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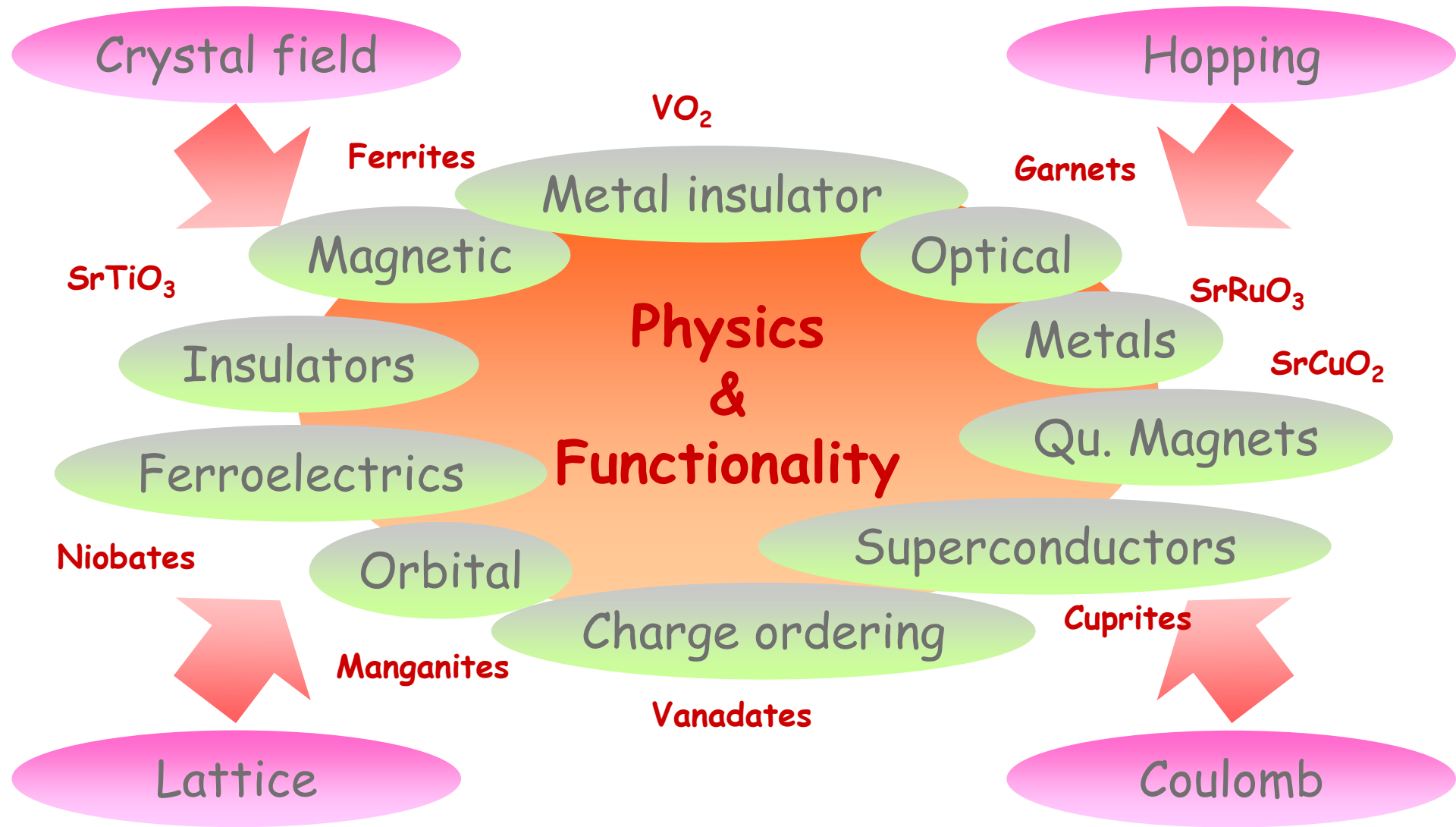
zernike institute for  
 advanced materials

# *Time domain experiments in Correlated matter*

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University of Groningen*

# Correlated Matter



# ***Time resolved views on matter***

- > Induced phase transitions
  - Novel states of matter
  - Ultrafast melting
  - Phase change media
  - Metal-Insulator, Ferro-Paramagnetic/electric, High/low spin, etc.
- > Coupling between orbital, lattice, charge and spin
  - Energy transfer
  - Decoupling through timescale
- > Inhomogeneities, static, dynamic
  - Stripes
  - Metal/insulator
- > Time domain spectroscopies
  - Electronic structure (PES/XAS)
  - Coherent lattice vibrations
  - Mossbauer
- > Magnetization reversal processes



# ***Time resolved views on matter***

## > Challenges

- Extend accessible physical properties dynamical state
  - How do correlations come about (TR-PES)
  - Lattice structure (TR-diffraction)
  - Spin structure (TR-Mössbauer diffraction)
  - Magnetization (TR-XMCD)
  - Electronic structure (TR-PES, XAS,...)
  - Inhomogeneity (TR-coherent imaging)
- Selective excitation
  - Excite particular lattice/orbital/charge/magnon modes to drive and control phase transitions
  - Excite non-thermal phases
  - Coherent control



# ***What can XFEL's do: Some dreams***

- › PES<sup>5</sup>
  - Place, Energy, Spin, Momentum & Time resolved
    - Optically induced electronic phase transitions
    - Formation of correlated states
    - Formation of Fermi surface
- › Two dimensional spectroscopy
  - Coherent links in the energy landscape
  - Hybridization (e.g. 3d-2p)
- › Coherent imaging on nano lengths and femto times
  - Charge inhomogeneity
  - Dynamic stripes
  - nucleation
- › Time resolved XMCD
  - Switching bits
- › Time resolved diffraction
  - Structural aspects of phase transitions
  - Melting

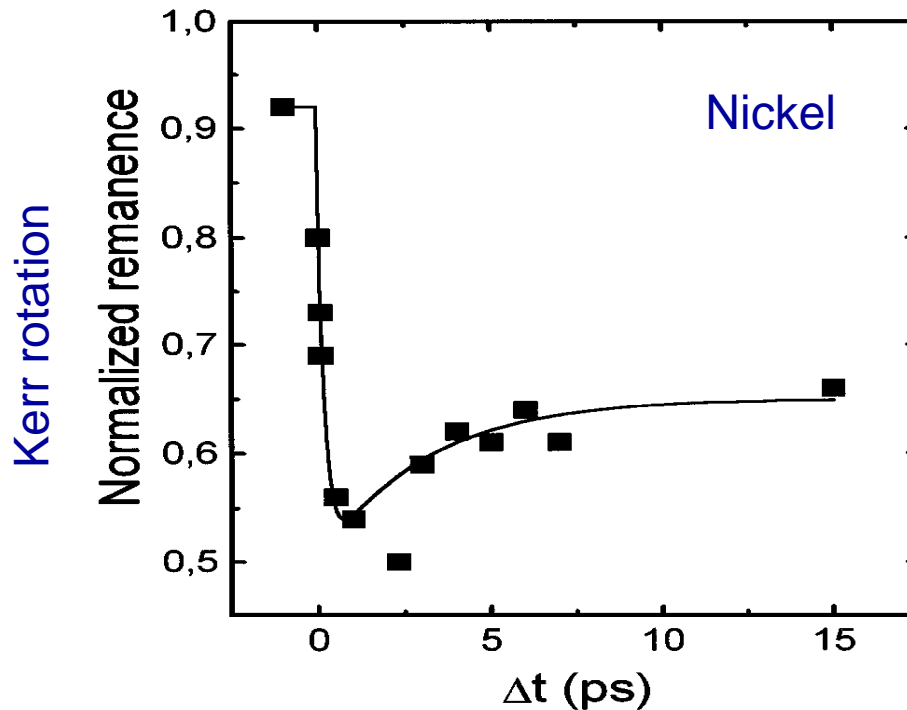


# ***Some examples***

- › Magnetization dynamics in EuO
- › Metamagnetic staircase in CuFeO<sub>2</sub>
- › Spin and orbital melting in YVO<sub>3</sub>
- › Jones-Peierls physics in the A7 metals



# Ultrafast magnetization dynamics



- De-magnetization by laser-heating (not a surprise)
- De-magnetization in 120 fs (faster than expected, ps-ns spin-lattice relaxation)
- Femto-second spin-lattice relaxation mechanism



# Magnetization dynamics in EuO

- > EuO  
Ferromagnetic ( $T_c=69$  K) semiconductor (1.2 eV bandgap)
- > Magnetic interaction mediated by 5d conduction electrons

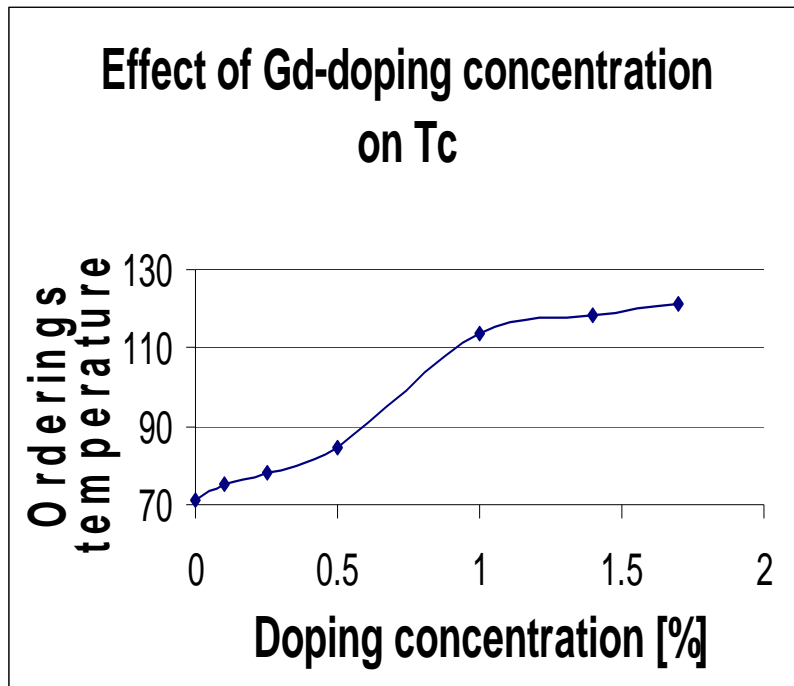
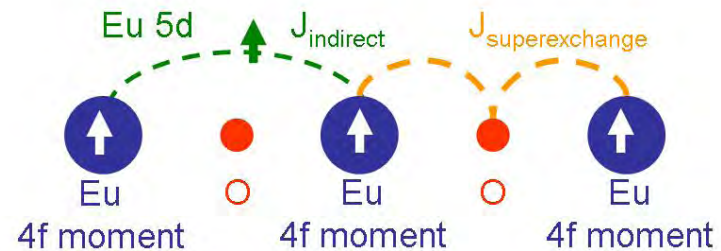
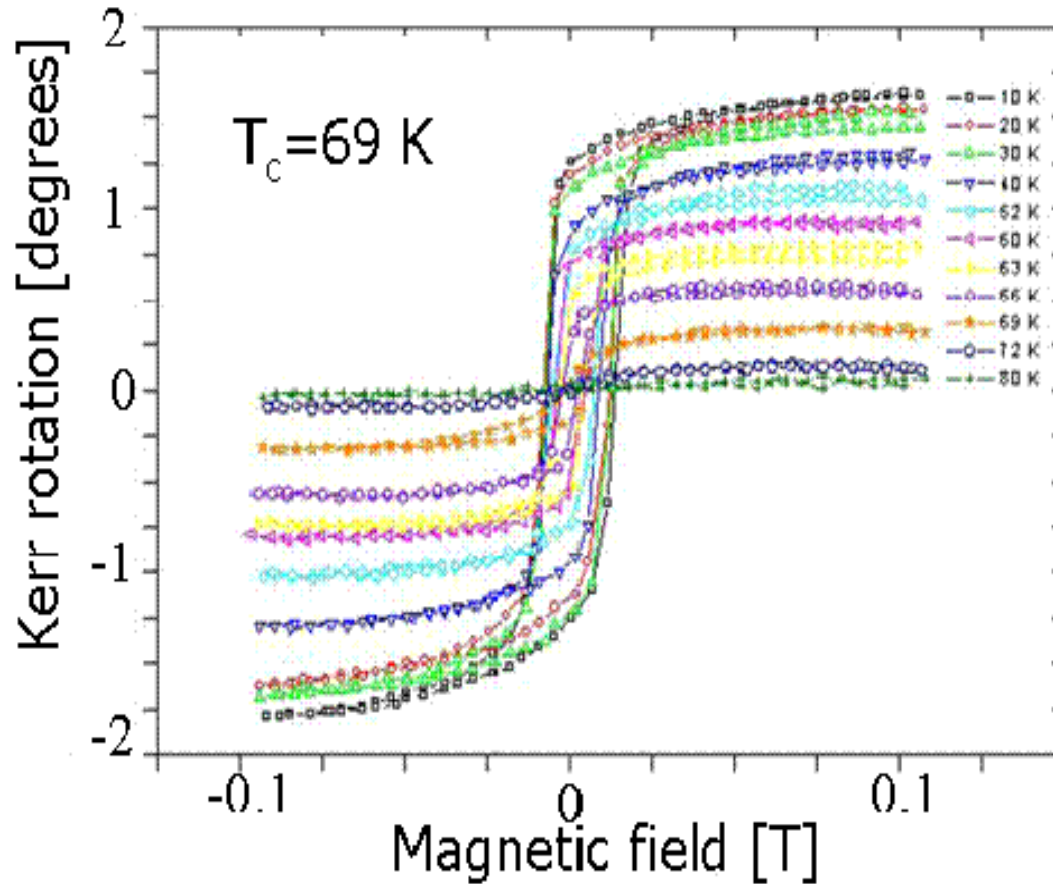


Photo doping  $\rightarrow$  Induce magnetism ?



# Magnetization dynamics in EuO

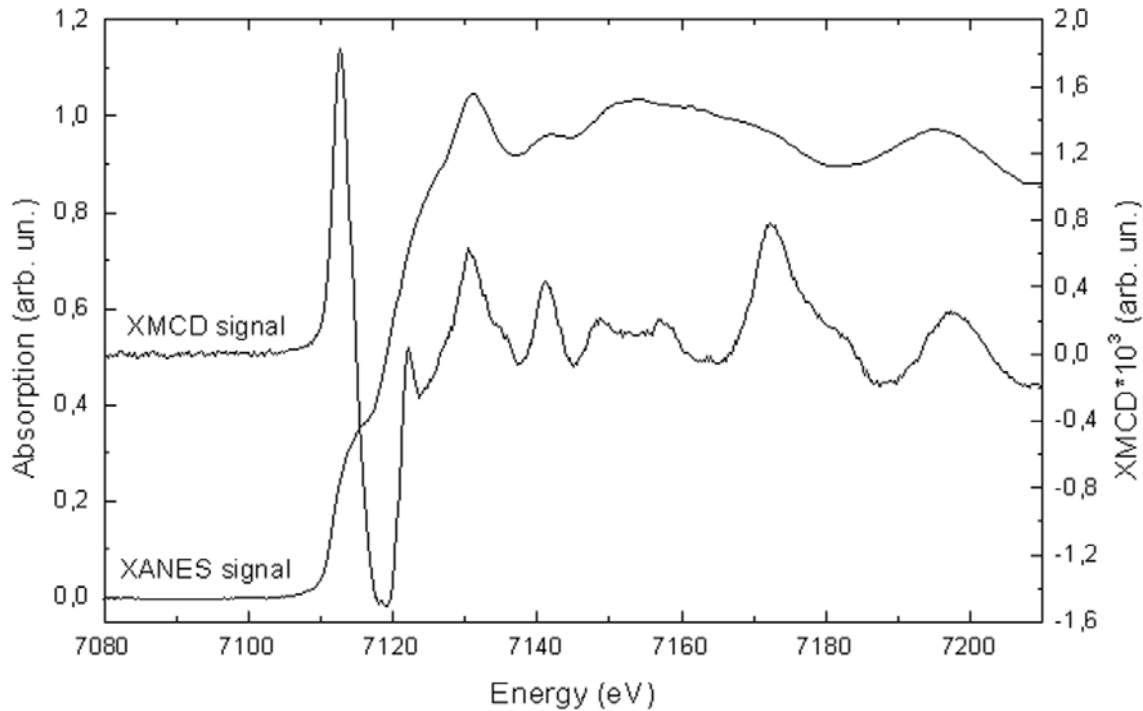
- Probing magnetism: MOKE



MOKE



# Fe K-edge XMCD



Main disadvantage: Small signal

Main advantage: Large penetration depth

# Relevant absorption edges

## PERIODIC TABLE OF THE ELEMENTS

<http://www.ktf-split.hr/periodni/en/>

PERIOD	GROUP I IA	GROUP IUPAC	GROUP CAS	RELATIVE ATOMIC MASS (1)	SYMBOL	ELEMENT NAME
1	1	IA	1	1.0079	H	HYDROGEN
2	3	IIA	2	6.941	Li	LITHIUM
2	4	IIA	2	9.0122	Be	BERYLLIUM
3	11	IIIA	13	22.990	Na	SODIUM
3	12	IIIA	13	24.305	Mg	MAGNESIUM
4	19	IVB	3	39.098	K	POTASSIUM
4	20	IVB	3	40.078	Ca	CALCIUM
4	21	VIB	4	44.956	Sc	SCANDIUM
4	22	VIB	4	47.867	Ti	TITANIUM
4	23	VIB	4	50.942	V	VANADIUM
4	24	VIB	4	51.996	Cr	CHROMIUM
4	25	VIB	4	54.938	Mn	MANGANESE
4	26	VIB	4	55.845	Fe	IRON
4	27	VIB	4	58.933	Co	COBALT
4	28	VIB	4	58.693	Ni	NICKEL
4	29	VIB	4	63.546	Cu	COPPER
4	30	VIB	4	65.39	Zn	ZINC
4	31	VIB	4	69.723	Ga	GALLIUM
4	32	VIB	4	72.64	Ge	GERMANIUM
4	33	VIB	4	74.922	As	ARSENIC
4	34	VIB	4	78.96	Se	SELENIUM
4	35	VIB	4	79.904	Br	BROMINE
4	36	VIB	4	83.80	Kr	KRYPTON
5	37	VIB	4	85.468	Rb	RUBIDIUM
5	38	VIB	4	87.62	Sr	STRONTIUM
5	39	VIB	4	88.906	Y	YTTORIUM
5	40	VIB	4	91.224	Zr	ZIRCONIUM
5	41	VIB	4	92.906	Nb	NIOBIUM
5	42	VIB	4	95.94	Mo	MOLYBDENUM
5	43	VIB	4	(98)	Tc	TECHNETIUM
5	44	VIB	4	101.07	Ru	RUTHENIUM
5	45	VIB	4	102.91	Rh	RHODIUM
5	46	VIB	4	106.42	Pd	PALLADIUM
5	47	VIB	4	107.87	Ag	SILVER
5	48	VIB	4	112.41	Cd	CADMIUM
5	49	VIB	4	114.82	In	INDIUM
5	50	VIB	4	118.71	Sn	TIN
5	51	VIB	4	121.76	Sb	ANTIMONY
5	52	VIB	4	127.60	Te	TELLURIUM
5	53	VIB	4	126.90	I	IODINE
5	54	VIB	4	131.29	Xe	XENON
6	55	VIB	4	132.91	Cs	CAESIUM
6	56	VIB	4	137.33	Ba	BARIUM
6	57-71	VIB	4	La-Lu	Lanthanide	
6	72	VIB	4	178.49	Hf	HAFNIUM
6	73	VIB	4	180.95	Ta	TANTALUM
6	74	VIB	4	183.84	W	TUNGSTEN
6	75	VIB	4	186.21	Re	RHENIUM
6	76	VIB	4	190.23	Os	OSMIUM
6	77	VIB	4	192.22	Ir	IRIDIUM
6	78	VIB	4	195.08	Pt	PLATINUM
6	79	VIB	4	196.97	Au	GOLD
6	80	VIB	4	200.59	Hg	MERCURY
6	81	VIB	4	204.38	Tl	THALLIUM
6	82	VIB	4	207.2	Pb	LEAD
6	83	VIB	4	208.98	Bi	BISMUTH
6	84	VIB	4	(209)	Po	POLONIUM
6	85	VIB	4	(210)	At	ASTATINE
6	86	VIB	4	(222)	Rn	RADON
7	87	VIB	4	(223)	Fr	FRANCIUM
7	88	VIB	4	(226)	Ra	RADIUM
7	89-103	VIB	4	Ac-Lr	Actinide	
7	104	VIB	4	(261)	Rf	RUTHERFORDIUM
7	105	VIB	4	(262)	Db	DUBNIUM
7	106	VIB	4	(266)	Sg	SEABORGIUM
7	107	VIB	4	(264)	Bh	BOHRIUM
7	108	VIB	4	(277)	Hs	HASSIUM
7	109	VIB	4	(268)	Mt	MEITNERIUM
7	110	VIB	4	(281)	Uuq	UNUNQUADIUM
7	111	VIB	4	(272)	Uuu	UNUNUNIUM
7	112	VIB	4	(285)	Uub	UNUNBIUM
7	114	VIB	4	(289)	Uuq	UNUNQUADIUM

K-edge 3-15 keV

L-edge 2-5 keV

L,M-edge 2-20 keV

Legend for element classification:

- Metal (Blue)
- Semimetal (Orange)
- Nonmetal (Green)
- Alkali metal (1)
- Alkaline earth metal (2)
- Transition metals (3-10)
- Lanthanide (Purple)
- Actinide (Pink)
- Chalcogens element (16)
- Halogens element (17)
- Noble gas (18)

STANDARD STATE (25 °C; 101 kPa):  
 Ne - gas, Fe - solid, Ga - liquid, Tc - synthetic

LANTHANIDE

57	138.91	58	140.12	59	140.91	60	144.24	61	(145)	62	150.36	63	151.96	64	157.25	65	158.93	66	162.50	67	164.93	68	167.26	69	168.93	70	173.04	71	174.97
La		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
LANTHANUM		CERIUM		PRASEODYMIUM		NEODYMIUM		PROMETHIUM		SAMARIUM		EUROPIUM		GADOLINIUM		TERBIUM		DYSPROSIUM		HOLMIUM		ERBIUM		THULIUM		YTTERIUM		LUTETIUM	

ACTINIDE

89	(227)	90	232.04	91	231.04	92	238.03	93	(237)	94	(244)	95	(243)	96	(247)	97	(247)	98	(251)	99	(252)	100	(257)	101	(258)	102	(259)	103	(262)
Ac		Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr	
ACTINIUM		THORIUM		PROTACTINIUM		URANIUM		NEPTUNIUM		PLUTONIUM		AMERICIUM		CURIUM		BERKELIUM		CALIFORNIUM		EINSTEINIUM		FERMIUM		MENDELEVIUM		NOBELIUM		LAWRENCIUM	

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)  
 Relative atomic mass is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.  
 However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netlink.com)



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[http://www.astro.virginia.edu/class/oconnell/astr121/im/periodic\\_table.gif](http://www.astro.virginia.edu/class/oconnell/astr121/im/periodic_table.gif)

# *Frustration in metamagnetic compounds*

## **The metamagnetic staircase of $\text{CuFeO}_2$**

### **Geometrical spin frustration:**

**'Personal' goal:** satisfy antiferromagnetic exchange interactions

**Obstructions:** competing exchange interactions with neighboring spins

**Emotional response:** anomalous magnetic behavior



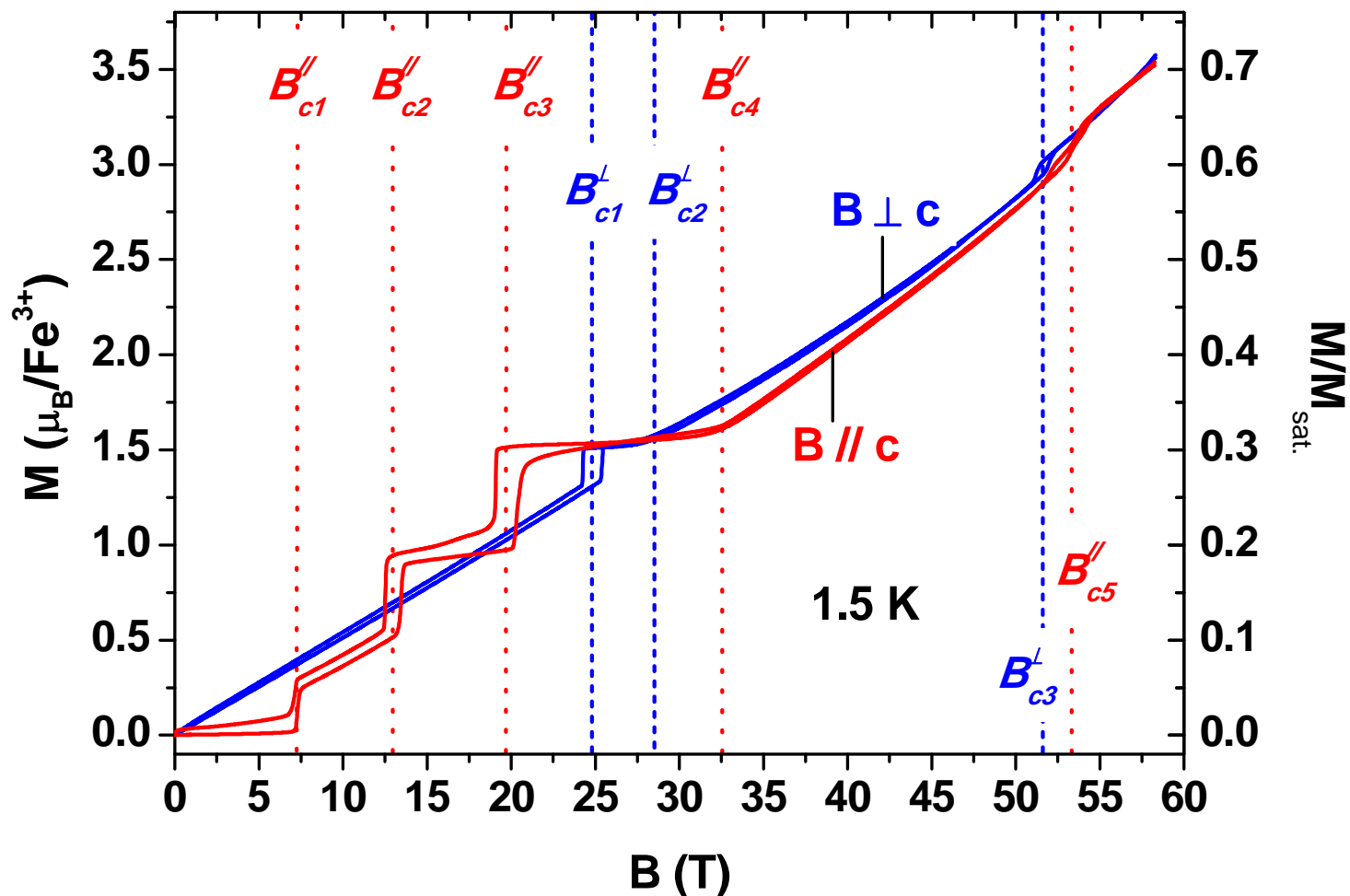
Frustration is an emotional response to circumstances where one is obstructed from arriving at a personal goal.





# Frustration in metamagnetic compounds

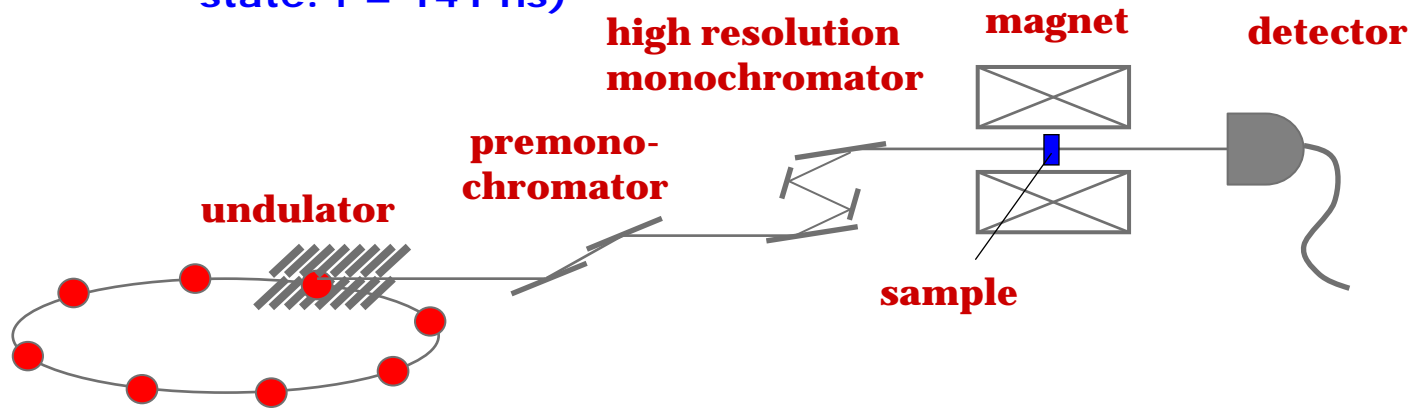
## The metamagnetic staircase of $\text{CuFeO}_2$



# Nuclear Forward Scattering in pulsed fields

## ➤ Time-based analogue of Mössbauer spectroscopy

- resonantly excite  $^{57}\text{Fe}$  nuclei with pulses of synchrotron radiation ( $\sim 100$  ps, 14.4 keV, 56.8 MHz)
- observe real-time  $\gamma$ -decay in the empty 176 ns time window ( $^{57}\text{Fe}$  excited state:  $\tau = 141$  ns)



**ESRF in 16-bunch mode**

- sample environment for extreme conditions possible (due to “laser beam-like” properties):
  - High-pressure measurements, very small samples, high magnetic fields (focusing power, intensity, source level-splitting in conventional Mössbauer)

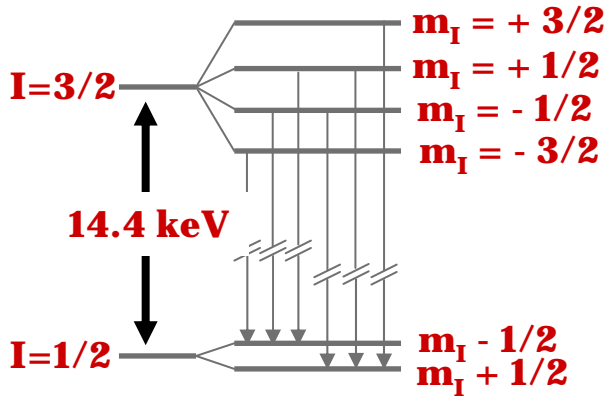


**ESRF, Grenoble**

# Nuclear Forward Scattering in pulsed fields

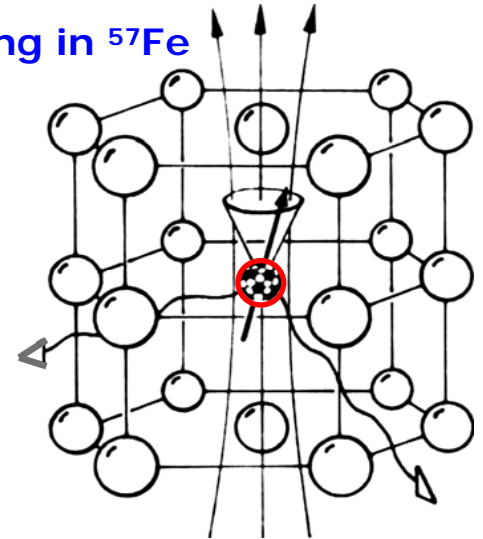
## ➤ Time-based analogue of Mössbauer spectroscopy

- probe the local magnetic field through hyperfine splitting in  $^{57}\text{Fe}$



Splitting dependent on:

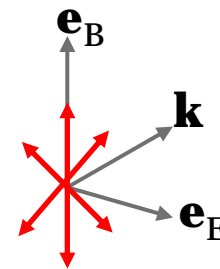
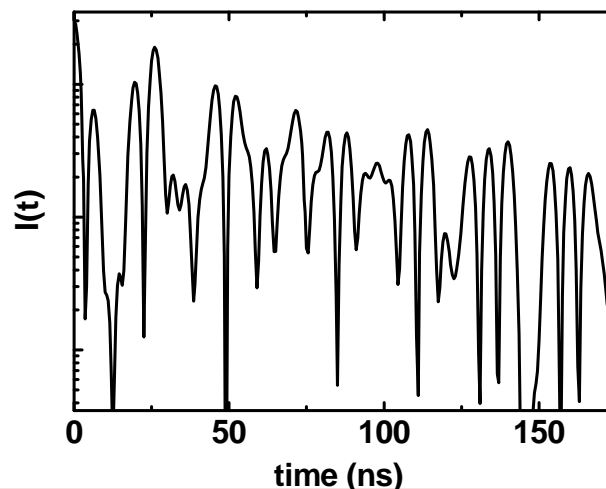
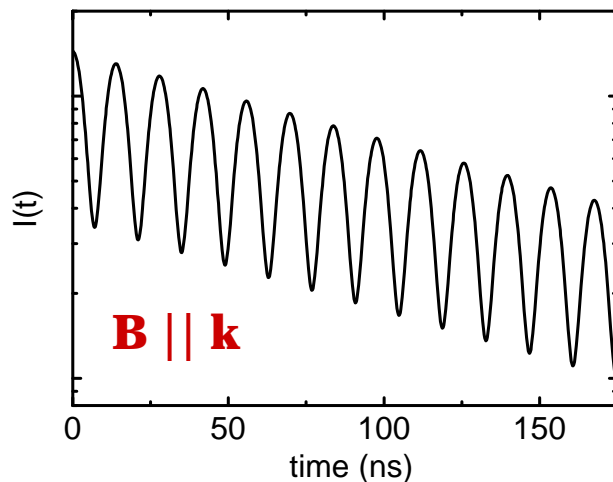
- local electric field (isomer shift)
- local magnetic field (level splitting)
- local electric field gradient (level splitting)
- local spin-direction



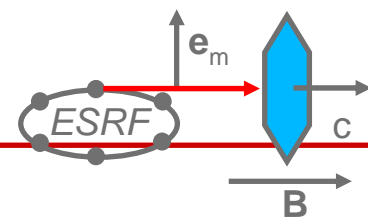
Schatz & Weidinger, ISBN 0-471-95479-9

exponential decay + beat frequency

distribution of spins

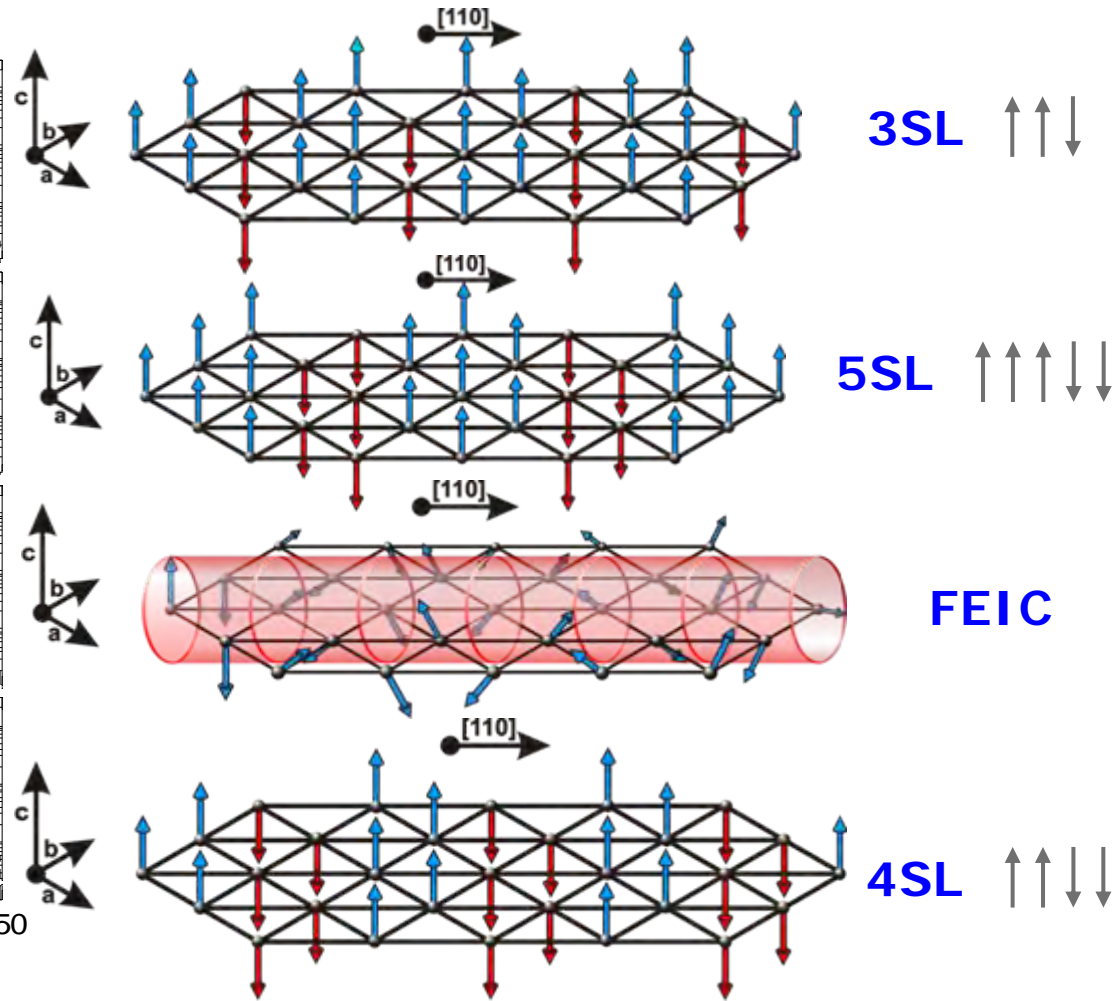
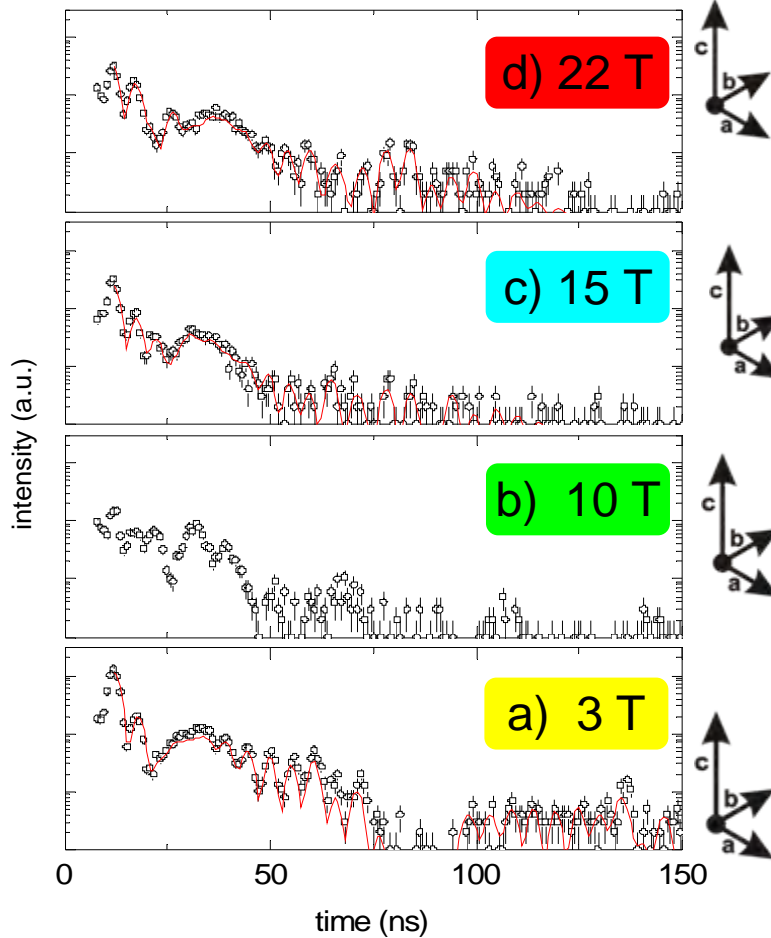


# NFS in pulsed fields: $B // c$



Lines: fits based on corresponding collinear models, 4SL, 5SL and 3SL

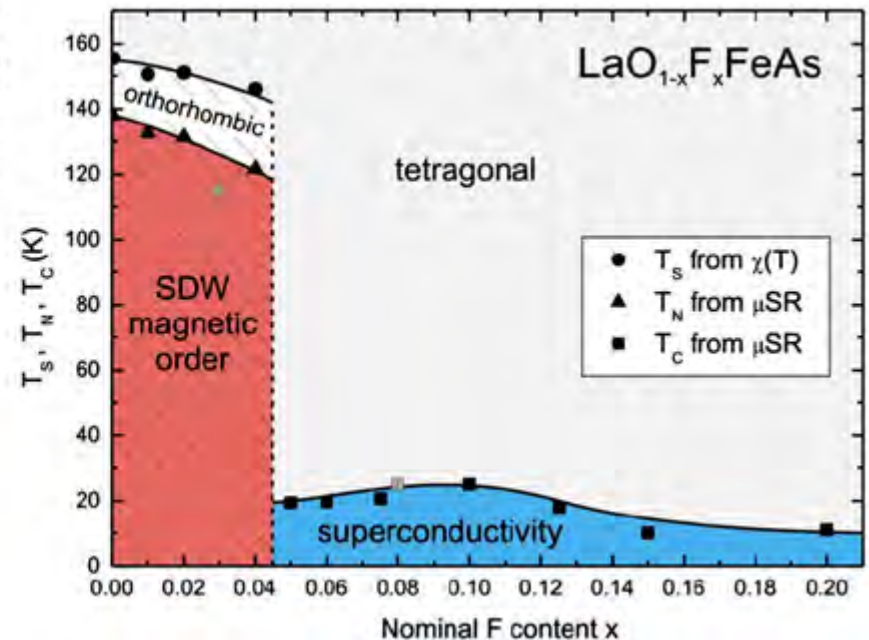
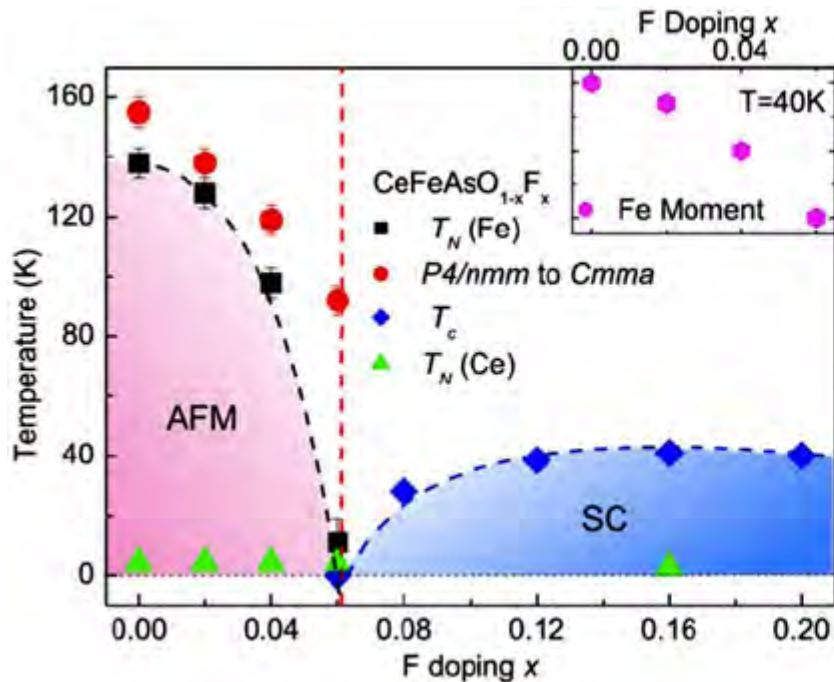
## NFS timespectra



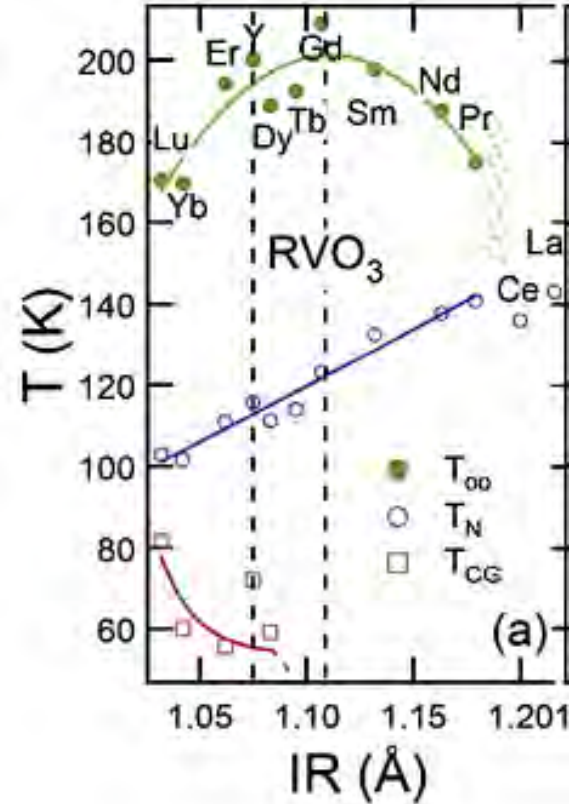
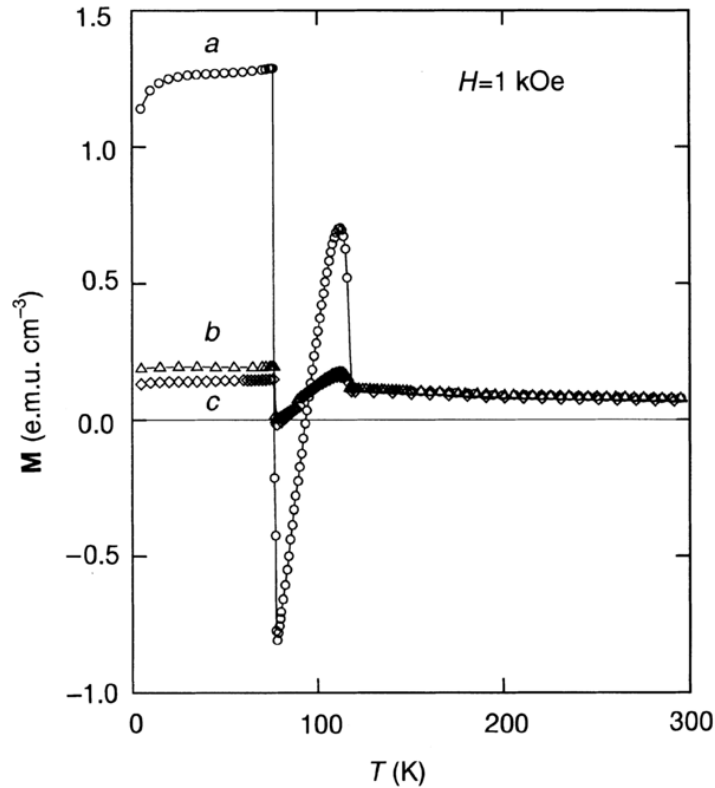
- › Counting statistics!
- › Interplay between Spin & Lattice order
- › Exotic spin structures
  
- › High field phases
  - TR-Xray in pulsed fields up to 100 T (easy up to 30T)
    - Structure evolution with field → anisotropy
  - Time domain Mössbauer in pulsed fields
    - Magnetic structure (polarized light, resonant diffr.)
    - small samples, extreme conditions (B,P,T)
  
- › LIESST compounds, magnetic switching,...
- › Non Iron compounds

# Iron Pnictide superconductors

Magnetic ordering at low doping  
Interplay between magnetism and superconductivity



# Spin & Orbital melting in YVO3



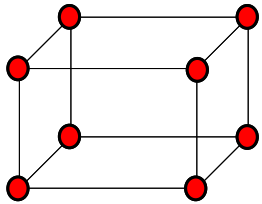
Ren et al, Nature **396**, 441 (1998)

Yan et al., PRL **99**, 197201 (2007)

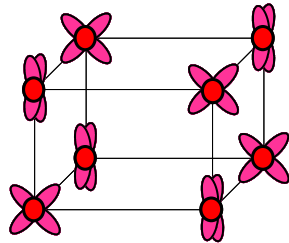


# Spin & Orbital melting in YVO3

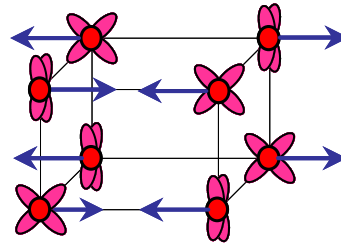
Spins disordered  
Orbitals disordered  
 $T > 196 \text{ K}$



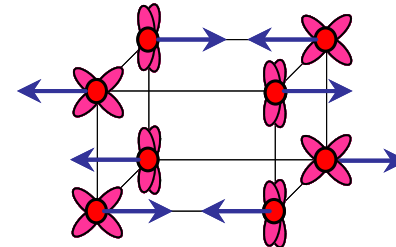
Spins disordered  
Orbitals G-ordered  
 $196 \text{ K} > T > 116 \text{ K}$



Spins C-ordered  
Orbitals G-ordered  
 $116 \text{ K} > T > 77 \text{ K}$



Spins G-ordered  
Orbitals C-ordered  
 $T < 77 \text{ K}$



Thermally induced transitions

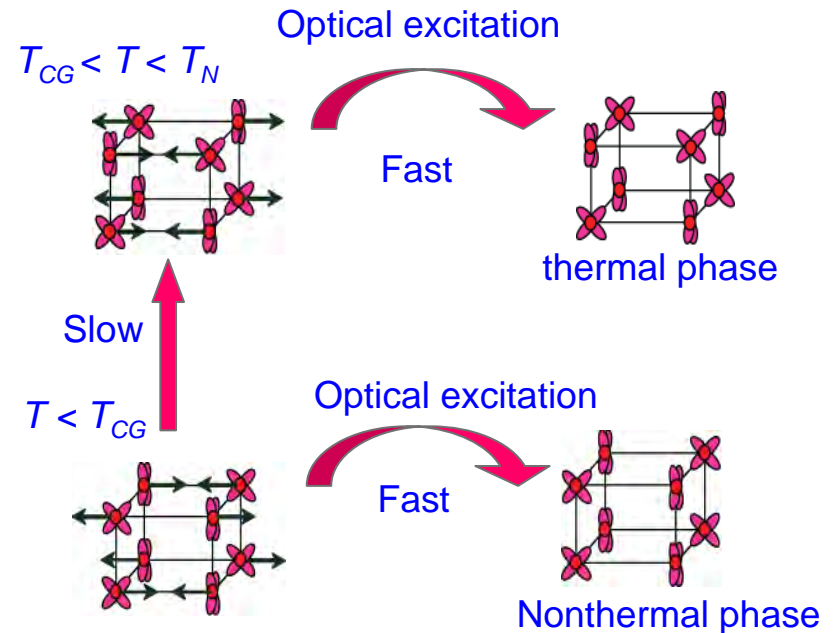
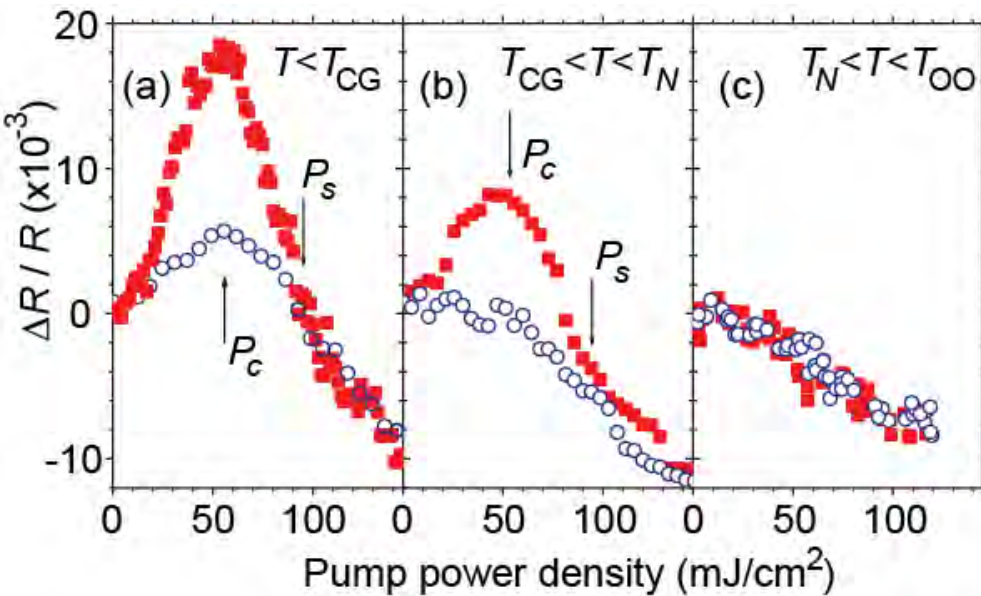
## Optically induced transitions ?

- How fast can it be done (current technology  $> 1 \text{ ns}$ )
- What are the restrictions
- Can one induce novel phases



# Melting spin order

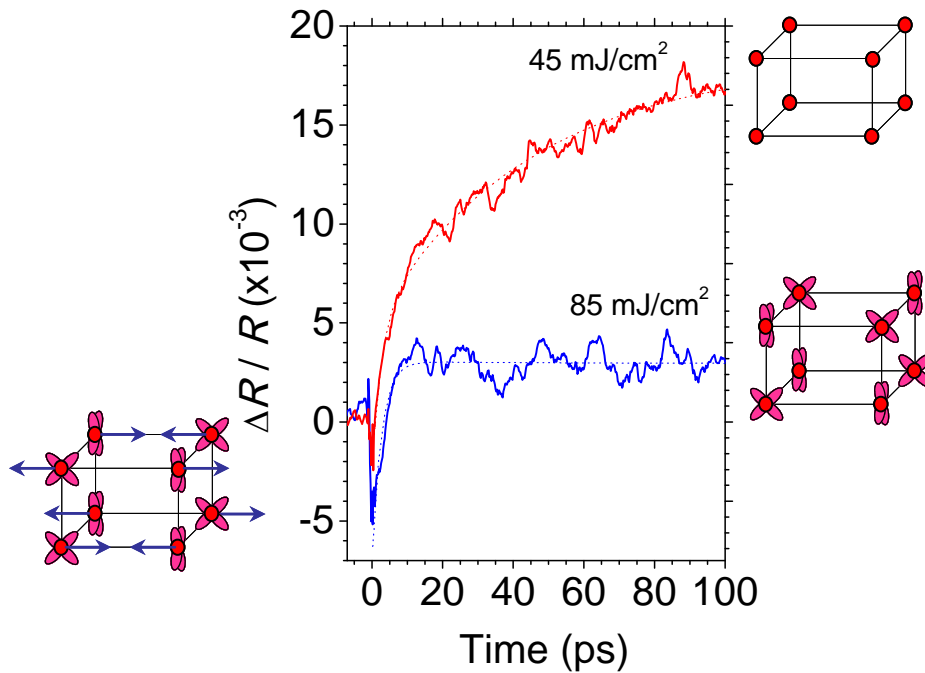
Time resolved reflectivity



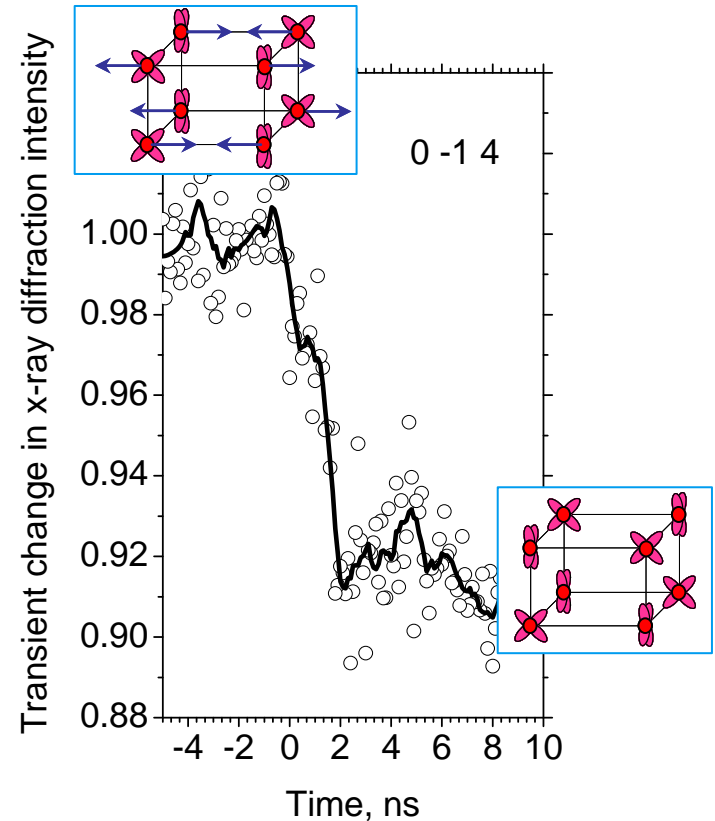
- Melting of spin order within 3 ps
- Phase transition to a non-thermal phase
- Transitions only fast when going to higher symmetry

# Melting orbital order

## TR-Optics

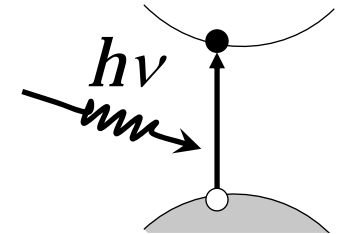


## TR-Xray

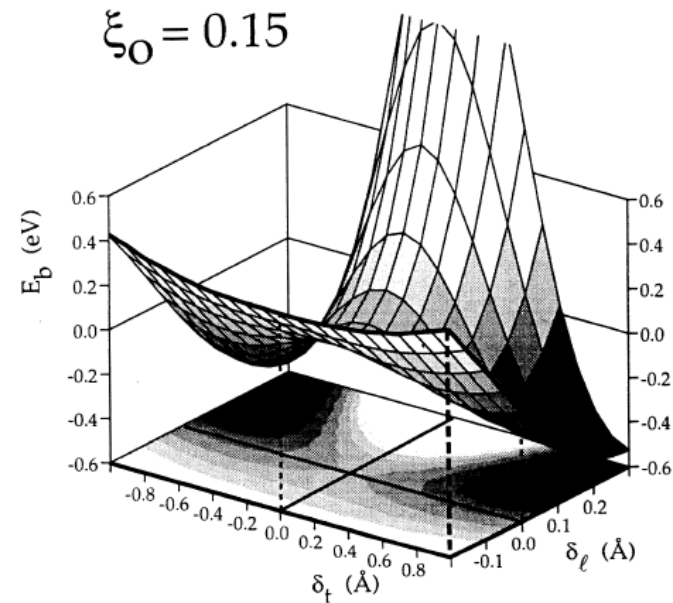
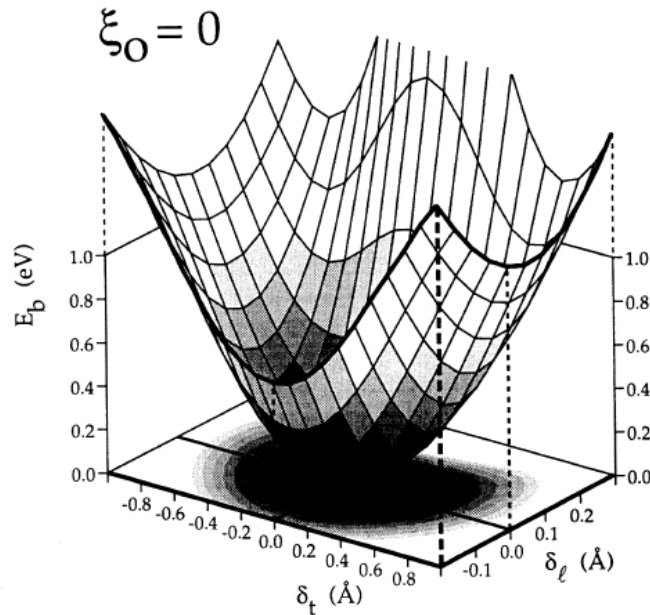


- > Spin melting
  - Ultrafast quenching of the magnetic order
    - XMCD is a more direct probe than TR-MOKE, far less problems with data interpretation
  
- > Orbital melting
  - ‘Slow’ process (>10-100 ps)
  - TR diffraction: indirect through lattice
  - TR resonant diffraction to more directly probe the orbital order.

# Jones-Peierls transition in the A7's

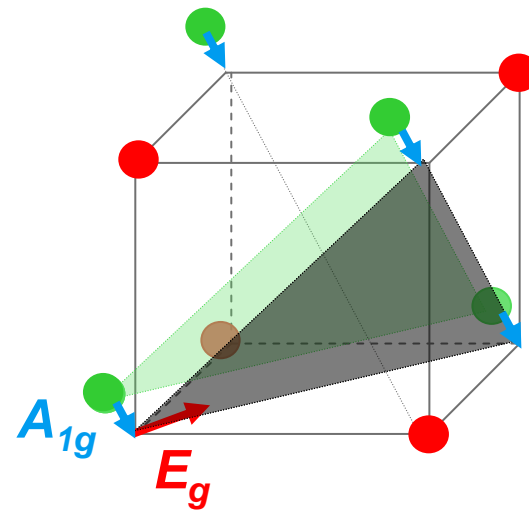
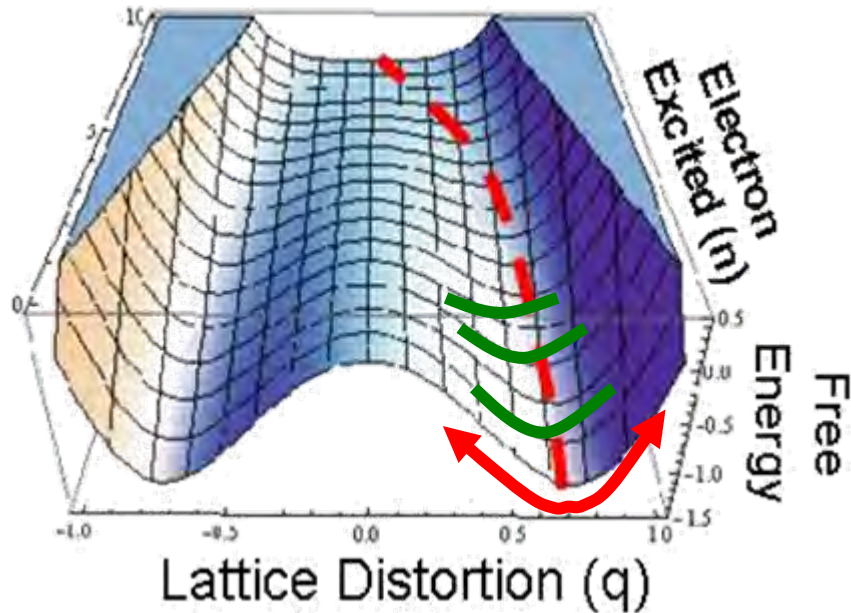


Charge excitation driven instability in GaAs and Si



# Jones-Peierls transition in the A7's

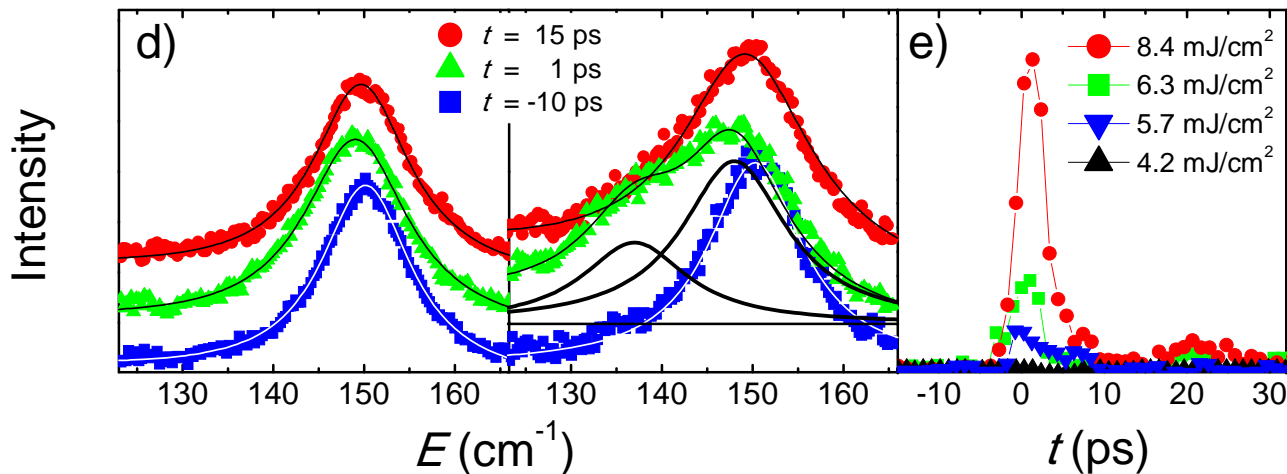
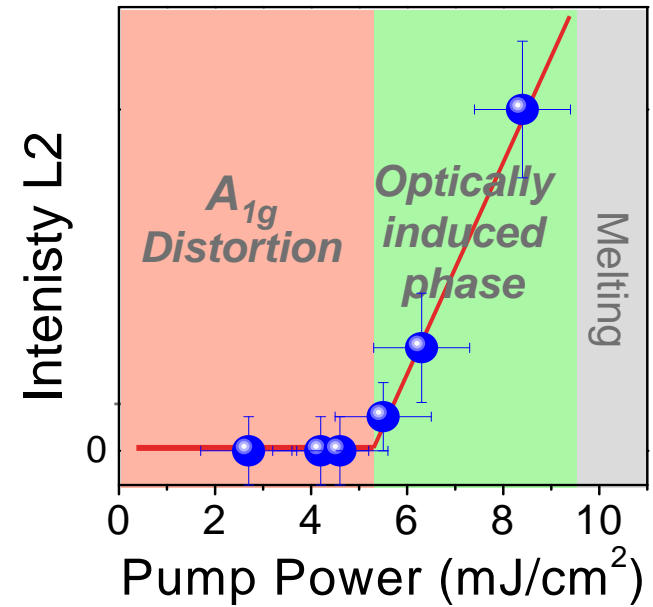
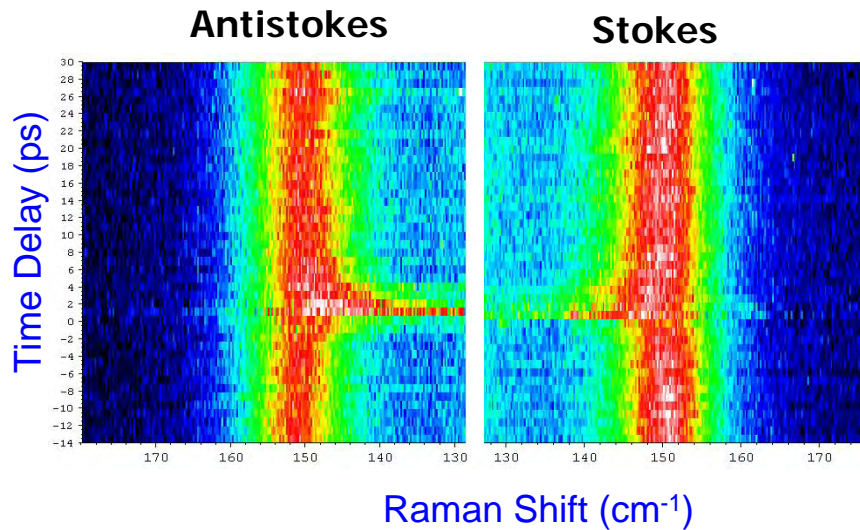
Charge excitation driven instability in the A7 semimetals



(111) Distorted from cubic



# Jones-Peierls transition in the A7's



- › Interplay between charge & lattice order
- › Full melting
  - TR-PES → Disappearance of peierls condensed state
  - TR-Xray → Structural dynamics
- › Induced structural phase transition
  - TR-PES → Nature of the new state
  - TR-Xray → Nature of the new state

- > Selective excitation
- > Novel states of matter
- > Detailed probing of physical properties of induced phenomena/novel states
- > Time scale vs degree of freedom
- > New techniques become feasible
  - Polarized time domain Mossbauer
  - Mossbauer diffraction??
  - 2 dimensional spectroscopy??
  - High magnetic fields and other extreme conditions more easy



# ***Acknowledgements***

- › **Dmitry Mazurenko**
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- › **Tom Lummen**
- › **Michiel Donker**
- › **Graeme Blake**
  
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- › **Eric Landahl (Argonne-APS)**
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- › **Hermann Durr (BESSY)**
- › **Hao Tjeng (Koln)**
- › **Simone Altendorf (Koln)**



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***Thank you***

***Open Ass. Prof. Position on T-Xray science: contact me***



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