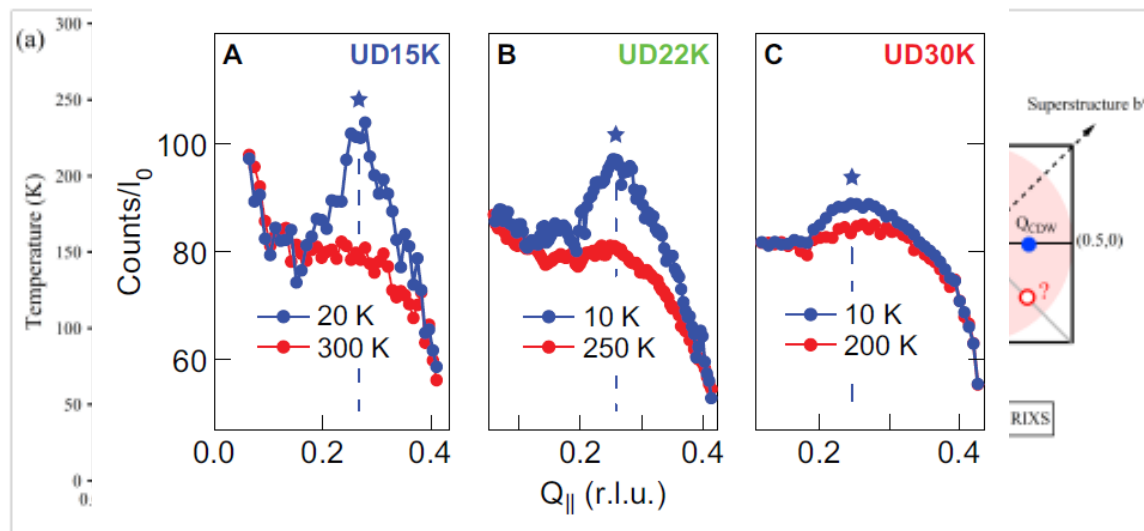


Max intensity at T_c : CDW compete with SC

RXS (and STM, XRD and NMR) has demonstrated that CDW are present in all underdoped cuprates. Are CDW related to Superconductivity?

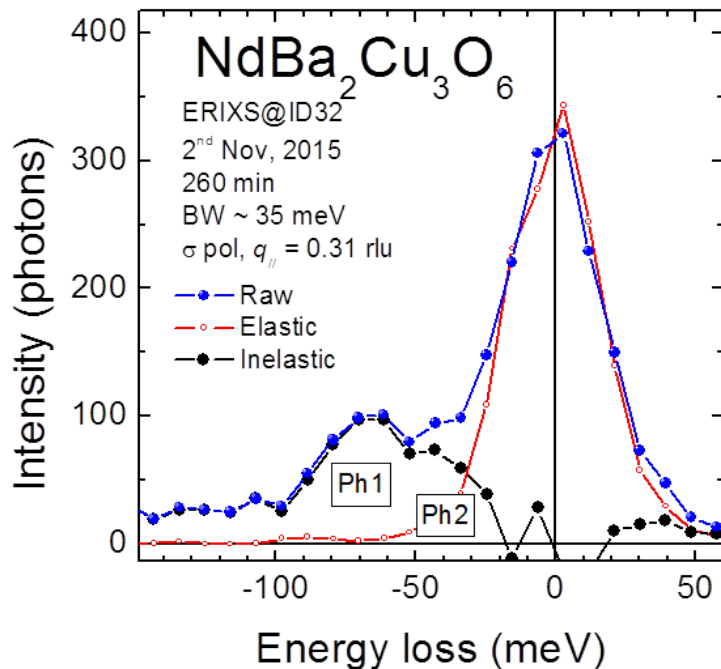
CDW and new generation RIXS

Higher sensitivity
reveals CDW in
optimally doped
Bi2201



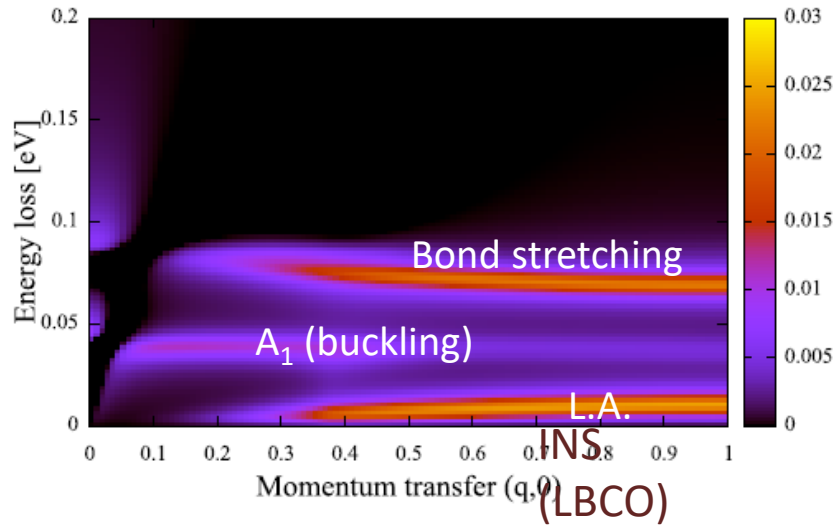
ERIXS: electron-phonon coupling

The very high resolution of ERIXS at ID32 allows the detection of phonons with RIXS. This is a very direct way of measuring the e-ph coupling.



The mapping of the e-ph coupling can clarify the role of CDW in superconductivity

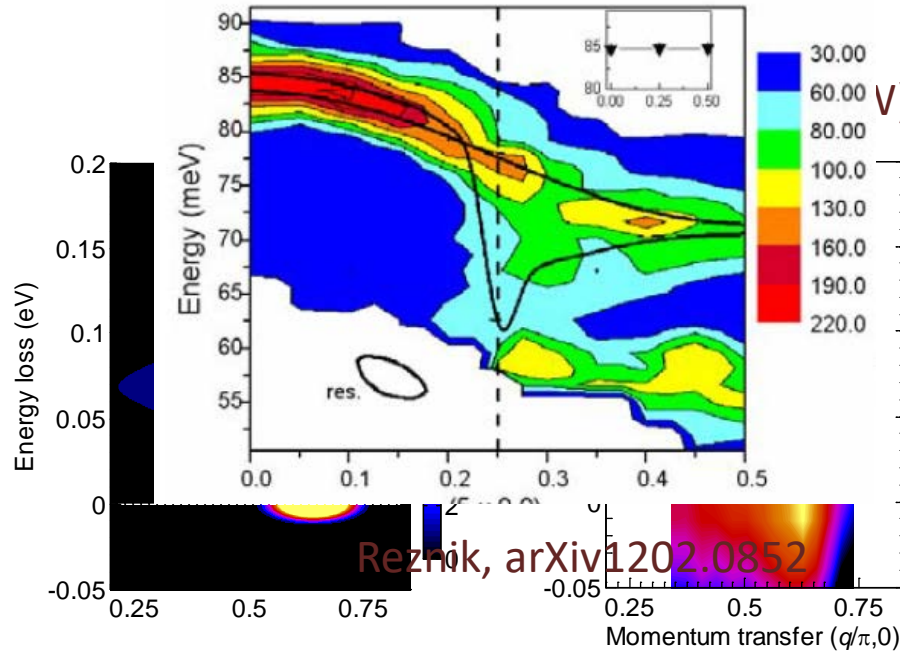
More work on e - ph coupling



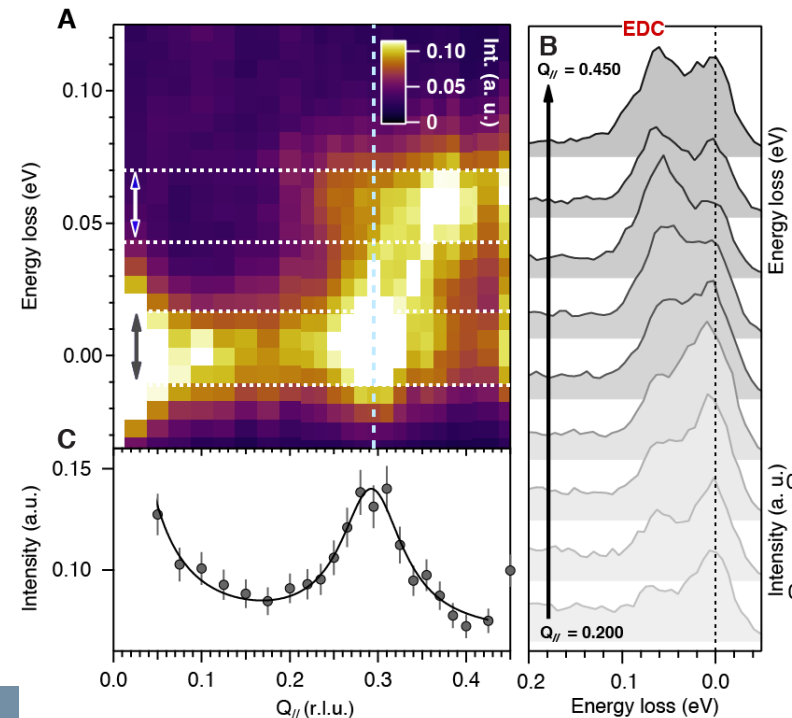
Theoretical phonon intensity in RIXS

T. P. Devereaux, A. M. Shvaika, K. Wu, K. Wohlfeld, C.-J. Jia, Y. Wang, B. Moritz, L. Chaix, W.-S. Lee, Z.-X. Shen, G. Ghiringhelli, and L. Braicovich, PRX **6**, 041019 (2016)

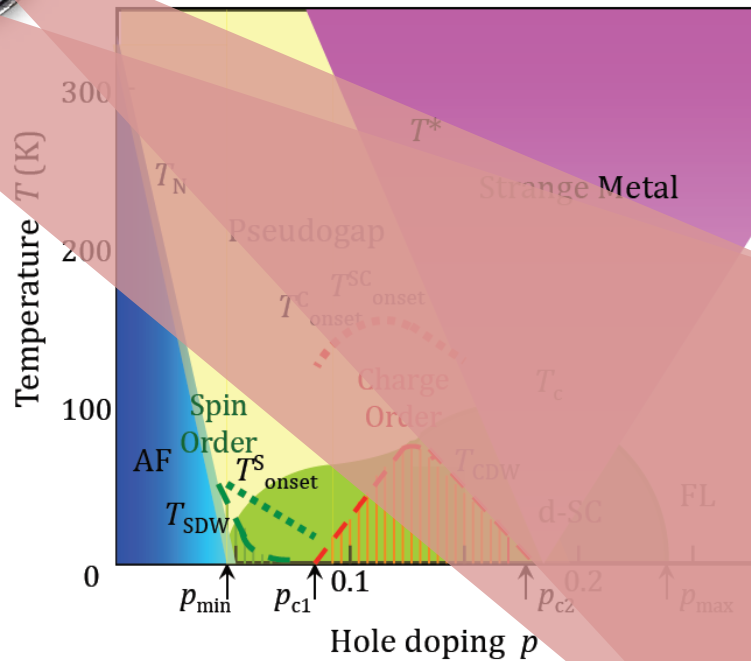
L. Chaix, G. Ghiringhelli, Y. Y. Peng, M. Hashimoto, Y. He, S. Chen, K. Kummer, N.B. Brookes, B. Moritz, S. Ishida, Y. Yoshida, H. Eisaki, L. Braicovich, Z.-X. Shen, T. P. Devereaux, W.-S. Lee, submitted



Exp. (40 meV BW)



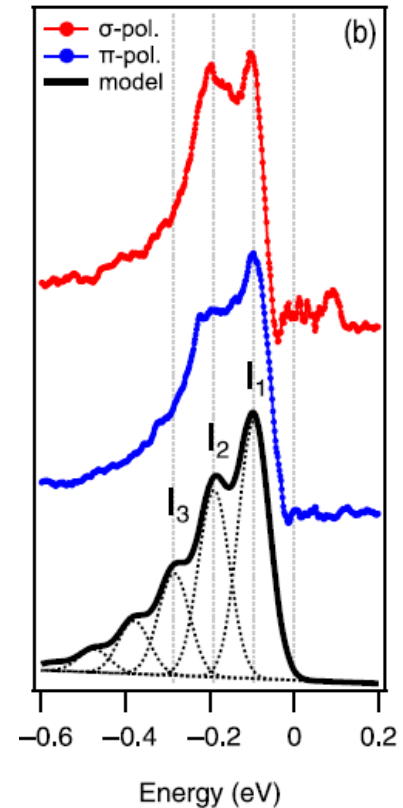
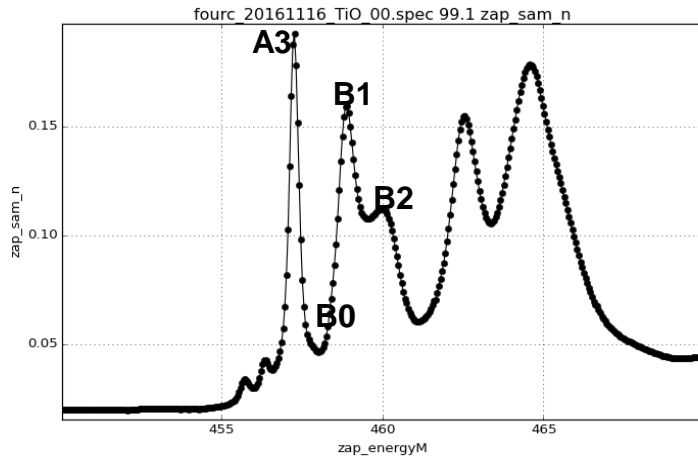
Conclusions



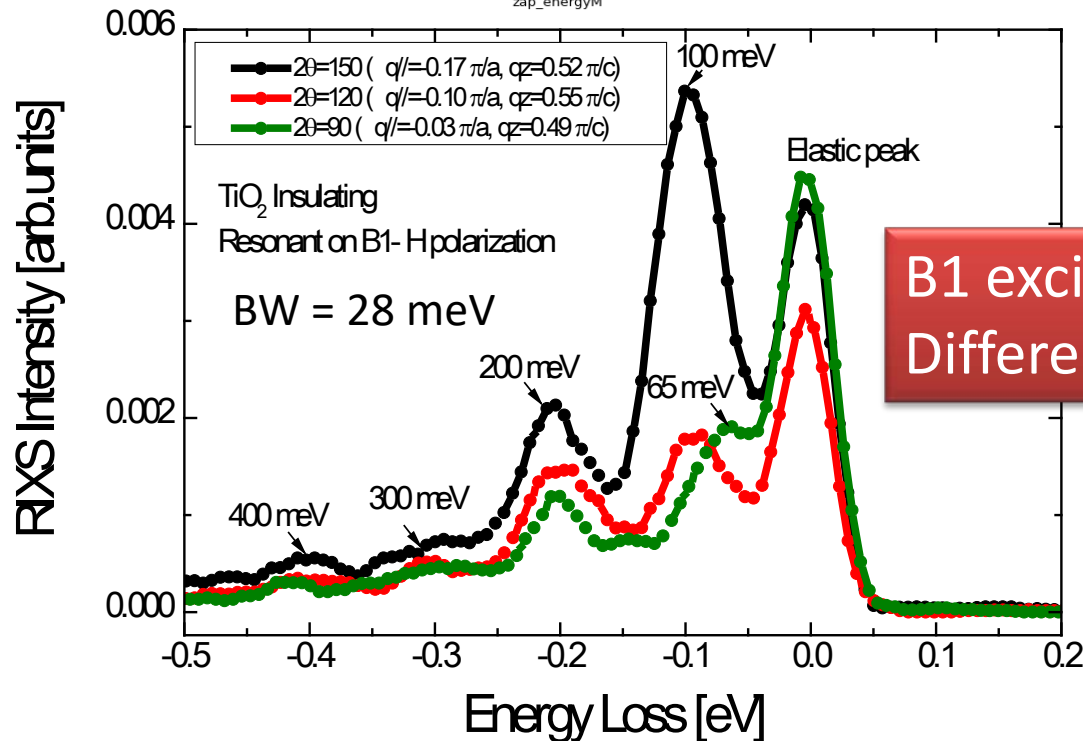
Thanks



Phonons in TiO₂



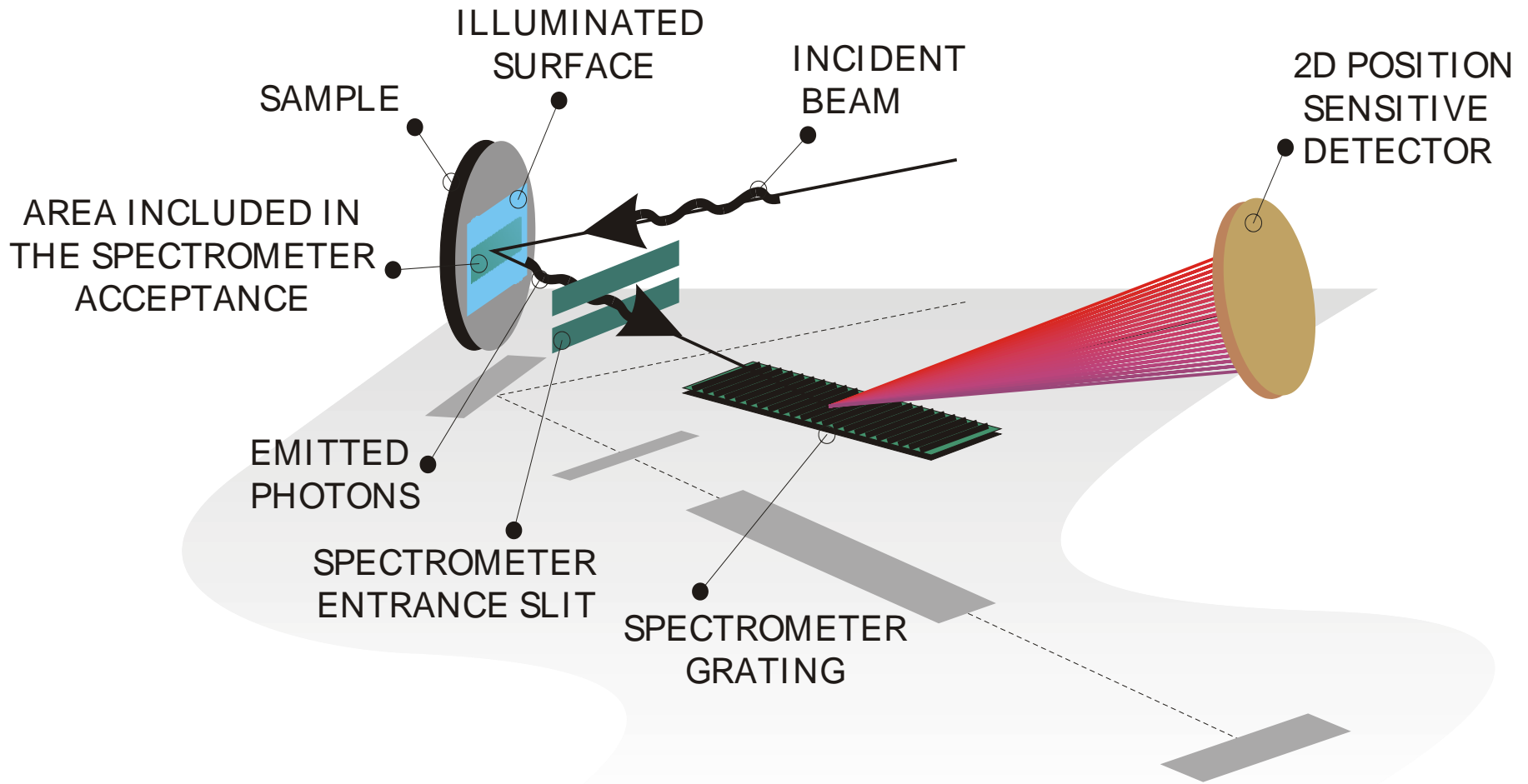
Moser et al, PRL **115**, 096404 (2015)



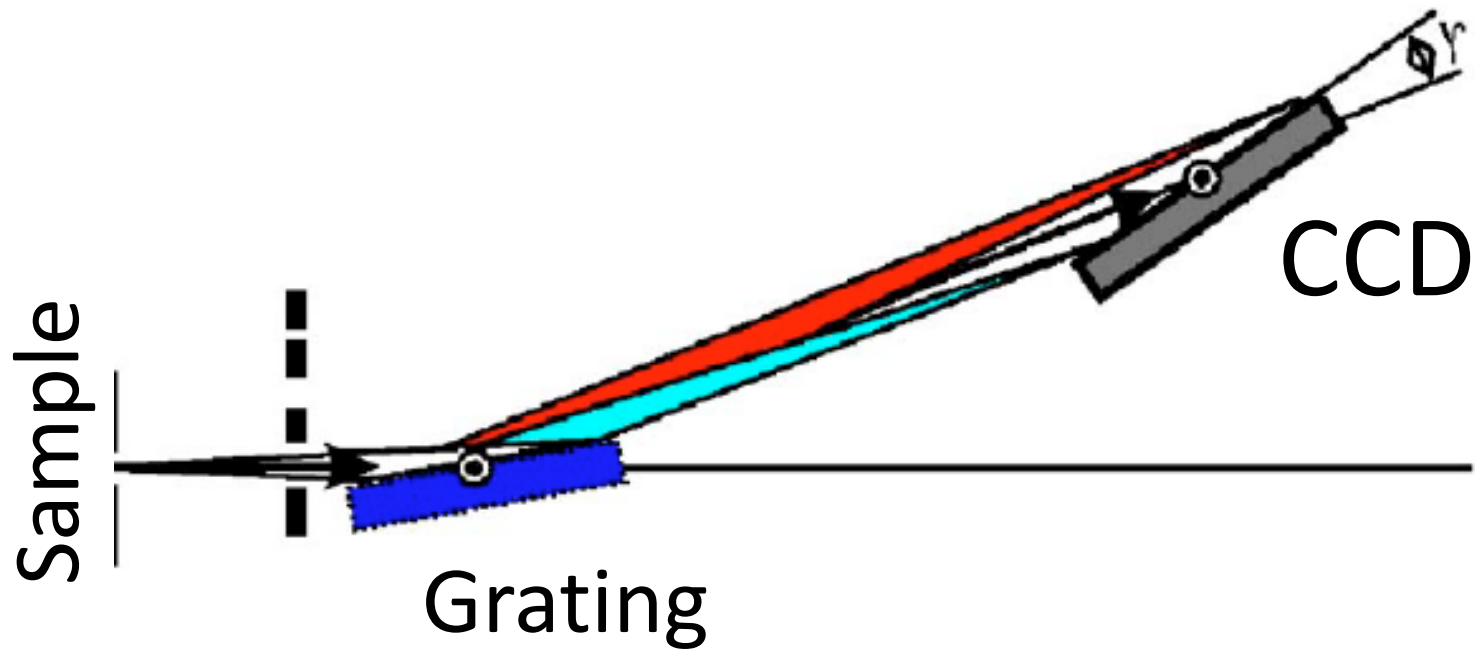
B1 excitation
Different q

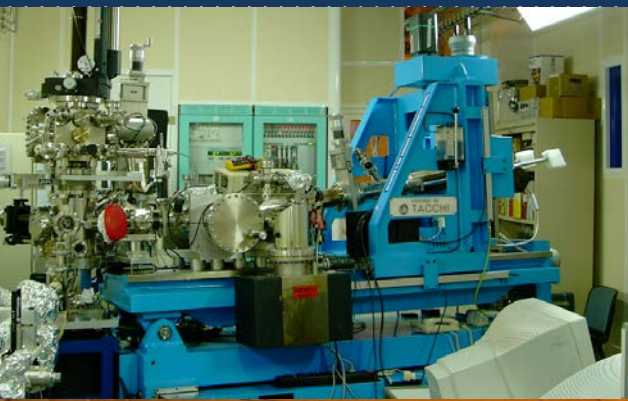
M. Salluzzo, G.M. De Luca, YY Peng, R. Fumagalli, D. Betto, L. Braicovich, G. Ghiringhelli, unpublished

Soft x-ray spectrometer



Longer instruments for better resolution





AXES: 2.2 m
ID12B and ID08



SAXES, SLS: 5 m



ERIXS, ID32: 10 m

ERIXS at ID32



Resolving power: 40,000
at 1 keV
3 times better than
previous record

Collimating Mirror
to increase
horizontal
acceptance

Two CCD detectors

Multi-layer mirror,
to measure
polarization of
scattered photons

Two Gratings,
to optimize for
resolution or
efficiency

