Magnetism at high pressures

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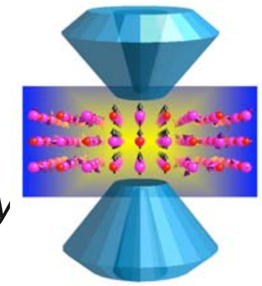
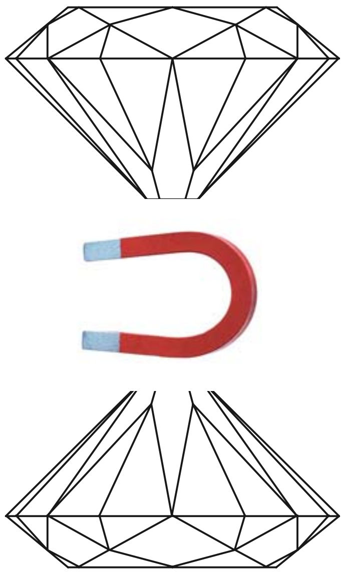


Outline

- Magnetism and Pressure
- SR, x-ray magnetic circular dichroism (XMCD)
- Challenges, experimental setup, detection method
- Examples of recent work
- Outlook

Energy Dispersive X-ray Absorption Spectroscopy: Scientific Opportunities and Technical Callenges, Grenoble (France) 2-5 February 2009.

Magnetism and Pressure



Pauli's exclusion principle

Heisenberg's Exchange- *J*

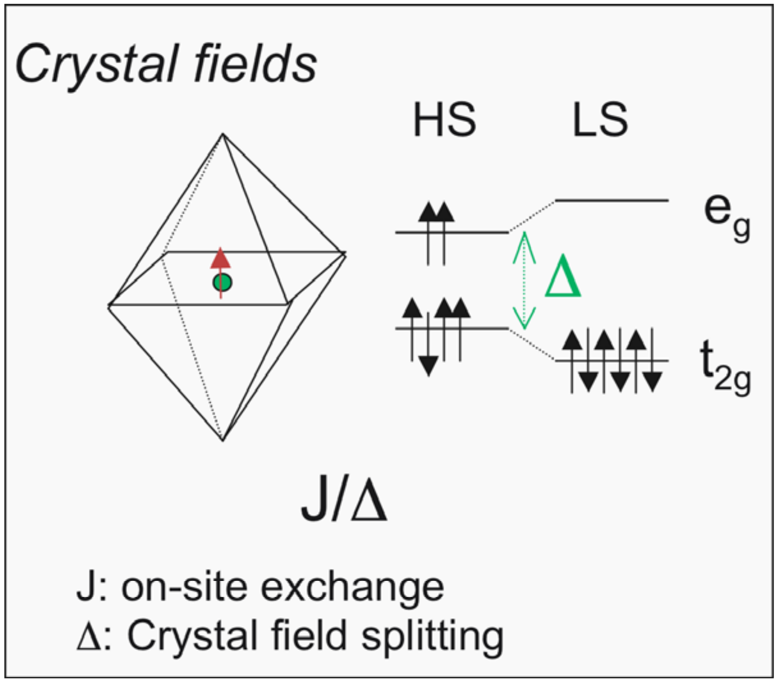
$$\psi = \psi_r(r_1, r_2) \otimes \psi_s(s_1, s_2)$$

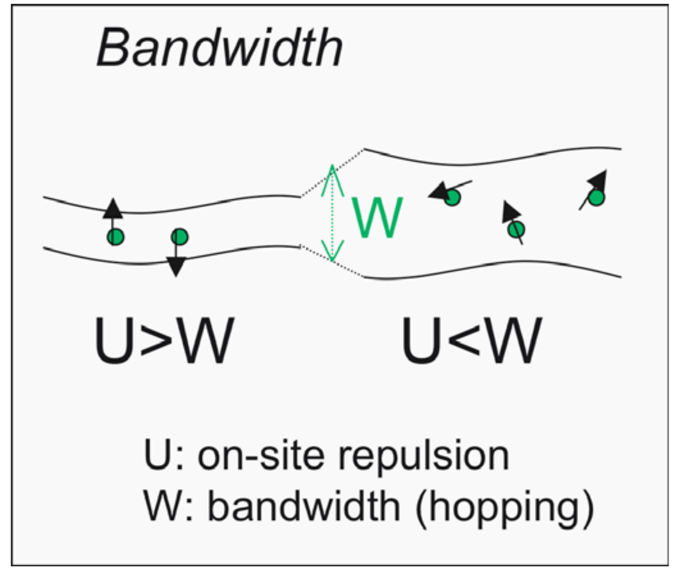
$$\psi_s(s_1, s_2) = \frac{1}{\sqrt{2}}[\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]$$

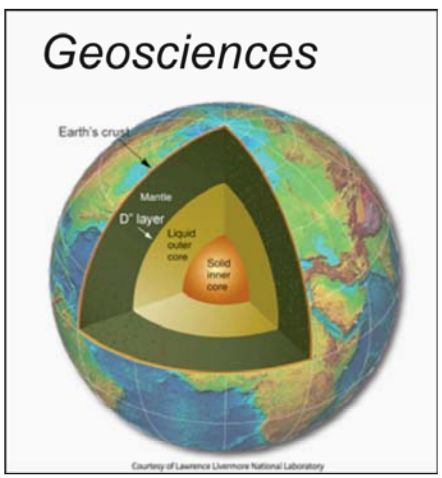
$$\psi_{t,m=1}(s_1, s_2) = \psi_\uparrow(s_1)\psi_\uparrow(s_2)$$

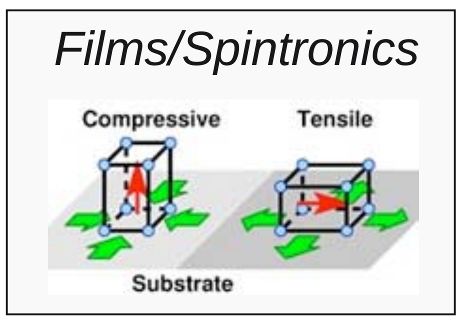
Pressure alters the overlap of electronic orbitals in a solid, modifying *electron-electron* interactions critical for magnetism.

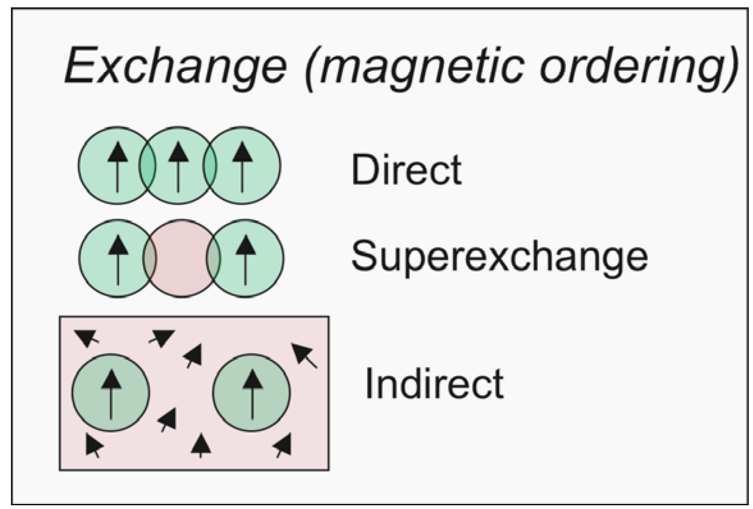
Magnetism and the High Pressure *knob*











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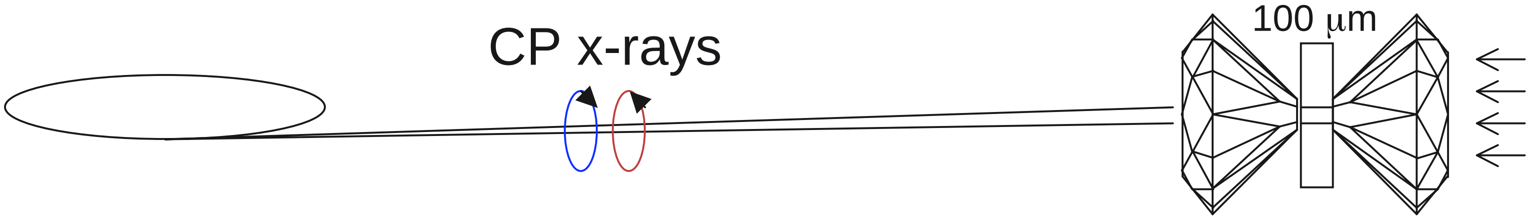
Why Synchrotron Radiation (SR)? Why XMCD?

- High-*brilliance* SR sources ideally suited for the small sample volumes needed for high-pressure research (1 Mbar ~ 1million atmospheres).
- SQUID magnetometry, Neutron diffraction, Mossbauer spectroscopy

m =120 kg
r =6 mm
P=100 atm

$$P = \frac{F}{A} = \frac{mg}{\pi r^2}$$

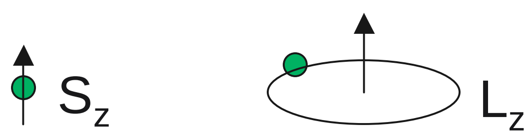
m =3,000 kg
r =15 cm
P=4 atm

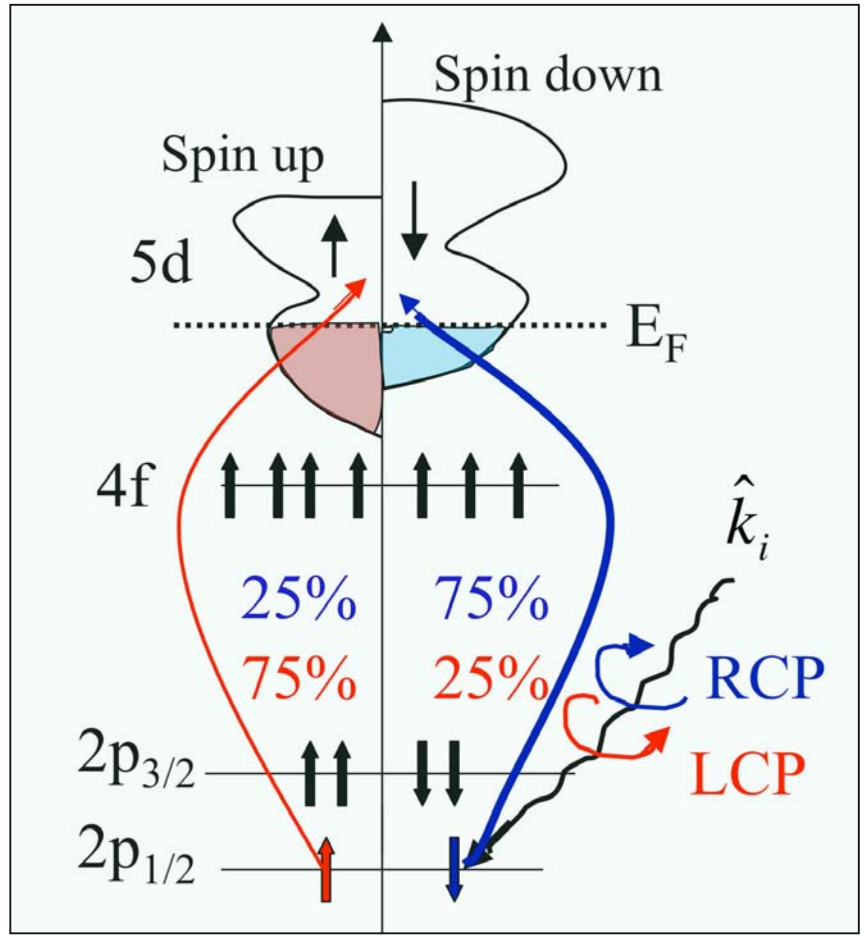


X-ray magnetic circular dichroism (XMCD)

Fano 1969; Schutz 1987

- Element- and orbital-selective probe.
- Sum rules may allow separation of S_z, L_z
- "Vectorial" probe (unlike XES, Mossbauer) requires net magnetization $\langle [\hat{k}_i \cdot \hat{m}] \rangle \neq 0$
  - ✓ Ferro/Ferri-magnets ($T<T_c$)
  - ✓ Paramagnets at high magnetic field
  - ✓ Canted antiferromagnets
  - ✓ Geoscience: Upper mantle conditions (20 GPa) since ordering Tc < 2000K





$$\mu_m = \mu^L - \mu^R \propto \rho(\uparrow) - \rho(\downarrow) \propto M[\hat{k}_i \cdot \hat{m}]$$

$$\mu_c = (\mu^L + \mu^R)/2$$

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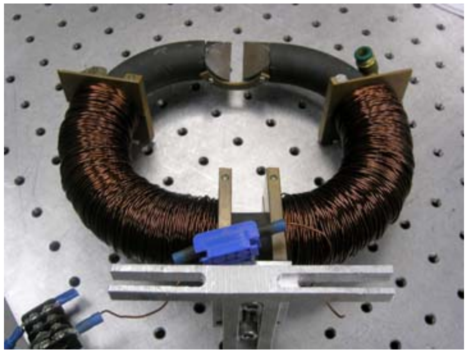
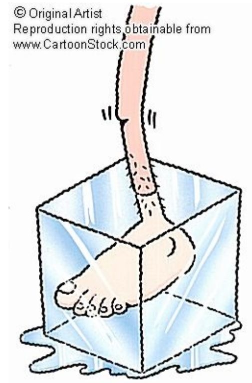
Some of the challenges for HP-XMCD experiments



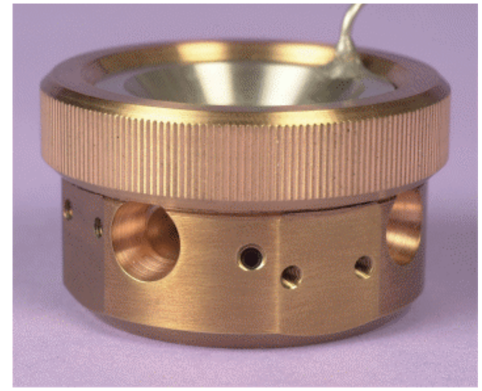
Magnetic field

As high as possible



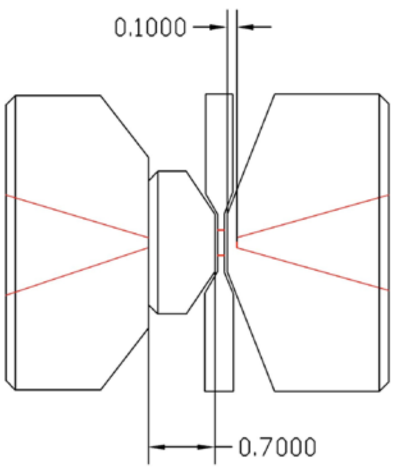
Low temperature

As low as possible



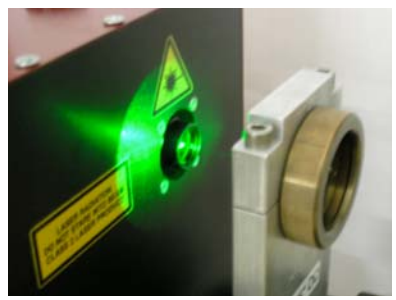
CuBe pressure cell

Non-magnetic, thermal conductor



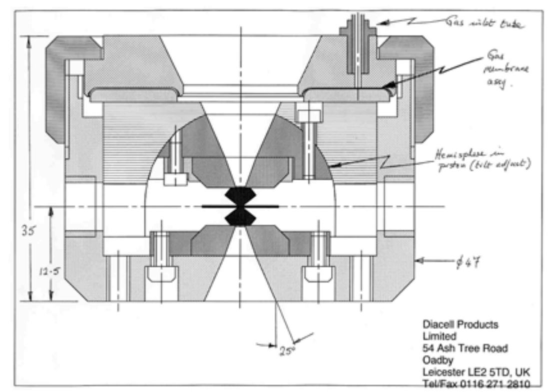
Perforated diamond anvils

As thin as possible



In-situ pressure calibration

Ruby, XAFS

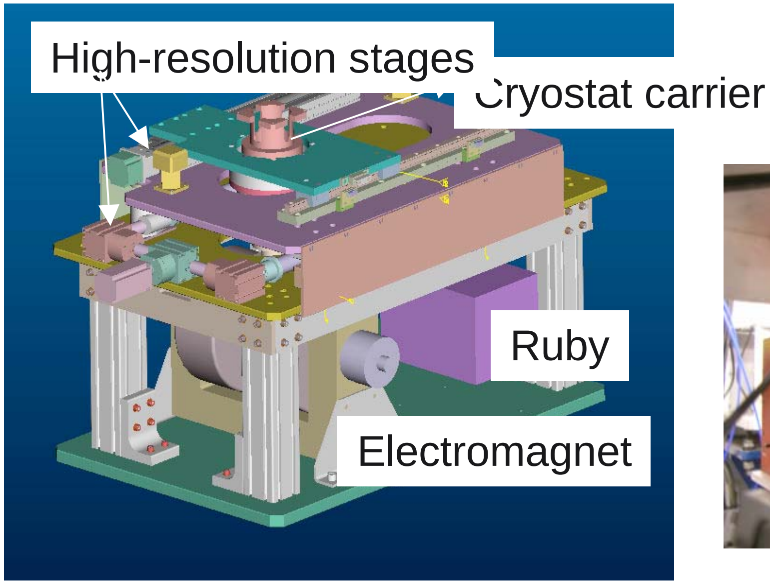


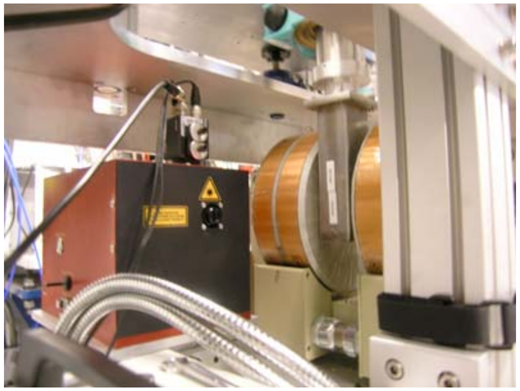
In-situ pressure change

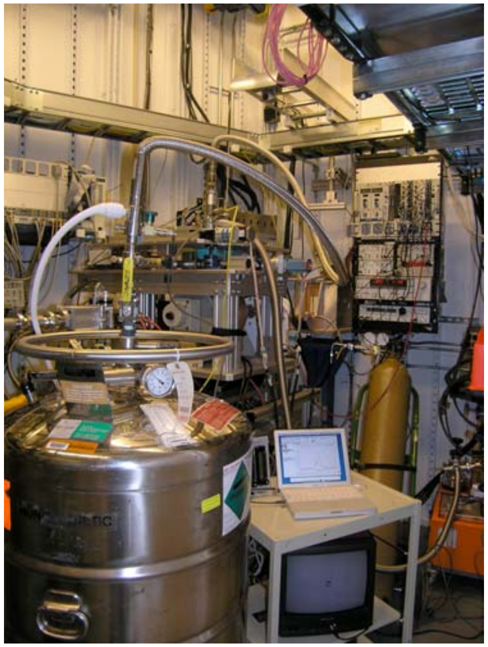
Gas Membrane cell

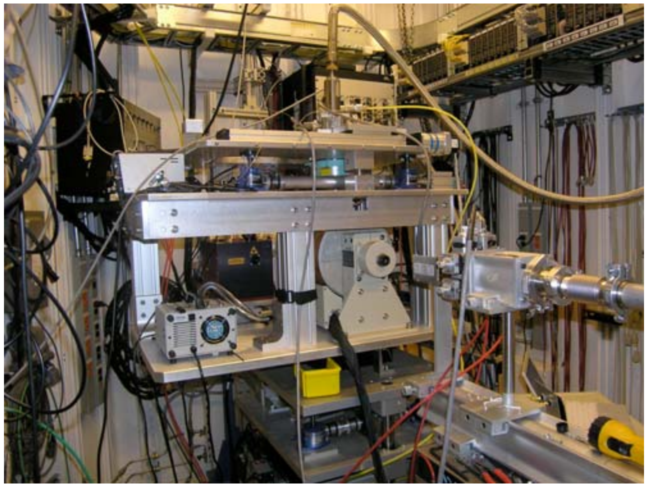
… Lock-in detection of small XMCD signals

Dedicated experimental setup at beamline 4-ID-D/XOR

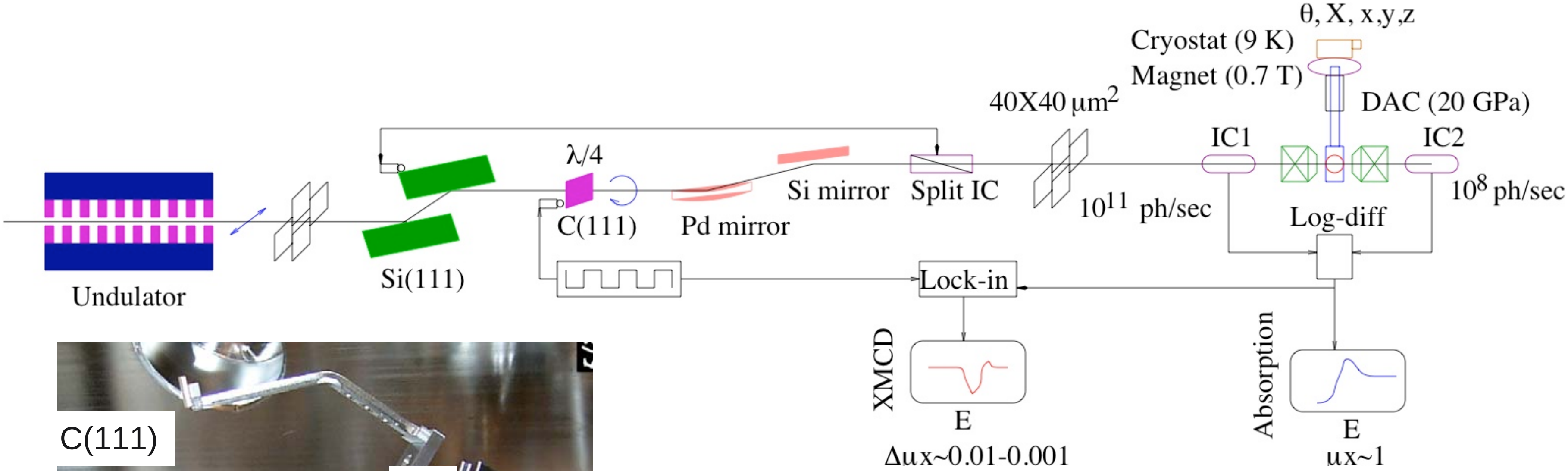


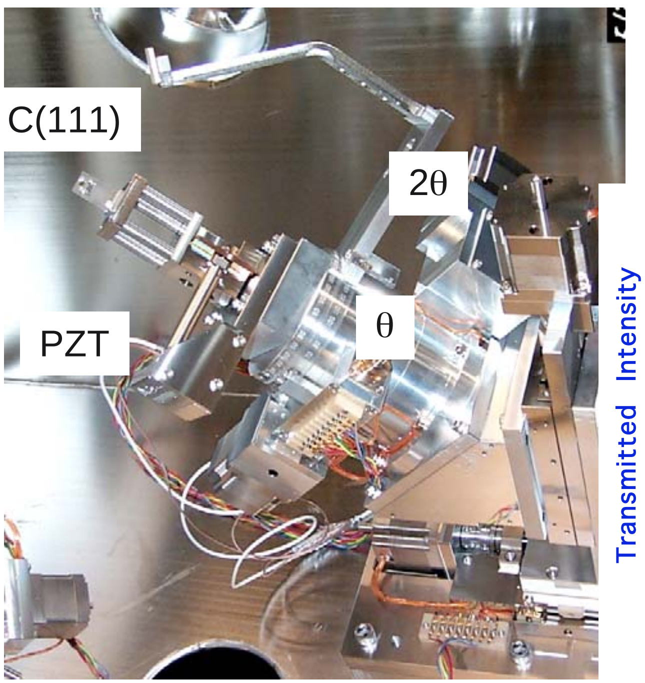


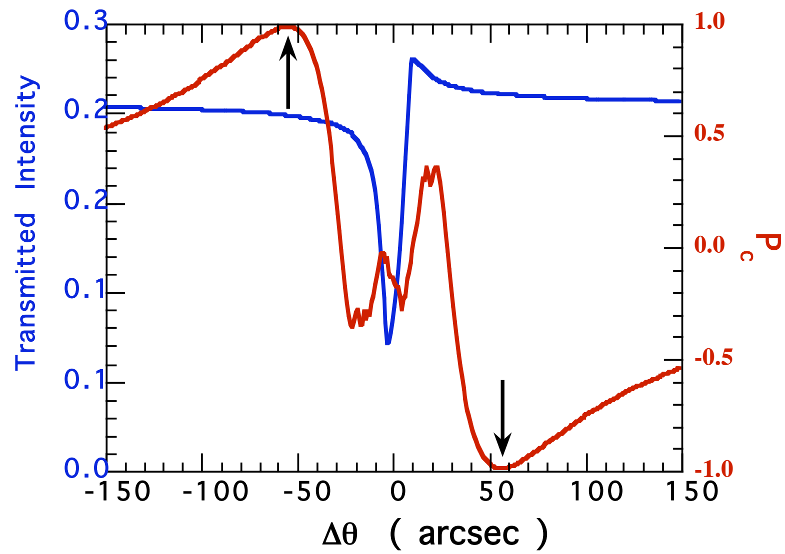




Beamline configuration, lock-in detection



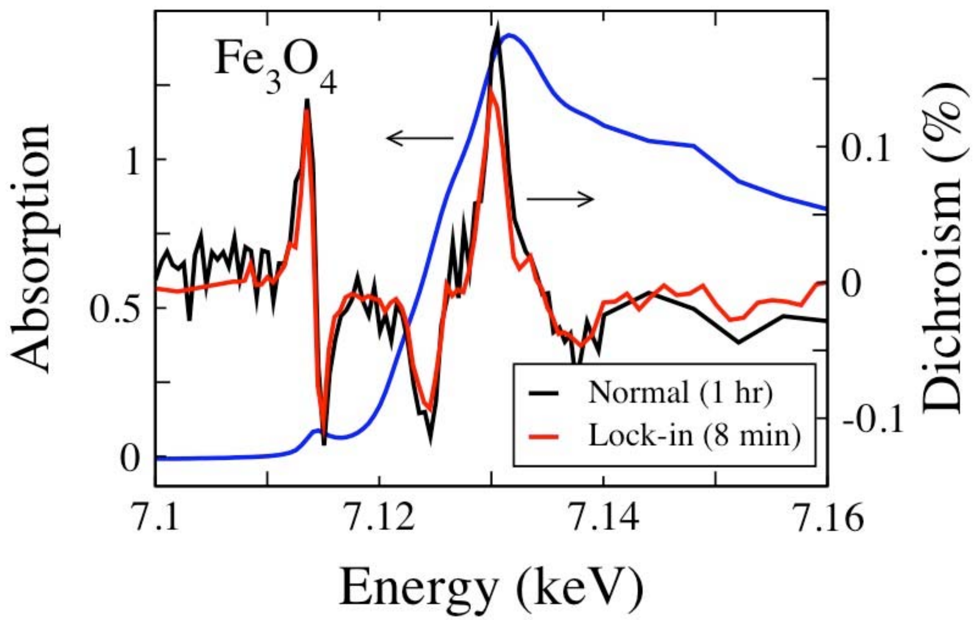




$$I_2 = I_1 e^{-\mu x}$$

$$\ln \frac{I_1}{I_2} = \ln I_1 - \ln I_2 = \mu x$$

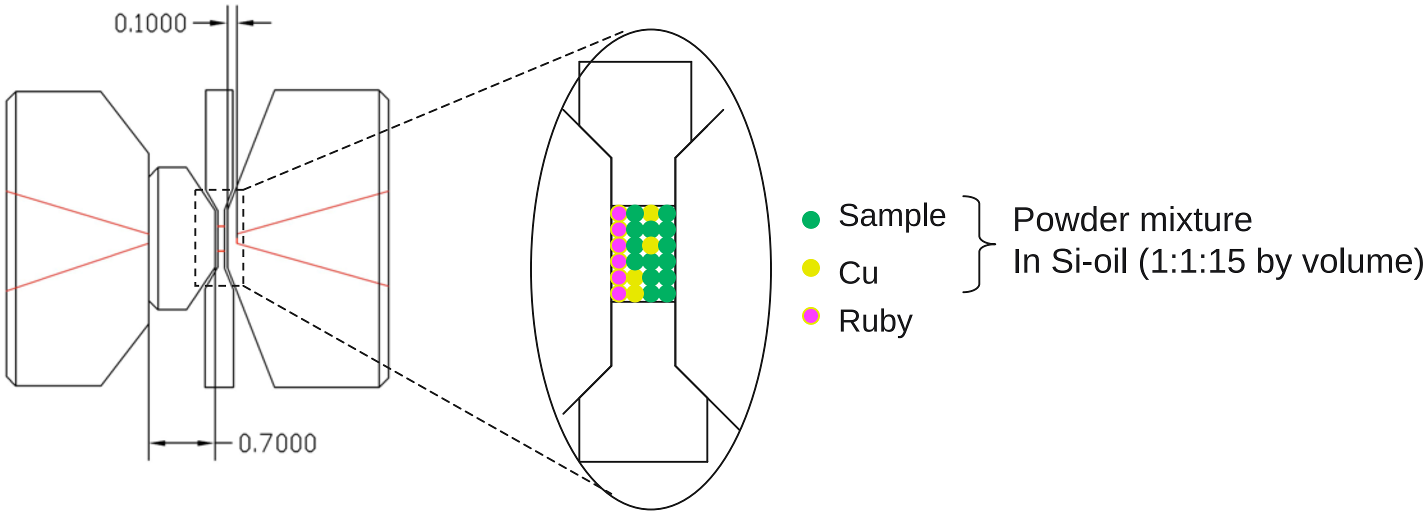
Haskel et al., RSI 78, 083904 (2007); Haskel et al., High Pressure Research 28, 185 (2008)

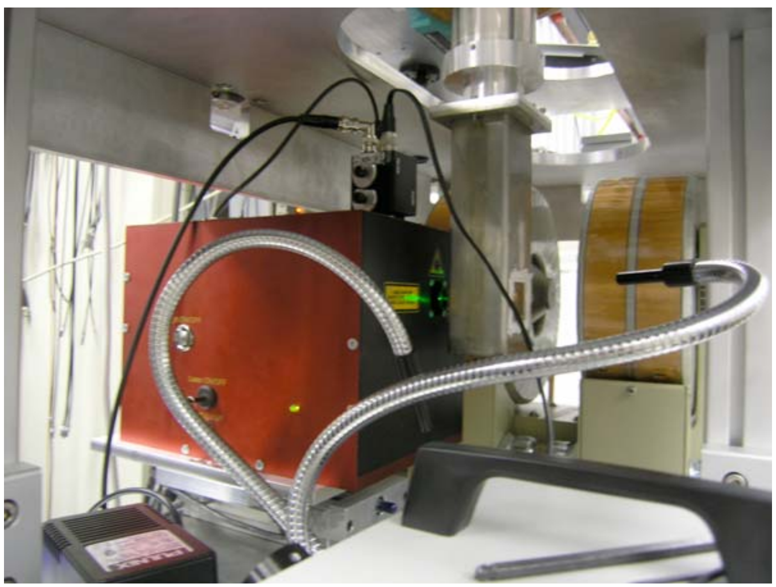


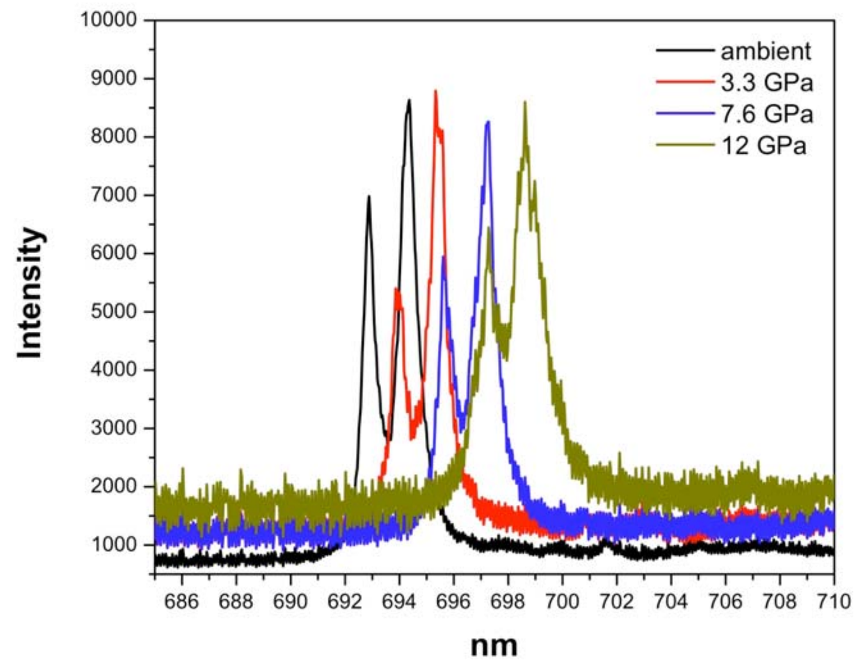
Detection Sensitivity ≥ 10ppm

- *K*-edges: 0.005 μ_B
- *L*-edges: 0.001 μ_B

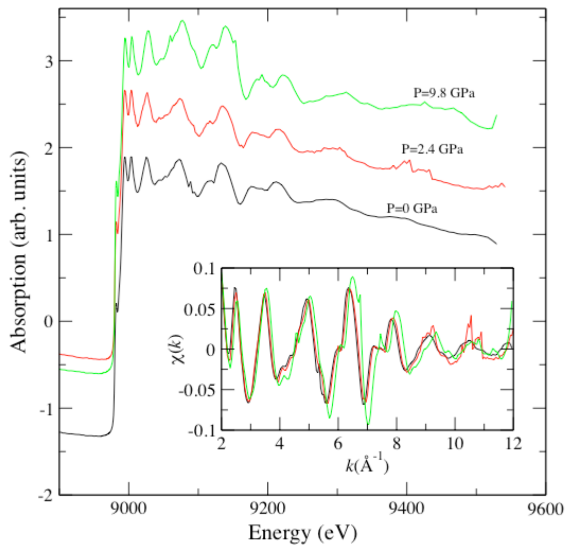
Pressure calibration

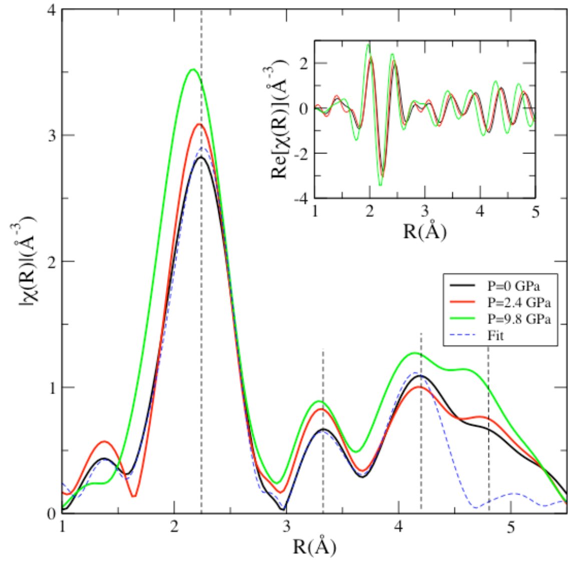


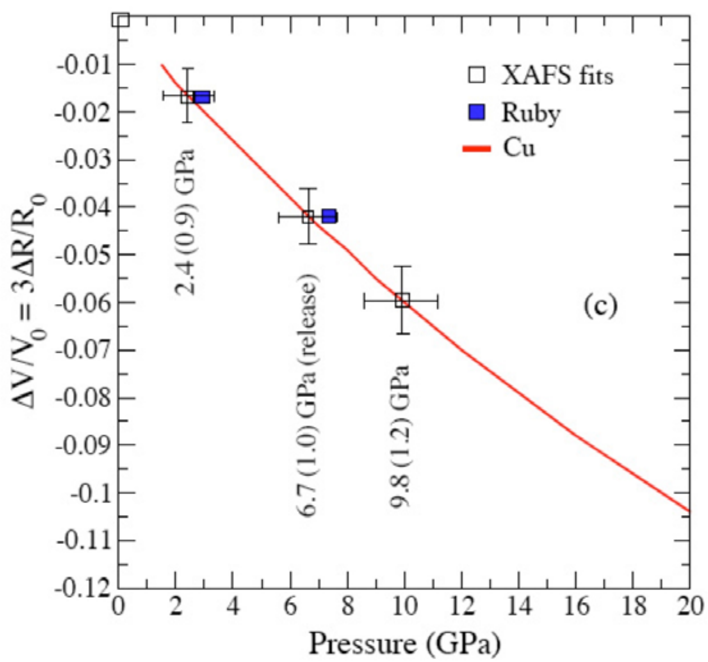




Haskel et al., RSI 78, 083904 (2007)







XAFS calibration useful
in the absence of optical access

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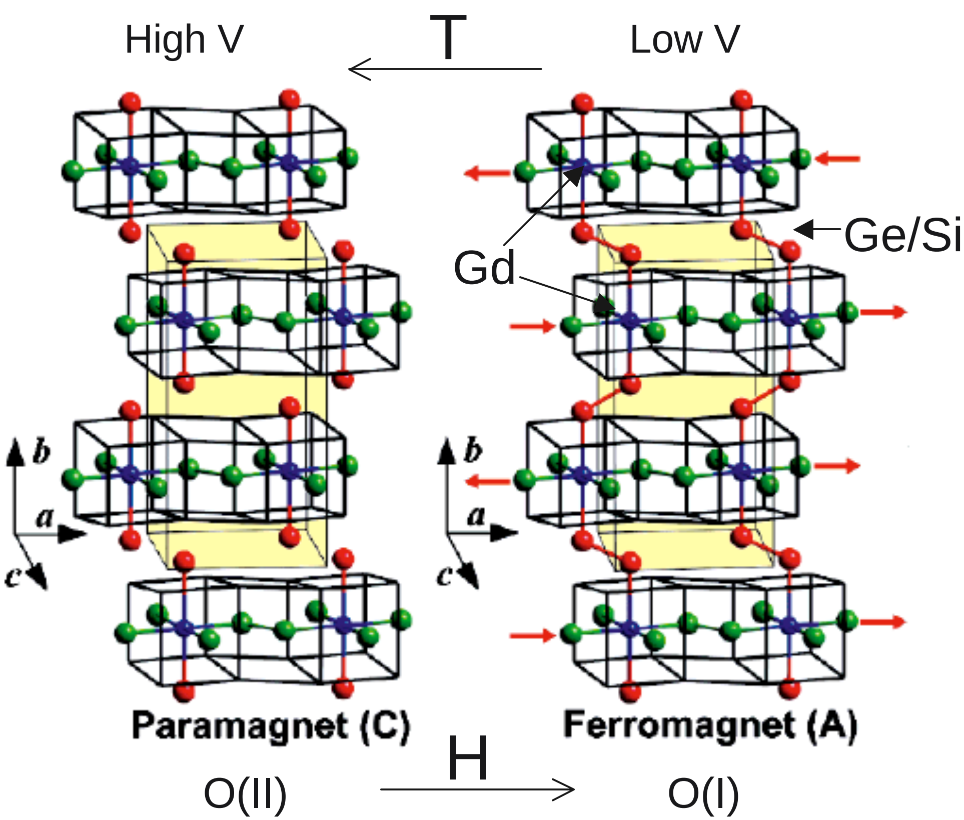
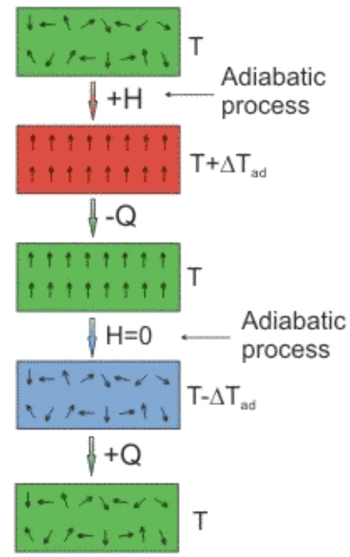
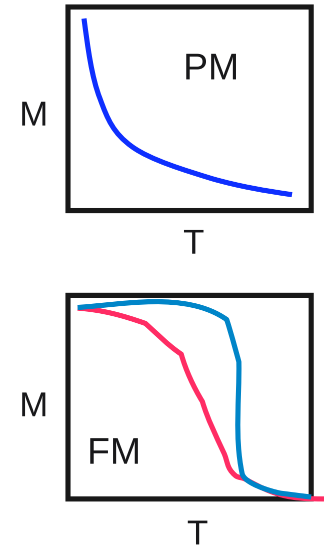
Giant Magnetocaloric materials $Gd_5(Si_xGe_{1-x})_4$





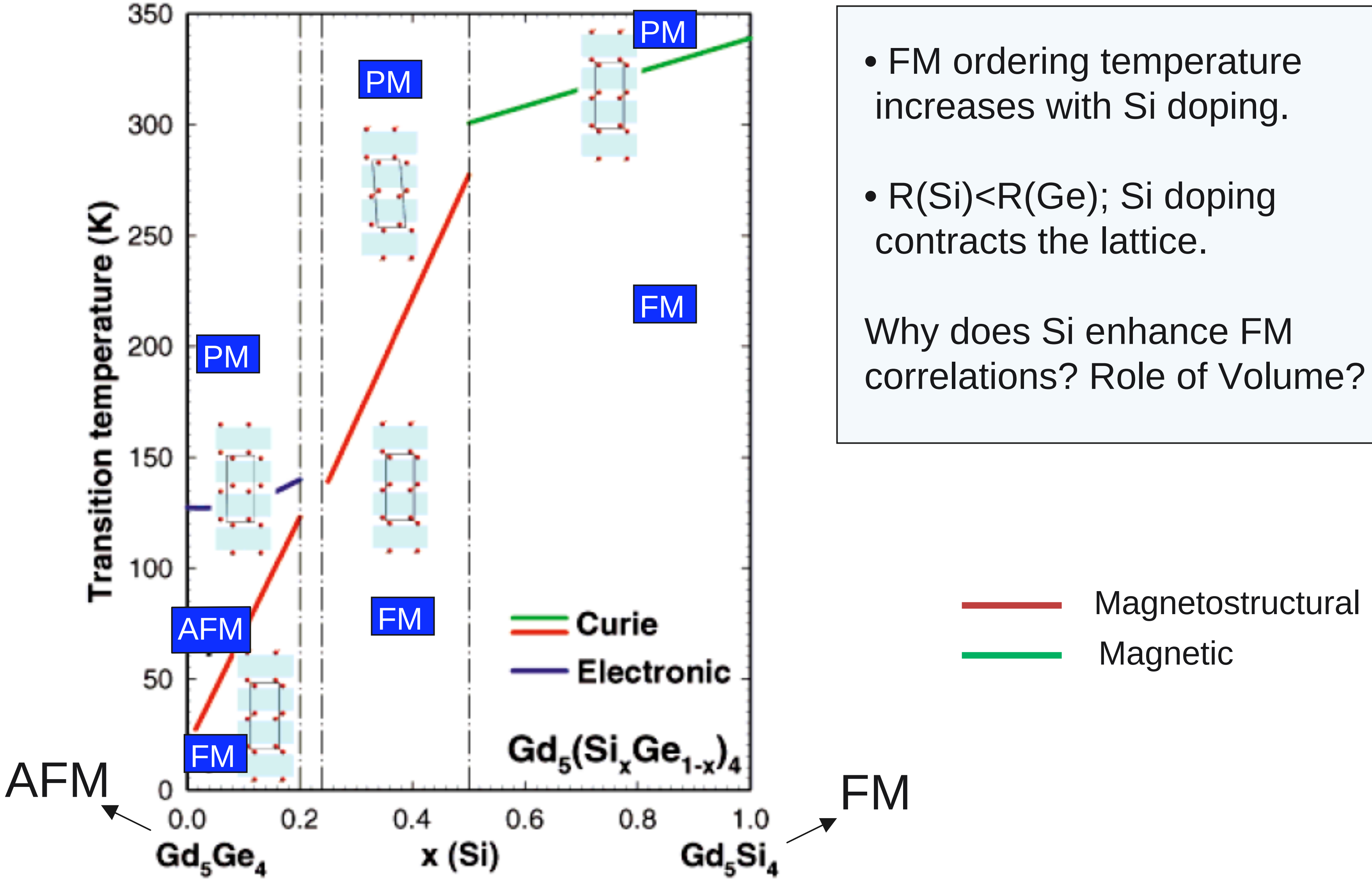


$$\Delta T_{ad}(T,\Delta B) = -\int_{B_i}^{B_f} \left(\frac{T}{C(T,B)} \times \frac{\partial M(T,B)}{\partial T} \right)_B dB$$

Pecharsky and Gschneidner
Advanced Materials 13, 683 (2001).

- First-order magneto-structural transition (H,T) yields large MCE.
- Breaking of Ge/Si bonds reduces Gd 5d overlap (4f-4f indirect FM exchange) across slabs.
- Cooling ΔT_{ad}~ 16 K at 280 K shown in H≤ 5T for $Gd_5Si_2Ge_2$.

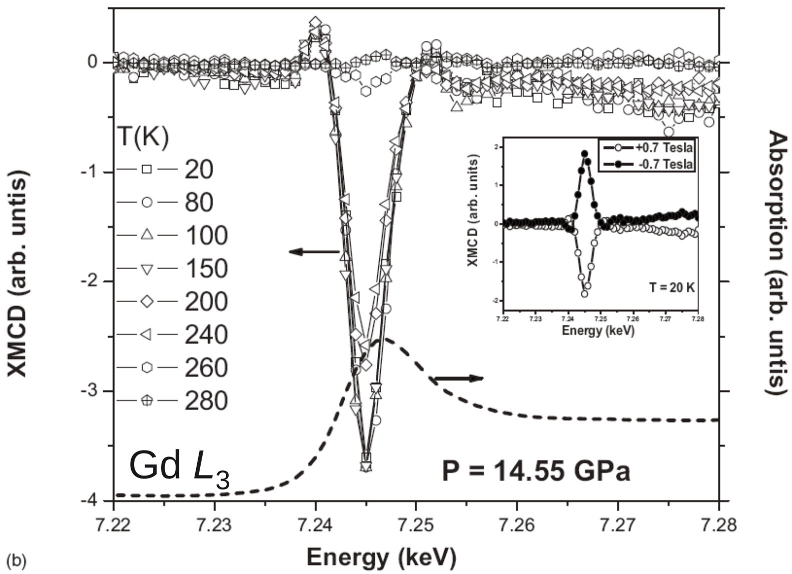
Phase diagram of $Gd_5(Si_xGe_{1-x})_4$: Si doping stabilizes FM phase



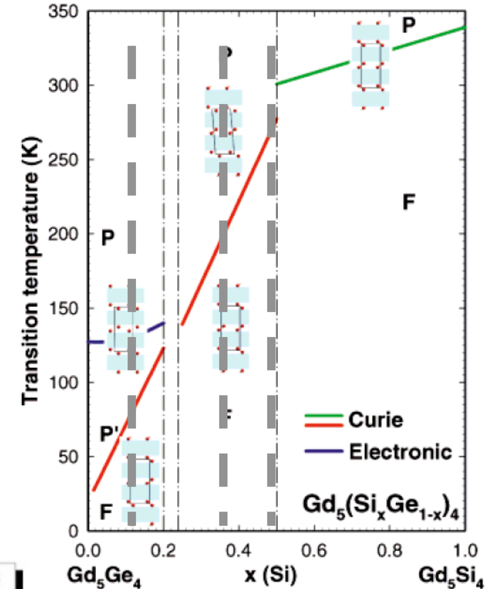
- FM ordering temperature increases with Si doping.
- R(Si)<R(Ge); Si doping contracts the lattice.

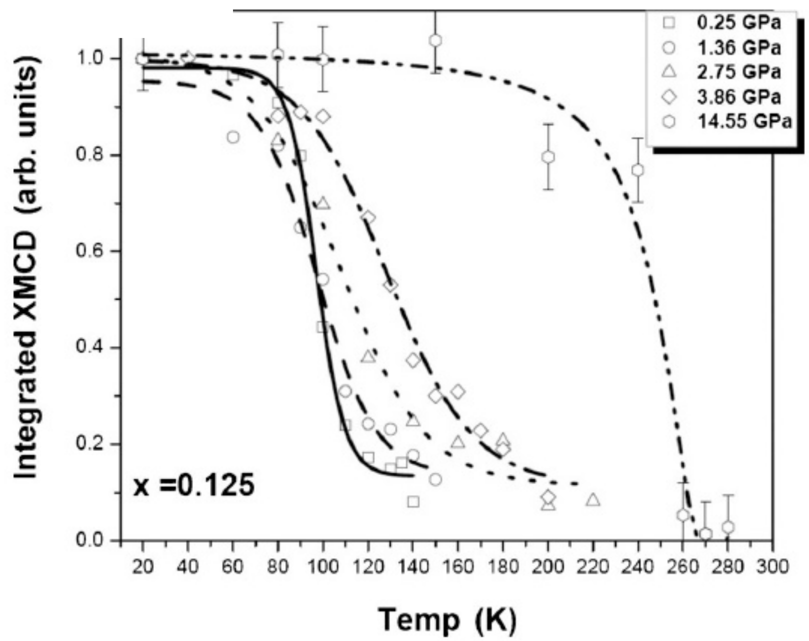
Why does Si enhance FM correlations? Role of Volume?

Volume effect on strength of FM interactions

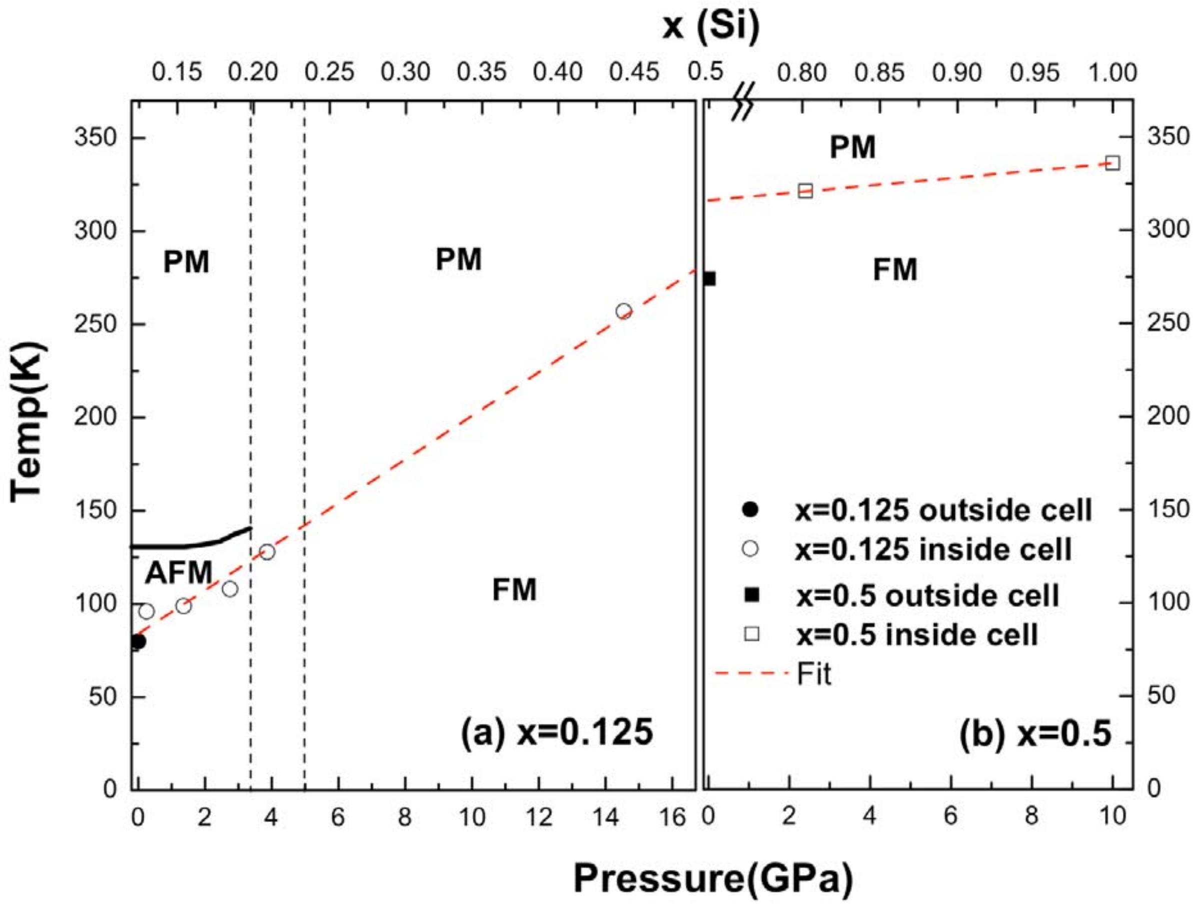


x=0.125, 0.375, 0.5

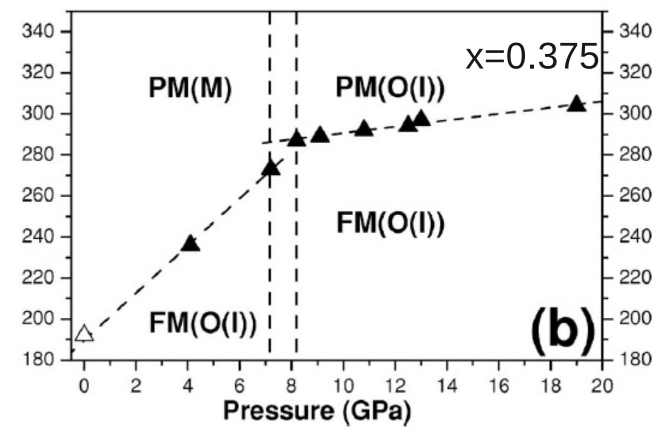




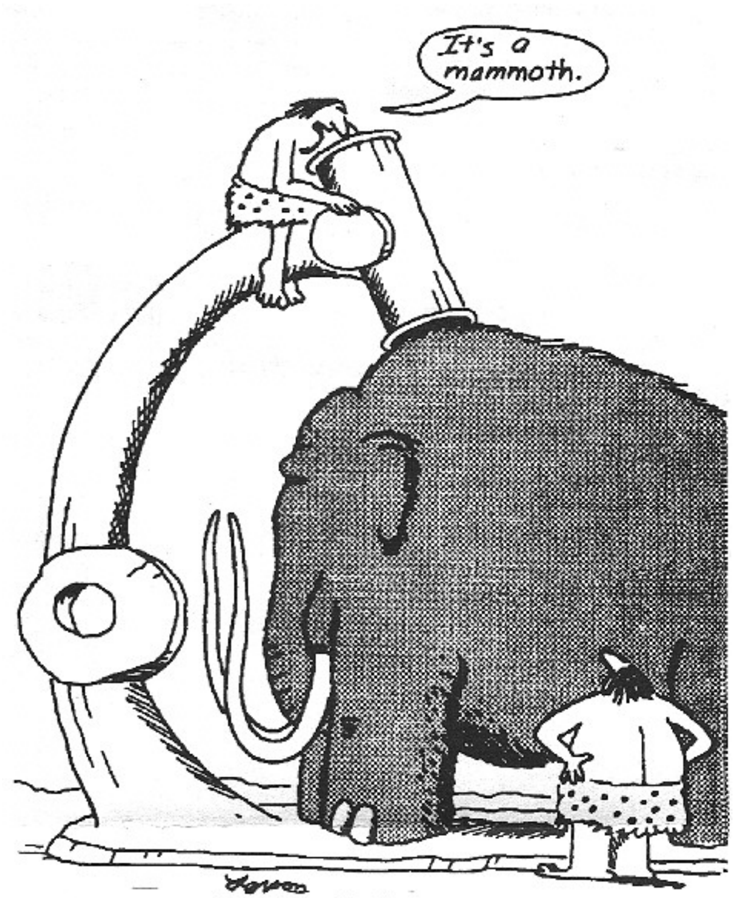
Morellon et al, JPCM (2004); Tseng, DH, et al., PRB 76, 014411 (2007)



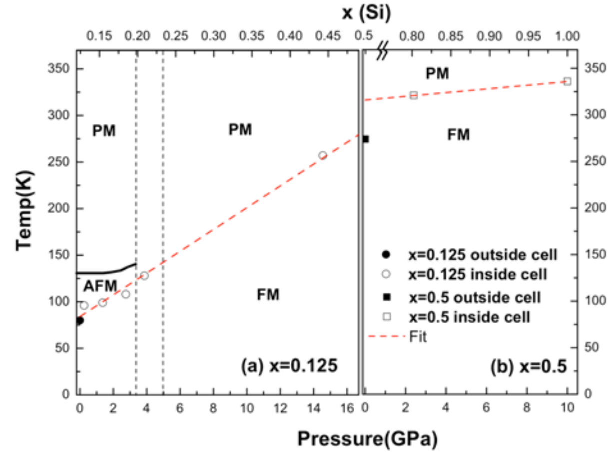
Δ(Si%)/ΔP=0.23(3) (Si%)/kbar

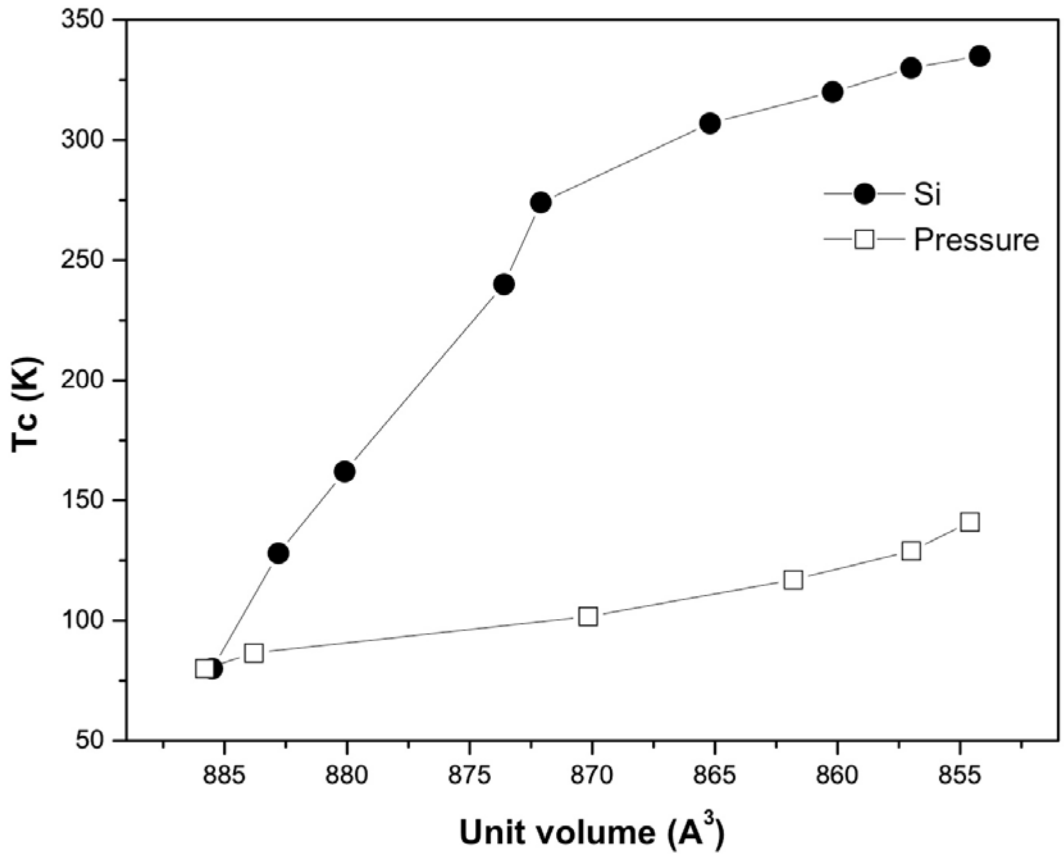


Are chemical pressure (Si) and applied pressure equivalent?



Early Microscope



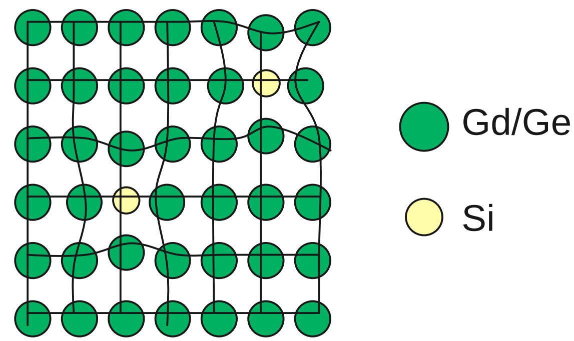


Si doping enhances Gd-Gd FM interactions (Tc) faster than a *uniform* lattice contraction.

Anisotropic lattice contraction

Need for XMCD expts under non-hydrostatic conditions !

Local lattice contraction (Si XAFS)



$$x \cdot a_{Si} + (1-x) \cdot a_{Ge} = a_{macroscopic}$$

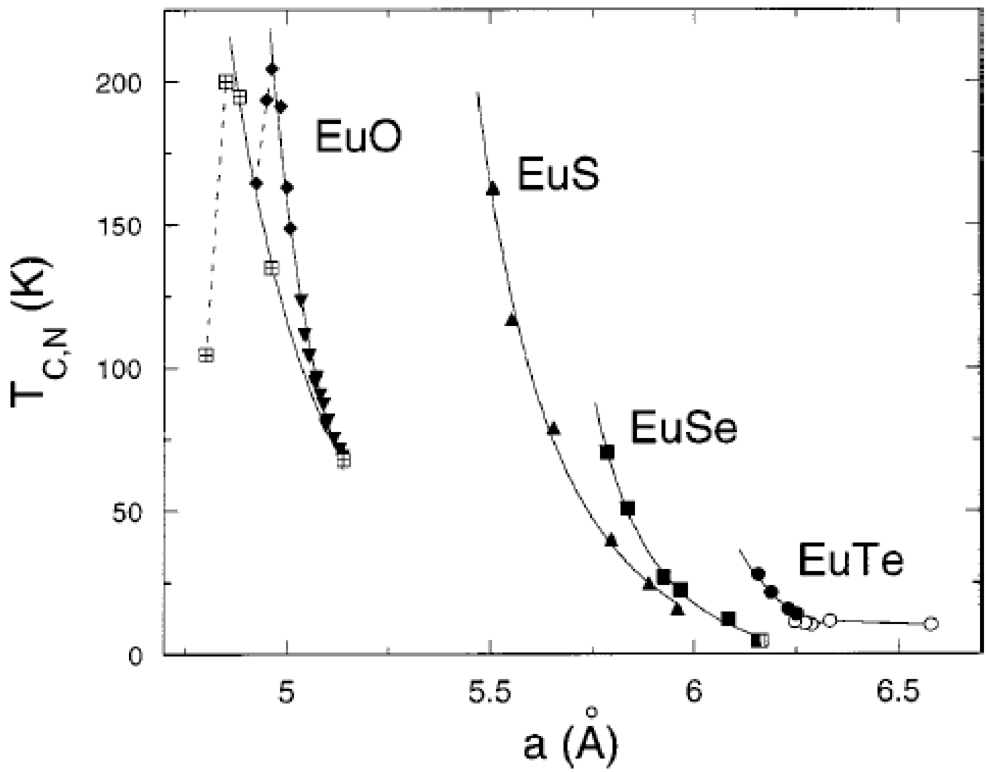
$$(\Delta V / V)_{Si} > (\Delta V / V)_{macroscopic}$$

- Ambient pressure Si XANES better simulated using lattice parameters from diffraction obtained at 10 Gpa- consistent with Si XAFS showing large (few %) local contraction around Si.

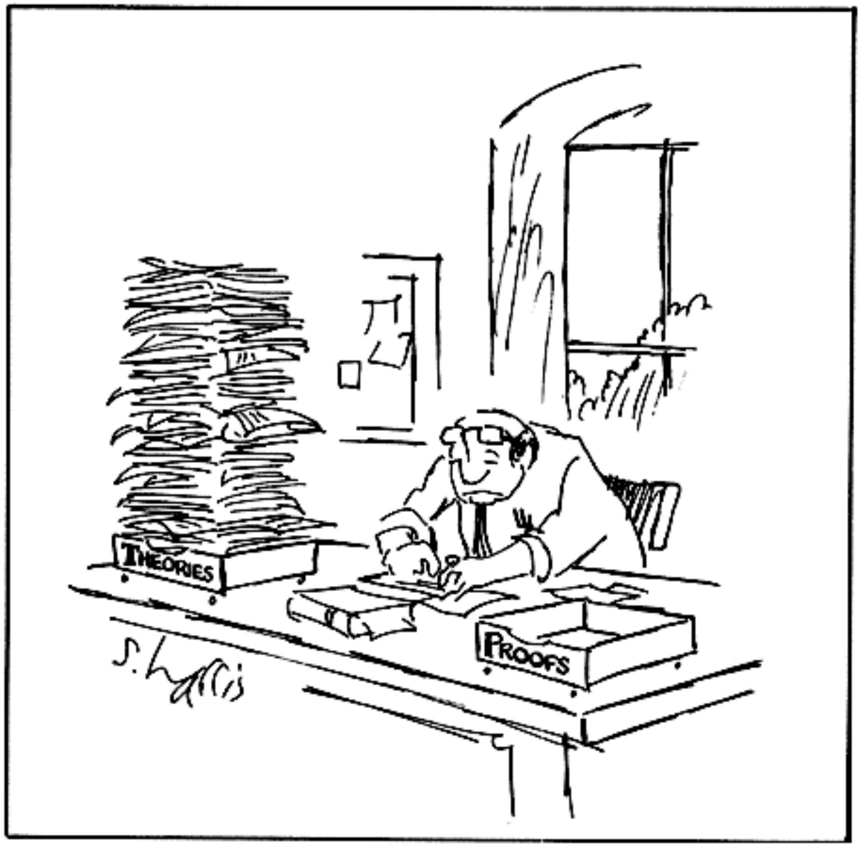
Tseng, DH, et al.,unpublished

EuX (X=O,S,Se,Te) Monochalcogenides (FM semiconductors)

- 100% spin-polarized, CMR materials (spintronics)
- Tc's are low (< 60 K), but strongly enhanced under strain/pressure
- Novel exchange (semiconductor, no conduction electrons)
- Eu^{2+} results in 4*f* states near E_F

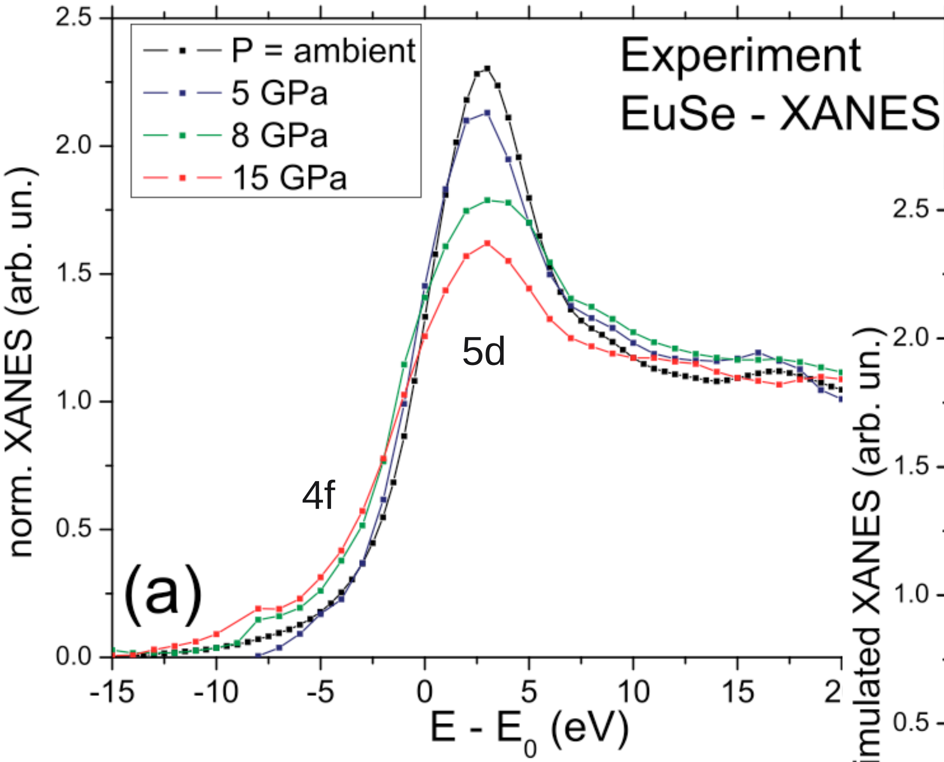


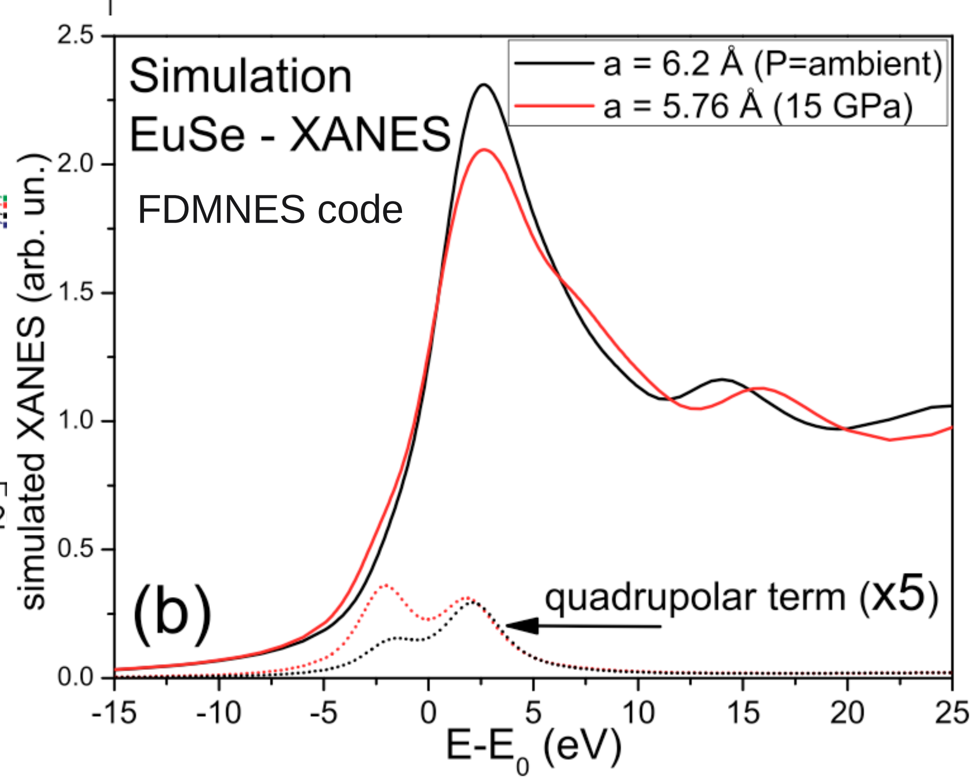
Goncharenko & Mirebeau, PRL 80, 1082 (1998)



X-ray spectroscopy of EuX (XANES, XMCD) at high pressures

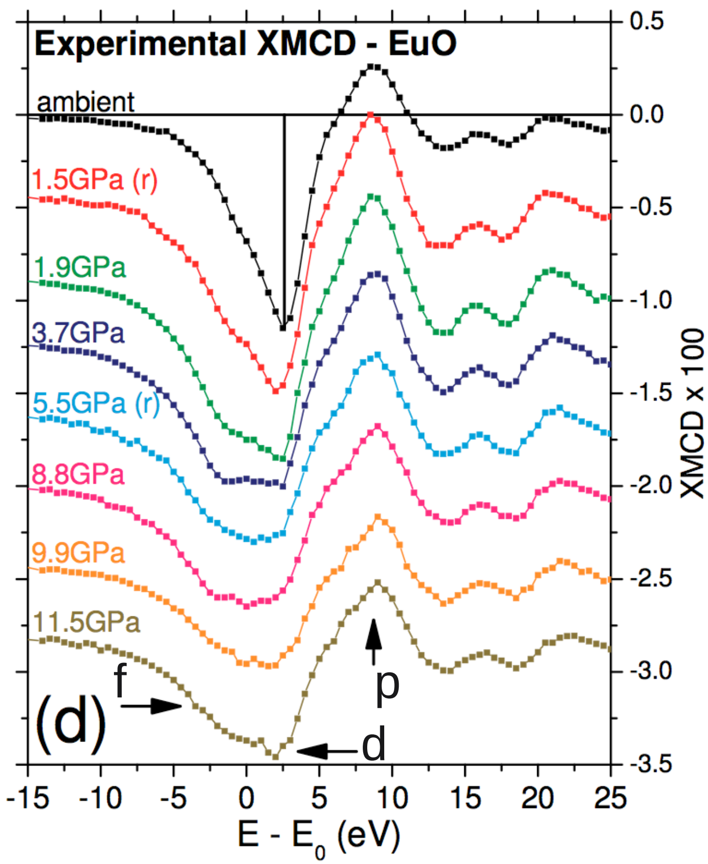
Eu L_3 edge (6.97 keV)
2p → 5d (dipolar)
2p → 4f (quadrupolar)

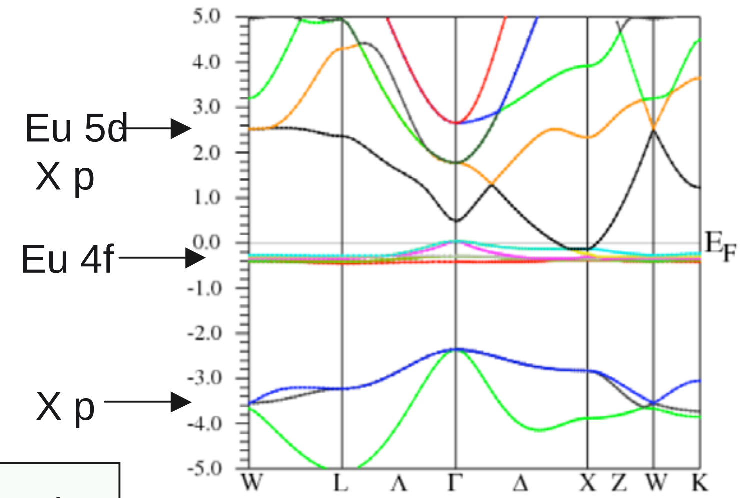




- Data for compressed lattices (pressure or X) shows d→f spectral weight transfer.

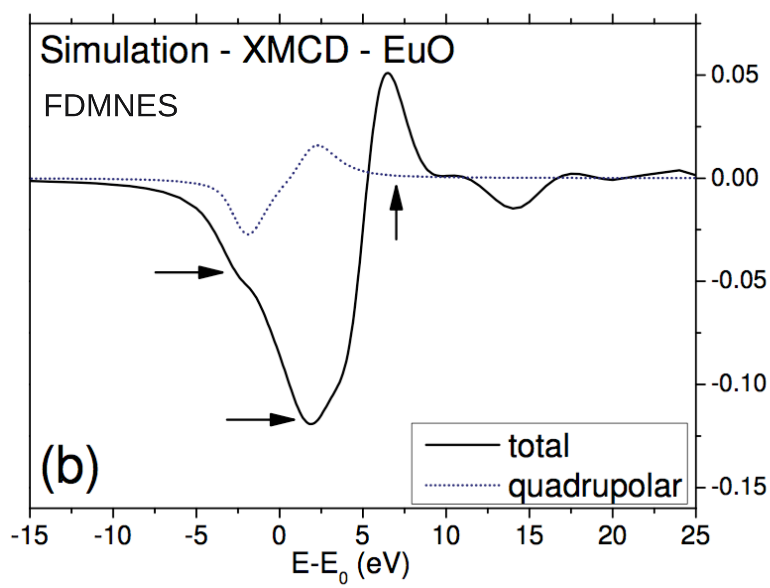
Souza-Neto, DH, et al., PRL Feb 2009 (in print)



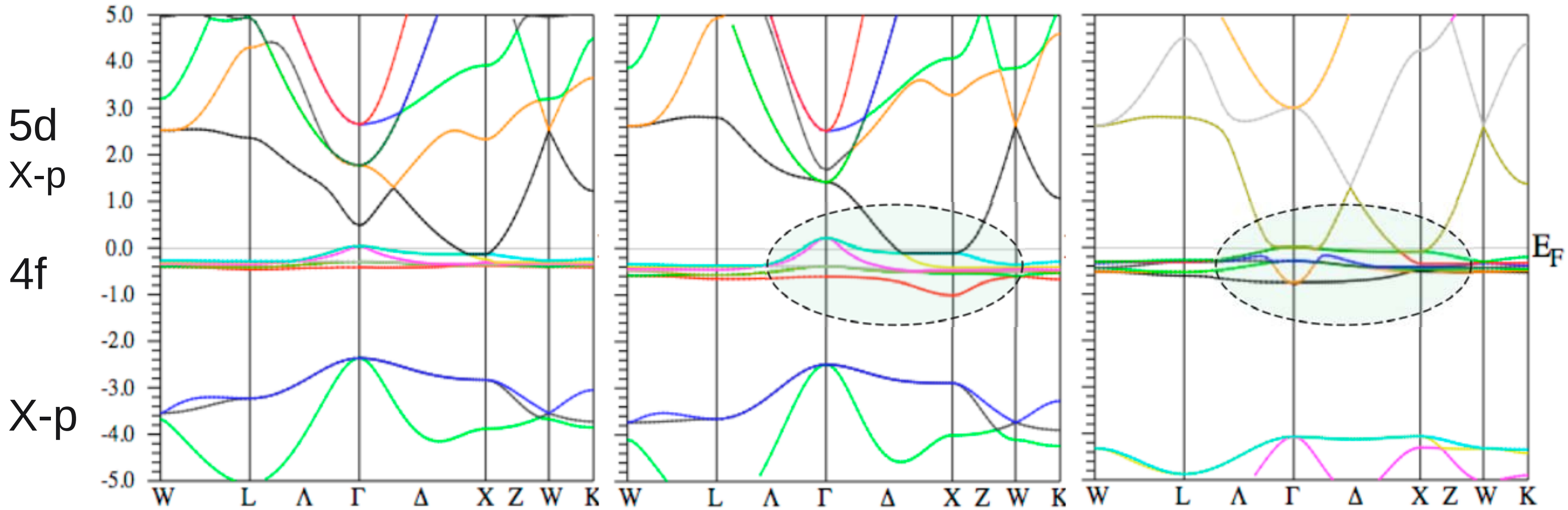


Eu L_3 edge (6.97 keV)
2p → 5d (dipolar)
2p → 4f (quadrupolar)

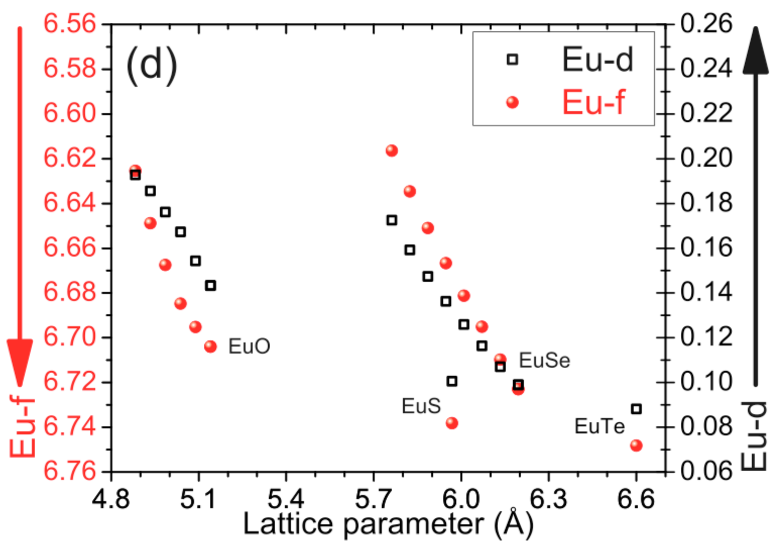
Kunes, Ku and Picket, JPSJ 74, 1408 (2005)



Density Functional Theory (LDA+ U band structure)

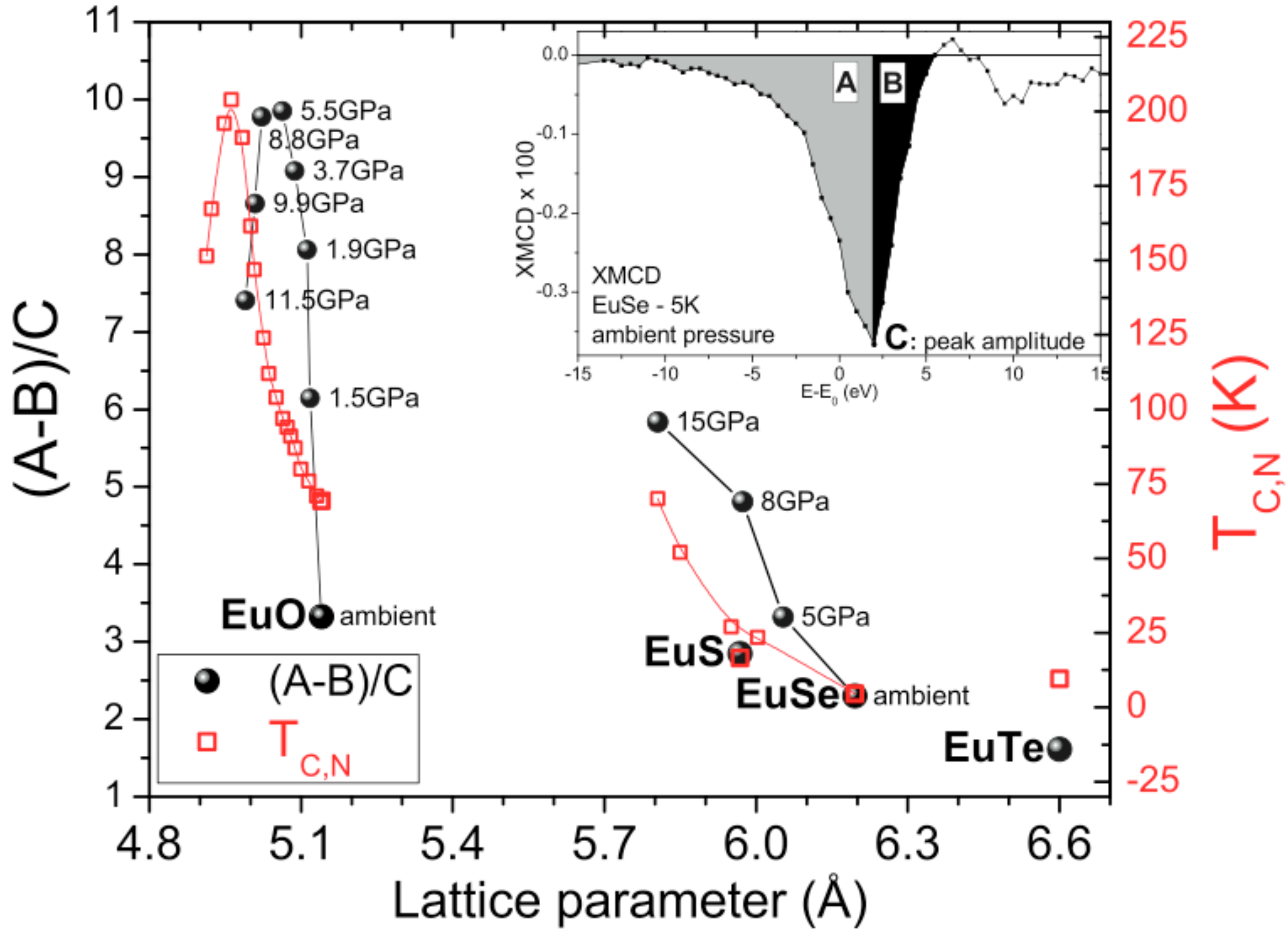


(a) EuSe (a = 6.2 Å) (b) EuSe (a = 5.76 Å, P = 15 GPa) (c) EuO (a = 5.14 Å)



- 4f states disperse, hybridize with 5d states.
- Increased CEF splitting lowers 5d t_{2g} states
- Net charge transfer f→d

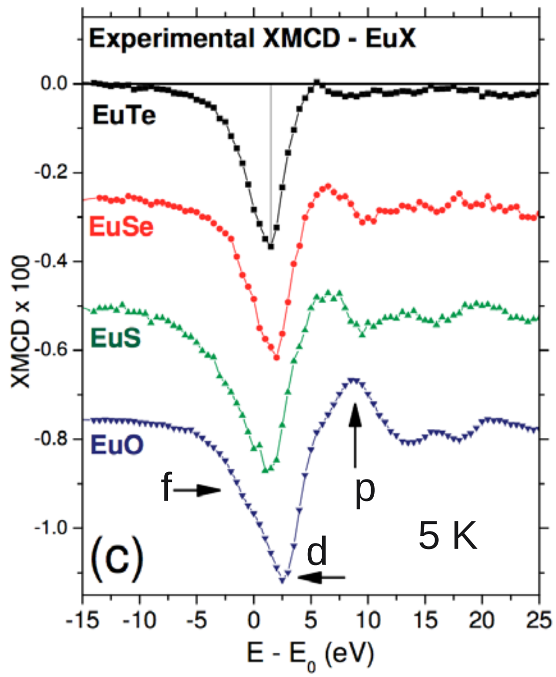
Souza-Neto, DH, et al., PRL Feb 2009 (in print)

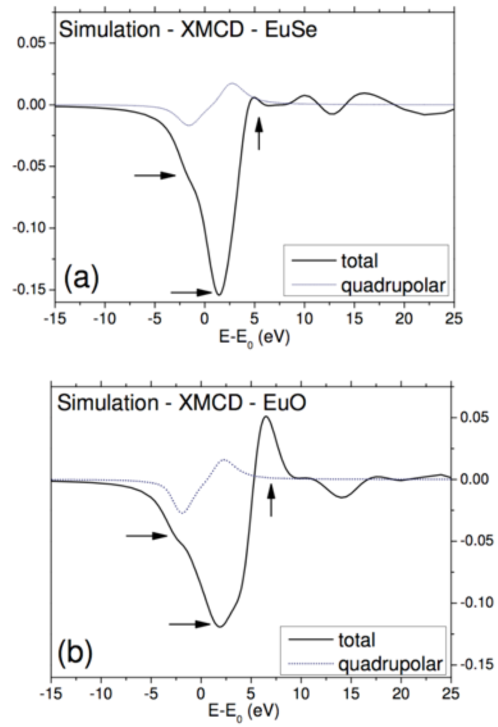


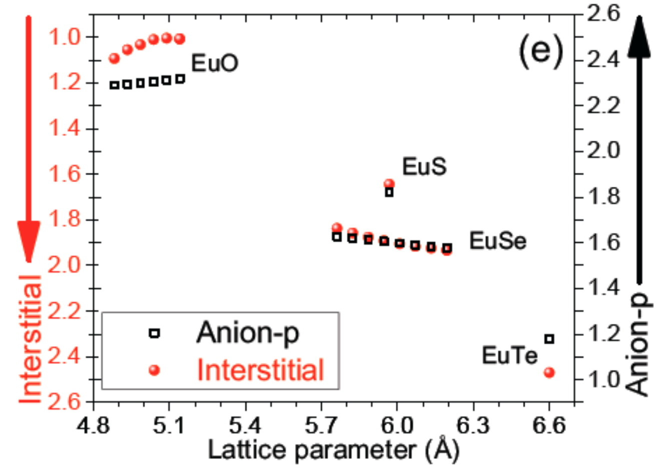
- 5d-4f (c-f) mixing dictates the strength of FM interactions, Tc

Souza-Neto, DH, et al., PRL Feb 2009 (in print)

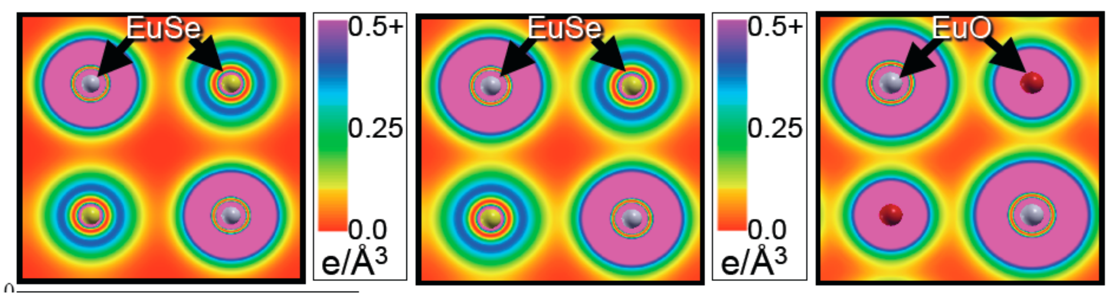
Why is P more effective than X-substitution in increasing Tc?







- Eu 5d - Anion p hybridization, ionicity, increase for Te →O: detrimental to FM interactions.



EuSe (Ambient) EuSe (15 Gpa) EuO (ambient)

Souza-Neto, DH, et al., PRL in print (2009)

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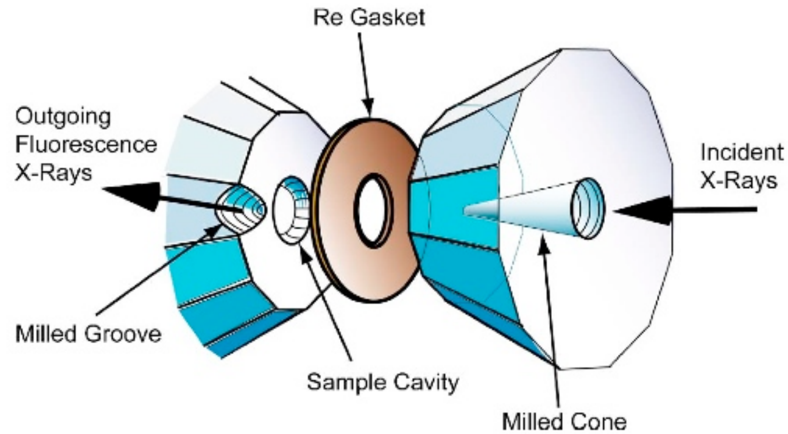
Outlook

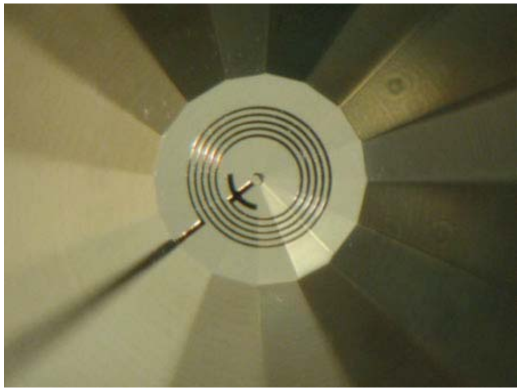
- Anisotropic materials, non-hydrostatic conditions (magneto-caloric, multiferroic,…):
  - →Single crystals
  - →Fluorescence geometry
  - →"Groovy" anvils, gaskets



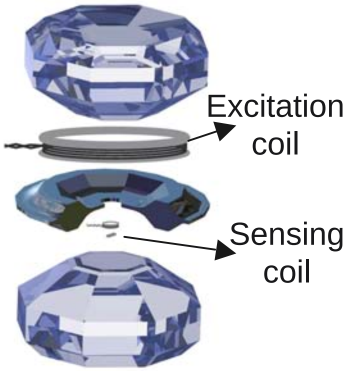
Bassett et al.

- Needs to probe AFM ordering at high P:
  - Neutrons, XRMS, XMS
  - XMLD?
  - AC susceptibility, designer anvils

- High Pressures (~1 Mbar), High Fields
  - Better focusing (10 μm)
  - 2D beam feedback (few μm)
  - Large bore solenoid (10 T)
  - Pulsed fields

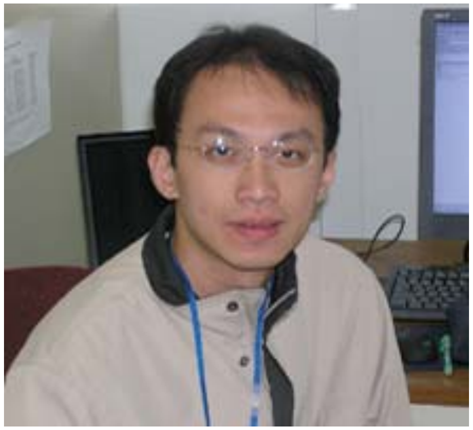


Vohra (Alabama)



Cambridge

Collaborators/Acknowledgments



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