

# Interaction of X-rays with matter

*A. Rogalev*

*European Synchrotron Radiation Facility (ESRF), Grenoble, France*



**What do you know?  
RUMSFELD**

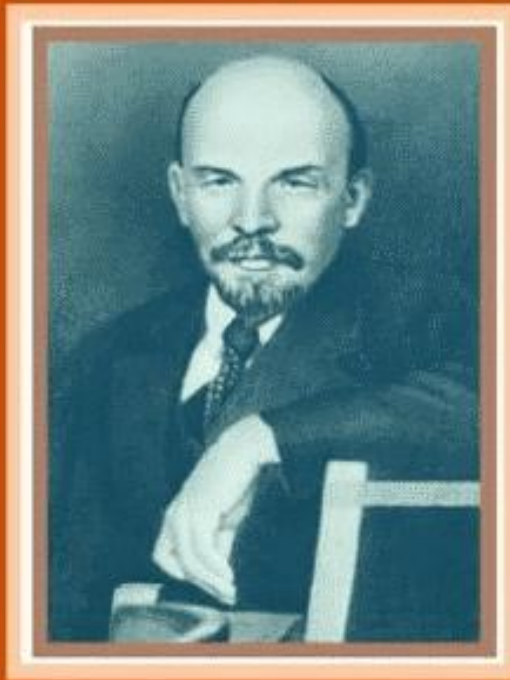
"That there are known knowns - there are things we know that we know"

"There are known unknowns - that is to say there are things we now know we don't know"

"But there are also unknown unknowns - there are things we do not know we don't know."

*The electron is as inexhaustible as the atom...*

**Materialism and  
Empirio-Criticism**  
Critical Comments on  
A Reactionary Philosophy



**Vladimir I. Lenin**

ТЕОРЕТИЧЕСКАЯ ФИЗИКА

VIII

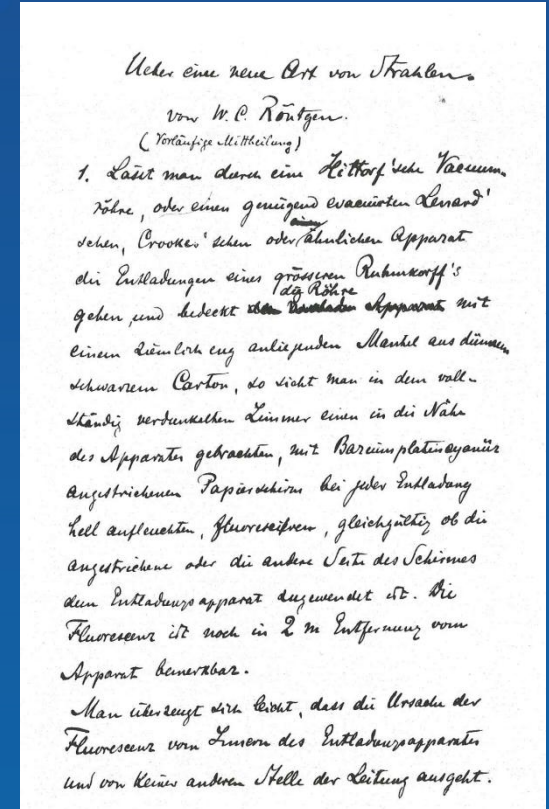
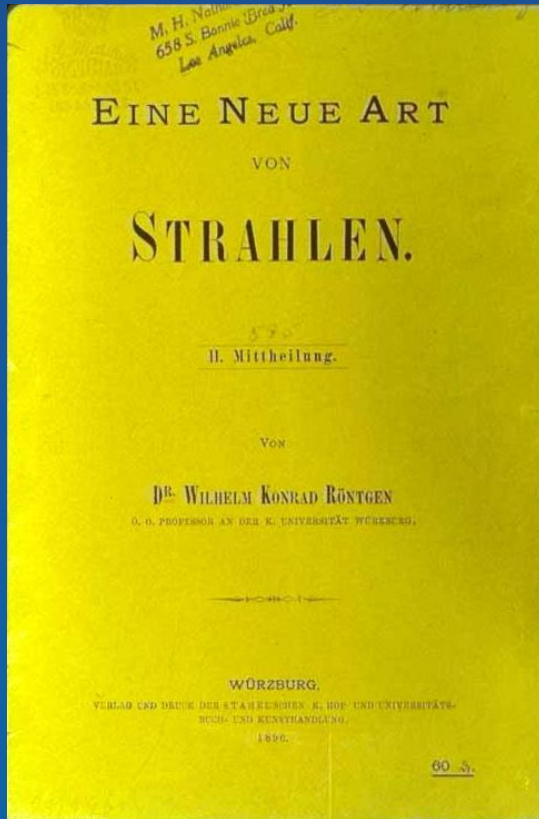
Л.Д. ЛАНДАУ  
Е.М. ЛИФШИЦ

**It is easy to show that**

$$\Delta\mu(\hbar\omega) \propto \sum_{b,\beta} (-1)^\beta T_\beta^{(b,\mathcal{G})}(\varepsilon, \varepsilon^*, k) \otimes Q_{-\beta}^{(b,\mathcal{G})}(\hbar\omega)$$



# In 1895 Dr. W.K.Röntgen has discovered "Eine Neue Art von Strahlen"



On December 28, 1895 W.C. Röntgen had submitted his manuscript  
"On a New Kind of Ray, A Preliminary Communication" to the Würzburg Physical Medical Society.  
On the 1<sup>st</sup> of January 1896 he sent copies of his manuscript to several renowned physicists.

# Comptes rendus hebdomadaires des séances de l'Académie des sciences

## Séance du lundi 23 Mars 1896

( 717 )

- » J'ai employé le dispositif de la chambre noire.
- » Un trou de petit diamètre ( $1^{mm}$ ), percé dans une plaque de laiton, située à quelques centimètres du tube, permettait d'obtenir l'image des régions actives sur une plaque photographique placée au delà.
- » Je vérifiai d'abord ainsi que les parties utiles de la plaque sont bien celles que frappent les rayons cathodiques.
- » Puis je disposai sur le trajet de ces rayons un obstacle en aluminium de forme simple (étoile ou croix); l'image de cet obstacle apparut très intense. Elle n'apparut pas lorsque, au moyen d'un aimant, on empêcha les rayons cathodiques de tomber sur l'obstacle.
- » Cet obstacle pouvait d'ailleurs être pris comme anode : cela ne changea rien à aucun de ces deux résultats.
- » L'expérience réussit également bien avec des corps moins perméables aux rayons X que l'aluminium et le verre, tels que le cristal et le platine. Pour le montrer, j'ai construit un tube en verre transparent aux rayons X, et, à l'intérieur de ce tube, je plaçai un obstacle mi-partie en platine, mi-partie en cristal. Naturellement la plaque photographique fut disposée de manière à recevoir les rayons X émis par celle des faces de l'obstacle que frappaient les rayons cathodiques. Les images obtenues furent encore nettes et très intenses.
- » Dans aucune de ces expériences, la cathode ne donna son image.

» En résumé, *aux points où une matière quelconque arrête les rayons cathodiques, se développent des rayons de Röntgen*, et il ne paraît pas s'en développer en d'autres points.

» Ces rayons divergent dans toutes les directions; seulement certaines substances, telles que le cristal, les absorbent rapidement; on comprend ainsi pourquoi les tubes en cristal ont un rendement faible, quoique la production y soit intense. Toute l'importance pratique des tubes à fluorescence verdâtre résulte de la transparence du verre dont ils sont formés<sup>(1)</sup>.

PHYSIQUE. — *Recherches concernant les propriétés des rayons X*. Note de MM. le Prince B. GALITZINE et A. DE KARNOJITZKY, présentée par M. L. Cailletet. (Extrait.)

« En poursuivant, avec de nouveaux tubes de Crookes, de formes diverses, les recherches que nous avons déjà soumises à l'Académie, nous avons obtenu de nouvelles photographies d'après lesquelles les centres d'émission des rayons X sont nettement caractérisés.

(1) Travail fait au Laboratoire de Physique de l'École Normale.

( 718 )

» D'après l'ensemble de nos recherches, l'existence, dans quelques cas, d'un centre d'émission d'origine anodique semble être mise désormais hors de doute. On observe en outre quelquefois que, si l'on intervertit l'anode et la cathode, le nouveau centre anodique se produit là où se trouvait auparavant le centre cathodique, mais ce dernier est toujours plus intense.

» Pour expliquer l'ensemble des faits observés, nous avons, dans notre Note précédente, proposé l'hypothèse des foyers, qui semble bien correspondre à tous les détails de nos expériences et qui, d'ailleurs, est d'accord avec ce fait, que les centres d'émission se trouvent d'ordinaire dans le voisinage de l'endroit où le verre du tube de Crookes devient fortement fluorescent, vu que c'est précisément là que l'action des rayons cathodiques se concentre. C'est cette hypothèse qui nous paraît offrir le plus de vraisemblance....

» Il se présente une autre question. Les rayons X correspondent-ils à des vibrations longitudinales ou à des vibrations transversales? Cette question pourrait être tranchée si l'on pouvait démontrer qu'ils se polarisent.

» Les premières recherches que nous avons entreprises à ce sujet ont échoué. Nous avons alors fait préparer trois petites plaques de tourmaline très minces (environ  $0^{mm},5$  d'épaisseur). Sur la plus grande se posaient les deux autres, une parallèlement et l'autre perpendiculairement à la première. S'il y a polarisation là où les plaques sont croisées, on doit s'attendre à voir l'action des rayons X affaiblie. Il va sans dire que l'action de la lumière ordinaire a été exclue et qu'on a changé plusieurs fois la position relative des petites plaques, afin d'éliminer toute influence d'inégale épaisseur ou de manque d'homogénéité. Dans les huit épreuves obtenues, on peut distinguer que là où les plaques ont été croisées l'action photochimique des rayons X a été moindre<sup>(1)</sup>.

» On peut en conclure que les rayons X se polarisent et, par suite, qu'ils correspondent à des vibrations transversales. »

(1) Pour renforcer ces épreuves, nous avons eu recours à M. Bourinsky, qui a récemment indiqué une méthode ingénieuse pour renforcer les négatifs faibles, méthode basée sur le principe de la superposition des pellicules (voir *Bulletin de l'Académie impériale des Sciences de Saint-Petersbourg*, n° 4, avril 1895). La différence des teintes a été mise ainsi hors de doute, comme on peut le voir sur les épreuves que nous avons l'honneur de soumettre à l'Académie.

C.R. Acad.Sci. Paris 122 (1896) 717-718

# Comptes rendus hebdomadaires des séances de l'Académie des sciences

## Séance du lundi 30 Mars 1896

( 783 )

PHYSIQUE. — *Sur la diffraction et la polarisation des rayons de M. Röntgen.*  
Note de M. G. SAGNAC, présentée par M. Lippmann.

« I. Pour obtenir, avec un réseau par transmission à intervalles égaux, des images réelles d'une fente lumineuse <sup>(1)</sup>, on placerait ce réseau en avant d'une image réelle fournie par un faisceau convergent. On ne peut le faire avec les rayons de M. Röntgen, qui divergent à l'extérieur du tube de Crookes et pour lesquels on ne possède pas de lentilles. Pour obtenir des images réelles d'une fente, j'ai diaphragmé par une seconde fente, derrière laquelle est placé le réseau, l'entrée d'une grande chambre noire.

« J'ai employé un réseau de  $\frac{1}{10}$  de millimètre, construit par M. Gaiffe avec des fils de platine de près de  $\frac{1}{20}$  de millimètre de diamètre. La partie inférieure d'un faisceau lumineux défini par deux fentes métalliques distantes de 7<sup>mm</sup>,5 passe au-dessous de la monture métallique du réseau et forme sur le verre dépoli de la chambre noire, à 35<sup>cm</sup> au delà du réseau, une image réelle de la première fente. La partie supérieure du même faisceau traverse à 2<sup>mm</sup>,5 derrière la seconde fente le réseau placé sous l'incidence de 45°, ce qui augmente ici les déviations et les intensités des faisceaux diffractés. Ces derniers ajoutent à l'image directe autant d'images diffractées dont quatre surtout sont bien nettes. Ces cinq images de la première fente supposée peu étroite (1<sup>mm</sup>) se renforcent en se superposant en partie et forment ainsi une image d'aspect cannelé, plus large de 7<sup>mm</sup> environ que l'image inférieure sans diffraction.

« Cela suffit pour conclure : *Les rayons de Röntgen qui ont impressionné la plaque sensible à travers le volet de bois du châssis ne possèdent pas de longueurs d'onde supérieures à 4 centièmes de micron <sup>(1)</sup>.*

« II. Les rayons de M. Röntgen sont-ils liés à un vecteur soit longitudinal, soit transversal et, dans ce dernier cas, comment les polariser ?

« On ne peut songer actuellement à les polariser par réflexion, ni par réfraction, ni sans doute par diffraction. L'émission et la diffusion seraient peut-être à essayer. Il est, en tout cas, plus simple de tenter de les polariser par absorption.

( 785 )

chroïsme. La plage des sections principales parallèles laisse passer une intensité dont l'excès sur celle de l'autre plage est mesuré par  $(\sigma^2 - e^2)$ .

» D'ailleurs pour les différences  $(\sigma - e)$ , de signes peut-être différents, relatives à différentes longueurs d'onde, les différences d'intensité correspondantes s'ajoutent toujours en faveur de la plage où les sections principales sont parallèles.

» J'ai recherché si l'effet se produit avec les rayons de M. Röntgen en disposant de tels systèmes de trois lames sur le double de papier noir qui recouvre la plaque sensible. Le temps de pose s'est élevé jusqu'à plusieurs heures. Les clichés obtenus avec l'intensité désirable n'ont pas révélé de dichroïsme sensible :

Corps employés.	Quartz.	Spath.	Tourmalines brunes <sup>(1)</sup> .	Mica.	Ferrocyanure de potassium.
Épaisseurs de chaque lame.	0 <sup>mm</sup> ,03	0 <sup>mm</sup> ,4	0 <sup>mm</sup> ,5	0 <sup>mm</sup> ,2	0 <sup>mm</sup> ,4 à 2 <sup>mm</sup>

« Une précaution est indispensable pour éliminer l'influence d'une petite différence de nature comme il est arrivé pour les tourmalines : on fait tourner de 90° sur place chacune des deux demi-lames supérieures de manière que les plages des sections principales parallèles et des sections croisées s'échangent mutuellement. Une différence d'intensité due au dichroïsme doit suivre, dans son déplacement, le parallélisme des sections principales. Or, la très petite différence d'intensité, aperçue avec les tourmalines, persistait toujours sur la même demi-lame.

« Si la méthode se prête à un contrôle aussi facile et se trouve indépendante de la complexité des radiations employées, elle n'est pas, malheureusement, bien sensible. On voit aisément, dans le cas de la lumière, que, pour déceler une différence de  $\frac{1}{10}$  par exemple, entre l'unité et le rapport  $\frac{\sigma}{e}$ , il faudrait que la photographie pût révéler une différence relative de  $\frac{1}{10}$  entre les intensités lumineuses qui impressionnent les deux plages contiguës, ce qui dépasse déjà beaucoup ce qu'on peut espérer.

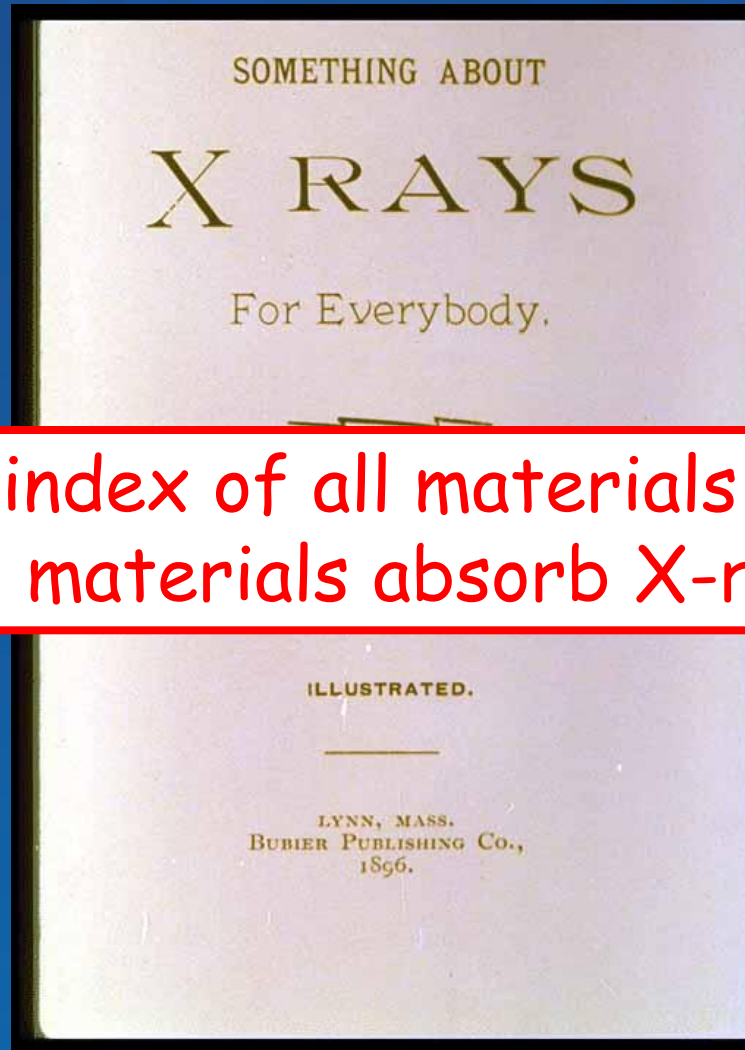
« On ne saurait donc tirer de ces expériences négatives de dichroïsme un argument de grande valeur en faveur de l'hypothèse d'un vecteur longitudinal. Elles ajoutent seulement une distinction particulière de plus entre les rayons X et les rayons lumineux que nous connaissons <sup>(2)</sup>. »

<sup>(1)</sup> Ces lames de quartz, de spath et de tourmalines, fournies par M. Verlain, étaient parallèles à l'axe. Les lames de mica et de ferrocyanure étaient obtenues par cliage.

<sup>(2)</sup> Travail fait au laboratoire de M. Bouty, à la Sorbonne, en février et mars. J'avais déjà réalisé quelques-unes de ces expériences, quand M. J.-J. Thomson a publié, dans le numéro du 27 février du journal *The Nature*, dont je viens d'avoir connaissance, la même expérience négative dans le cas de la tourmaline.

### C.R. Acad.Sci. Paris 122 (1896) 783-785





Refractive index of all materials is close to 1  
 All materials absorb X-rays

*How-to book gave step-by-step instructions on making radiographs, and included forms for ordering the equipment described.*



The refractive index of a material in the x-ray range

$$n = 1 - \delta + i\beta \quad \text{or} \quad n = 1 - \frac{r_0 \lambda^2}{2\pi} N_{\text{at}} (f_1 - if_2)$$

BUT

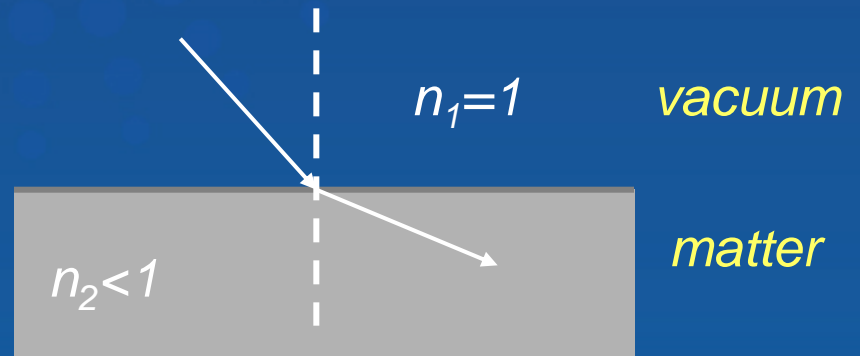
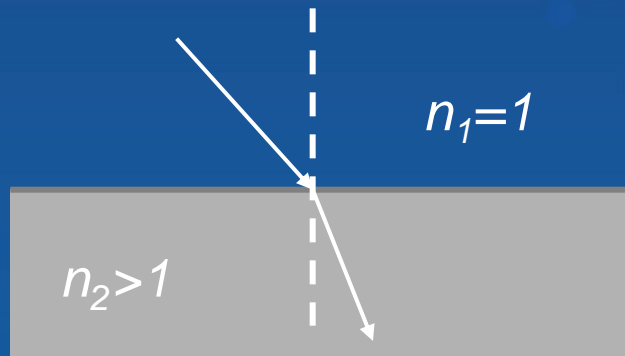
$$1/n \neq v/c$$

**The great challenge for X-ray optics !!!**

Snell's law:  $n_1 \cos(\theta_1) = n_2 \cos(\theta_2)$

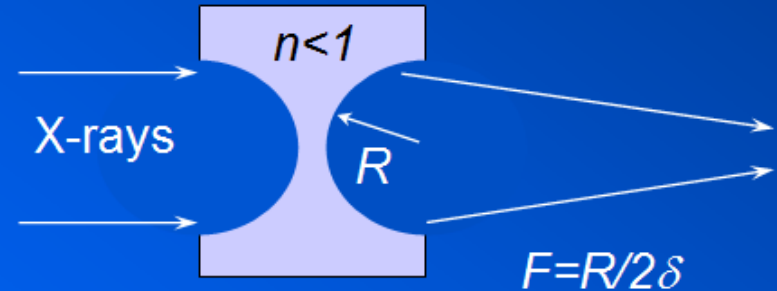
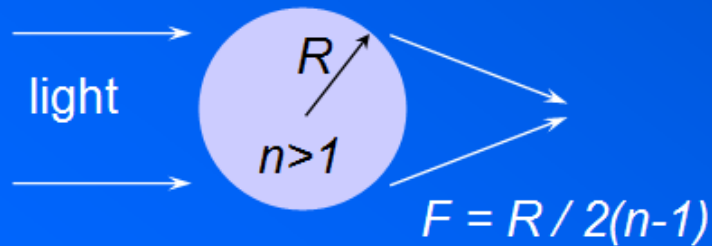
visible light

X-rays



convex lens

concave lens



$n > 1$   
 $n-1 \sim 0.1$

$Re(n) = 1 - \delta + i\beta < 1$   
 $1-n \sim 10^{-5} - 10^{-6}$

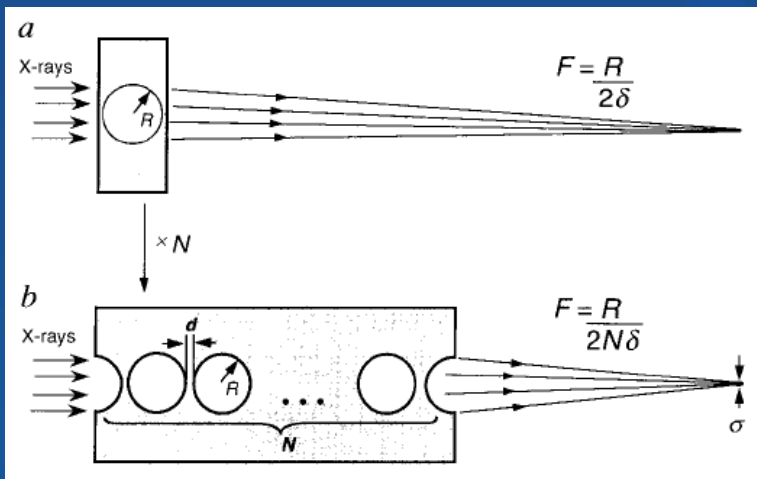
NATURE · VOL 384 · 7 NOVEMBER 1996

# A compound refractive lens for focusing high-energy X-rays

A. Snigirev\*, V. Kohn†, I. Snigireva\* & B. Lengeler\*‡

\* European Synchrotron Radiation Facility, BP220, F-38043 Grenoble Cedex, France

† Kurchatov, I. V., Institute of Atomic Energy, 123182 Moscow, Russia



Refractive optics after ~15 years development

standard tool at SR beamlines worldwide.

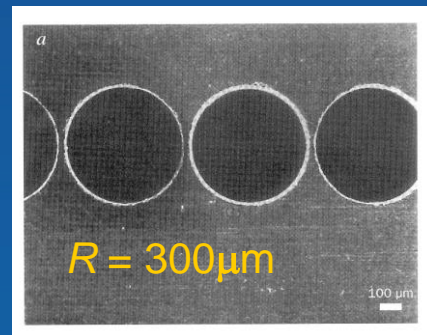
~ 50% of ESRF beamlines use refractive lenses

*the most versatile and adaptable X-ray optics*

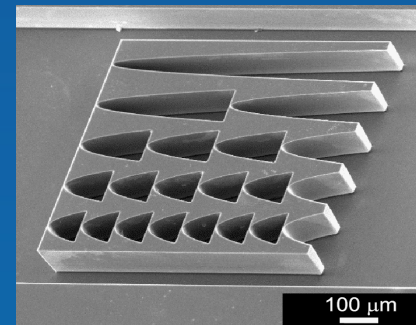
- energy range -from a few keV to hundreds of keV
- focal length -from a few millimeters to tens of meters
- focal spot -from tens of nanometers to tens of microns
- microradian collimation
- high stability and low cost

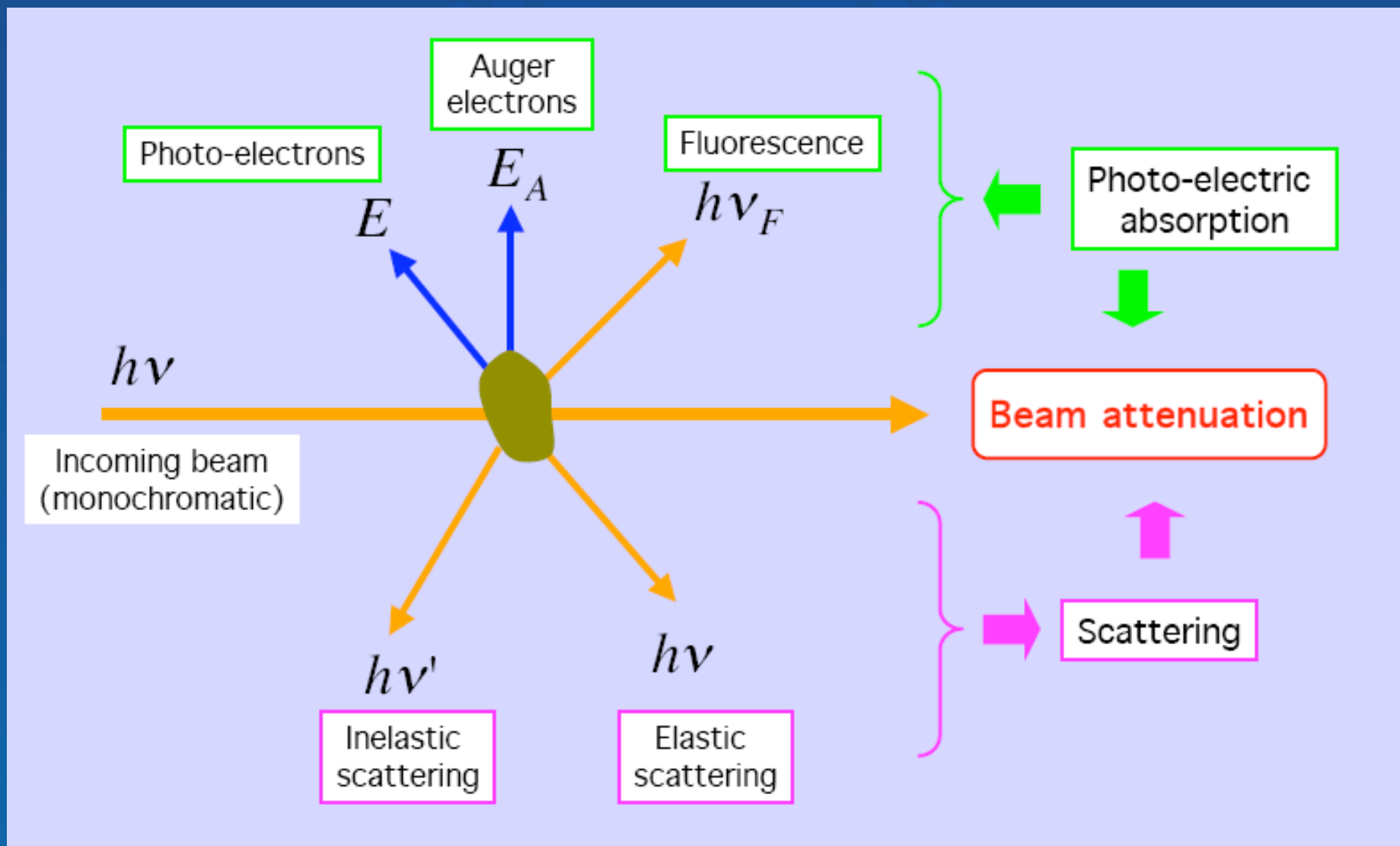
*applications: microdiffraction, microfluorescence and imaging, standing wave microscopy etc.*

## The first AL CRL

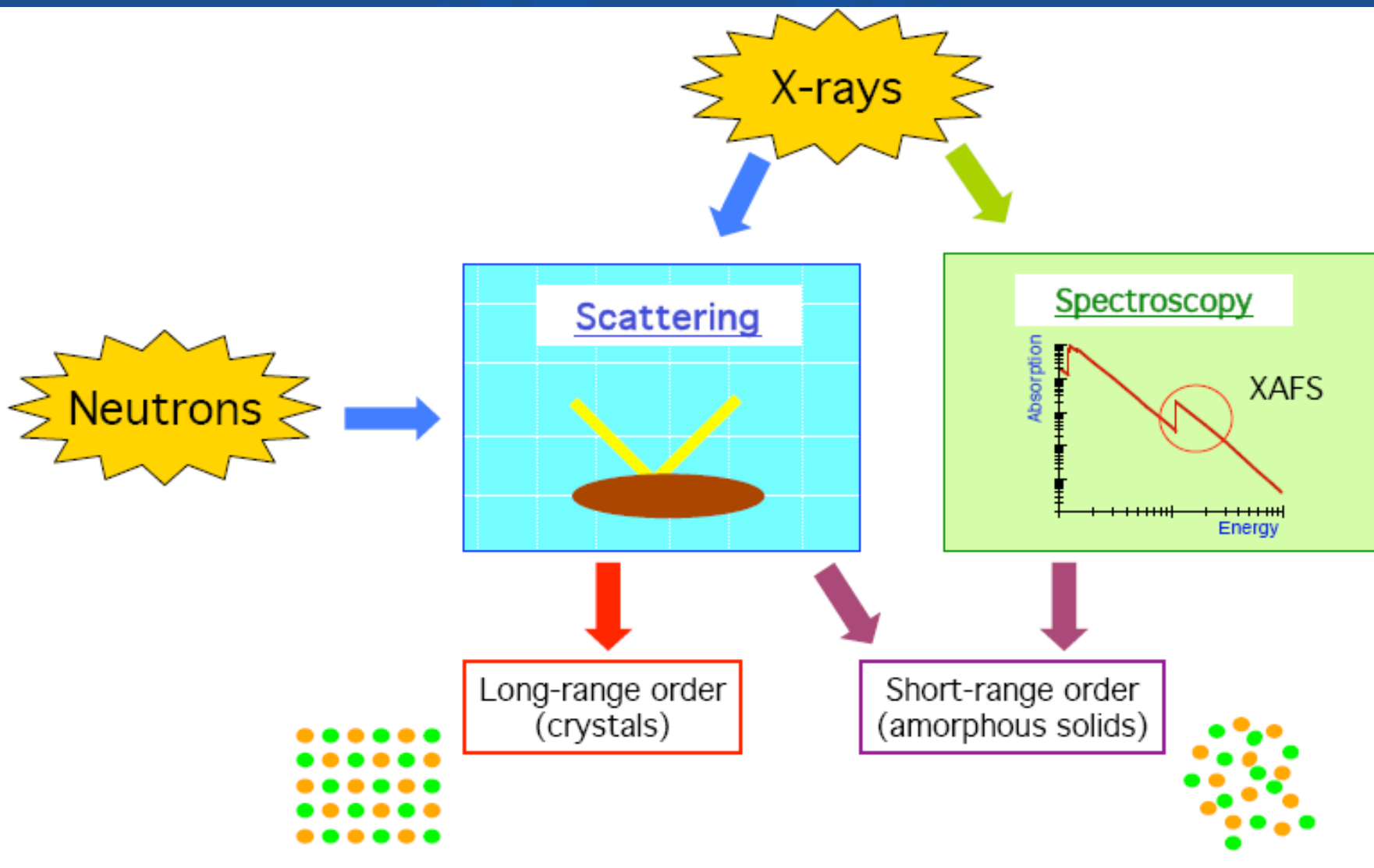


## Si parabolic lens

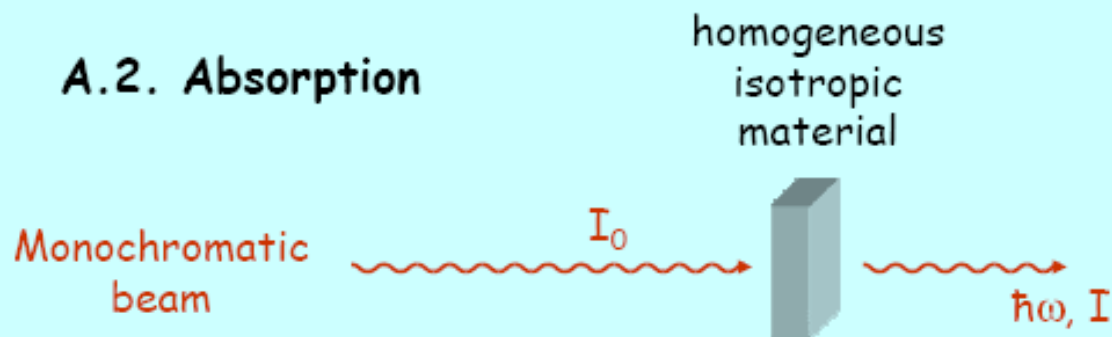








## A.2. Absorption



$$I = I_0 \exp(-\mu D)$$

Beer-Lambert law :

$\mu$ : total linear absorption coefficient  
 D: sample thickness

$$\ln(I_0/I) = \mu D$$

For a crystalline solid :

$$\mu = \frac{1}{V} \sum_{i=1}^n \sigma_i$$

V : cell volume with n atoms

$\sigma_i$  = absorption cross section

cm<sup>2</sup> or Mbarn

$$1 \text{ Mbarn} = 10^{-18} \text{ cm}^2$$

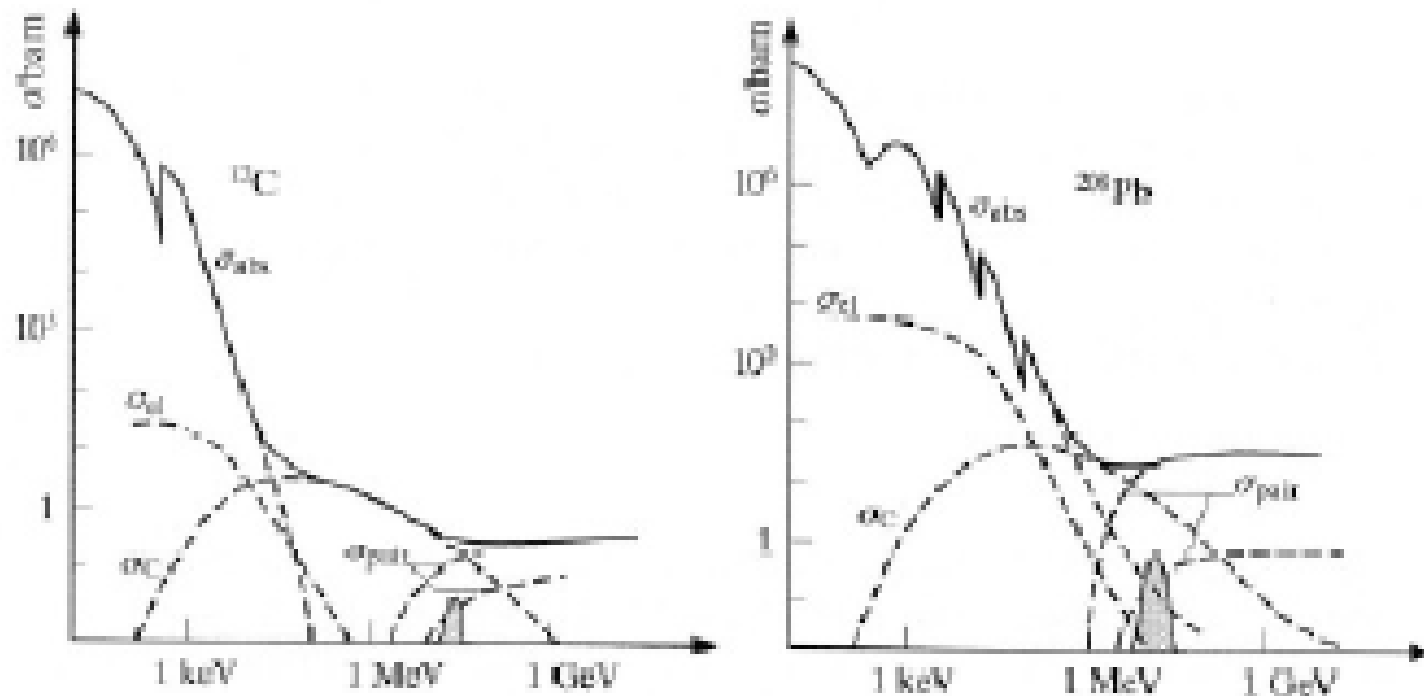
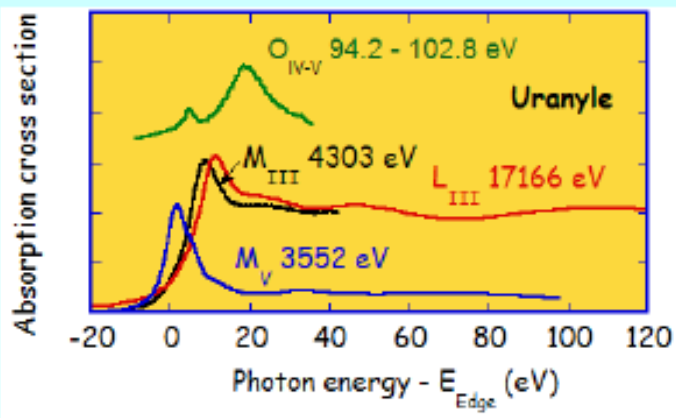
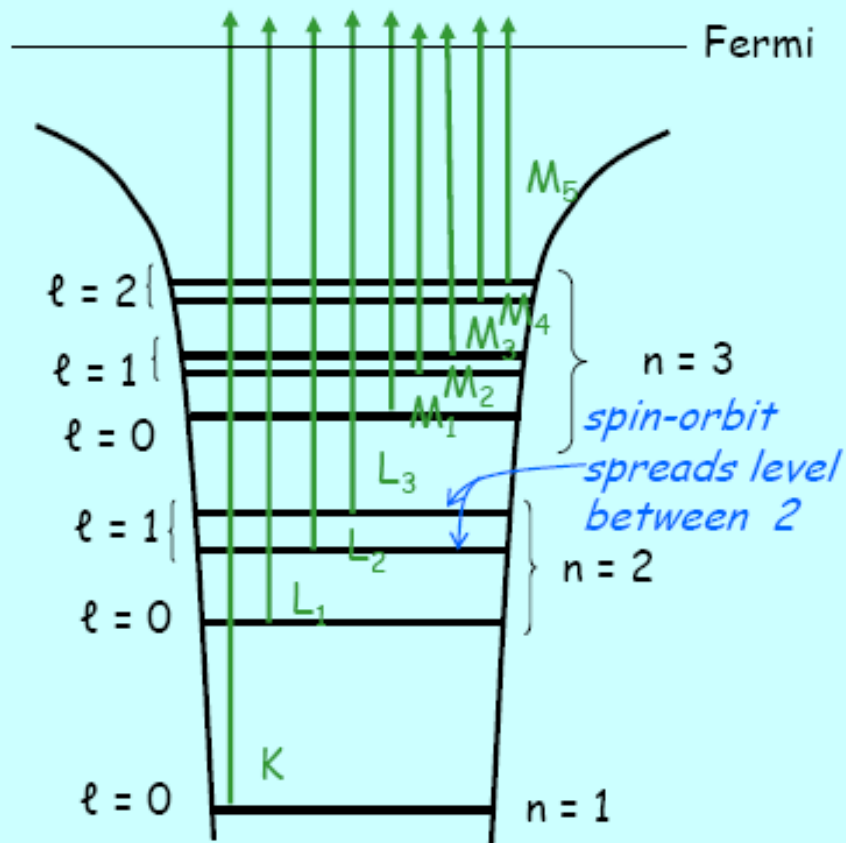


Fig. 7. Energy dependence of the cross-sections for the interaction of x-rays with a carbon and lead atom. The full line corresponds to the total cross-section  $\sigma_{\text{tot}}$ ,  $\sigma_{\text{abs}}$  is the photoelectric absorption,  $\sigma_{\text{el}}$  corresponds to elastic scattering and  $\sigma_{\text{C}}$  to inelastic (Compton) scattering,  $\sigma_{\text{pair}}$  to the creation of electron-positron pairs. The shaded areas are the nuclear absorption cross-section ([24])

For any chemical element there is a set of absorption edges

Some edges (eV)

	K	L <sub>2</sub>	M <sub>2</sub>
H	13.6		
C	284.2		
Fe	7112	720	52.7
Ag	25514	3524	604
U	115606	20948	5182



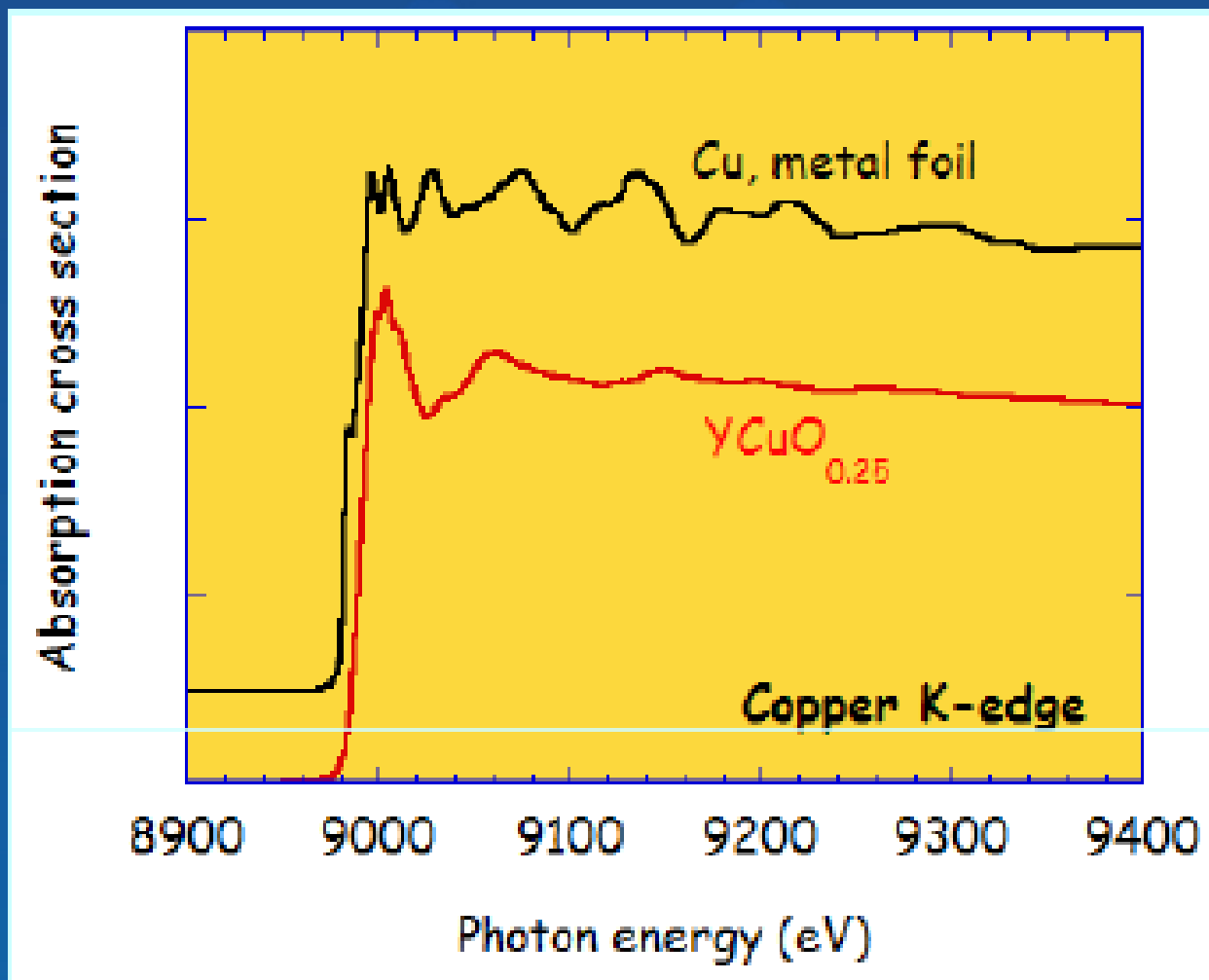
Experiment Ch. Den Auwer *et al.*

*Deeper is the edge*

*→ Shorter is the time life*

*→ Broader is the edge*





X-ray absorption spectrum reflects local electronic and atomic structure of a material

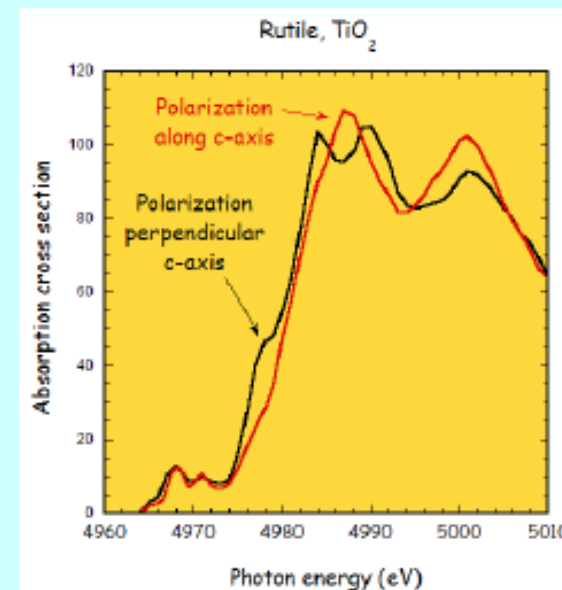
### A.3. Dependence on the polarization light

Pleochroism or dichroism is the change in color evident as the mineral is rotated under plane-polarized light.

Due to adsorption of particular wavelengths of light.  
 → transmitted light to appear colored.

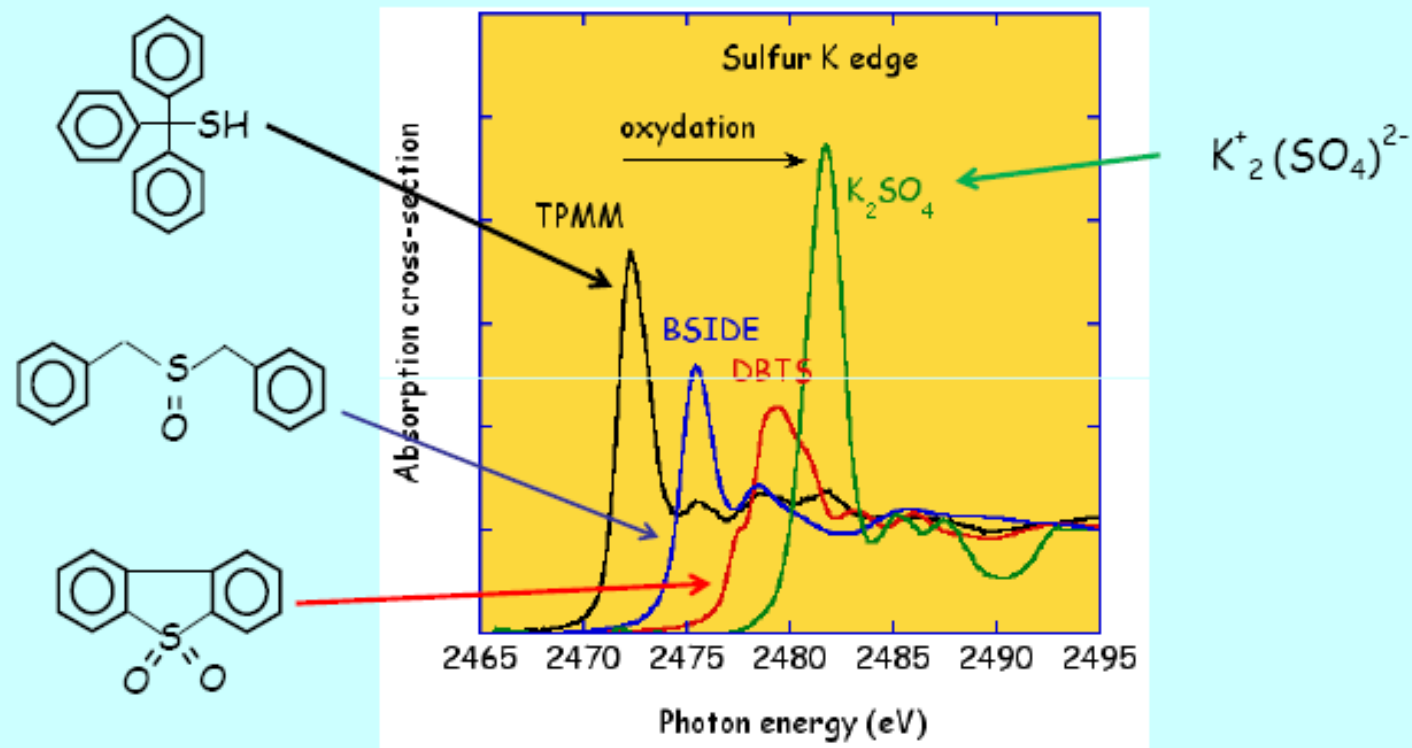
Function of the thickness and the particular chemical and crystallographic nature of the mineral.

Also true in the X-ray energy range :



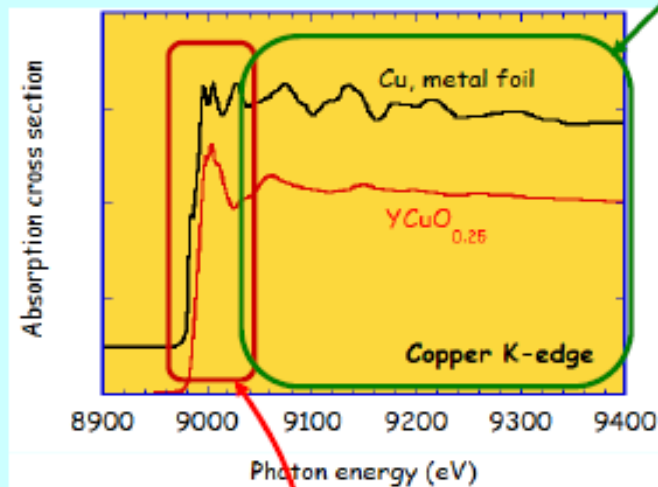
*B. Poumellec et al., DCI-LURE*

## A.4. Dependence on the oxidation state



Pichon *et al.* IFP, LURE

## EXAFS and XANES

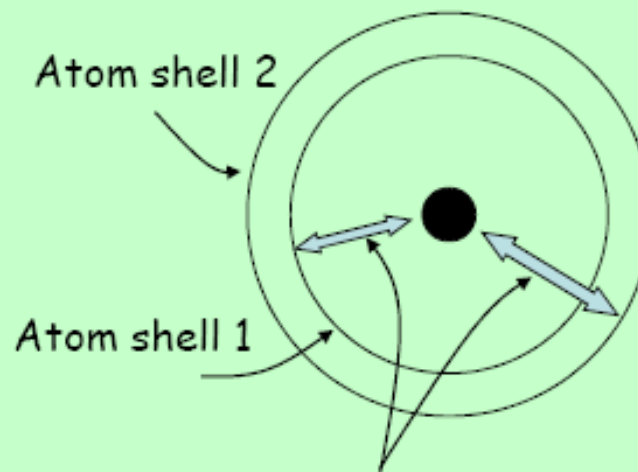


### XANES

XANES gives information on

- 3D arrangement
- Local symmetry,
- Electronic and magnetic structure

### EXAFS



*Final states are calculated by simple interference between the outgoing wave and the backscattered waves by the different shells*

EXAFS gives information on

- The number of atoms per shell,
- The distance of the shells



### D.3. Characteristic times

1 - Time of the process « absorption of the photon »

$$t_1 = 1/W_{fi}, \quad W_{fi} \text{ absorption probability}$$

$$t_1 < 10^{-20} \text{ s}$$

*multi-electronic process can be seen at low energy of the photoelectron*

2 - Time life of the core hole

$$t_2 = \hbar / \Delta E_i, \quad \Delta E_i \text{ width of the level}$$

for 1s for Z = 20 up to 30,  $E_i \approx 1 \text{ eV}$

$$t_2 \approx 10^{-15} \text{ à } 10^{-16} \text{ s}$$

3 - Relaxation time of the electron

Effect on all the electrons of the field created by the hole and the photoelectron. Many kinds of process, multielectronic.

$$t_3 \approx 10^{-15} \text{ à } 10^{-16} \text{ s}$$

4 - Transit time of the photoelectron outward from the atom

Depends on the photoelectron kinetic energy, for  $E_c = 1 \text{ à } 100 \text{ eV}$

$$t_4 \approx 10^{-15} \text{ à } 10^{-17} \text{ s}$$

5 - Thermic vibration

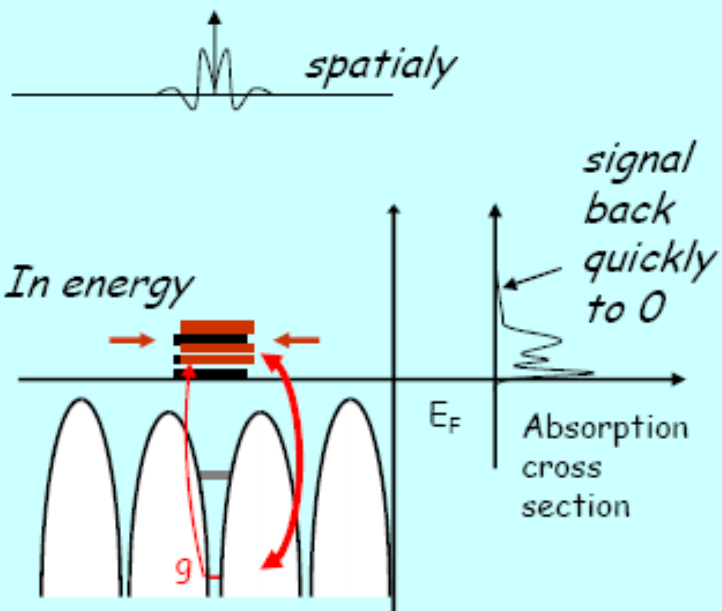
$$t_5 \approx 10^{-13} \text{ à } 10^{-14} \text{ s}$$

*X-ray absorption takes a snap shot of the pertubated material*

53

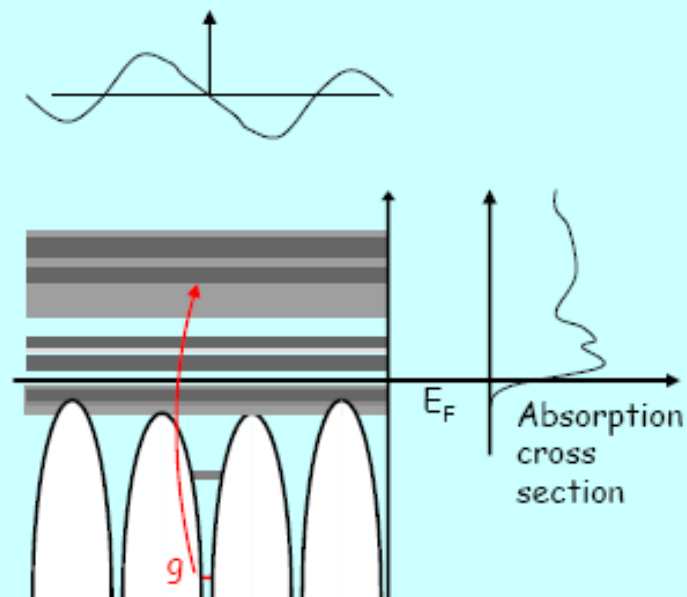
## D.4. Mono and multi-electronic approaches

### Localized final states



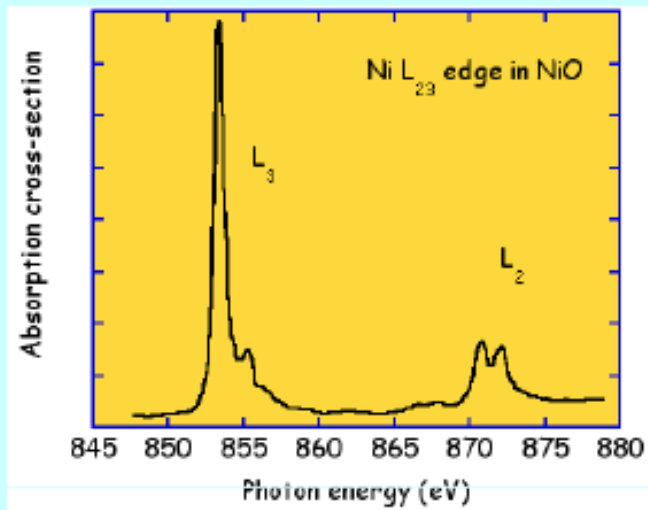
- Interaction with the hole
- Several possible electronic states...

### Non localized final states



- The photo-electron sees far from the absorbing atom

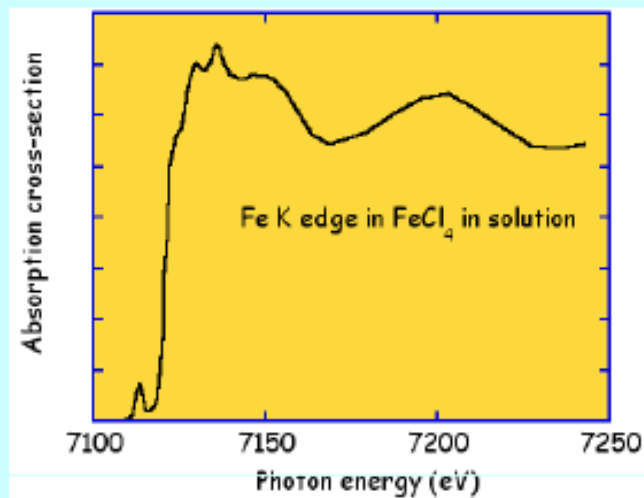
## Localized final states



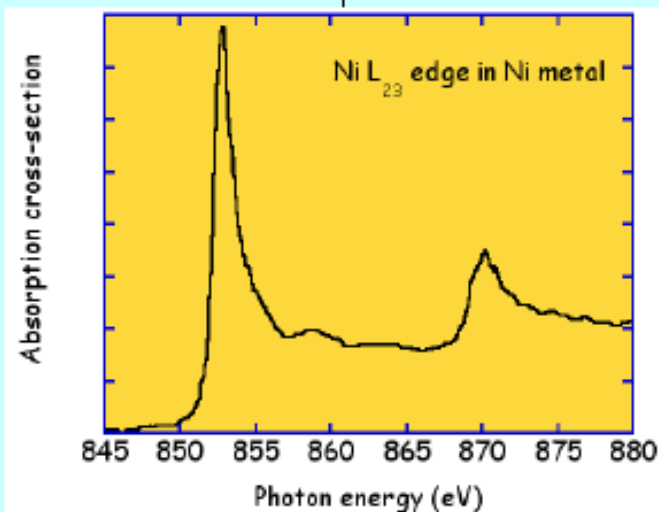
multiplet

 A. Scherz, PhD  
Thesis, Berlin

## Non localized final states



mono-electronic theory

 O. Proux *et al.*  
FAME, ESRF

 Intermediate  
situation ...

55

# X-ray Absorption Cross-section

$$\sigma = \sum_{fi} |\langle \psi_f | \hat{O} | \psi_i \rangle|^2 \delta(\hbar\omega - (E_f - E_i))$$

In the x-ray regime, the magnetic part of the electromagnetic field can be neglected the operator  $\hat{O}$  is reduced to its electric part (multipolar expansion of this electric field)

$$\hat{O} = \vec{\epsilon} \cdot \vec{r} \left( 1 - \frac{1}{2} i \vec{k} \cdot \vec{r} \right)$$

E1    E2

$$\begin{aligned} \sigma = & \sum_{\alpha\beta} \epsilon_{\alpha}^* \epsilon_{\beta} D_{\alpha\beta} - \frac{i}{2} \sum_{\alpha\beta\gamma} \epsilon_{\alpha}^* \epsilon_{\beta} k_{\gamma} (I_{\alpha\beta\gamma} - I_{\beta\alpha\gamma}^*) \\ & + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \epsilon_{\alpha}^* \epsilon_{\beta} k_{\gamma} k_{\delta} Q_{\alpha\beta\gamma\delta} \end{aligned}$$

$$D_{\alpha\beta} = \sum_{fi} \langle \psi_i | r_{\alpha} | \psi_f \rangle \langle \psi_f | r_{\beta} | \psi_i \rangle$$

$$I_{\alpha\beta\gamma} = \sum_{fi} \langle \psi_i | r_{\alpha} | \psi_f \rangle \langle \psi_f | r_{\beta} r_{\gamma} | \psi_i \rangle$$

$$Q_{\alpha\beta\gamma\delta} = \sum_{fi} \langle \psi_i | r_{\alpha} r_{\beta} | \psi_f \rangle \langle \psi_f | r_{\gamma} r_{\delta} | \psi_i \rangle.$$

Dipole-Dipole E1.E1 Contribution

Dipole-Quadrupole E1.E2 Contribution

Quadrupole-Quadrupole E2.E2 Contribution

$$\sigma = \sum_{\alpha\beta} \epsilon_{\alpha}^* \epsilon_{\beta} \boxed{D_{\alpha\beta}} - \frac{i}{2} \sum_{\alpha\beta\gamma} \epsilon_{\alpha}^* \epsilon_{\beta} k_{\gamma} (I_{\alpha\beta\gamma} - I_{\beta\alpha\gamma}^*) + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \epsilon_{\alpha}^* \epsilon_{\beta} k_{\gamma} k_{\delta} Q_{\alpha\beta\gamma\delta}$$

This rank-2 tensor is fully symmetric and reflects anisotropy of the electronic structure of absorbing atom:  
**linear birefringence and linear dichroism effects.**

In the presence of an external magnetic field or spontaneous magnetic order, it has an antisymmetric part that is responsible for **the Faraday effect and the magnetic circular dichroism.**

Further terms in the symmetric part are quadratic in the magnetization and describe **the Cotton-Mouton effect and the magnetic linear dichroism.**

$$\sigma = \sum_{\alpha\beta} \epsilon_{\alpha}^* \epsilon_{\beta} D_{\alpha\beta} - \frac{i}{2} \sum_{\alpha\beta\gamma} \epsilon_{\alpha}^* \epsilon_{\beta} k_{\gamma} (I_{\alpha\beta\gamma} - I_{\beta\alpha\gamma}^*) + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \epsilon_{\alpha}^* \epsilon_{\beta} k_{\gamma} k_{\delta} Q_{\alpha\beta\gamma\delta}$$

This rank-4 tensor may give rise to an optical anisotropy in cubic crystals.

In the presence of an external magnetic field or spontaneous magnetic order, it is also giving rise to linear magneto-optical effects: **the Faraday effect and the magnetic circular dichroism.**

$$\sigma = \sum_{\alpha\beta} \epsilon_{\alpha}^* \epsilon_{\beta} D_{\alpha\beta} - \frac{i}{2} \sum_{\alpha\beta\gamma} \epsilon_{\alpha}^* \epsilon_{\beta} k_{\gamma} (I_{\alpha\beta\gamma} - I_{\beta\alpha\gamma}^*) + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \epsilon_{\alpha}^* \epsilon_{\beta} k_{\gamma} k_{\delta} Q_{\alpha\beta\gamma\delta}$$

This rank-3 tensor is fully asymmetric and in the absence of any external magnetic field or spontaneous magnetic order describes effects related to natural optical activity:  
**circular birefringence and circular dichroism effects.**

In the presence of an external magnetic field or spontaneous magnetic order, it is responsible for non-reciprocal or directional optical effects: **x-ray non-reciprocal linear dichroism and magnetochiral dichroism.**

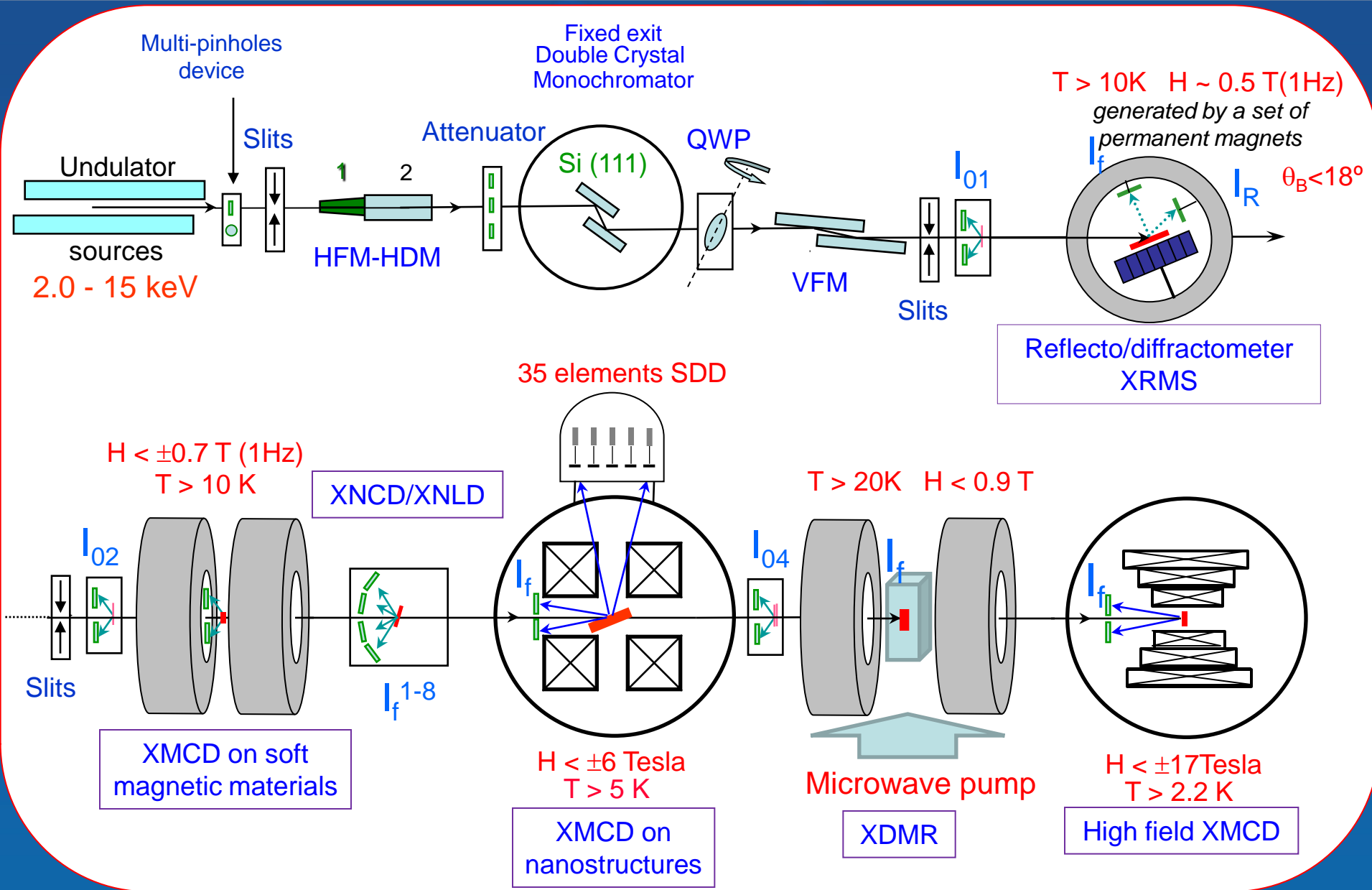


# Polarization dependent X-ray absorption spectroscopy

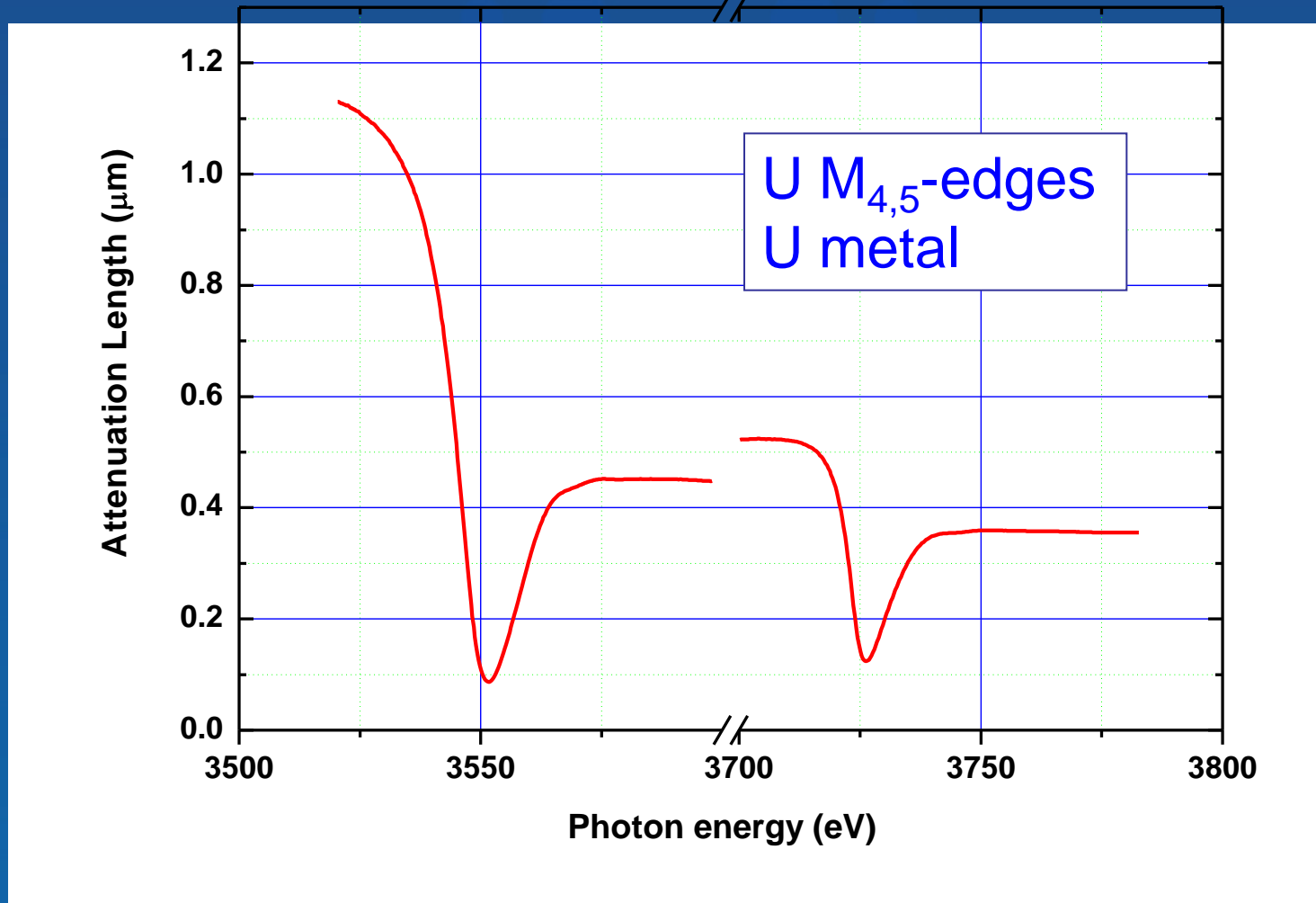
**X-ray dichroism is difference in X-ray absorption between two orthogonal polarizations of incoming beam**

Quantity to measure:  $\Delta\mu = \mu^+ - \mu^-$  (CD);  $\Delta\mu = \mu^{\parallel} - \mu^{\perp}$  (LD)

Dichroisms	Multipoles	Parity	Time-Reversal +1	Time-Reversal -1
Rotational Anisotropy	$E1E1$ + $E2E2$	Even and Odd	XNLD Alexander <i>et al.</i> (1963)	
Magneto-Optics	$E1E1$ + $E2E2$	Even and Odd	XMLD Van der Laan <i>et al.</i> (1986)	XMCD Schütz <i>et al.</i> (1987)
Optical Activity	$E1E2$ ( $E1M1$ )	Odd <u>only</u>	XNCD ID12 team (1998)	XnrLD+ XM $\chi$ D ID12 team (2000-2001)



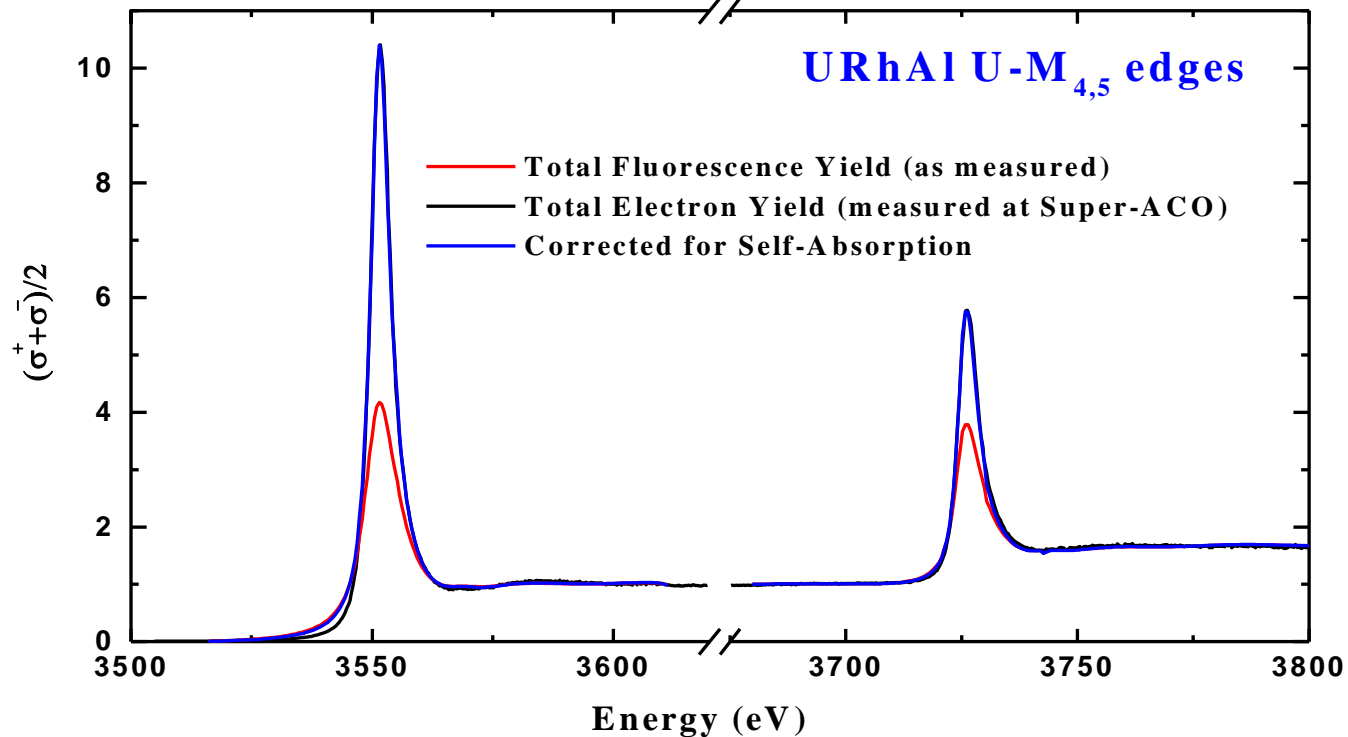
Strongly absorbing (*single crystals*) or nearly transparent (*thin films*) samples



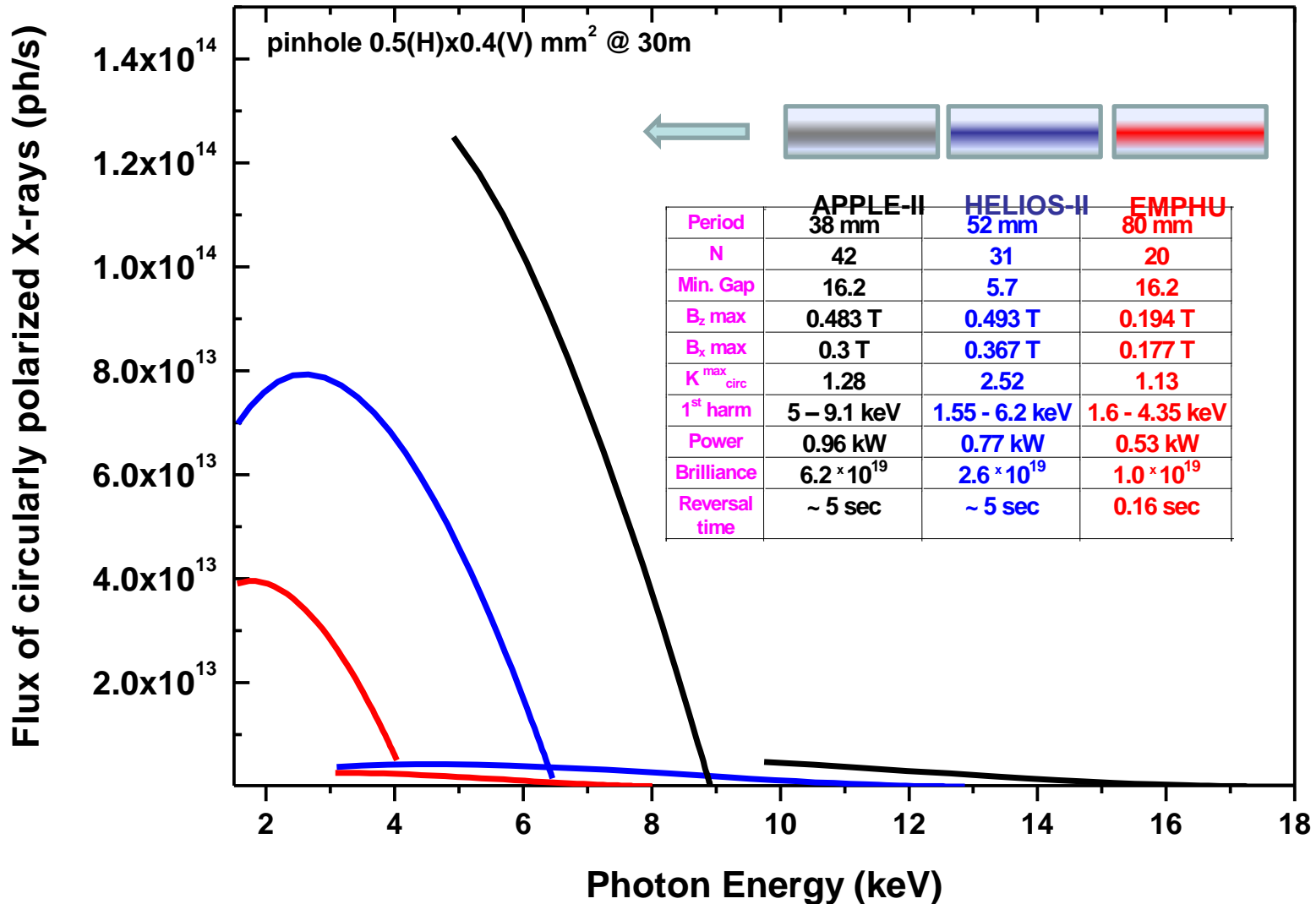
Transmission experiments is hardly possible

## Total Fluorescence Yield Detection Mode

- Well suitable for single crystals, thin films, *etc.*
- Probing the bulk properties
- Does not depend on the magnetic field



**Self-absorption corrections are needed**

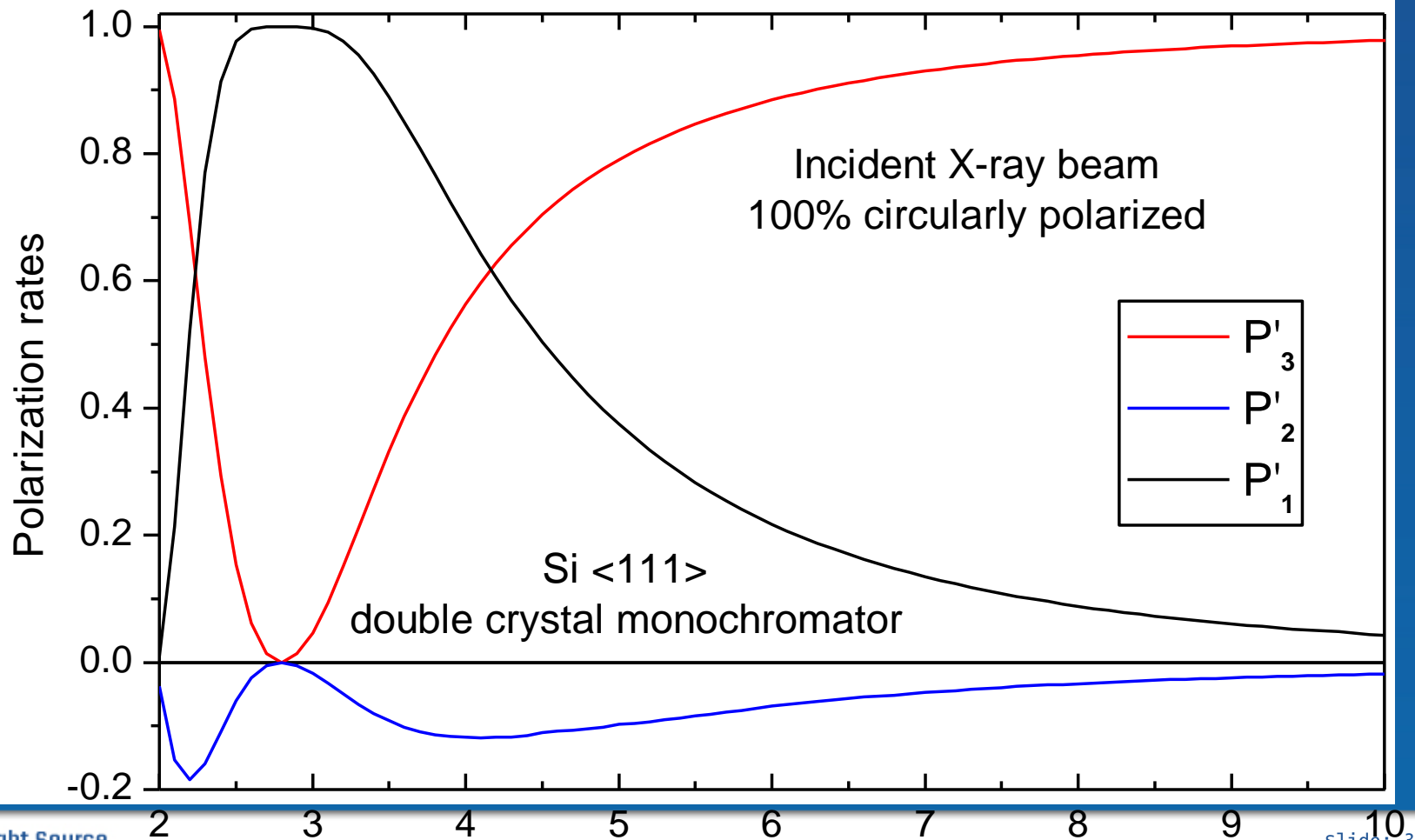


# Wide energy range at the ID12 beamline

**2.05 keV - 15 keV**

IA																				0									
1 H 1.008	IIA																			2 He 4.003									
3 Li 6.941	4 Be 9.012										5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18													
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95												
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80												
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3												
55 Cs 132.9	56 Ba 137.3	57* La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)												
87 Fr (223)	88 Ra (226.0)	89** Ac (227)	104 Rf	105 Ha	106 Unh	107 Uns	108	109 Une																					
* 58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0																
** 90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (244)	94 Pu (242)	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 (260)																

# Polarisation transfer by monochromator



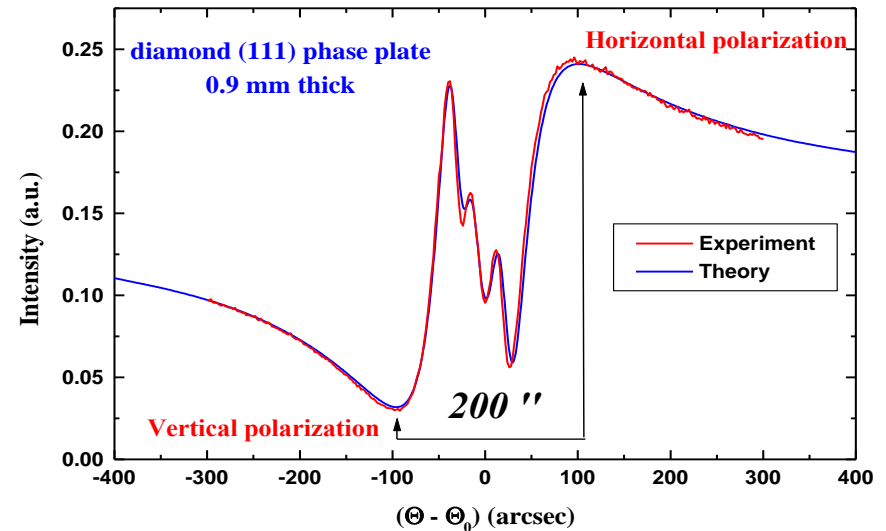


# Quarter wave plate chamber

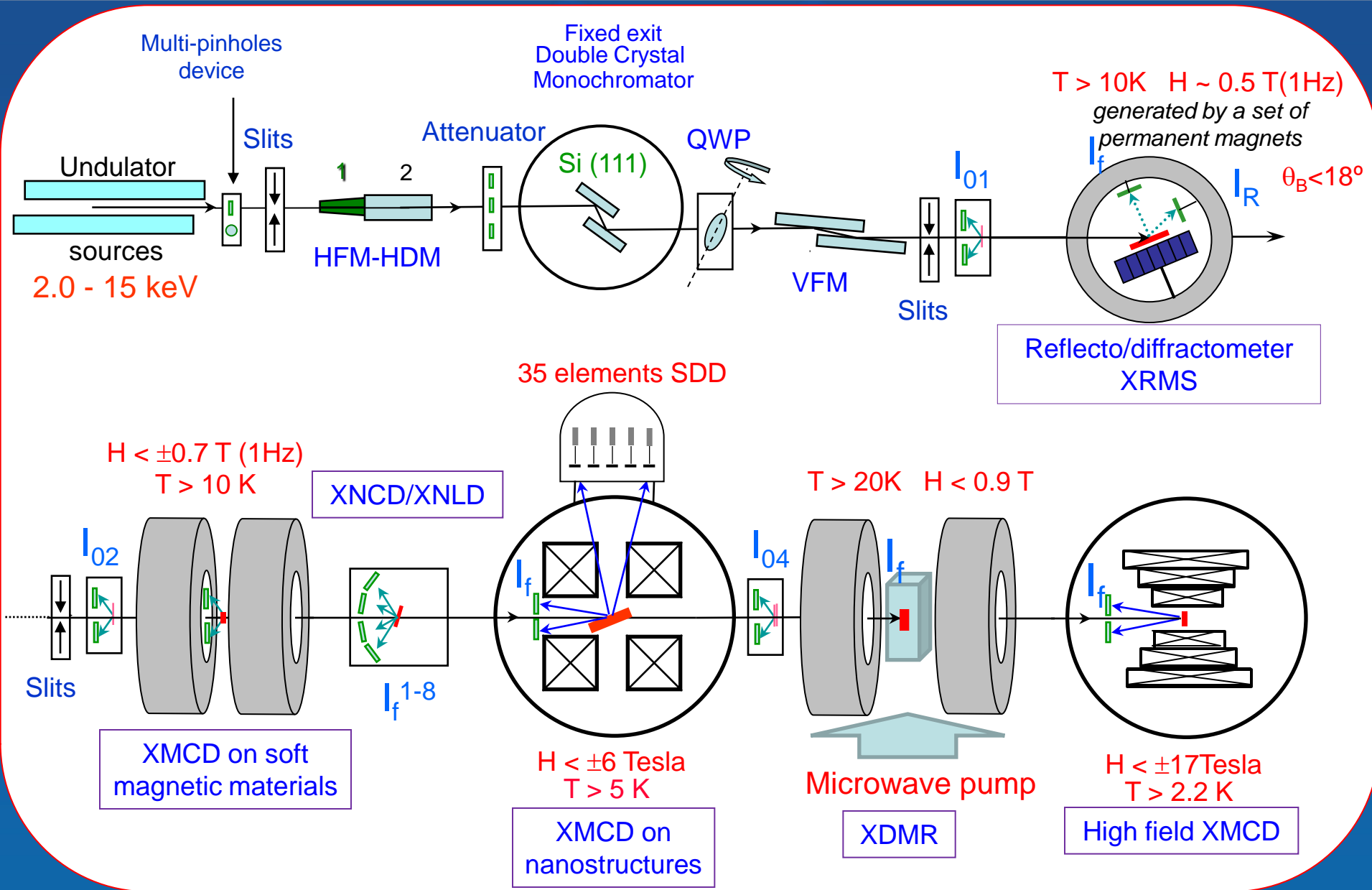
Phase shift between  $\sigma$  and  $\pi$  component of polarization induced by a diffracting crystal:

$$\varphi = \frac{\pi}{2} \left( \frac{r_e}{\pi V} \right)^2 \frac{F_h \cdot F_h^- \cdot \lambda^3 \cdot \sin 2\theta_0}{\theta - \theta_0} \cdot z$$

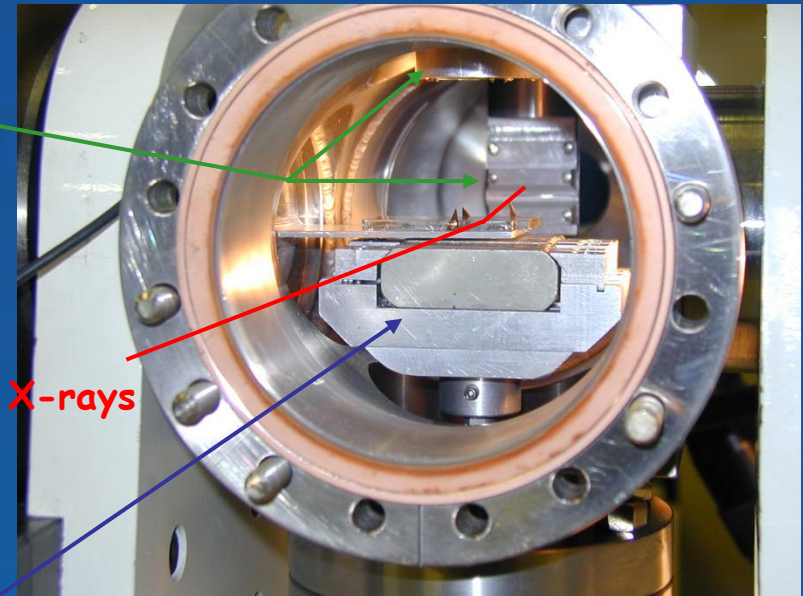
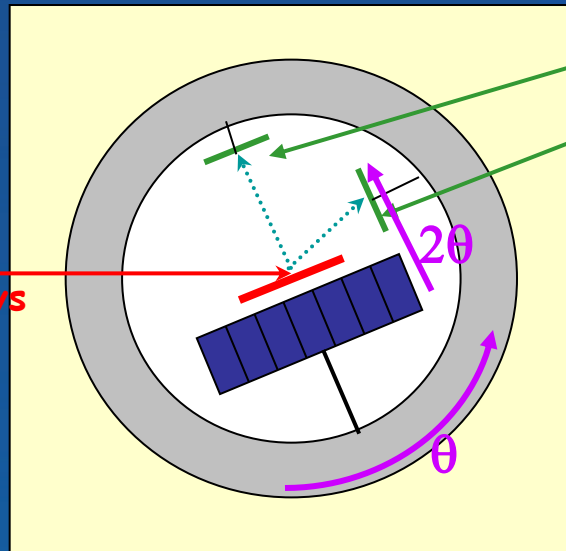
Transmission profile of a diamond QWP at 7.2 keV



Very powerful tool for X-ray linear (natural or magnetic) dichroism experiments.



# Reflectometer/Diffractometer



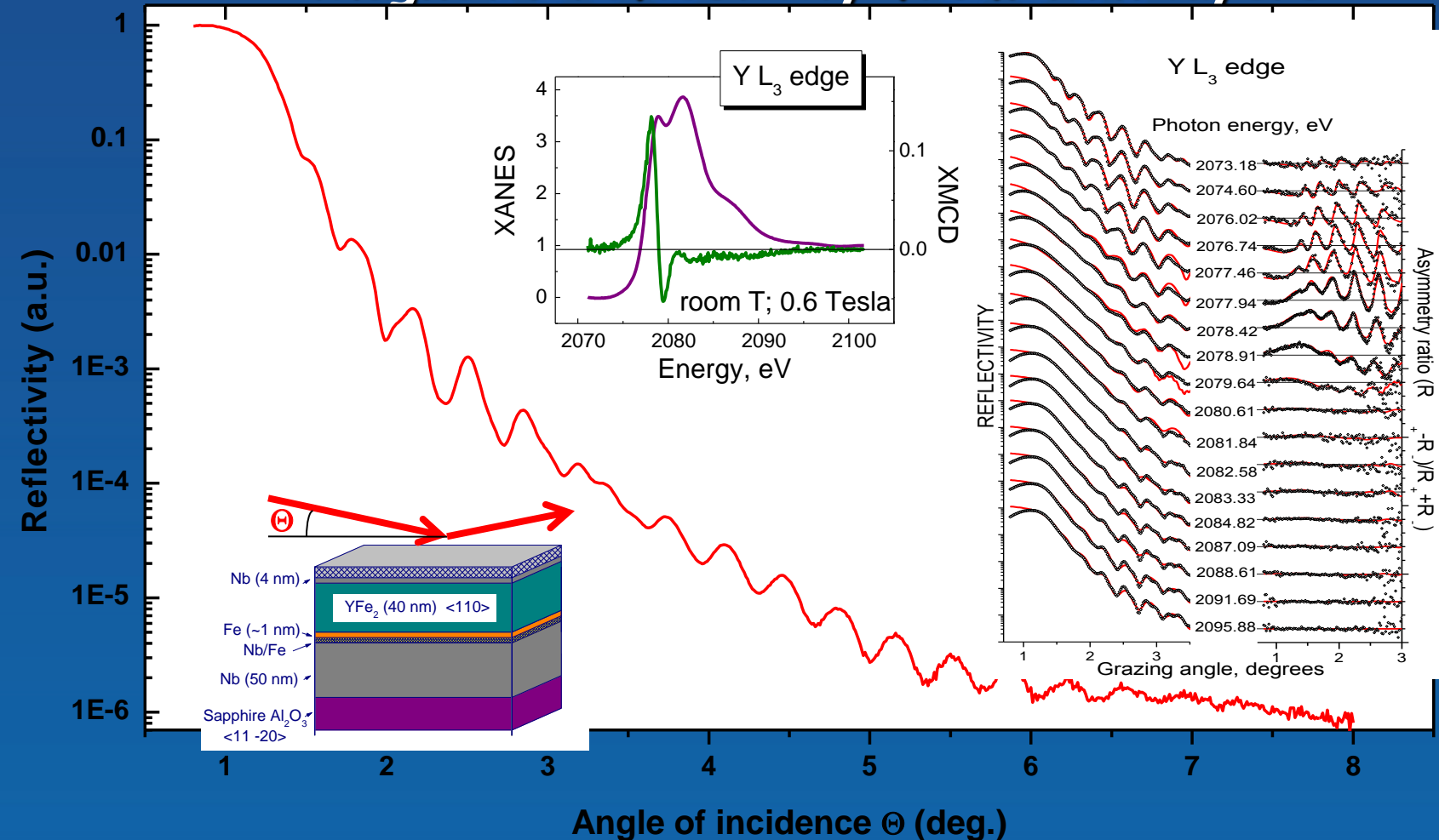
Magnetic field of 0.5 Tesla generated by one magnetic period of Helios-I

## Performances

- 0.001° precision
- Incident beam vertical size: ~ 100µm
- Entrance slits: 40 µm
- UHV
- Temperature from (20K to 300K)

*Simultaneous measurements of reflected intensity and Fluorescence Yield*

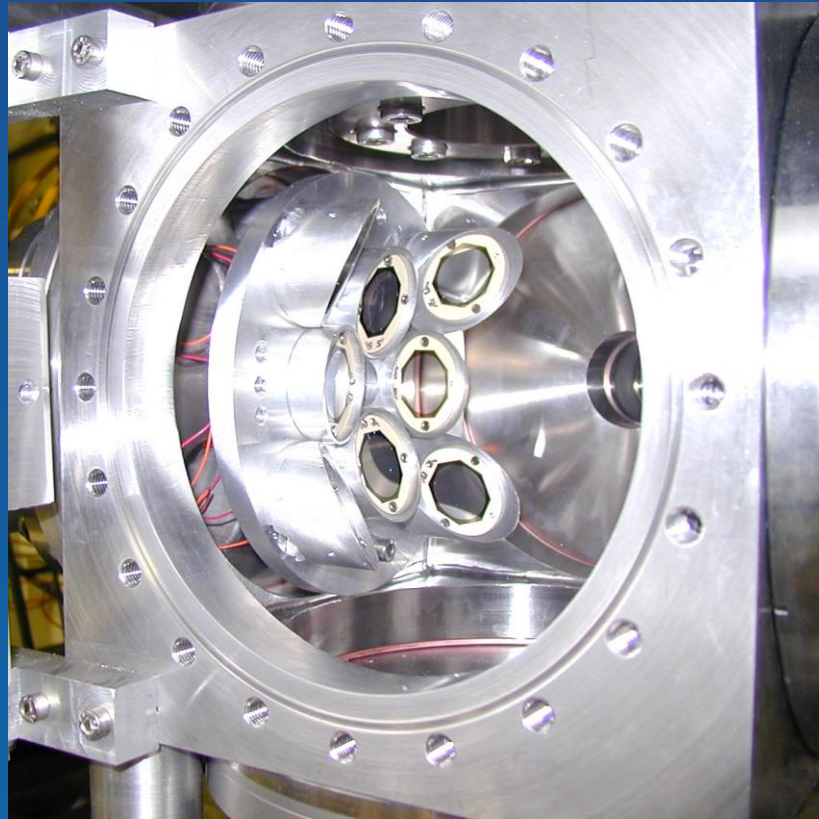
# Magnetic reflectivity from thin layers



From the analysis of Kiessig fringes one gets unique information about properties at the interfaces (magnetic incl.)



# Experimental station for X-ray Natural Linear and Circular Dichroisms



## *X-ray Linear Dichroism:*

*<E1.E1> transitions and <E2.E2> transitions*

*Brouder Ch., J. Phys.: Condensed Matter 2 (1990), 701-738*

*For <E1.E1> transitions and sample without symmetry*

$$\begin{aligned} \sigma^{Dxx} = & \sigma^D(0, 0) - 1/\sqrt{2} (3 \sin^2 2\theta - 1) \sigma^D(2, 0) - \sqrt{3} \sin(\theta) \\ & \times (\cos \varphi \sigma^{Dr}(2, 1) + \sin \varphi \sigma^{Di}(2, 1)) - \sqrt{3} \cos^2 \theta (\cos(2\varphi) \sigma^{Dr}(2, 2) \\ & + \sin(2\varphi) \sigma^{Di}(2, 2)) \end{aligned} \quad (A39a)$$

$$\begin{aligned} \sigma^{Dxy} = \sigma^{Dyx} = & \sqrt{3} \sin \theta (\sin \varphi \sigma^{Dr}(2, 1) - \cos \varphi \sigma^{Di}(2, 1)) \\ & + \sqrt{3} \cos \theta (\sin(2\varphi) \sigma^{Dr}(2, 2) - \cos(2\varphi) \sigma^{Di}(2, 2)) \end{aligned} \quad (A39b)$$

$$\sigma^{Dyy} = \sigma^D(0, 0) + 1/\sqrt{2} \sigma^D(2, 0) + \sqrt{3} (\cos(2\varphi) \sigma^{Dr}(2, 2) + \sin(2\varphi) \sigma^{Di}(2, 2)). \quad (A39c)$$

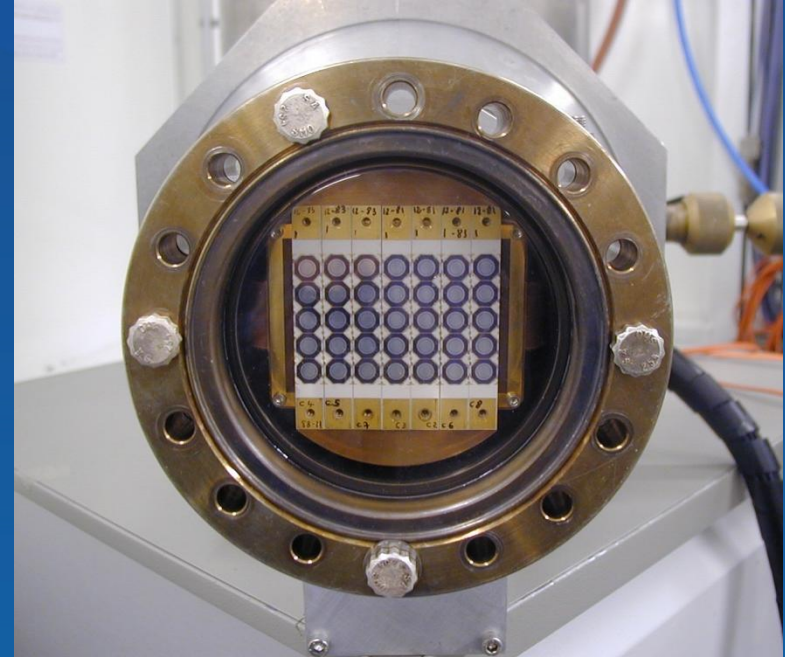
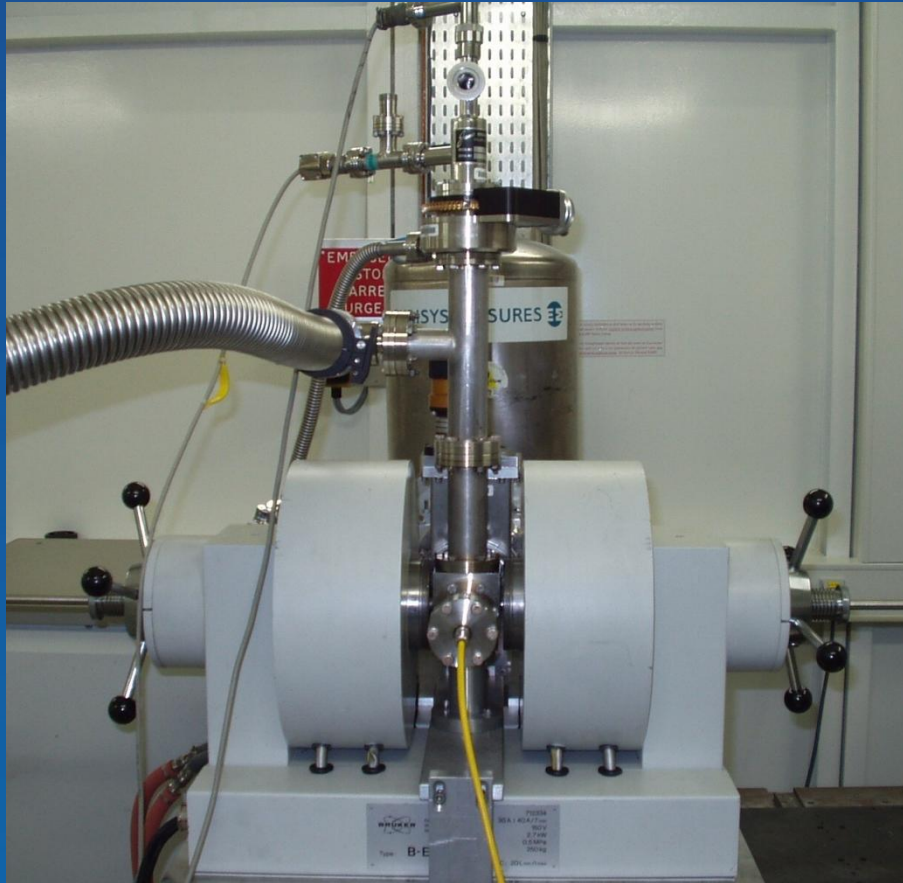
## *X-ray Natural Circular Dichroism:*

*<E1.E2> transitions*

*Natoli C.R. et al, Eur.Phys.J. B4 (1998), 1-11*

Backscattering detection geometry is the most convenient:  
sample can be rotated either around an axis parallel to the  
X-ray wavevector ( $\varphi$ ) or perpendicular to the beam direction ( $\theta$ )

# X-ray magnetic circular dichroism on nanomaterials



**Windowless chamber**  
**Cryogenically cooled:  $T = 150 \text{ K}$**   
**High solid angle:  $\sim 350 \text{ mm}^2 @ 20 \text{ cm}$**   
**High counting rate:  $> 10^5 \text{ cps/channel}$**

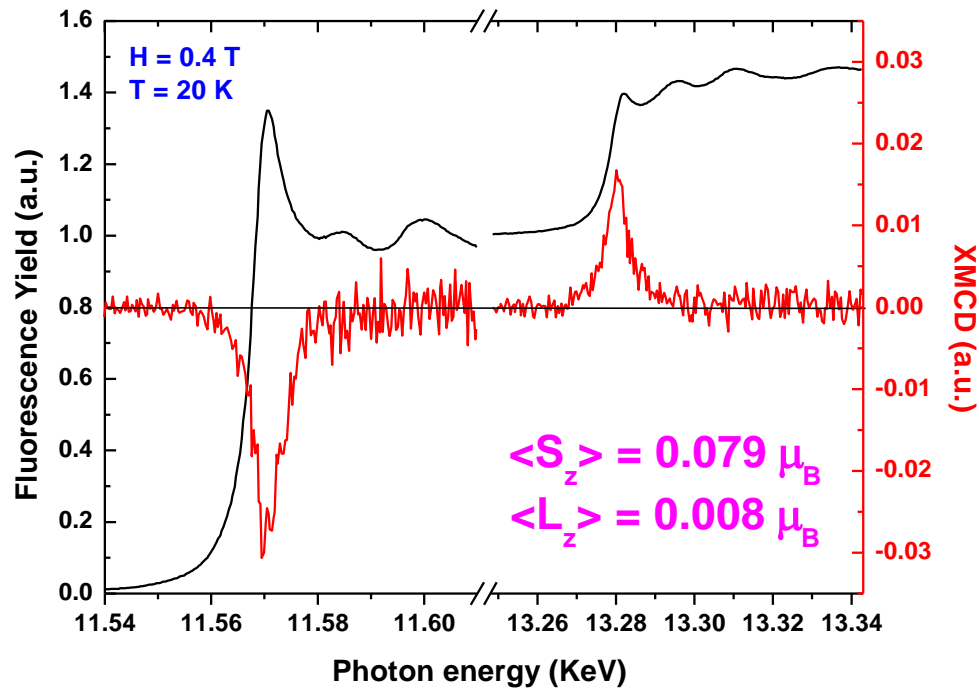
**Adapted now for XMCD experiments:  $T > 4.2 \text{ K}$ ; external magnetic field  $H < \pm 6 \text{ T}$**

# Typical example of an XMCD experiment

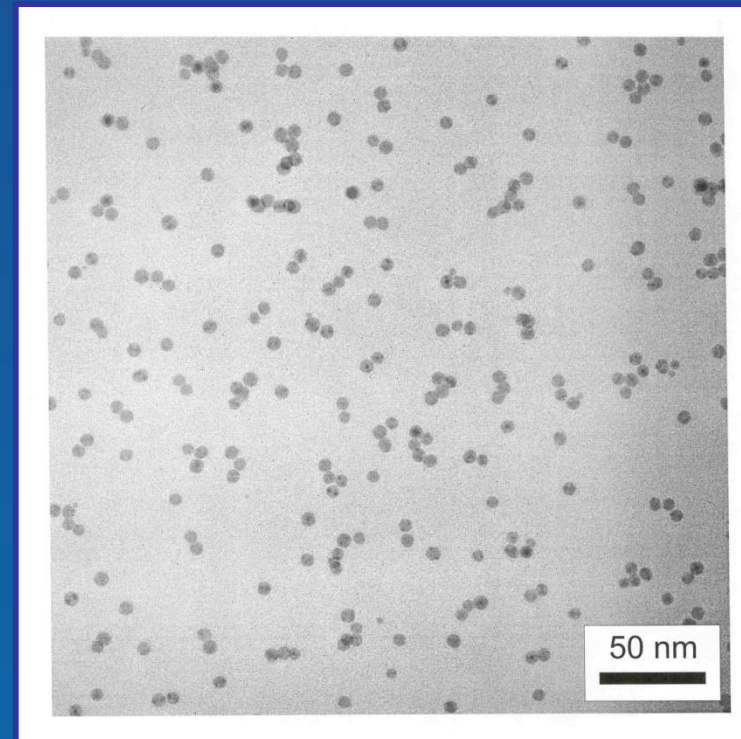
*Pt magnetism in monodispersed  $Fe_{70}Pt_{30}$  nanoparticles deposited on a Si wafer*

**XMCD at the Pt  $L_{II-III}$  Edges**

*Useful counting rate : 20 kcps per channel*



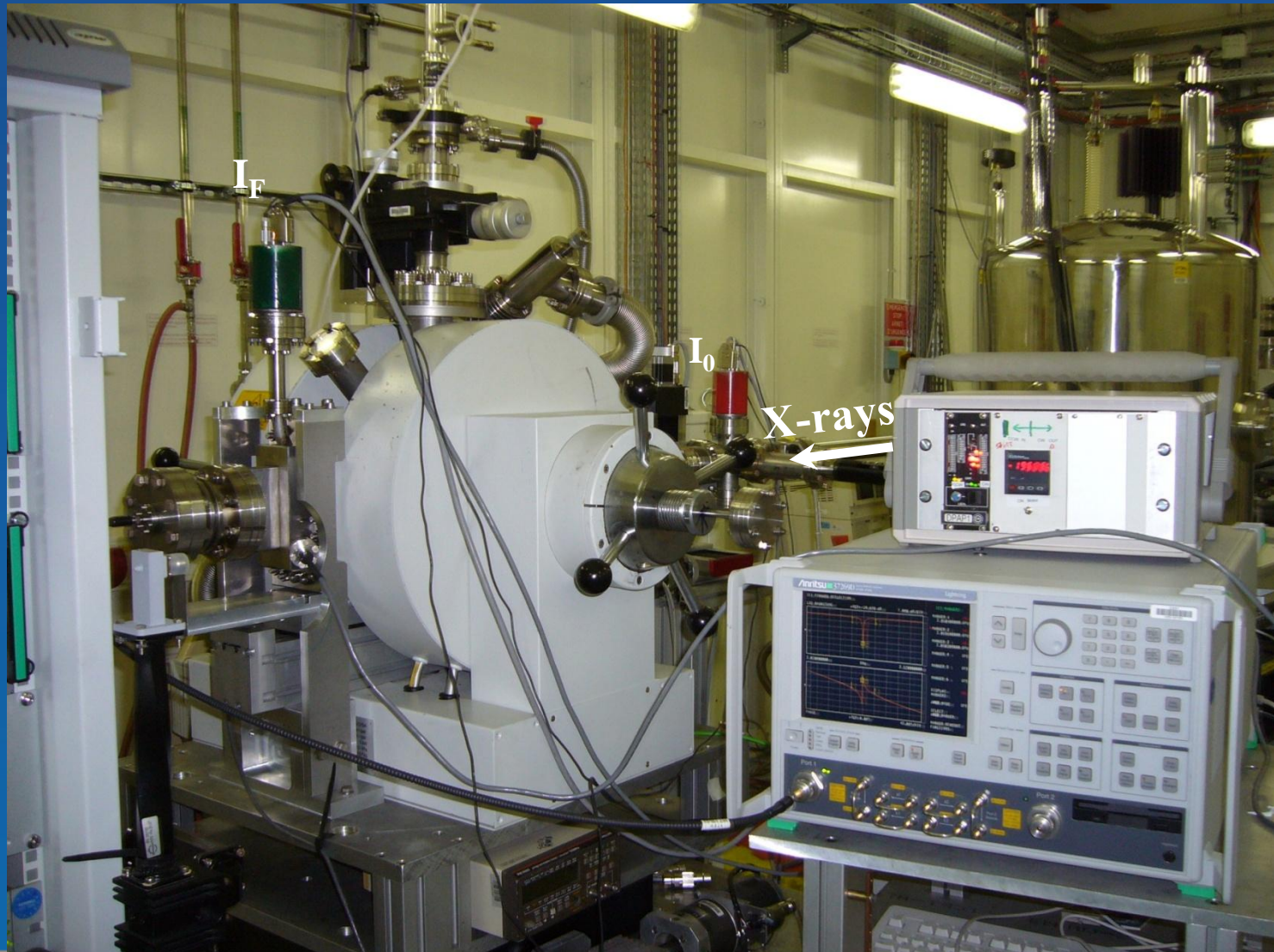
**Concentration  $< 10^{13}$  atoms/cm<sup>2</sup>**  
**Average particle diameter : 6 nm**



*Sample has been provided by M. Spasova, M. Farle  
 (Univ. Duisburg, Germany)*



# Experimental Set-Up for X-ray Detection of Magnetic Resonance



# Towards very high magnetic fields

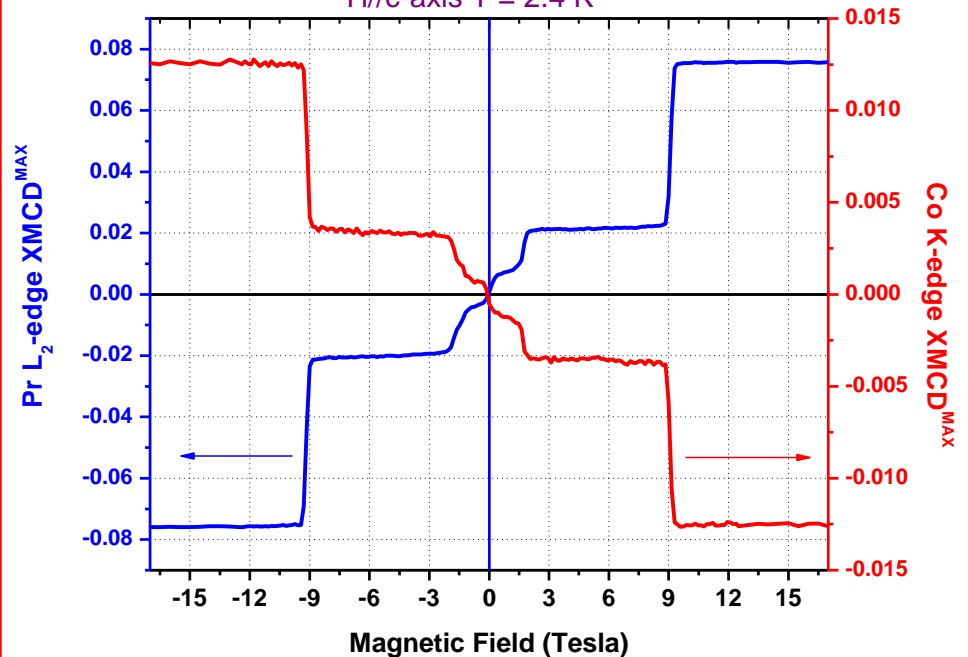


Solenoid magnet built by Cryogenic Ltd:  
 $H_{\max} = 17 \text{ T}$ ; Sweep rate = 2 T/min  
 Amagnetic cryostat  $2.3 \text{ K} < T < 300 \text{ K}$

Very first experimental results:

$\text{PrCo}_2\text{Ge}_2$  single crystal

H//c-axis T = 2.4 K



# X-ray Linear Dichroism



# GaN:Mn diluted magnetic semiconductor

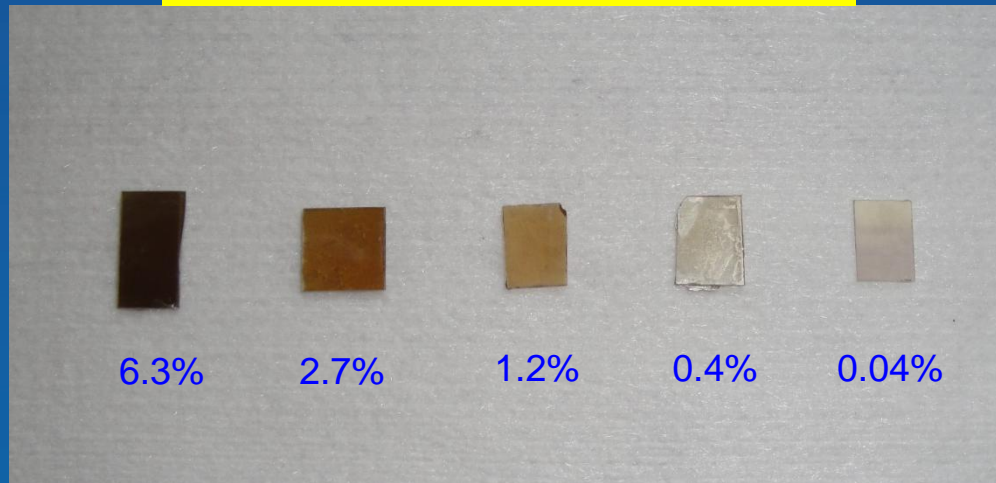
Samples were grown by plasma assisted molecular beam epitaxy (PAMBE)

E. Sarigiannidou\*, E. Monroy and H. Mariette

*Equipe mixte CEA-CNRS-UJF "Nanophysic and Semiconductors", DFRMC/SP2M CEA, Grenoble, France*

*\* LMGP/LTM, INP -Minatec, Grenoble, France*

Ga<sub>1-x</sub>Mn<sub>x</sub>N epitaxial film (400nm)



6.3%

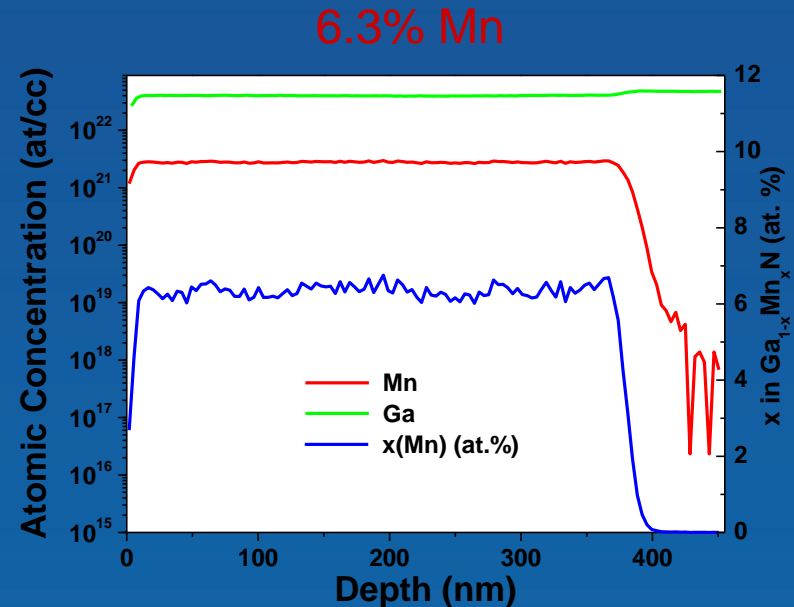
2.7%

1.2%

0.4%

0.04%

dark red → transparent



**Homogeneous** Incorporation of Mn from 0.04 up to max. 6.3 at.%

## ➤ in-situ RHEED

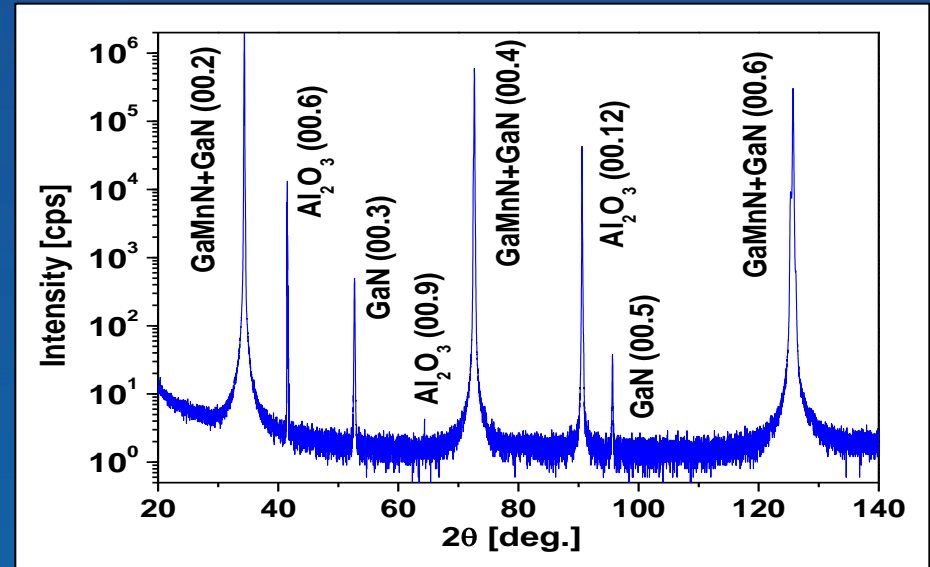
monitoring the growth



- ❖ smooth surfaces
- ❖ absence of secondary phases
- ❖ no information about the incorporation

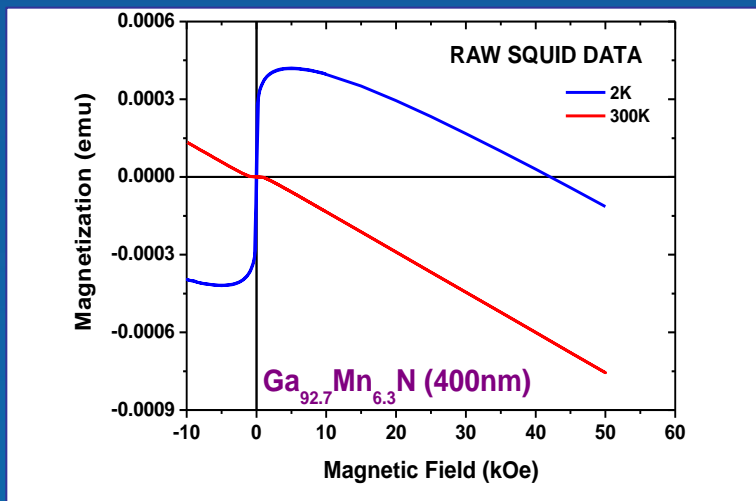
## ➤ High Angle X-ray Diffraction

- ❖ detection limit of ~1% of sample volume
- ❖ absence of secondary phases
- ❖ difference in the lattice parameter
- ❖ not sensitive to amorphous phases

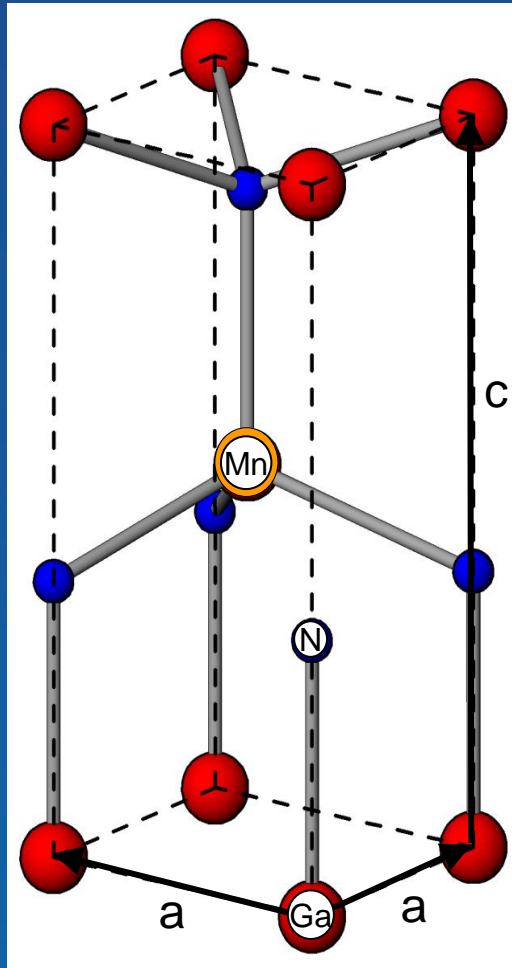


## ➤ SQUID

- ❖ measure the whole sample including substrate, cap layer, inclusions, impurities
- ❖ non trivial extraction of a true magnetic response



# What do we need to know more ?



Space group 186  
 Structure :  $P6_3mc$   
 Non-centrosymmetric

## 1. How are Mn atoms incorporated in the lattice?

- Single phase
- Presence of (magnetic) secondary phases
- Clusters formation

Concentration limit ?

## 2. What is the site of Mn atoms ?

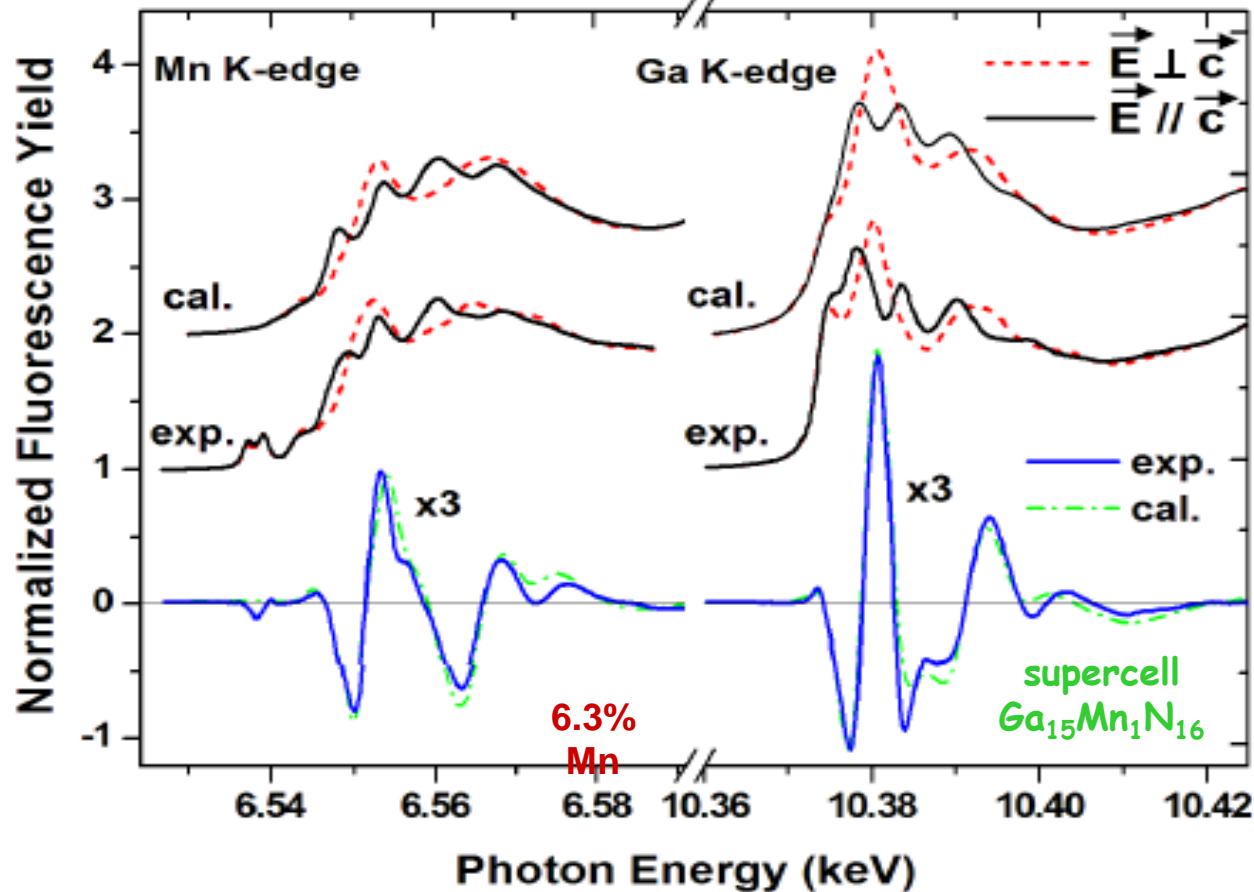
- Ga or N substitution
- Interstitial
- Substitution and interstitial

## 3. What is the valence state of Mn atoms?

## 4. Is it really a diluted magnetic semiconductor or ferromagnetic compound diluted in semiconductor ?

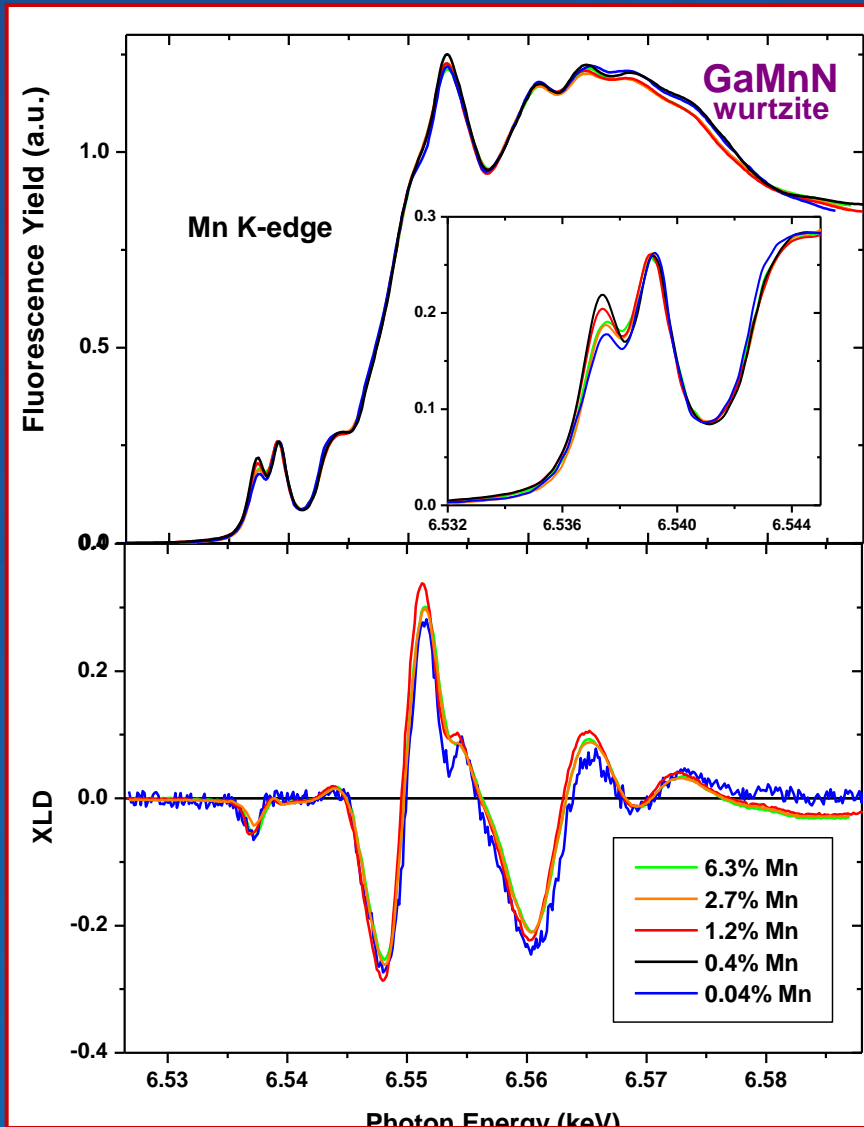
# X-ray Linear Dichroism (XLD) Results

*E. Sarigiannidou et al. Phys. Rev. B74, 041306(R) (2006)*



- Mn atoms are Ga substituted
- No secondary parasitic or clusters phases





□ All the Mn K-edge XANES spectra have similar spectral shape

➤ small differences are observed at the first pre-edge peak (narrowing of 3d band)

□ XLD spectra are identical for all samples from 0.04% up to 6.3% of Mn

➤ No secondary parasitic or clusters phases  
 0.04% Mn is the reference spectrum  
 (presence of secondary phases is unlikely)

**Mn is perfectly incorporated up to at. concentration of 6.3%**

# X-ray Magnetic Circular Dichroism



# On a question about the magnetic rotation of plane polarised primary X-rays



886

Zeitschrift für Physik, 39, 886-900 (1926)

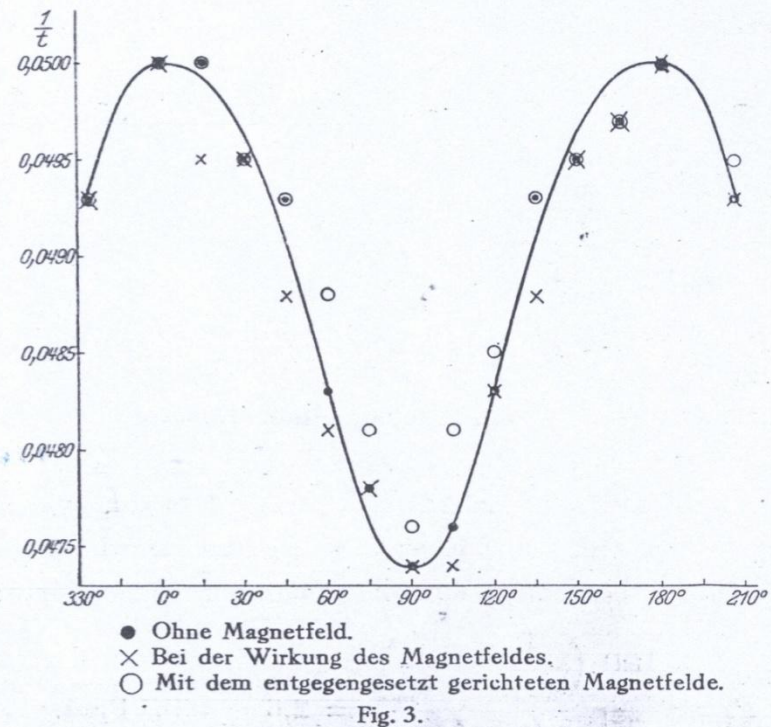
## Zur Frage nach der magnetischen Drehung der Polarisationsebene primärer Röntgenstrahlen.

Von W. Kartschagin und E. Tschetwerikowa in Moskau.

Mit 3 Abbildungen. (Eingegangen am 16. September 1926.)

In der vorliegenden Arbeit wurde eine Wirkung des magnetischen Feldes auf die Polarisationsebene der Röntgenstrahlen bei ihrem Durchgang durch Paraffin und Eisen untersucht. Auf Grund der Resultate der Arbeit und der Versuche bei einigen Annahmen, die Folgerungen der Elektronentheorie der Dispersion auf die zu behandelnde Frage anzuwenden, ziehen wir folgenden Schluß: Beim Durchgang primärer Röntgenstrahlen durch Paraffin kann die magnetische Drehung der Polarisationsebene wegen der Kleinheit des Drehungswinkels nicht beobachtet werden. Beim Durchgang der primären Strahlen durch Eisen kann man eine Drehung der Polarisationsebene erwarten, aber eine genaue Messung des Drehungswinkels ist sehr schwierig.

In this work, an effect of a magnetic field on plane polarised X-rays scattered by Paraffin and Iron is studied. Far from the absorption edge the rotation can not be observed due the weakness of the rotation angle. Whereas at an absorption edge of ferromagnetic materials one can expect to measure the magnetic rotation eventhough precise measurements are very difficult.



# BASICS OF XMCD

*The first serious approach to the problem*

PHYSICAL REVIEW B

VOLUME 12, NUMBER 11

1 DECEMBER 1975

## Calculation of the $M_{23}$ magneto-optical absorption spectrum of ferromagnetic nickel

J. L. Erskine\*

*Department of Physics, University of Illinois, Urbana, Illinois 61801*

E. A. Stern†

*Department of Physics, University of Washington, Seattle, Washington 98195*

(Received 28 April 1975)

The  $M_{23}$  magneto-optical absorption spectrum of ferromagnetic nickel is calculated using an approach similar to the component state-density method that has been successfully used in obtaining valence-band emission and absorption x-ray spectra of metals. The  $M_{23}$  magneto-optical effects result predominantly from spin-orbit splitting of the  $3p$  core state in conjunction with the final  $d$ -state spin polarization. The calculated spectrum exhibits features that are directly related to electronic structure parameters including the  $3p$  core spin-orbit splitting, and the unfilled  $d$ -band spin polarization. Temperature variations in the magneto-optical structure can be used to determine separately the exchange-splitting variation and spin-wave excitation contributions to the decrease in the magnetization. Experimental verification of these predictions should provide insight into the applicability of the Stoner model to ferromagnetic nickel and may be helpful in resolving some of the apparently conflicting results of other experimental probes of the spin polarization near the Fermi level in nickel.

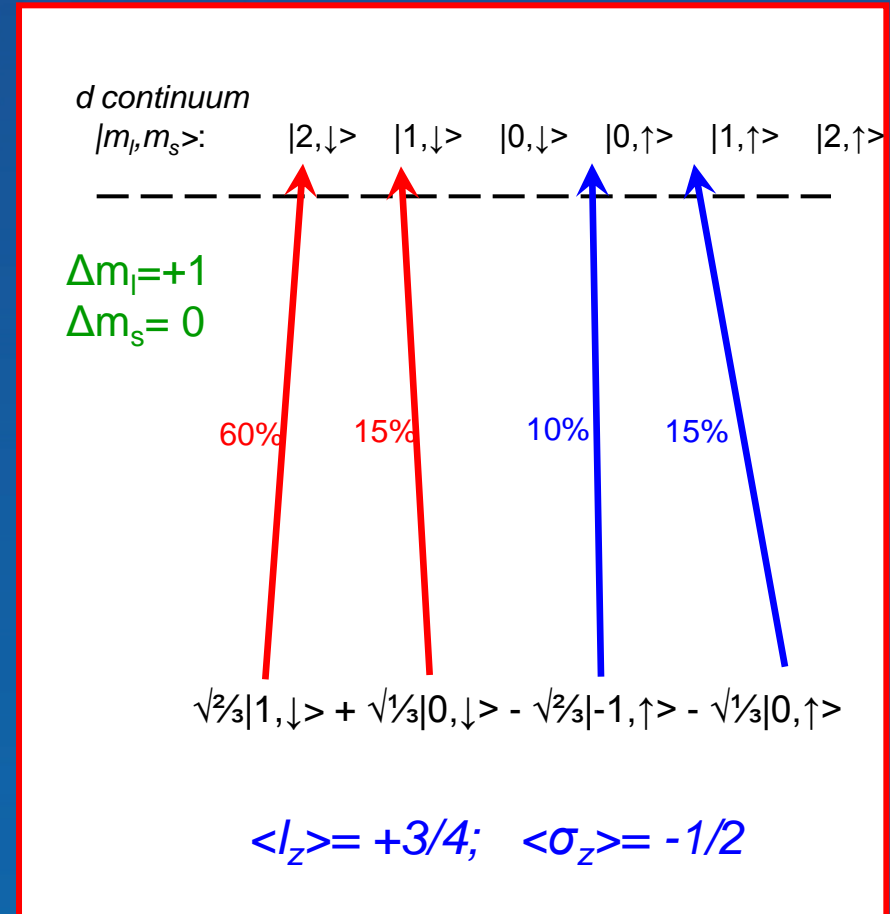
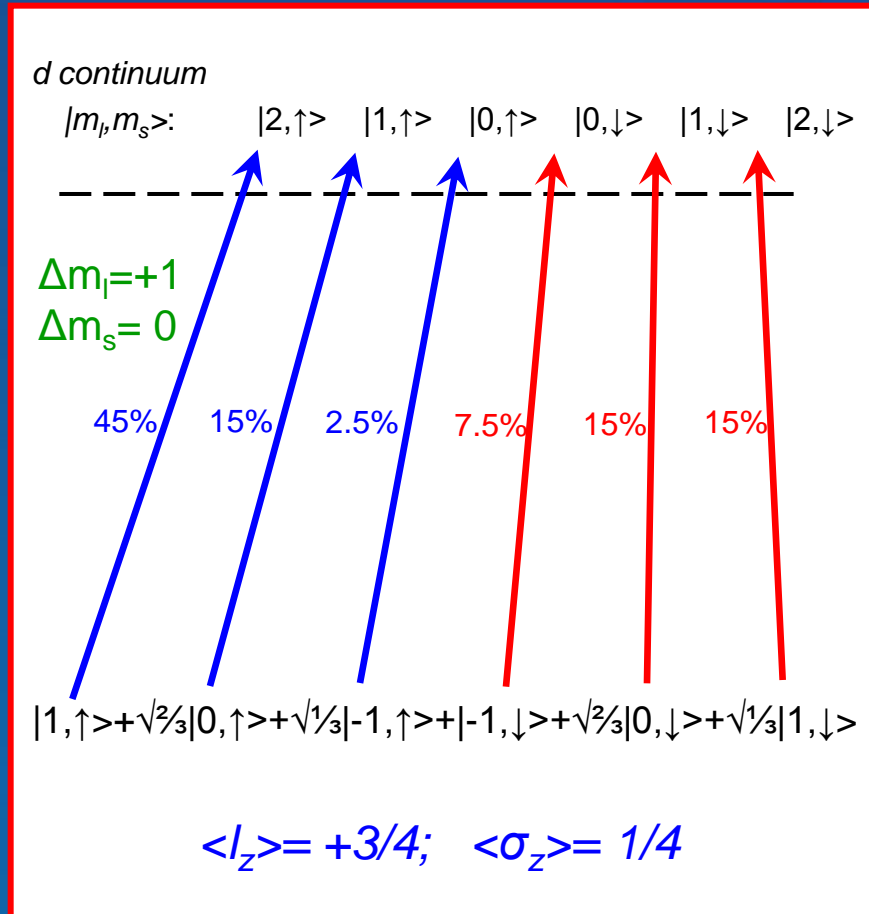
*Two-step model*

# TWO STEP MODEL OF XMCD

Absorption of a right circularly polarized photon

$L_{III}$ -edge ( $2p_{3/2}$ )

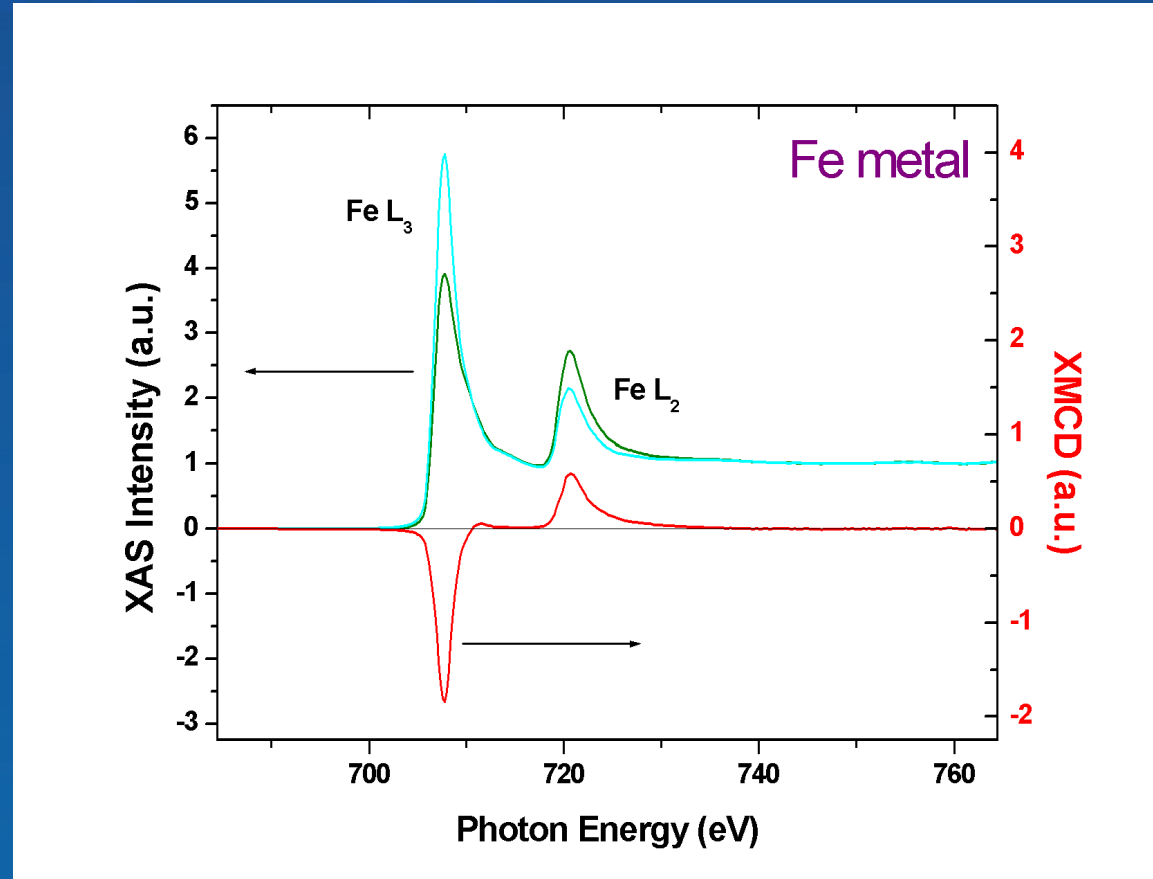
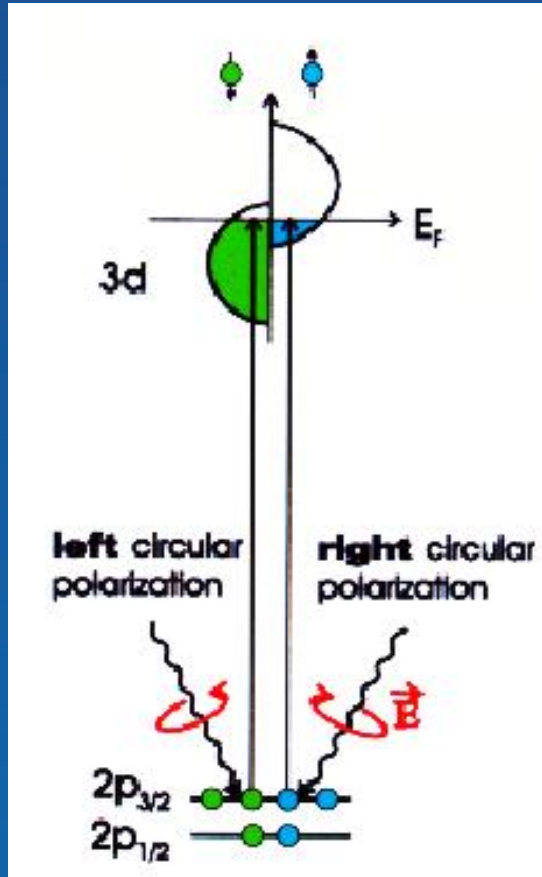
$L_{II}$ -edge ( $2p_{1/2}$ )



*Excited photoelectrons are spin polarized*

# TWO STEP MODEL OF XMCD

Exchange splitting of the valence band is driving the second step



XMCD is the direct probe of unoccupied spin up and spin-down density of states



# First experimental evidence of XMCD

VOLUME 58, NUMBER 7

PHYSICAL REVIEW LETTERS

16 FEBRUARY 1987

## Absorption of Circularly Polarized X Rays in Iron

 G. Schütz, W. Wagner, W. Wilhelm, and P. Kienle<sup>(a)</sup>
*Physik Department, Technische Universität München, D-8046 Garching, West Germany*

R. Zeller

*Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5175 Jülich, West Germany*

and

R. Frahm and G. Materlik

*Hamburger Synchrotronstrahlungslabor am Deutsches Elektronen-Synchrotron DESY, D-2000 Hamburg 52, West Germany*

(Received 22 September 1986)

The transmission of synchrotron radiation through magnetized iron at energies above the  $K$ -absorption edge shows relative differences for right and left circular polarization of several times  $10^{-4}$ . The observed spin dependence of the near-edge photoabsorption is proportional to the difference of the spin densities of the unoccupied bands. In the extended absorption region up to 200 eV above the Fermi level a small spin-dependent absorption is observed and thus is expected to give information on the magnetic neighborhood of the absorbing atom.

PACS numbers: 75.50.Bb, 75.10.Lp, 75.25.+z, 78.70.Dm

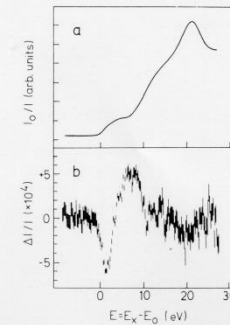


FIG. 1. (a) Absorption  $I_0/I$  of x rays as function of the energy  $E$  above the  $K$  edge of iron and (b) the difference of the transmission  $\Delta I/I$  of x rays circularly polarized in and opposite to the direction of the spin of the magnetized  $d$  electrons.

## *XMCD is a new approach to study ferromagnetic system*

RAPID COMMUNICATIONS

PHYSICAL REVIEW B

VOLUME 42, NUMBER 11

15 OCTOBER 1990-1

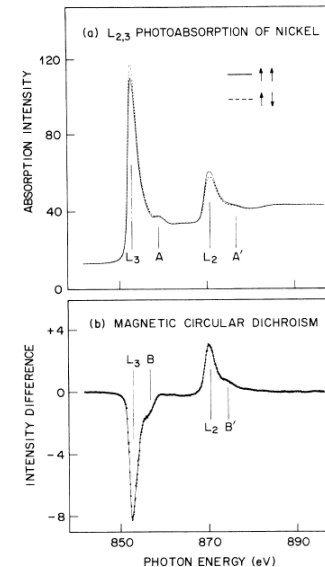
### Rapid Communications

*Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in Physical Review B should be no longer than 4 printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

### Soft-x-ray magnetic circular dichroism at the $L_{2,3}$ edges of nickel

C. T. Chen, F. Sette, Y. Ma, and S. Modestri  
 AT&T Bell Laboratories, Murray Hill, New Jersey 07974  
 (Received 2 March 1990)

Magnetic circular dichroism (MCD) has been observed at the  $L_{2,3}$  absorption edges of ferromagnetic nickel by use of circular-polarized soft-x-ray synchrotron radiation. The MCD intensity ratio between the  $L_2$  and the  $L_3$  edges is found to differ appreciably from that predicted by a simple exchange-split-valence-band model. Fine MCD features, imperceptible in the absorption spectra, are also observed and a tentative interpretation is given. This work, demonstrating the feasibility of MCD measurements in the soft-x-ray region, provides a new approach to study  $3d$  and  $4f$  ferromagnetic systems with their respective dipole-permitted  $2p \rightarrow 3d$  and  $3d \rightarrow 4f$  transitions.



# Sum rules relate experimental XMCD spectra to the spin and orbital moments

VOLUME 68, NUMBER 12

PHYSICAL REVIEW LETTERS

23 MARCH 1992

## X-Ray Circular Dichroism as a Probe of Orbital Magnetization

 B. T. Thole,<sup>(1)</sup> Paolo Carra,<sup>(2)</sup> F. Sette,<sup>(2)</sup> and G. van der Laan<sup>(3)</sup>
<sup>(1)</sup>Department of Chemical Physics, Materials Science Centre, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

<sup>(2)</sup>European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble CEDEX, France

<sup>(3)</sup>Daresbury Laboratory, Science and Engineering Research Council, Warrington, WA4 4AD, United Kingdom (Received 2 December 1991)

A new magneto-optical sum rule is derived for circular magnetic dichroism in the x-ray region (CMXD). The integral of the CMXD signal over a given edge allows one to determine the ground-state expectation value of the orbital angular momentum. Applications are discussed to transition-metal and rare-earth magnetic systems.

## Orbital sum rule

$$\int_{j^+ + j^-} (\mu^+ - \mu^-) = \frac{2l(l+1)}{l(l+1) + 2 - c(c+1)} \times C \times \langle L_z \rangle$$

## Spin sum rule

$$\int_{j^+} (\mu^+ - \mu^-) - \frac{c+1}{c} \int_{j^-} (\mu^+ - \mu^-) = C \times [A \langle S_z \rangle + B \langle T_z \rangle]$$

VOLUME 70, NUMBER 5

PHYSICAL REVIEW LETTERS

1 FEBRUARY 1993

## X-Ray Circular Dichroism and Local Magnetic Fields

 Paolo Carra,<sup>(1)</sup> B. T. Thole,<sup>(1),(2)</sup> Massimo Altarelli,<sup>(1)</sup> and Xindong Wang<sup>(3)</sup>
<sup>(1)</sup>European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble CEDEX, France

<sup>(2)</sup>Department of Chemical Physics, Materials Science Center, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

<sup>(3)</sup>Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011 (Received 13 July 1992)

Sum rules are derived for the circular dichroic response of a core line (CMXD). They relate the intensity of the CMXD signal to the ground-state expectation value of the magnetic field operators (orbital, spin, and magnetic dipole) of the valence electrons. The results obtained are discussed and tested for transition metals and rare earths.

$$T = \sum_i (s_i - 3r_i(r_i \cdot s_i) / r_i^2) \quad C = \frac{1}{n_h} \int_{j^+ + j^-} (\mu^+ + \mu^- + \mu^0) \quad - \text{X-ray absorption cross section per hole;}$$

$$A = \frac{l(l+1) - 2 - c(c+1)}{3c}$$

$$B = \frac{l(l+1)[l(l+1) + 2c(c+1) + 4] - 3c(c-1)^2(c+2)^2}{6c \cdot l(l+1)}$$

**Quantity to measure:  $\Delta\mu = \mu^+ - \mu^-$**

$\mu^{(+,-)}$  => Absorption cross-sections for CP X-rays with (+ / -) helicity or with helicity *parallel / antiparallel* to the sample magnetization

Two ways to record XMCD spectra:

- to reverse the helicity or magnetization after each scan
- to flip the helicity at each energy point of the scan

Uranium X-ray absorption edges:

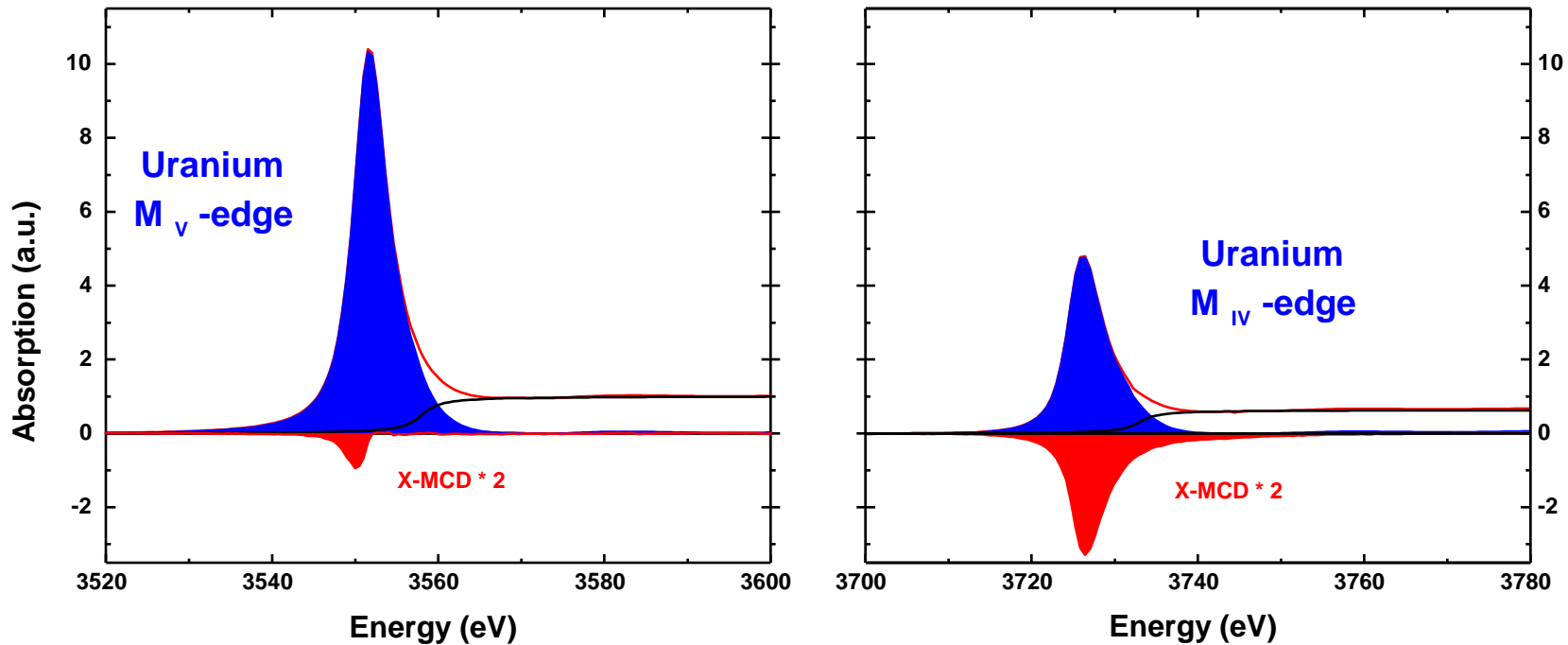
**M<sub>V</sub>-edge (3d<sub>5/2</sub> -> 5f<sub>5/2,7/2</sub>)**  
**3.552 keV**

**M<sub>IV</sub>-edge (3d<sub>3/2</sub> -> 5f<sub>5/2</sub>)**  
**3.728 keV**

**L<sub>III</sub>-edge (2p<sub>3/2</sub> -> 6d<sub>3/2,5/2</sub>)**  
**17.166 keV**

**L<sub>II</sub>-edge (2p<sub>1/2</sub> -> 6d<sub>3/2</sub>)**  
**20.948 keV**

# Application of the sum rules



$$\langle L_z \rangle = n_h (\Delta I_{M5} + \Delta I_{M4}) / (I_{M5} + I_{M4}) = \mu_L$$

$$2\langle S_z^{\text{eff}} \rangle = 2\langle S_z \rangle + 6\langle T_z \rangle = n_h (2\Delta I_{M5} - 3\Delta I_{M4}) / (I_{M5} + I_{M4}) = \mu_S \quad (\text{if } T_z \approx 0)$$

$$\langle L_z \rangle / \langle S_z^{\text{eff}} \rangle = 2(\Delta I_{M5} + \Delta I_{M4}) / (2\Delta I_{M5} - 3\Delta I_{M4}) \quad \text{is independent of } n_h$$

$$\langle l.s \rangle = -3/4 n_h (2I_{M5} - 3I_{M4}) / (I_{M5} + I_{M4}) + \delta$$

# Application of the sum rules

$$\langle S_z^{\text{eff}} \rangle = \langle S_z \rangle + 3 \langle T_z \rangle$$

$\langle T_z \rangle$  is a measure of a spin moment anisotropy induced either by a charge quadrupole moment or by the spin-orbit interaction

In the case of 5f-electrons:  $\langle T_z \rangle \neq 0$

**In the intermediate spin-orbit coupling scheme (for free ions):**

- for  $5f^2$                        $R_T = \langle T_z \rangle / \langle S_z \rangle = \mathbf{1.15}$
- for  $5f^3$                          $R_T = \langle T_z \rangle / \langle S_z \rangle = \mathbf{0.57}$

**There are no any direct measurements of this term (so far !!!)**

Possibility to estimate  $\langle T_z \rangle$  *via* combination of XMCD, Neutron and Compton scattering with SQUID measurements

# UFe<sub>2</sub>

fcc Laves phase with  $a_0=7.058$

ferromagnet with Curie temperature  $T_c = 160$  K

total magnetic moment  $1.09 \mu_B$ / formula unit

strong spin-orbit coupling in the 5f states => orbital moment

third Hund's rule:

5f spin and orbital moments are of opposite sign

**Polarized neutron scattering experiments:**

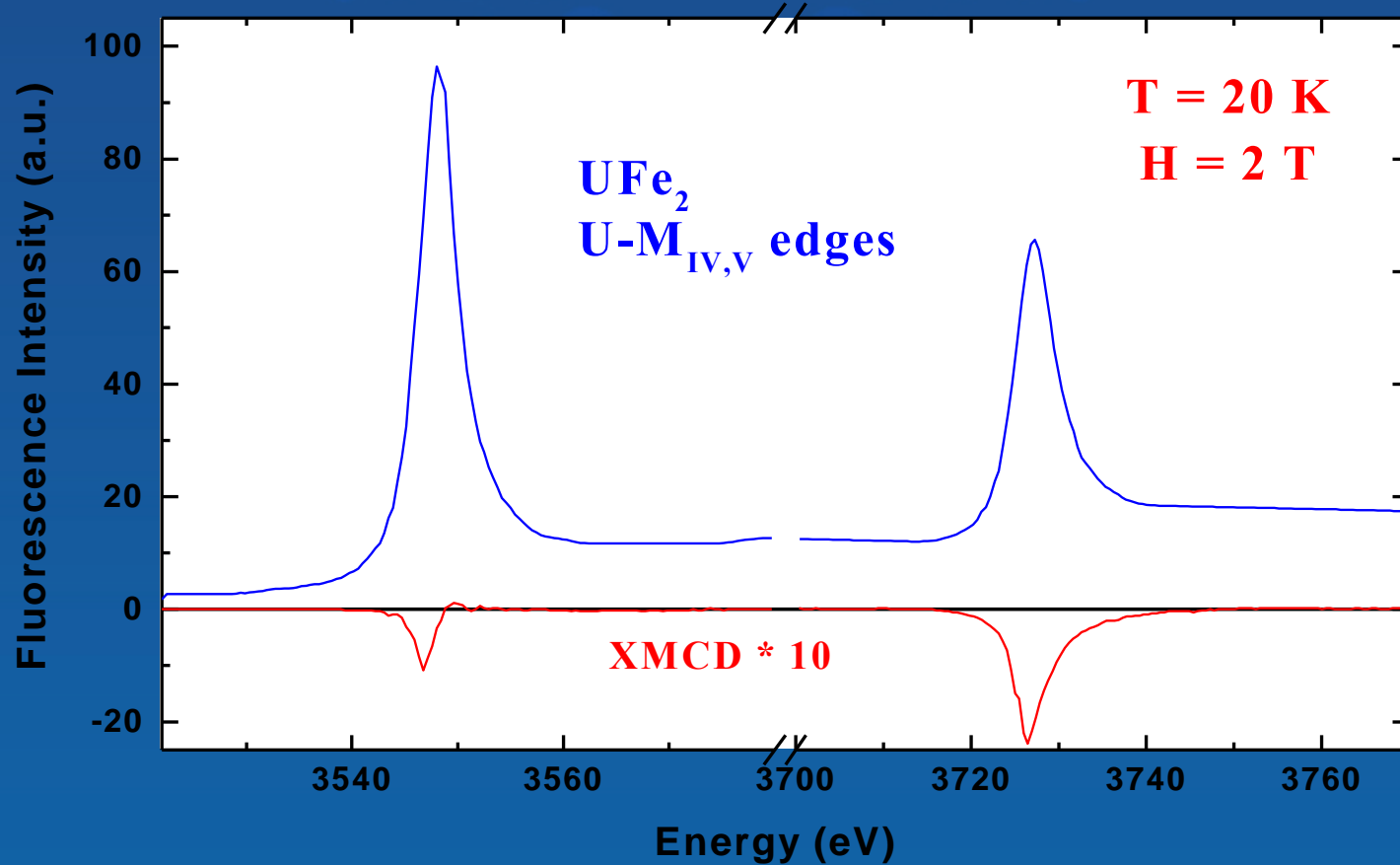
**a total U 5f moment  $< 0.01 \mu_B$**

**with  $\mu_L \sim -\mu_S \sim 0.23 \mu_B$**

M. Wulff, G. H. Lander, B. Lebech, and A. Delapalme, Phys. Rev. B **39**, 4719 (1989).



polycrystalline sample  $T_c = 160 \text{ K}$   $\mu_{\text{TOTAL}} = 1.16 \mu_B$

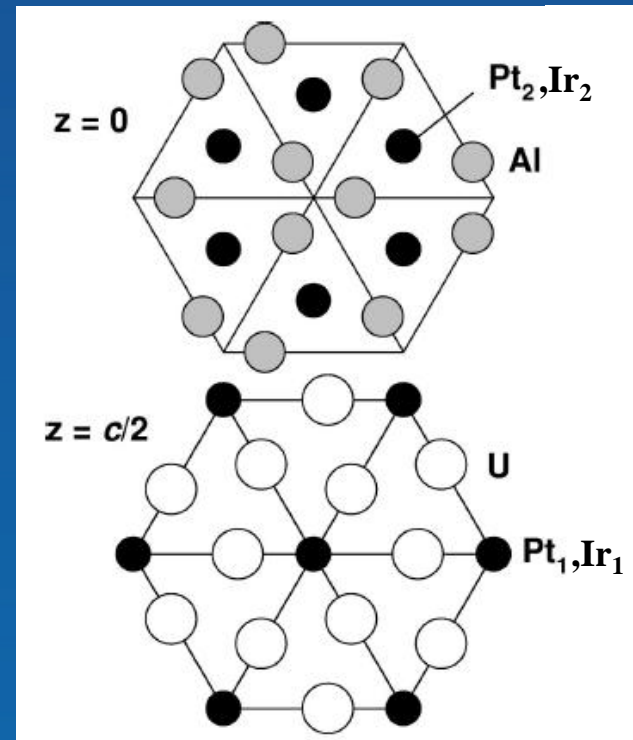
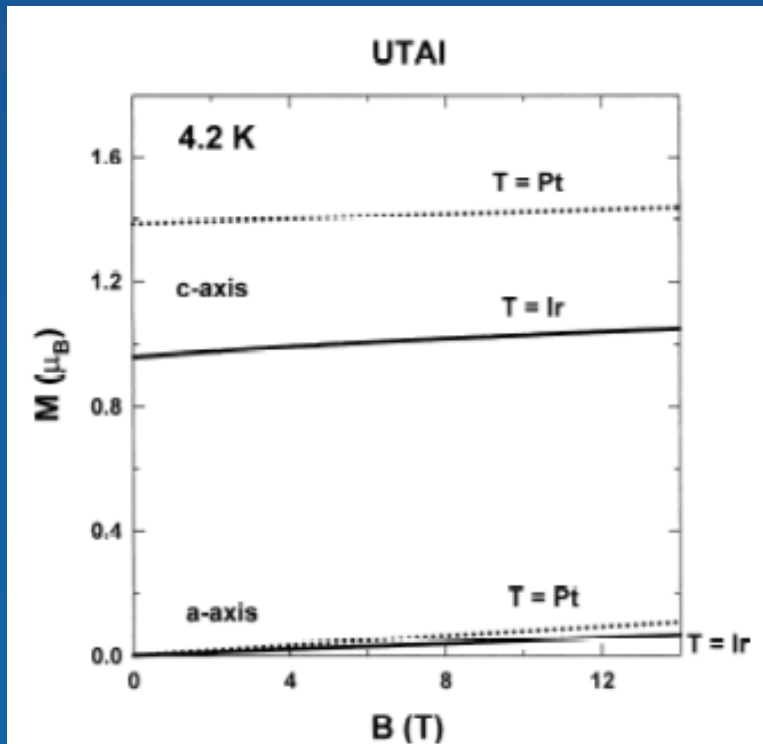


	$\mu_L (\mu_B)$	$\mu_S (\mu_B)$	$-\mu_L / \mu_S$
<b>X M C D</b>	<b><math>0.21 \pm 0.02</math></b>	<b><math>-0.20 \pm 0.02</math></b>	<b><math>0.97 \pm 0.05</math></b>
<b>Neutron</b>	<b><math>0.23 \pm 0.01</math></b>	<b><math>-0.22 \pm 0.02</math></b>	<b><math>1.05 \pm 0.05</math></b>
<b>Theory</b>	<b>0.47</b>	<b>-0.58</b>	<b>0.81</b>

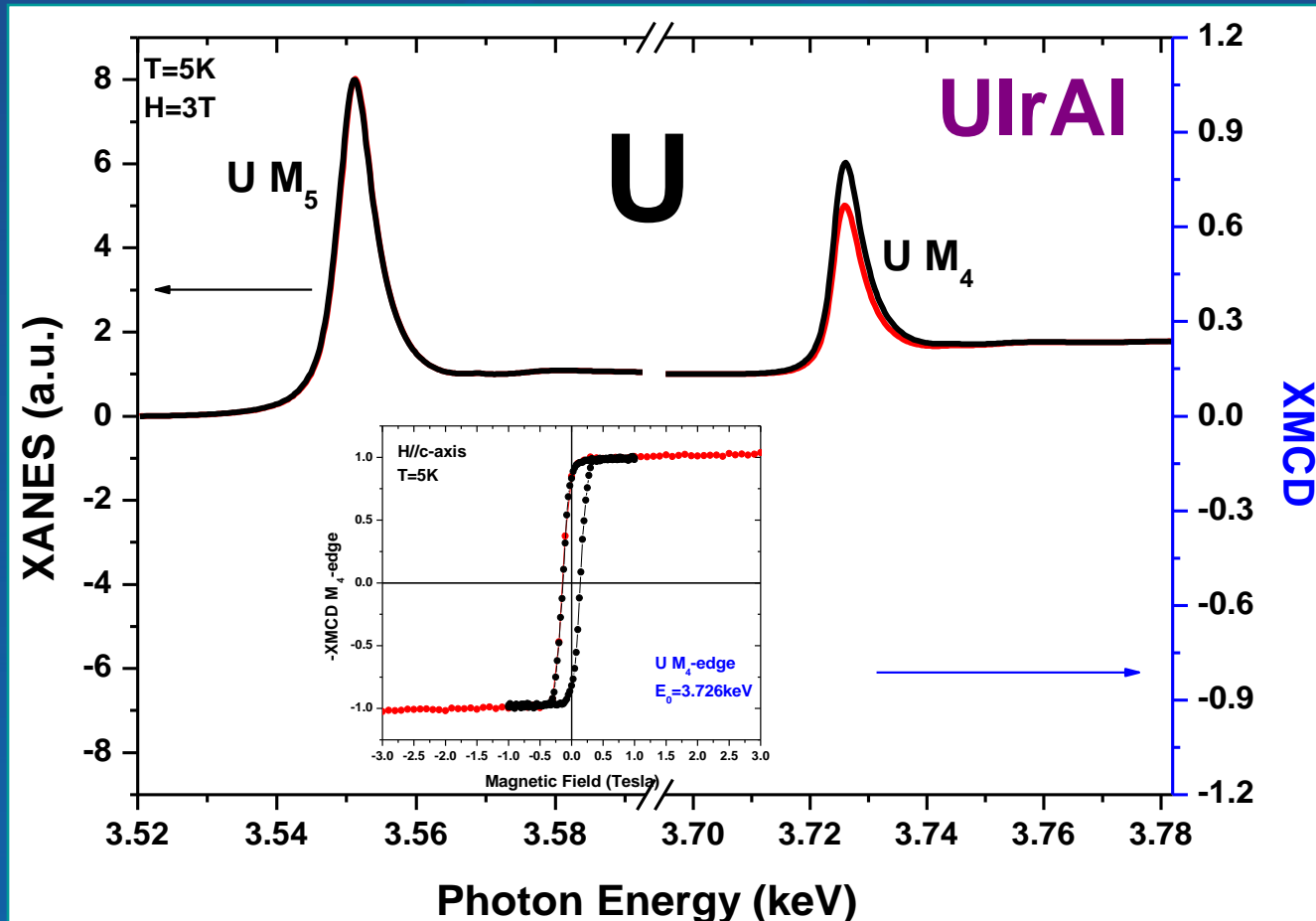
# UTX ternary compounds

Both are ferromagnets

- UIrAl ( $\mu_{TOT} = 0.98 \mu_B$ )  $T_C = 64K$
- UPtAl ( $\mu_{TOT} = 1.38 \mu_B$ )  $T_C = 43K$

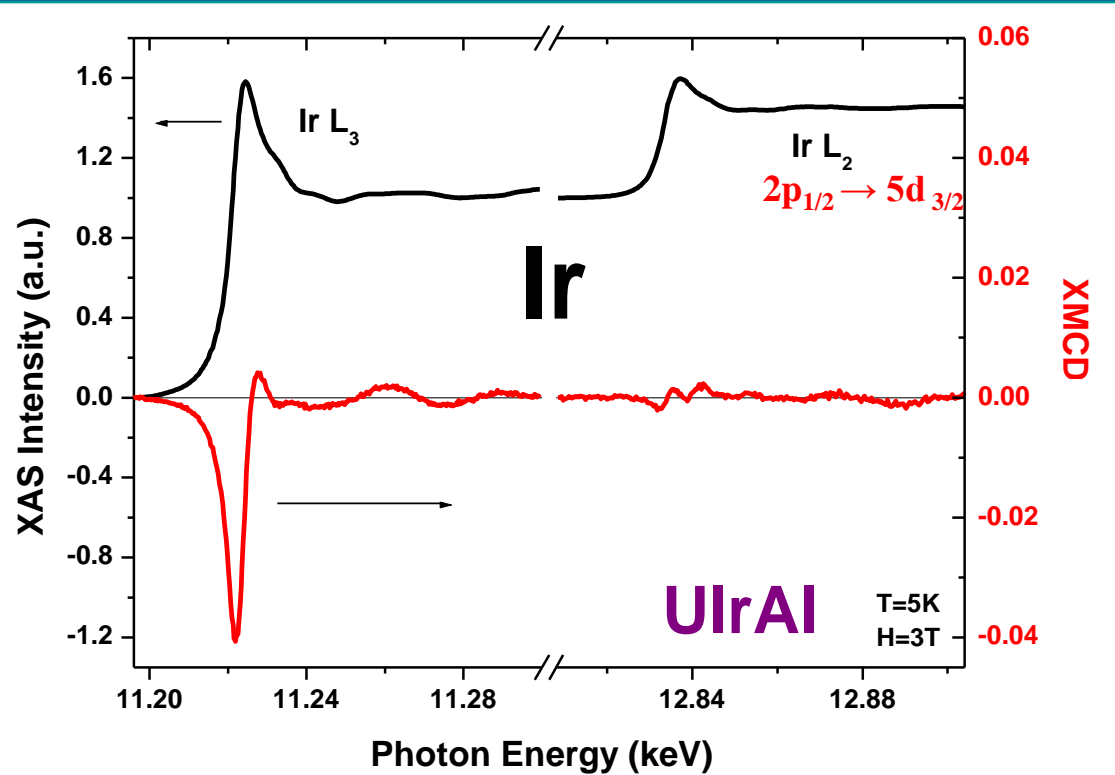


*A.V. Andreev, J. Alloys Compd. 336, 77 (2001)*



	$\mu_L^U(5f)$ ( $\mu_B$ /atom)	$\mu_S^U(5f)$ ( $\mu_B$ /atom)	$\mu_{tot}^U(5f)$ ( $\mu_B$ /atom)	$\mu_L^U(5f)/\mu_S^U(5f)$
<b>f=2</b> ( $U^{4+}$ )	<b>1.29</b>	<b>-0.37</b>	<b>0.92</b>	<b>-3.45</b>
<b>f=3</b> ( $U^{3+}$ )	<b>1.18</b>	<b>-0.56</b>	<b>0.62</b>	<b>-2.10</b>

# XMCD at the Ir $L_{2,3}$ -edges in UIrAl



- Strong XMCD at the  $L_3$ -edge
- Small XMCD at the  $L_2$ -edge
- Large Ir 5d orbital moment aligned parallel to the spin

$\mu_L^{\text{Ir}(5d)}$ ( $\mu_B$ /atom)	$\mu_S^{\text{Ir}(5d)}$ ( $\mu_B$ /atom)	$\mu_{\text{tot}}^{\text{Ir}(5d)}$ ( $\mu_B$ /atom)	$\mu_L^{\text{Ir}(5d)} / \mu_S^{\text{Ir}(5d)}$
0.028	0.048	0.076	0.60

# Analysis combining VSM magnetometry and XMCD

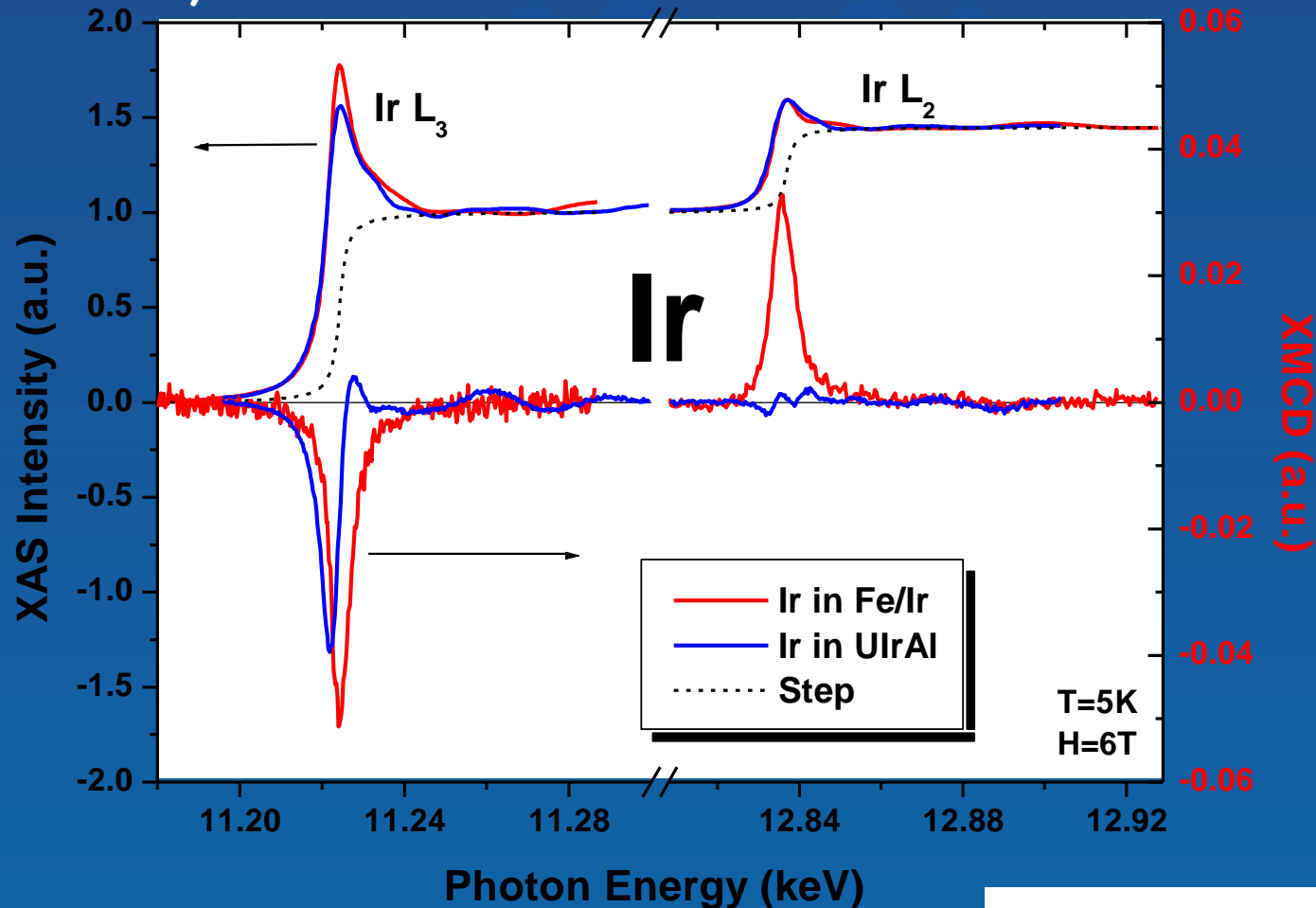
- $M^{\text{U}}(5f) = 0.92 \mu_{\text{B}} / \text{U atom}$  for  $n_f=2$  ( $\text{U}^{4+}$ )
- $M^{\text{U}}(5f) = 0.62 \mu_{\text{B}} / \text{U atom}$  for  $n_f=3$  ( $\text{U}^{3+}$ )
- $M^{\text{Ir}}(5d) = 0.076 \mu_{\text{B}} / \text{Ir atom}$  (sum over two Ir sites)

$$M_{\text{total}} = M^{\text{U}} + M^{\text{Ir}} = 0.996 \mu_{\text{B}}$$

Al and U(6d) contributions are neglected

VSM Data:  $M_{\text{total}} = 0.98 \mu_{\text{B}}$  at 6 Tesla and 4.2K

# Ir $L_{2,3}$ -edges XMCD: UIrAl versus Fe/Ir



**XMCD  $\Rightarrow$  different spectral shape !!**  
**XANES  $\Rightarrow$  small charge transfer**

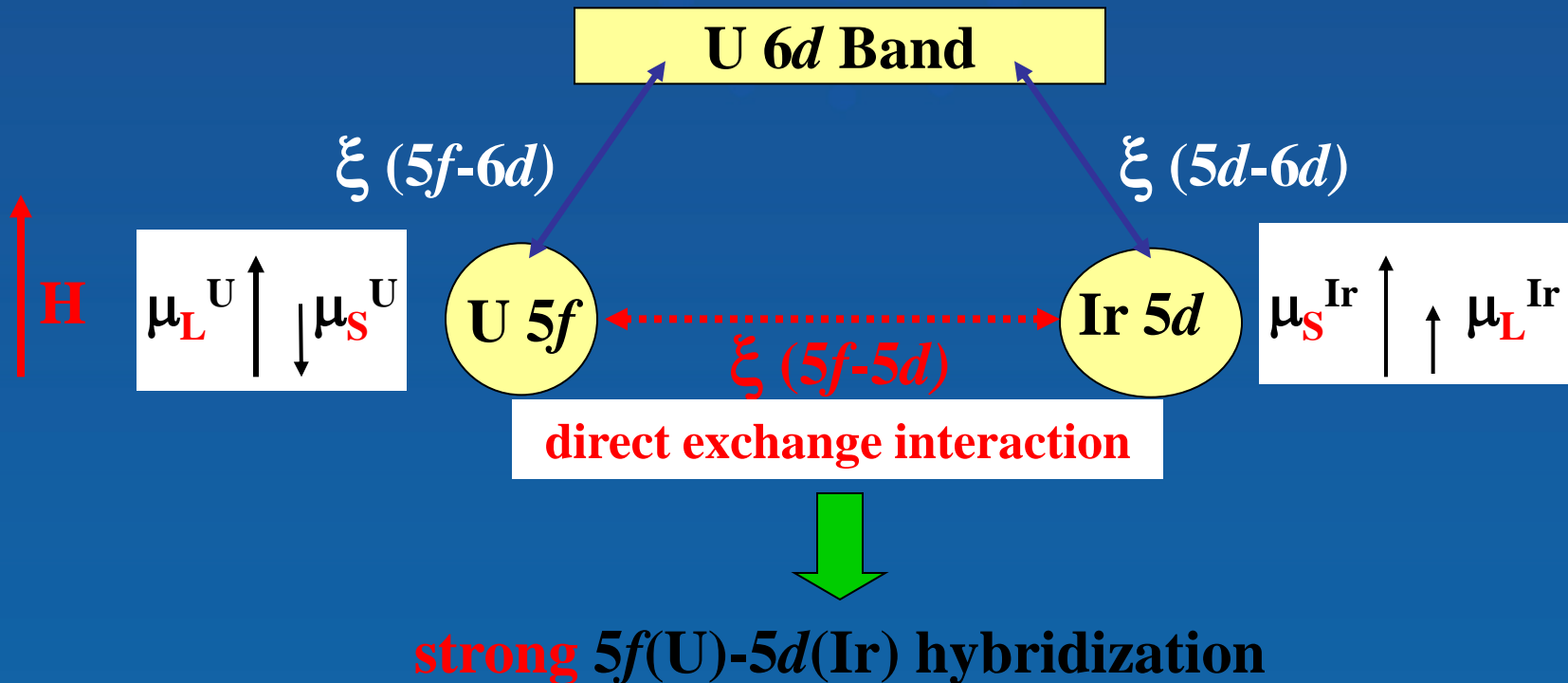
**Fe/Ir**       $\mu_L / \mu_S \sim 0.10$

**UIrAl**       $\mu_L / \mu_S \sim 0.60$



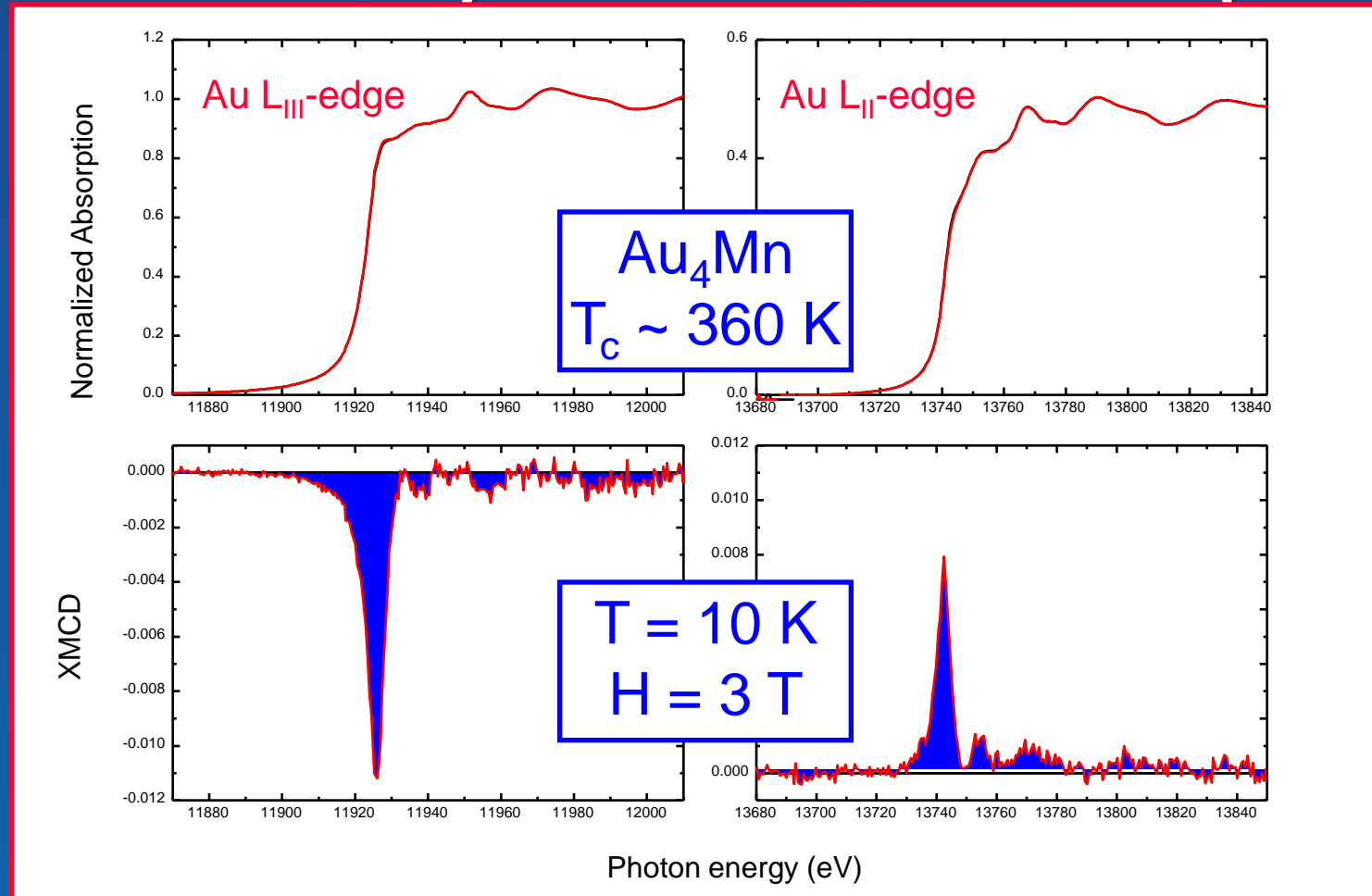
# Induced magnetism on Ir 5d states

Indirect exchange interaction



**Ir orbital moment feels the strong U spin-orbit coupling  
 $\Rightarrow$  Enhanced Ir orbital moment**

# Sensitivity of the XMCD technique



$\langle S_z \rangle = 0.0353(5)\mu_B$   $\langle L_z \rangle = 0.0054(5)\mu_B$  (per Au atom)  
 To compare with  $4.15\mu_B$  per Mn atom

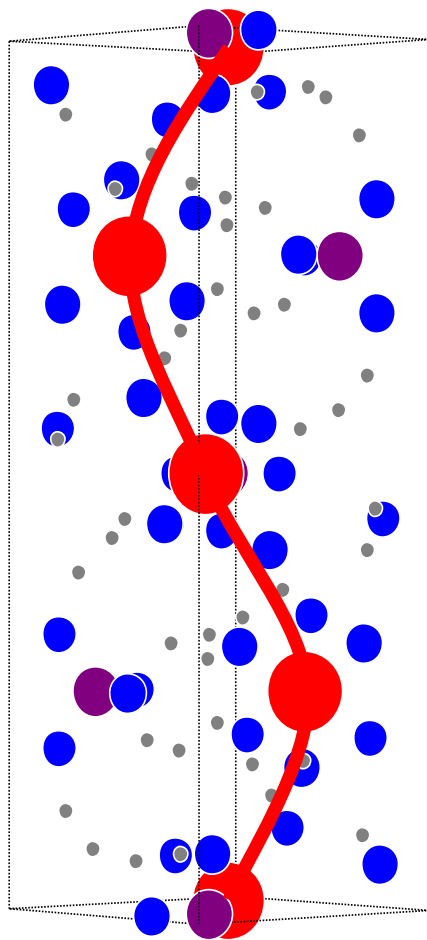
# X-ray Natural Circular Dichroism

# Irreducible Parts of Optical Activity Tensor

*J. Jerphagnon et D.S.Chemla J. Chem. Phys. 65, 1524 (1976)*

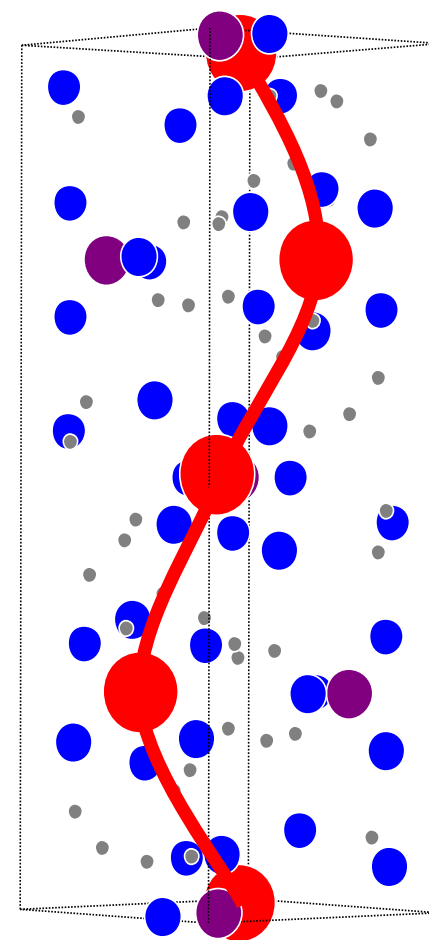
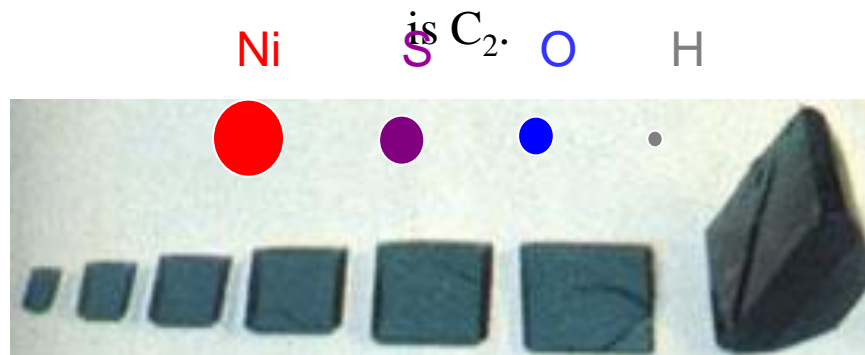
Non-Centro-Symmetrical Crystal Classes	Point Groups	Pseudo-Scalar	Polar Vector	Pseudo-Deviator
		Enantio-morphism E1.M1	Voigt/Fedorov OA E1.M1+E1.E2	XNCD E1.M1+E1.E2
$\bar{4}3m; \bar{6}m2; \bar{6}$	$T_d; D_{3h}; C_{3h}$	No	No	No
432; 23	O ; T	Yes	No	No
622; 32; 422	$D_6; D_3; D_4$	Yes	No	Yes
6mm; 3m; 4mm	$C_{6v}; C_{3v}; C_{4v}$	No	Yes	No
6; 3; 4	$C_6; C_3; C_4$	Yes	Yes	Yes
$\bar{4}2m$	$D_{2d}$	No	No	Yes
$\bar{4}$	$S_4$	No	No	Yes
mm2	$C_{2v}$	No	Yes	Yes
222	$D_2$	Yes	No	Yes
2	$C_2$	Yes	Yes	Yes
m	$C_s$	No	Yes	Yes
1	$C_1$	Yes	Yes	Yes

# Structure of $\alpha$ -Nickel Sulfate Hexahydrate



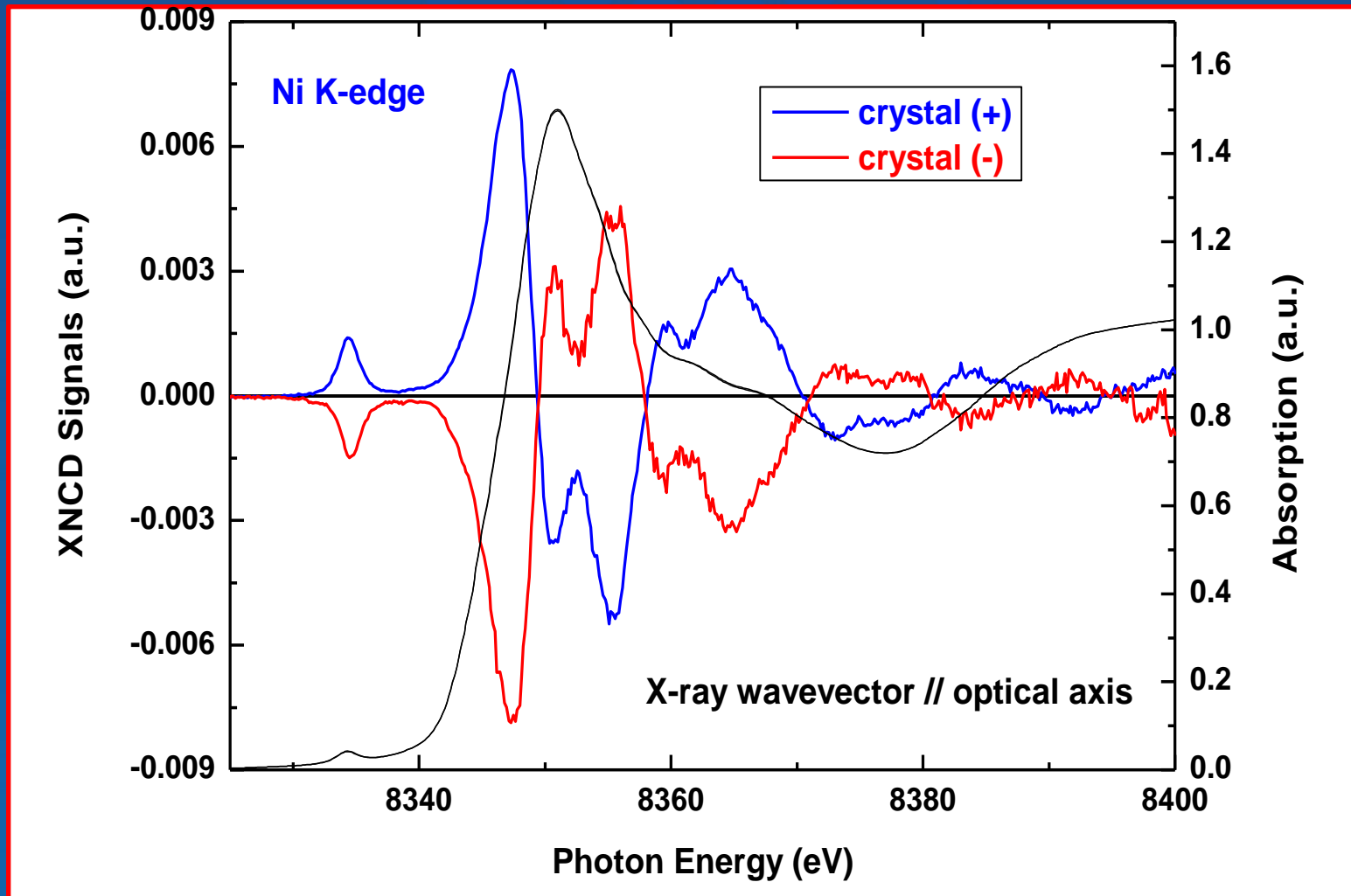
$P4_12_2$

$\alpha$ -NiSO<sub>4</sub>·6H<sub>2</sub>O is a uniaxial crystal with four formula units per unit cell that belongs to the **enantiomorphous** tetragonal space groups,  $P4_12_2$  or  $P4_32_12$ . Four nearly perfect Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> octahedrons are identical, except for orientation, and are related through a **screw axis** which is parallel to the tetragonal axis of the crystal, *i.e.* crystallographic *c* axis or optical axis. The point group symmetry at each Ni<sup>2+</sup> site



$P4_32_12$

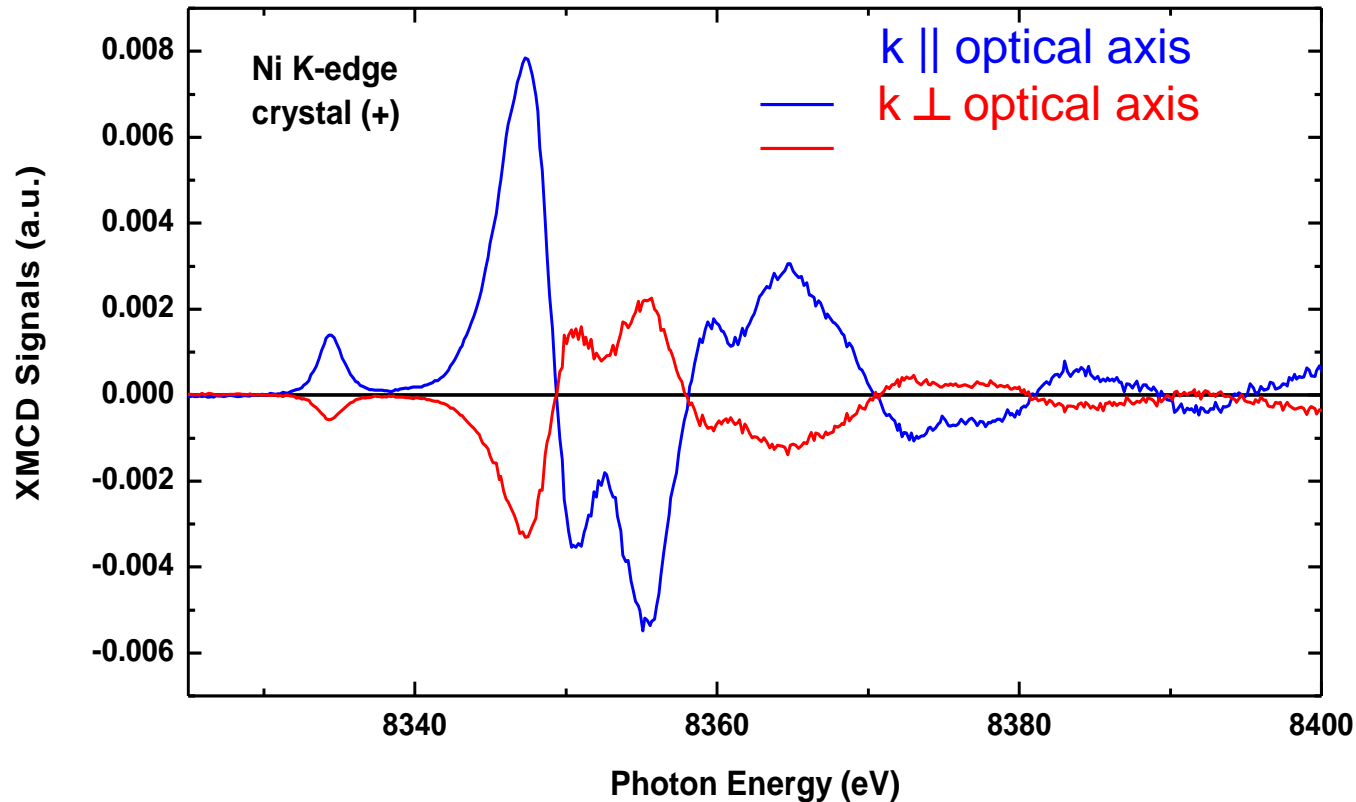
# XNCD spectra of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ crystals



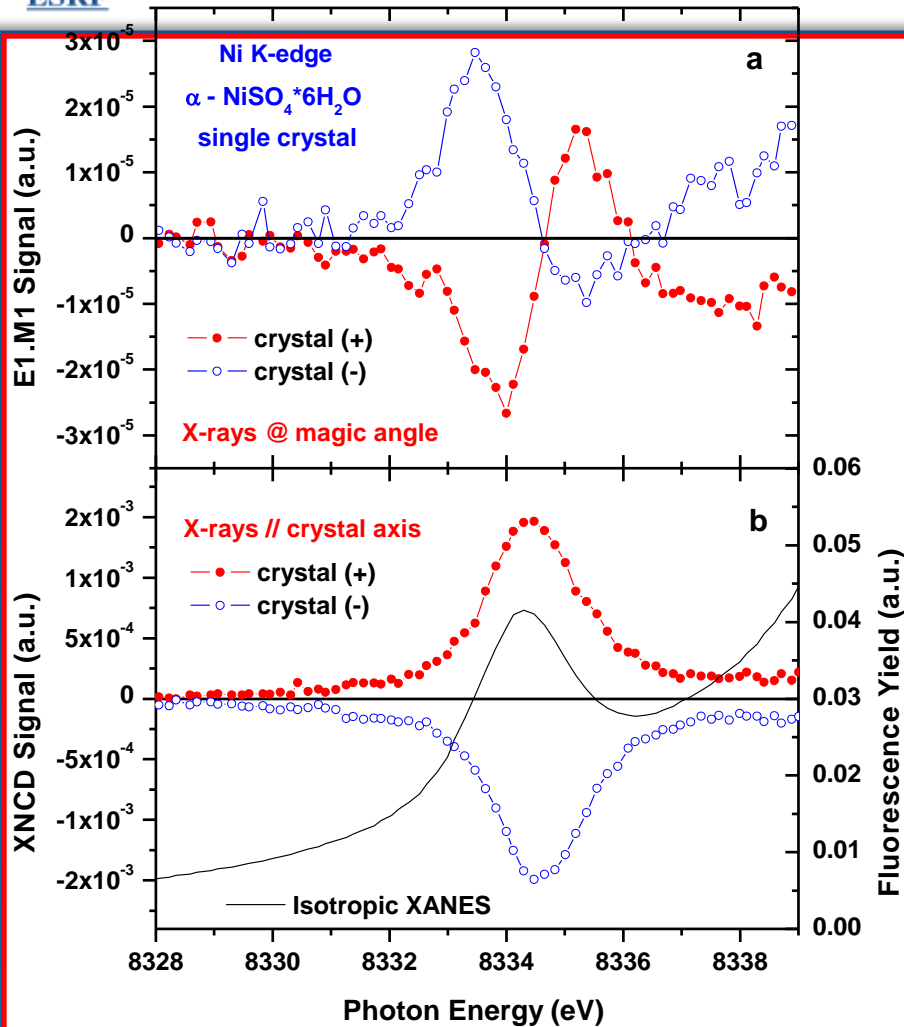
Amplitude of the XNCD signal is nearly 1% with respect to the edge jump !



# Angular dependence of the XNCD signal



This result confirms  $(3\cos^2\Theta - 1)$  dependence of the E1.E2 XNCD signal. To measure a weak scalar E1.M1 signal one has to perform angular scans in the vicinity of the magic angle  $\Theta = 54.73^\circ$



$\langle E1.M1 \rangle$  contribution  
 is as small as  $3 \cdot 10^{-5}$  and  
 is 60 times smaller than  
 $\langle E1.E2 \rangle$  contribution

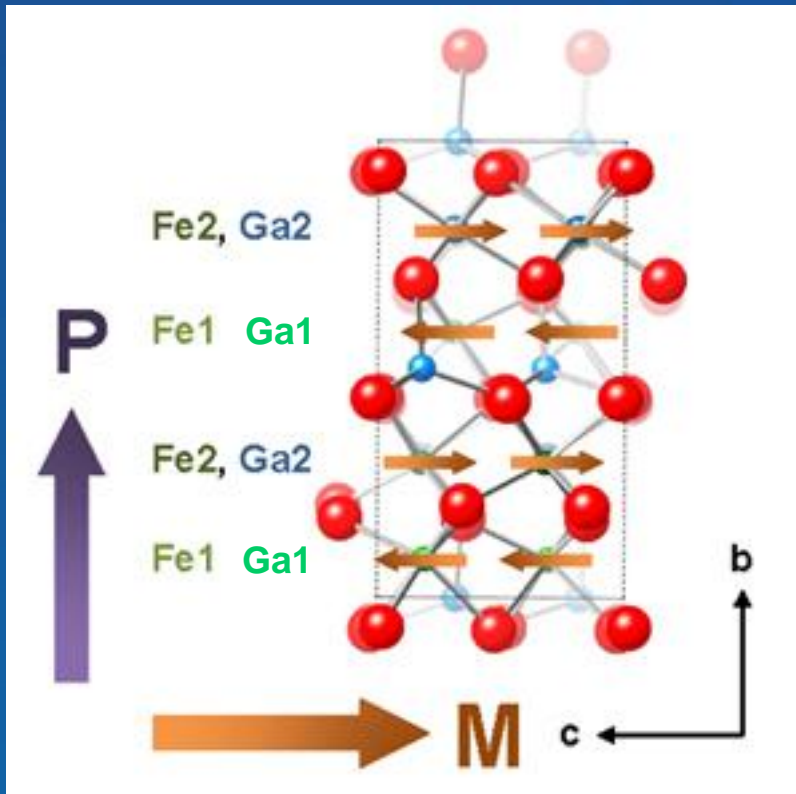
*Monoelectronic M1 transitions from 1s core levels are forbidden in non-relativistic approach*

*BUT*

*they are allowed in the relativistic theory:*

*M1 transition selection rules are:  $\Delta l=0, \pm 1, \pm 2$ ,  $\Delta j=1$ ; except  $s \leftrightarrow p$  transitions*

# *GaFeO<sub>3</sub> is the mostly studied multiferroic*



**Orthorhombic unit cell**  
 **$a=8.72\text{\AA}$ ,  $b=9.37\text{\AA}$ ,  $c=5.07\text{\AA}$**   
 **$C_{2v}$  polar crystal class**  
**Space group  $Pc2_1n$**   
**Polarization along b axis**

**Ferrimagnet with  $T_c \leq 270\text{ K}$**   
**Easy magnetization along c**

**Magnetic point group  $m'2'm$**

Anapole spin moment is estimated to be  $24.155\mu_B \text{\AA}$  per unit cell.

Yu. F. Popov, A. M. Kadomtseva, G. P. Vorob'ev et al JETP, **87** (1998), 146

# Irreducible Parts of Optical Activity Tensor

*J. Jerphagnon et D.S.Chemla J. Chem. Phys. 65, 1524 (1976)*

Non-Centro-Symmetrical Crystal Classes	Point Groups	Pseudo-Scalar	Polar Vector	Pseudo-Deviator
		Enantio-morphism E1.M1	Voigt/Fedorov OA E1.M1+E1.E2	XNCD E1.M1+E1.E2
$\bar{4}3m; \bar{6}m2; \bar{6}$	$T_d; D_{3h}; C_{3h}$	No	No	No
432; 23	O; T	Yes	No	No
622; 32; 422	$D_6; D_3; D_4$	Yes	No	Yes
6mm; 3m; 4mm	$C_{6v}; C_{3v}; C_{4v}$	No	Yes	No
6; 3; 4	$C_6; C_3; C_4$	Yes	Yes	Yes
$\bar{4}2m$	$D_{2d}$	No	No	Yes
$\bar{4}$	$S_4$	No	No	Yes
mm2	$C_{2v}$	No	Yes	Yes
222	$D_2$	Yes	No	Yes
2	$C_2$	Yes	Yes	Yes
m	$C_s$	No	Yes	Yes
1	$C_1$	Yes	Yes	Yes

# X-ray Natural Circular Dichroism in $\text{GaFeO}_3$

$$\Delta\sigma_{\text{NCD}} = \sigma^+ - \sigma^-$$

Only two interference terms contribute to the dichroic signal :

$$\langle i | \hat{\varepsilon} \cdot r | f \rangle \langle f | (k \times \hat{\varepsilon}) \cdot (L + gs) \cdot i \rangle$$

**E1.M1**

**Origin of OA in the visible**  
**Very small in the X-ray range**

$$\langle i | \hat{\varepsilon} \cdot r | f \rangle \langle f \cdot \hat{\varepsilon} \cdot r k \cdot r | i \rangle$$

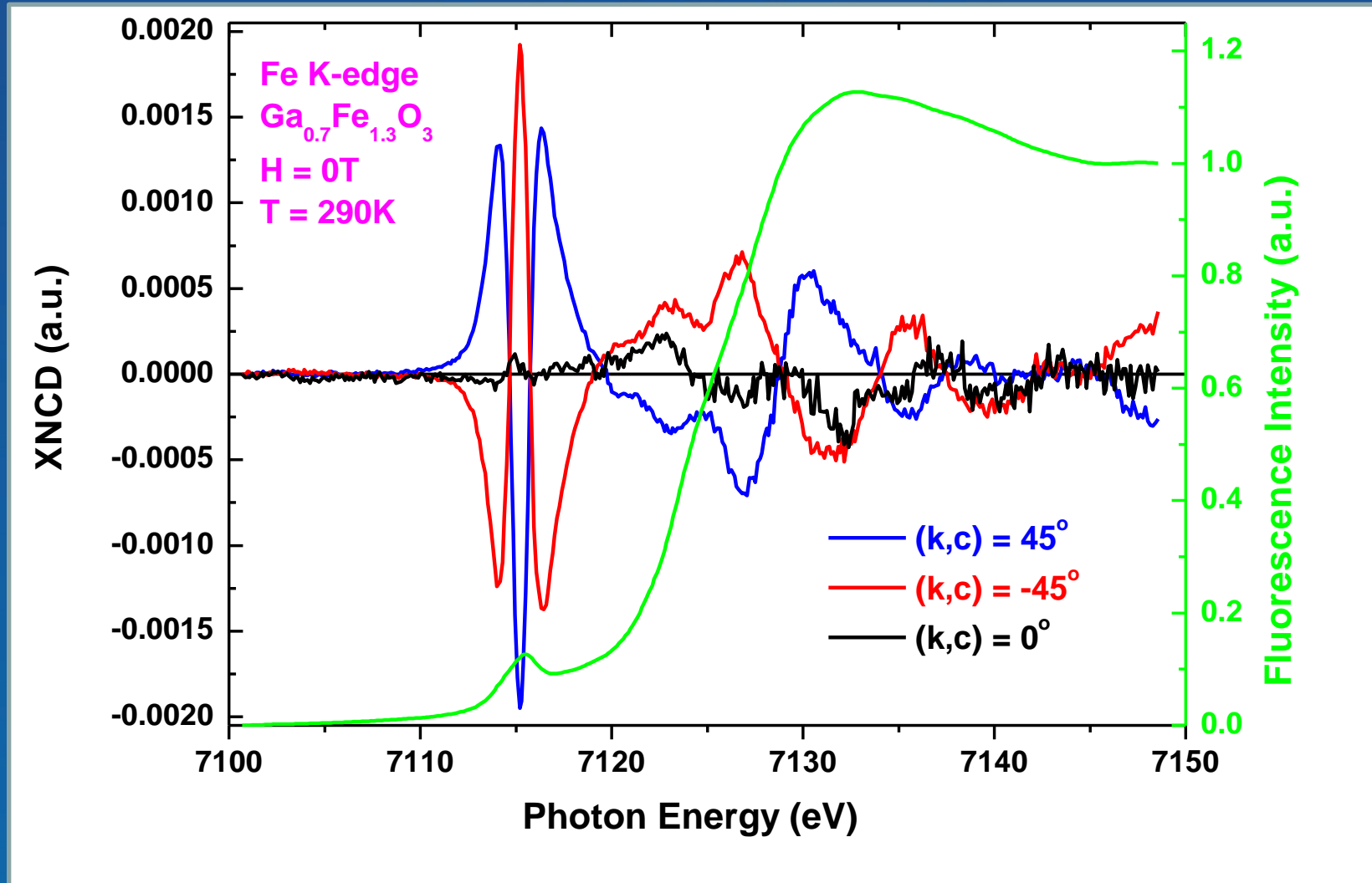
**E1.E2**

**only for anisotropic systems**  
**Sizeable in the X-ray range**

**Space group  $\text{Pc}2_1\text{n}$  (class  $\text{mm}2$ )  $\Leftrightarrow$  *Non-enantiomorphous crystal***  
*No optical activity along  $c$  axis*

$$\Delta\sigma_{\text{NCD}} \propto P_c \sin^2\Theta \sin 2\varphi$$

# X-ray Natural Circular Dichroism in $\text{Ga}_{0.7}\text{Fe}_{1.3}\text{O}_3$





# Can we quantify Optical Activity of an atom with X-rays ?

## XNCD Sum Rule

P. Carra , A. Jerez & I. Mari - Phys. Rev. B67 45111 (2003)

$$\int_{\text{Edge}} \frac{\sigma_{EIE2}}{(\hbar\omega)^2} d(\hbar\omega) = \frac{-16\pi^2\alpha_0}{\hbar c} \frac{S_3}{S_0} (2\ell_c + 1) \sum_{\ell, \ell'} \mathbf{R}_\ell^{(1)} \mathbf{R}_{\ell'}^{(2)} \mathbf{a}^{(2,+1)}(\ell, \ell'; \ell_c) \times \sqrt{\frac{3}{2}} \langle \Psi | [L, \Omega]^{(2)} | \Psi \rangle$$

$$\mathbf{R}_\ell^{(1)} = \int_0^{P_{\text{MT}}} r^3 dr \varphi_c(r) \varphi_\ell(r)$$

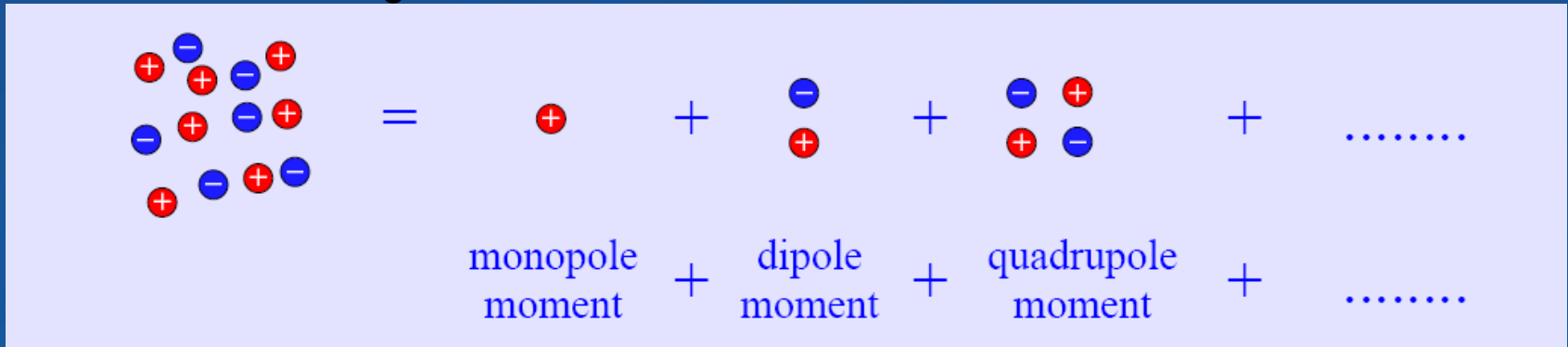
$$\mathbf{R}_{\ell'}^{(2)} = \int_0^{P_{\text{MT}}} r^4 dr \varphi_c(r) \varphi_{\ell'}(r)$$

$$\mathbf{a}^{(2,+1)} = \frac{2(2\ell + 1)(2\ell' + 1)[6 + 3\ell_c(\ell_c + 1) - 2\ell(\ell + 1) - \ell'(\ell' + 1)]}{(\ell + \ell' + 1)(\ell_c - 3\ell' + 2\ell)(\ell_c + 3\ell' - 2\ell + 1)(\ell_c + \ell)^2(\ell_c + \ell + 2)^2}$$

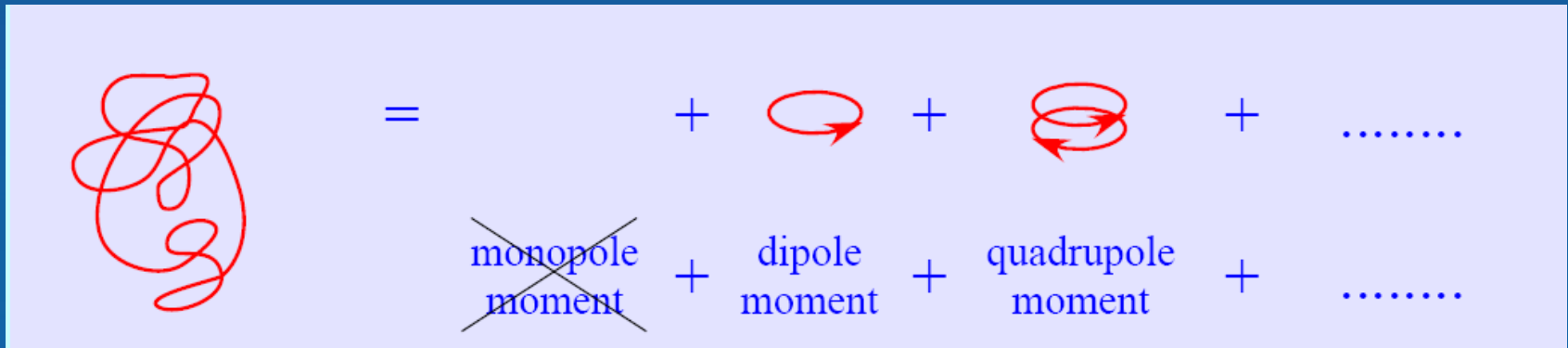
*Radial integrals to be calculated numerically*

# Multipole moments

distribution of charges



distribution of currents



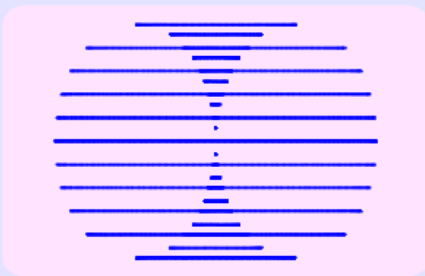
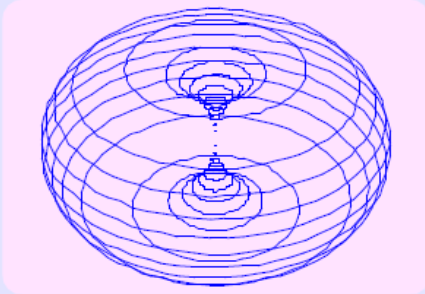
*All these multipole moments conserve parity*

# Picture of a parity-odd atom

parity conserving atom

$$|\Psi\rangle = |P_{1/2}\rangle$$

current = circles on torus



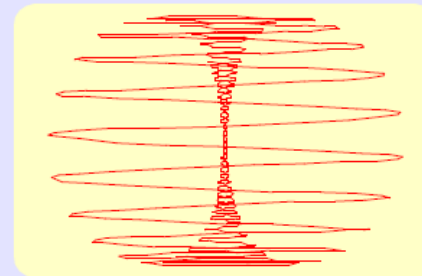
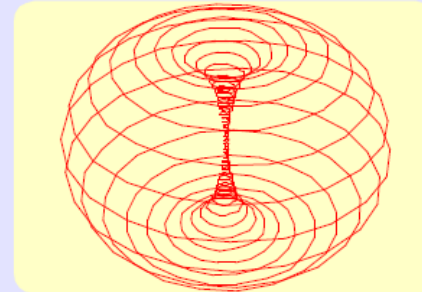
parity violating atom

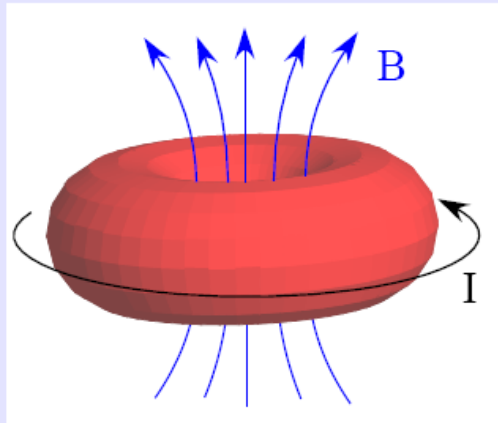
$$|\Psi\rangle = |P_{1/2}\rangle + i \varepsilon_{pv} |S_{1/2}\rangle$$

in H-atom:  $\varepsilon = 10^{-11}$

here:  $\varepsilon = 5\%$

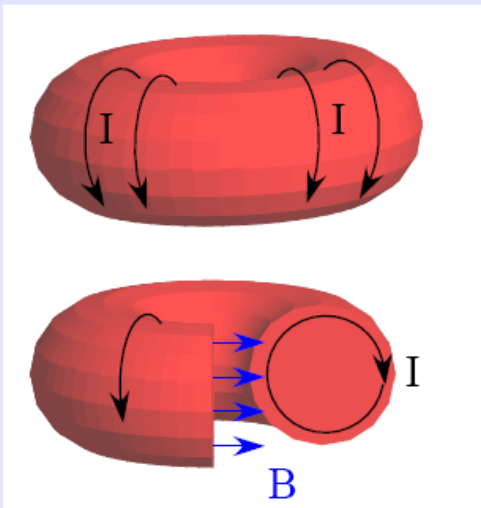
current = helix on torus





magnetic dipole moment  
= circular current loop

→ magnetic field in all space



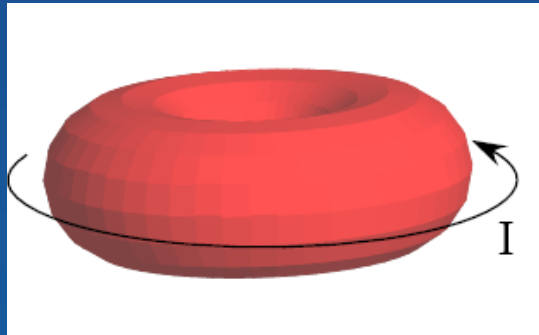
magnetic anapole moment

= toroidal current

→ magnetic field confined inside of torus

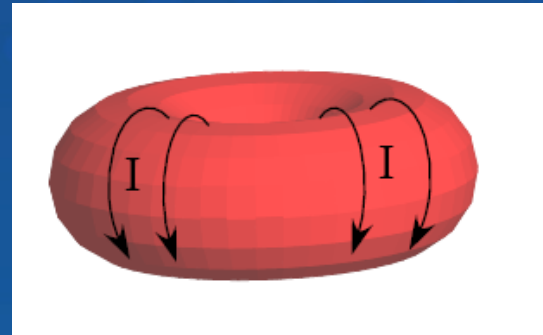
*the lowest order parity-odd magnetic multipole distribution of a current*

dipole current



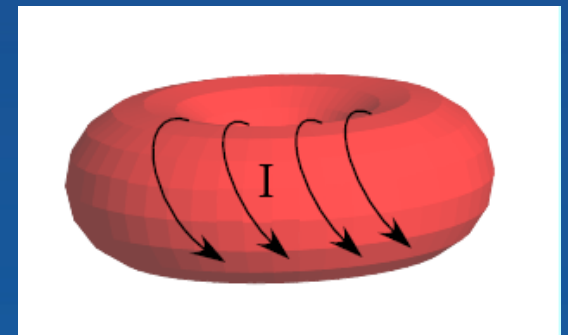
+

anapole current



=

helico-toroidal current



**Coexistence of dipole and anapole moments violates parity**

**Anapole Moment  
link together Chirality & Magnetism**

## *Acknowledgements:*

F. Wilhelm, N. Jaouen, A. Smekhova,  
J. Goulon, Ch. Goulon-Ginet,

# THANK YOU