Inelastic scattering spectroscopy with neutrons and X-rays to study superconducting materials:

Part II magnetic superconductors and magnetic excitations

Matteo d'Astuto

Institut Néel CNRS/UGA UPR2940

matteo.dastuto@neel.cnrs.fr

Summary

- *Magnetism in “exotic” superconductors*
- *Magnetic spectroscopies with X-rays and neutrons*
- *Resonant Inelastic X-ray Scattering spectroscopy*
- *(Para)Magnon dispersion in cuprates with INS and RIXS*

Further readings

Basic textbooks in neutron and x-ray physics

- “Introduction to the Theory of Thermal Neutron Scattering”, G.L. Squires (Dover Publications,1996)
- “Theory of Neutron Scattering from Condensed Matter”, Stephen W. Lovesey (Clarendon Press, 1986)
- “Elements of Modern X- ray Physics”, Jens Als- Nielsen Des McMorrow (John Wiley & Sons, 2011)
- “JDN 16 – Diffusion Inélastique des Neutrons pour l'Étude des Excitations dans la Matière Condensée”, S. Rols, S. Petit, J. Combet et F. Leclercq-Hugeux (Eds.) (EDP Sciences, 2010)

Further readings

Advanced readings in x-ray physics

- "Core Level Spectroscopy of Solids", Frank de Groot, Akio Kotani (2008, CRC Press)
- "Resonant inelastic x-ray scattering studies of elementary excitations", L. J. P. Ament, M. van Veenendaal, T. P. Devereaux, J. P. Hill, J. van den Brink, *Reviews of Modern Physics* **83** (2011)

Further readings

Basic textbooks in superconductivity

...there are many, my preferred one is:

- "Theory of Superconductivity" (Advanced Books Classics), J. Robert Schrieffer (Perseus Books, 1999)

Further readings

Advanced readings in cupates superconductivity (non exhaustive list by far...)

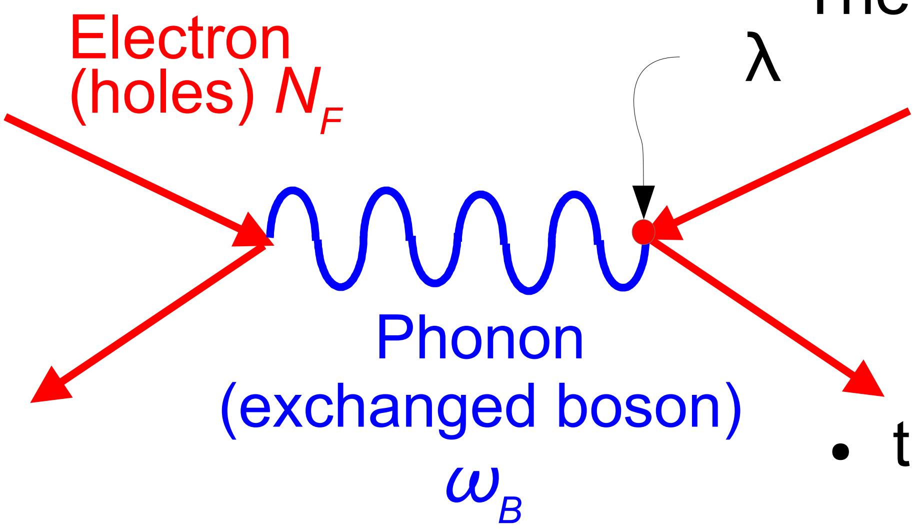
- A. Damascelli *et al.*, *Rev. Mod. Phys.* **75** (2003) 473;
- D. A. Bonn, *Nature Physics* **2** (2006) 159;
- D. J. Scalapino, *Rev. Mod. Phys*. **84** (2012) 1383.

Electron - phonons interactions and superconductivity in a nutshell

Superconductivity basic idea:

creation of “Cooper pairs” ⇨ “bosonic” charge carriers

Reciprocal space



The transition temperature (Tc) is function of:

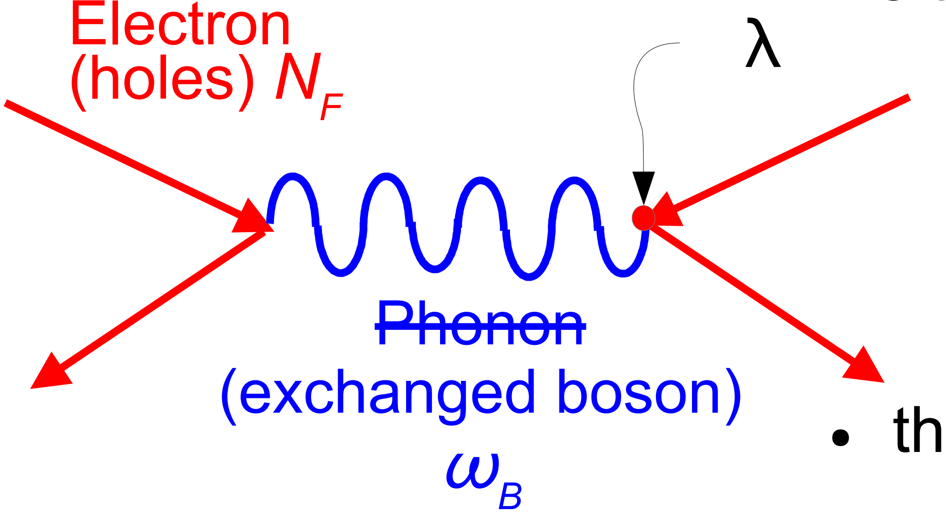
- the boson frequency (ω_B);
- the interaction strength (λ);
- the electron density @ Fermi surface (N_F).

Electron - phonons interactions and superconductivity in a nutshell

Superconductivity basic idea:

creation of “Cooper pairs” ⇨ “bosonic” charge carriers

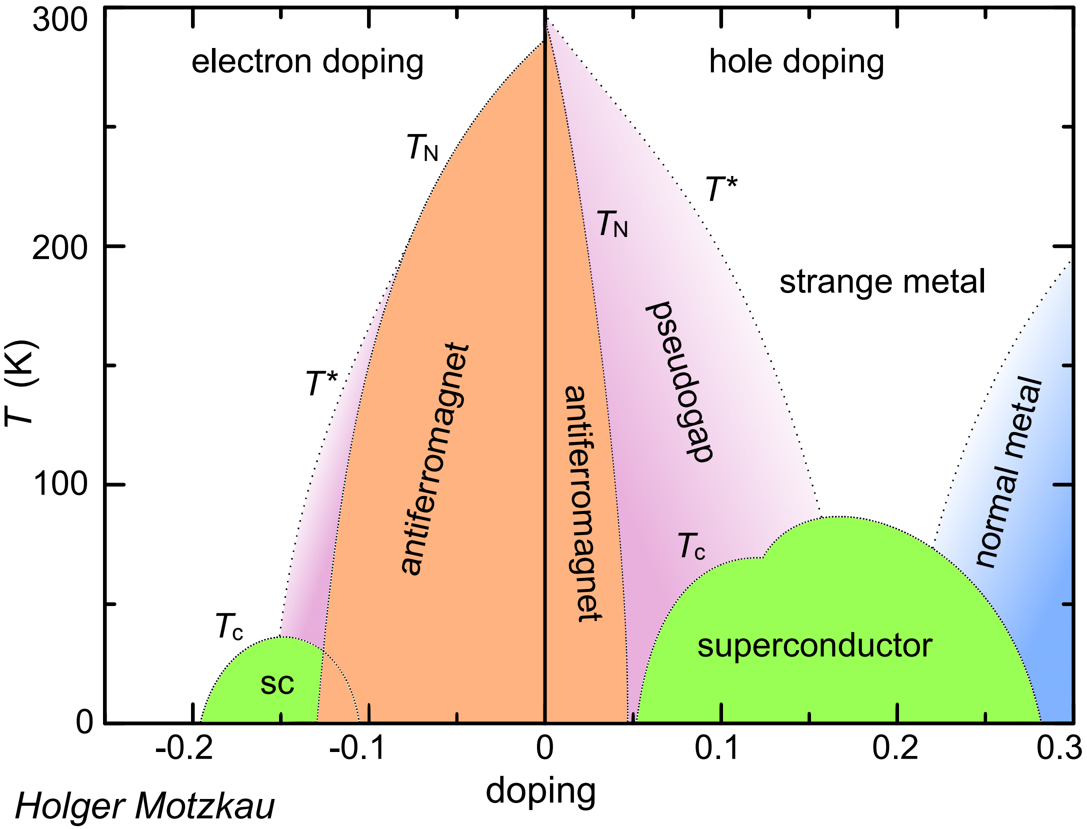
Reciprocal space



The transition temperature (Tc) is function of:

- the boson frequency (ω_B);
- the interaction strength (λ);
- the electron density @ Fermi surface (N_F).

Background HTS cuprate



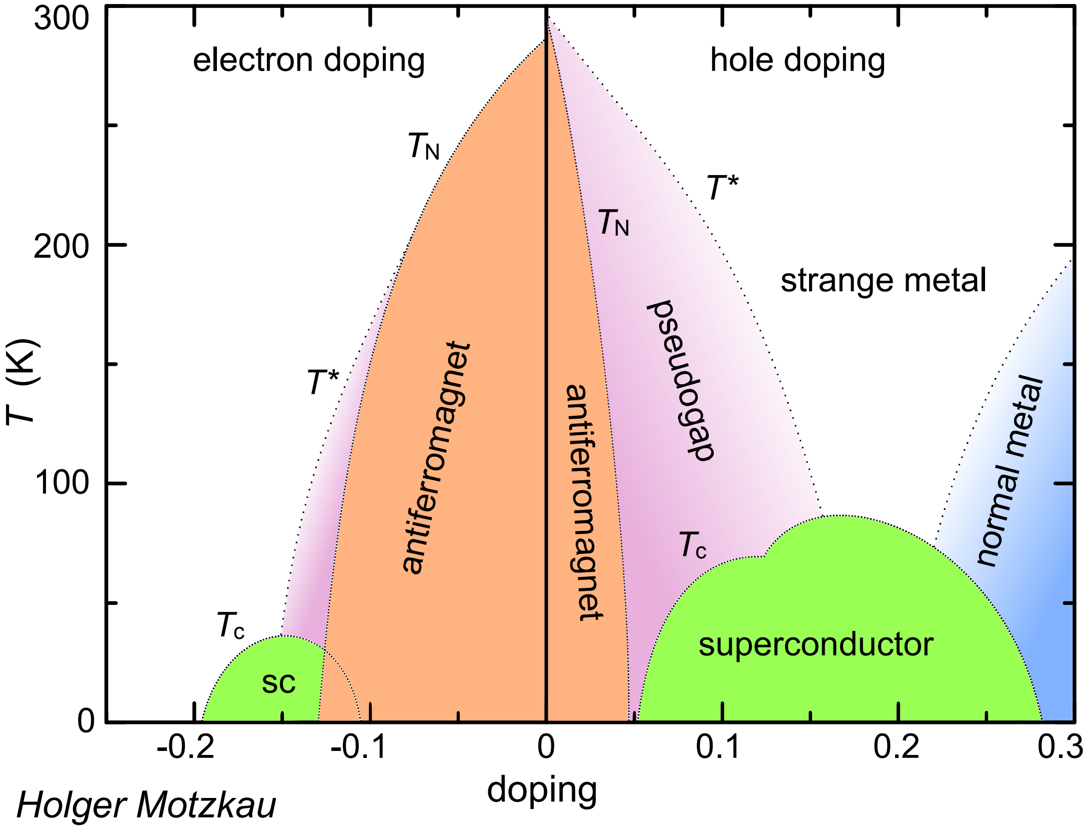
Holger Motzkau
[CC BY-SA 3.0] *Wikimedia Commons*

- *Mott-Hubbard insulator (charge transfer): Coulomb on-site repulsion*

Insulator

Strong exchange (antiferromagnet)

Background HTS cuprate



Holger Motzkau
[CC BY-SA 3.0] *Wikimedia Commons*

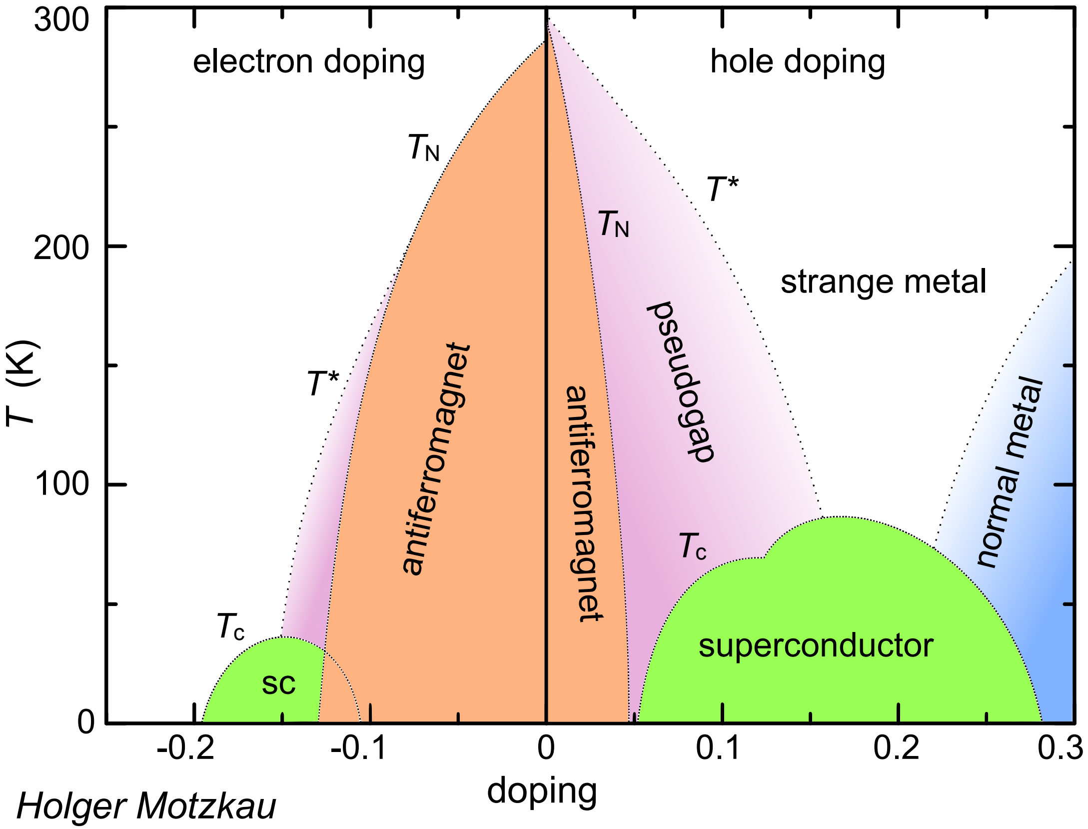
- *Mott-Hubbard insulator (charge transfer): Coulomb on-site repulsion*

Insulator

Strong exchange (antiferromagnet)

- *Doping induce transition to metal with:*
  - *superconductivity*

Background HTS cuprate



Holger Motzkau
[CC BY-SA 3.0] *Wikimedia Commons*

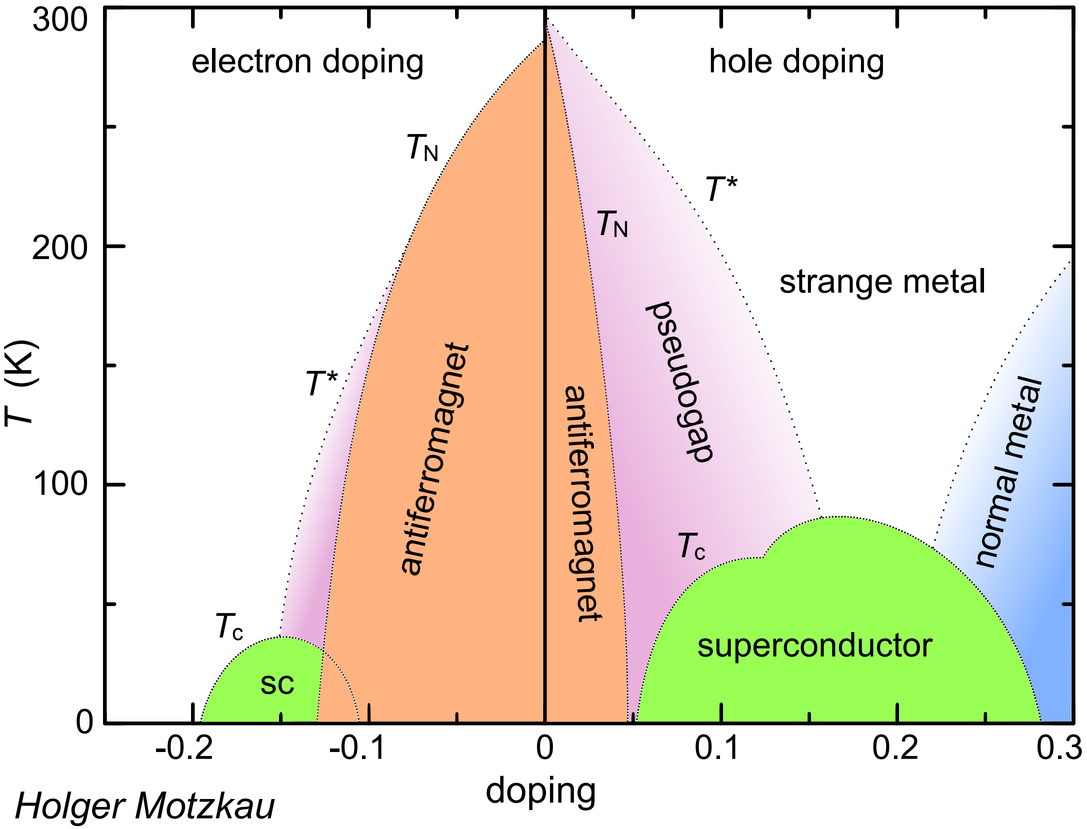
- *Mott-Hubbard insulator (charge transfer): Coulomb on-site repulsion*

Insulator

Strong exchange (antiferromagnet)

- *Doping induce transition to metal with:*
  - *superconductivity*
  - *persistent exchange*

Background HTS cuprate



Holger Motzkau
[CC BY-SA 3.0] *Wikimedia Commons*

- Mott-Hubbard insulator (charge transfer): Coulomb on-site repulsion

Insulator

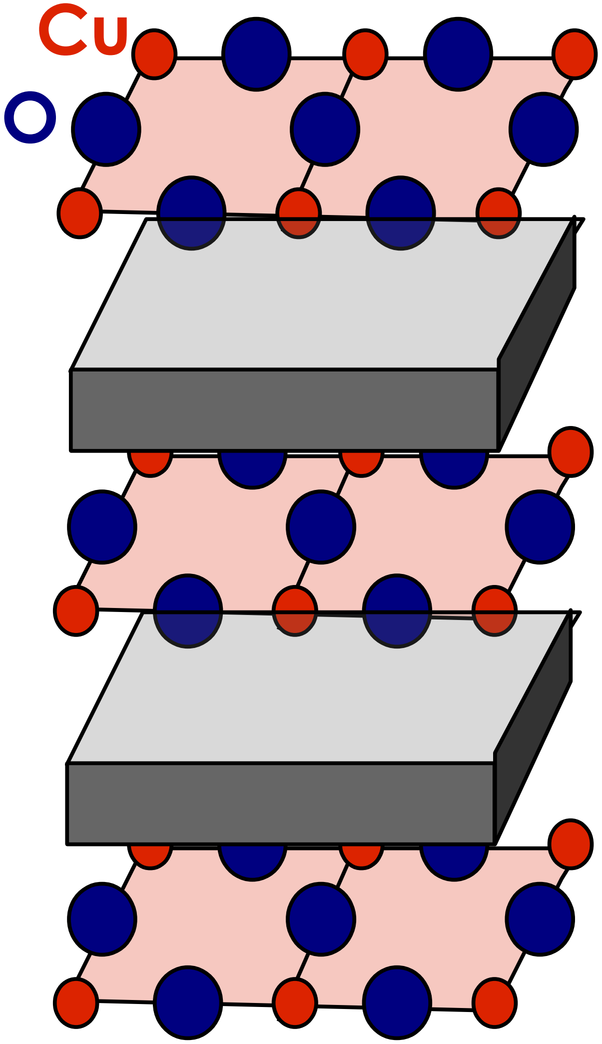
Strong exchange (antiferromagnet)

- Doping induce transition to metal with:

- *- superconductivity*
- *- persistent exchange*
- *- pseudo-gap phase*
- *- 1/8 anomaly in the SC dome*

Structure type perovskite des cuprates

Structure à 1 plan



Plan CuO_2

Bloques d'oxyde

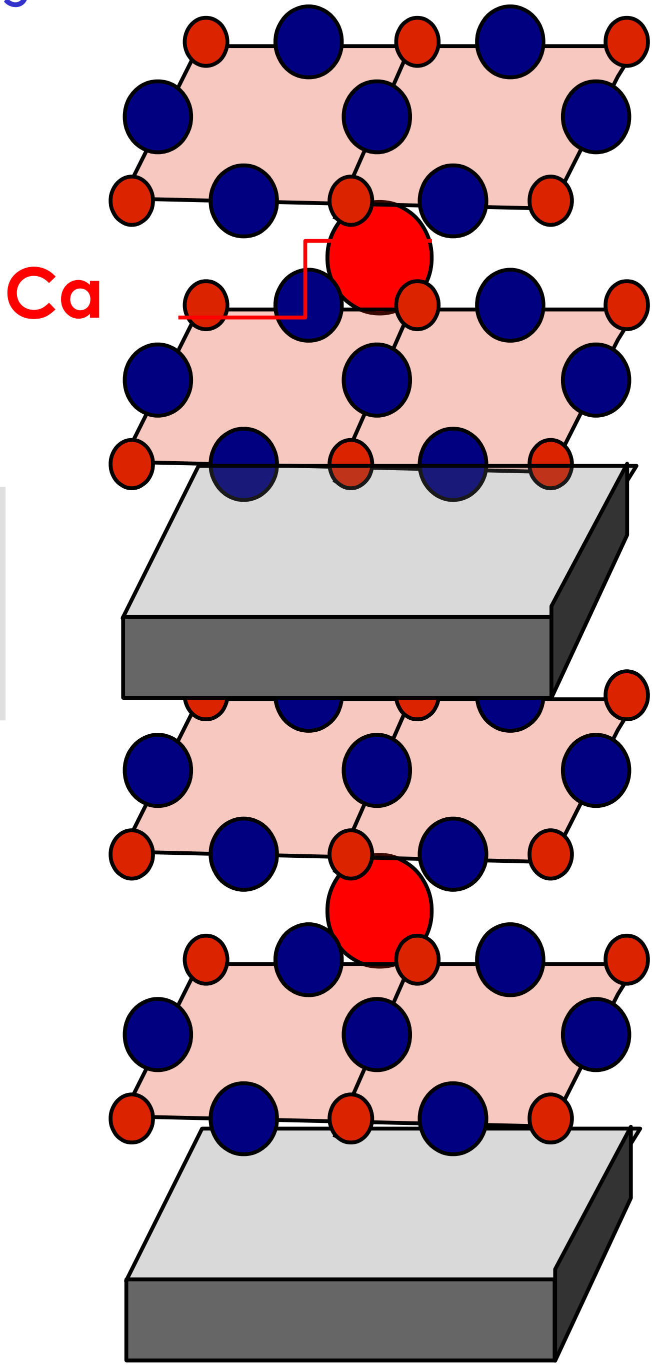
(réservoirs de charge)

1 plan Tc : 24 - 40 K

2 plans Tc : 80 - 100 K

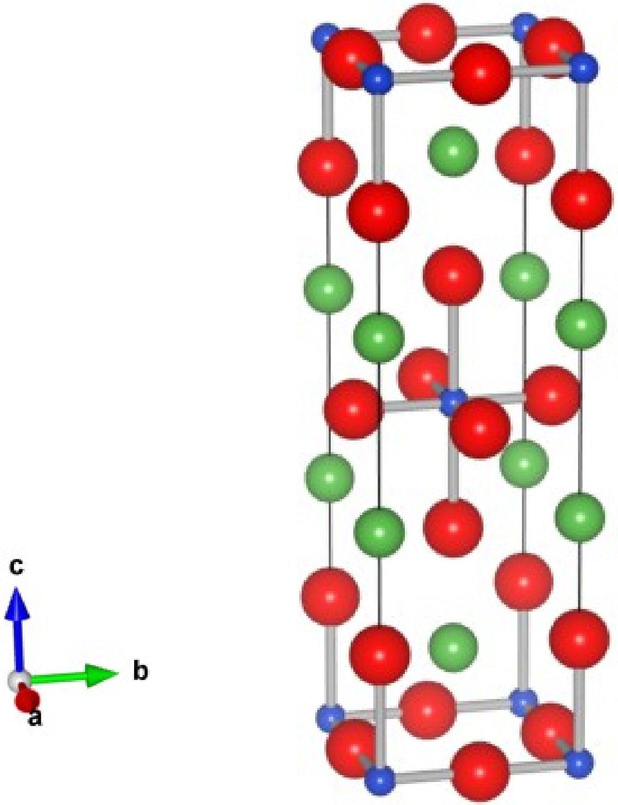
3 plans Tc : 100 - 140 K

Structure à 2 plans

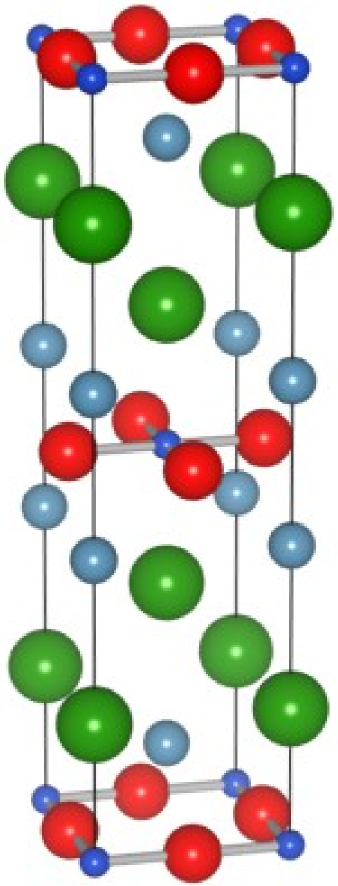


Single layer I4/mmm structure: Oxychloride & normal cuprates

"214" I4/mmm
cuprate
(La_2CuO_4)



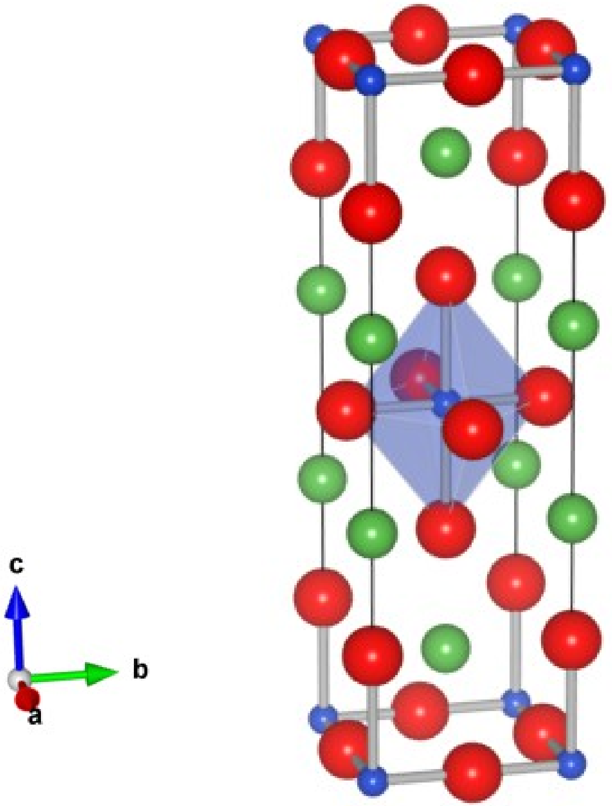
"2122" I4/mmm
oxychloride
($Ca_2CuO_2Cl_2$)

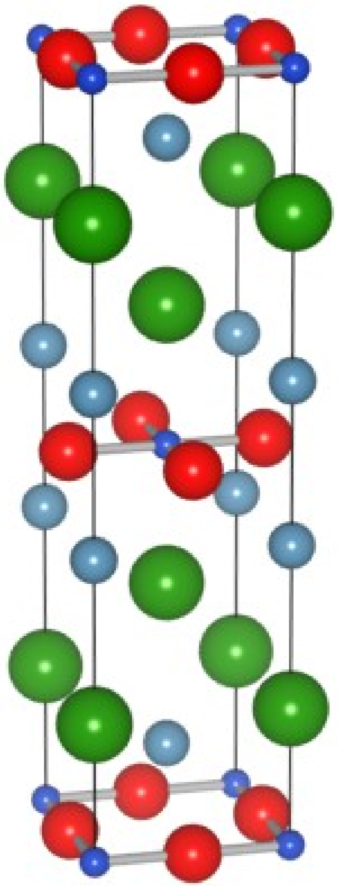


Single layer I4/mmm structure: Oxychloride & normal cuprates

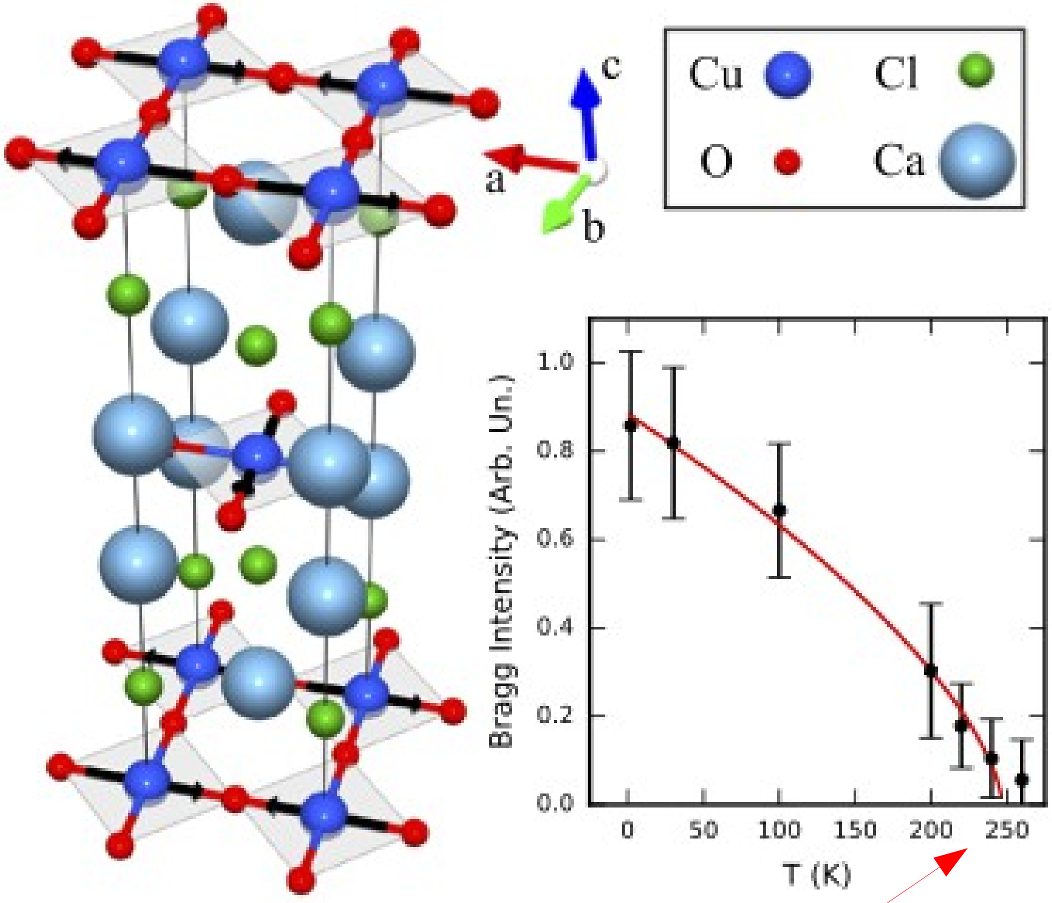
“214” I4/mmm
cuprate
(La_2CuO_4)

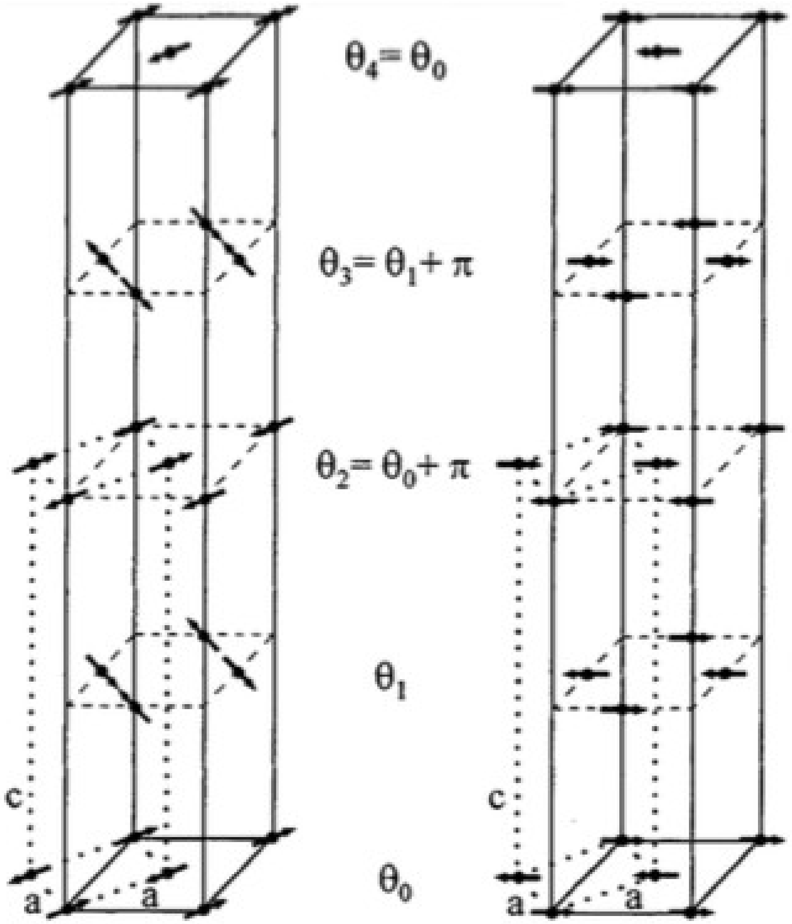
“2122” I4/mmm
oxychloride
($Ca_2CuO_2Cl_2$)





Oxychloride cuprates magnetic structure





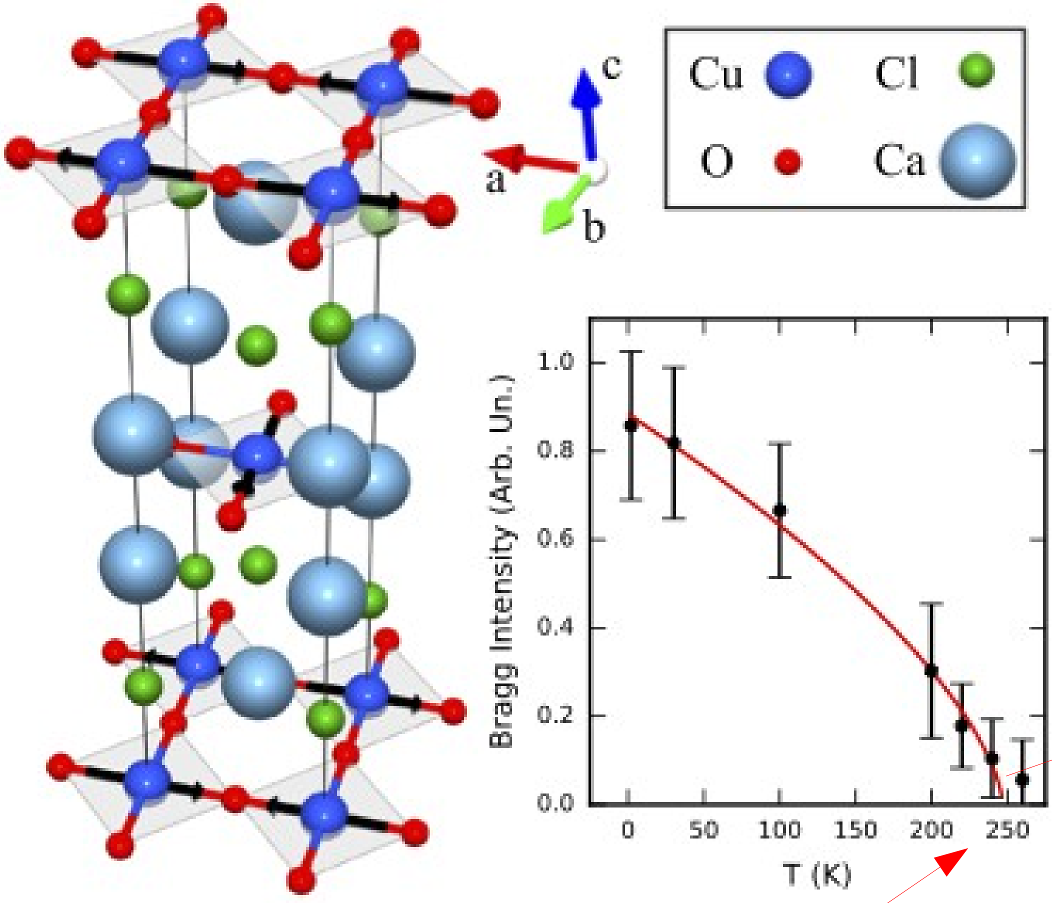
Parent compound:

$Ca_2CuO_2Cl_2$ $T_N \approx 245$ K

B. Lebert *et al.*, *PRB* **95** (2017) 155110

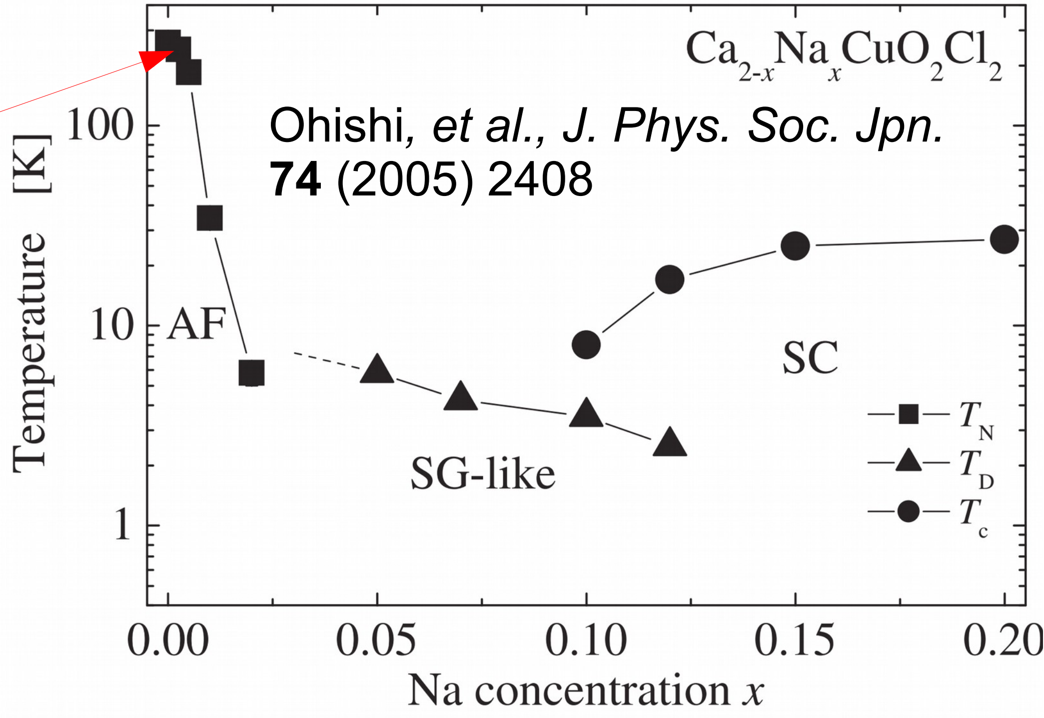
Oxychloride cuprates phase diagram

$Ca_2D_xCuO_2Cl_2$
(D = Na or vacancies):



Parent compound:
$Ca_2CuO_2Cl_2$ $T_N \approx 245$ K

B. Lebert *et al.*, *PRB* **95** (2017) 155110



Ohishi, *et al., J. Phys. Soc. Jpn.* **74** (2005) 2408

Oxychloride & “normal” cuprates phase diagram

cuprate

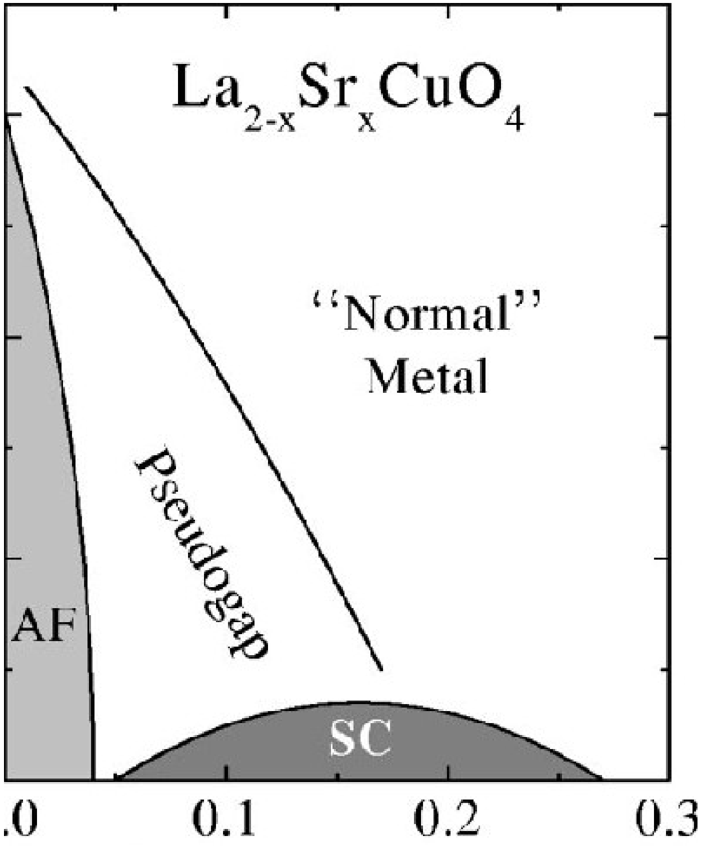
$La_{2-x}M_xCuO_4$

(M=Sr, Ba)

oxychloride

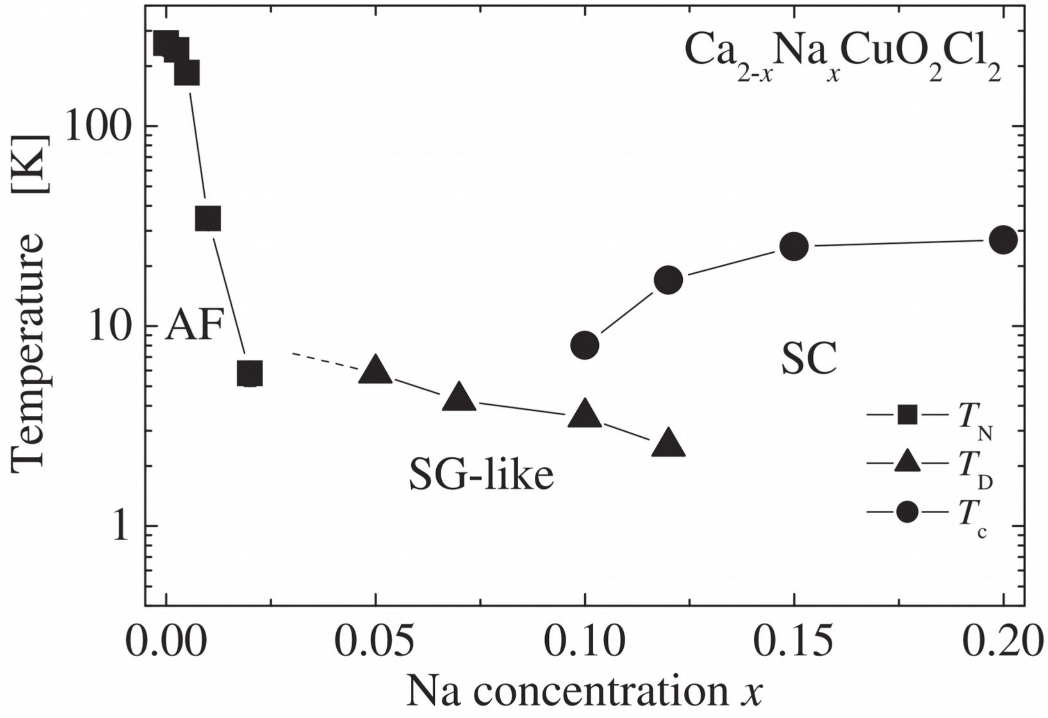
$Ca_2D_xCuO_2Cl_2$

(D = Na or vacancies)



hole doping

A. Damascelli *et al., Rev. Mod. Phys.* **75** (2003)



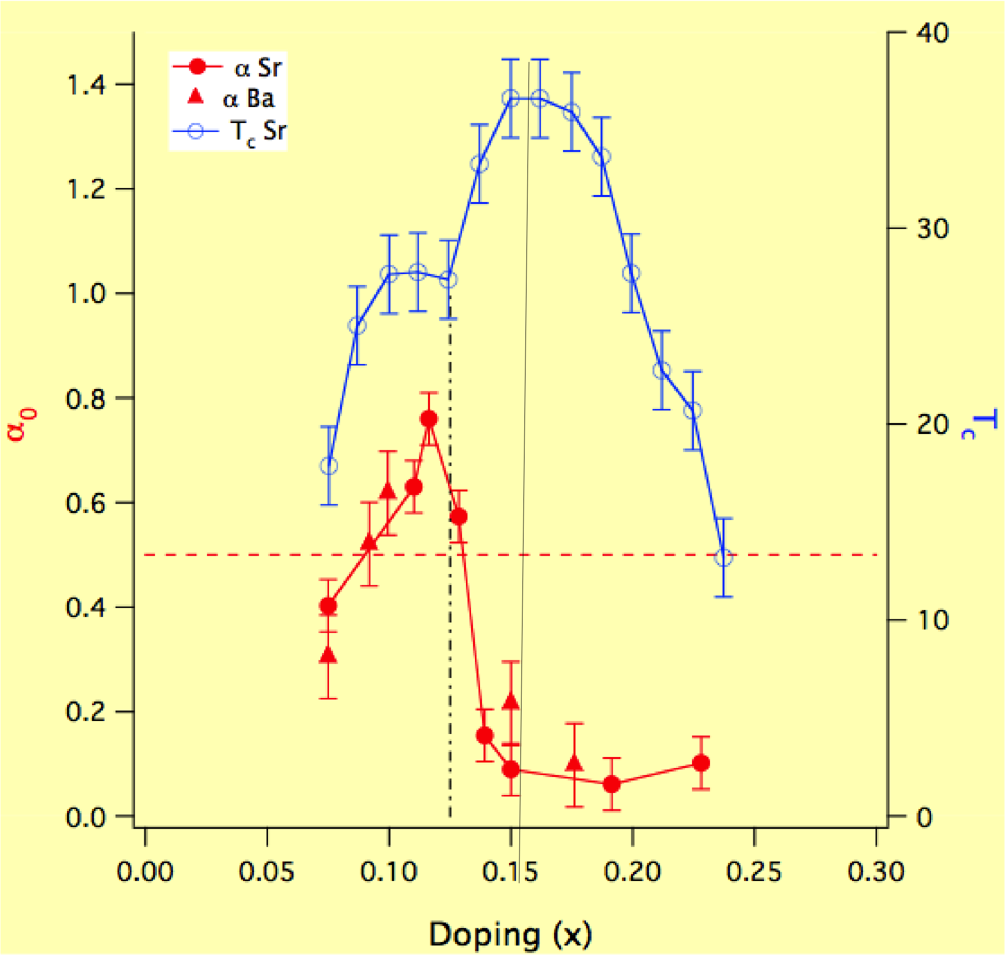
Ohishi*, et al., JPSJ.* **74** (2005)

Oxychloride & “normal” cuprates phase diagram

cuprate

$La_{2-x}M_xCuO_4$

(M=Sr, Ba)

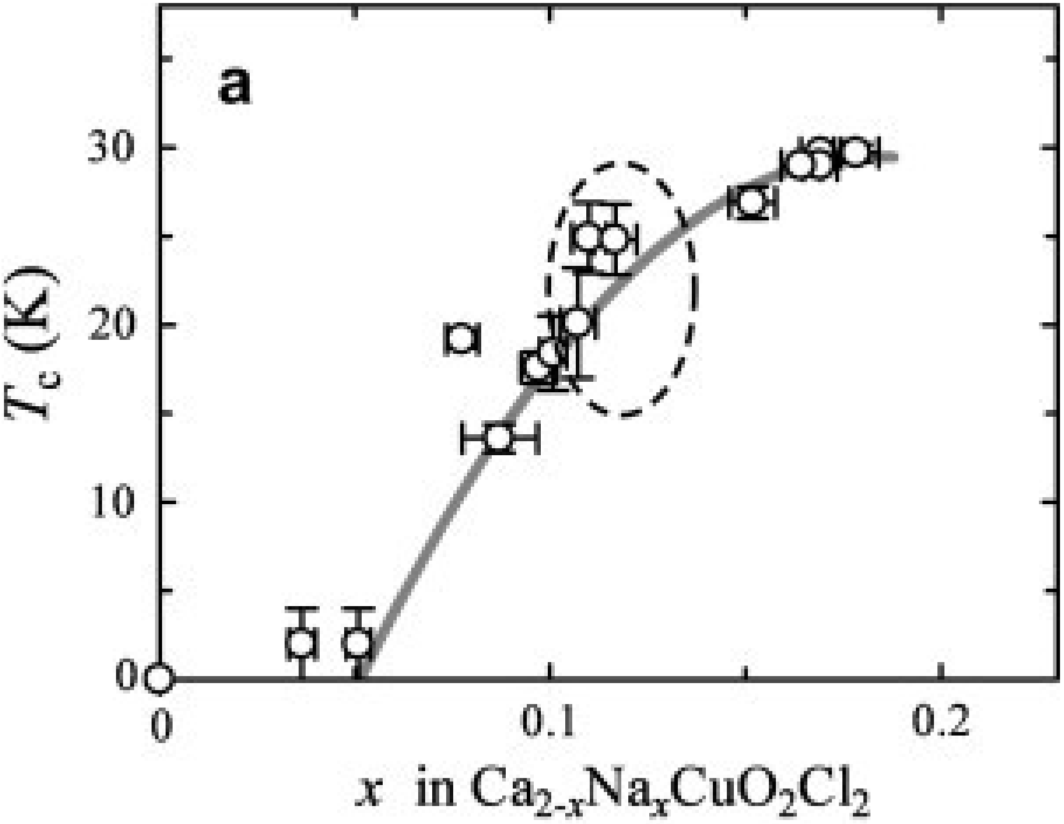


M. K. Crawford, *et al. Science* **250** (1990)
et P.G. Radaelli *et al. PRB* **49** (1994)

oxychloride

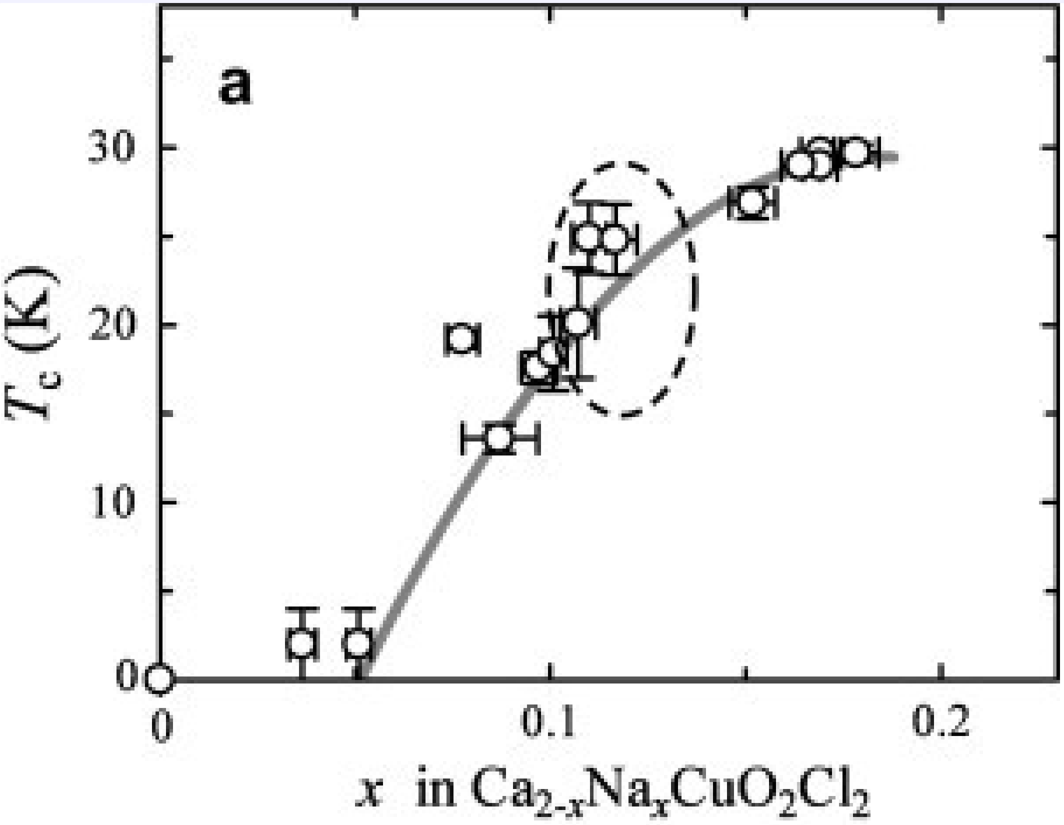
$Ca_2D_xCuO_2Cl_2$

(D = Na or vacancies)



Hirai *etal., Physica C* **463-465** (2007)

Oxychloride cuprates



Hirai, Sasagawa, Takagi, *Physica C* **463-465** (2007)

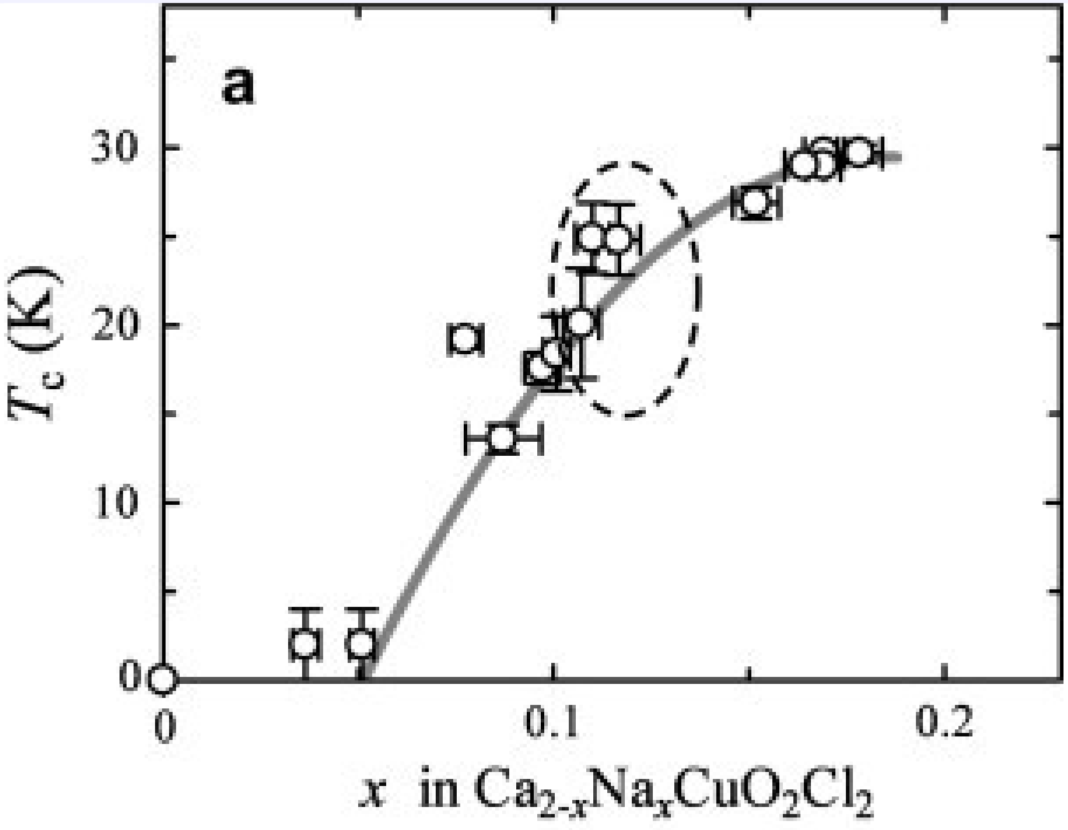
$Ca_2D_xCuO_2Cl_2$
(D = Na or vacancies):

- perfect under-doped SC dome

- only light elements

Simple system for ab-initio and multi-electronic calculations

Oxychloride cuprates



Hirai, Sasagawa, Takagi, *Physica C* **463-465** (2007)

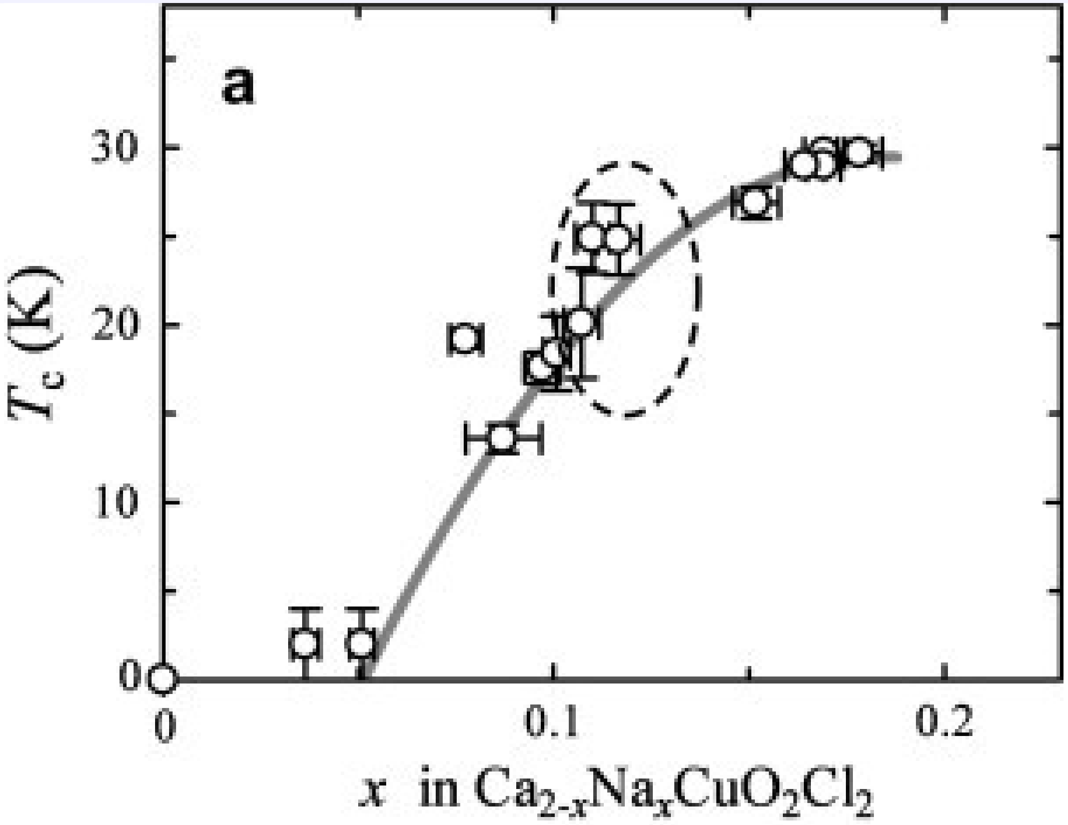
$Ca_2D_xCuO_2Cl_2$
(D = Na or vacancies):

- perfect under-doped SC dome

- **only light elements**

Simple system for ab-initio and multi-electronic calculations

Oxychloride cuprates



Hirai, Sasagawa, Takagi, *Physica C* **463-465** (2007)

$Ca_2D_xCuO_2Cl_2$
(D = Na or vacancies):

- perfect under-doped SC dome

- **only light elements**

Simple system for ab-initio and multi-electronic calculations

However: relatively few experimental results (for a cuprate)

Spectroscopies with synchrotron and neutrons

synchrotron light sources

- ***Photon in - photon out***
  - *absorption*
  - *fluorescence*
  - *inelastic scattering*
  - *resonant inelastic scattering*
- ***Photoemission***

neutrons

Neutron in - neutron out

- *inelastic scattering*

We can explore many excitations in solids,

but here we will focus on.... phonons

Spectroscopies with synchrotron and neutrons

synchrotron light sources

- ***Photon in - photon out***
  - *absorption*
  - *fluorescence*
  - *inelastic scattering*
  - *resonant inelastic scattering*
- ***Photoemission***

neutrons

Neutron in - neutron out

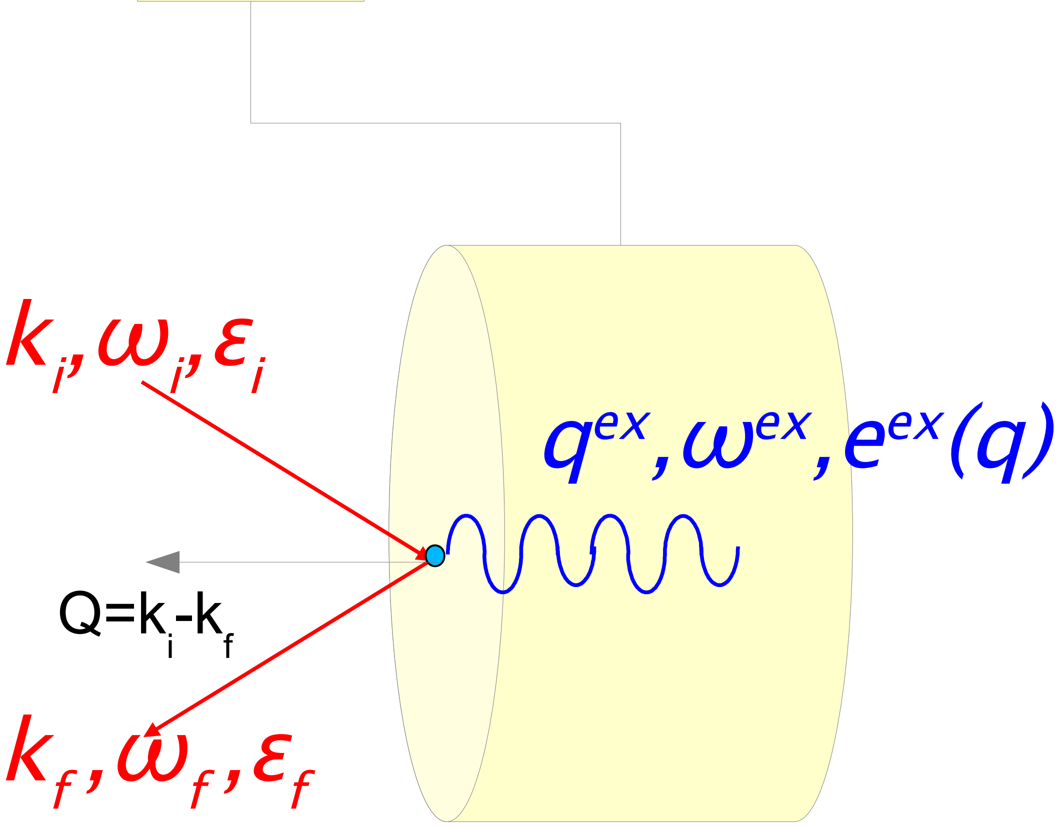
- *inelastic scattering*

We can explore many excitations in solids,

but here we will focus on.... and (para)magnons (afternoon lecture).

Inelastic X-ray Scattering spectroscopy

A particle (photon, neutron, electron He atom...) probe a sample (in this lecture a crystal)

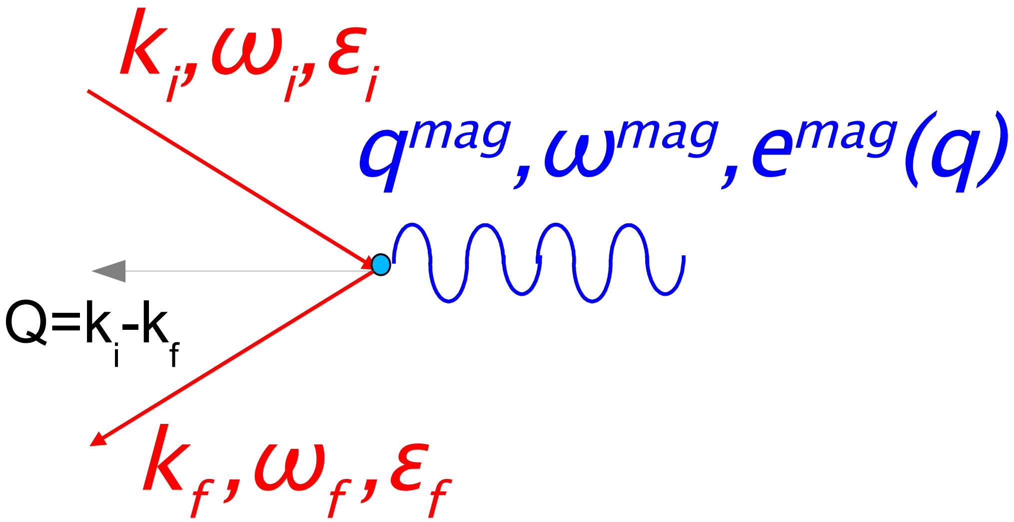


and exchange energy and momentum with an internal excitation (*e.g.* a phonon..)

With visible light is known since the works of Raman and Brillouin

Inelastic Scattering: kinematic

Knowing energy (frequency), momentum (wave-vector) of both incident and scattered probes, one get energy and momentum of the ~~phonon~~ magnon



$$\hbar\omega_i - \hbar\omega_f = \hbar\omega_{mag}$$

$$\hbar k_i - \hbar k_f = \hbar Q$$

Spectroscopies with synchrotron and neutrons

neutrons

Several types of spectrometer:

- *3-axis*
  - *standard (meV resolution)*
  - *backscattering (eV resolution)*
- *time-of-flight*
- *spin-echo*
- *plus coupled ones (3-axis/spin-echo)*

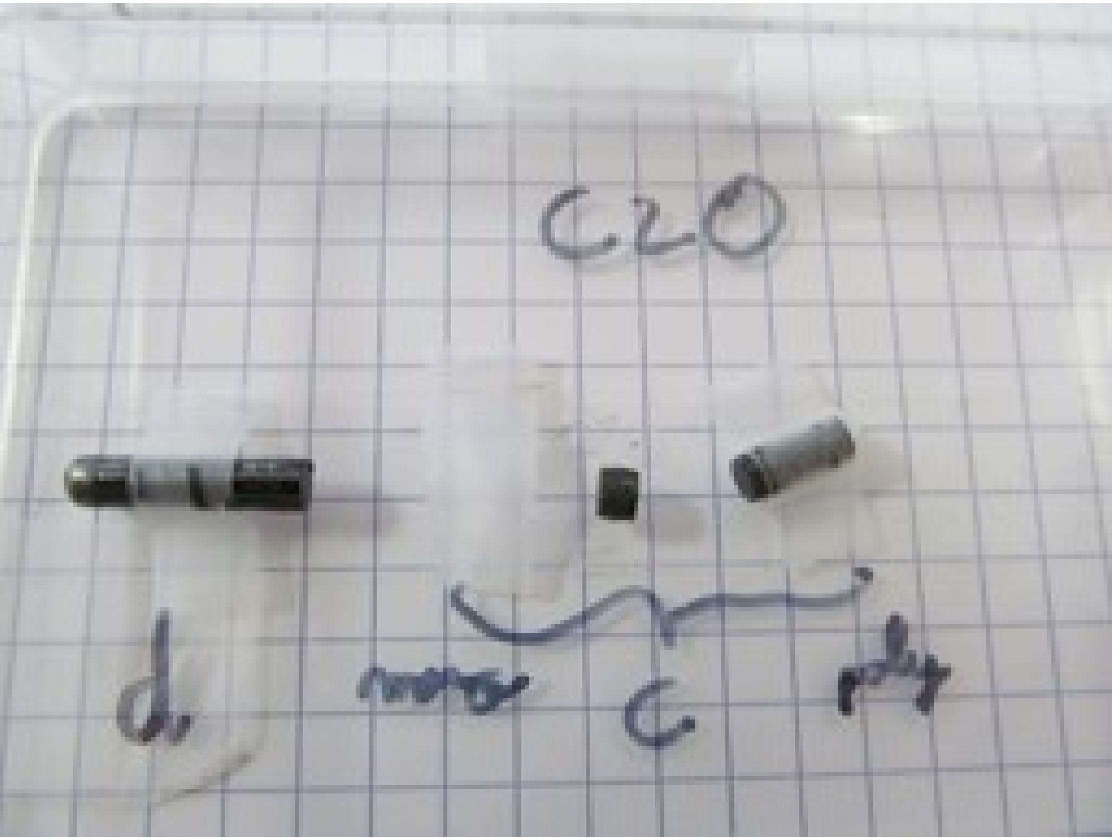
synchrotron light sources

Too many types, I'll focus on:

- *3-axis Rowland geometry*
  - *backscattering (phonons)*
  - *soft X-ray (magnons)*

$La_{2-x}M_xCuO_4$ (M=Sr, Ba) case : large volume crystal growth

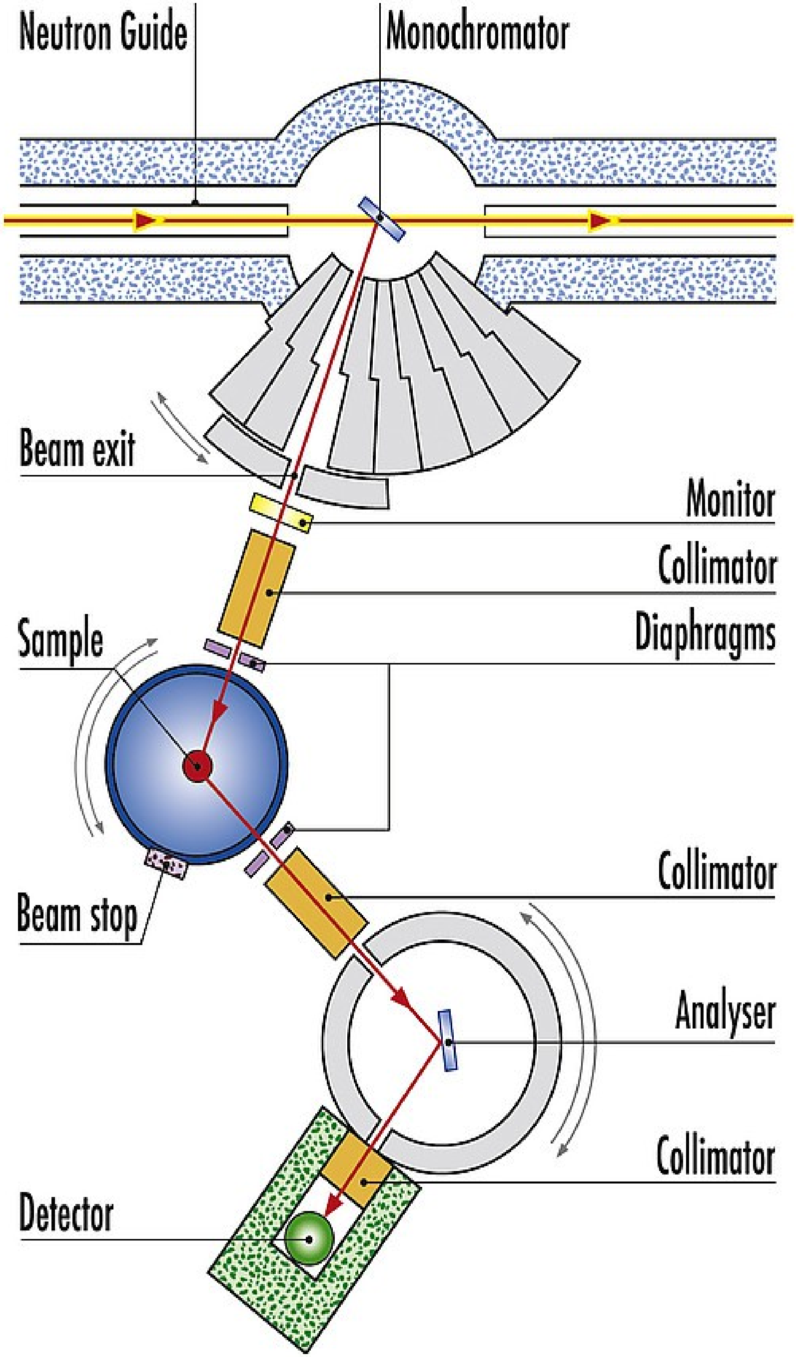
cm^3 size single crystals available:



Example : $(La,Nd)_{2-x}Sr_xCuO_4$ crystals, growth by Travelling Solvent Floating Zone (TSFZ)

Sylvain Denis (*PhD Université Paris Sud - Paris XI*, 2014)

I can do inelastic neutron scattering !



IN3 instrument layout
(ILL, Grenoble, France)

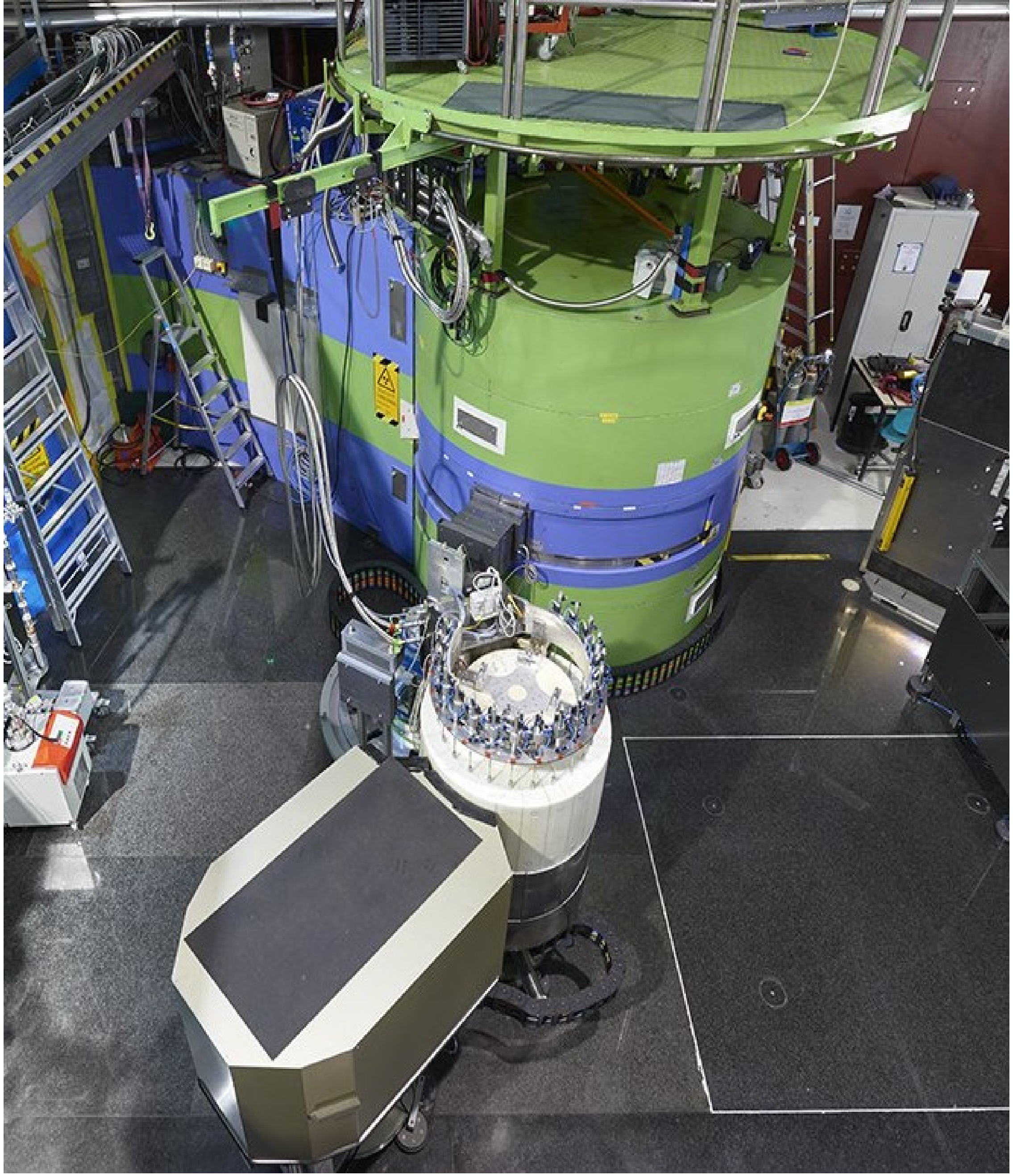
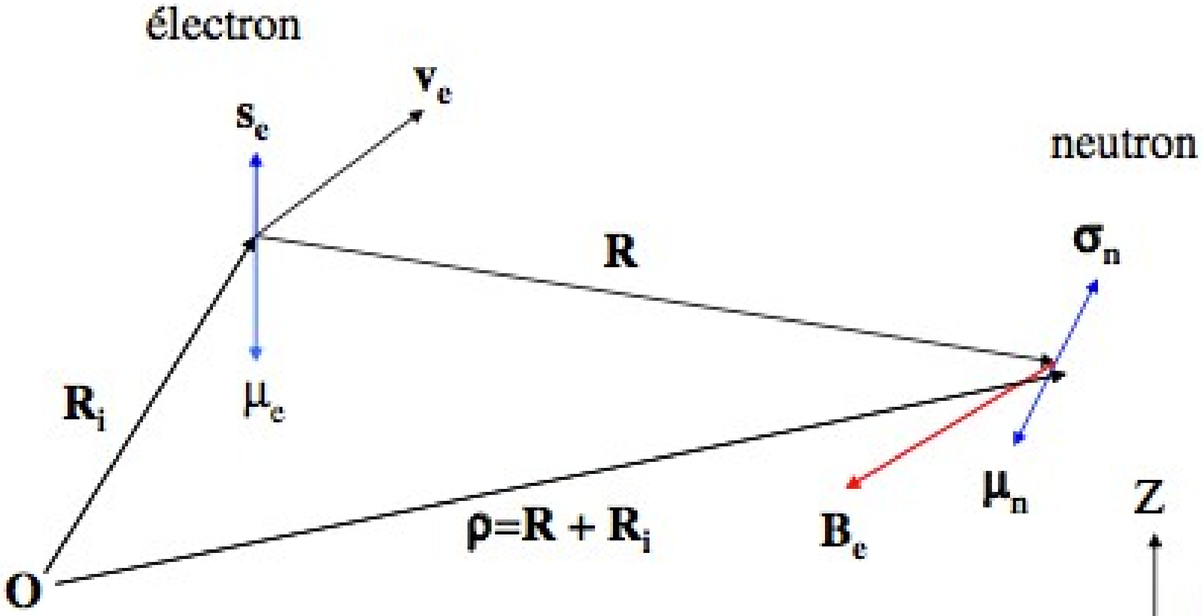
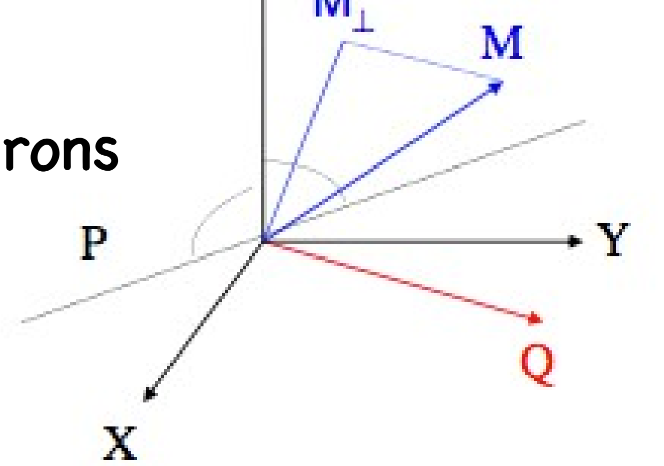


Image of PANDA at FRM-II
(Garching, Germany)



General magnetic cross section for neutrons



$$\frac{\partial^2\sigma}{\partial\Omega\partial E'} = \frac{k'}{k}(\gamma r_o)^2 \sum_{\ell,\sigma,\sigma'} p_\ell p_\sigma \frac{1}{2\pi\hbar}\int dt\ \langle \ell\sigma|\ \sigma\cdot\mathbf{M}_\perp(t=0)|\ \sigma'\rangle\langle\sigma'|\ \sigma\cdot\mathbf{M}_\perp(t)\ |\ell\sigma\rangle\ e^{-i\omega t},$$

$$\mathbf{M}_\perp(t) = \sum_i e^{i\mathbf{Q}\mathbf{R}_i(t)}\left(\tilde{\mathbf{Q}}\times(\mathbf{s}_i(t)\times\tilde{\mathbf{Q}}) - \frac{i}{\hbar|\mathbf{Q}|}\tilde{\mathbf{Q}}\times\mathbf{p}_i(t)\right).$$

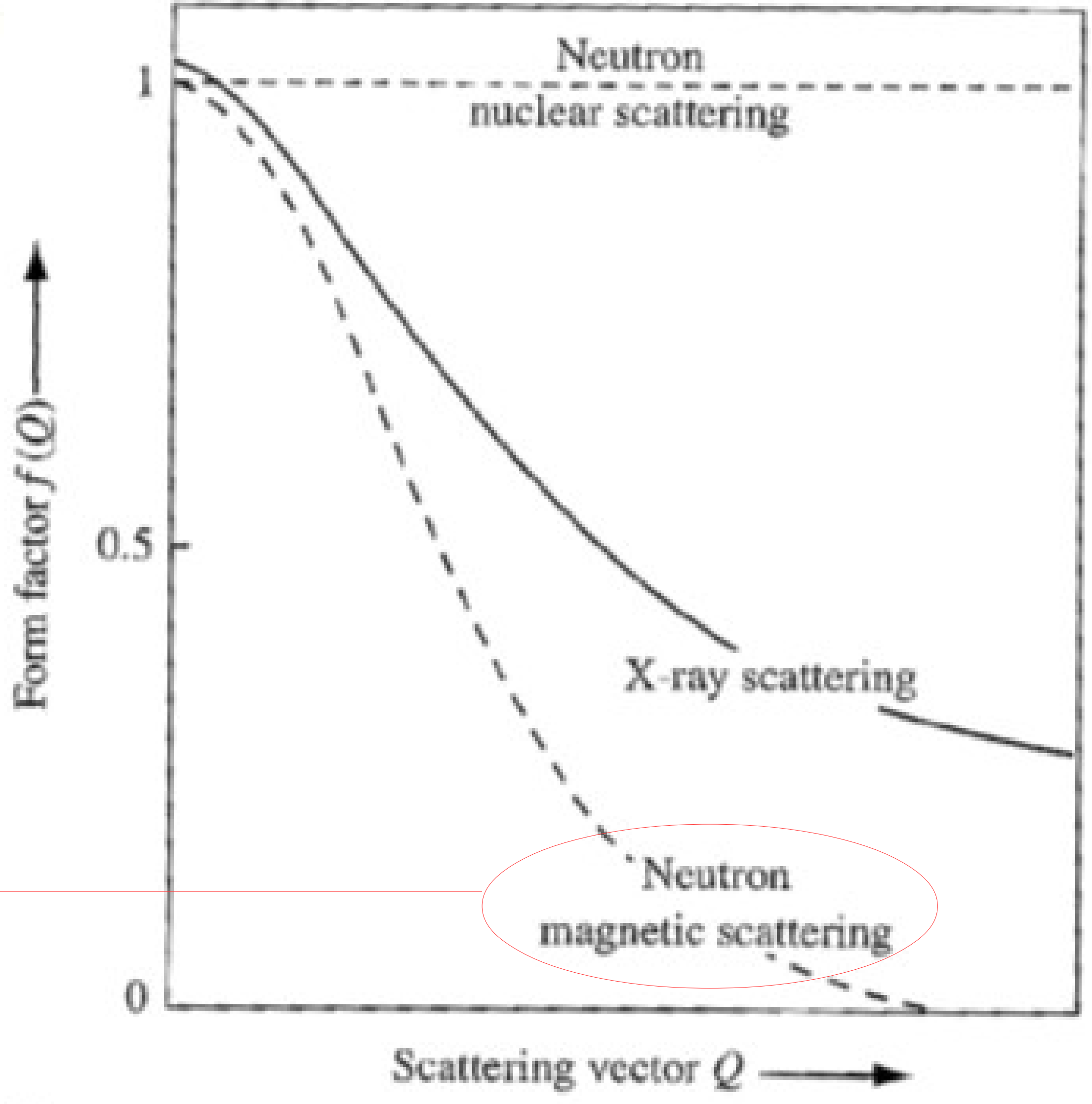
F. Moussa, S. Petit,
JDN **10** 337-354 (2010)

Spin only cross section for neutrons

F. Moussa, S. Petit,
JDN **10** 337-354 (2010)

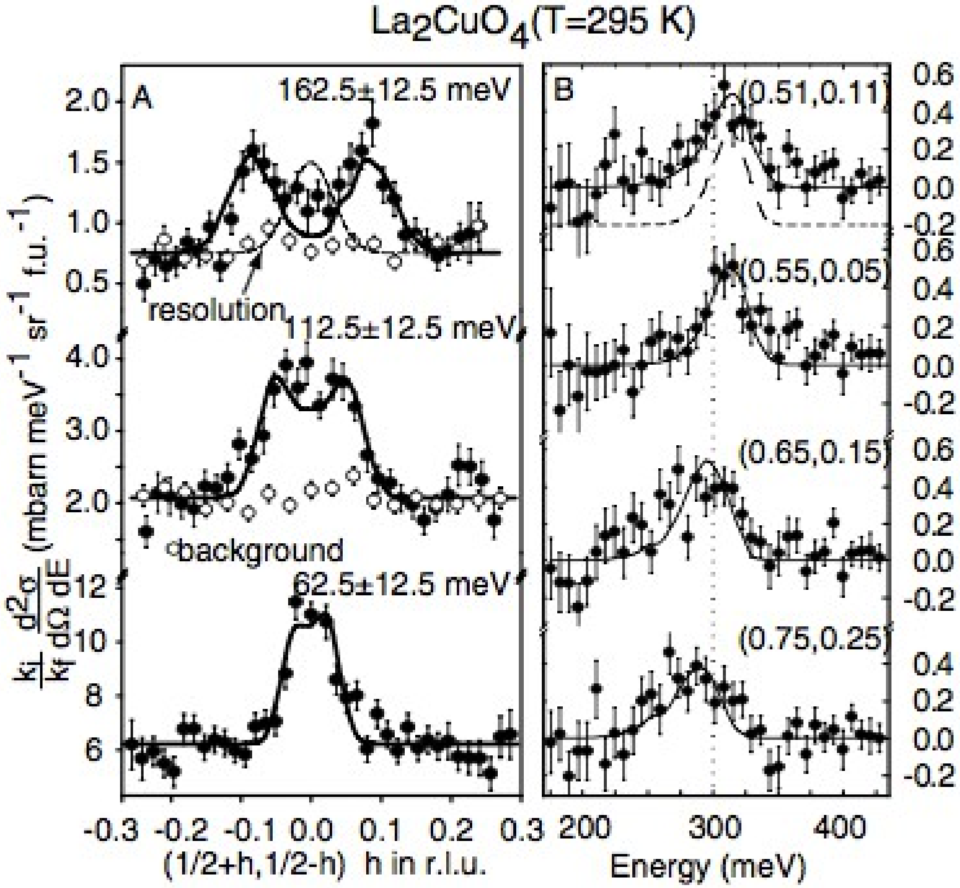
$$\frac{\partial^2\sigma}{\partial\Omega\partial E'} = \frac{k'}{k}(\gamma r_o)^2\frac{1}{2\pi\hbar}\sum_{\ell,\ell',d,d'} F_d(\mathbf{Q})F^*_{d'}(\mathbf{Q})$$

$$\times \int dt\, \langle e^{i\mathbf{Q}\mathbf{R}_{\ell,d}} e^{-i\mathbf{Q}\mathbf{R}_{\ell',d'}(t)}\, \mathbf{S}_{\perp,\ell,d}(t=0).\mathbf{S}_{\perp,\ell',d'}(t)\rangle\, e^{-i\omega t}.$$



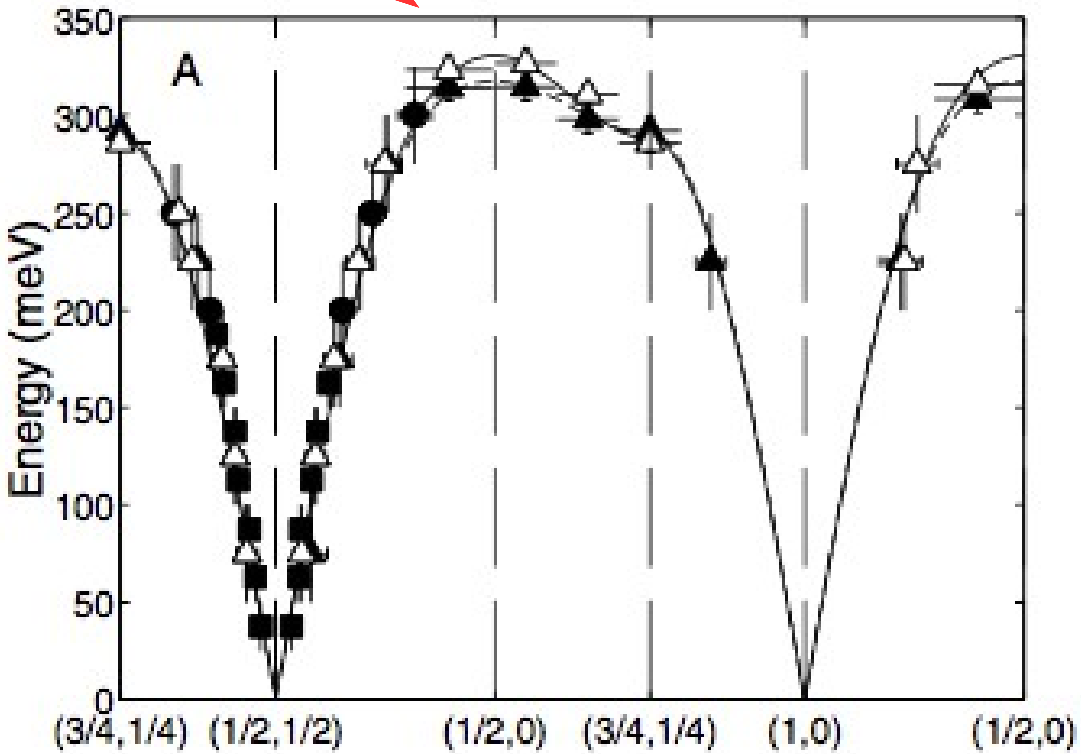
(See yesterday lectures by Claire Colin)

Spin waves in parent compound: La_2CuO_4



Just as for phonons: scattered intensity

Dispersion relations



Calculated dispersion:

Heisenberg model

$$H = J\,\Sigma_{<ij>} S_i S_j$$

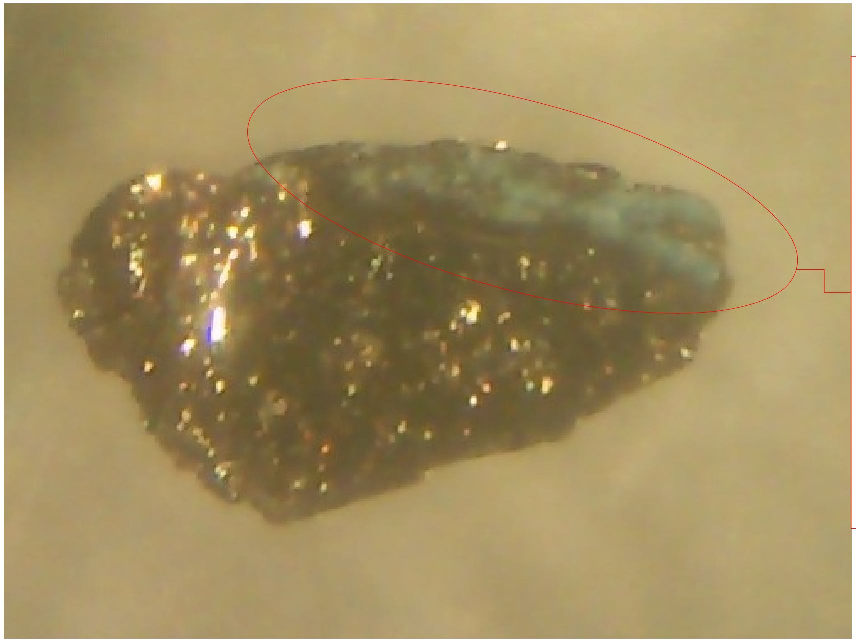
with higher-order couplings

Coldea, *et al.* *PRL* **86**, (2001)

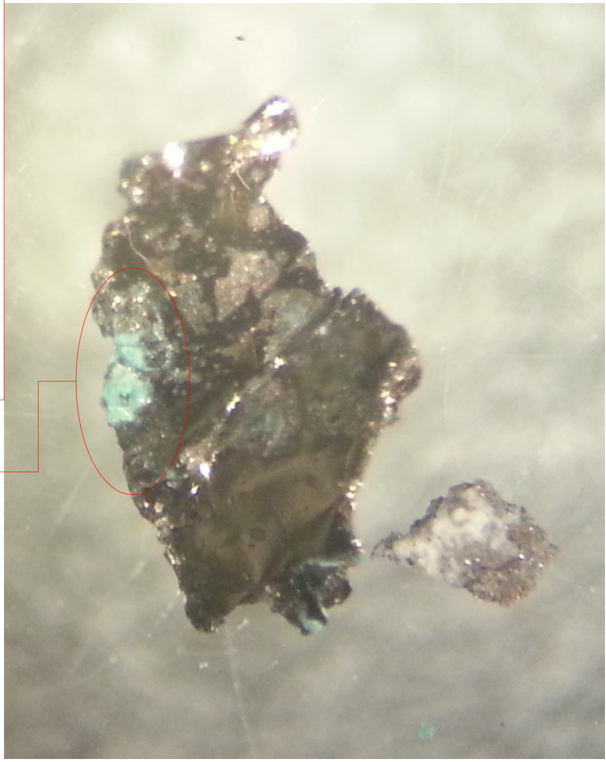
Oxychloride cuprates : material science

a) Doped at high P (4-6 GPa) → small (< 1 mm) crystals, *e.g.* for neutron scattering

b) Sensitive to moisture :



they form beautiful blue needle-like crystals of hydroxides



Unfortunately the hydroxide are not superconducting!

...so to handle in vacuum or controlled atmosphere

Oxychloride cuprates : material science

...so to handle in vacuum or controlled atmosphere

Synchrotron progress in energy resolution

For very small sample, today we can probe:

- (para)magnon with RIXS
- phonons with IXS

Cu L_3 experiment on ADRESS (SLS) – **ΔE ≈ 130 meV**

Cu L_3 experiment on ID32 (ESRF) – **ΔE ≈ 30 meV**

(non resonant) IXS at

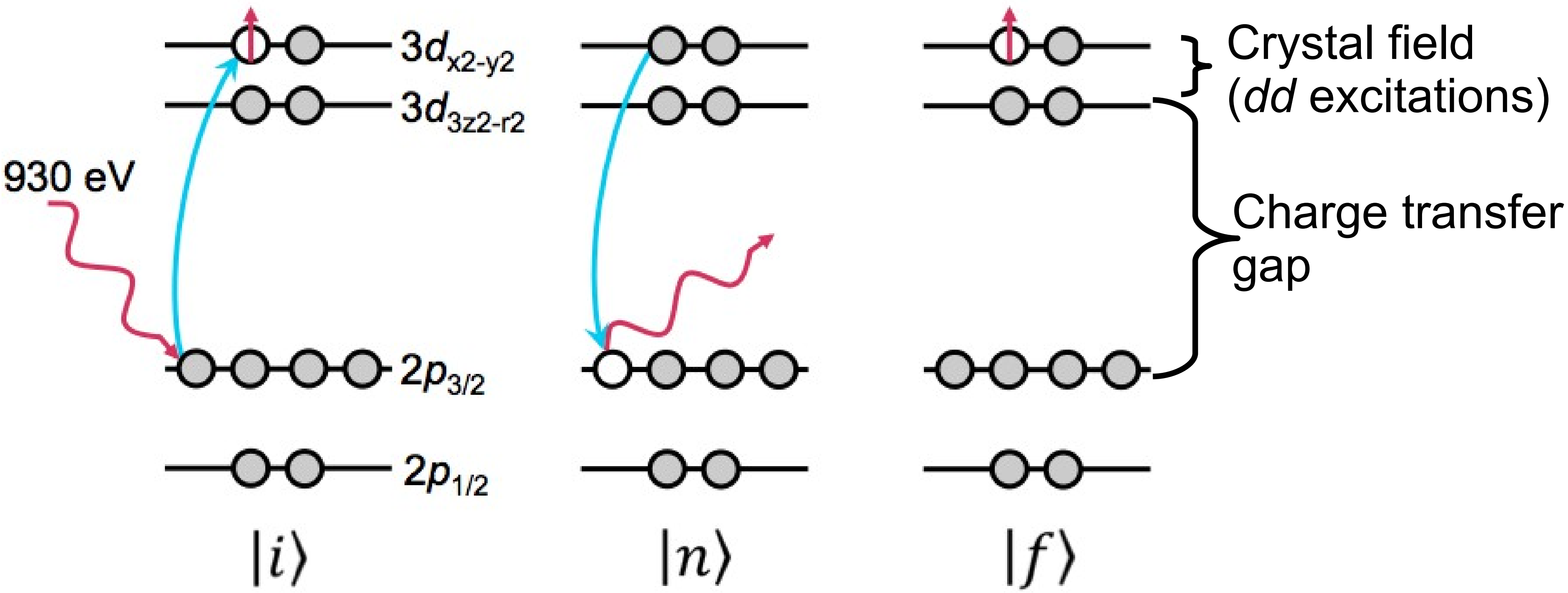
ID28 (ESRF, Grenoble) and

BL35XU (Spring-8, XXX)

ΔE ≤ 3 meV

RIXS experiments

Elastic process:



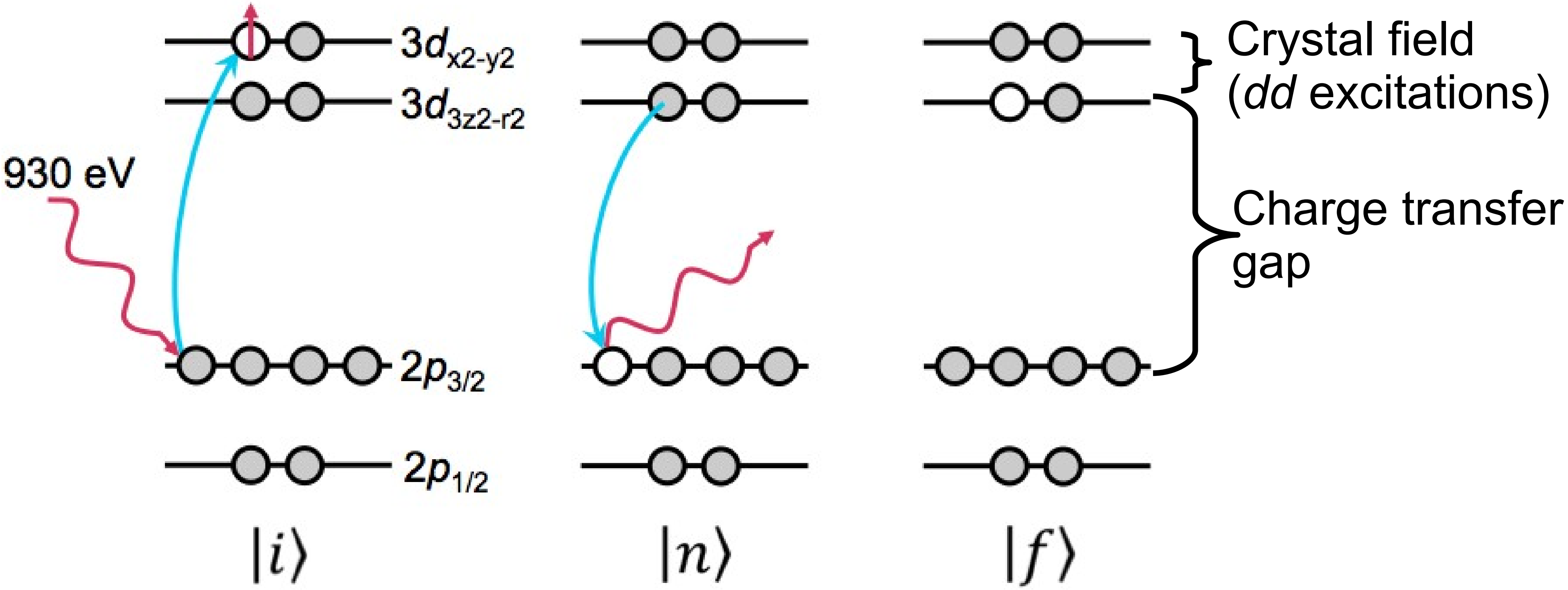
Crystal field (*dd* excitations)

Charge transfer gap

Dean *J. Magn. Magn. Mater.* **376** (2015)

RIXS experiments

dd excitations:



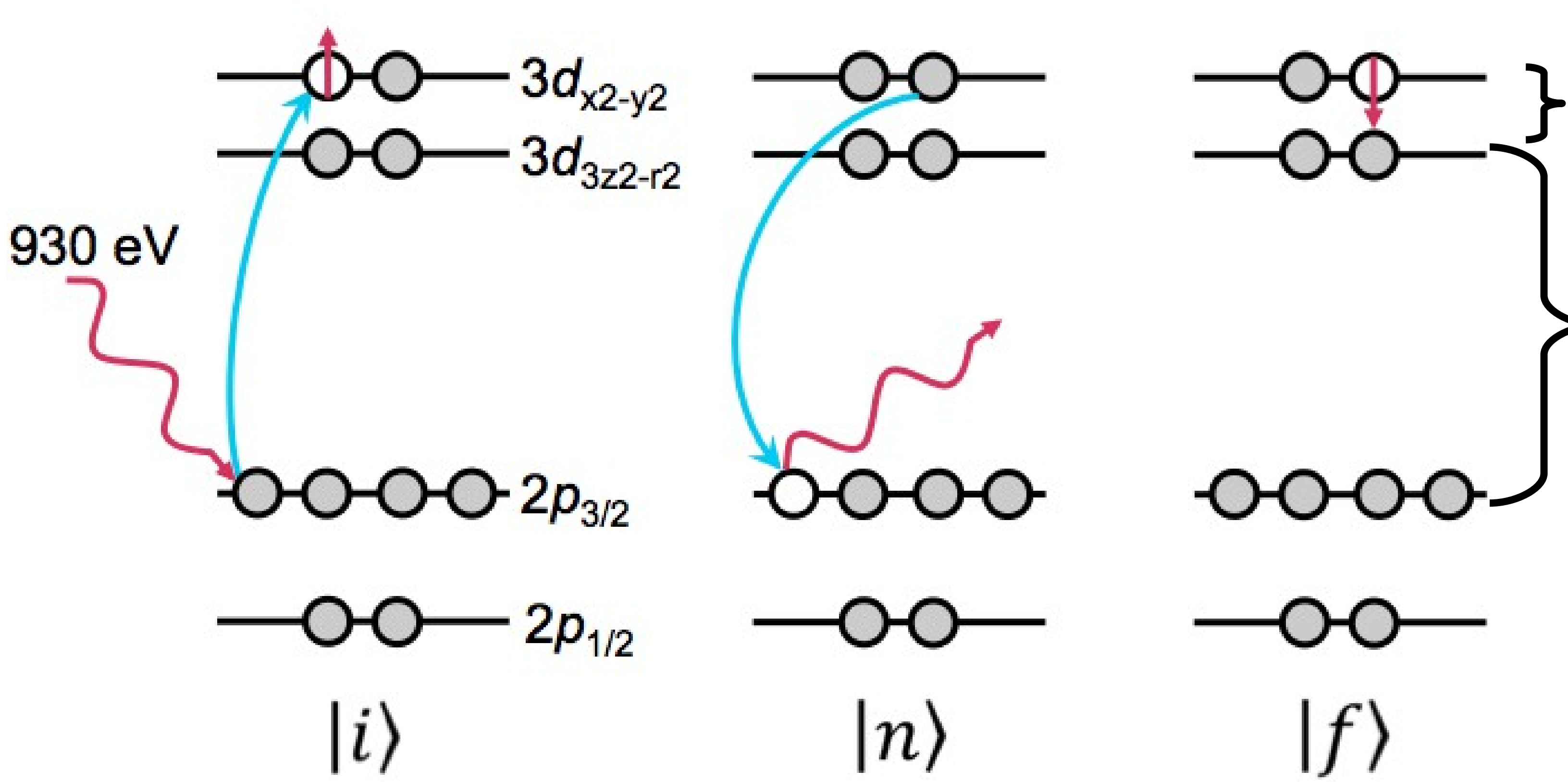
Crystal field (*dd* excitations)

Charge transfer gap

Dean *J. Magn. Magn. Mater.* **376** (2015)

RIXS experiments

Spin flip (magnons):

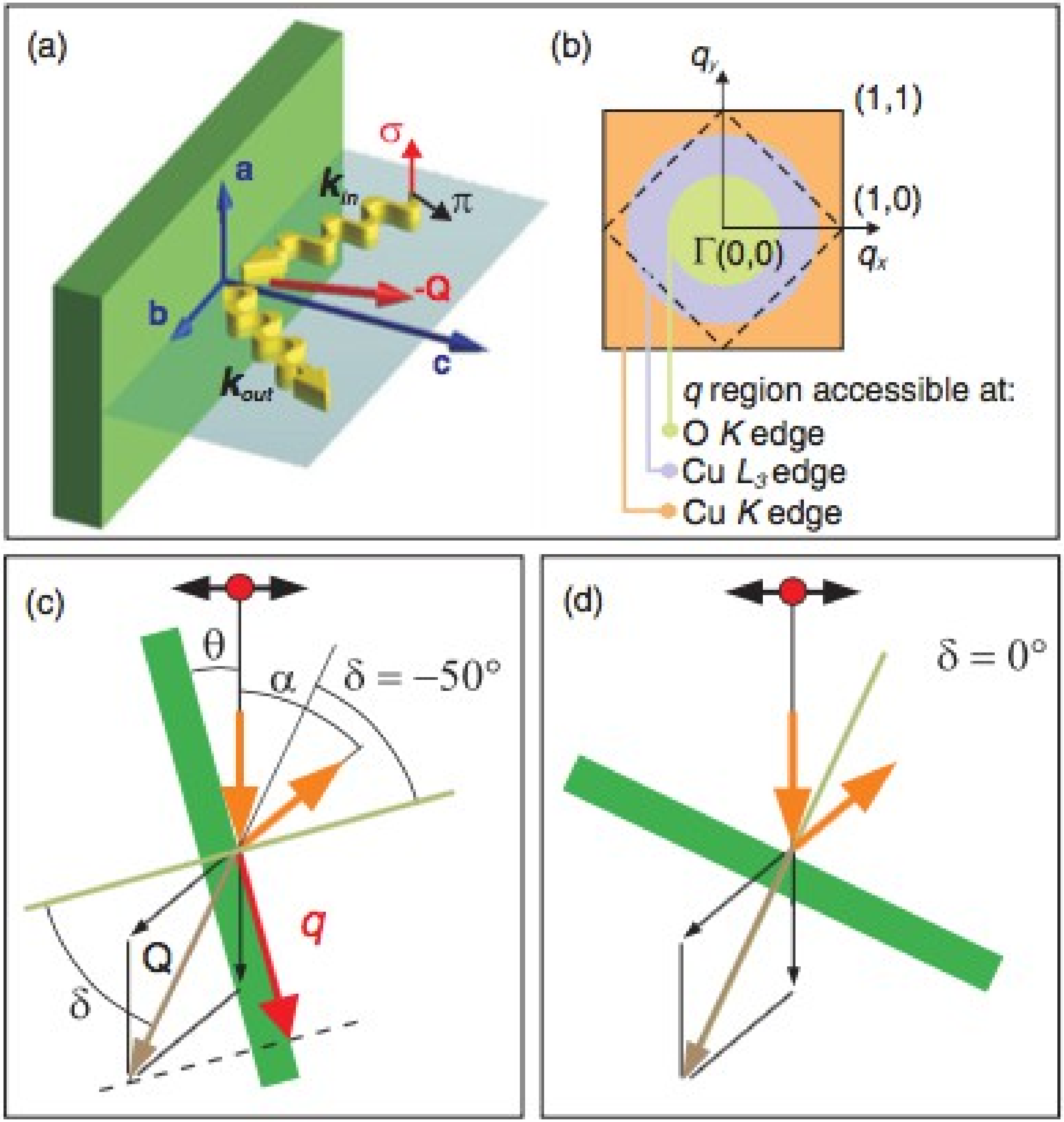


Crystal field (*dd* excitations)

Charge transfer gap

Dean *J. Magn. Magn. Mater.* **376** (2015)

RIXS experiments



O K edge Ѓ 530 eV (bi-magnon)

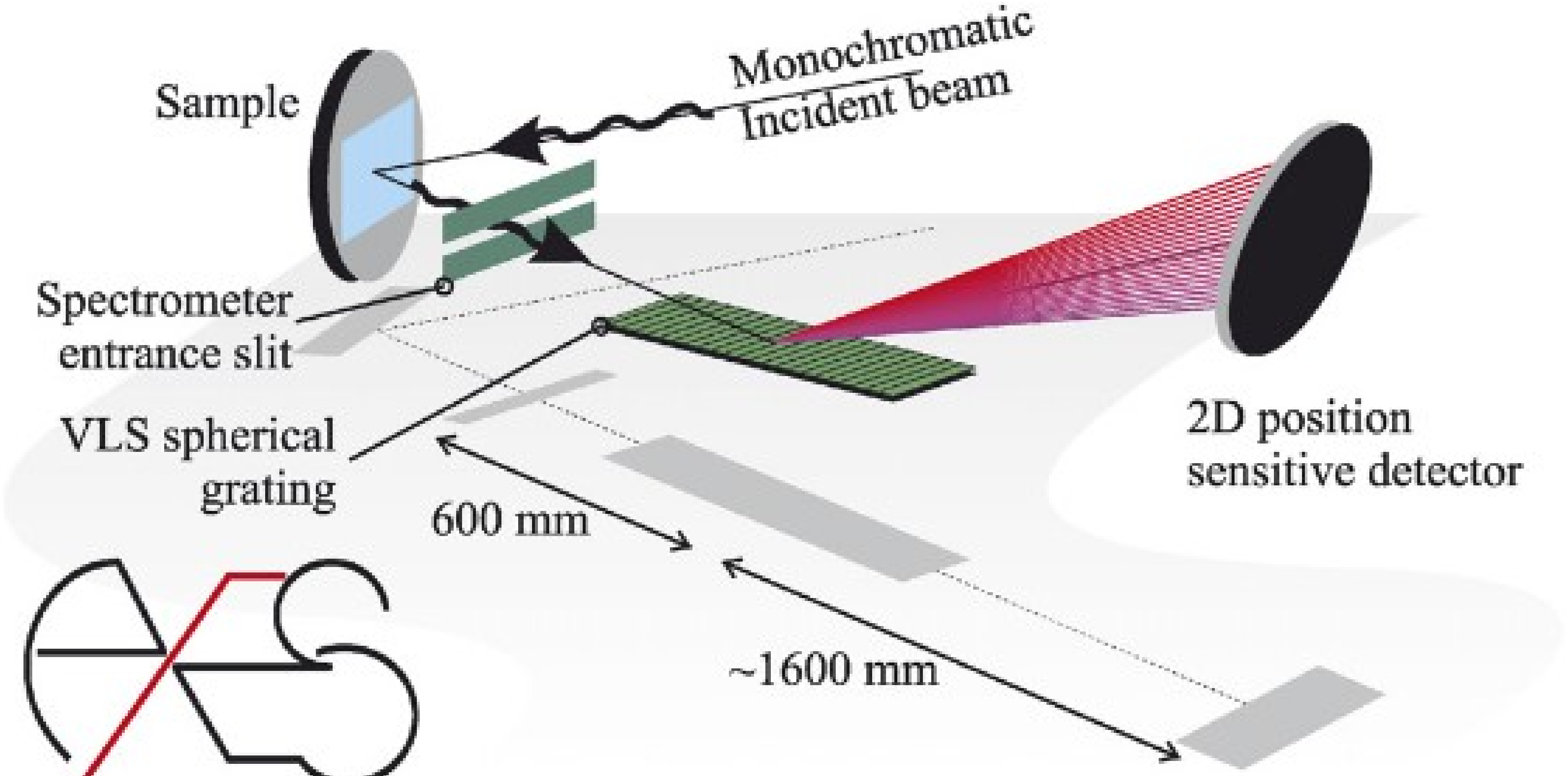
Cu L_3 edge Ѓ 930 eV (single magnon + bi-magnon)

Cu k-edge ~ 8992.5 eV

V. Bisogni *et al., PRB* **85** (2012)

RIXS spectrometer

First realisation - ΔE = 130 meV @ Cu L_3

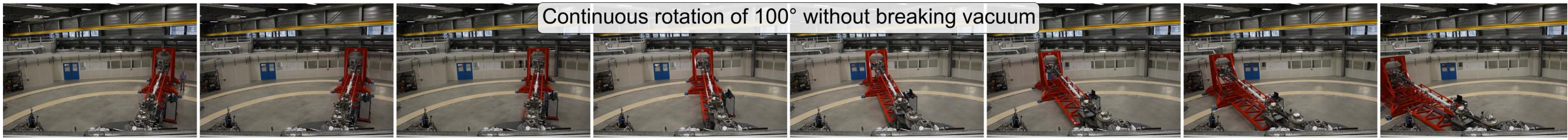


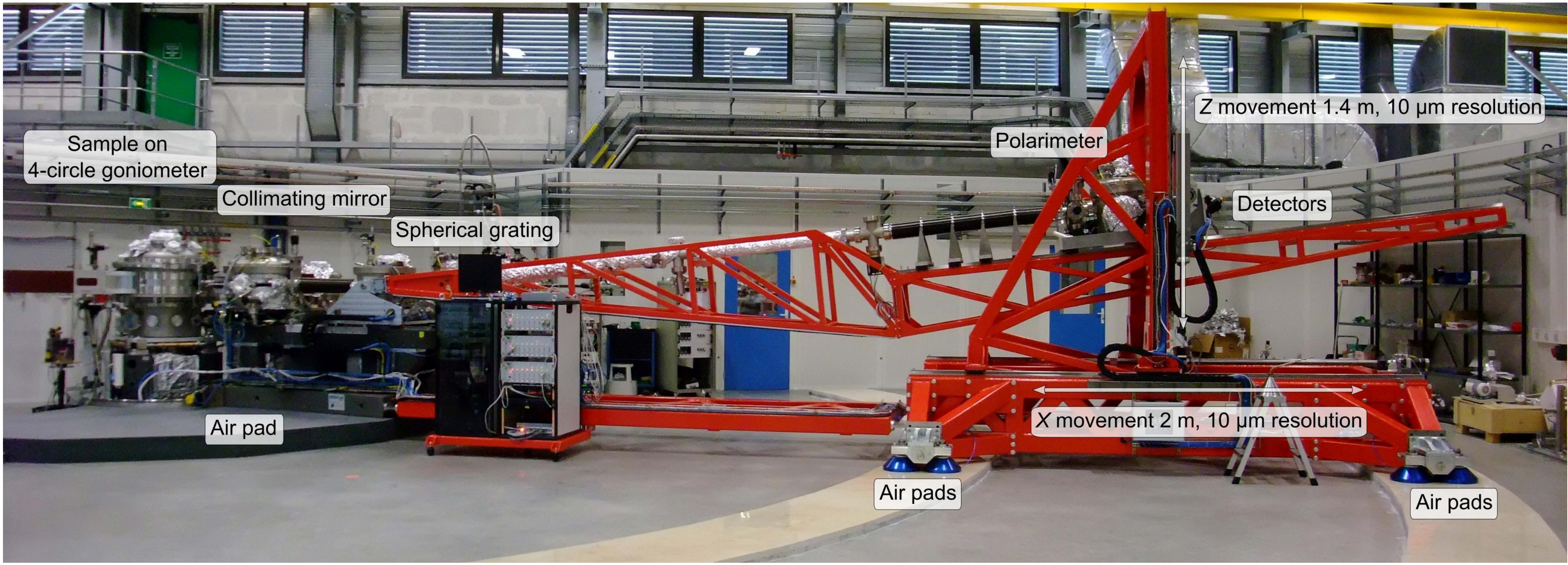
M.E. Dinardo et al. *NIM A* **570** (2007)

RIXS spectrometer

Today record on ID32 (ESRF)- $\Delta E = 30$ meV @ Cu L_3

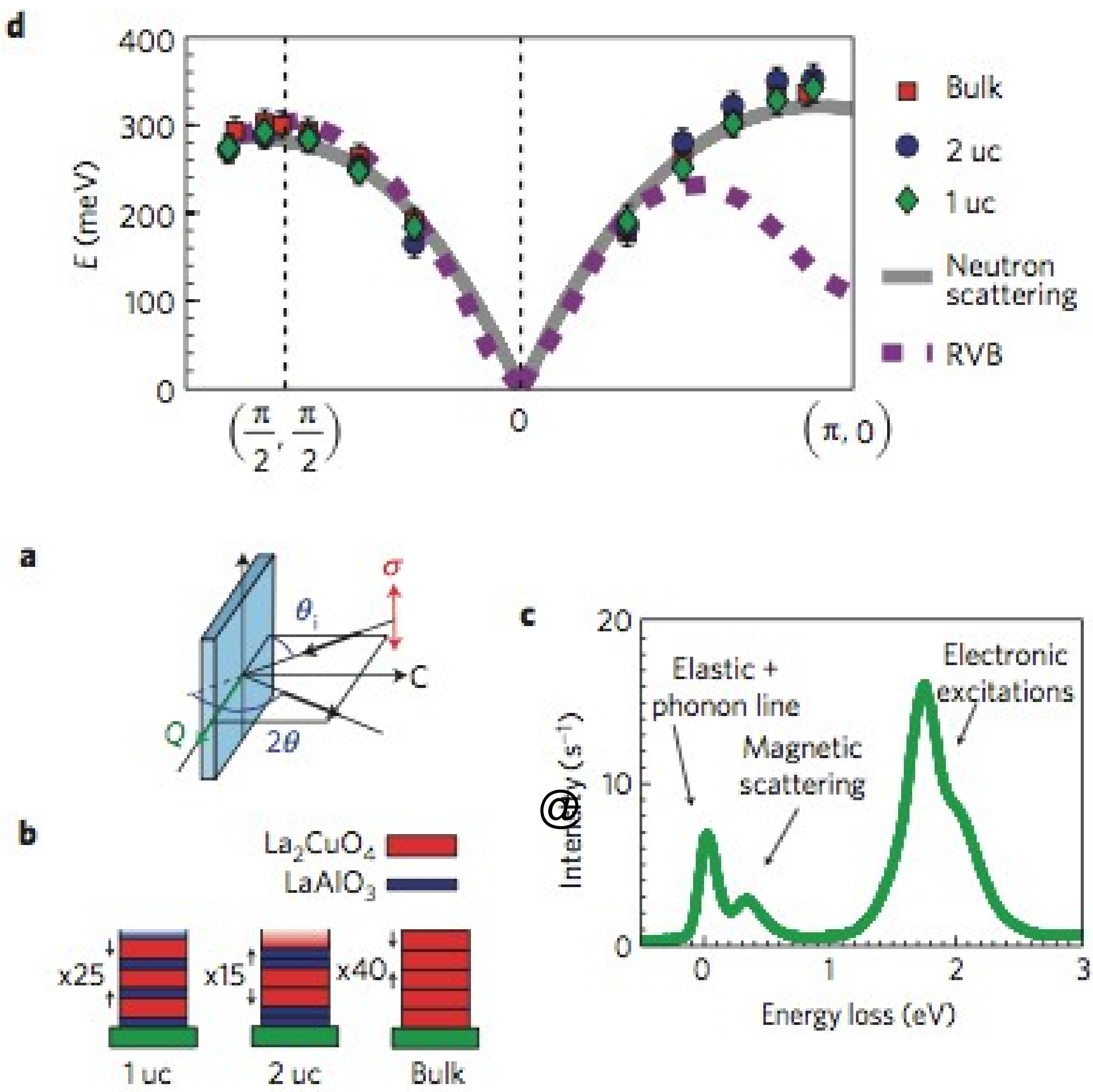
Including polarisation analysis !





L. Braicovich *et al., Rev. Sci. Instrum.* **85** (2014),
picture from http://www.esrf.eu/ID32

RIXS Neutron comparison in La_2CuO_4



Comparing Neutron with RIXS: same La_2CuO_4 dispersion

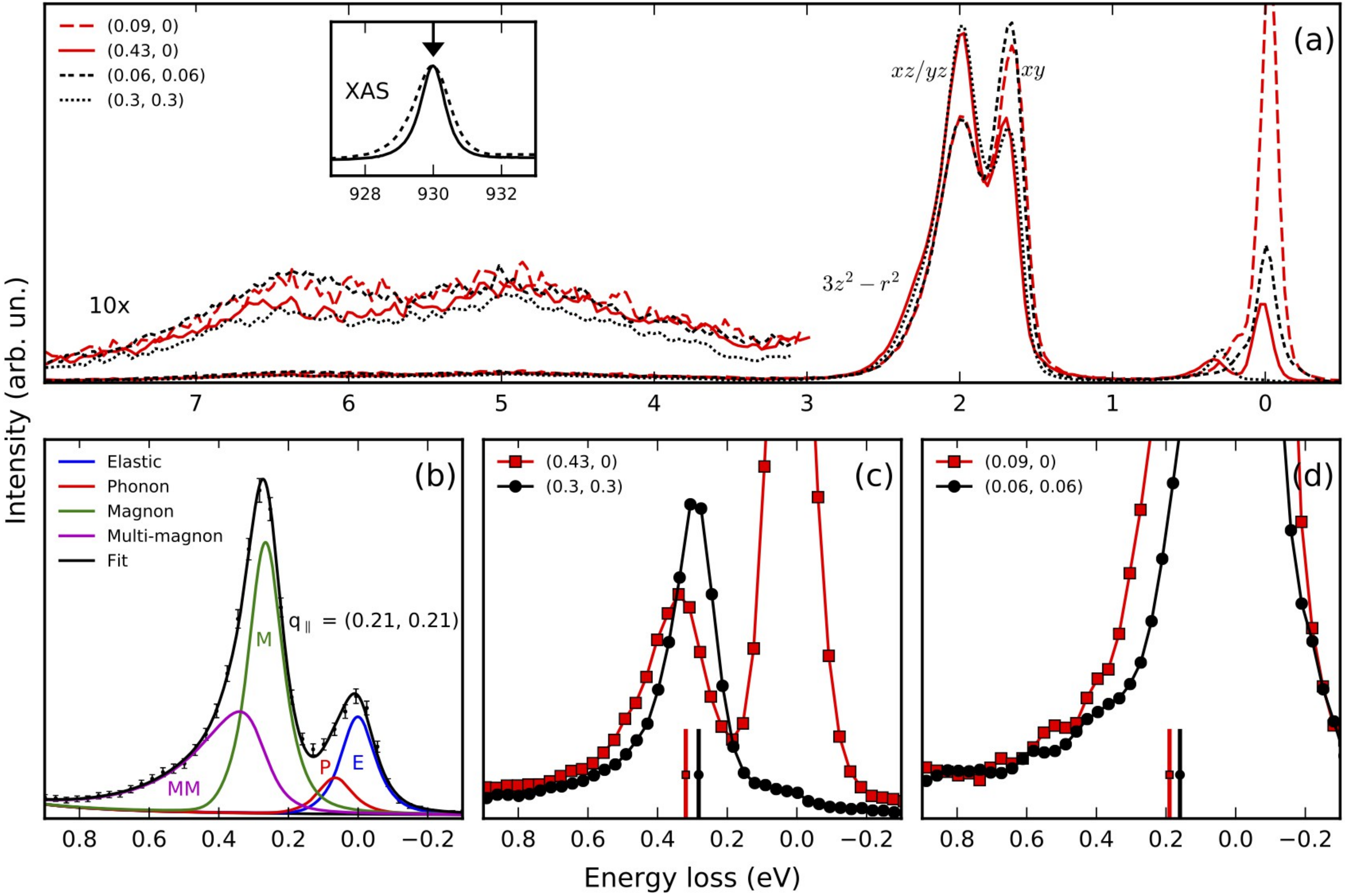
But much smaller samples!

1 isolated La_2CuO_4 layer

Dean *et al., Nature Materials* **11** (2012)

Results parent compound: $Ca_2CuO_2Cl_2$

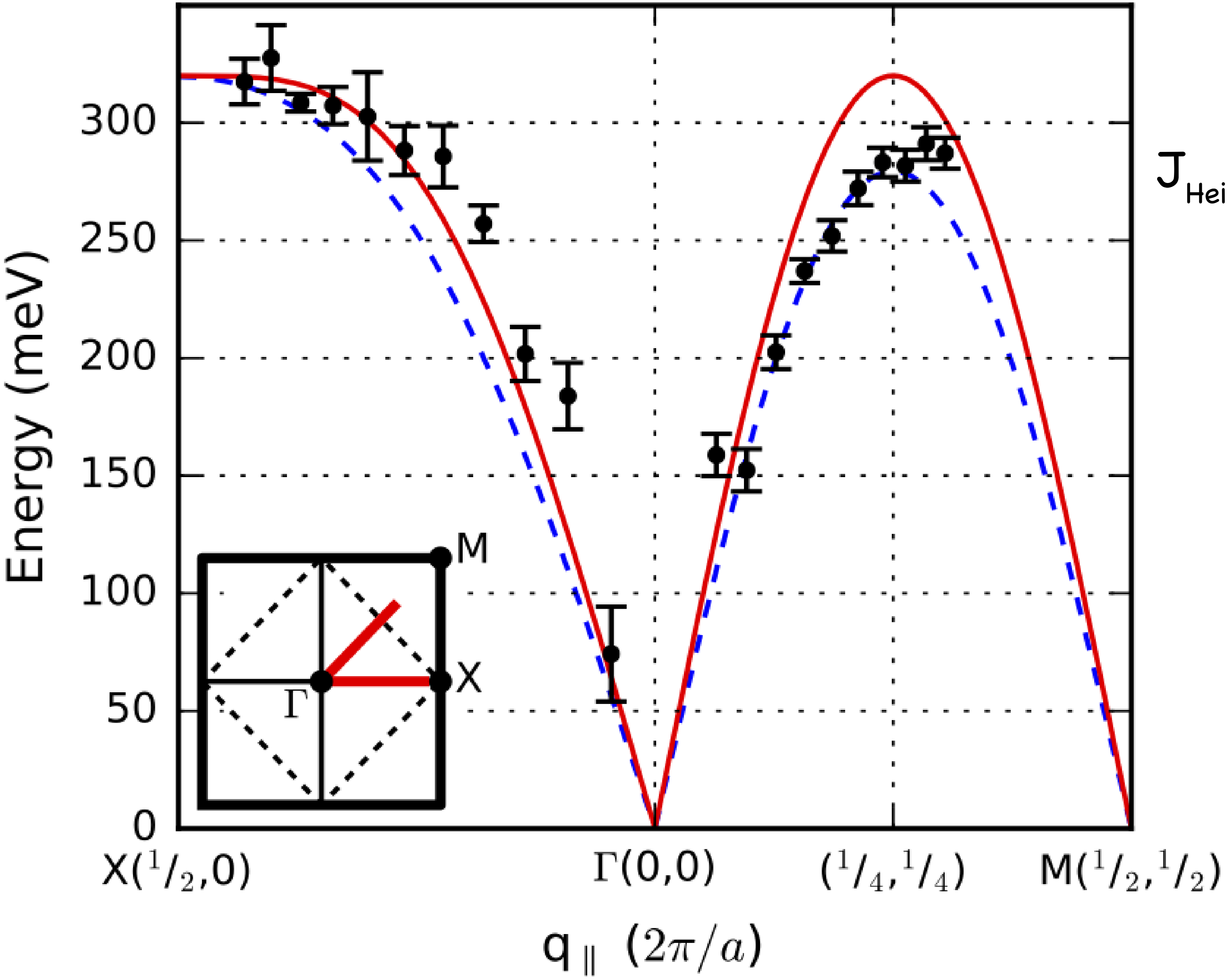
Cu L_3 experiment on ADESSS (SLS) Resolution = 130 meV



B. Lebert *et al.*, *PRB* **95** (2017) 155110

Results parent compound: $Ca_2CuO_2Cl_2$

Cu L_3 experiment Resolution = 130 meV



Disp. param. (red)
$J_{Heisenberg}$(meV) = 135±4

Zone boundary
dispersion

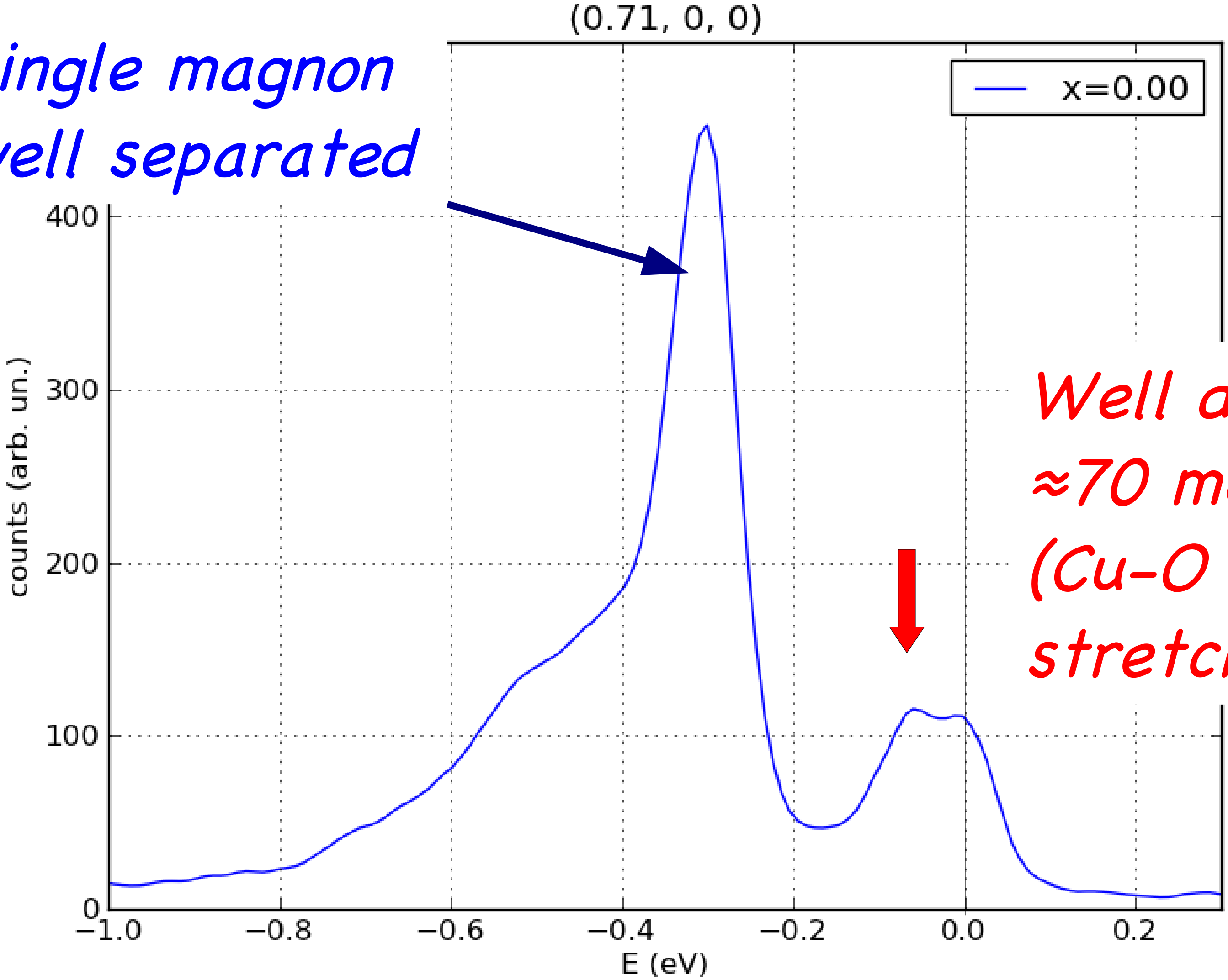
Heisenberg
with higher-order
couplings

B. Lebert *et al.*, *PRB* **95** (2017) 155110

Na-CCOC Cu L_3 experiment on ID32 (ESRF)

$Ca_2CuO_2Cl_2$

Resol. = 70 meV

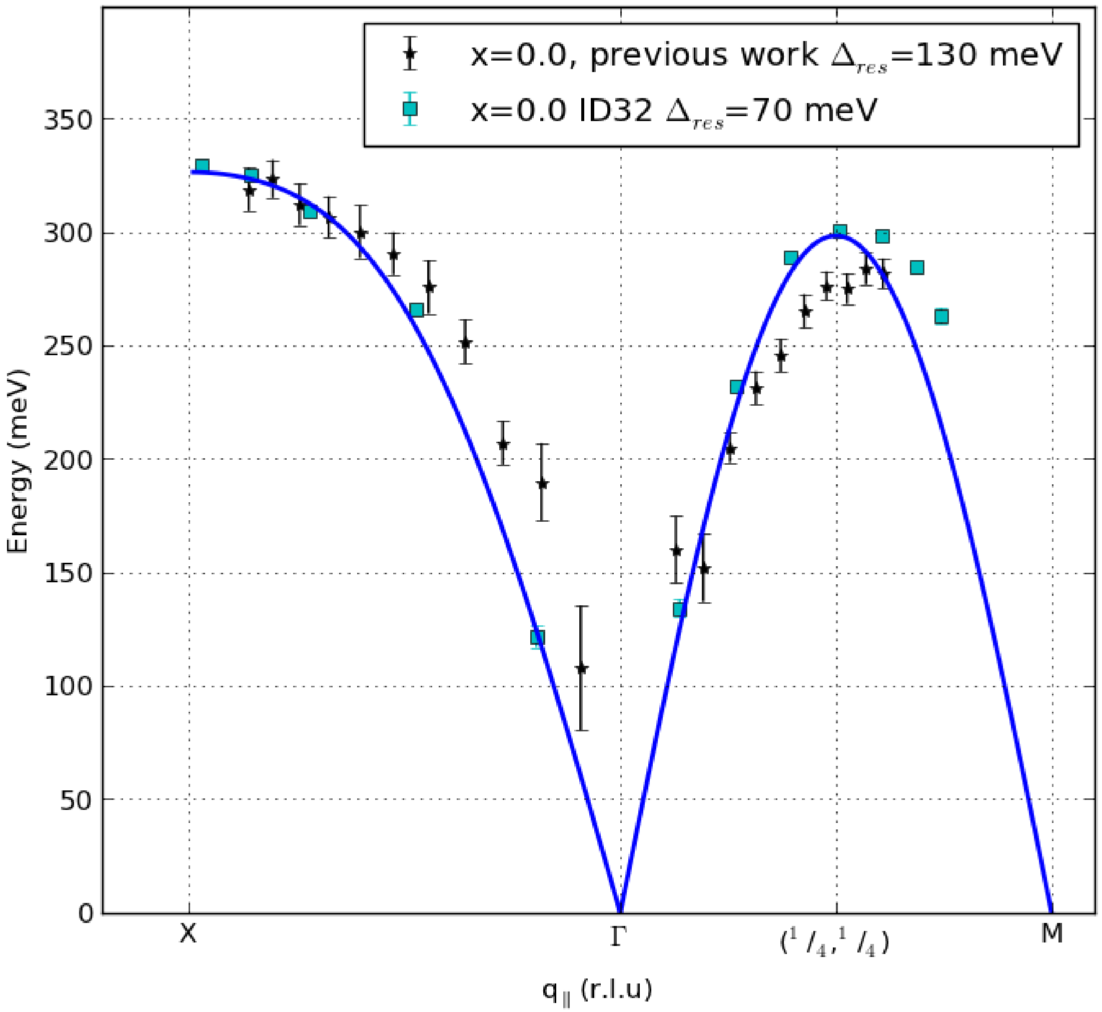


Single magnon well separated

Well defined phonon ≈70 meV (Cu-O bond stretching energy)

B. Lebert *et al.*, *ESRF experiment HC-2702 (2016)*

Results ESRF Parent compound: $Ca_2CuO_2Cl_2$



Disp. param. (opt. ESRF data)

$t_{hopping}$(meV)= 340.0

U_{Coul}(meV)= 3000.0

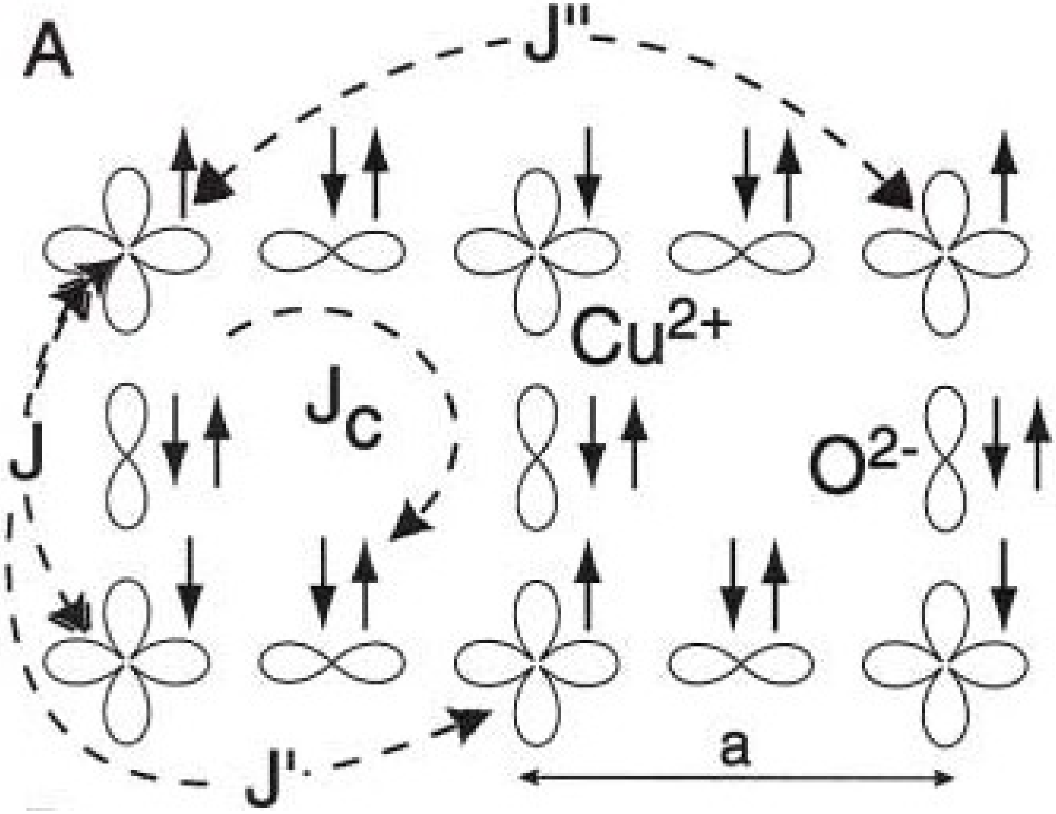
$J_{Heisenberg}$(meV)= 142.

J_{cyclic}(meV)= 40.

$J_1=J_2$(meV)= 1.98

B. Lebert *et al., ESRF experiment HC-2702 (2016)*

Results parent compound: $Ca_2CuO_2Cl_2$



from Coldea, *PRL* **86**, (2001)

$t_{hopping}$(meV)= 295.0

U_{Coul}(meV)= 2200.0

J_0 (meV)= 141;

J_{cyclic}(meV)= 57; J_1=J_2(meV)= 3

	J_0 (meV)	
System	Experiment	QMC (QC)
$Ca_2CuO_2Cl_2$	141(4)	--
$CaCuO_2$	-- (120-130)**	140(20)* (132)**
La_2CuO_4	146***	160(13)*

* K. Foyevtsova, *et al. Phys. Rev. X* **4**, (2014)
Minola, *et al. PRB* **87, (2013)
***Coldea, *et al. PRL* **86**, (2001)

B. Lebert *et al., PRB* **95** (2017) 155110