HFI/NQI 2010 (September 14, 2010, Geneva)

Investigations on Thin Fe Films and Heusler Alloy Films Using Synchrotron-Radiation-Based Mössbauer Spectroscopy

K. Mibu

Nagoya Institute of Technology

JANAN

Three world centers for synchrotron-based Mössbauer spectroscopy

CREST project for synchrotron-based Mössbauer spectroscopy

(CREST = Core Research for Evolutional Science and Technology)

FY 2005 ~ 2010 (~ JPY 400,000,000 / 5.5 years)

M. Seto, Kyoto University
Project Leader

Y. Yoda, JASRI/SPring-8
Methodological improvements on the beam line (@BL09XU)

T. Mitsui, Japan Atomic Energy Agency
Methodological improvements on the beam line (@BL11XU)

S. Kishimoto, High Energy Accelerator Research Institute (KEK)
Improvements of detector systems

H. Kobayashi, Hyogo Prefectural University
Applications to material research (High pressures)

K. Mibu, Nagoya Institute of Technology
Applications to material research (Thin films & Nano-structures)

Outline

- Focusing on the measurements of hyperfine fields for thin films -

Introduction

* Quick introduction to synchrotron-radiation-based Mössbauer spectroscopy

* Conventional Mössbauer spectroscopy for thin films and nano-structures

* Background of the test samples (Fe films & Co_2MnSn films)

Results on Synchrotron-Radiation-Based Mössbauer Spectroscopy

* Measurements in time domains for Fe films and Co_2MnSn films

* Measurements in energy domains using a nuclear Bragg monochromator for Fe films

* Measurements in energy domains using a standard absorber for Co_2MnSn films

Conclusion

Advantages and disadvantages of synchrotron radiation as a source for Mössbauer spectroscopy

Advantages

* Small beam size
  (Around 1 mm without focusing devices,10 μm or less with focusing devices)
* Low angular divergence
* High intensity
* Polarization
* Pulse structures
* Energy selectivity

Disadvantages

* Broad energy bandwidth
  (Wider than 1 meV even after monochromatization in general)

Special techniques are required to use synchrotron radiation as a source for Mössbauer spectroscopy.

Historical Backgrounds

* Proposal for the use of synchrotron radiation as a Mössbauer source
  S. L. Ruby
  Journal de Physique, Colloq. **35**, C6 - 209 (1974)

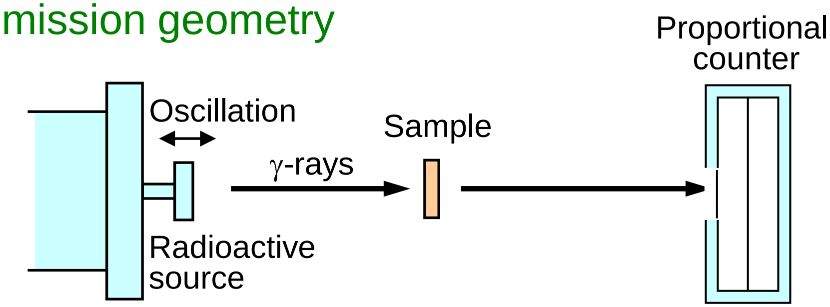
* Conclusive observation of Mössbauer spectra using synchrotron radiation and nuclear Bragg monochromator
  E. Gerdaw, R. Rüffer, H. Winkler, W. Tolksdorf, C. P. Klages, J. P. Hannon
  Phys. Rev. Lett. **54**, 835 (1985)

* Observation of time spectra for nuclear forward scattering (NFS) of synchrotron radiation
  J. B. Hastings, D. P. Siddons, U. van Bürck, R. Hollatz, U. Bergmann
  Phys. Rev. Lett. **66**, 770 (1991)

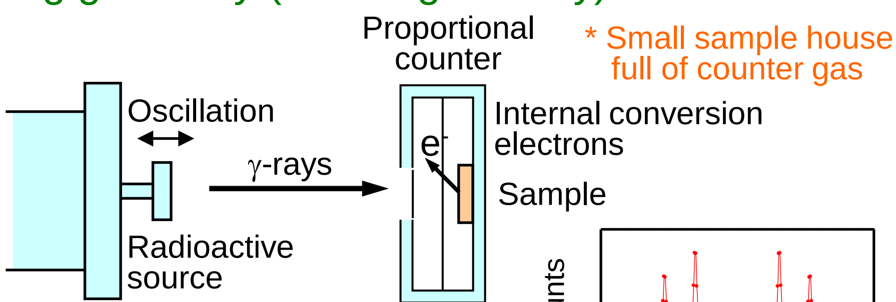
* Development of new method to measure Mössbauer spectra in energy domain using synchrotron radiation
  M. Seto, R. Masuda, S. Higashitaniguchi, S. Kitao. Y. Kobayashi, C. Inaba, T. Mitsui, Y. Yoda
  Phys. Rev. Lett. **102**, 217602 (2009)

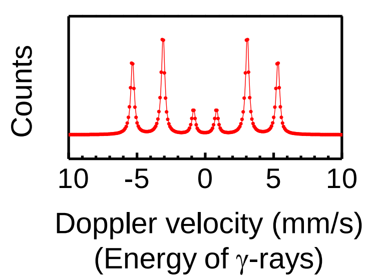
Conventional Mössbauer spectroscopic setups for for thin films and nano-structures on single crystal substrates

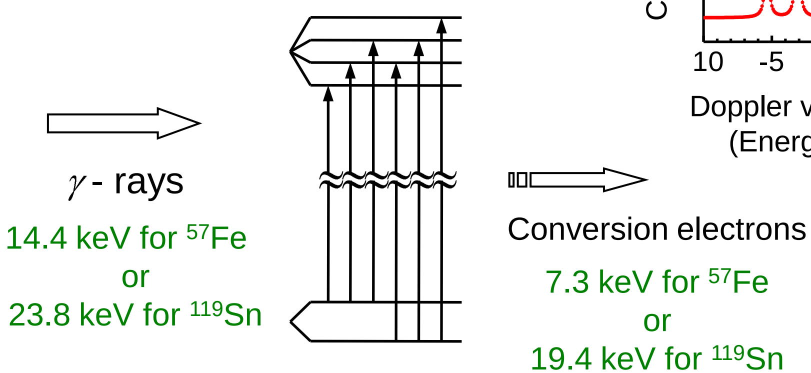
Transmission geometry



Scattering geometry (CEMS geometry)







~ 70 K (w/ He+2% CH_4 gas)
~ 30 K (w/ H_2 gas)

Advantages of synchrotron-radiation-based Mössbauer spectroscopy for the investigations on thin films and nano-structures

- In comparison with conversion electron Mössbauer spectroscopy (CEMS) using a radioactive source and a proportional gas counter –

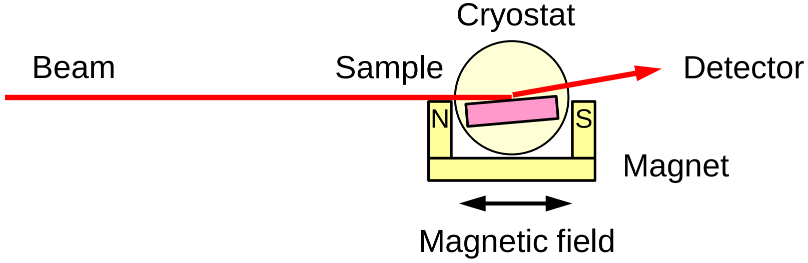
1. Easier to measure at low temperatures, in magnetic fields, with electric fields, and under other special sample conditions
2. Possible to detect in-plane magnetic anisotropy using the polarization characters
3. Not necessary to maintain radioactive sources, and applicable to all the Mössbauer nuclei in principle

☞ Large potential needs from the field of material science

But・・・ Difficult to get sufficient number of probe nuclei in the narrow beam path in comparison with the case of bulk powder or single crystal samples

☞ Required to measure in an oblique incidence (or grazing angle) geometry

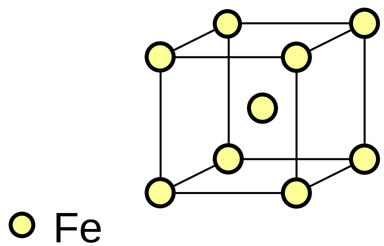
☞ Sometimes necessary to enrich probe nuclei in the sample appropriately

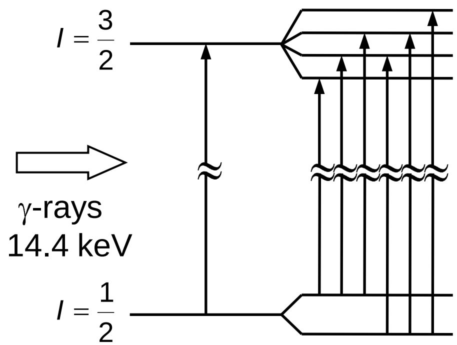


Test samples and Mössbauer nuclei

(1) Fe firms, nano-structures, monatomic layers

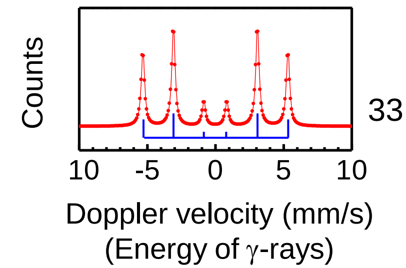
For ^{57}Fe Mössbauer spectroscopy





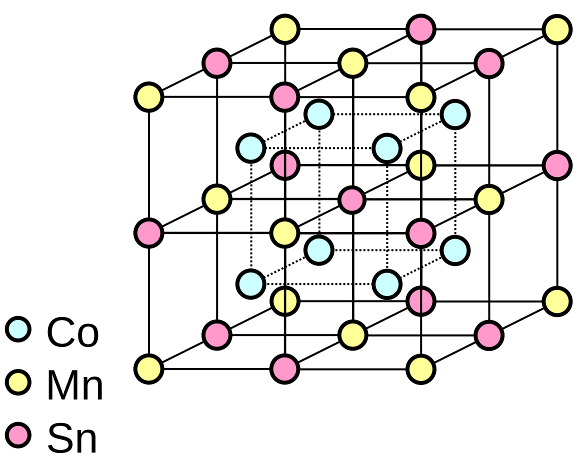
^{57}Fe nuclear energy levels

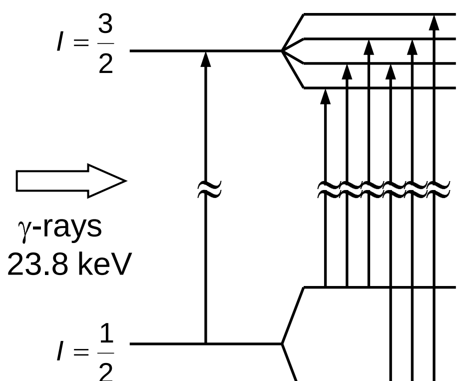
Calculated CEMS spectrum



(2) Co_2MnSn Heusler alloy films

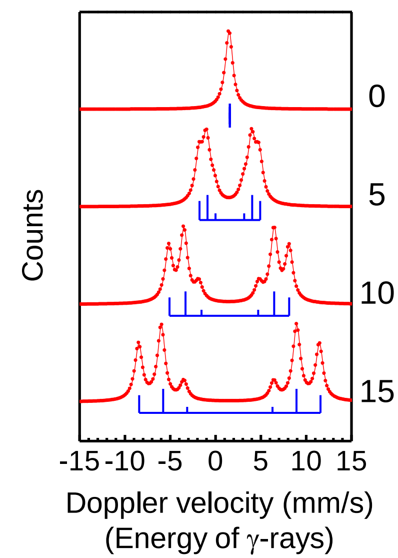
For ^{119}Sn Mössbauer spectroscopy





^{119}Sn nuclear energy levels

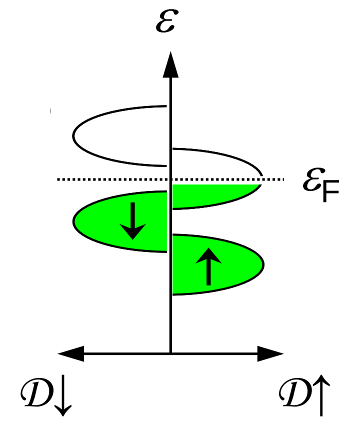
Calculated CEMS spectra for various hyperfine fields



Background of the test samples

Heusler alloys with an $L2_1$-type structure

* Theoretically predicted to be "half metallic"
  (or w/ highly spin-polarized conduction electrons)
* Promising materials for spin-electronics devices

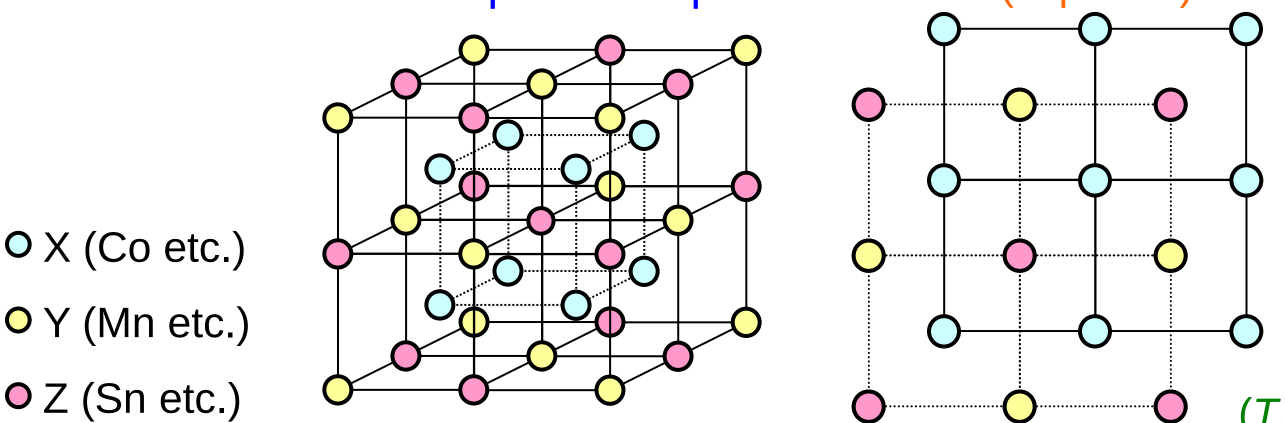


Strategy

Preparation of $L2_1$-type alloy films by atomically controlled alternate deposition

* Control of local crystallographic structures
* Control of interfacial atomic species
* Stabilization of non-equilibrium phases

(Top view)

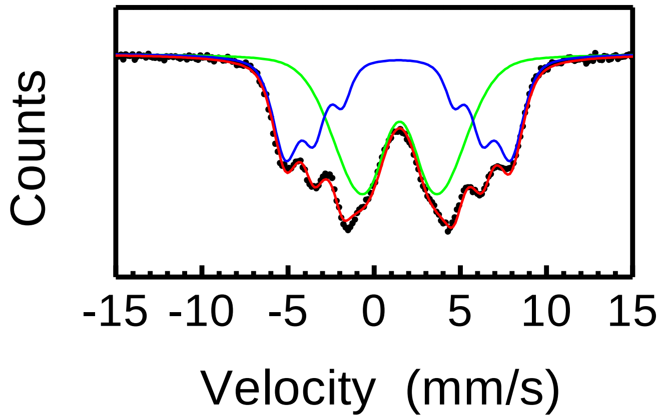


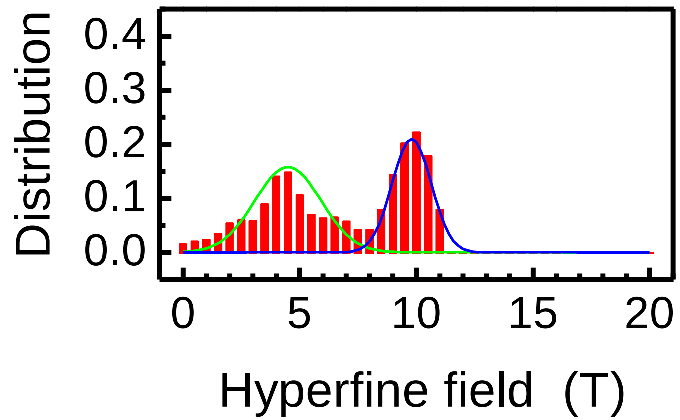
Co_2MnSn
(T_c = 811 K, $\mu \sim 5\ \mu_B$)

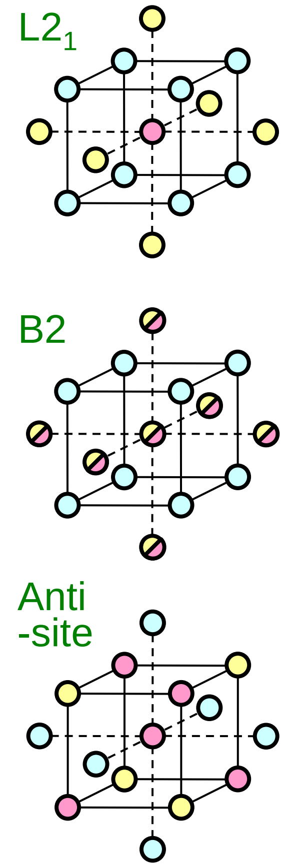
Mössbauer spectra for Co_2MnSn measured using a radioactive source

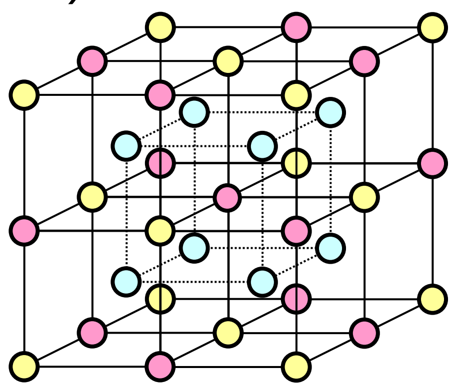
Bulk Co_2MnSn alloy prepared by arc-melting

(Long range $L2_1$ order parameter = 0.9)







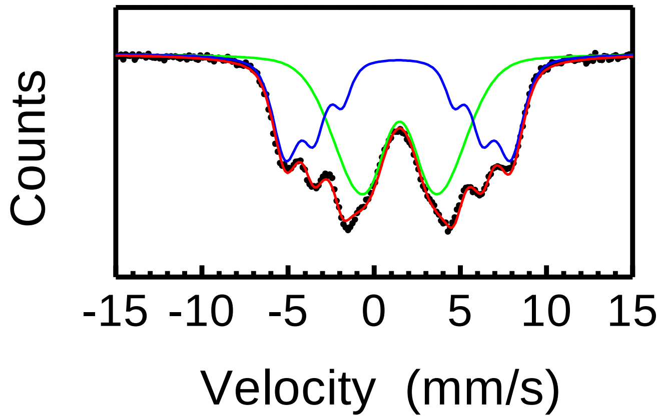


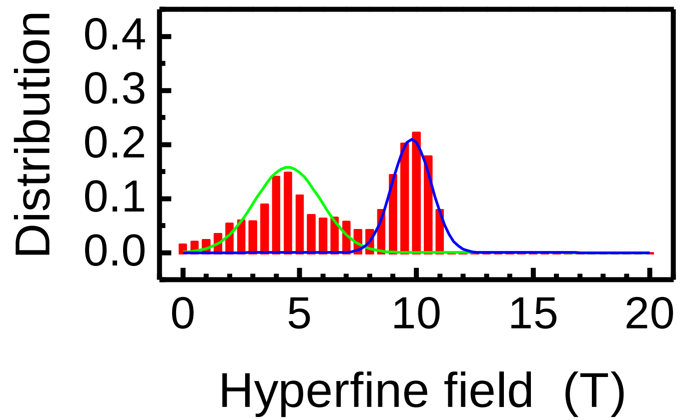
Similar spectra:

J. M. Williams *et al.*, J. Phys. C, **1** (1968) 473, etc.
R. A. Dunlap *et al.*, Can. J. Phys. **59** (1981) 1577, etc.
A. G. Gavriliuk *et al.*, J. Appl. Phys. **77** (1995) 2648.

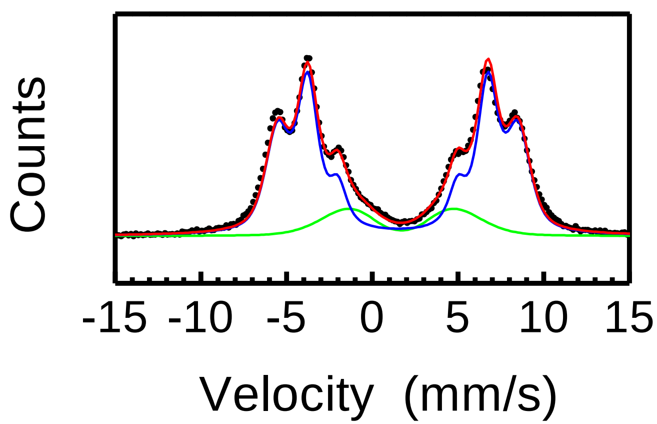
Mössbauer spectra for Co_2MnSn measured using a radioactive source

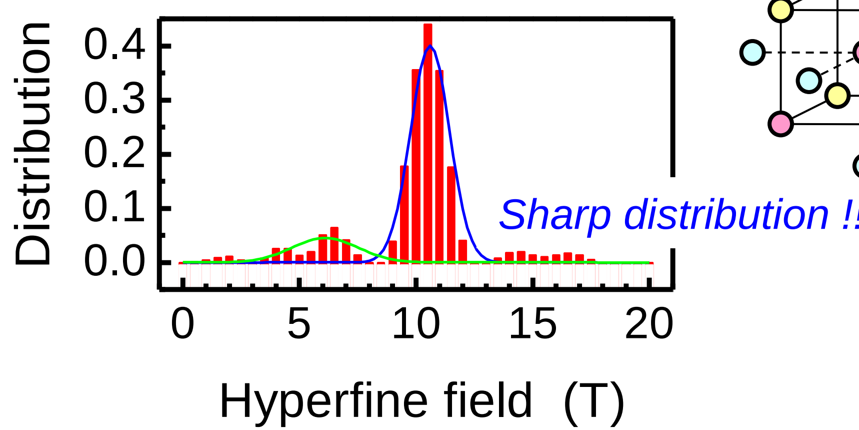
Bulk Co_2MnSn alloy prepared by arc-melting
(Long range $L2_1$ order parameter = 0.9)

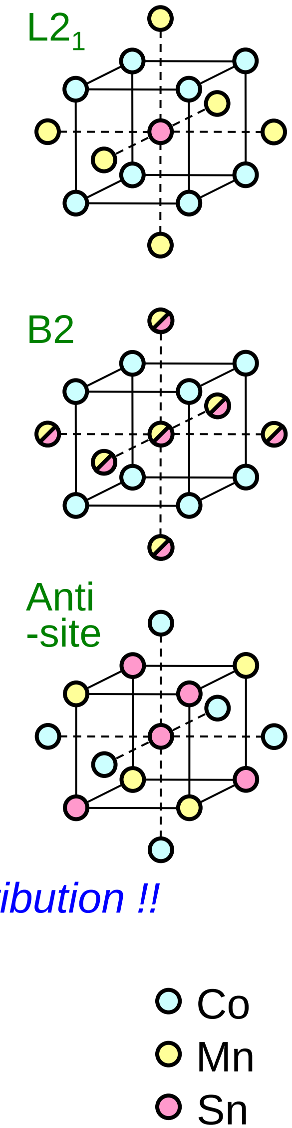




Co_2MnSn(40.2 nm) film prepared by atomically controlled alternate deposition
(T_{sub} = **500℃**)







☞ Available to investigate magnetic interface effect or size effect of Co_2MnSn!!

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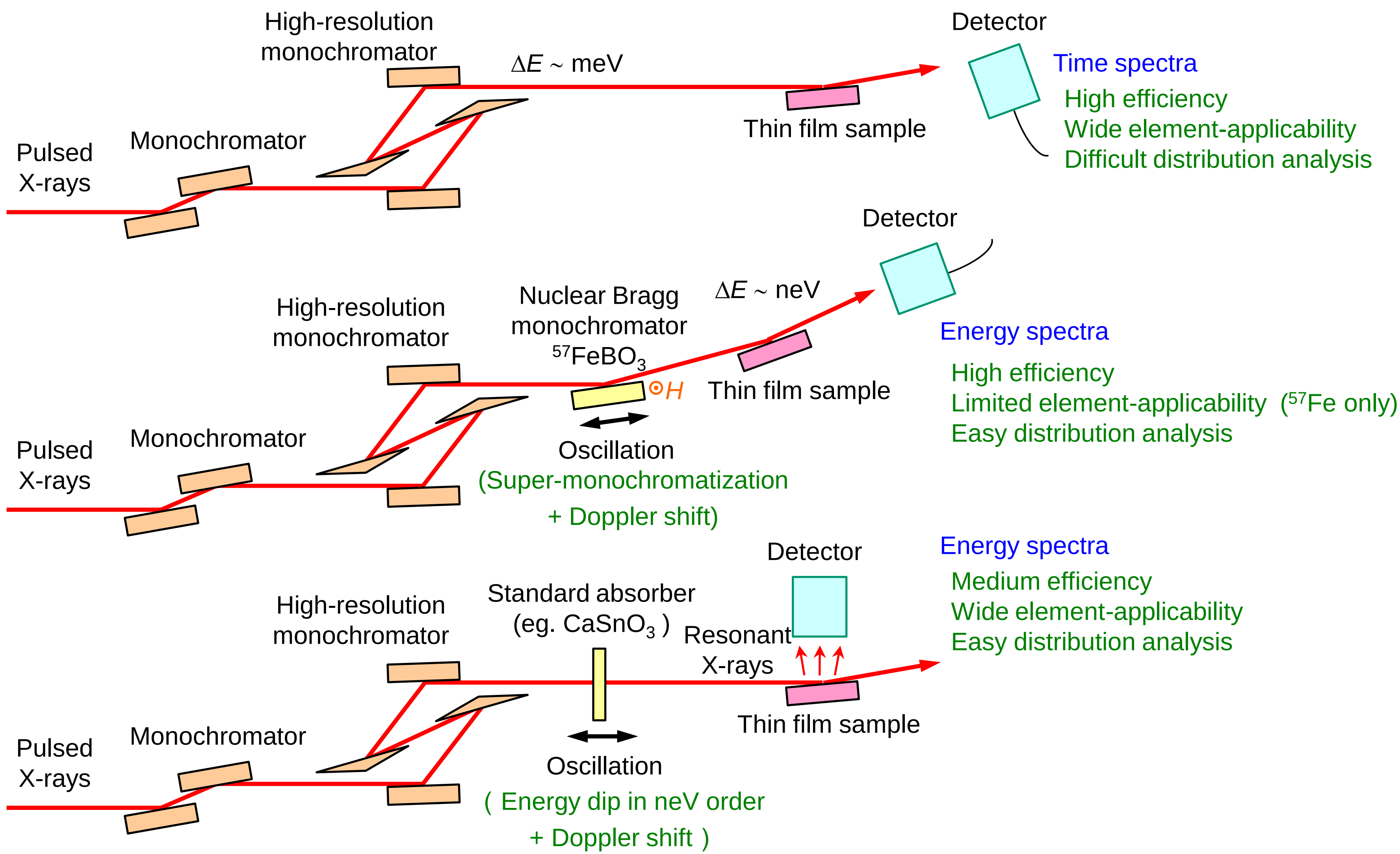
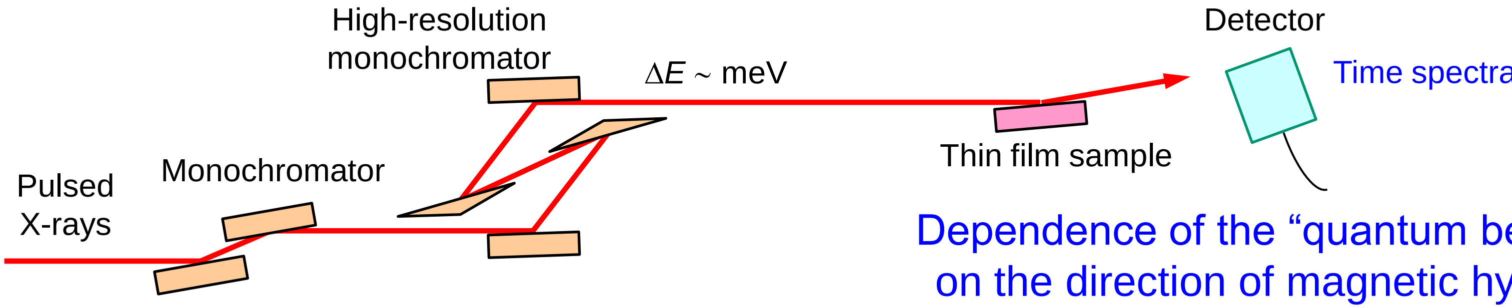
Conclusion

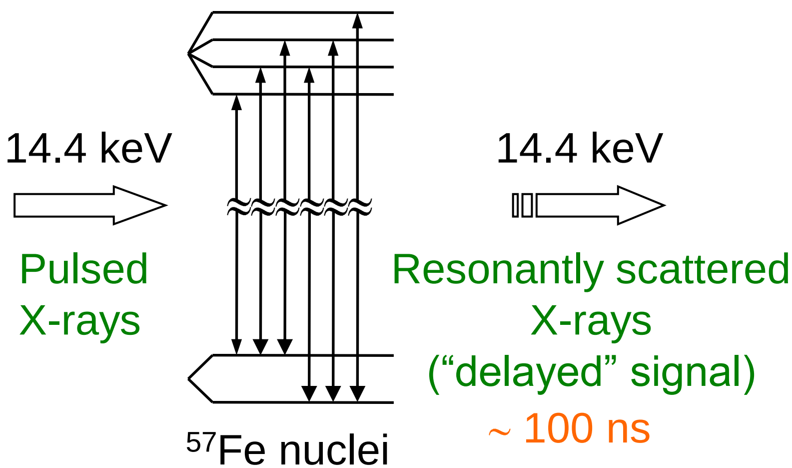
Setups of synchrotron-based Mössbauer spectroscopy

For the investigations on thin films

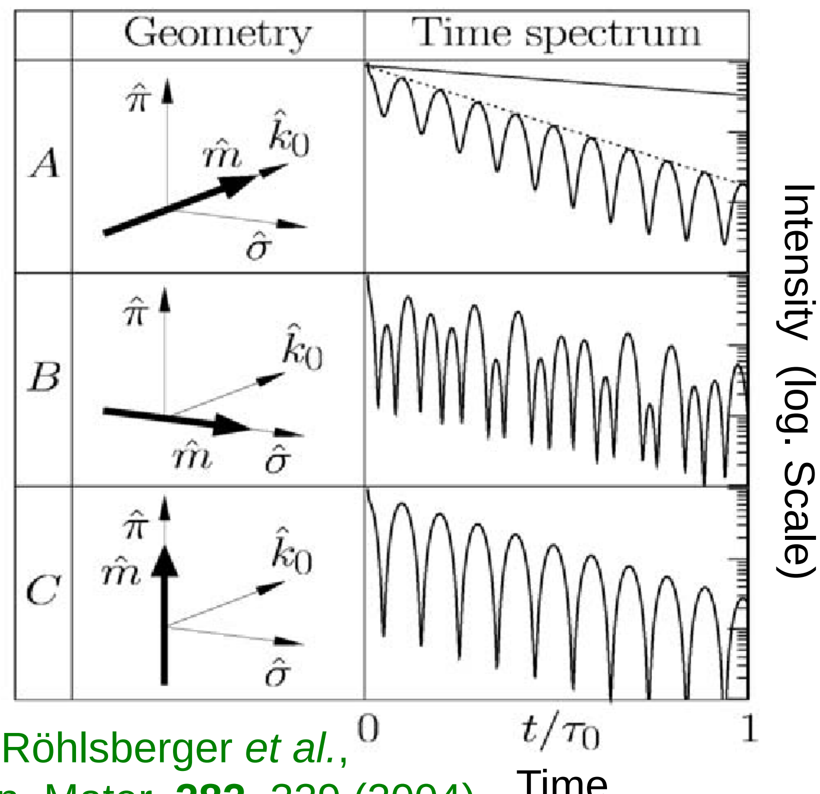


Measurements of nuclear resonant time spectra





Dependence of the “quantum beat” patterns on the direction of magnetic hyperfine field (rel. to the beam polarization)



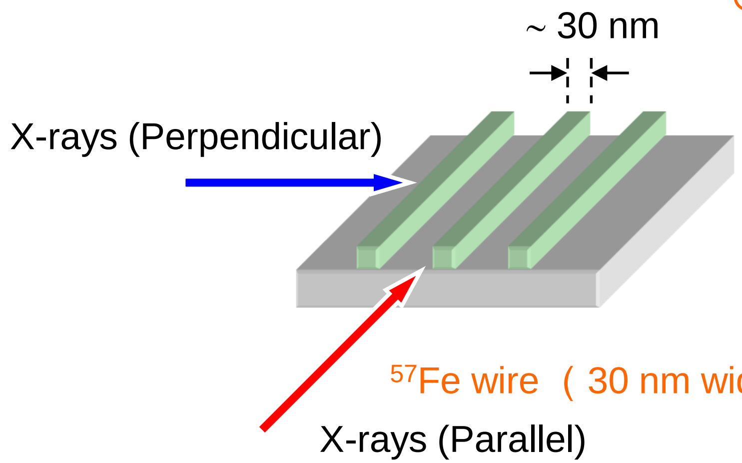
* Interference beat frequency
=> Inversely proportional to the hyperfine field

* Interference beat pattern
=> Dependent on the direction of hyperfine field

Cited from R. Röhlsberger *et al.*, J. Magn. Magn. Mater. **282**, 329 (2004).

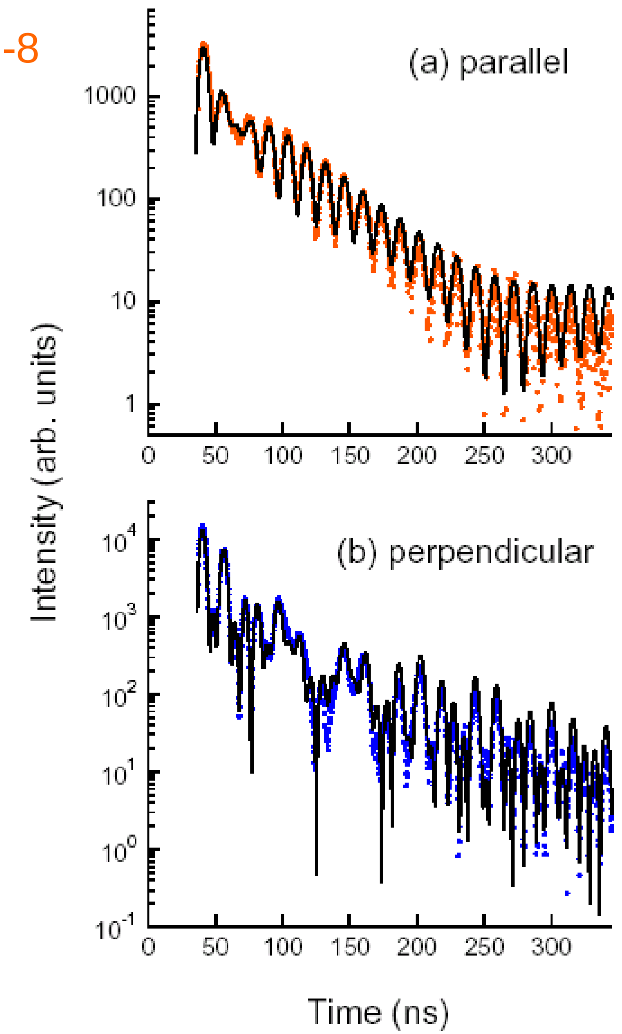
Nuclear resonant time spectra for Fe nanowires

@ BL11XU, SPring-8



^{57}Fe wire (30 nm wide, 30 nm thick)

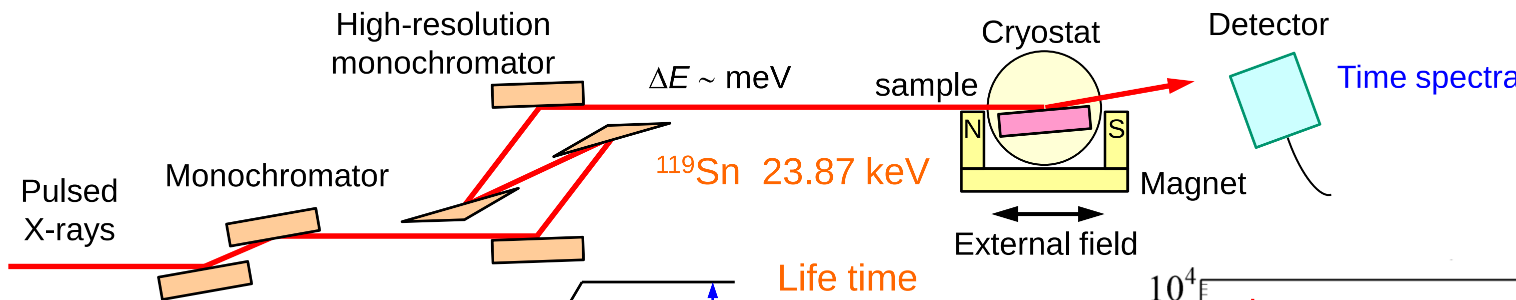
Quantum beat
+
Dynamical beat

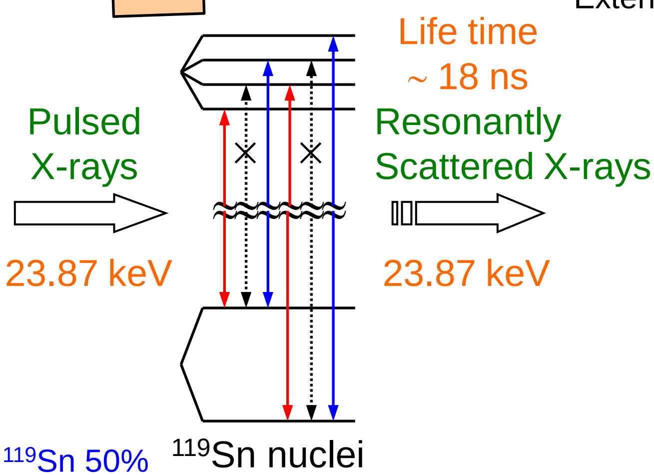


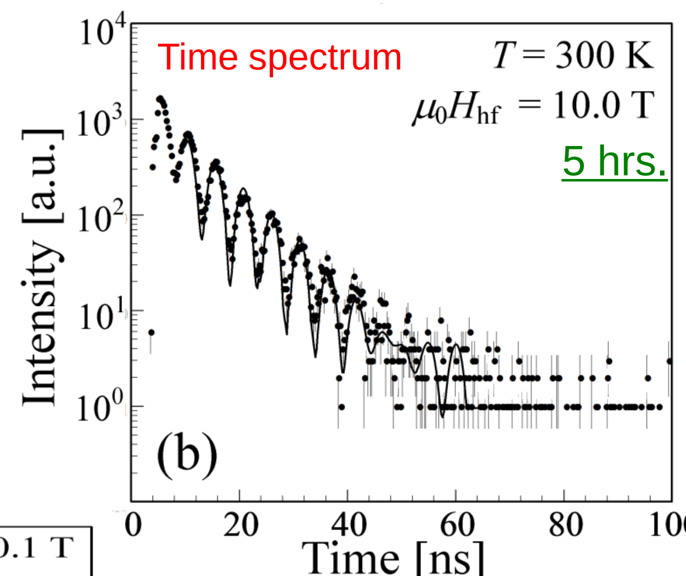
Excellent works on the determination of magnetization direction in thin film samples have been published by:

ESRF group (*e.g.*, R. Röhlsberger *et al.*, Phys. Rev. Lett. 89, 237201 (2002))
APS group (*e.g.*, C. L'abbé *et al.*, Phys. Rev. Lett. 93, 037201 (2004))

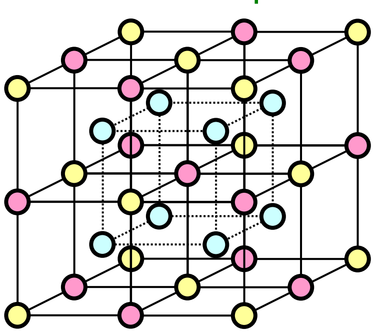
Nuclear resonant time spectrum for a “thick” Co_2MnSn film

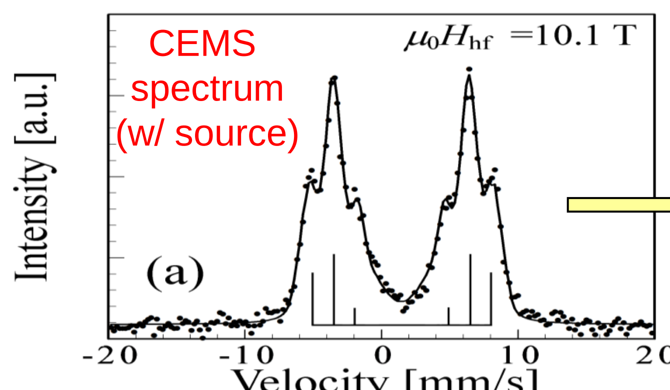


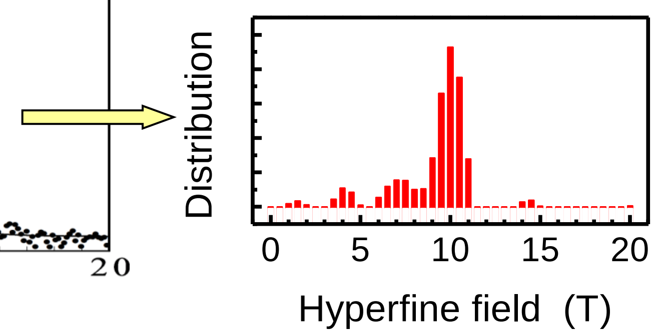




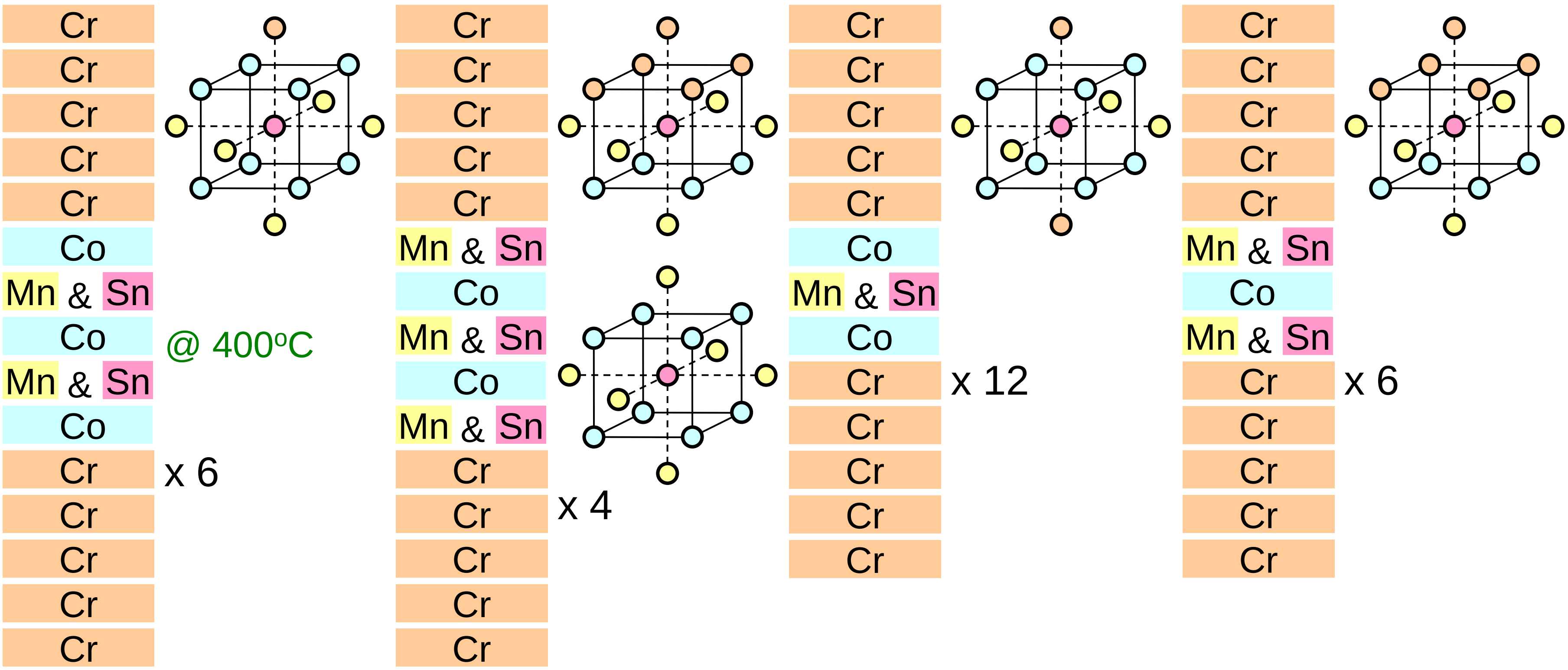
Co_2MnSn (40.2 nm) w/ ^{119}Sn 50%
(Prep. by atomically controlled alternate deposition)







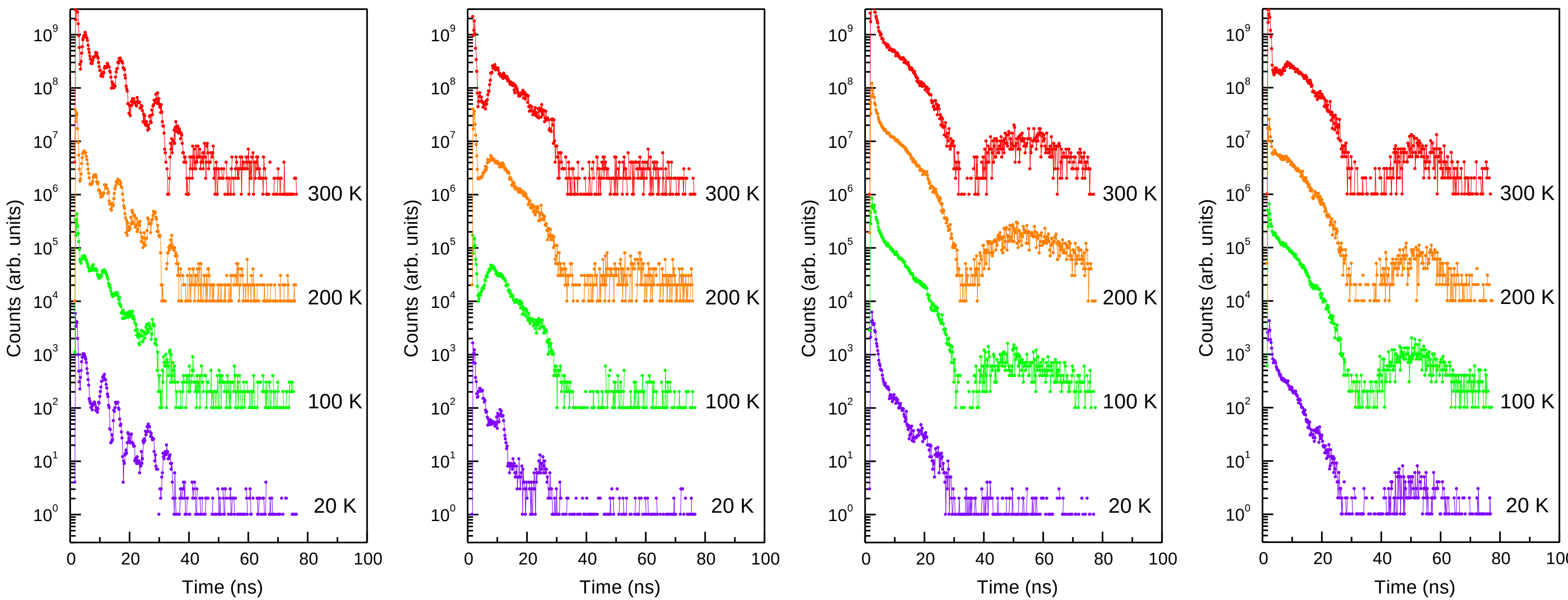
“Ultra-thin” Co_2MnSn films for Mössbauer measurements



^{119}Sn total 1.2 nm (~ 6 atomic layers)

Nuclear resonant time spectrum for “ultra-thin” Co_2MnSn films

Measurement time ~ 3 hrs./ each



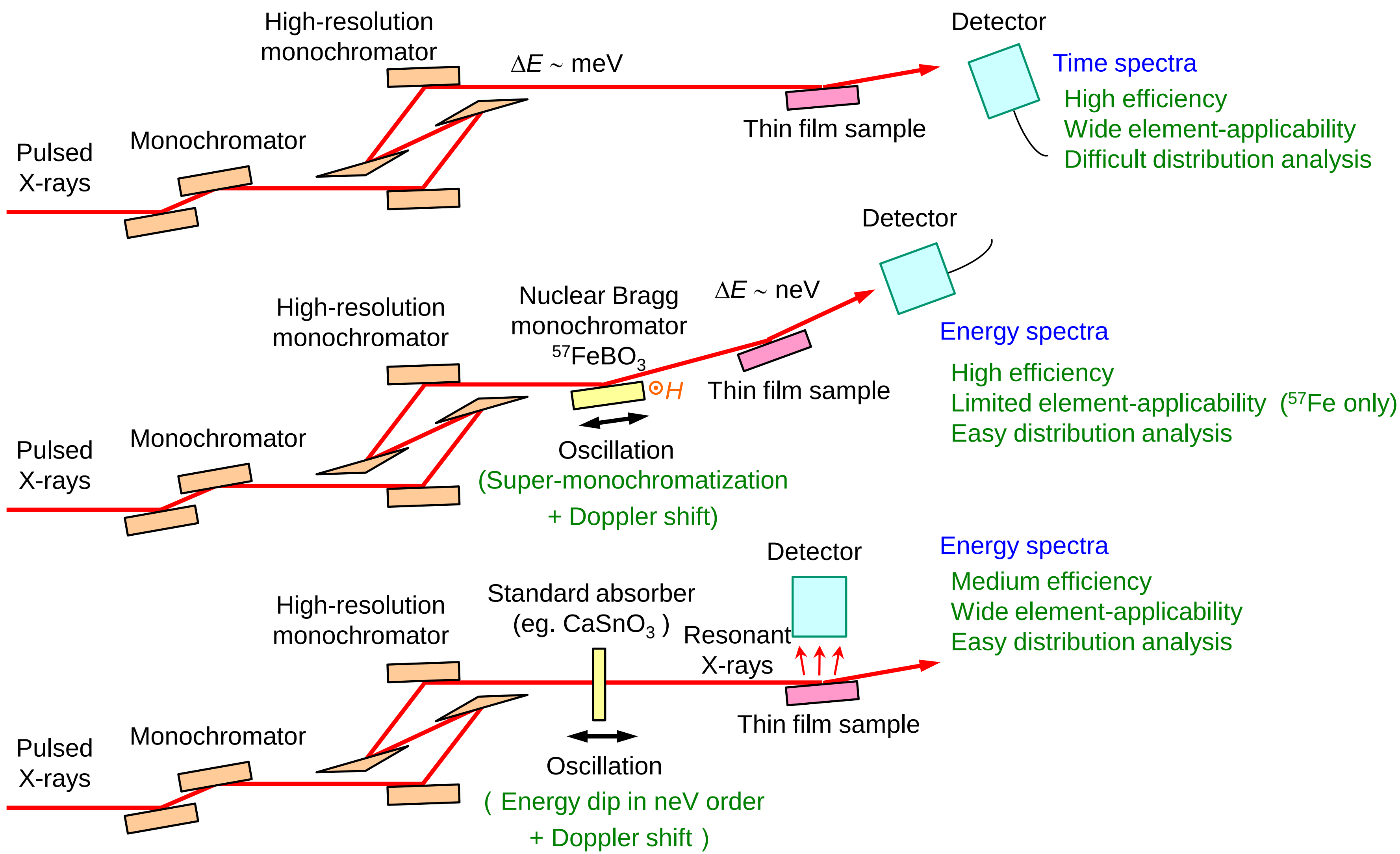
Co	Mn & Sn	Co	Mn & Sn
Mn & Sn	Co	Mn & Sn	Co
Co	Mn & Sn	Co	Mn & Sn
Mn & Sn	Co		
Co	Mn & Sn		

^{119}Sn total 1.2 nm (~ 6 atomic layers)

→ Smaller hyperfine fields

Setups of synchrotron-based Mössbauer spectroscopy

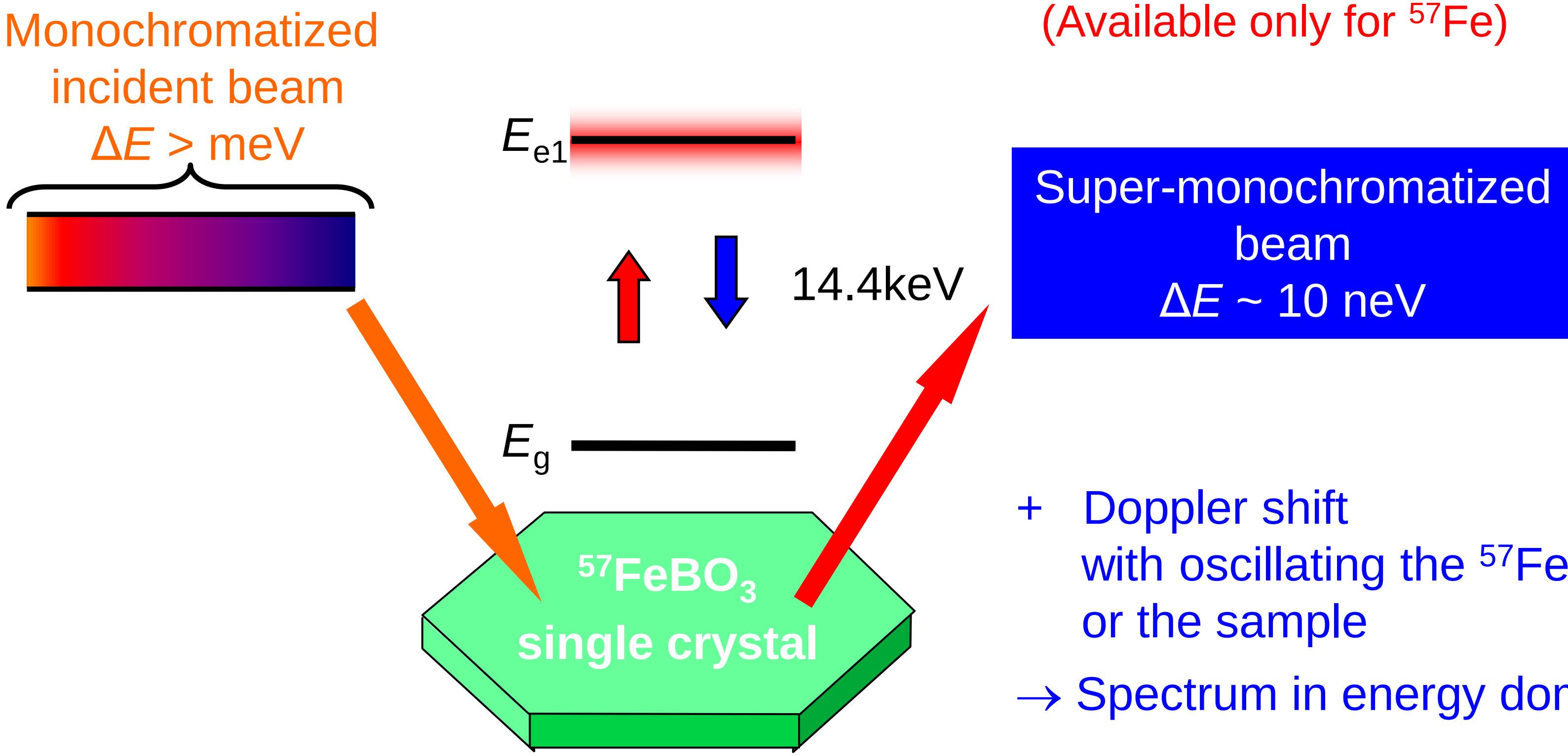
For the investigations on thin films



Single-line Mössbauer source using nuclear Bragg reflection

Use of electronically forbidden but nuclear allowed Bragg reflection from an antiferromagnetic single crystal kept near the Néel temperature

(Available only for ^{57}Fe)



\+ Doppler shift with oscillating the $^{57}FeBO_3$ or the sample

→ Spectrum in energy domain

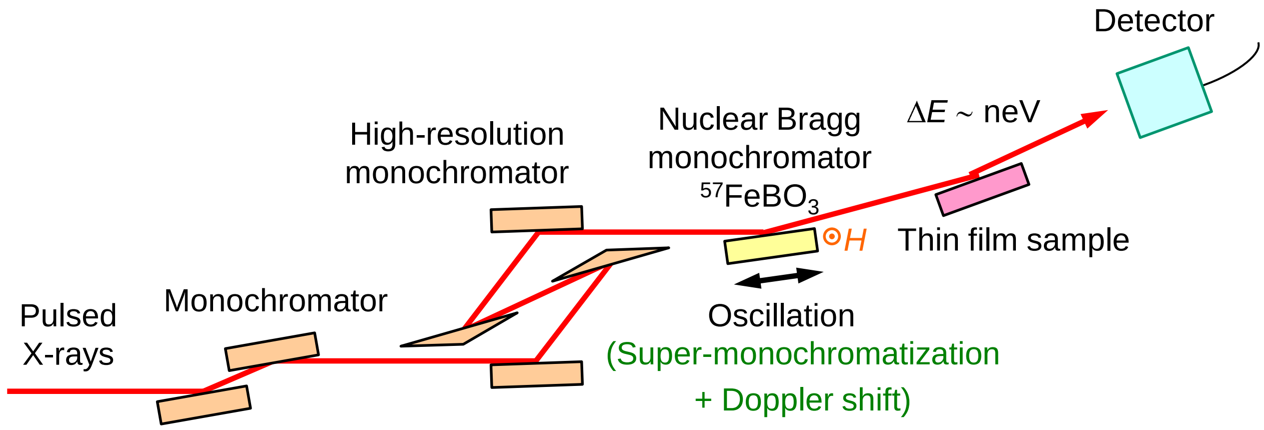
G. V. Smirnov *et al*., JETP Lett. **43**, 352(1986).

A. I. Chumakov *et al.*, Phys. Rev. B **41**, 9545(1990).

G. V. Smirnov *et al.*, Phys. Rev. B **55**, 5811(1997).

G. V. Smirnov, Hyperfine Interactions **125**, 91(2000).

Strategy for the use of nuclear Bragg monochromator for the studies on thin films and nano-structures



Key techniques:

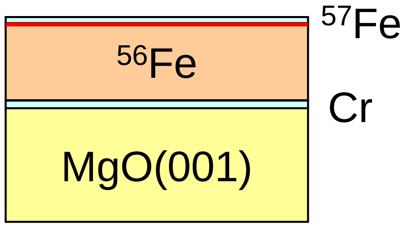
T. Mitsui, M. Seto, R. Masuda, Jpn. J. Appl. Phys. 46 L930 (2007)

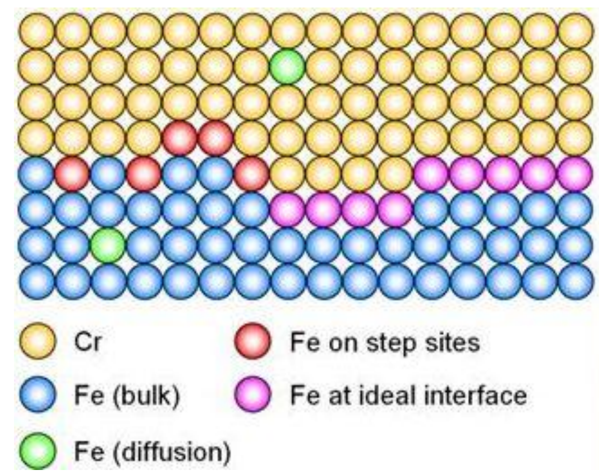
1. Use of a top-quality $^{57}FeBO_3$ single crystal for intense super-monochromatized beams

2. Realization of energetically-modulated monochromatized beams at a fixed angle and position

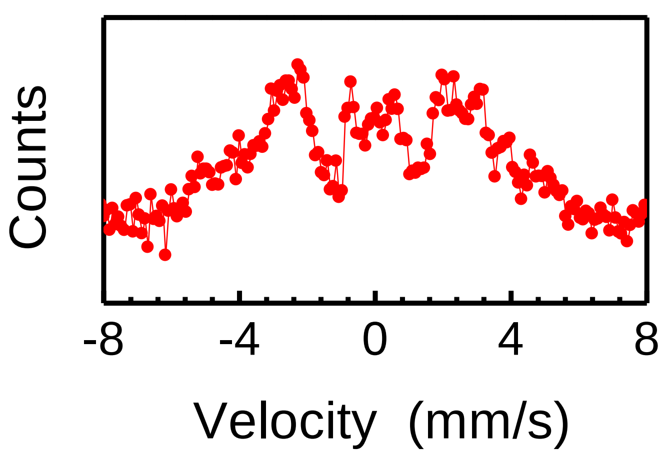
Measurements of ^{57}Fe monolayer using a radioactive source

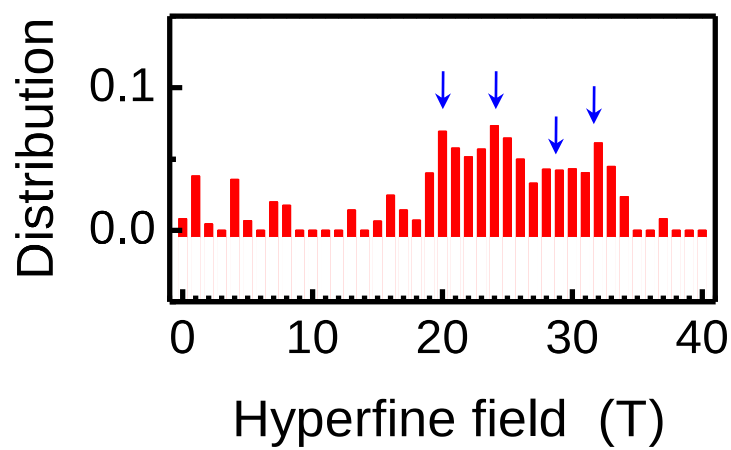
MgO(001)/Cr(1.0 nm)/ ^{56}Fe(10.0 nm)/ ^{57}Fe(0.2 nm)/Cr(1.0 nm)





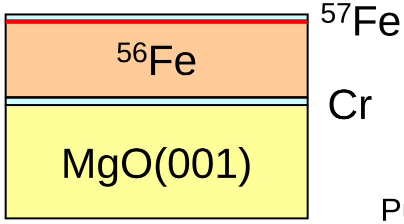
CEMS w/ a radioactive source
(46 mCi (1.7 GBq), 7 days, RT)
Effect = 0.36%

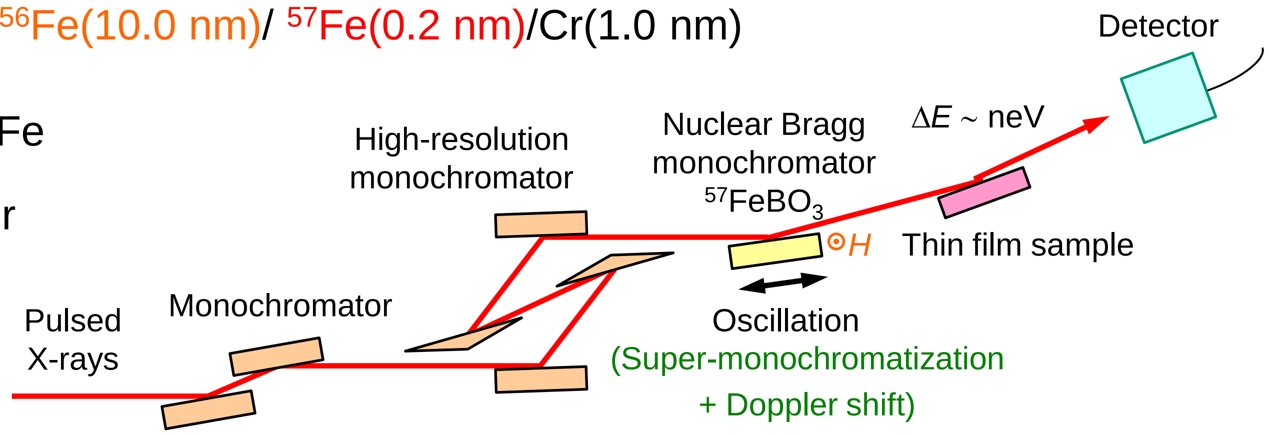




Measurements of ^{57}Fe monolayer using nuclear Bragg monochnomator

MgO(001)/Cr(1.0 nm)/ ^{56}Fe(10.0 nm)/ ^{57}Fe(0.2 nm)/Cr(1.0 nm)





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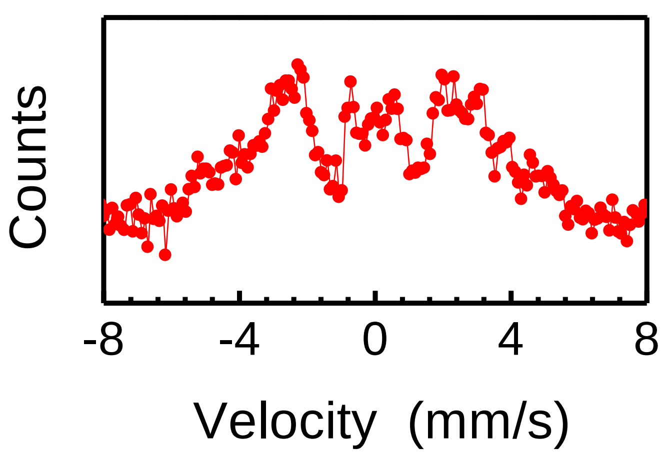
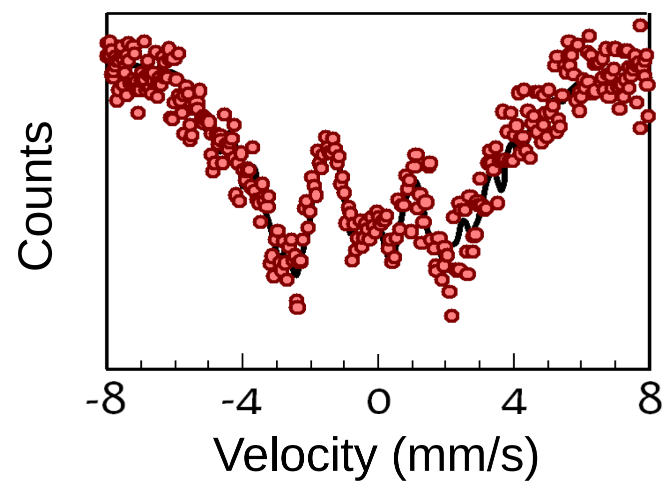
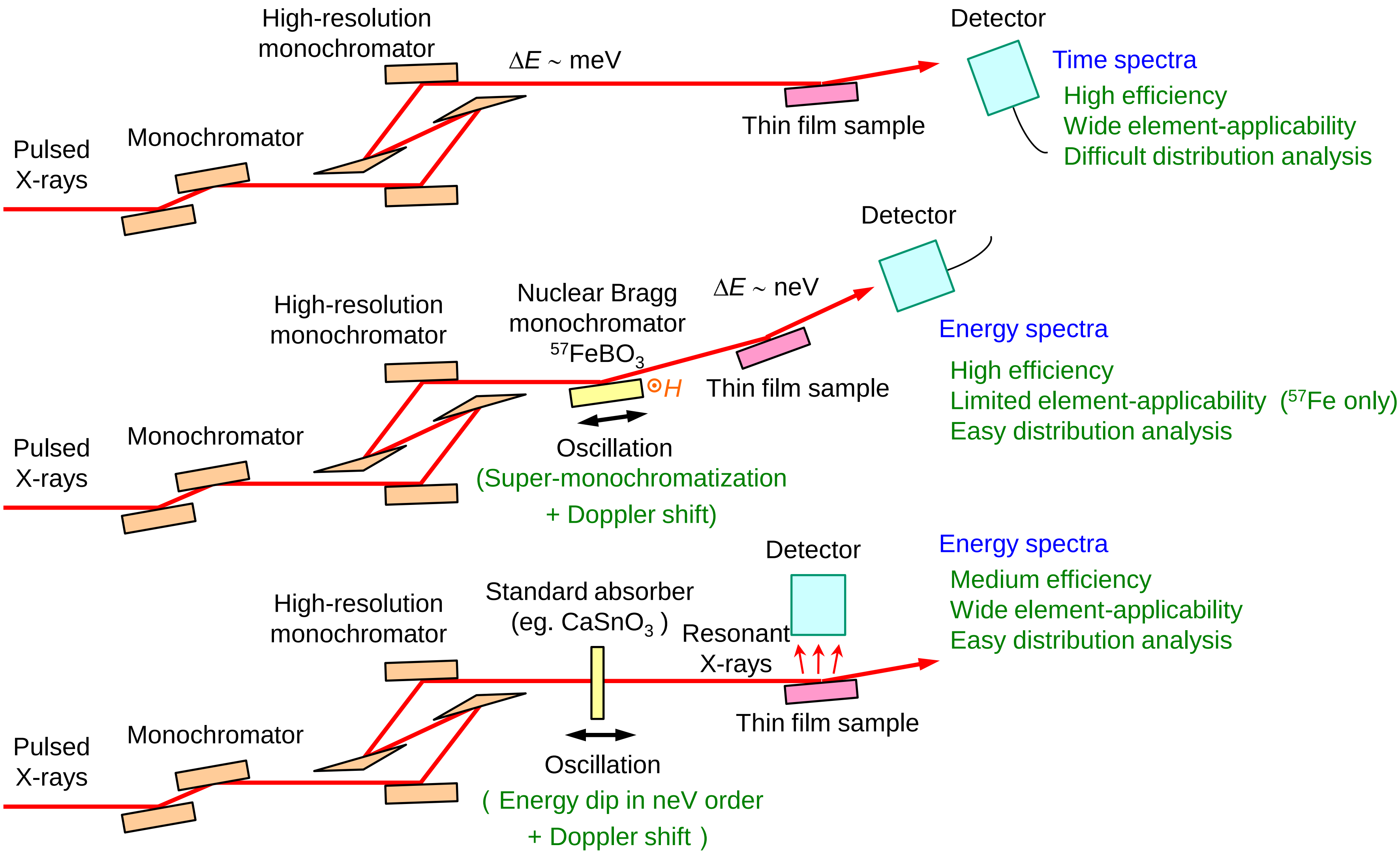


Synchrotron w/ nuclear Bragg monochnomator
(Incident angle ~ 1.6°, Measurement ~ 3 hrs)

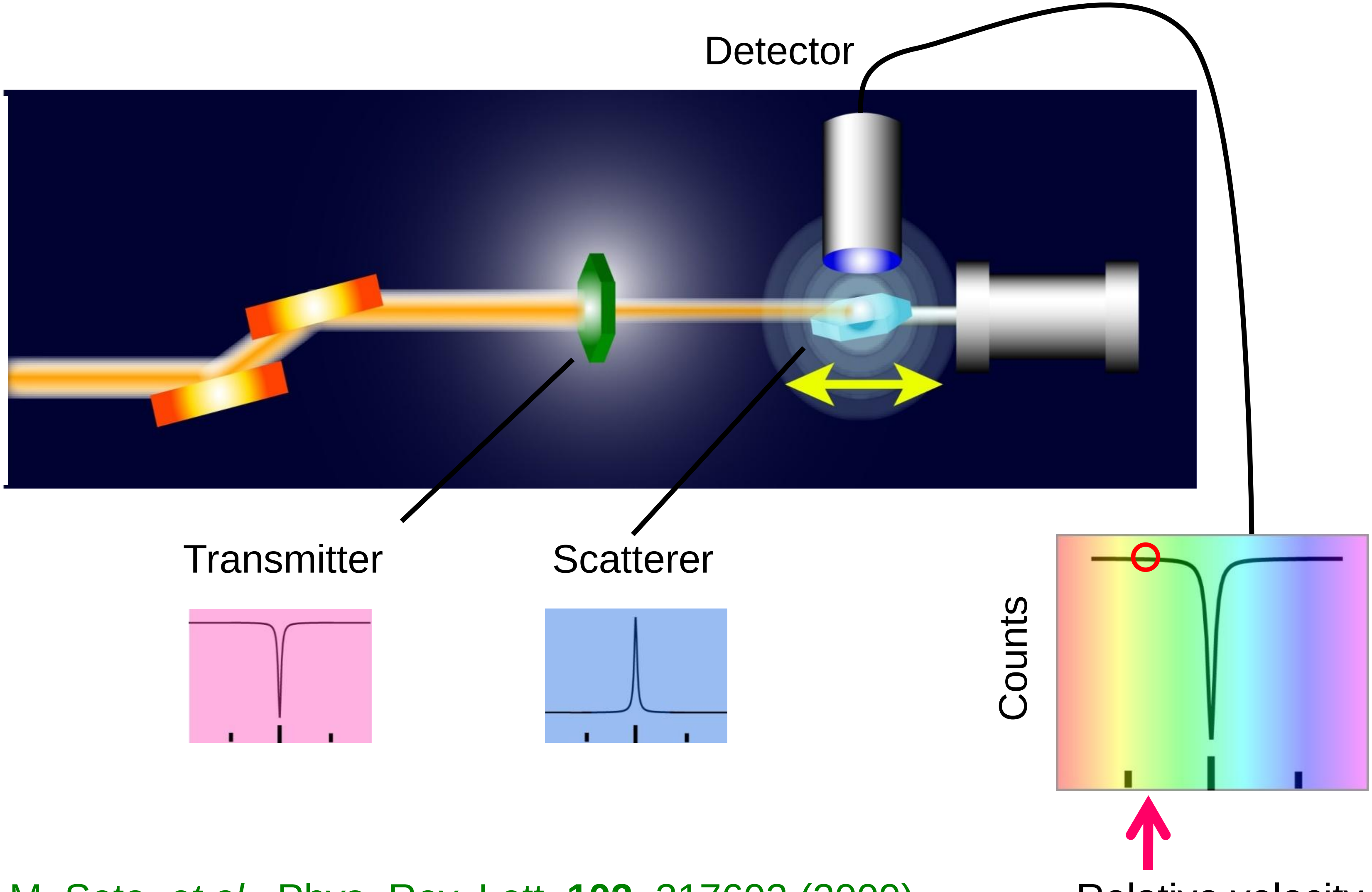


Setups of synchrotron-based Mössbauer spectroscopy

For the investigations on thin films



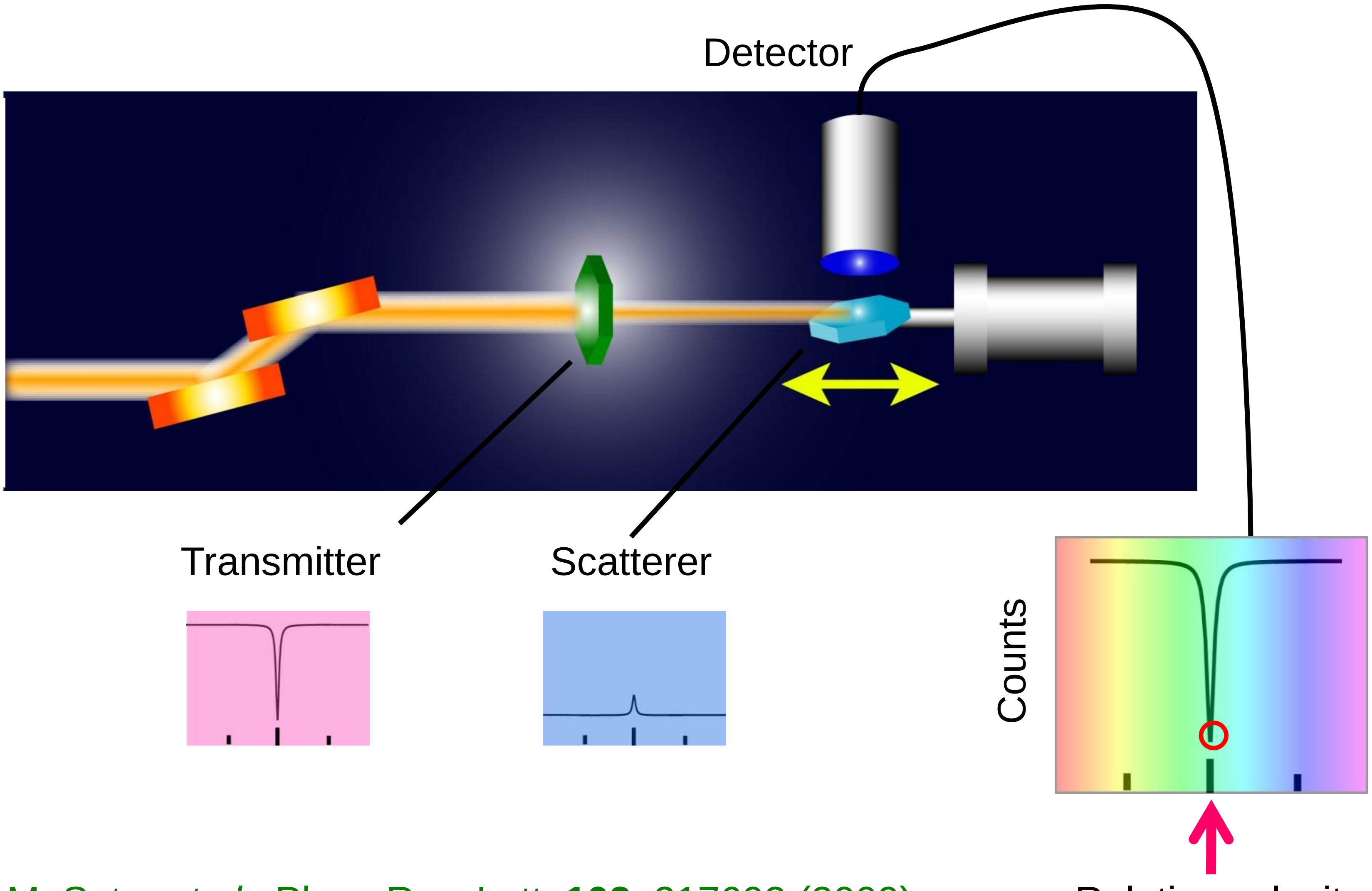
New method for SR Mössbauer spectroscopy in energy domain



M. Seto, *et al.*, Phys. Rev. Lett. **102**, 217602 (2009)

* The transmitter can be a sample and the scatterer can be a standard absorber, or vice versa

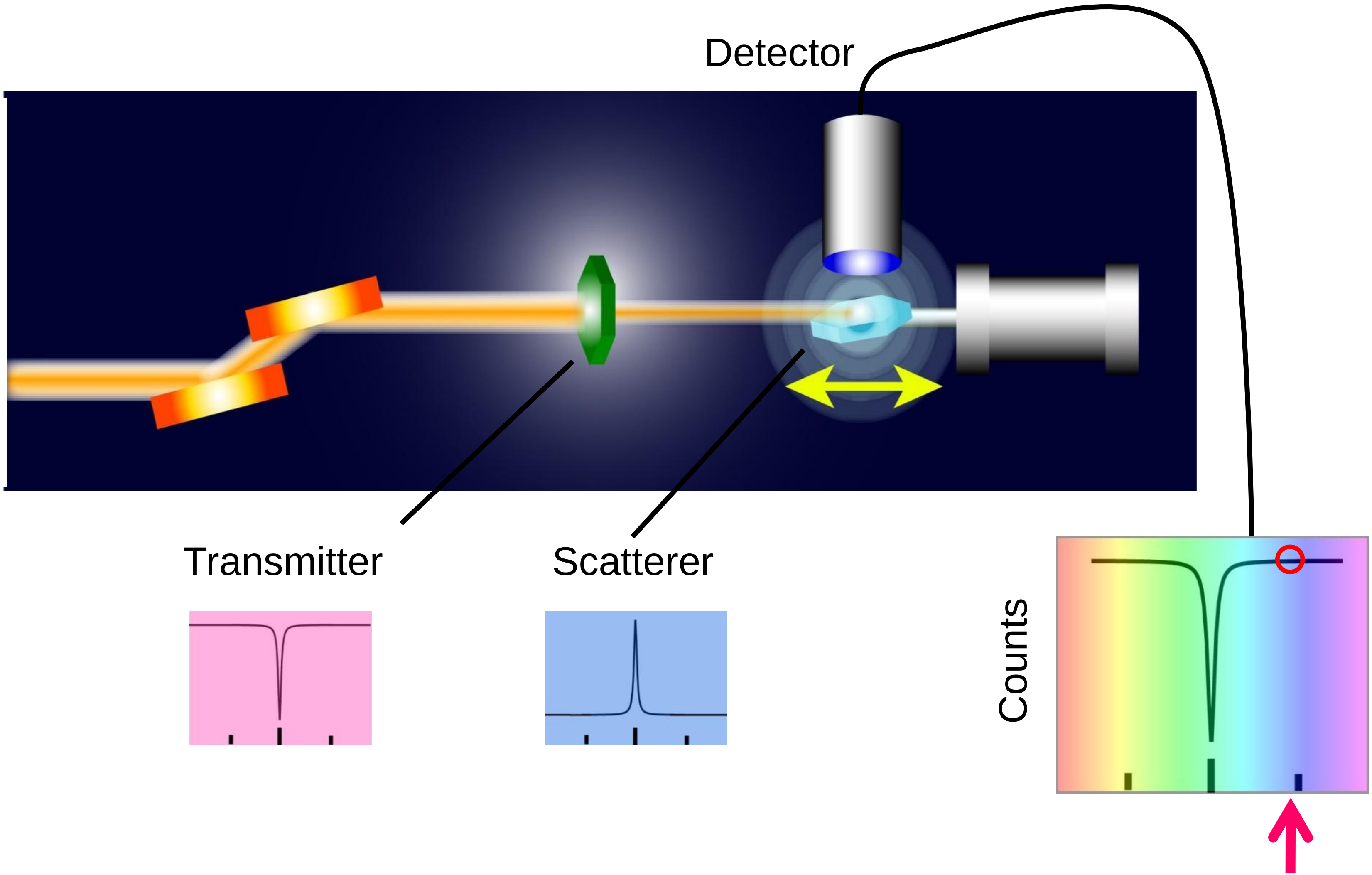
New method for SR Mössbauer spectroscopy in energy domain



M. Seto, *et al.*, Phys. Rev. Lett. **102**, 217602 (2009)

* The transmitter can be a sample and the scatterer can be a standard absorber, or vice versa

New method for SR Mössbauer spectroscopy in energy domain



M. Seto, *et al.*, Phys. Rev. Lett. **102**, 217602 (2009)

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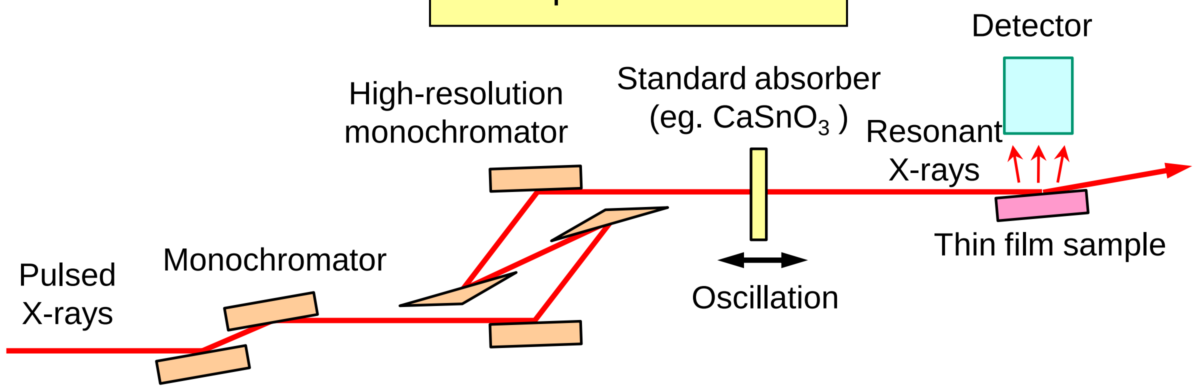
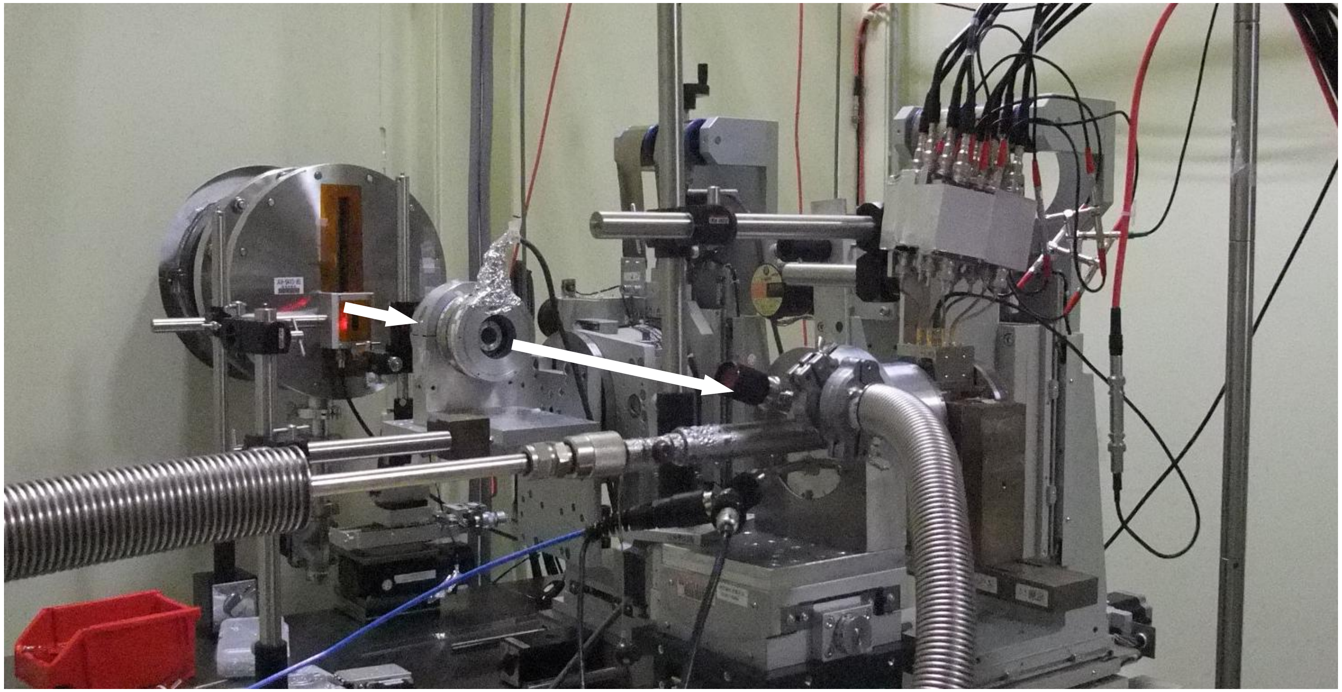
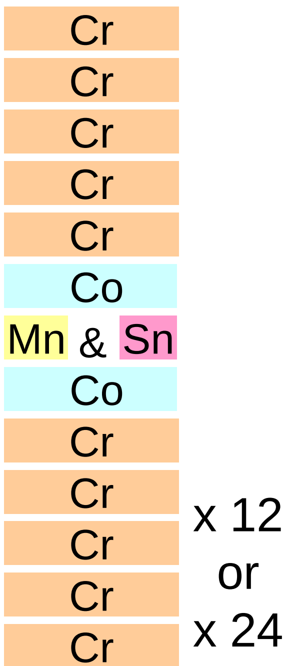
New method for SR Mössbauer spectroscopy in energy domain

Setups for thin films

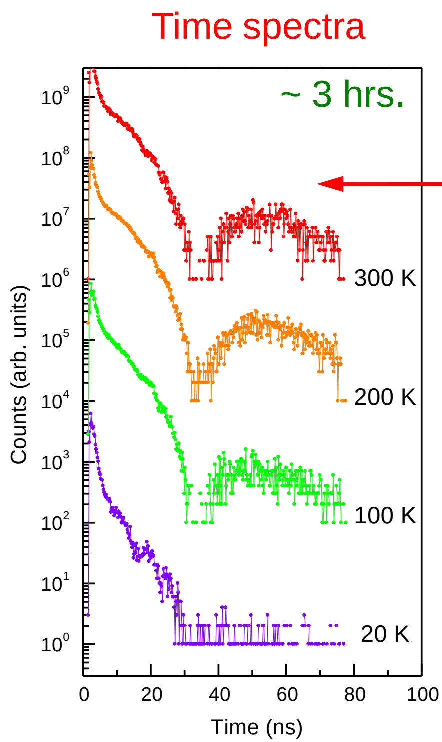


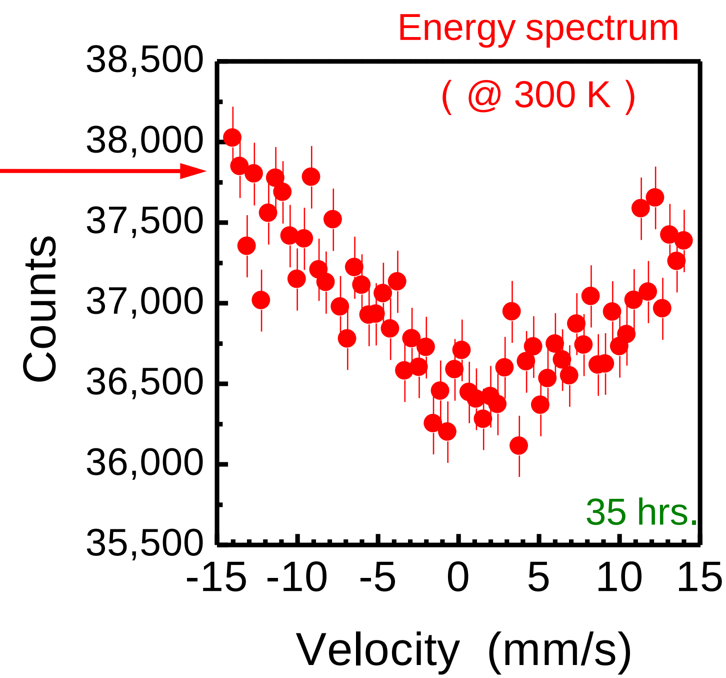


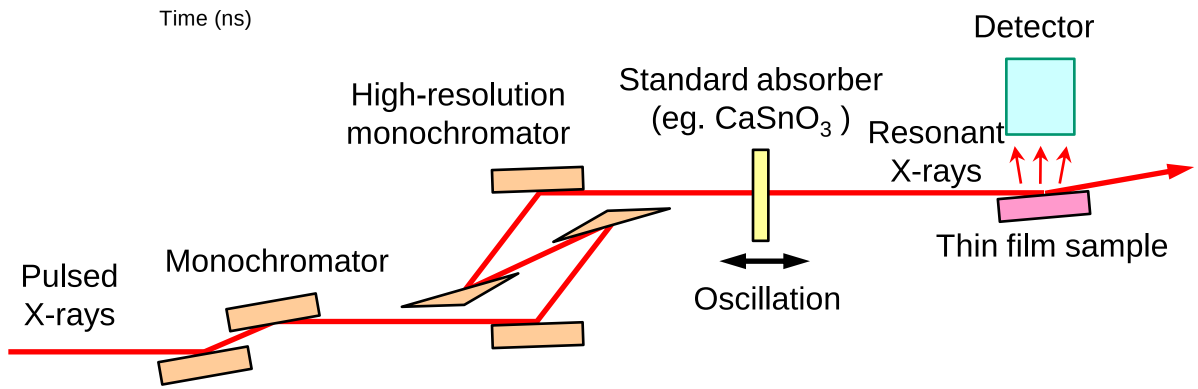
SR Mössbauer spectrum of a ultra-thin Co_2MnSn film in energy domain



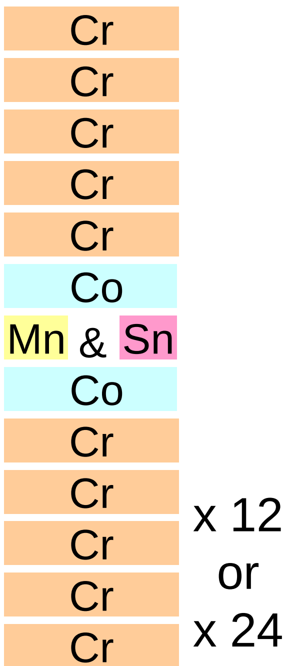
^{119}Sn total
1.2 nm
(~ 6 atomic layer)
or
2.4 nm
(~ 12 atomic layer)







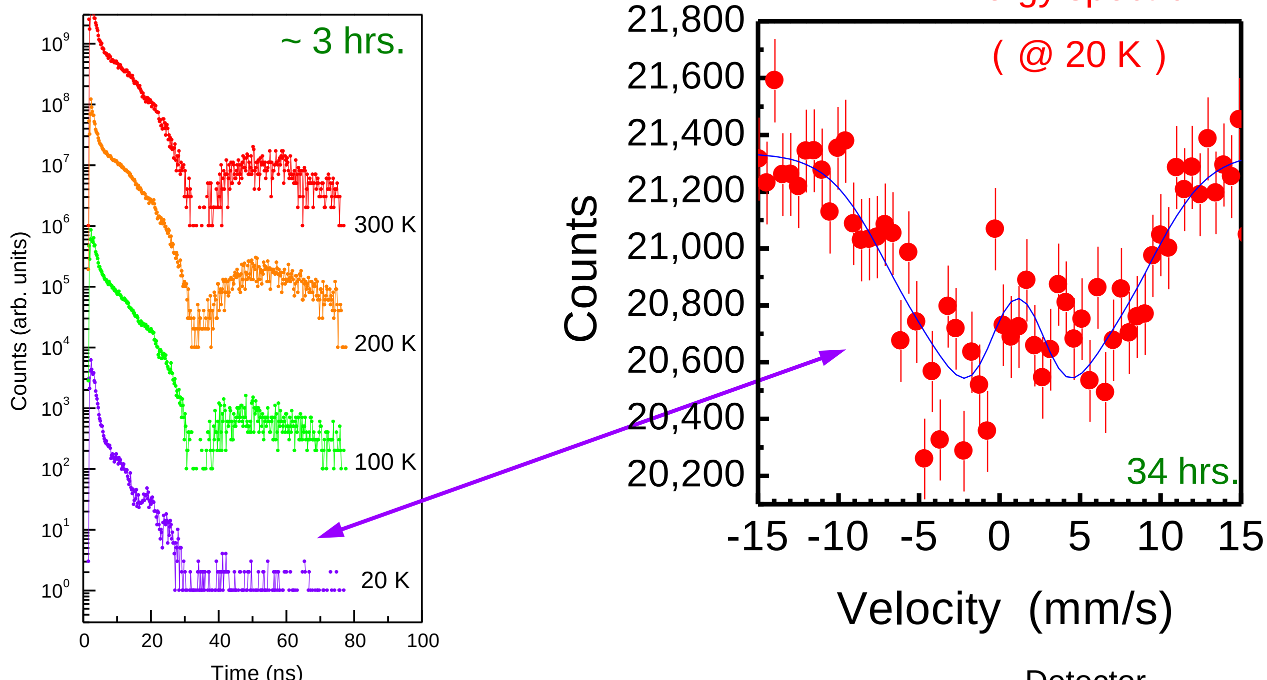
SR Mössbauer spectrum of a ultra-thin Co_2MnSn film in energy domain

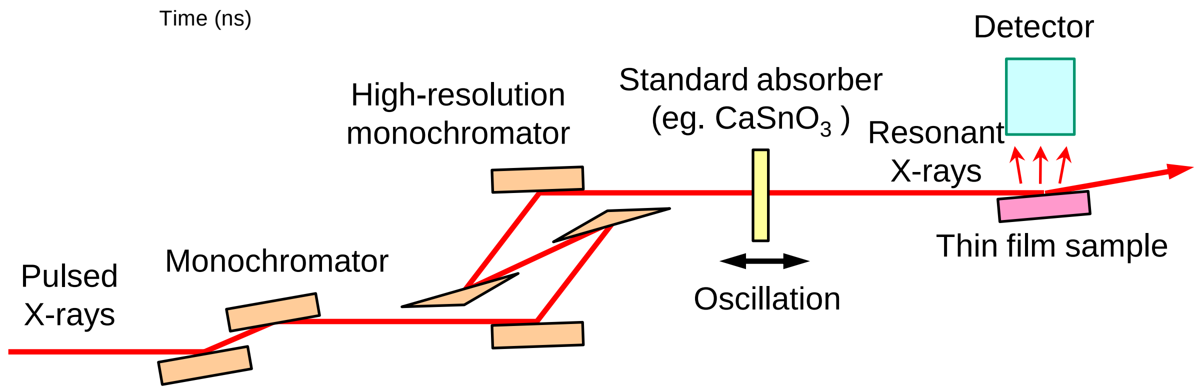


^{119}Sn total
1.2 nm
(~ 6 atomic layer)
or
2.4 nm
(~ 12 atomic layer)

Time spectra

Energy spectrum





Still necessary to be improved for thin films

Conclusion

Synchrotron-radiation-based Mössbauer spectroscopy in energy domain
for the studies on thin films and nano-structures

From

the development and demonstration phase

to

the application phase for material researches

Thank you