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Magnetic Spectroscopy of Functional Materials

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Outline

- Magnetic contrast with CP x-rays
- The needs and opportunities
- Best permanent magnets [PRL 95, 217207 (2005)]
- Giant magnetocaloric materials [PRL 98, 247205 (2007)]

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U.S. Department of Energy
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Office of Science U.S. DEPARTMENT OF ENERGY
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Magnetic Spectroscopy of Functional Materials

- → Magnetic contrast with CP x-rays
- The needs, the tools
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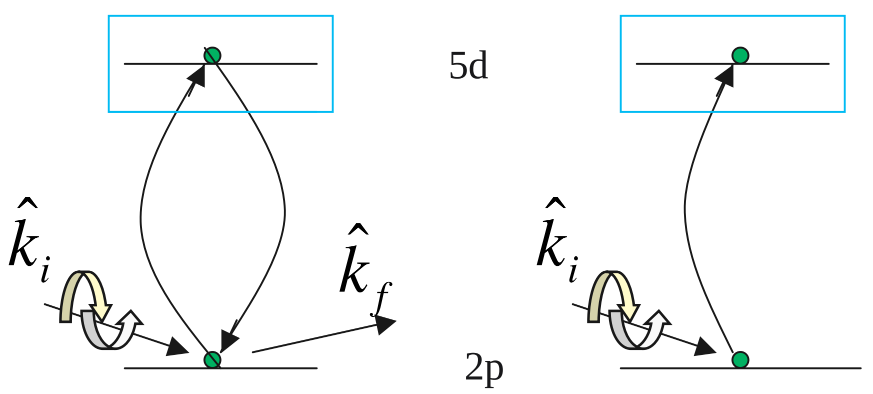
Magnetic contrast with CP x-rays

Fano 1969; Schutz 1987

- Element- and orbital specific (resonance)
- Separation of S_z, L_z (sum rules)
- Resonant scattering adds Q dependence

Scattering | Absorption

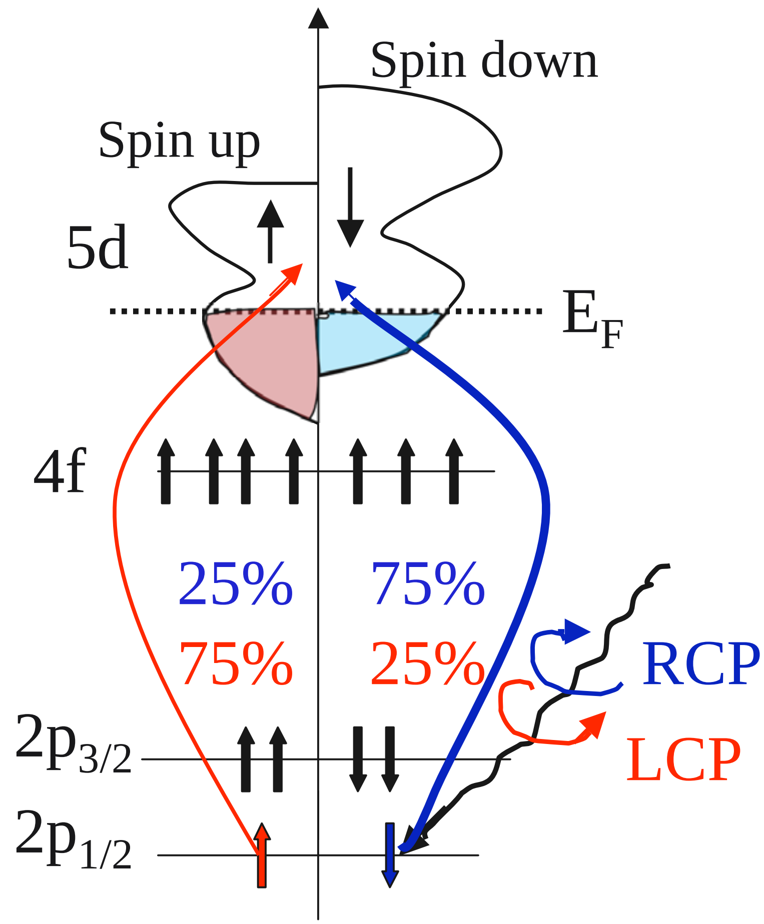


$$I_m = I^L - I^R$$

$$I_m \propto f_c^* f_m[(\hat{k}_i \cdot \hat{m}) + (\hat{k}_f \cdot \hat{m})\cos 2\Theta]$$

$$\mu_m = \mu^L - \mu^R$$

$$\mu_m \propto \mathrm{Im}(f_m)[\hat{k}_i \cdot \hat{m}]$$



Magnetic contrast with CP x-rays

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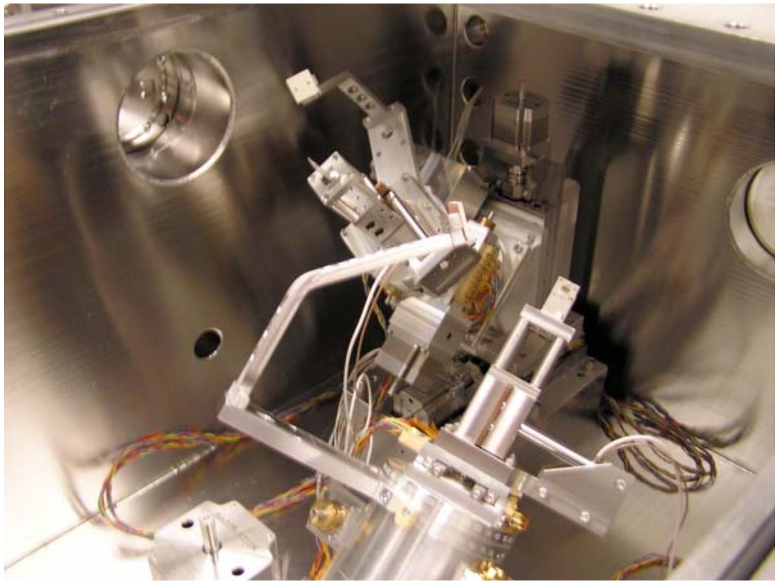

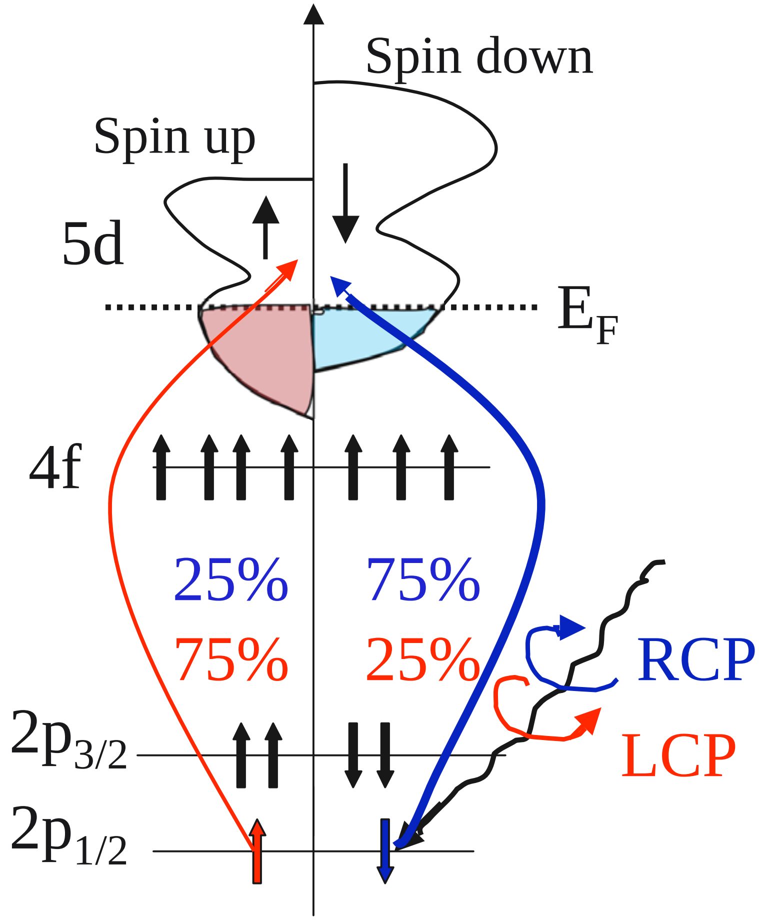

Magnetic Spectroscopy of Functional Materials

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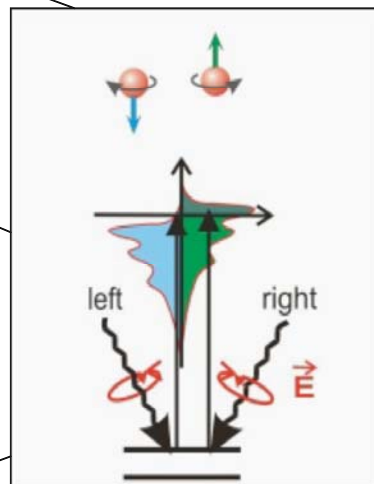
The needs and opportunities, the tools

High Field studies

Mineral Physics, Geosciences (High Pressure)

Magnetic Domains (Imaging)

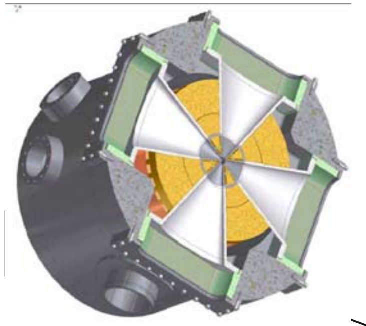


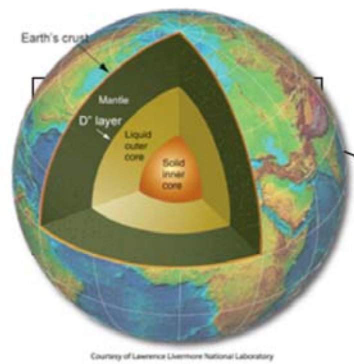
Interfacial Magnetism (Magnetic Reflectivity)

Site-specificity in Crystals (Magnetic DAFS)

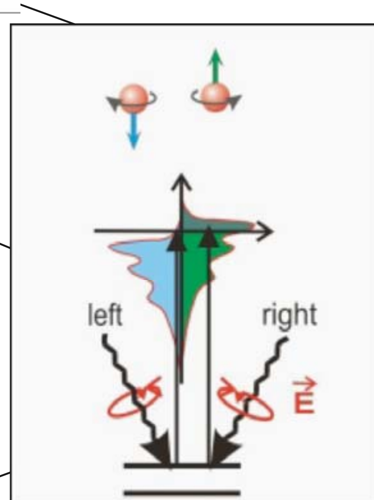
Spin disorder (MXAFS)

Magnetization Dynamics (Time-resolved studies)

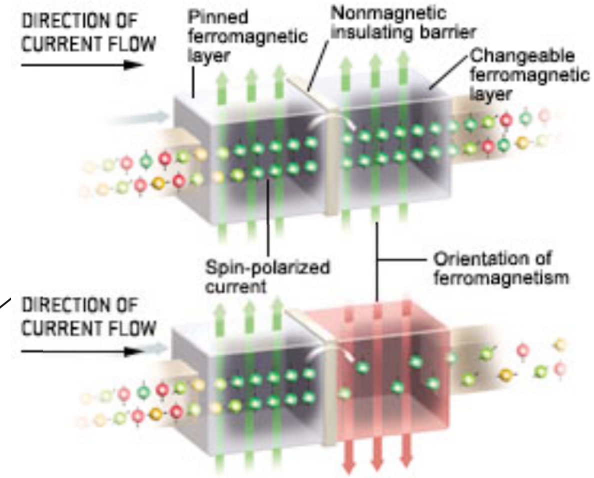




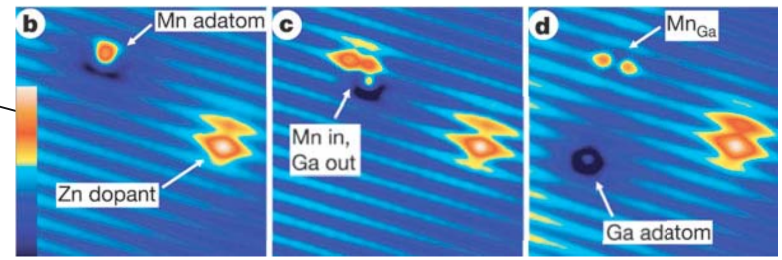
Earth's crust
Mantle
D" layer
Liquid outer core
Solid inner core
Courtesy of Lawrence Livermore National Laboratory



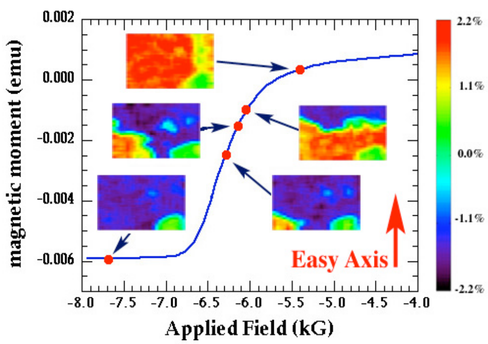
left
right
$\vec{E}$



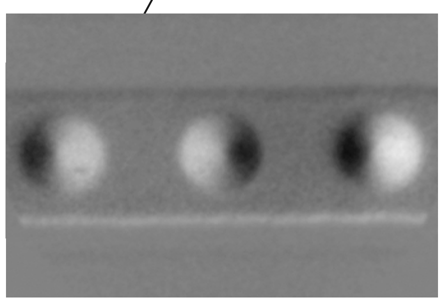
DIRECTION OF CURRENT FLOW
Pinned ferromagnetic layer
Nonmagnetic insulating barrier
Changeable ferromagnetic layer
Spin-polarized current
Orientation of ferromagnetism
DIRECTION OF CURRENT FLOW

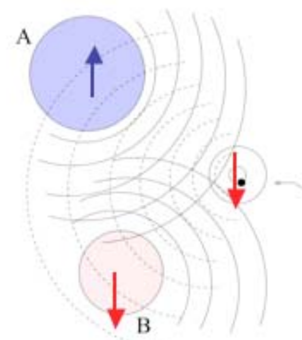


b
Mn adatom
Zn dopant
c
Mn in, Ga out
d
Mn_{Ga}
Ga adatom



magnetic moment (emu)
0.002
0.000
-0.002
-0.004
-0.006
-8.0
-7.5
-7.0
-6.5
-6.0
-5.5
-5.0
-4.5
-4.0
Applied Field (kG)
Easy Axis
2.2%
1.1%
0.0%
-1.1%
-2.2%





A
B

Magnetic Spectroscopy of Functional Materials

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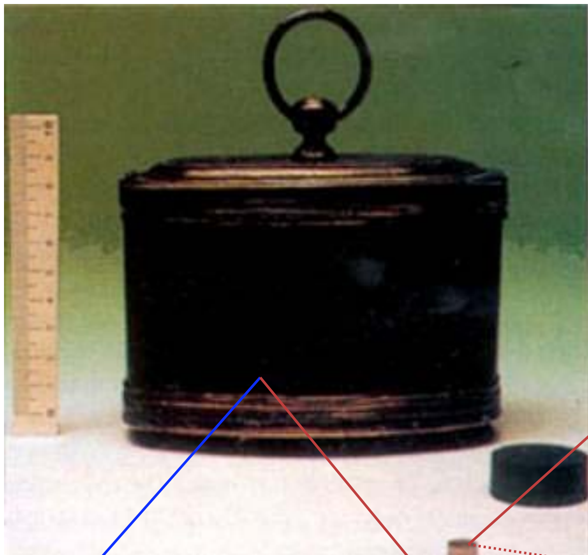
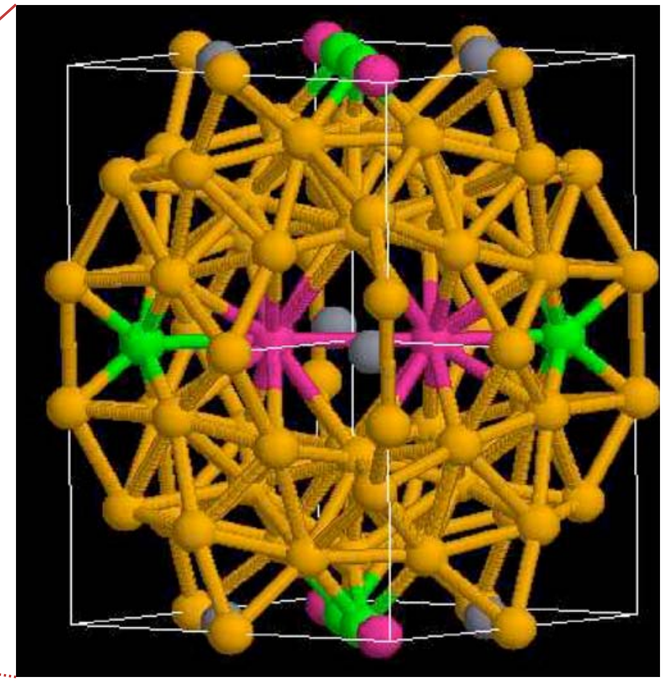
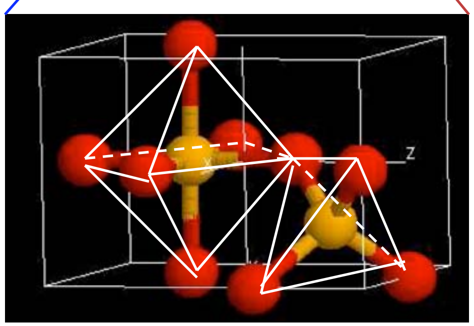
- The needs and opportunities
- → Best permanent magnets
- Giant magnetocaloric materials

Permanent Magnets: Evolution brings complexity





$Nd_2Fe_{14}B$
(artificial)



Magnetite

O
Fe

Fe Nd1 B
Nd2

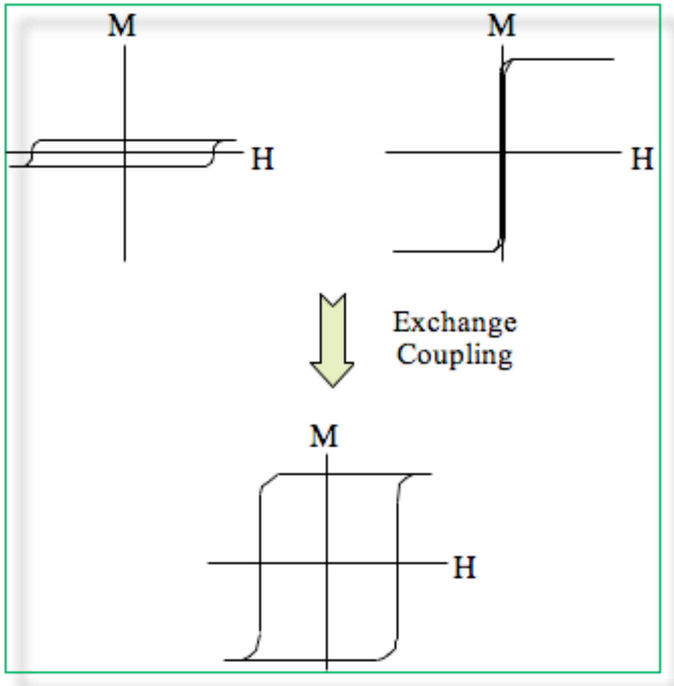
64 magnetic atoms

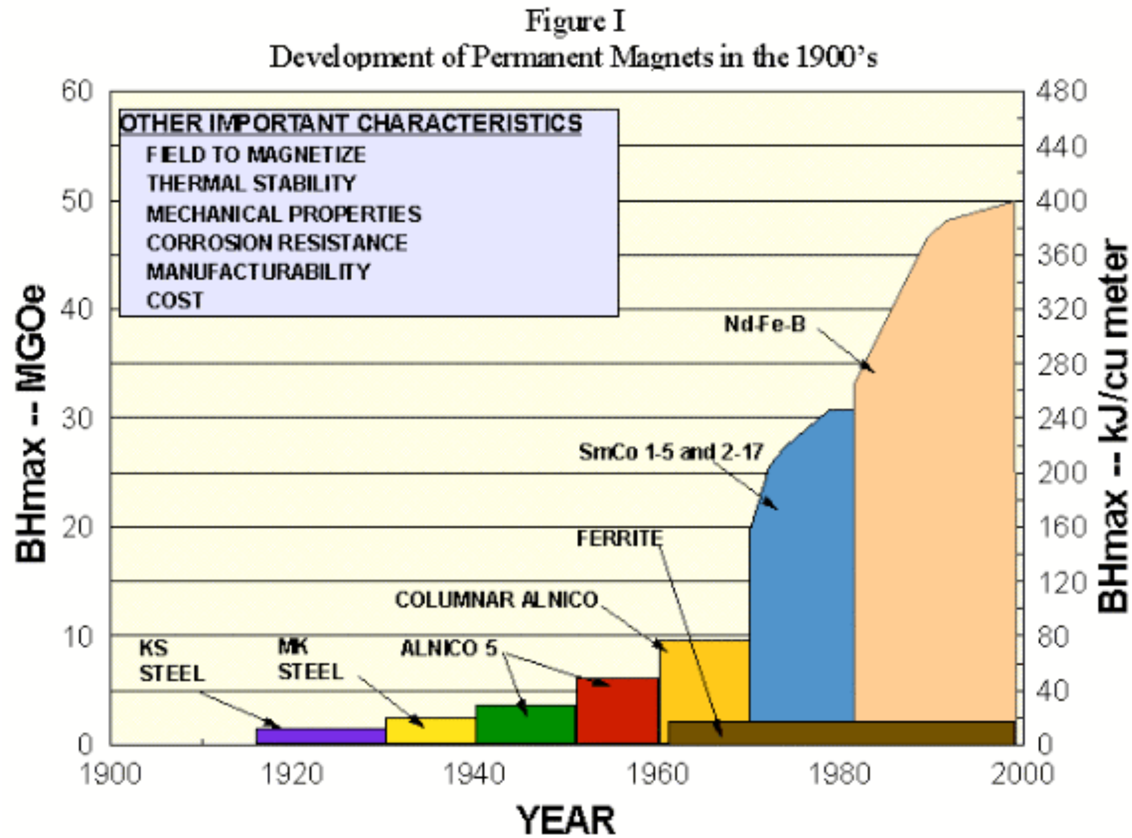
2 magnetic elements (Fe, Nd)

Modern magnets and the Rare-Earth role

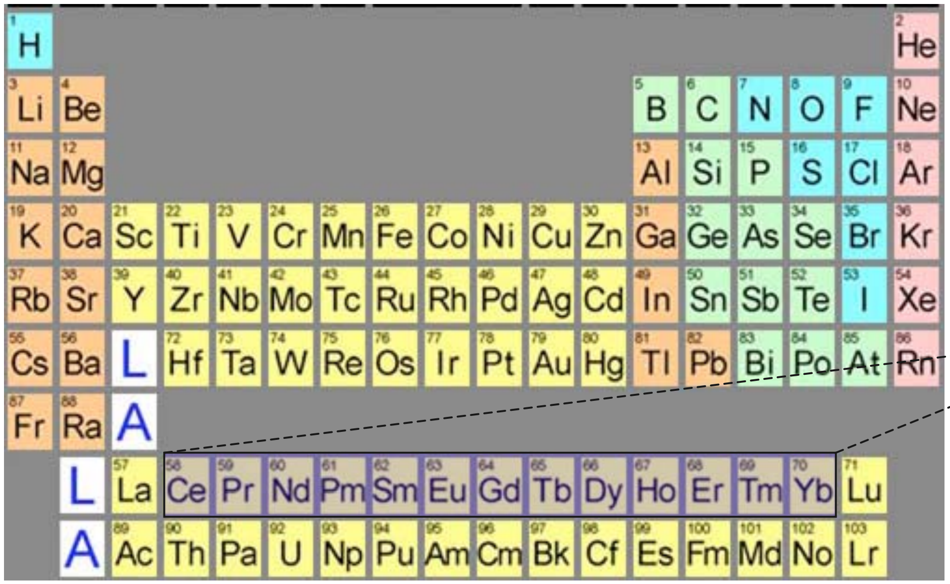
Recipe for a good magnet:

- Large magnetization (pack high density of magnetic ions).
- Large coercivity (“magnetic hardness”, add rare-earth ions).

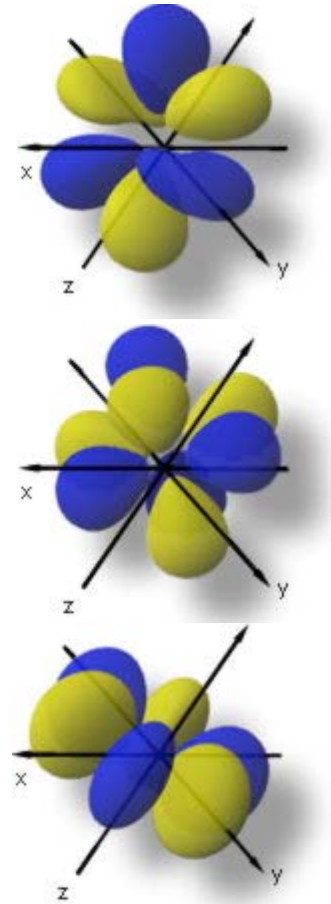


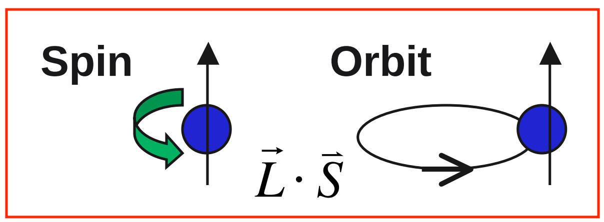


Modern magnets and the Rare-Earth role



Rare-Earths:
4f electrons

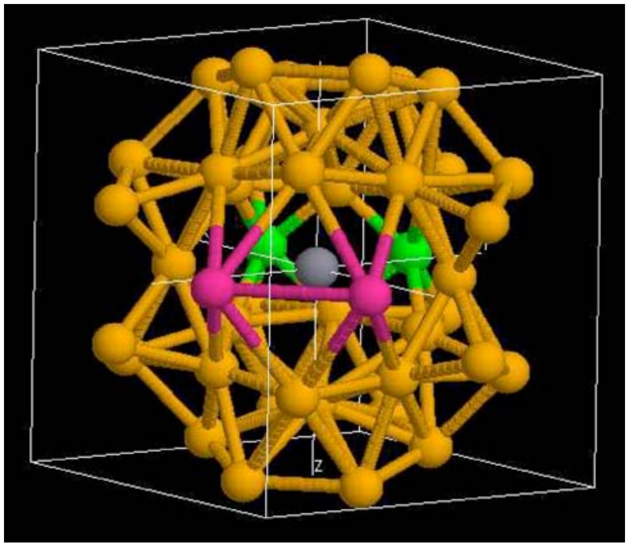




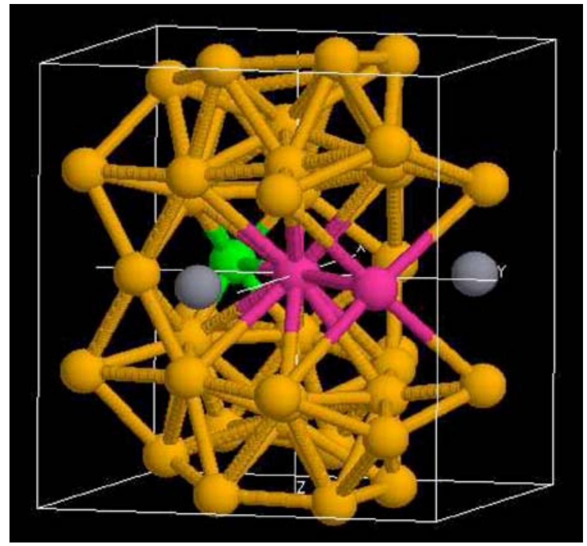
- *Aspherical* 4f orbitals interact with surrounding electrons (crystal field).
- *Spin-orbit coupling* + crystal field determine preferred spin orientation, "pinning" the magnetic moments.

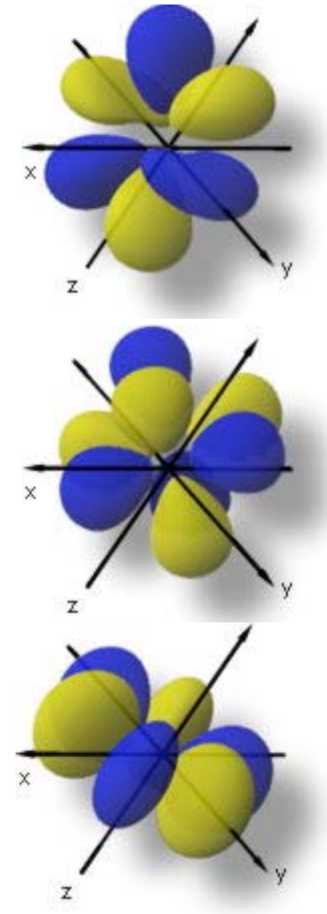
$Nd_2Fe_{14}B$: *Best in its class*

- Fe: ~ 31 μ_B/f.u; Nd: ~ 6 μ_B/f.u. (element-specificity)
- Magnetocrystalline anisotropy [001] dominated by Nd RE ions.



Nd *g*
Nd *f*
B
Fe



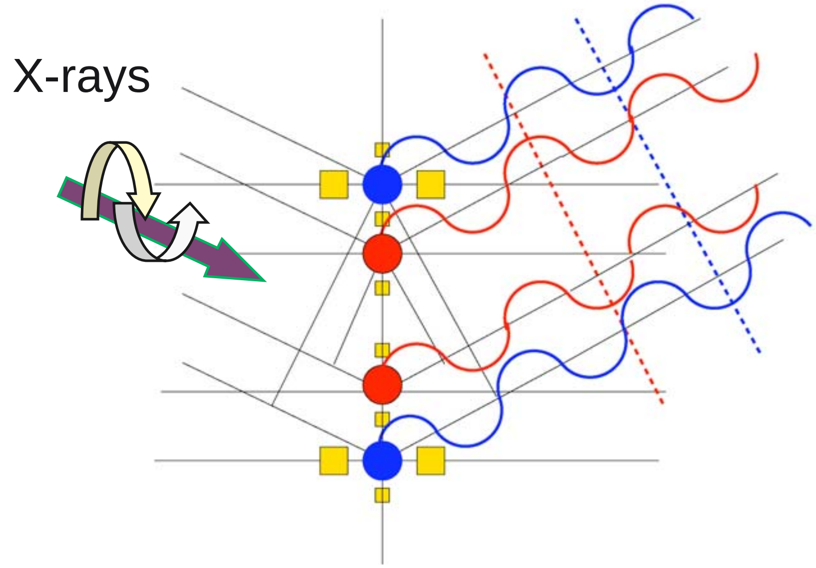


Rare-earth Nd ions are simultaneously present in two different crystalline environments.
What are their roles?

Exploiting the crystal's symmetry for site separation

$$F_{hkl} = f_{Nd}(Q,E)\sum_{i=1}^{4} e^{i\vec{Q}\cdot\vec{r}_i}$$

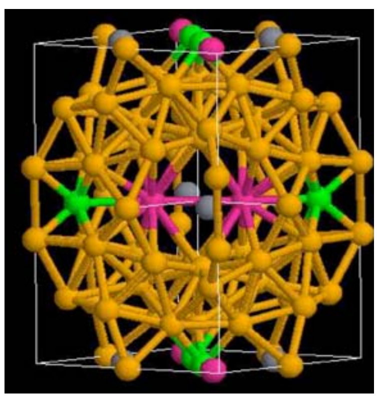
$$[\vec{Q} = 2\pi(\frac{h}{a},\frac{k}{b},\frac{l}{c}), \vec{r}_i = (x_i a + y_i b + z_i c)]$$



$$(4g)\ (x,\bar{x},0);(\bar{x},x,0);(\frac{1}{2}+x,\frac{1}{2}+x,\frac{1}{2});(\frac{1}{2}-x,\frac{1}{2}-x,\frac{1}{2})$$

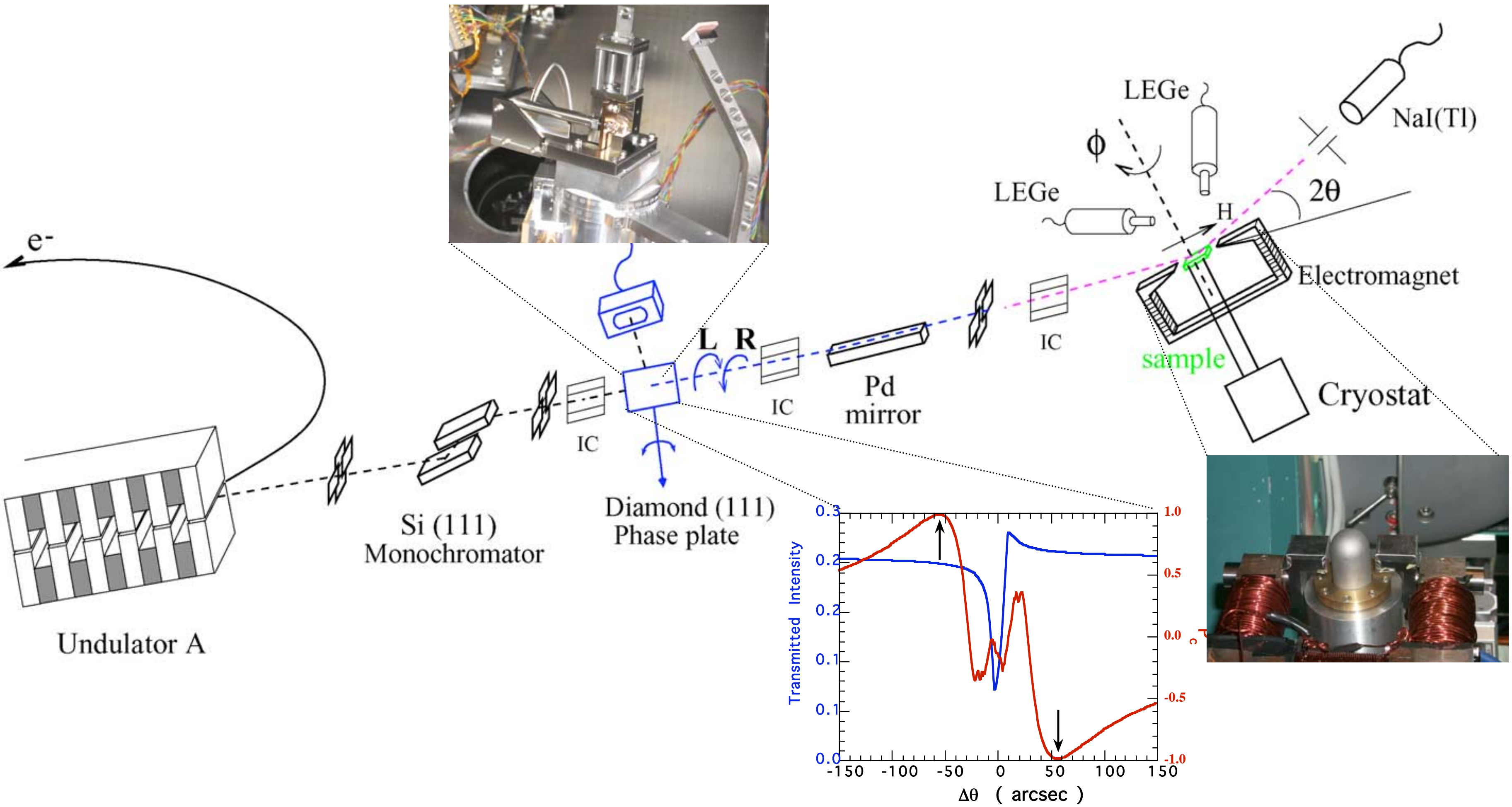
$$(4f)\ (x,x,0);(\bar{x},\bar{x},0);(\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2});(\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2})$$

- Nd (*4f*)
- Nd (*4g*)
- B
- Fe

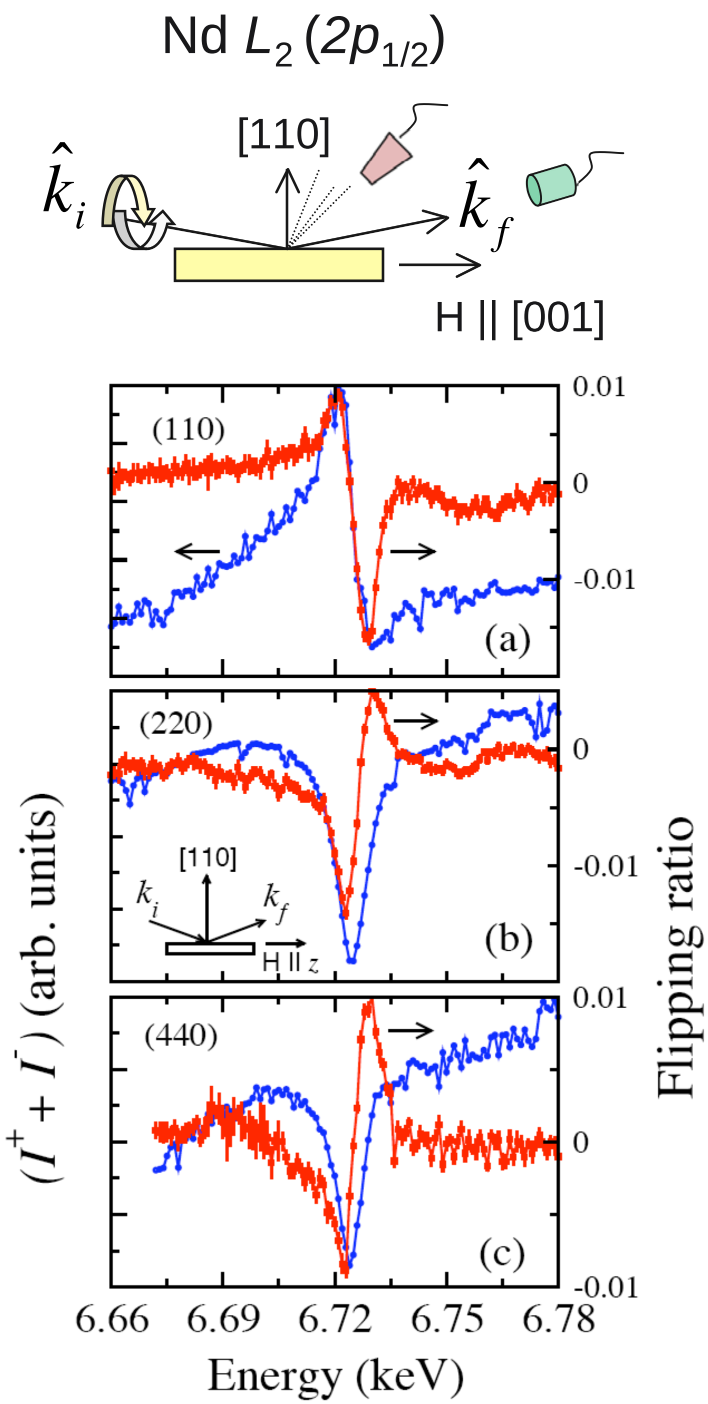


Site	(110)	(220)	(440)
Nd (*4f*)	3%	96.4%	48.5%
Nd (*4g*)	97%	3.6%	51.5%

Beamline 4-ID-D, Advanced Photon Source



- Resonant diffraction at fix Q: scan ID gap, monochromator, phase plate, and sample angles with E. Digital lock-in detection of *$(I^L - I^R)/(I^L+I^R)$*.



$$I_m \propto f_c^* f_m [(\hat{k}_i \cdot \hat{m}) + (\hat{k}_f \cdot \hat{m}) \cos 2\Theta]$$

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Nd (4*f*)	3%	96.4%	48.5%
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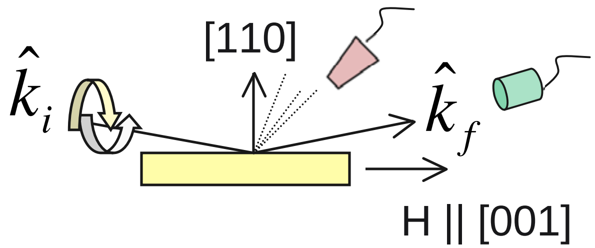
- (110) and (220) reflections probe element *and* site-specific magnetism.

Nd L_2 ($2p_{1/2}$)



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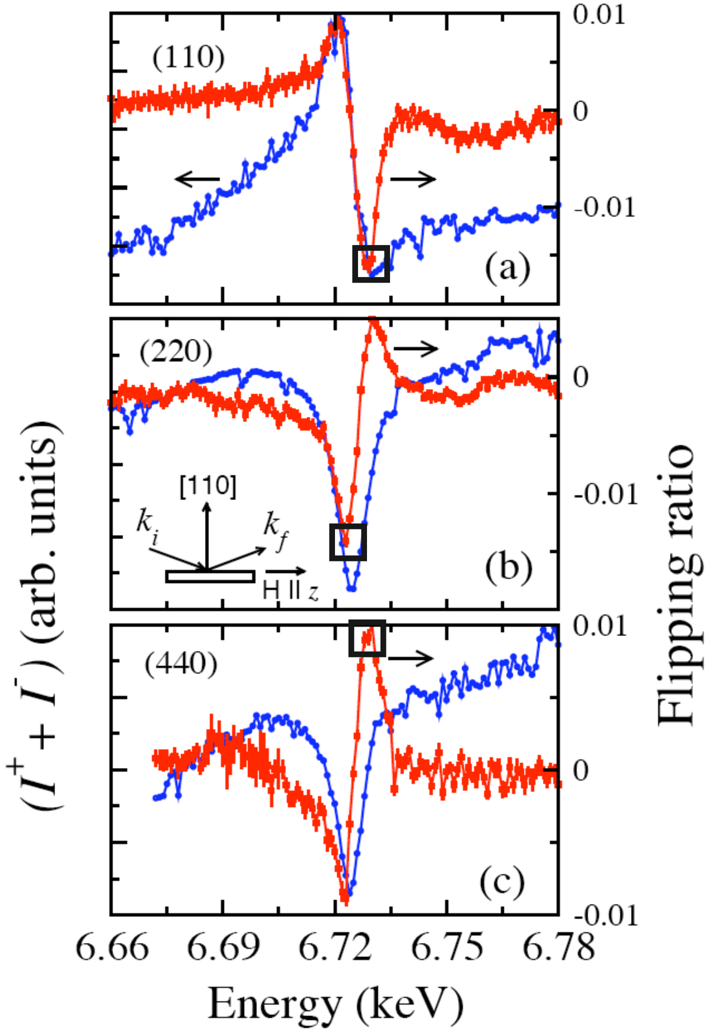
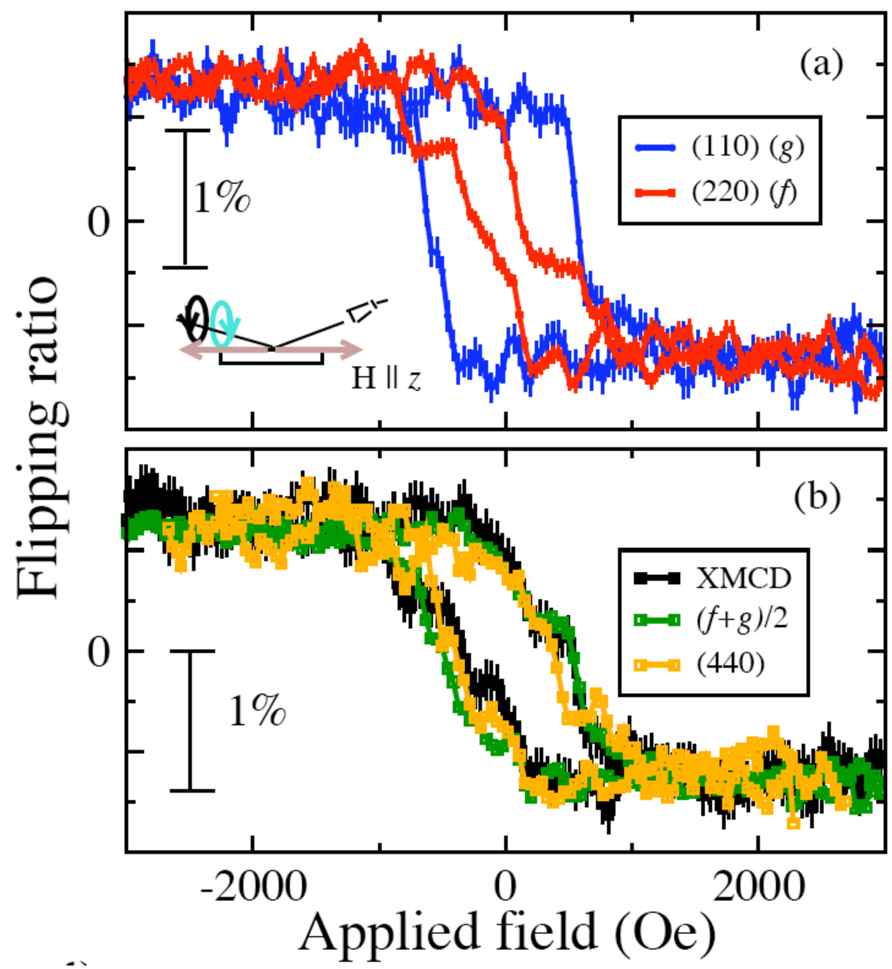
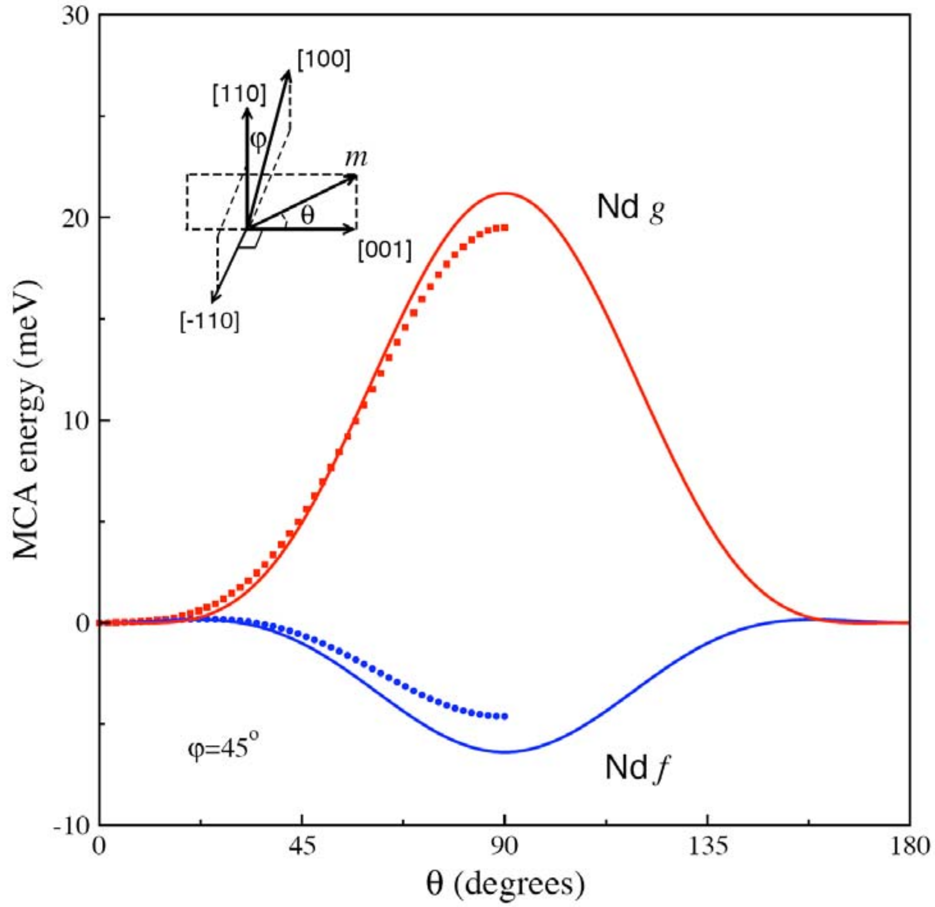
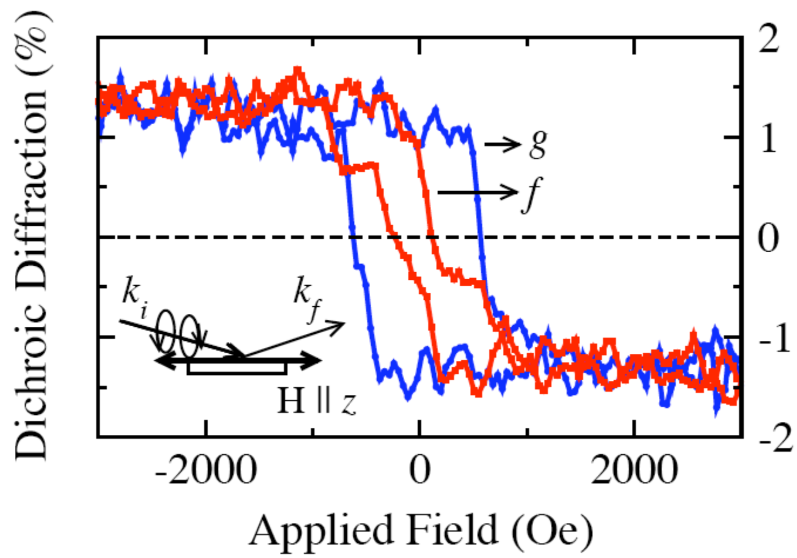




Theoretical calculations (M. van Veenendaal, NIU-ANL)



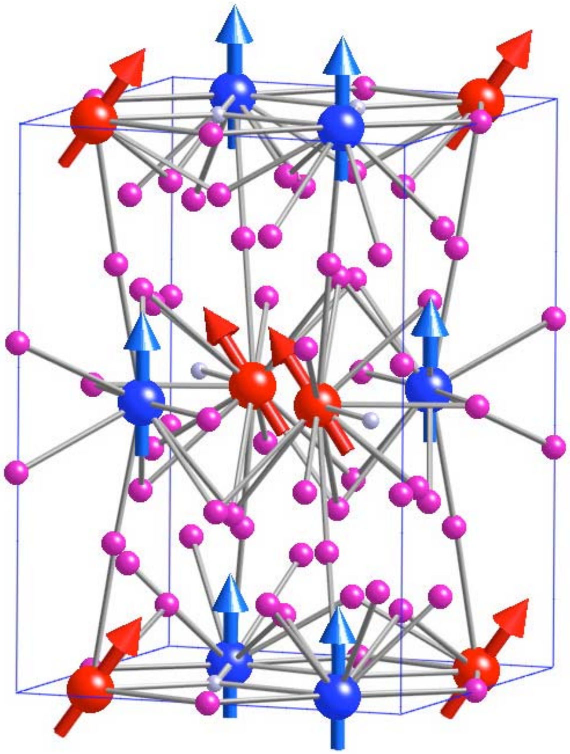


$$\langle LSJ, M=-J \mid H_{CEF} \mid LSJ, M=-J \rangle$$

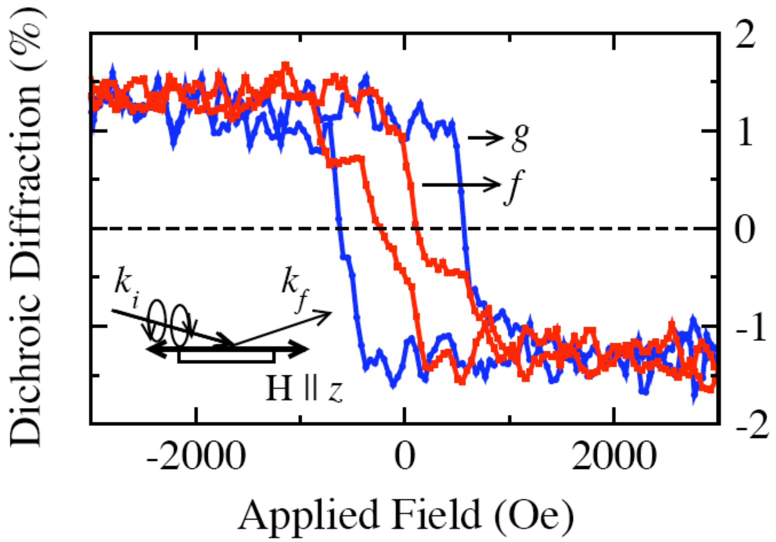
$$H_{CEF} = e\sum_i V(\vec{r}_i) = \sum_i B_{kq}\left(C_q^k\right)_i$$

CEF parameters M. Yamada *et al* (1988).

Manipulate magnetic hardness by atomic engineering



Phys. Rev. Lett. **95**, 217207 (2005)

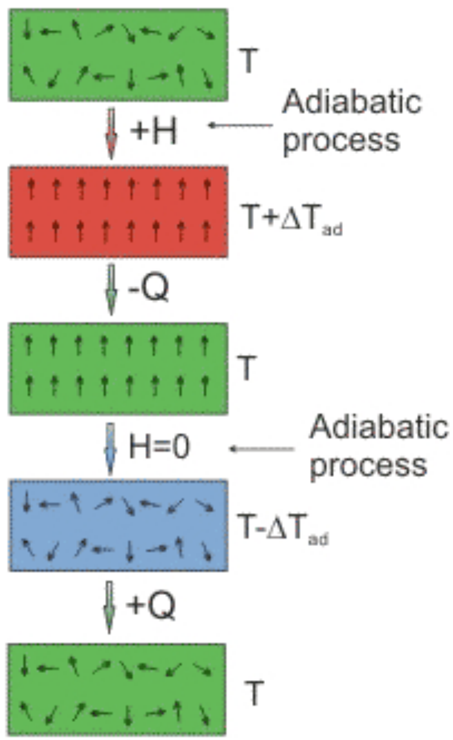


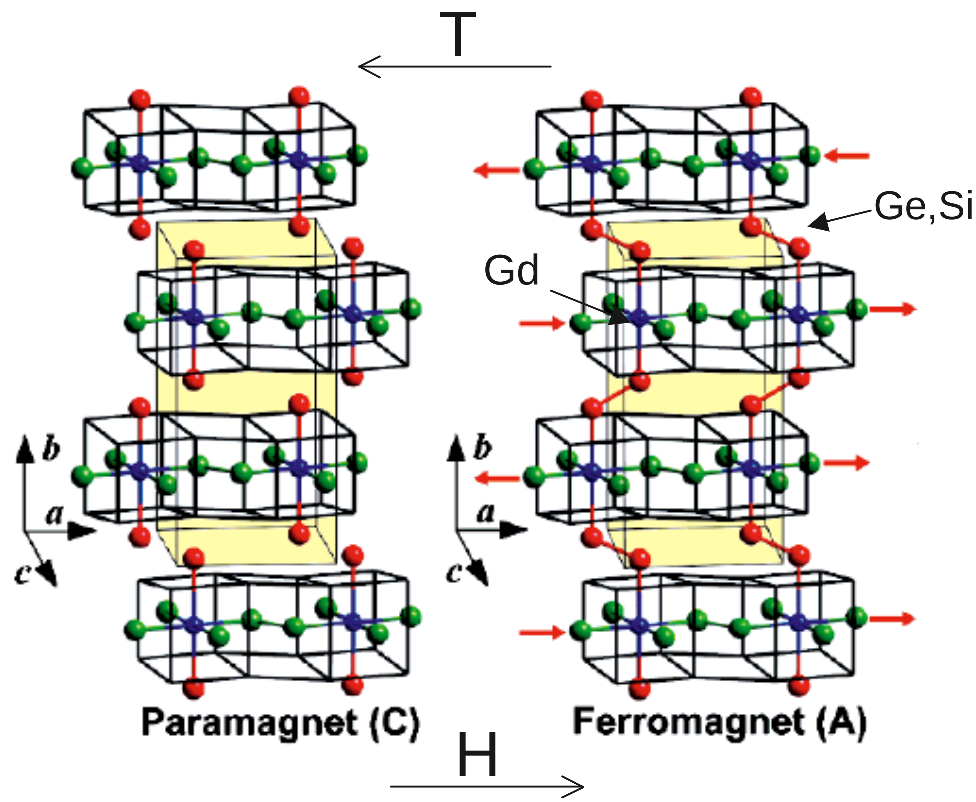
- Only one Nd site responsible for magnetic hardness.
- Replace “faulty” ions with other RE ions, or even Gd (isotropic).

Magnetic Spectroscopy of Functional Materials

- Magnetic contrast with CP x-rays
- The needs and opportunities
- Best permanent magnets
- → Giant magnetocaloric materials

Giant magneto-caloric material $Gd_5(Si_xGe_{1-x})_4$

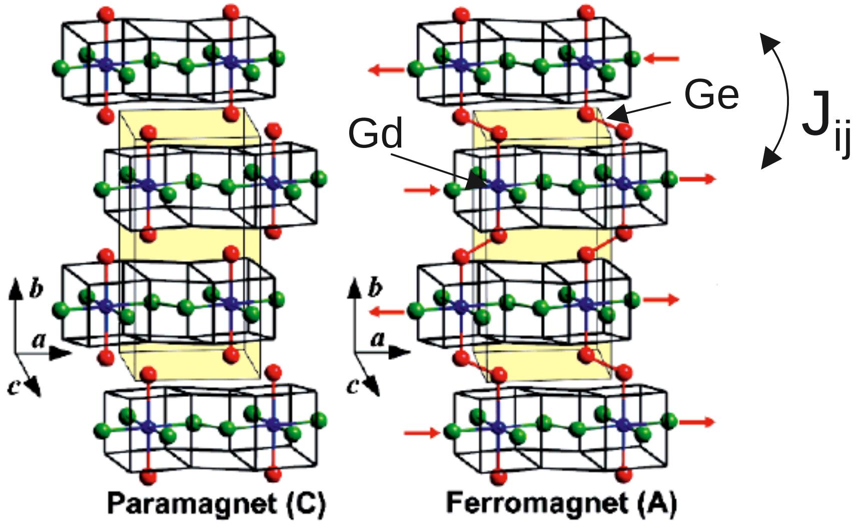




Pecharsky and Gschneider
Advanced Materials 13, 683 (2001).

- First-order magneto-structural transition yields large magnetic and structural entropy changes that can be harnessed for magnetic refrigeration.
- Transition temperature can be tuned with Si doping to near RT.

What is the role of Ge in mediating inter-layer exchange interactions?
Why does Si doping enhance magnetic ordering?



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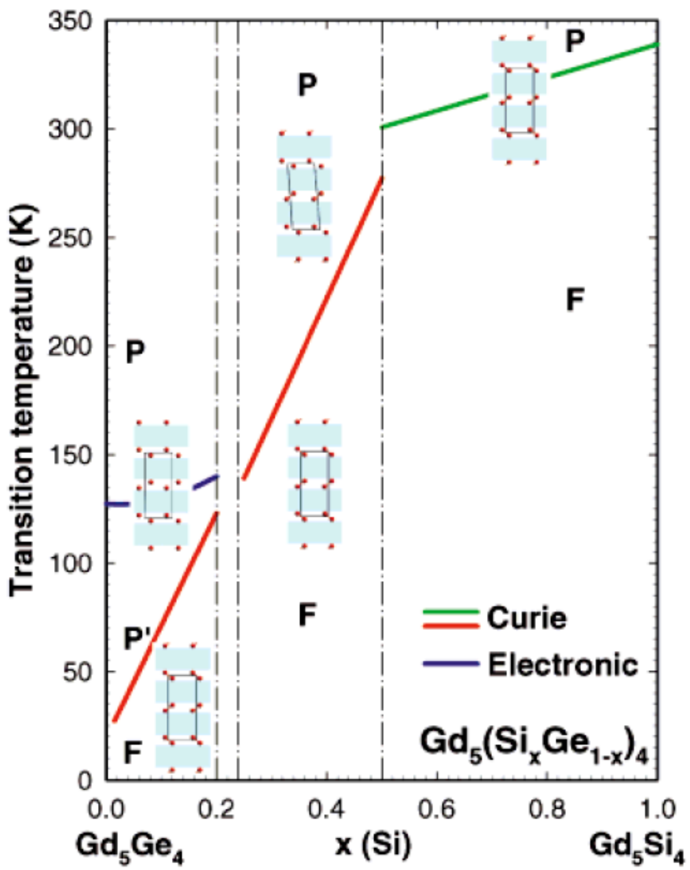
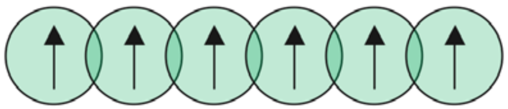
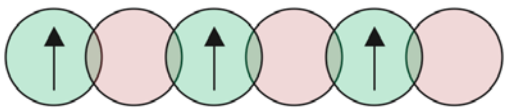


What is the role of Ge in mediating Gd-Gd exchange interactions?

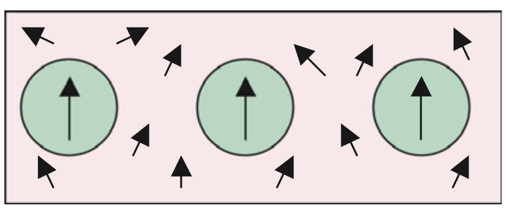
- No direct exchange interaction between Gd 4*f* electrons (atomic-like).



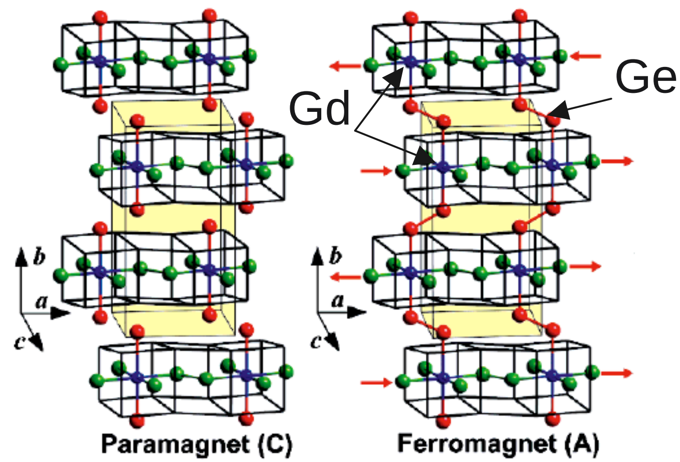
Direct Exchange
(overlap)
Pauli 1925, Heisenberg 1926



Superexchange
(overlap non-magnetic ion)
P.W. Anderson 1950

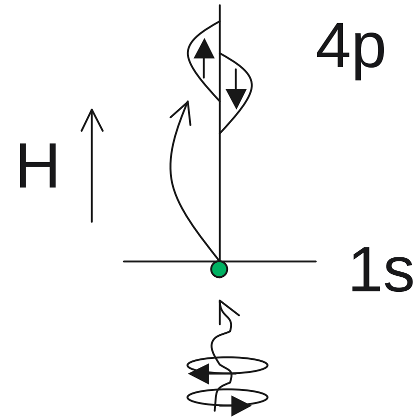


Indirect Exchange
(conduction electrons)
Ruderman and Kittel 1954

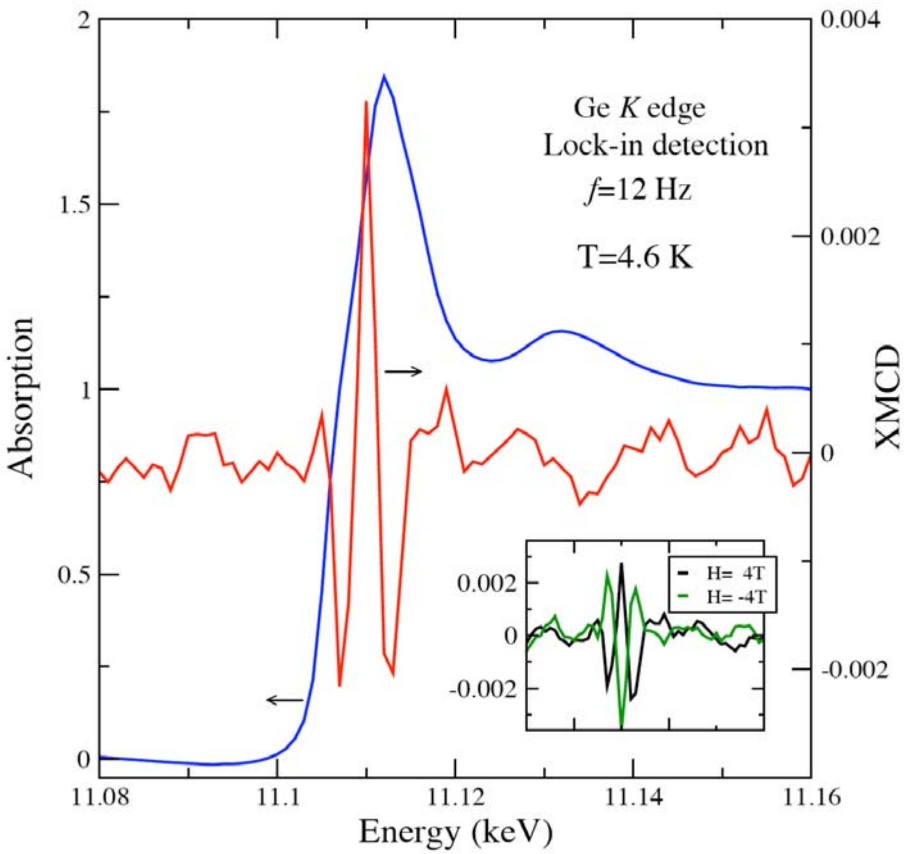


- Since Ge is non-magnetic, SE is believed to be responsible.

Is Ge *really* non-magnetic?



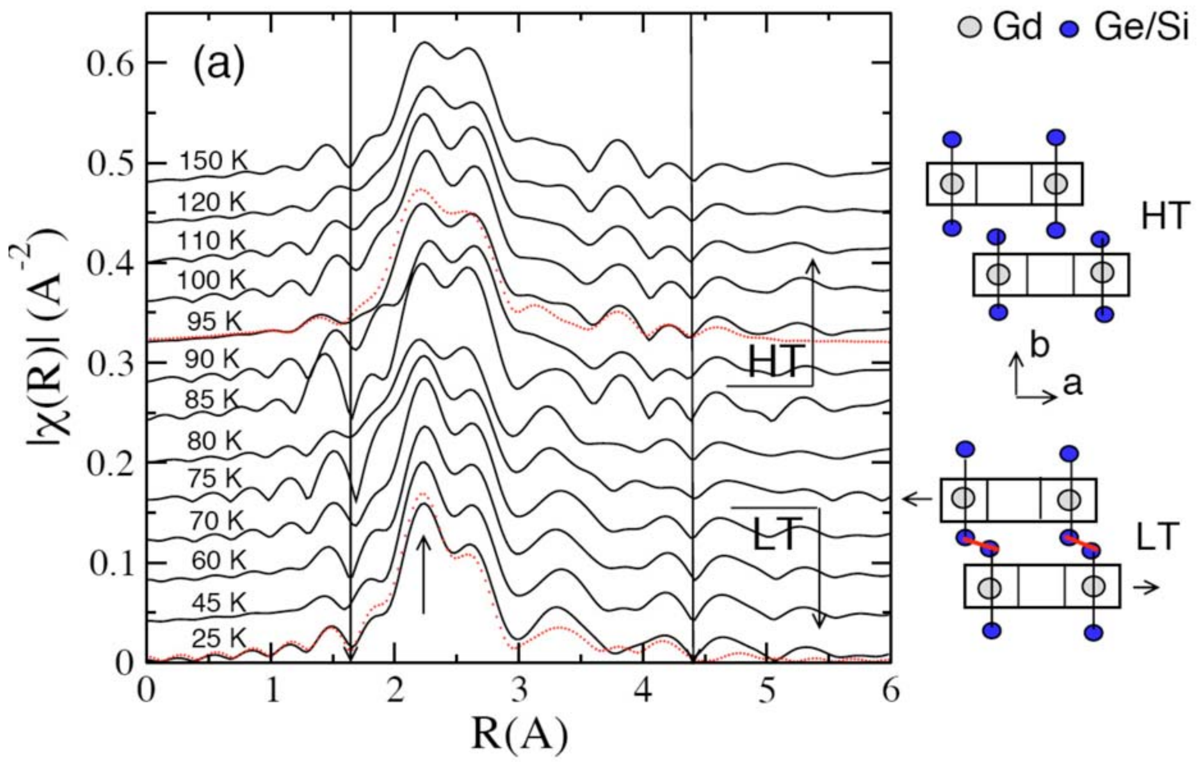
$$\frac{d\langle l_z \rangle}{dE} \neq 0$$



- Ge *K*- XMCD comparable to Fe,Co,Ni, but Ge is $3d^{10}$.

Is Ge magnetism tied to Gd magnetism and to the structural transition; i.e. intrinsic?

$Gd_5(Si_{0.125}Ge_{0.875})_4$



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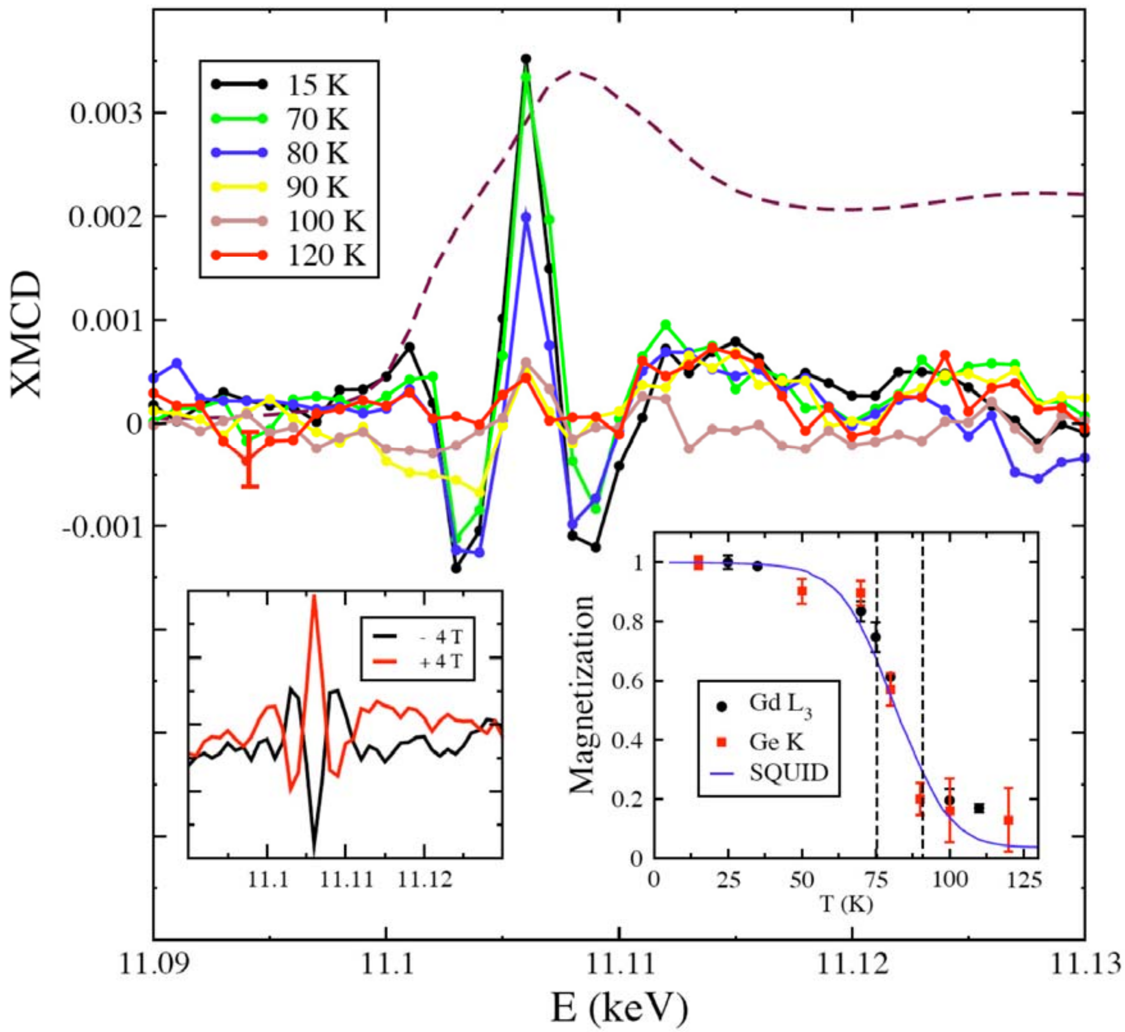

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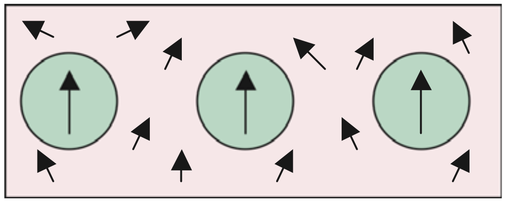
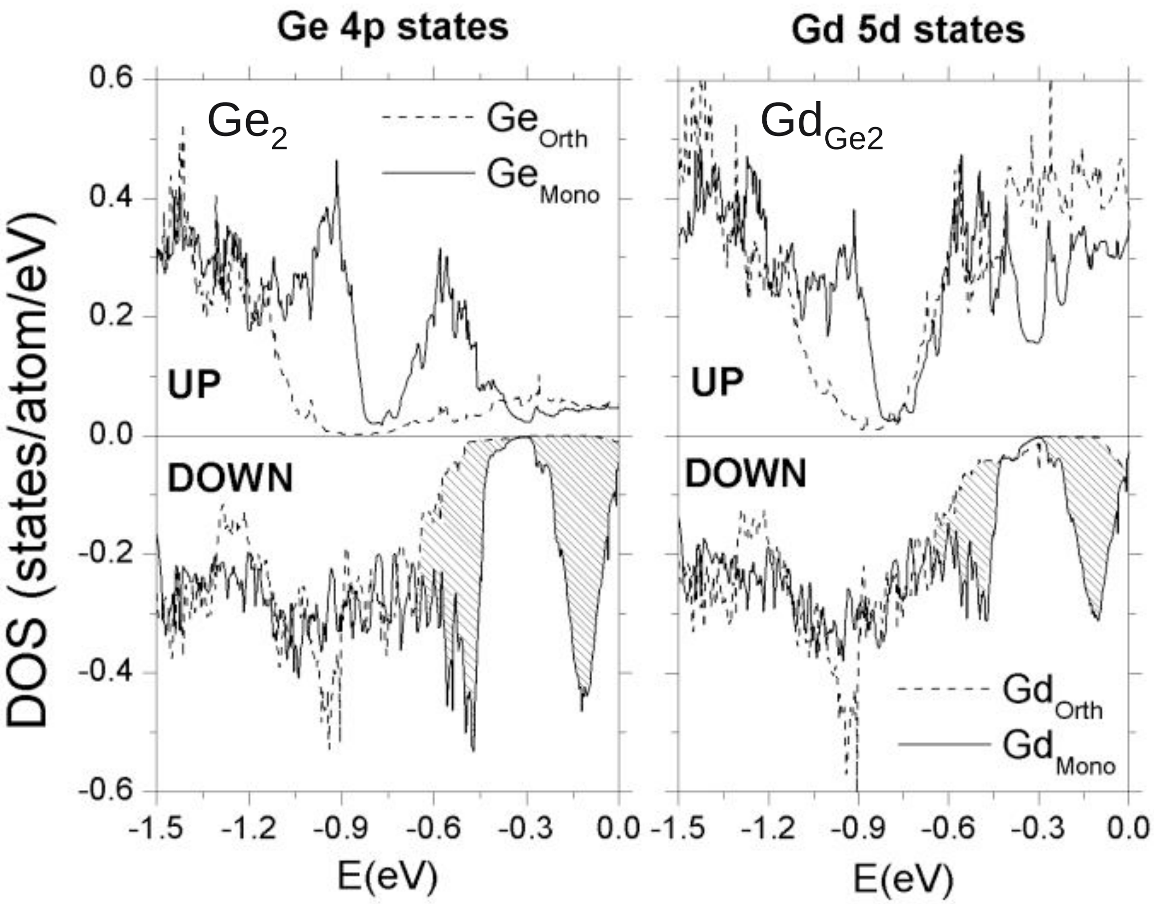
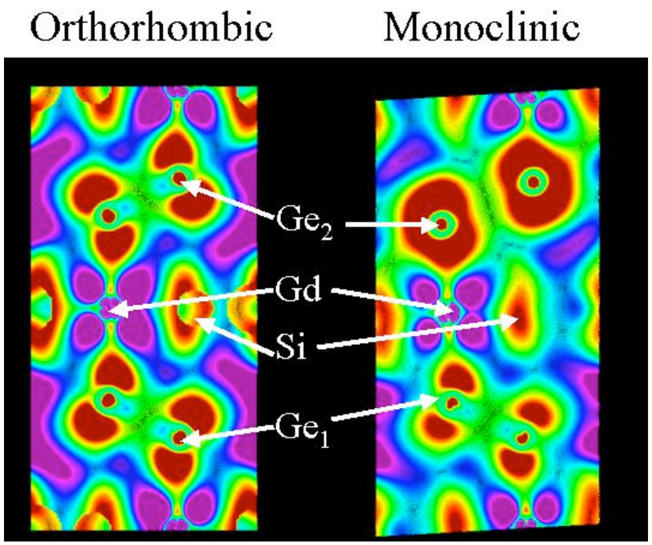


Gd 5*d*- Ge 4*p* hybridized band mediates indirect exchange?

DFT calculations (Y. B. Lee, B. Harmon- Ames)





S_z (μ_B) for Ge 4*p*, Gd 5*d*

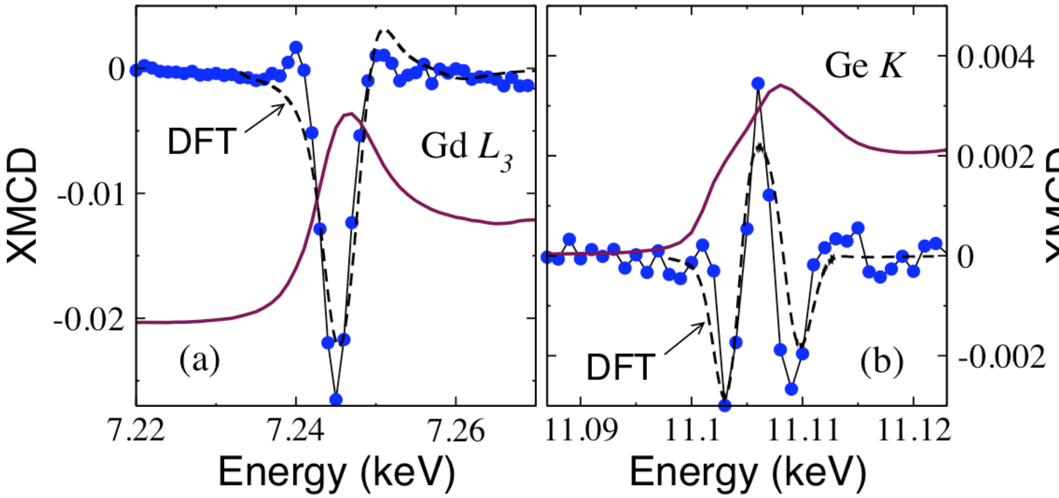
	Ortho	Mono	Δ (%)
Ge_1	-0.033	-0.038	15%
Ge_2	-0.033	-0.06	100%
Gd_{Ge2}	+0.341	+0.23	30%

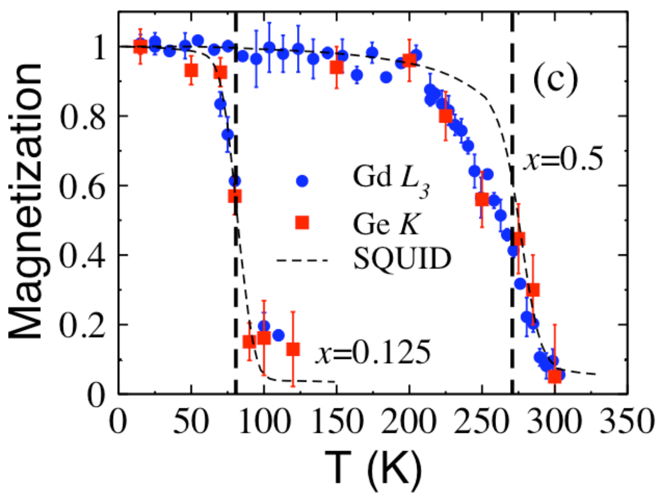
Bond breaking reduces the overlap of Gd 5d wavefunctions across disconnected slab $J_{ij} \propto \sum_k \left\langle P_{5d_i}\psi_k \mid P_{5d_j}\psi_k \right\rangle$

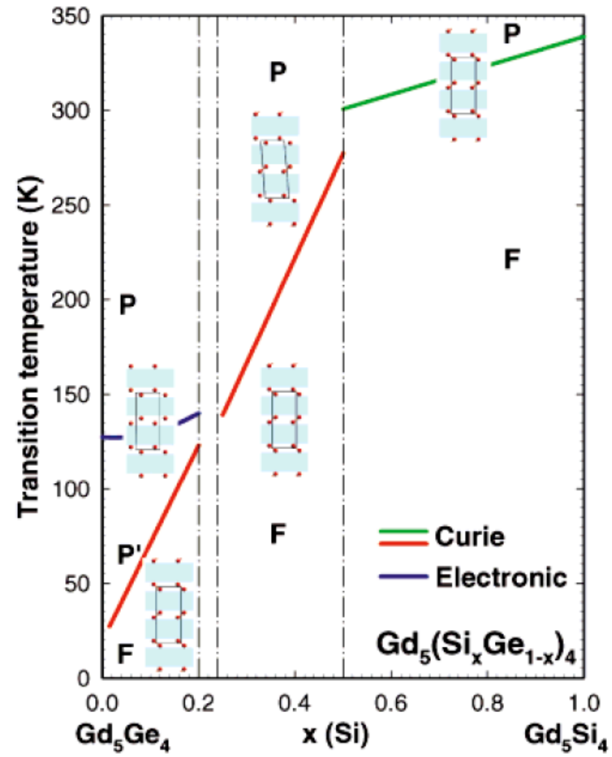
PRL 98, 247205 (2007)

DFT calculations validated by XMCD data.

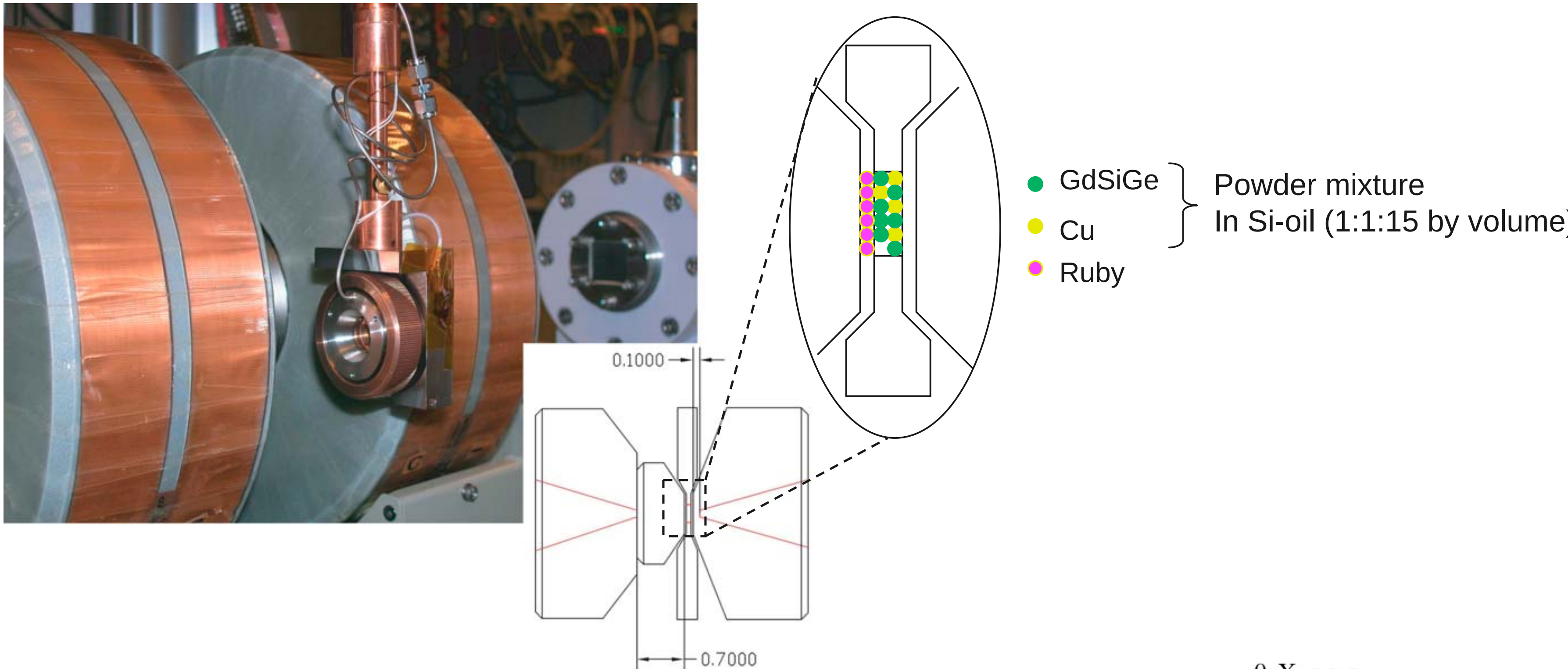
PRL 98, 247205 (2007)

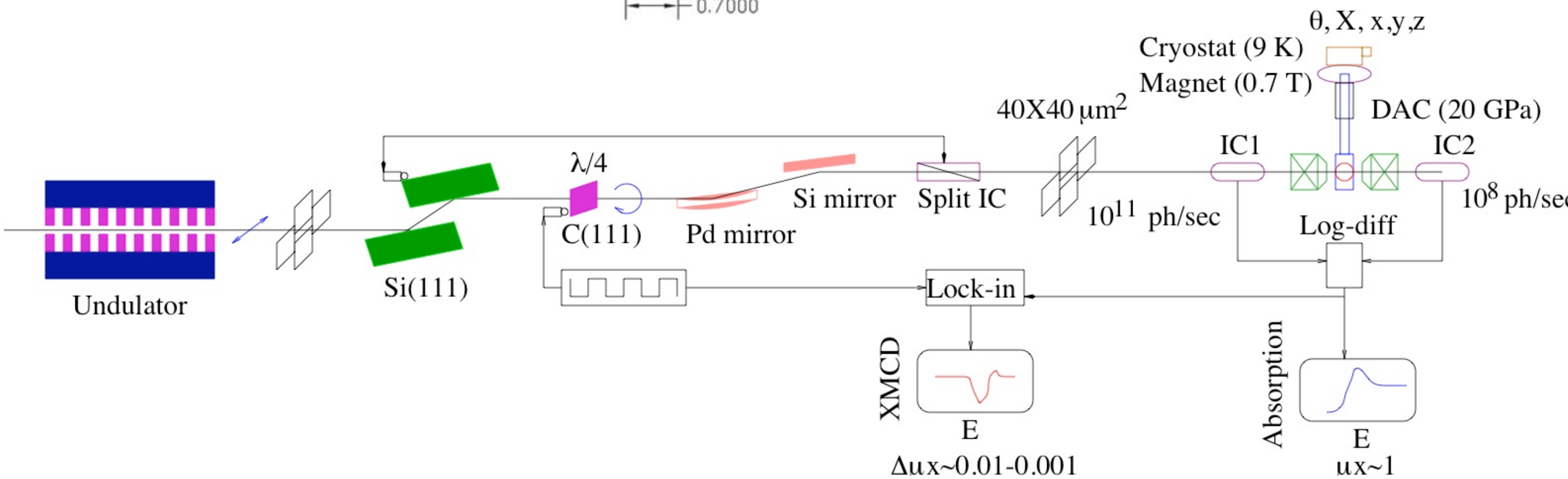




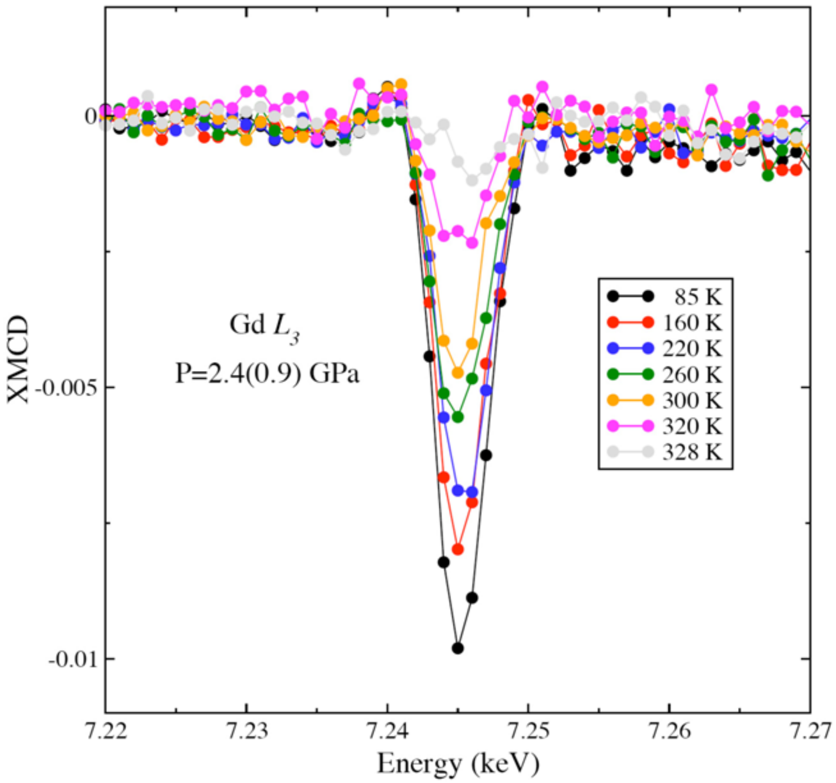


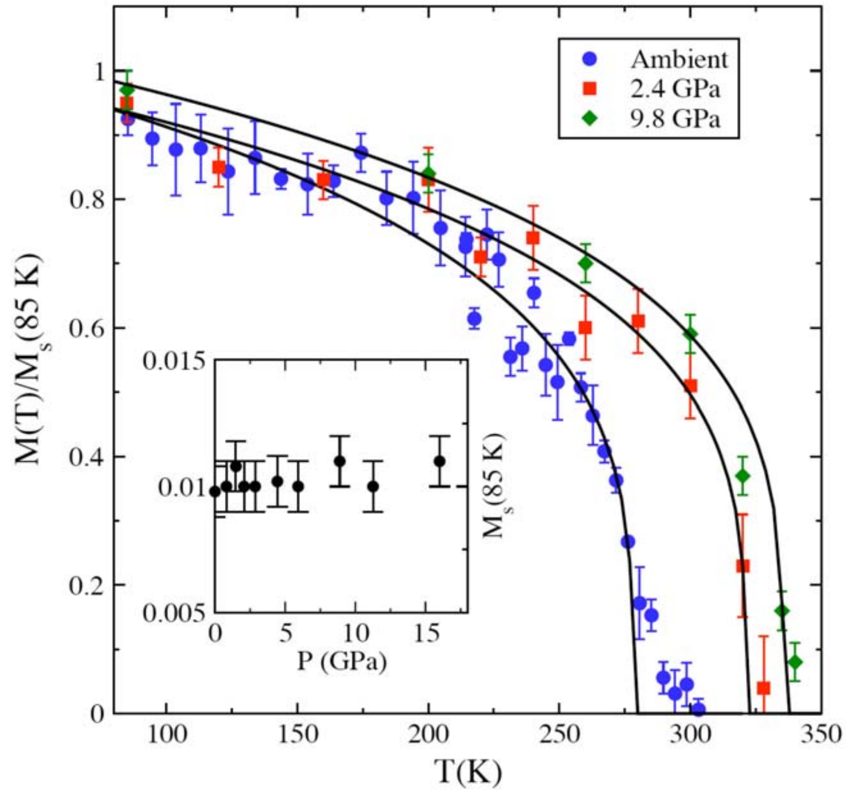
Why does Si doping enhance Tc?

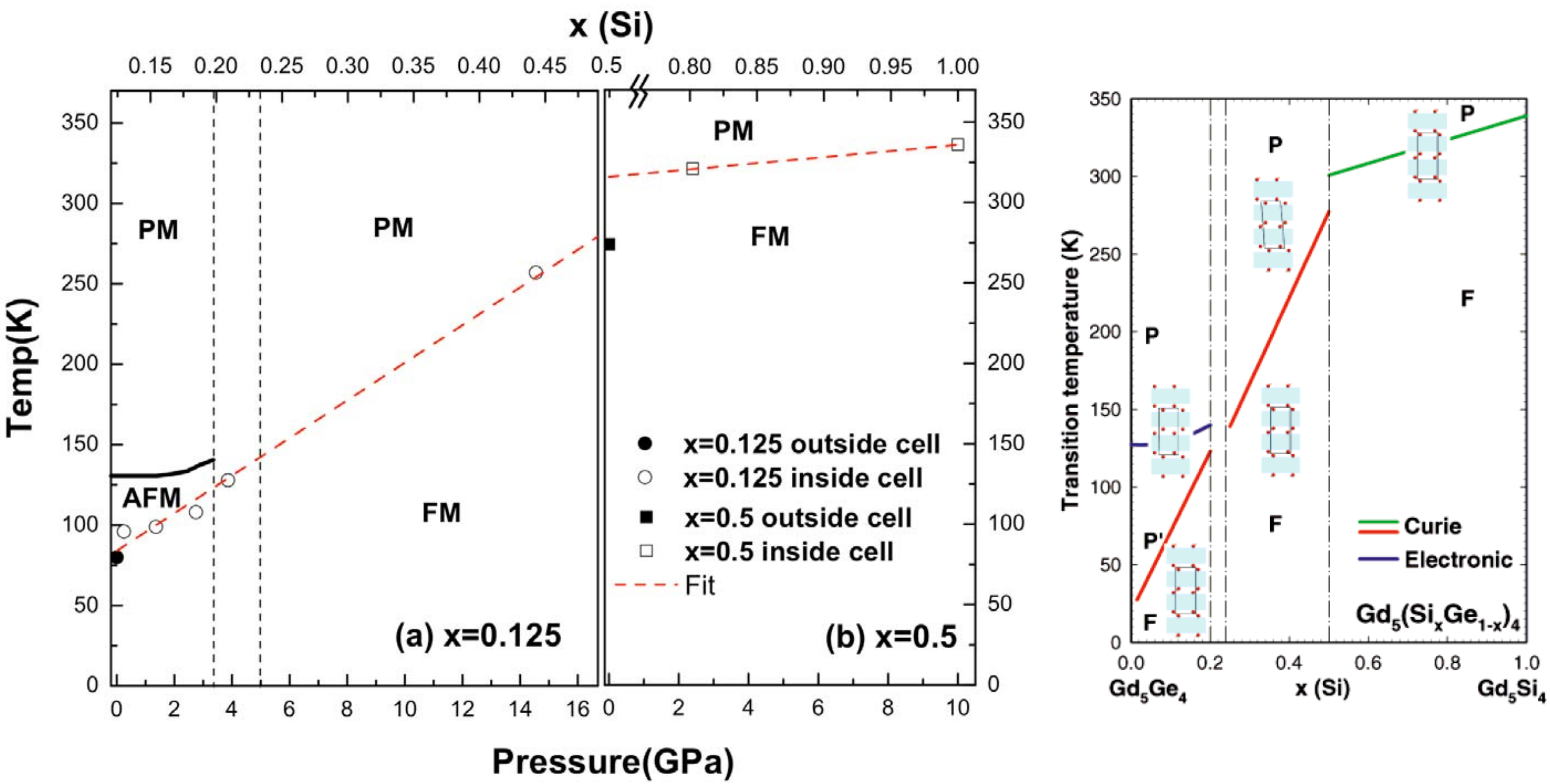




Review of Scientific Instruments 78, 083094 (2007)


Gd L_3
P=2.4(0.9) GPa
85 K
160 K
220 K
260 K
300 K
320 K
328 K
XMCD
Energy (keV)
0
-0.005
-0.01
7.22
7.23
7.24
7.25
7.26
7.27


Ambient
2.4 GPa
9.8 GPa
M(T)/M$_s$(85 K)
T(K)
0
0.2
0.4
0.6
0.8
1
100
150
200
250
300
350
M$_s$(85 K)
P (GPa)
0.015
0.01
0.005
0
5
10
15



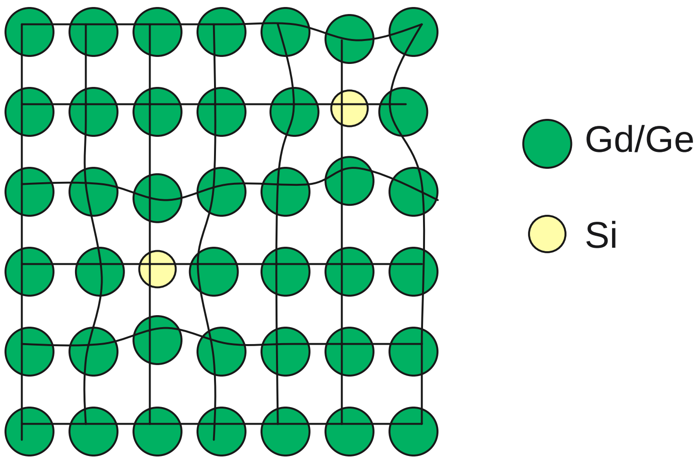
Enhanced magnetic order with Si doping is volume-driven

Increased overlap enhances indirect exchange

Tseng *et al.*, PRB 76, 014411 (2007)

… but … for the same macroscopic volume change Tc increases x3 faster with Si doping than with pressure…

$$(\Delta T_c / T_c)_{x,P} / (\Delta V / V)_{x,P}$$



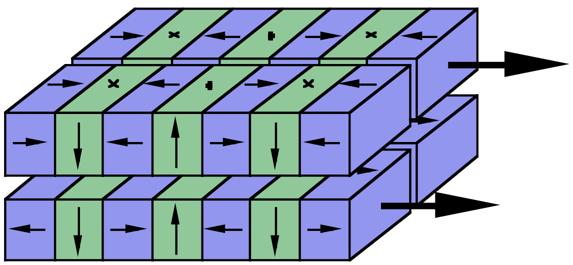
$$(\Delta V / V)_{local} > (\Delta V / V)_{macroscopic}$$

We postulate that compressed local regions around Si act as efficient FM exchange pathways and stabilize FM order faster than a smaller uniform compression of the lattice.

Tseng *et al.*, PRB 76, 014411 (2007)

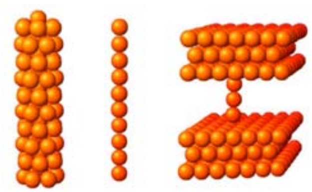
Future directions

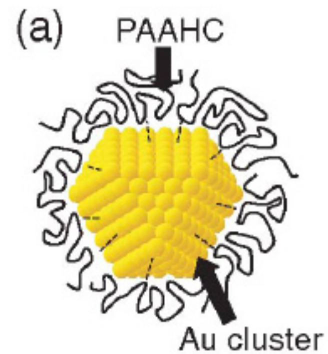
• Extend energy range of CP x-rays to 2.5-3.5 keV to include $L_{2,3}$ edges of 4*d* elements and $M_{2,3}$ edges of 5*d* elements.



Apple-type undulator

Pd





Au

• Improve focusing capabilities to enable 1 Mbar XMCD experiments.

Collaborators

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