High pressure activity at the ESRF ID12 beamline

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OUTLINE

- ❑ **ID12 beamline**

- ❑ **2 selected exemples:**

- pressure induced electron density redistribution in $EuCo_2P_2$
- pressure dependence of the orbital to spin moment ratio in UGe_2

- ❑ **Conclusion / Perspective**

ID12 beamline

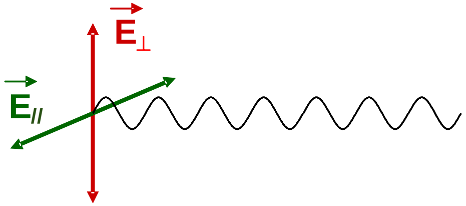
The ID12 beamline is a beamline dedicated to *polarization dependent* X-ray absorption spectroscopies.

Strength of X-ray spectrocopy: element-specific and orbital-selective

Any state of polarization of X-ray beam generated by *helical undulators:*

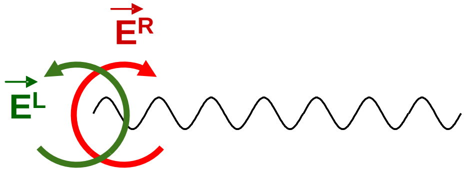
- **linear polarization (horizontal or vertical)**

$$XNLD = \mu^{\perp}(E) - \mu^{//}(E)$$



- **circular polarization (right or left)**

$$XMCD = \mu^{R}(E) - \mu^{L}(E)$$



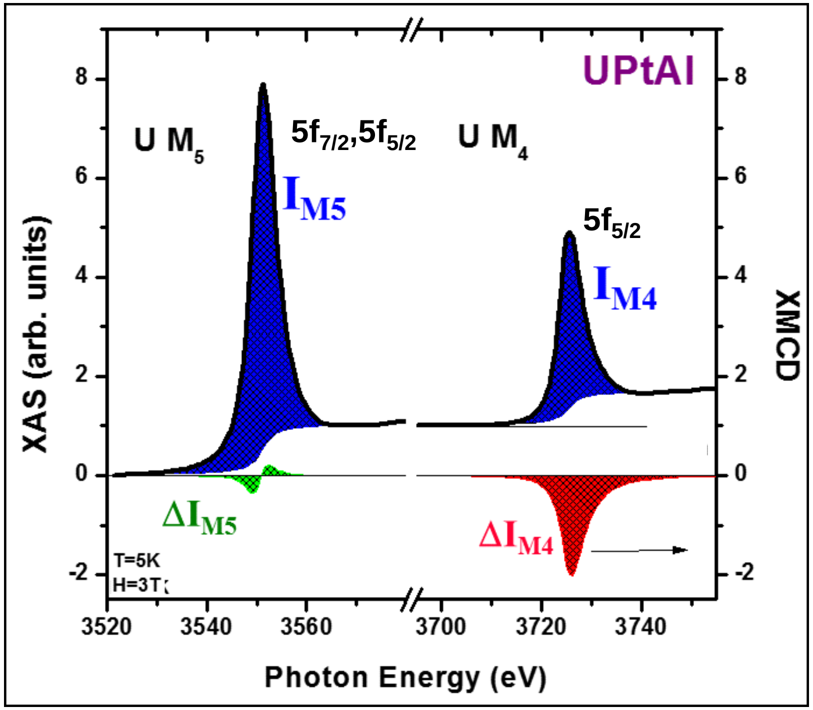
to investigate *electronic structure* and *magnetic properties* of the absorbing atom

Ground state values of various effective operators can be deduced via a set of sum rules.

1. **Charge sum rule:**
   $I_{M5}+I_{M4} \propto$ number of 5f holes

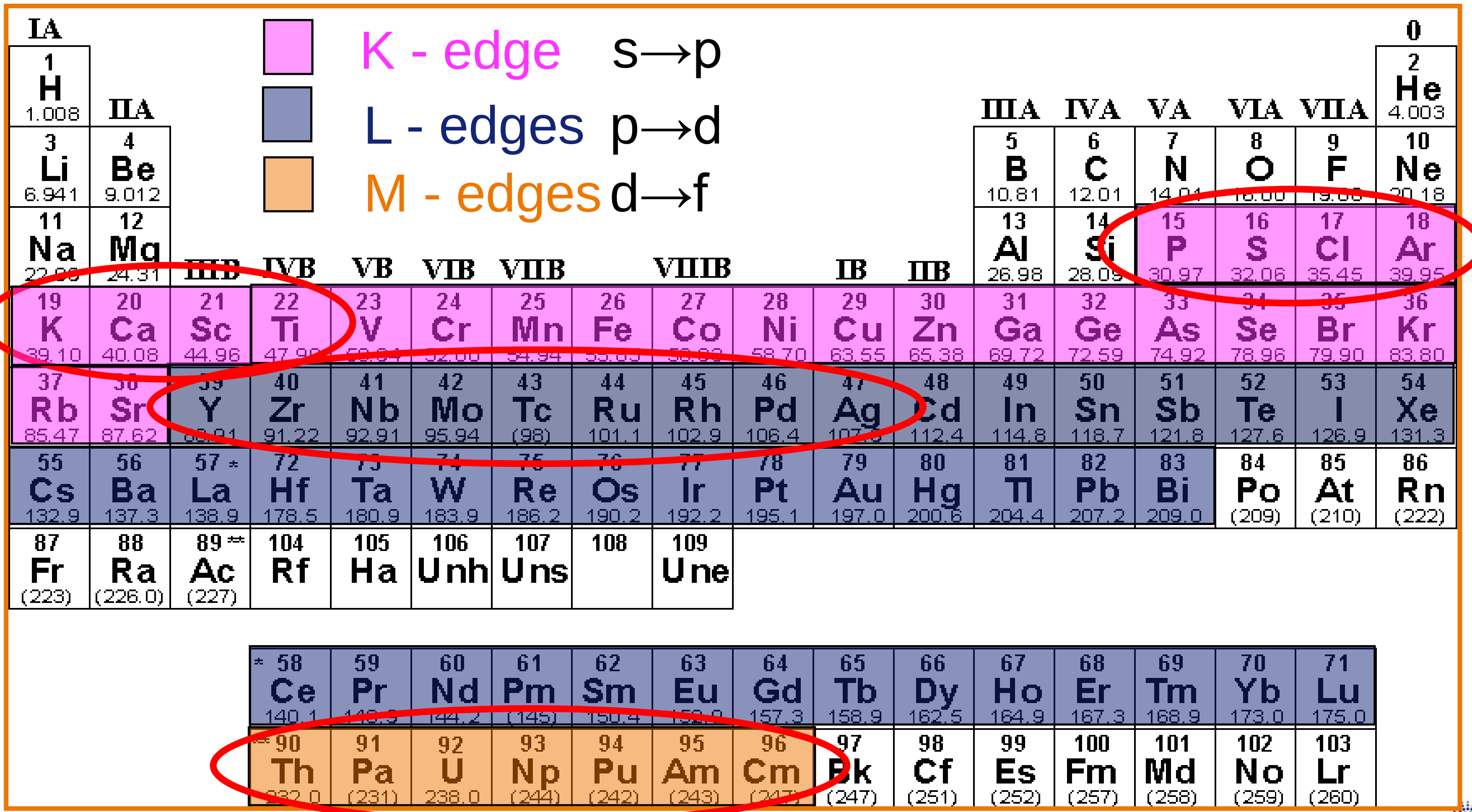
2. **Spin-Orbit sum rule:**
   $I_{M5}/(I_{M5}+I_{M4})$ => the occupancy of the spin-orbit split sub-shells ($5f_{5/2}$, $5f_{7/2}$)
   i.e. anisotropy of the spin-orbit interaction

3. **Orbital and Spin sum rules:**
   linear combination of ΔI_{M5} and ΔI_{M4}
   => the orbital magnetic moment
   => the spin magnetic moment



ID12 beamline

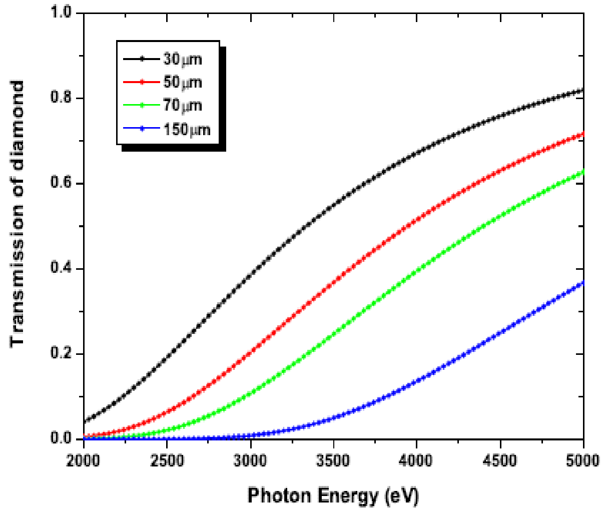
- **fixed exit DCM with Si<111> : energy range 2 < E < 15 keV**
- **Extension of HP XANES and XMCD to photon energies below 5 keV**



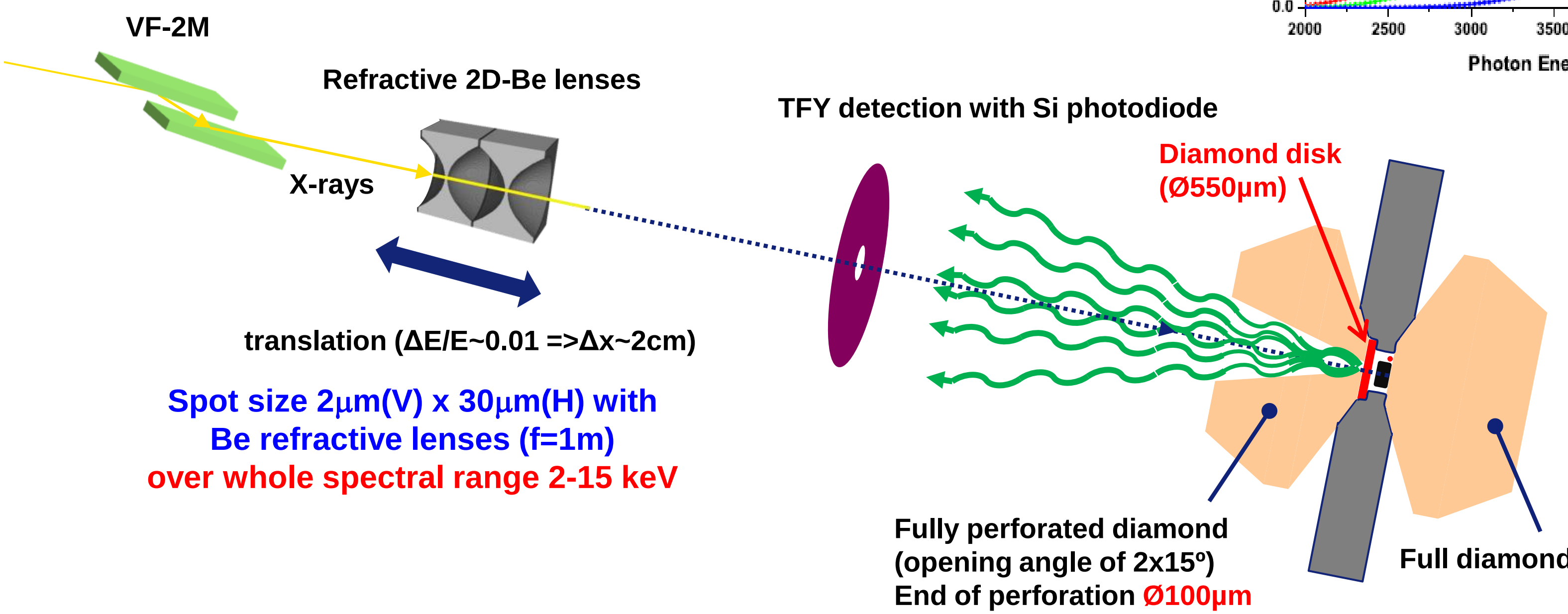
ID12 diamond anvil cell dedicated for tender x-rays

Specific membrane He driven DAC: ESRF development (ID12 and HP lab)
combine a fully perforated diamond + a thin diamond disk

- **Fully perforated diamonds → to minimize the attenuation of X-rays**
- **Diamond disks: 30µm (up to 10 GPa) and 80µm (up to 20 GPa)**
  => 30µm thin diamond window => 60% transmission @ 3.6keV

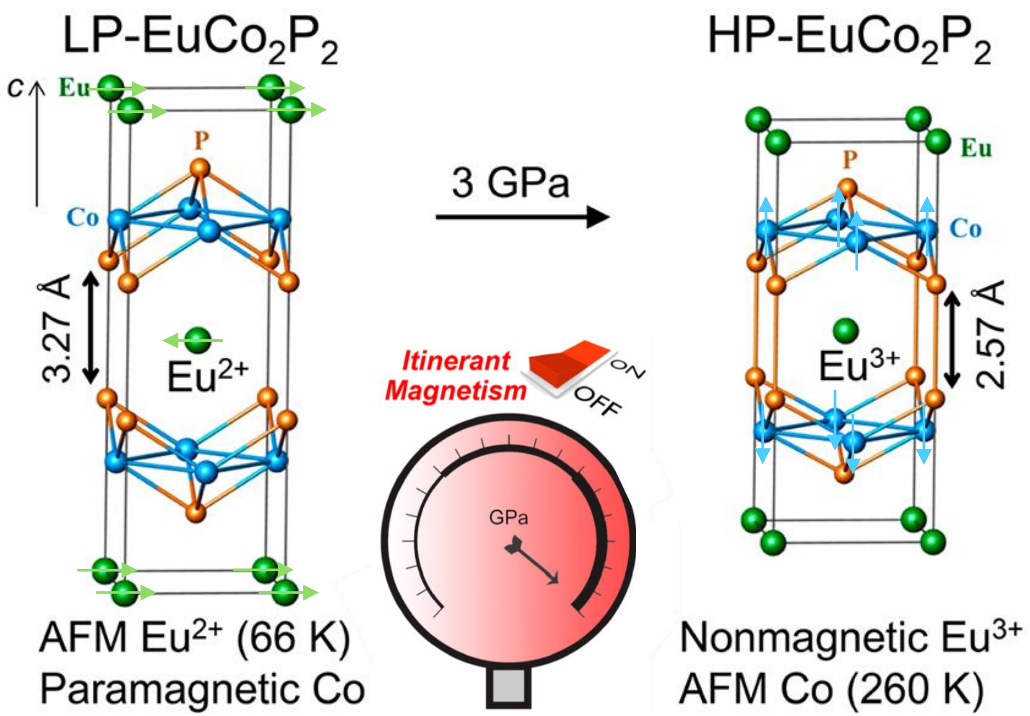


ESRF ID12 beamline



Spot size 2µm(V) x 30µm(H) with
Be refractive lenses (f=1m)
over whole spectral range 2-15 keV

Electron redistribution in $EuCo_2P_2$ under pressure



Normal
localized AFM

Collapsed
itinerant AFM

A traditional Zintl–Klemm electron counting approach suggests:

	Zintl charges Normal (LP)		Zintl charges Collapsed (HP)
Eu	+2	e^- →	+3
Co	+2		+0.5
P	−3	e^- →	−2

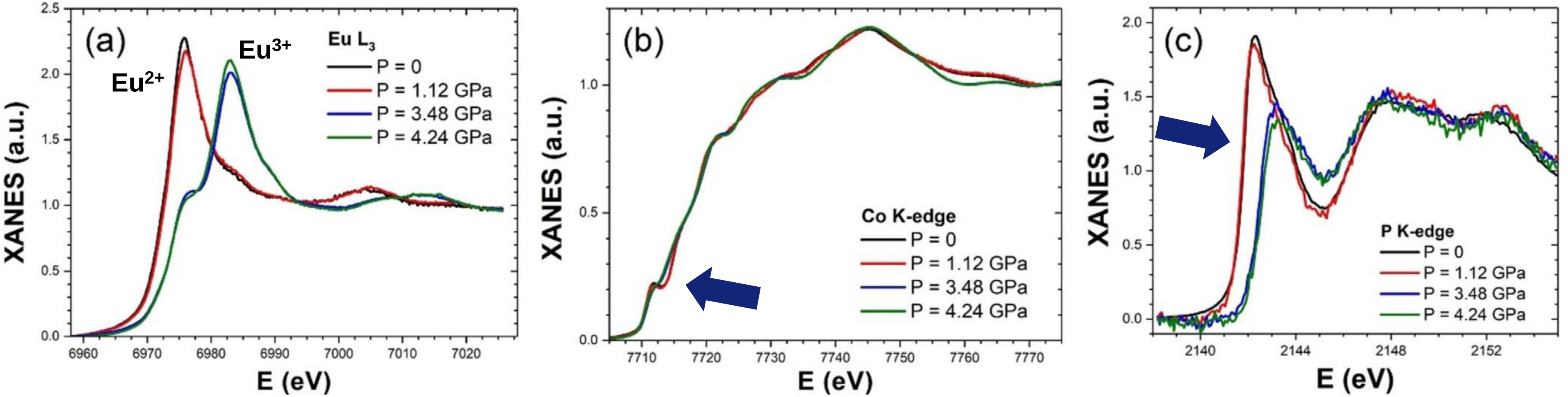
M. Chefki et al., PRL 80, 802 (1998)
N. Bi et al., PRB 63, 100102(R) (2001)

➡ **band filling effect of Co 3*d* band**

This formal treatment of charge balance hardly conveys the realistic physical picture in the metallic systems with strong covalent bonding, where electronic states of different elements are strongly mixed.

HP XANES of Eu L3-edge, Co and <u>P K-edges</u>

Electron redistribution in $EuCo_2P_2$ under pressure



$Eu^{2+} \Rightarrow Eu^{3+}$

$4f^{7} \Rightarrow 4f^{6}$

minor change of Co K-edge

some broadening: increase in the metallic character of the Co electronic states

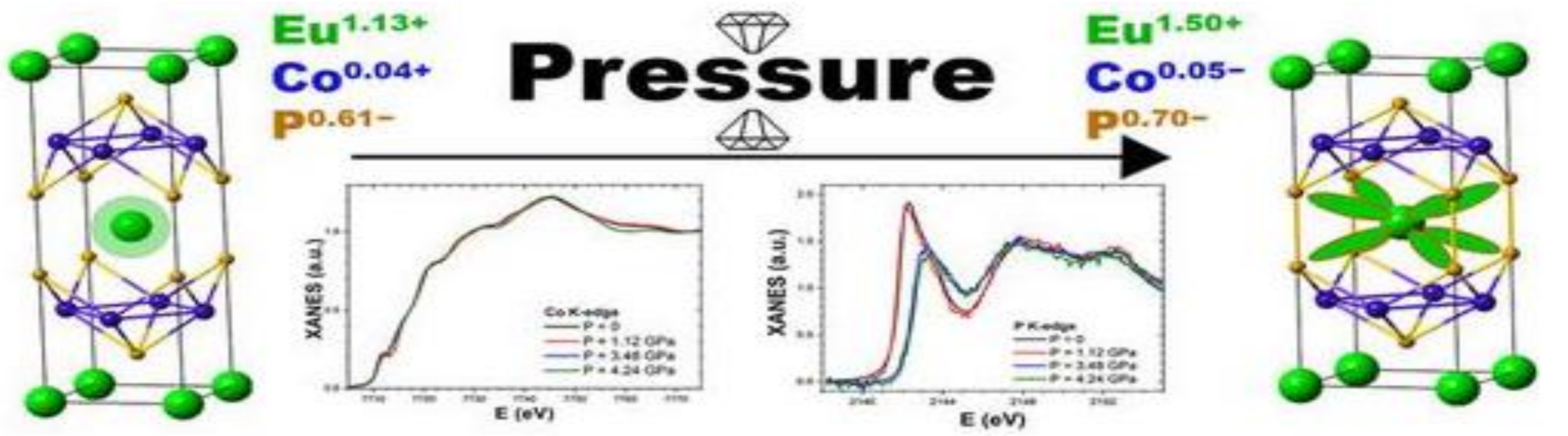
decreased intensity of the "white line" at higher pressure:

increase in the electron density occupation of the phosphorus 3p states

Vincent Yannello,[a] Francois Guillou,[b, h] Alexander A. Yaroslavtsev,[c, d] Zachary P. Tener,[a] Fabrice Wilhelm,[b] Alexander N. Yaresko,[e] Serguei L. Molodtsov,[c, f, g] Andreas Scherz,[c] Andrei Rogalev,*[b] and Michael Shatruk*[a]

Chem. Eur. J. 2019, 25, 5865 – 5869

Electron redistribution in $EuCo_2P_2$ under pressure



High pressure "squeezes out" electrons from the localized Eu 4f levels into the delocalized Co 3d – P 3p band supported by quantum-chemical calculations.

These changes explain the increased electron density on P atoms, deduced from the P K-edge XANES spectra.

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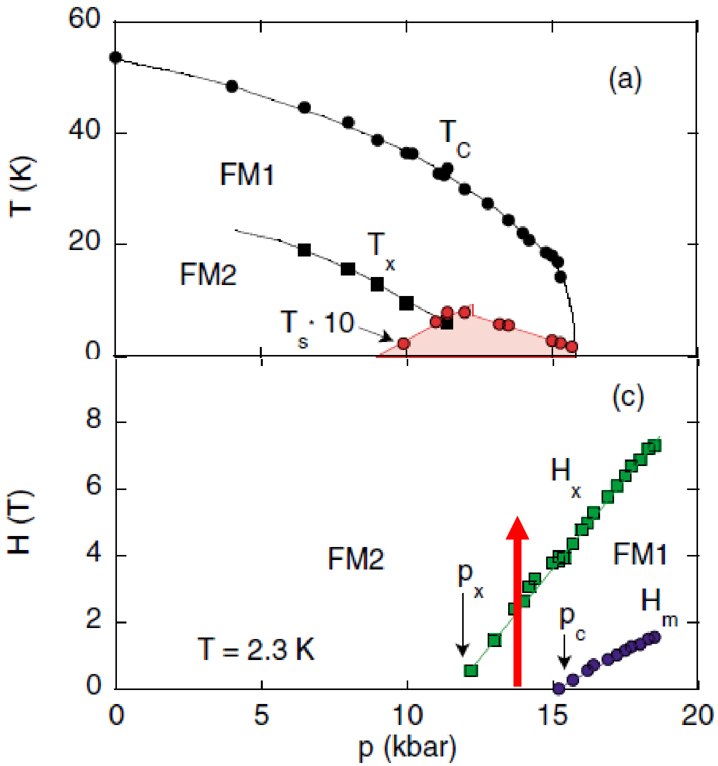
Magnetism of UGe_2 under pressure

UGe_2 represents the first example of materials where ferromagnetism and superconductivity coexist but are not competing.

S. Saxena *et al., Nature* **406,** 587 (2000)



As a function of pressure, one observes a cross-over from a strongly polarized FM2 phase (~1.5μ_B) to a weakly polarized FM1 phase (~0.9 μ_B).
Superconductivity appears in FM1 phase.

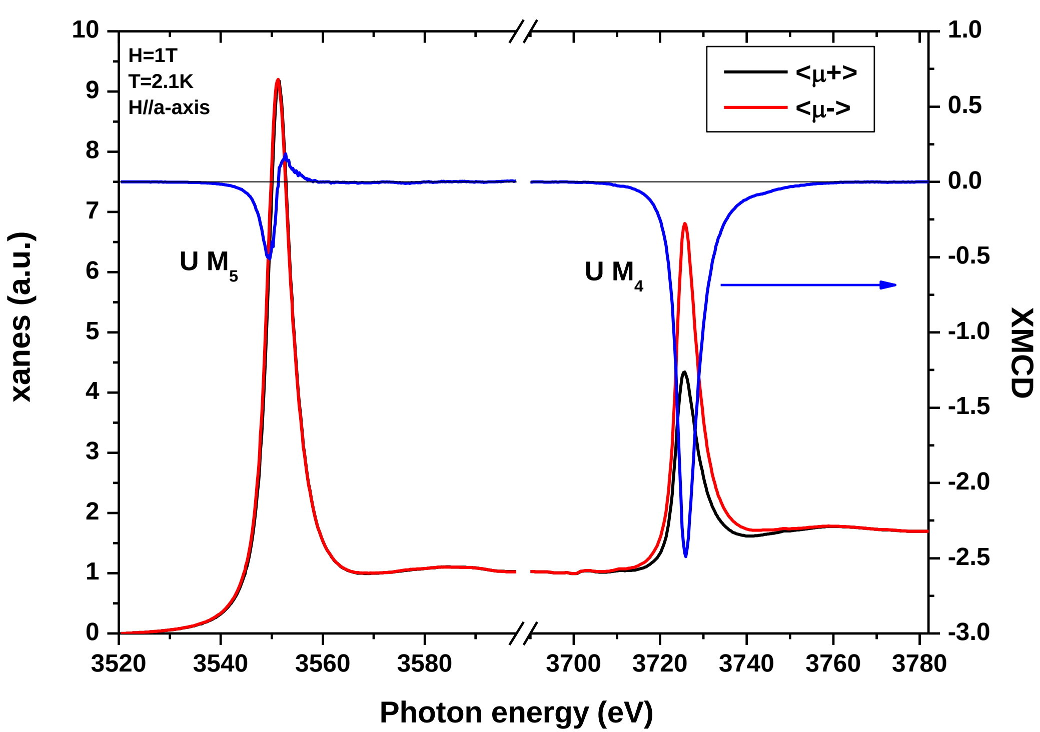
How are the uranium 5*f* orbital and spin magnetic moments affected by the FM1- FM2 phase transition?

C. Pfleiderer and A. D. Huxley, *Phys. Rev. Lett.* **89**, 147005 (2002)
V. Taufour, *et al.*, *Phys. Rev. Lett.* **100**, 217201 (2010)

Electronic and magnetic properties of Uranium: 5f states => $M_{4,5}$ -edges

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

μ^+, μ^- => Absorption cross-sections for CP X-rays with (+) right helicity
(-) left helicity



XMCD

Sum-rules: - U 5*f* Orbital moment
- U 5*f* Spin moment

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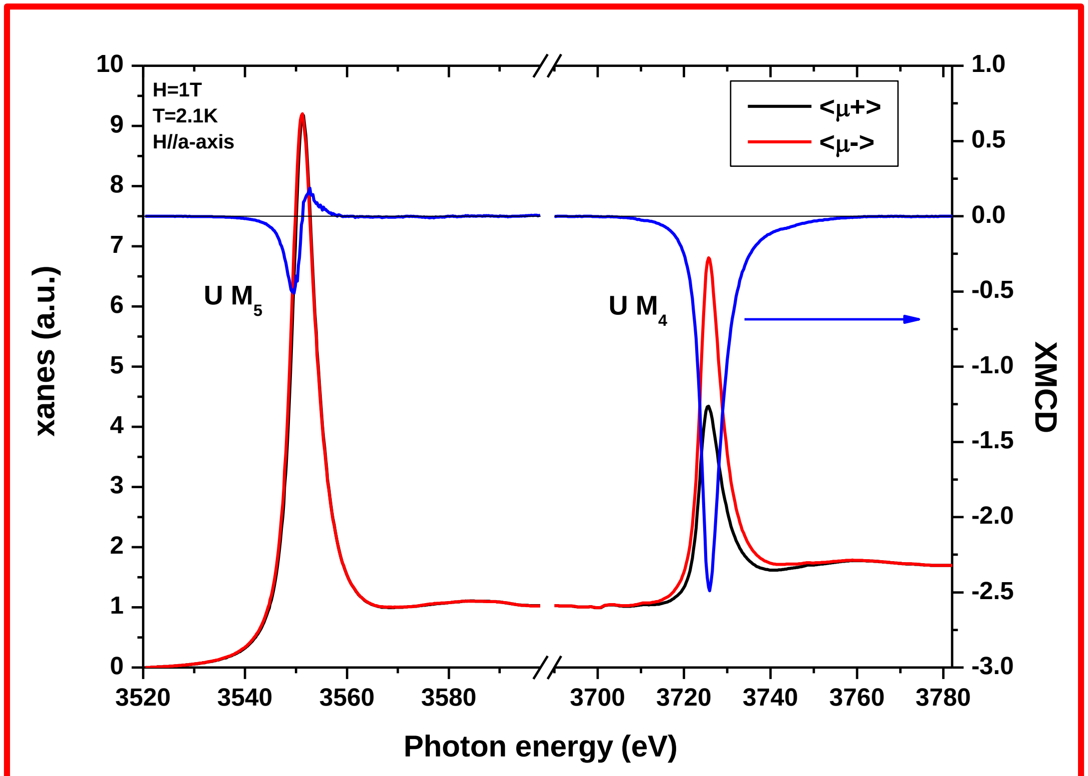

CONCLUSION / PERSPECTIVE

- **XANES spectra can be recorded under high pressure in the tender X-ray range down to 2.1 keV that covers the K-edge of P, S, Cl, K…, L-edges of the 4d transition metals and the M-edges of actinides.**

- **unique possibility to measure XMCD under multiple extreme conditions of high pressure up to 60 GPa, at temperature down to 2.7K and under magnetic field up to 8T.**

Perspective:

Reach higher pressure in the DAC dedicated for tender X-rays => 20 GPa
=> will be possible with EBS due to smaller beam: nearly round focal spot ~3μm

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UGe_2

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Thank you for your attention
Welcome to ID12 in 2020