Timing Needs for Nuclear Resonant Spectroscopy

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XSD-APS-ANL

Workshop on new science opportunities provided by a multi-bend achromat lattice at the APS

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We acknowledge & thank our "USERS" for their creativity & support

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6	R. Scheidt	University of Notre Dame	Chemistry
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9	J. Lie	University of Michigan	Geophysics
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16	B. Roldan Cuenaya	Central Florida University	Materials Science
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23	B. Fultz	California Institute of Technology	Materials Science
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26	J. Tse	University of Saskatchewan	Physics
27	F. Weber	Karlsruhe Institute of Technology	Physics
28	S. Couet	Katholike Universitat Leuven	Physics
29	M. Greven	University of Minnesota	Physics
30	D. Reznik	University of Colorado	Physics
31	D. Farber	Lawerence Livermore Nat.Lab	Physics
32	P. Abbamonte	UIUC	Physics
33	Z. Hasan	Princeton	Physics
34	J. Hill	BNL	Physics
35	A. Walters	University College London	Physics

Timing needs for nuclear resonant scattering

1) Spectral flux per pulse needs to be maximized.

2) There should be “adequate” time, i.e. one or preferably two lifetime between two consecutive bunches.

3) Bunch purity should be at the level of 10^{-10}.

4) Adjacent buckets to the main bucket should be clean at the same level.

5) Keep the current bunch structure of 24 bunches, introducing new injection components to clean up the adjacent buckets.

6) Introducing “beam scrapers” to address impurity issues developed during top-up.

- **One little request** - $\sigma_{y'}$ (MBA) < $\sigma_{y'}$(APS) to preserve beamline optic efficiency

- **One more little request - GIVE US 12. 5 m long straight section (why not ?..)**

Scientific scope of nuclear resonant scattering

1) Measurement of hyperfine interaction parameters to extract valence and spin state, local atomic symmetry, and magnetization
2) Measurement of thermodynamic and elastic properties of wide range of materials through the measurement of phonon excitation spectrum (NRVS).

- **materials of current technological interest**:
  - energy storage and conversion : Li-ion battery, skutterudites, clathrates, pnictides, multiferroics
- **proteins, enyzmes¨**
  - mechanism of metabolic and catalytic reactions
  - porphyrins, cubanes, bioinorganic mimics
- **minerals**:
  - crust, mantle, outer core, inner core
  - sound velocity, spin state, shear modulus under extreme conditions
- **nanomaterials**,
  - nanocatalysts, semiconductors, superconductors
- **thin layers, multilayers**
  - buried layers, interfaces, wedges, terraces, magnetism & superconductivity

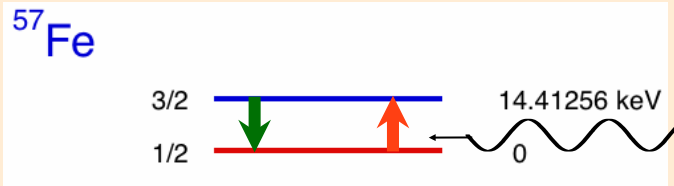
Mössbauer transitions in the periodic table

Periodic table of Mössbauer active elements [hide]

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Mössbauer-active elements | Gamma-ray sources | Unsuitable for Mössbauer

Transitions to ground state with a relatively low energy is what makes a nuclei a Mössbauer nuclei, because there is a finite probability of recoil-free absorption and emission



Argonne National Laboratory campus

Nuclear Resonances excited with synchrotron radiation

	Isotope	Energy (keV)	Lifetime (ns)
1	^{181}Ta	6.2155	14138
2	^{169}Tm	8.4013	5.77
3	^{83}Kr	9.4035	212
4	**^{57}Fe**	**14.4125**	**141.1**
5	^{151}Eu	21.5414	13.99
6	^{149}Sm	22.496	10.2
7	^{119}Sn	23.8794	25.67
8	^{161}Dy	25.6514	40.68
9	^{201}Hg	26.2738	0.91
10	^{129}I	27.770	24.2
11	^{40}K	29.834	6.13
12	^{125}Te	35.460	2.06
13	^{121}Sb	37.129	6.5
14	^{61}Ni	67.419	7.35
15	^{73}Ge	68.752	2.68

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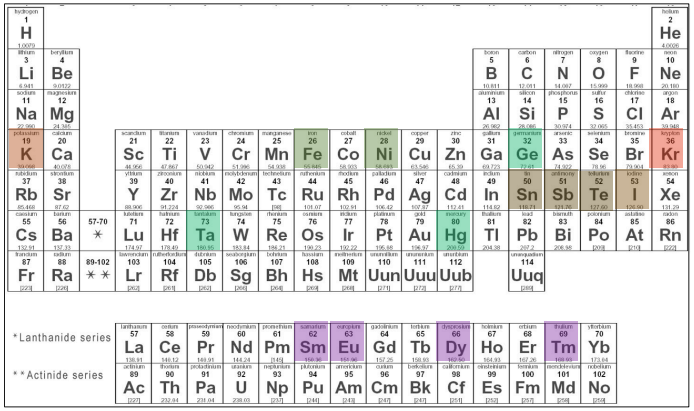
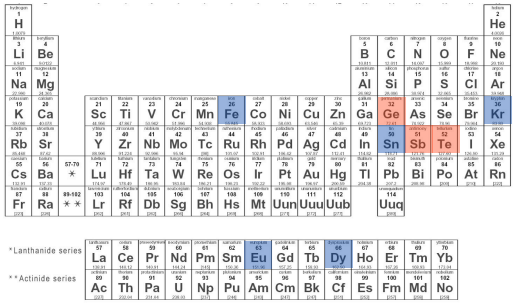
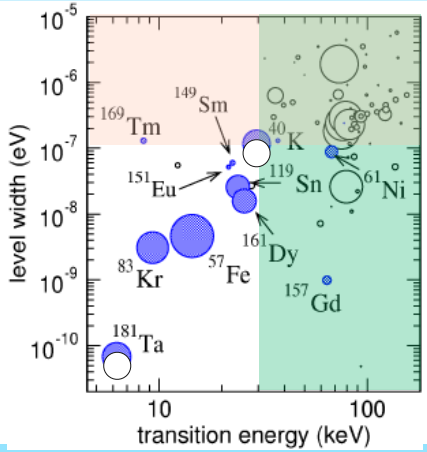


Why limited number of isotopes ?

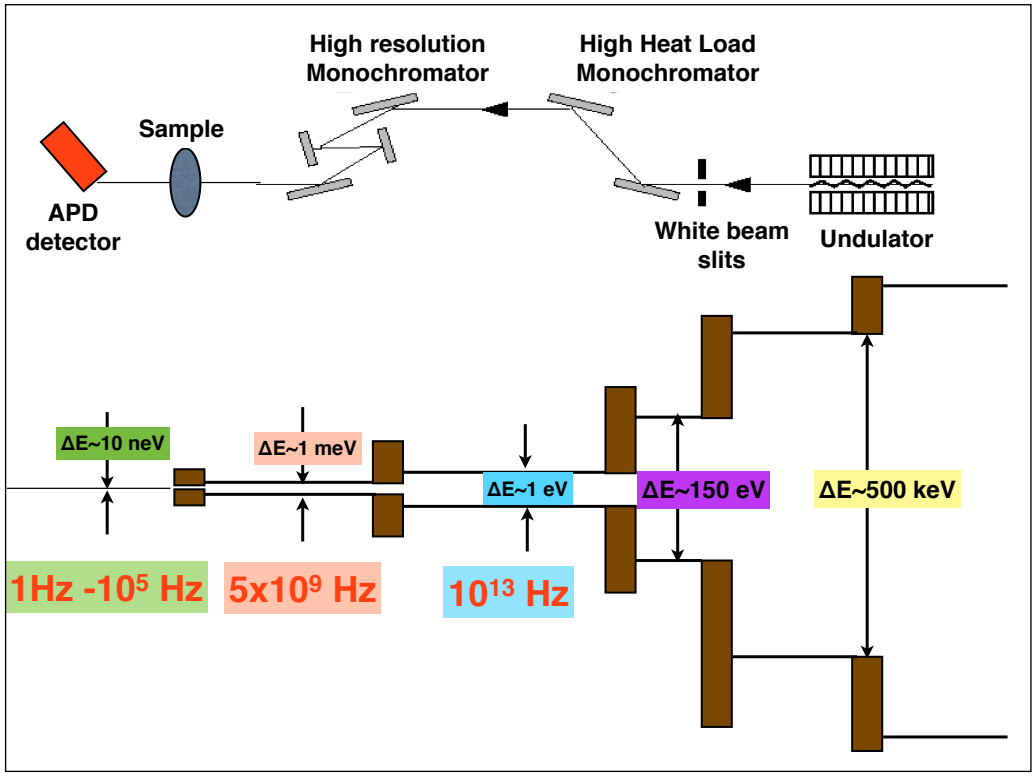
Absorption **cross-section**, nuclear **life time**, and **resonance energy** must be suitable for a General User program with wide applicability



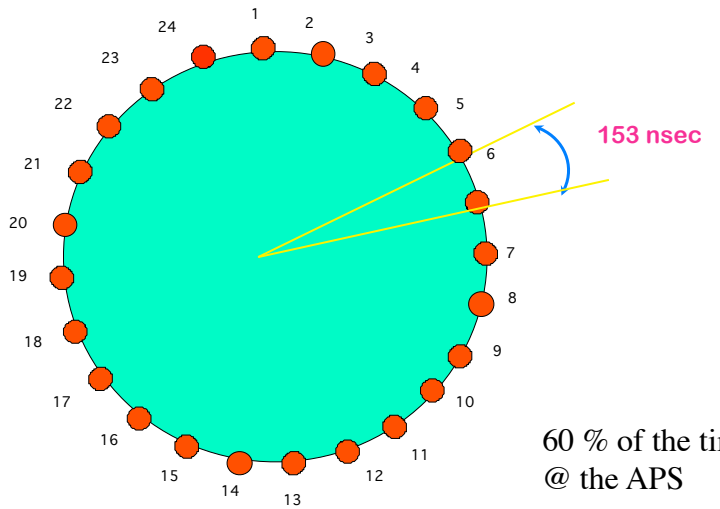


- With **Fe** (3d-element), **Sn,** (semi-metal), **Eu** and **Dy** (Rare earth), and **Kr** (Noble element) a diverse scientific program has already been created.

- Sb, Te, and Ge can be added in the future, if new resources, and undulators become available..


High resolution Monochromator
High Heat Load Monochromator
Sample
APD detector
White beam slits
Undulator
ΔE~10 neV
ΔE~1 meV
ΔE~1 eV
ΔE~150 eV
ΔE~500 keV
1Hz -10^5 Hz
5x10^9 Hz
10^13 Hz

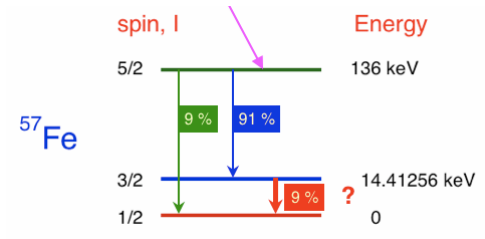
Standard Time structure @ APS

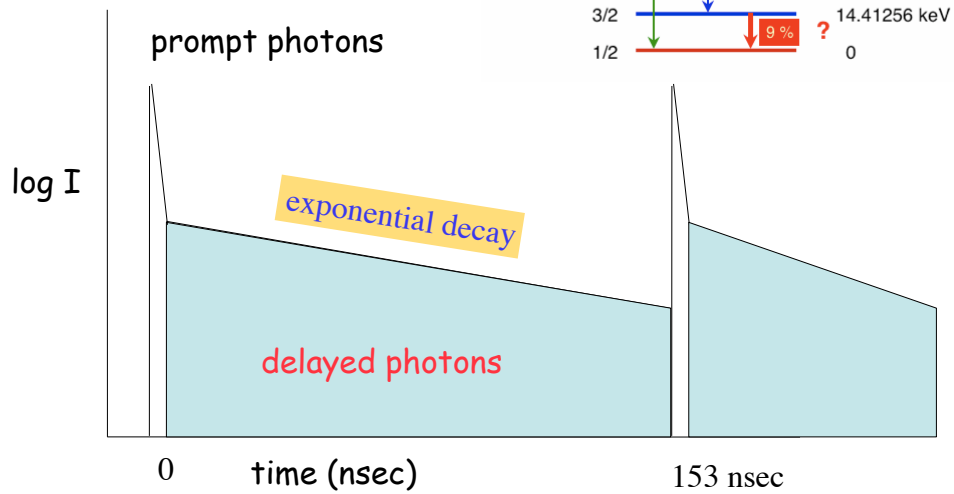


60 % of the time
@ the APS

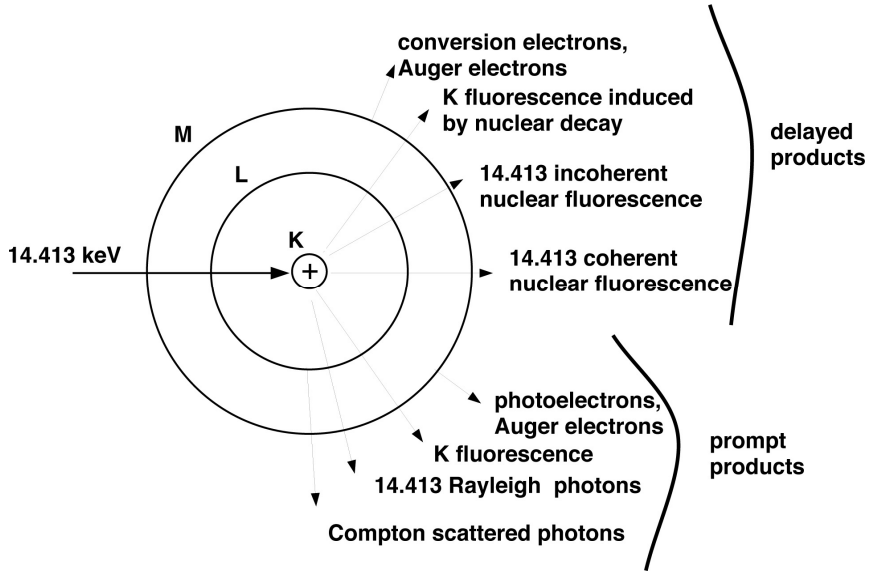
1 revolution=3.68 μsec =>1296 buckets

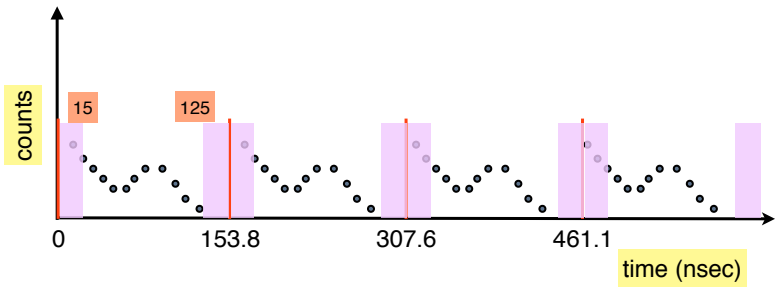
Detection of nuclear decay

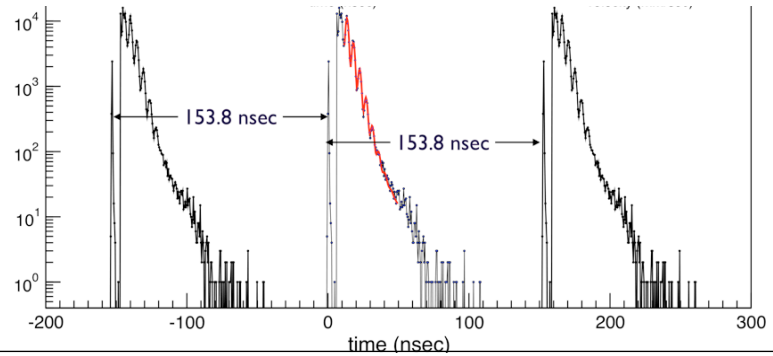




Decay channels in Nuclear Resonance of ^{57}Fe




counts
15
125
0
153.8
307.6
461.1
time (nsec)


153.8 nsec
153.8 nsec
-200
-100
0
100
200
300
time (nsec)

The basic difficulty of the Mössbauer experiments at a synchrotron

- Synchrotron is a pulsed source +
  - There is 10^6-10^7 photons/pulse/eV in 0.1 nsec

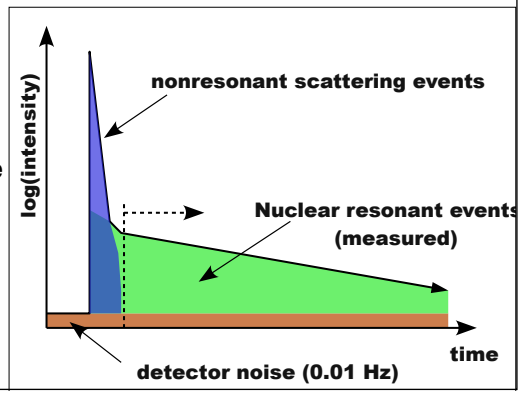
- With crystal monochromators, you can reduce the bandwidth to "acceptable" levels +

- There is a "cost" to monochromatization - (5-50 %) -

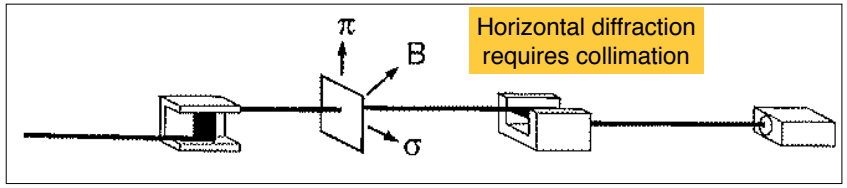
- Resonant/non-resonant ratio is still very large ; 1-to-10^8
  Resonant count rate : 10^{-2}-10^{-1} ph/pulse, 10^4-10^5 ph/sec

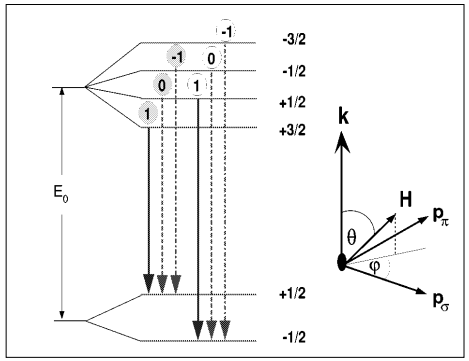
- Currently, no efficient photon pulse detector with nanosecond time resolution with a dynamic range of 10^{10}

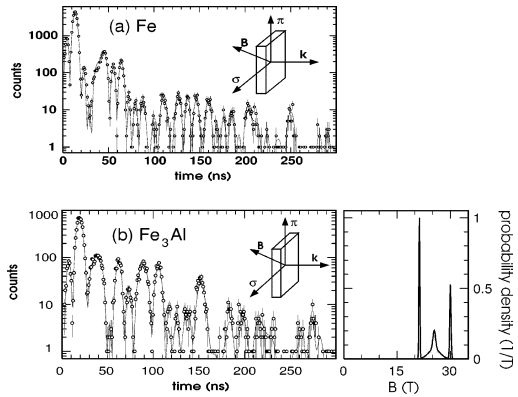
- Many strategies are developed to mitigate "prompt" signal issue.



Mitigating the prompt: Polarizer/Analyzer optics







Managing the "Prompt"

- Developed Strategies
  - Pure nuclear reflections & artificially layered systems
    - *requires sample with very specific properties*
  - Nuclear Lighthouse Effect
    - *requires sample to spin at a million rpm*
  - Crossed polaroids
    - *requires optically active sample*
  - High-resolution Monochromator (HRM)
    - *bandwidth reduction ⇨ prompt reduction*

- Excellent prompt suppression
- Very difficult to implement focusing optics
- Easy access to early times
- Only transmits σ → π scattering channel

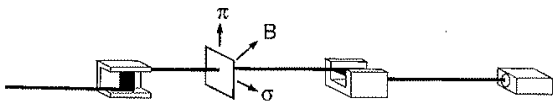
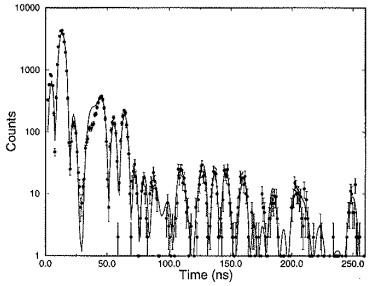


FIG. 1. Experimental setup of the polarizer, Fe foil with magnetic field (B), analyzer, and detector.



from T.S. Toellner et al., Applied Phys. Lett.., ***67*** *1993-4 (1995)*

Polarizer/Analyzer optics: Is it "universal" ?

Table 2
Performance characteristics of channel-cut polarizers using $\Theta_B \approx 45°$ Bragg reflections in silicon/germanium at selected Mössbauer transition energies.

Isotope	Energy (keV)	$\tau_{1/2}$ (ns)	Crystal reflection	Θ_B (deg.)	$\Delta\theta^a$ (μrad)	$\int R_\sigma^2 \, d\theta$ (μrad)	δ_o
^{181}Ta	6.215	6800	Si(4 0 0)	47.28	142.0	59.8	5.5×10^{-4}
			Ge(4 0 0)	44.88	318.0	126.2	4.8×10^{-9}
^{169}Tm	8.410	4.0	Si(3 3 3)	44.85	44.4	19.0	1.2×10^{-8}
^{83}Kr	9.410	147	Si(5 3 1)	45.86	31.2	14.1	1.5×10^{-5}
^{57}Fe	14.413	97.8	Si(8 4 0)	45.10	10.2	6.1	1.0×10^{-8}
^{151}Eu	21.532	9.7	Ge(8 8 8)	44.87	0.78	0.15	1.7×10^{-9}
			Si(12 4 4)	44.69	0.31	0.26	9.1×10^{-6}
^{149}Sm	22.494	7.1	Ge(11 9 3)	45.07	0.55	0.05	6.0×10^{-11}
			Si(8 8 8)	44.68	0.25	0.21	9.7×10^{-6}
^{119}Sn	23.878	17.8	Ge(15 3 1)	44.73	0.35	0.03	1.6×10^{-8}
			Si(12 6 6)	44.63	0.19	0.16	1.5×10^{-5}

Mitigating the prompt: Fast shutter

Synchrotron Mössbauer spectroscopy using high-speed shutters

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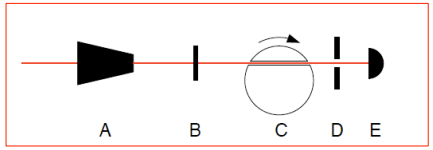
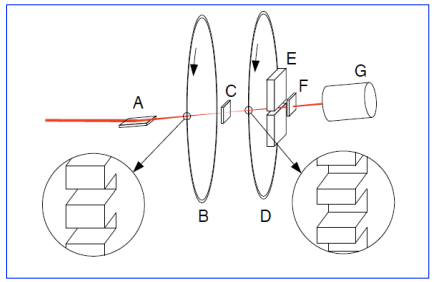
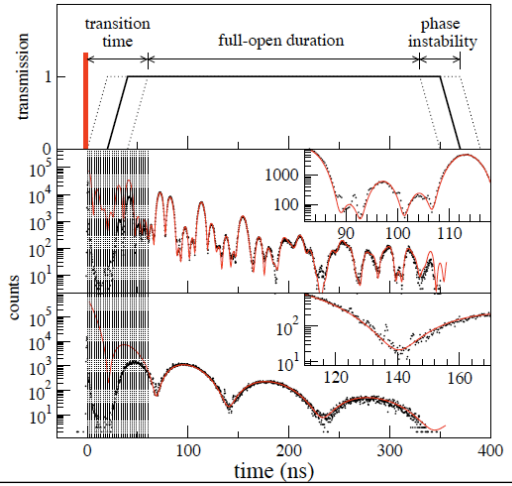
G. Shenoy[a] and W. Sturhahn[a]†

J. Synchrotron Radiation (2010)



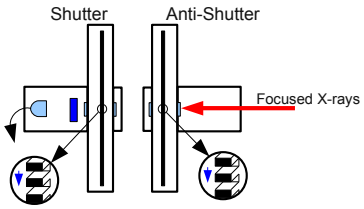


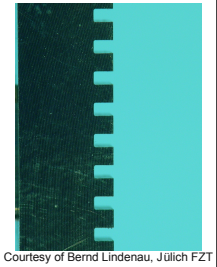


High-Speed Shutter System for Hybrid Fill Mode

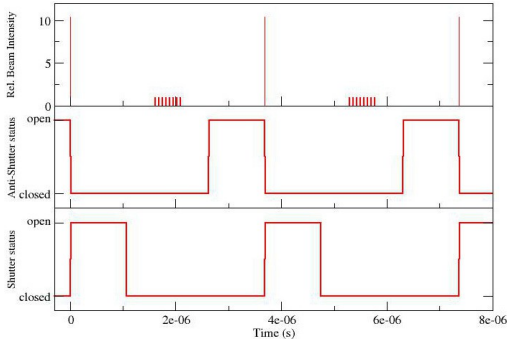
- *X-ray flux = 10^{14} ph/s (average incident X-ray power = 0.23 W)*
- *X-ray beam size = 10 µm (V) x <2000 µm (H)*
- Rep. rate of transmission window = 271554 Hz
- Transmission window width = 1.2 ± 0.1 µs

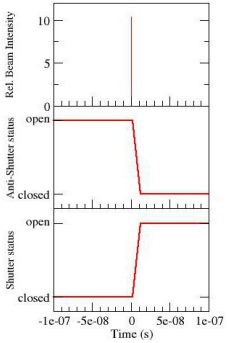
Side View





Courtesy of Bernd Lindenau, Jülich FZT



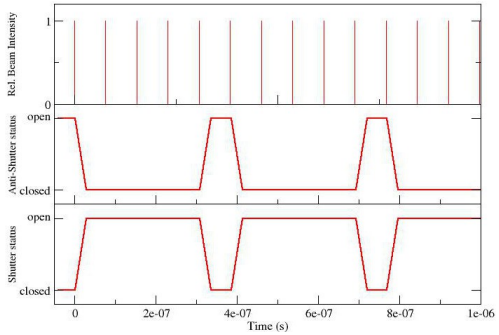


- *Shutter must transition from full close to full open as fast as possible (< 15ns) and with excellent periodicity (instability of start of transmission window < 10 ns)*

T. Toellner (under procurement)

High-Speed Shutter System for MBA 48-bunch Mode

- NRS needs adequate “dark time” between pulses to register time spectra (^{57}Fe lifetime = 141 ns)
- Difficult to manufacture high rep. rate shutter with ns transmission-window-stability
- Perhaps can use 20% of X-ray pulses (in 48-bunch mode)
  - 2.6 MHz shutter
  - Technology limited



- 48-bunch mode
  - 76.72 ns period
  - 4.2 mA per bunch
- Anti-Shutter rejects 4 out of 5 pulses
  - Notch density ≈ 3.74 mm^{-1} (2880 notches)
  - Notch width ≈ 40 um
- Shutter
  - 280 ns transmission window duration
  - Notch density ≈ 3.74 mm^{-1}
  - Notch width ≈ 207 um (60 um teeth)

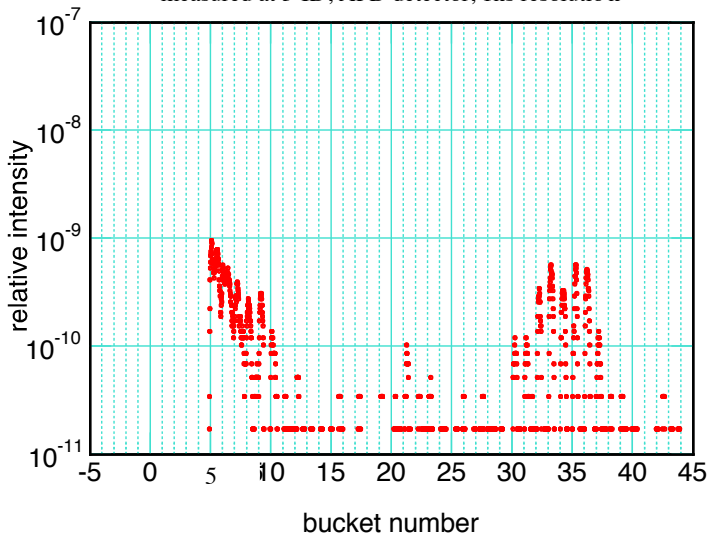
NB. assumes 245mm disk at 700m/s

T. Toellner (under procurement)

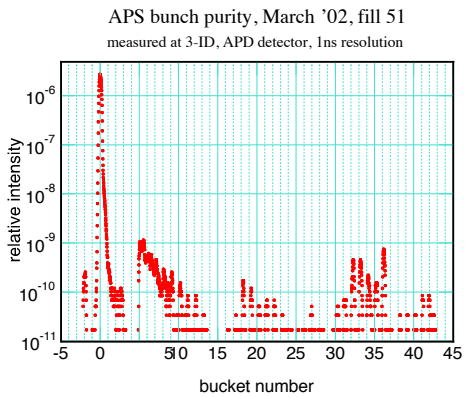
Bunch Purity

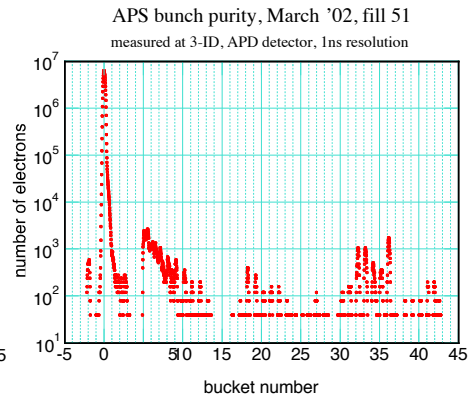
APS bunch purity, March '02, fill 52

measured at 3-ID, APD detector, 1ns resolution



How many electrons can we actually see ?





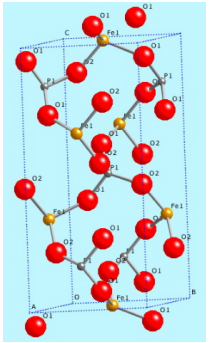
1 Ampere = 1 Coulomb/sec = $6.24 \cdot 10^{18}$ electron/sec

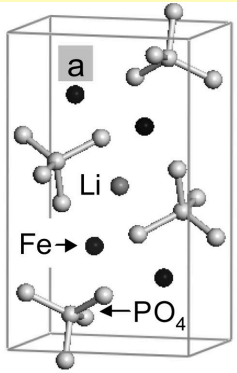
1 bunch at 5 mA has $1.15 \cdot 10^{11}$ electrons

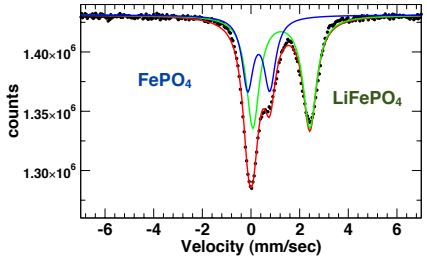
Photon flux = 10^{10} Hz/1meV, i.e $5 \cdot 10^{8}$ Hz/bunch/meV

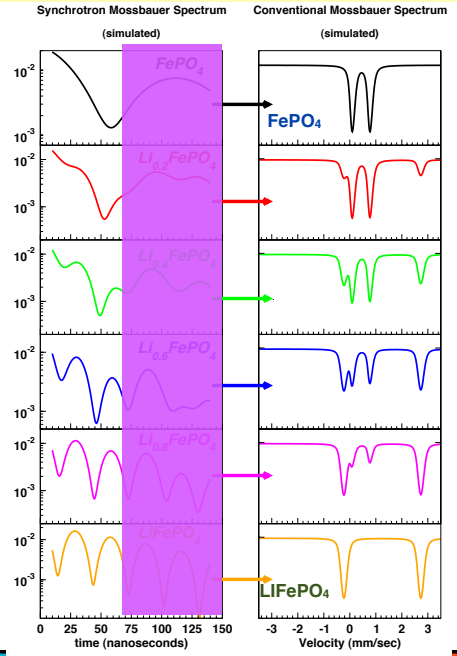
APD noise ~ 0.01 Hz => 1 part in 10^{10} purity ideal

1. Upcoming scientific applications : Battery materials

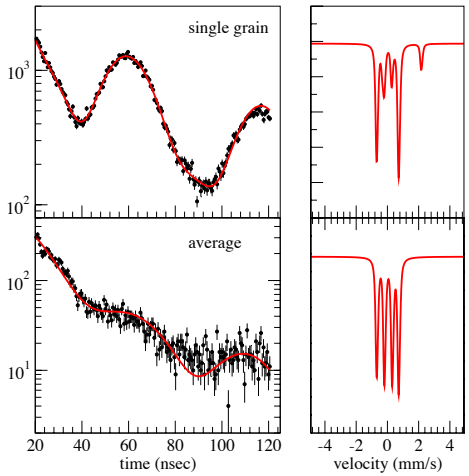




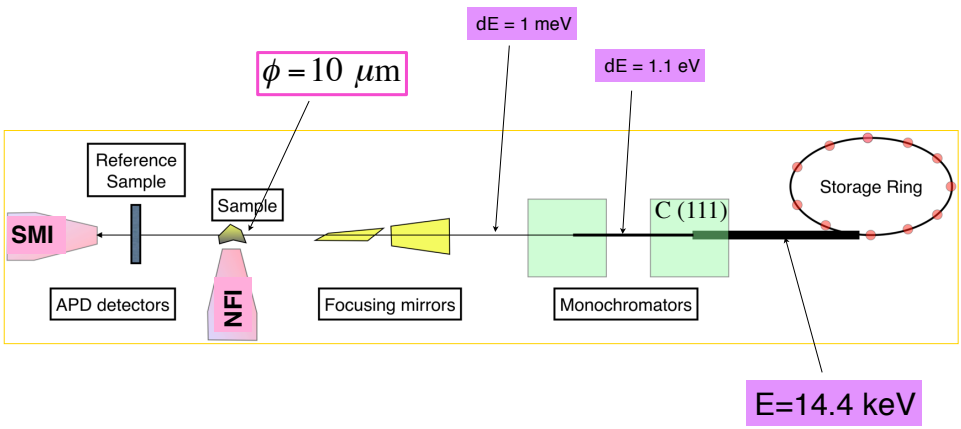


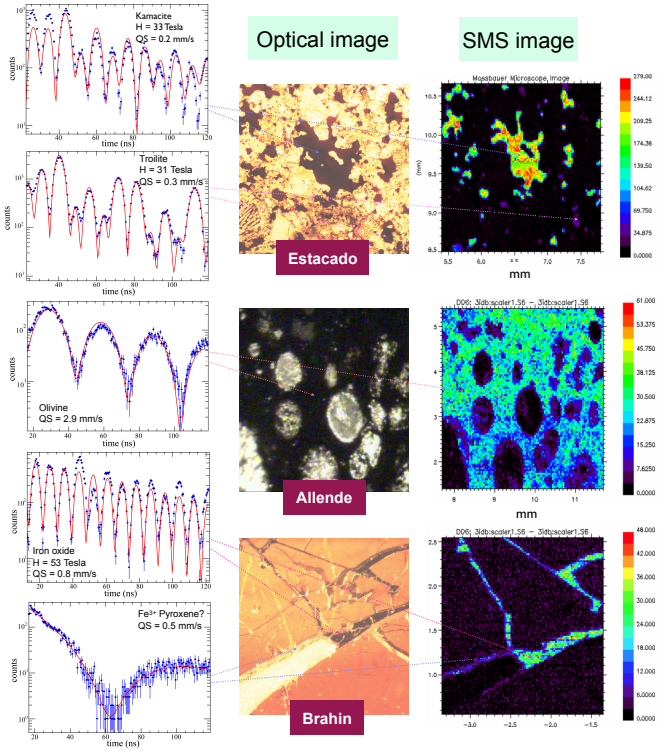


1. Upcoming scientific applications : Battery materials

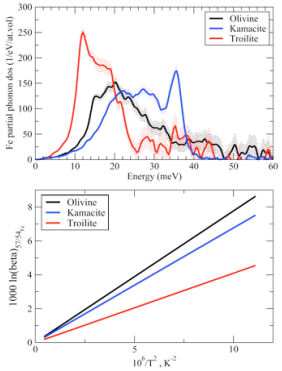


Mössbauer Microscope at 3-ID-B





Phonon density of states



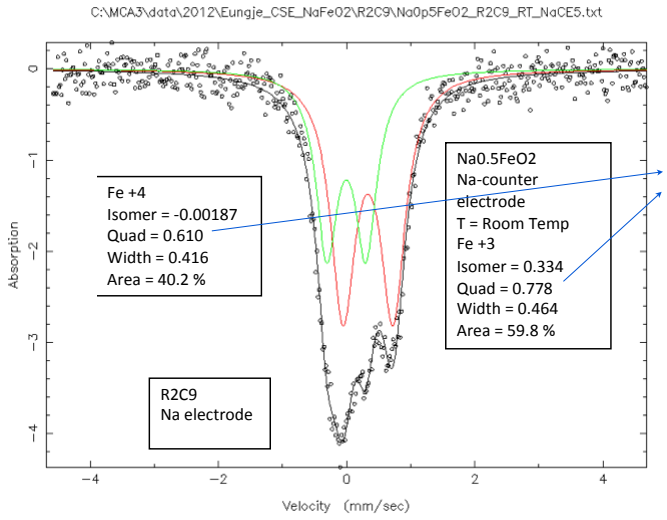
Iron 57/54 isotope fractionation

$$KE_{^{57}Fe} = \frac{3}{2}\int_0^{E_{max}} g(e)E(e,T)\mathrm{d}e$$ Kinetic energy / iron atom

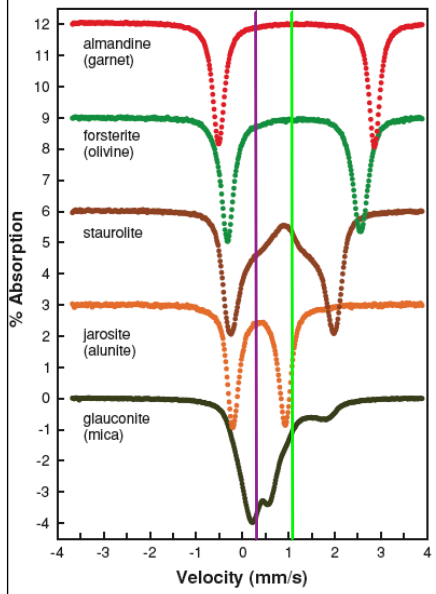
$$E(e,T) = \frac{e}{\exp(e/kT)-1} + \frac{1}{2}e$$ Energy of a Bose-Einstein oscillator

$$\ln \beta_{^{57/54}Fe} = \left(\frac{3}{2}KE_{^{57}Fe} - \frac{3}{2}\right)\frac{\Delta m}{m}$$ Reduced isotopic partition function ratio

1. Upcoming scientific applications : Unusual oxidation states



Small variations in quadrupole splitting and isomer shift can only be observed when there is sufficient time between the bunches.

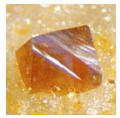


Fe^{2+}, cubic $Fe^{2+}Al_2Si_3O_{12}$

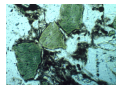
Fe^{2+}, octahedral $(Mg,Fe)_2SiO_4$

Fe^{2+}, tetrahedral $Fe_2Al_9(SiO_4)_4(O,OH)_2$

Fe^{3+}, octahedral $KFe^{3+}{}_3(OH)_6(SO_4)_2$



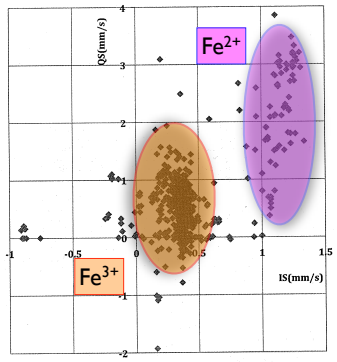
Fe^{3+}, tetrahedral $(K,Na)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$



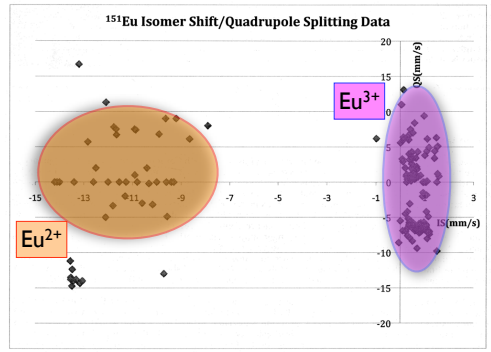
M. Darby Dyar, et al, Ann. Rev. Earth. Planet. Sci, 34 (2006) 83

Why isomer shift & quadrupole splitting is used for valence identification in Mössbauer Spectroscopy ?

^{57}Fe



^{151}Eu



What does Mossbauer spectroscopy measure ?

- isomer shift:

  s-electron density on the nucleus

  related to bonding and valence

- quadrupole splitting:

  Electric field gradient on the nucleus

  related to deviations from cubic symmetry & ligands

- magnetic hyperfine splitting:

  internal magnetic hyperfine field

  related to spin state and long-range order

- Lamb-Mossbauer factor:

  recoil-free fraction of the absorption-emission

  related to lattice dynamics & bonding strength

What does nuclear resonant vibrational spectroscopy measure?

- phonon density of states
  - force constant,
  - Debye sound velocity, longitudinal and shear velocity
  - vibrational specific heat and free energy,
  - shear modulus,
  - recoil-free fraction (i.e. Lamb-Mössbauer factor),

- kinetics of reactions

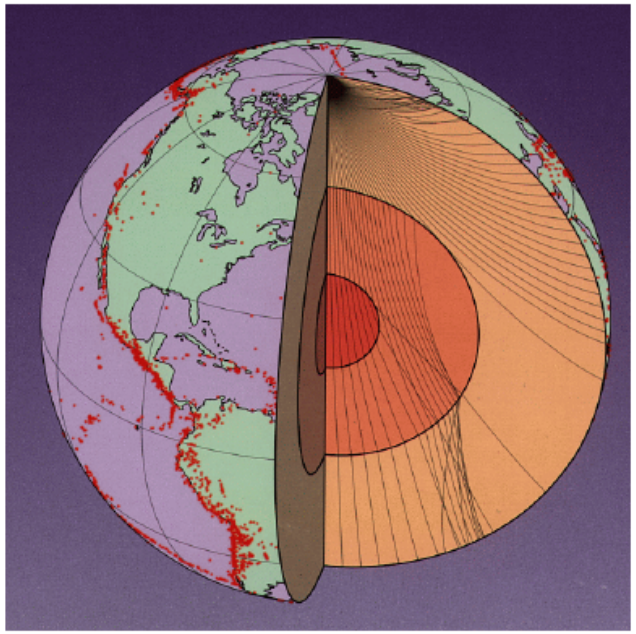
  minutes or seconds

- extreme conditions

  high pressure, monolayers, buried layers, etc…

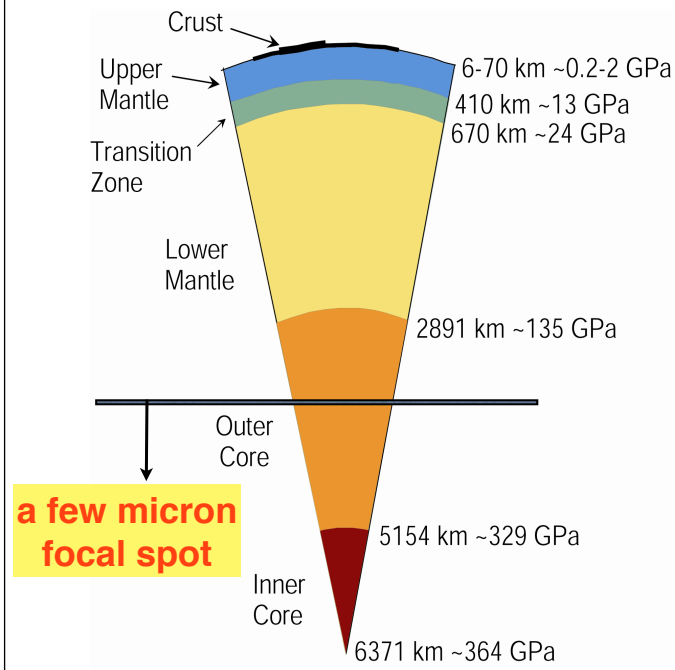
- spatially resolved spectromicroscopy

high pressure applications

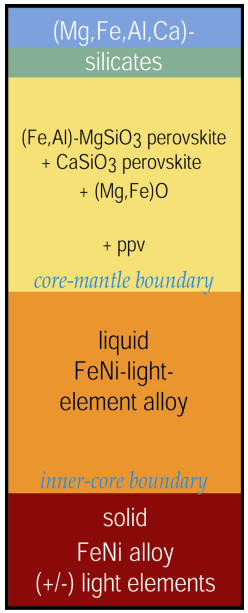


high pressure applications

^{57}Fe



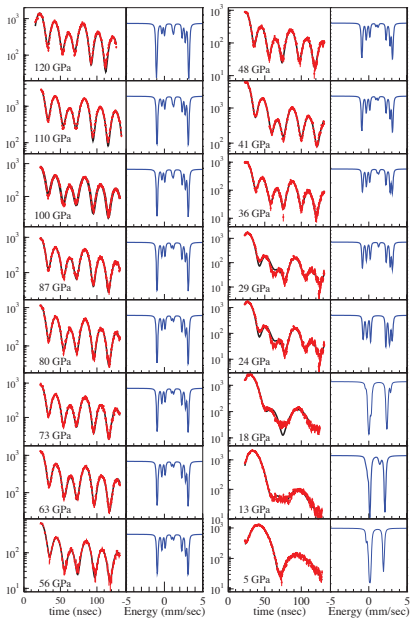
a few micron focal spot



American Mineralogist, Volume 97, pages 592–597, 2012

Electronic spin states of ferric and ferrous iron in the lower-mantle silicate perovskite

JUNG-FU LIN,[1,*] ERCAN E. ALP,[2] ZHU MAO,[1] TORU INOUE,[3] CATHERINE MCCAMMON,[4] YUMING XIAO,[5] PAUL CHOW,[5] AND JIYONG ZHAO[2]



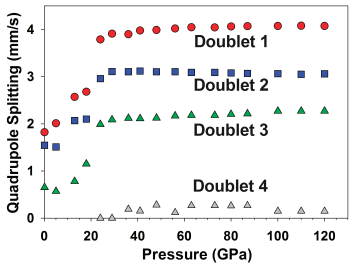
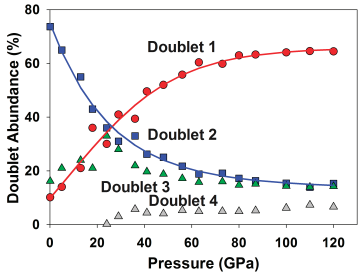


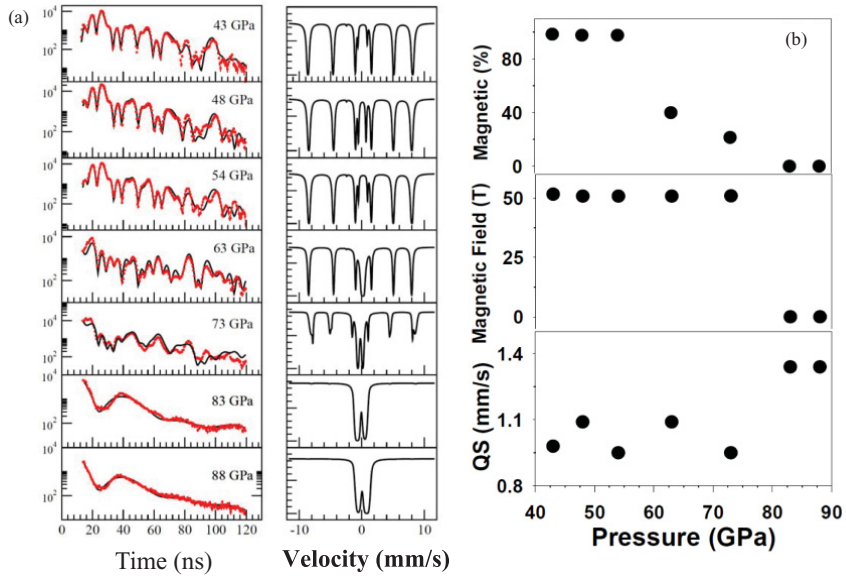
FIGURE 4. Derived quadrupole splitting (QS) of iron in $(Mg_{0.9},Fe_{0.1})SiO_3$ silicate perovskite at high pressures and 300 K. (Color online.)



PHYSICAL REVIEW B **84**, 064424 (2011)

Phonon density of states of Fe_2O_3 across high-pressure structural and electronic transitions

Jung-Fu Lin,[1,*] John S. Tse,[2] Esen E. Alp,[3] Jiyong Zhao,[3] Michael Lerche,[4] Wolfgang Sturhahn,[3]
Yuming Xiao,[5] and Paul Chow[5]



Timing needs for nuclear resonant scattering

1) Spectral flux per pulse needs to be maximized.

2) There should be “adequate” time, i.e. one or preferably two lifetime between two consecutive bunches.

3) Bunch purity should be at the level of 10^{-10}.

4) Adjacent buckets to the main bucket should be clean at the same level.

5) Keep the current bunch structure of 24 bunches, introducing new injection components to clean up the adjacent buckets.

6) Introducing “beam scrapers” to address impurity issues developed during top-up.

- **One little request** - $\sigma_{y'}$ (MBA) < $\sigma_{y'}$(APS) to preserve beamline optic efficiency

- **One more little request - GIVE US 12. 5 m long straight section (why not ?..)**

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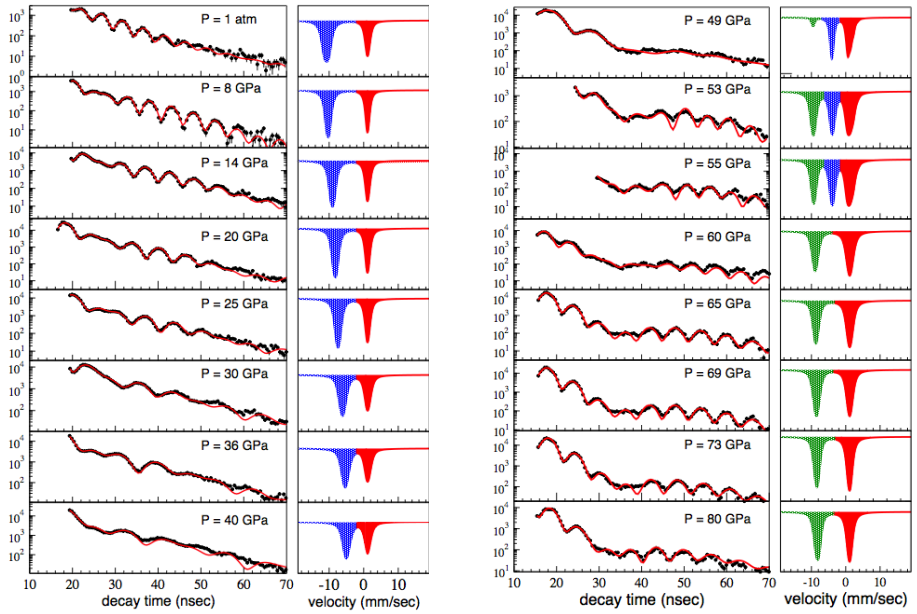
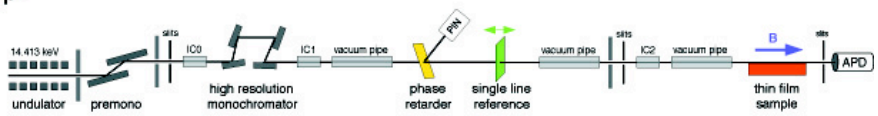
Pressure induced valence transition in EuO: something new?



Thank you ....

Nuclear resonant magnetometry with circularly polarized x-rays

Setup:

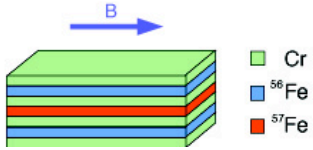


Phase retarder : to convert linear polarization to circular polarization

Single line : nuclear resonant reference sample to increase sign-sensitivity

Sample : thin film in grazing incidence geometry

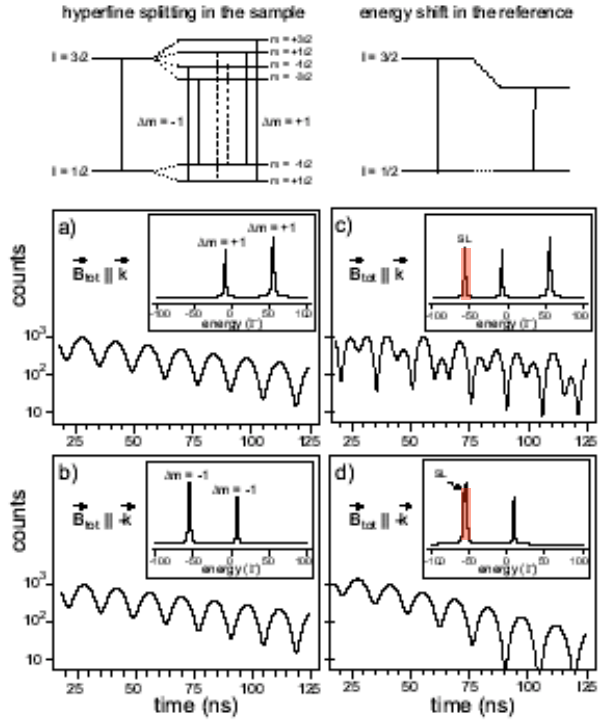
Sample:



MgO/Cr(111)/Fe(50)/Cr(11)/Fe(50)/Cr(11)/Fe(50)/Cr(44)

only the middle Fe layer contains ^{57}Fe

C. L'abbé, et al, Phys. Rev. Lett. 93 (2004) 037201

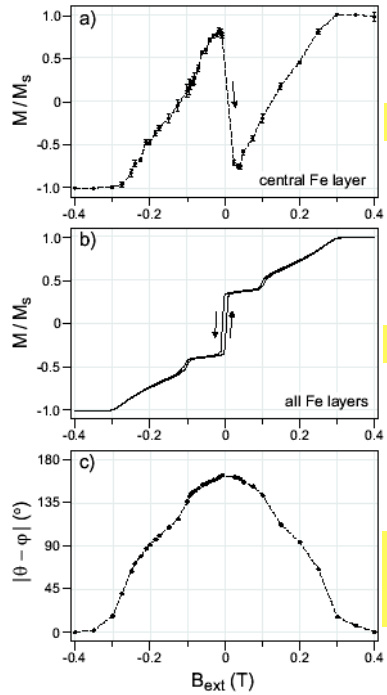


C. L'abbé, et al, Phys. Rev. Lett. 93 (2004) 037201

Synchrotron Mössbauer Spectroscopy with circularly polarized x-rays is used to measure the sign of the magnetization vector in a buried multilayer system.

The interlayer coupling of the Fe/Cr magnetic moments depend on the Cr layer thickness, and it can be NON-LINEAR, in addition to the known parallel, anti-parallel, or perpendicular couplings.

By using the isotope slectivity, we can study the interlayer coupling of the central ^{57}Fe layer distinctly separated fromthe rest of the ^{56}Fe layers



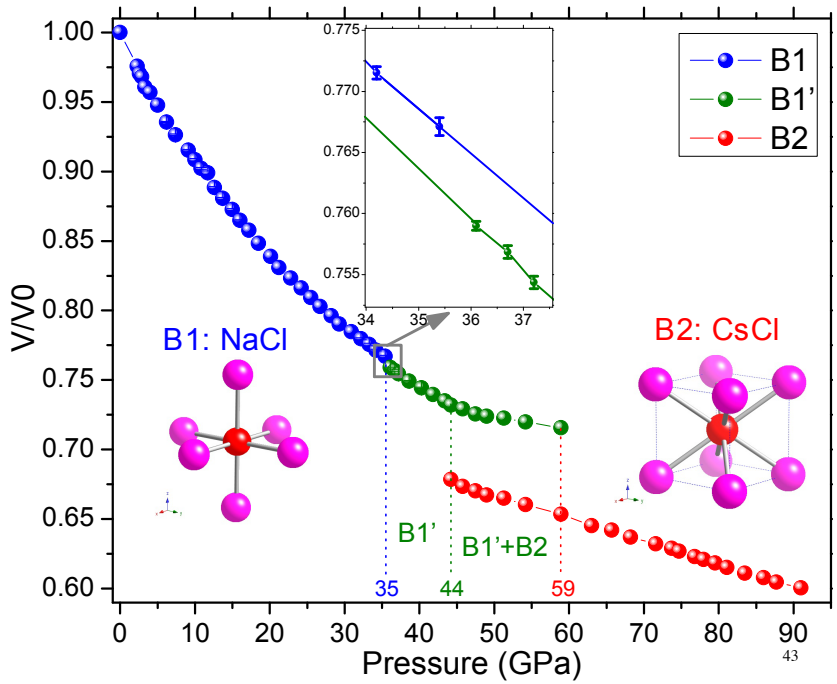
Central Fe layer

All Fe layers

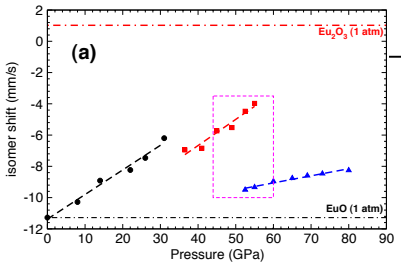
Angle between central and outer layer magnetization vectors

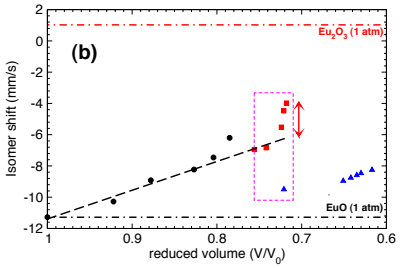
C. L'abbé, et al, Phys. Rev. Lett. 93 (2004) 037201

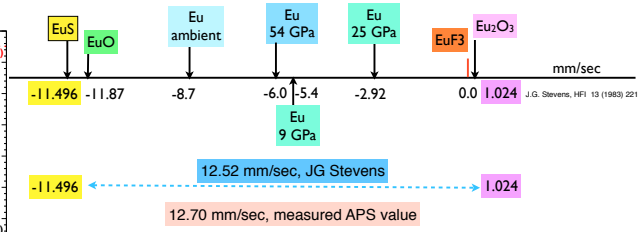
Pressure induced valence transition in EuO: something new?

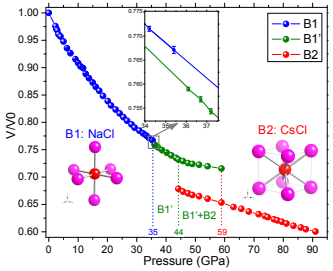


Pressure induced valence transition in EuO: something new?









M*ixed-valency* in *f*-electron systems occurs when otherwise localized *f*-orbitals of Rare-Earth or Actinide elements hybridize with delocalized *s,p, or d* electrons. This novel reentrant valence transition in Eu ions at higher pressures into a *lower* valence state is cocurrent with a 7% volume collapse. The results call for revisiting the literature on mixed-valent *f*-electron systems where electronic valence is inferred from structural data alone.

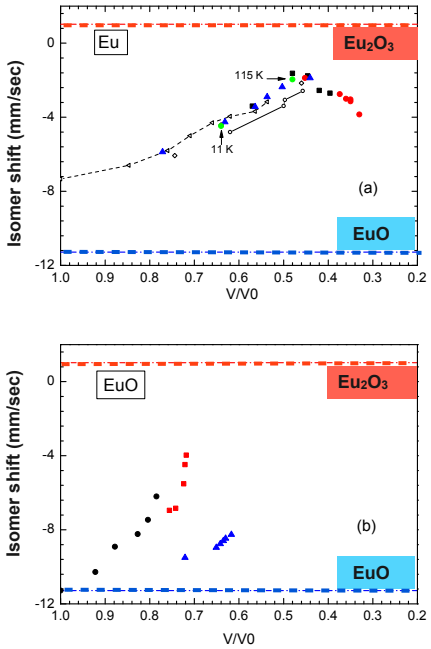
6. Pressure induced mixed valency in Eu and EuO revisted

Rare earths can display mixed valence states in the same compound. Lanthanide atoms are **trivalent**, except Eu and Yb, which are **divalent** as elemental metals.

If they remain divalent is dictated by the relative stability of their half-filled 4f orbitals.

Eu is 40–50% larger than other lanthanides, and it is highly compressible. Hence, the application of pressure would prompt Eu to become trivalent whereby one 4f electron would be promoted into the conduction band.

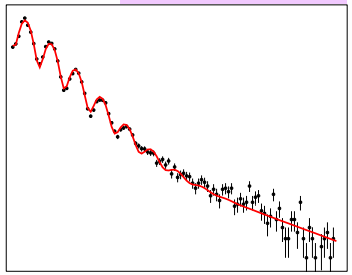
We demonstrate the discrepancy between the results obtained from bond-valence model and the direct measurements of the valence state of EuO. We also demonstrate that Eu-metal remains nearly divalent to the highest pressures reached.



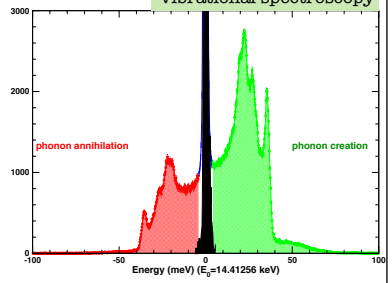
Excitation of the Mössbauer nuclei with synchrotron radiation

Proposed by Stan Ruby at Argonne, in 1974, it took 10 years to pump 14.4 keV level of ^{57}Fe (DESY) and another 10 years to realize phonon measurements (Argonne-KEK).

Time-domain Mössbauer spectroscopy



Nuclear resonant vibrational spectroscopy



^{57}Fe

τ = 141 ns, ΔE = 4.6 neV

ΔE= 0