

Mössbauer Spectroscopy – Part 2

D.H. Ryan

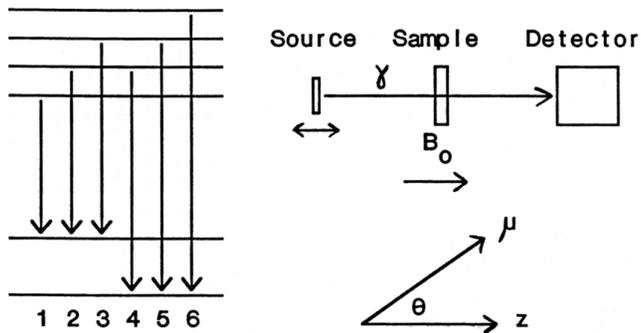
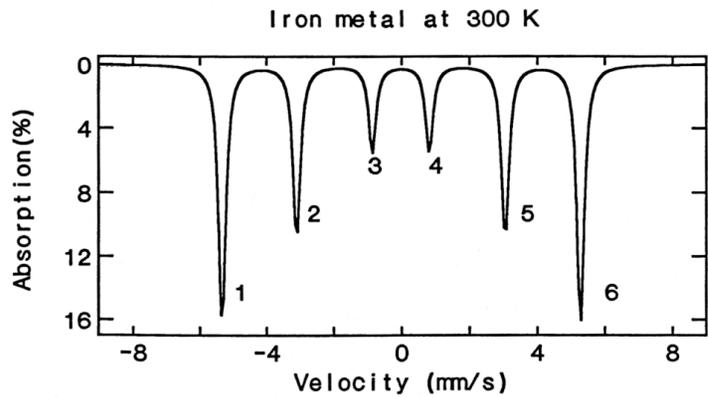
Centre for the Physics of Materials and
Physics Department,
McGill University, Montreal, Quebec



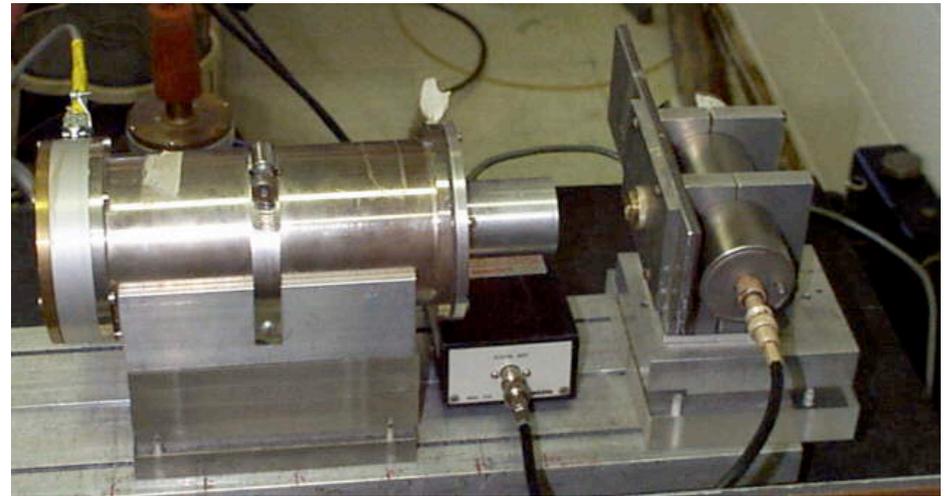
McGill

ISU Physics-590B 25/27 Feb 2019

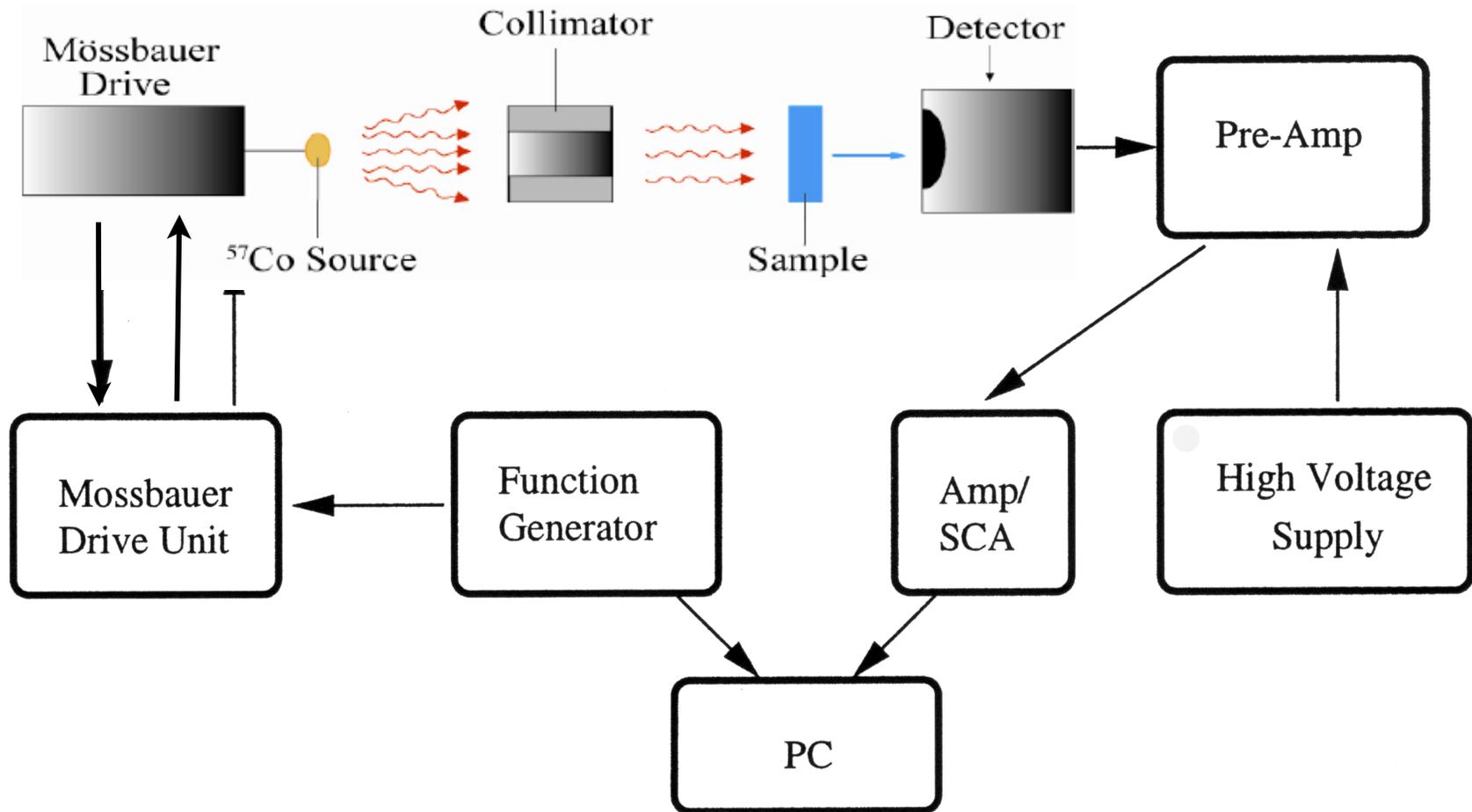
Instant Mössbauer



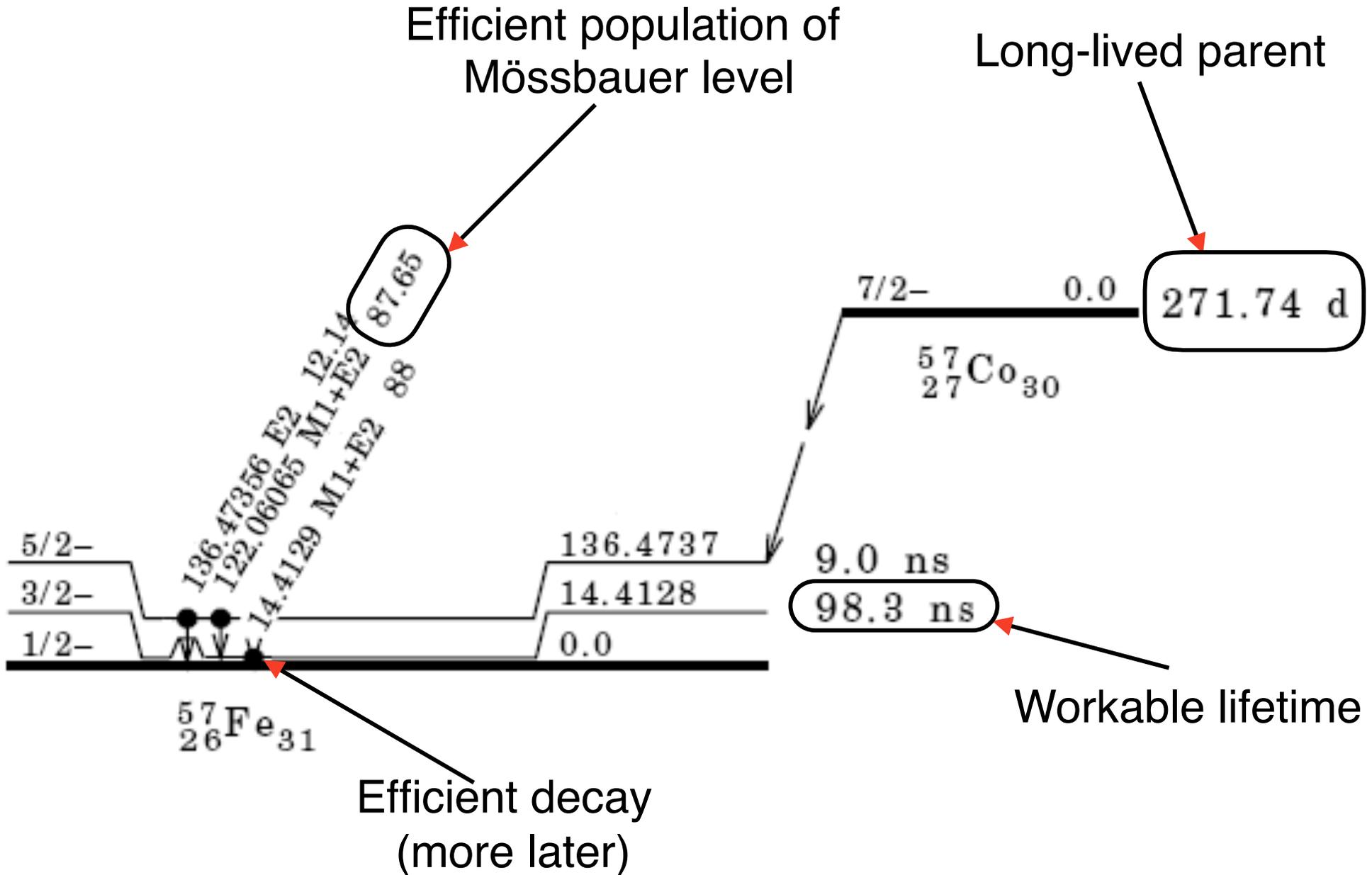
$$I_{2,5} = \frac{4\sin^2\vartheta}{1 + \cos^2\vartheta}$$



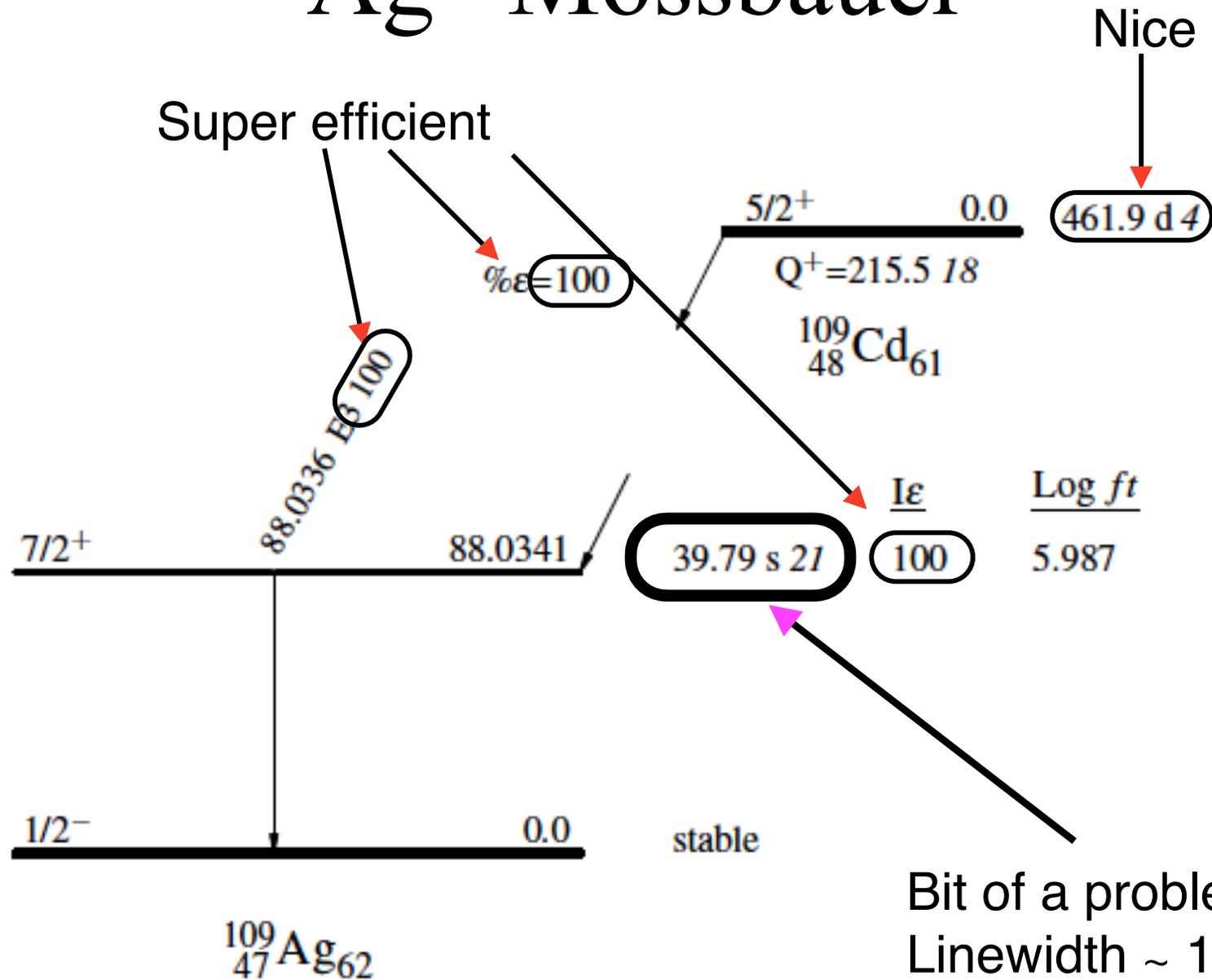
Typical spectrometer components



^{57}Fe Mössbauer



^{109}Ag “Mössbauer”



Valence

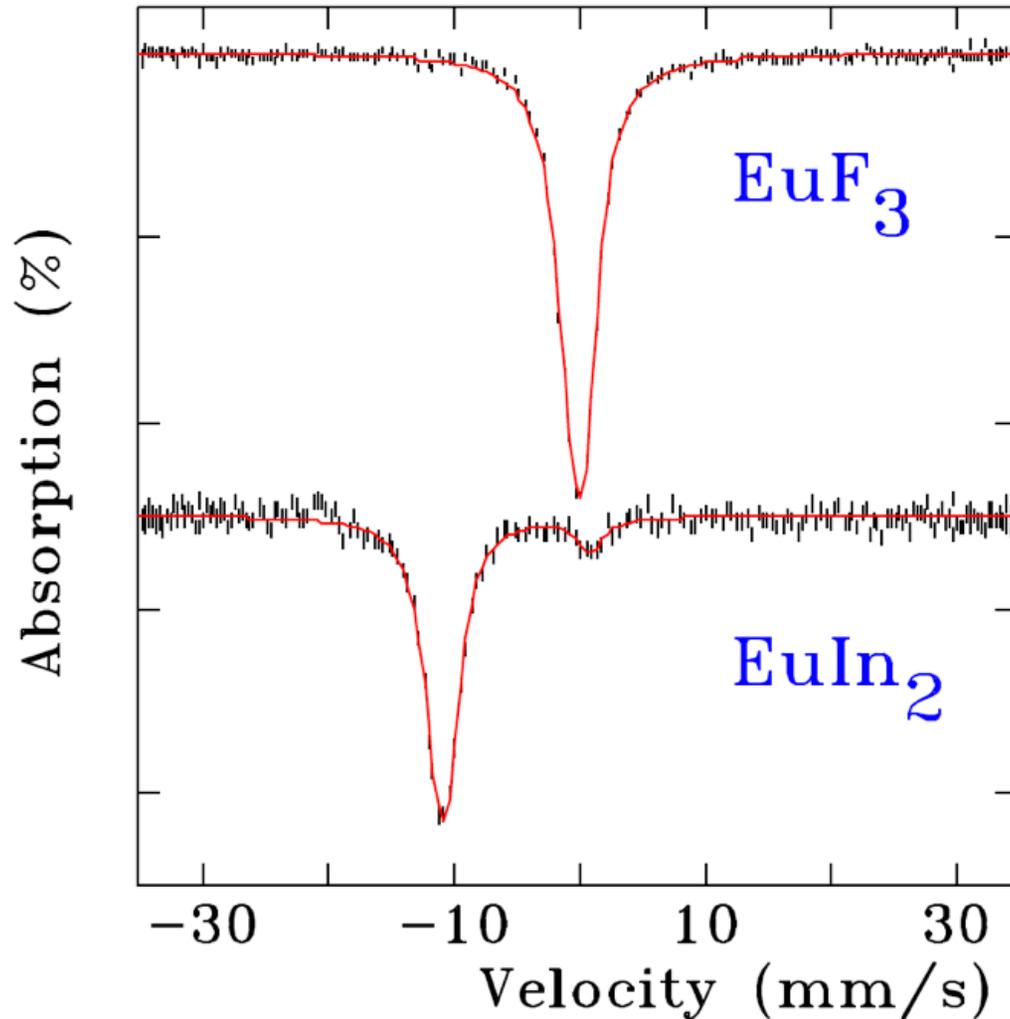
Determining the valence of a Mössbauer-active element is frequently quite easy.

It is also an extremely useful and basic piece of information.

As a result, it can be surprisingly lucrative.

However, it does not always come from the isomer shift.

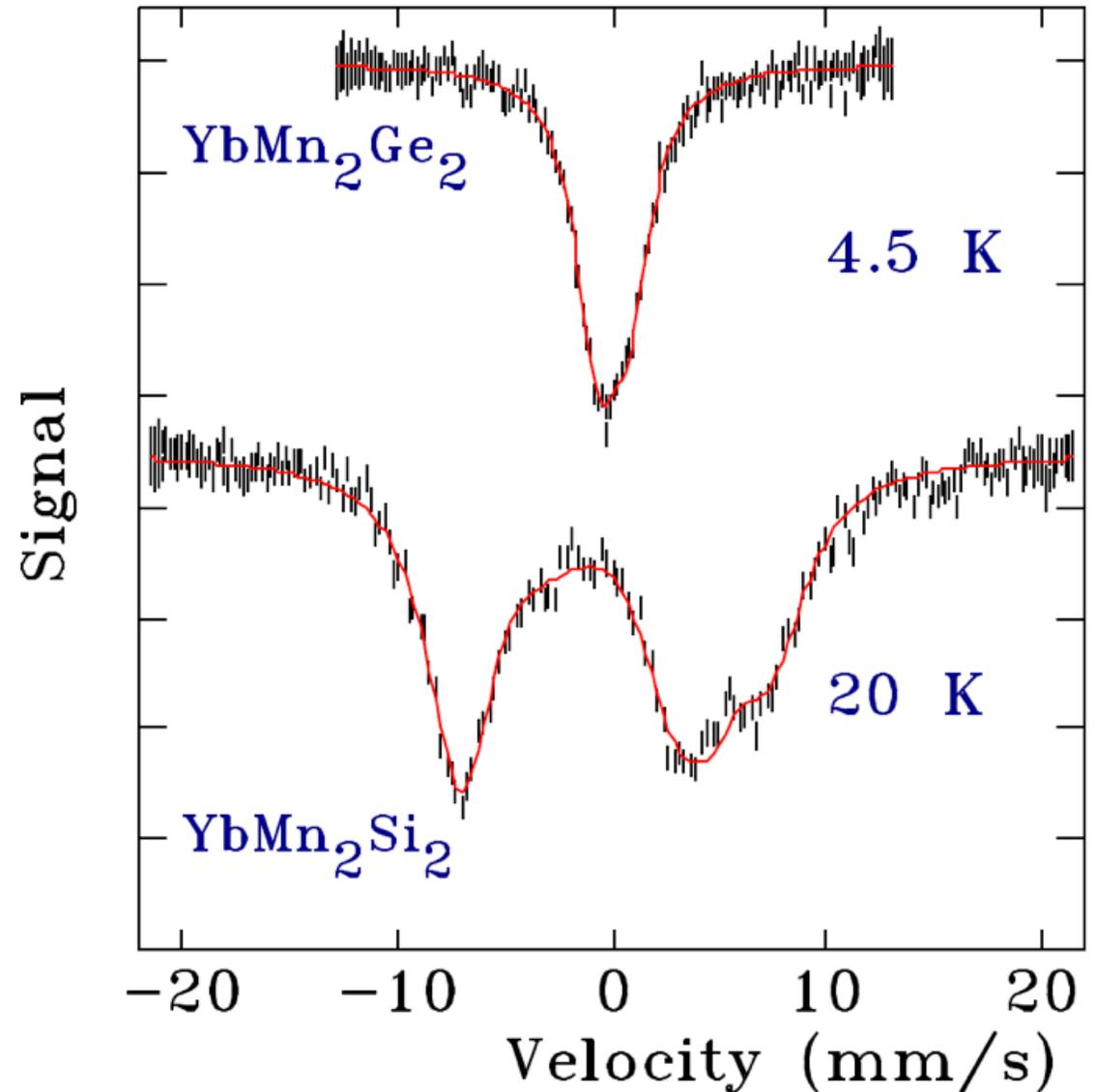
^{151}Eu has one of the largest $2^+/3^+$ changes in isomer shift

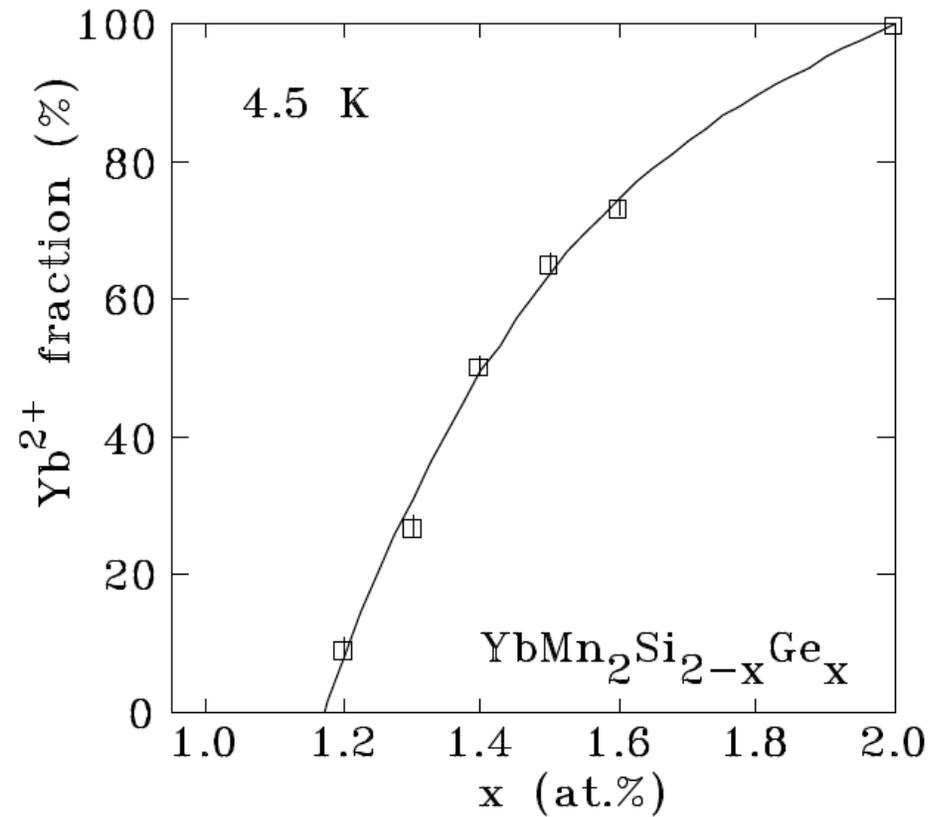
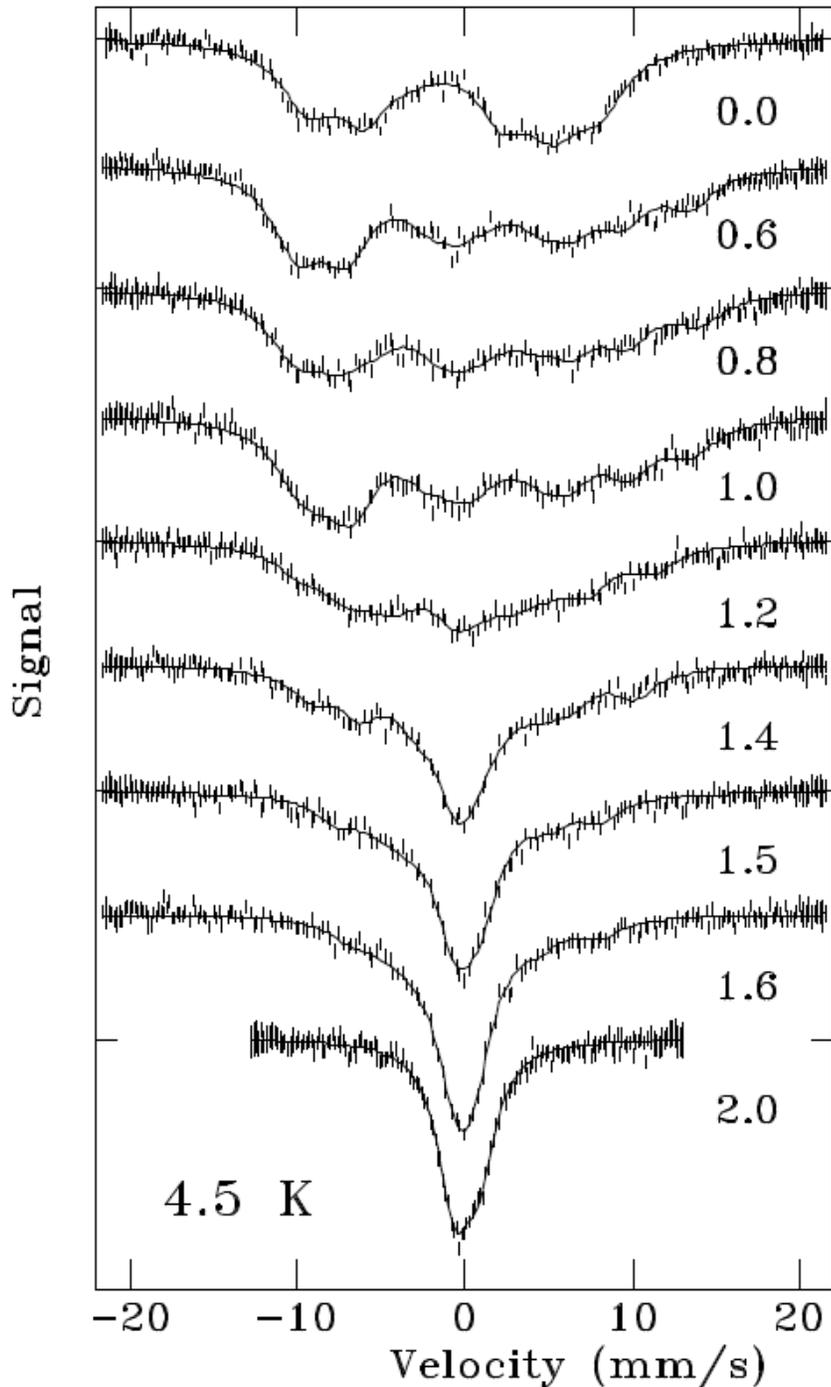


but almost no quadrupole contribution in either state

^{170}Yb has *no* change in isomer shift

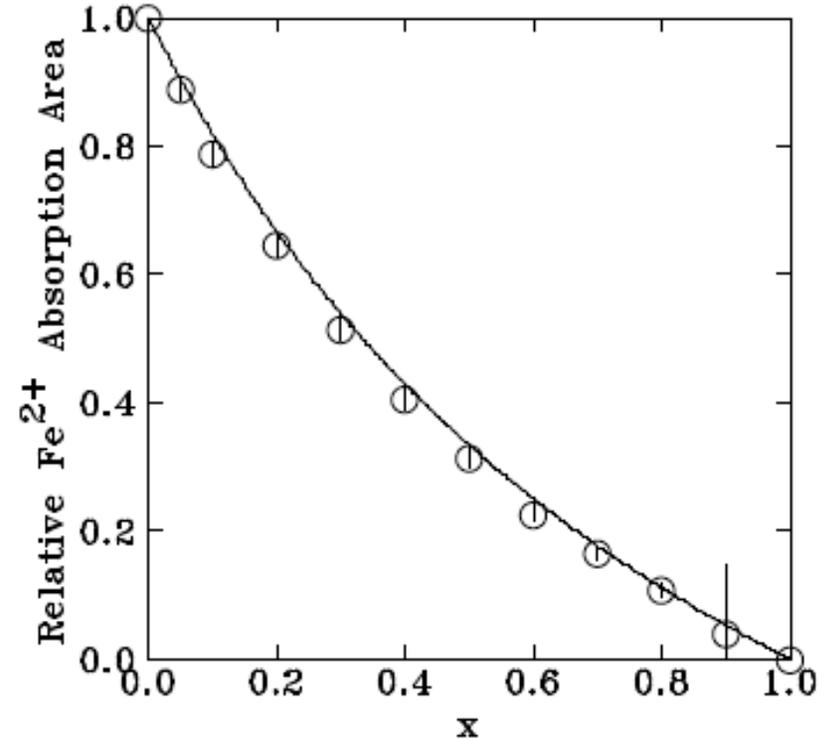
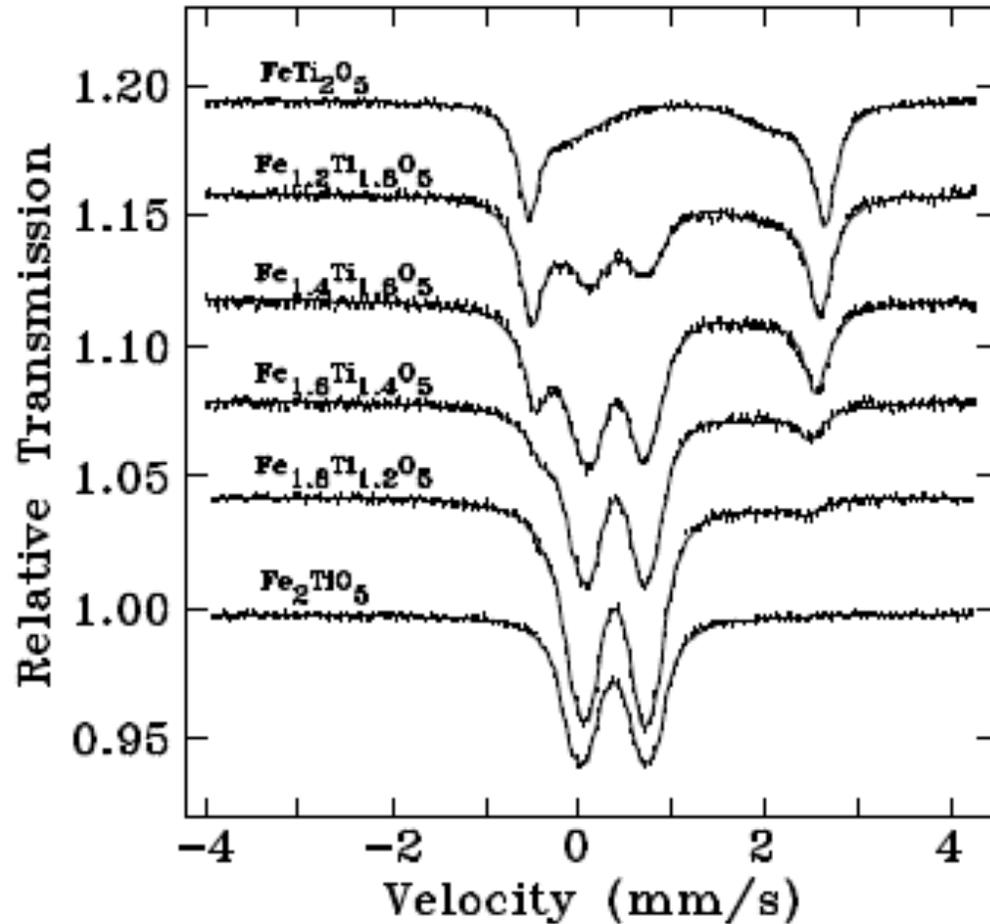
but a clear difference in quadrupole contribution makes the two valence states distinct.





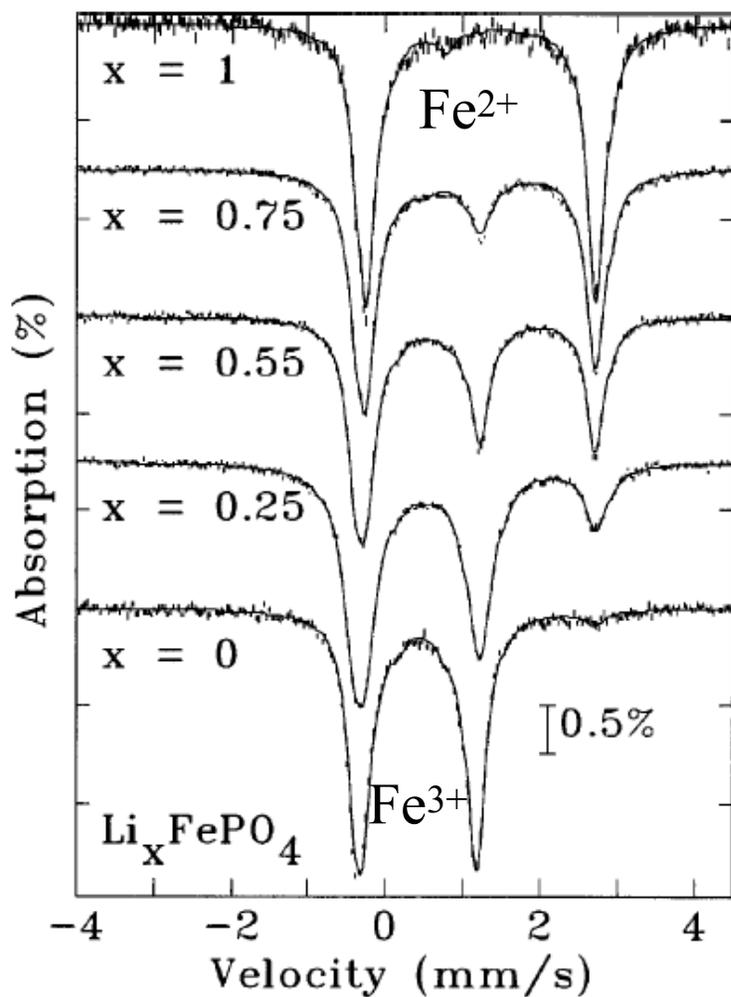
This makes tracking the evolution of the ytterbium valence quite easy.

^{57}Fe shows changes in both the isomer shift and quadrupole splitting



W Q Guo†‡, S Malus†, D H Ryan† and Z Altounian†
J. Phys.: Condens. Matter **11** (1999) 6337–6346.

Li_xFePO_4

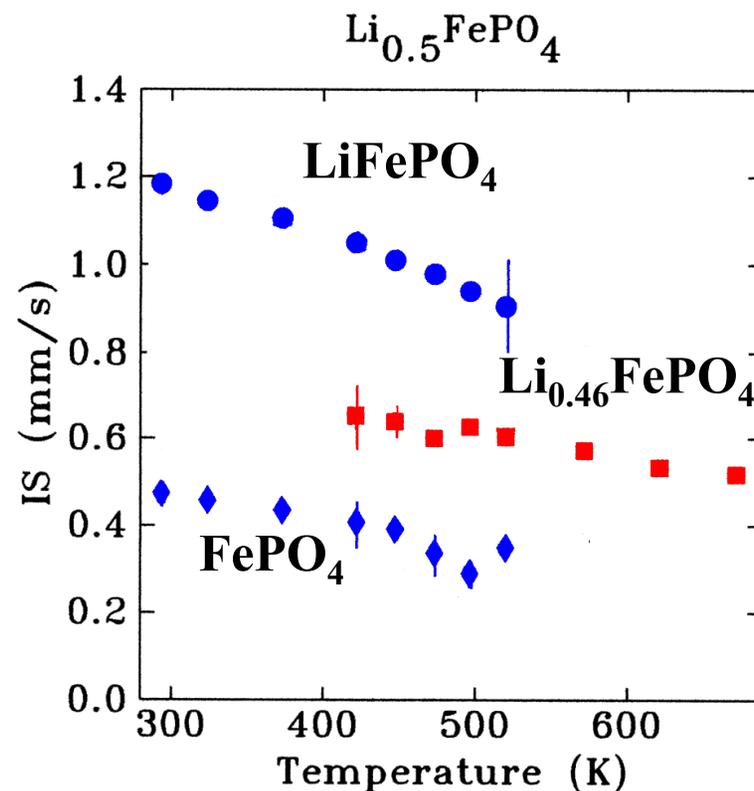
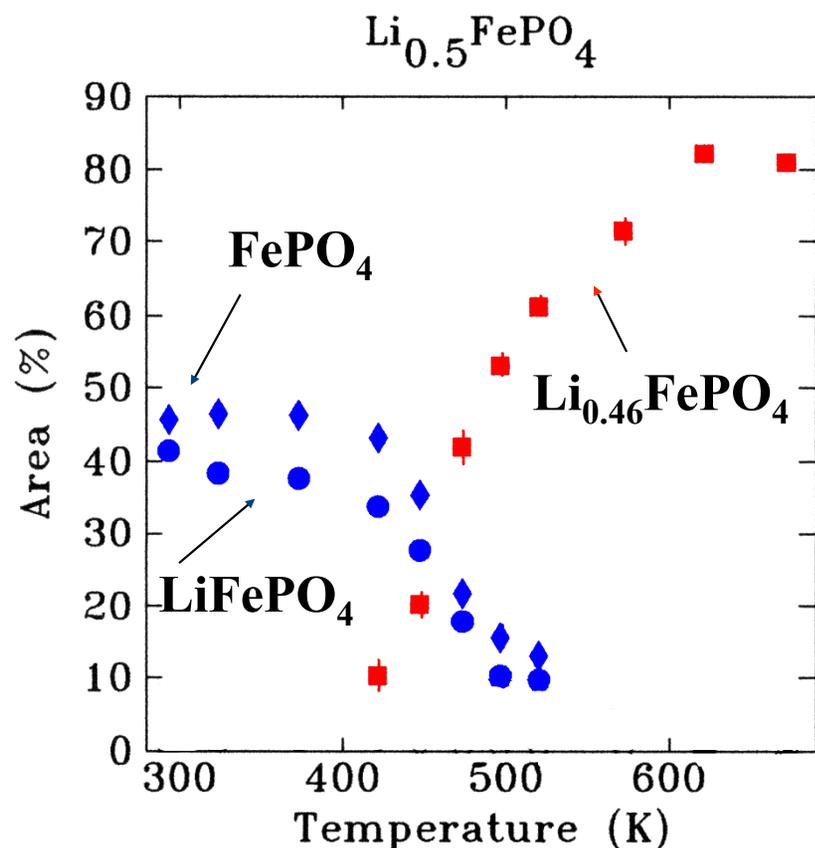


- Spectra from Fe^{2+} and Fe^{3+} are distinct
- Progressive oxidation of the iron is clearly seen.
- Information is *quantitative* and can be compared *directly* with electrochemical charge state

Rapid e- hopping in Li_xFePO_4

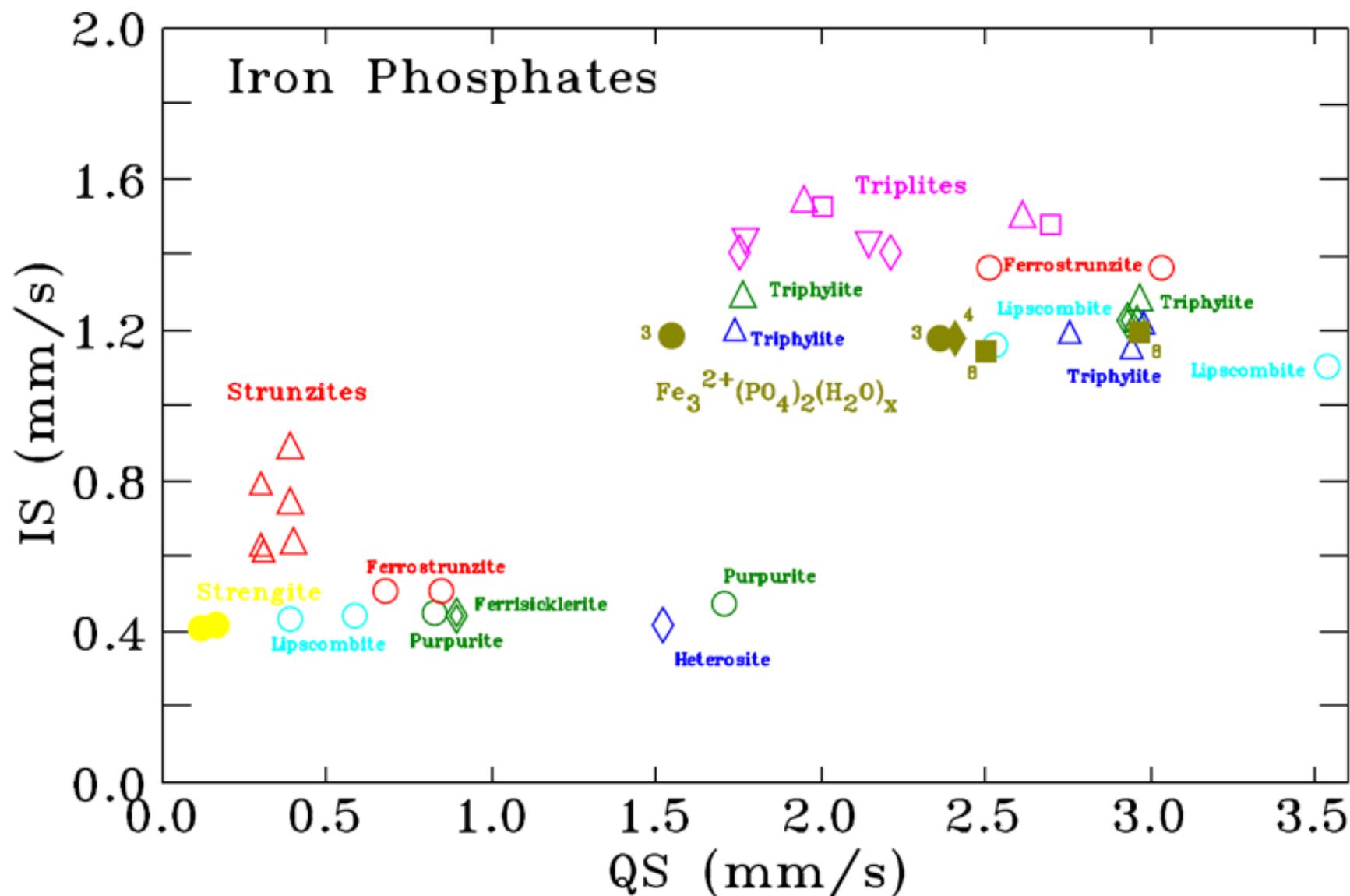
Variable temp Mössbauer data for $\text{LiFePO}_4/\text{FePO}_4$

- in collaboration with Prof. Linda Nazar, Waterloo



- Fast hopping on the Mössbauer time scale ($10^{-8} - 10^{-6}$ sec) seen at 420K
- – transition occurs at same temp as seen by diffraction
- Averaged environment $\text{Fe}^{2.5+}$ > 420K, \rightarrow NO intermediate region
- Co-existence of two-phase regime and solid solution regime (420-500K)

“Fingerprinting” for mineral identification can be very useful, but it is not without problems

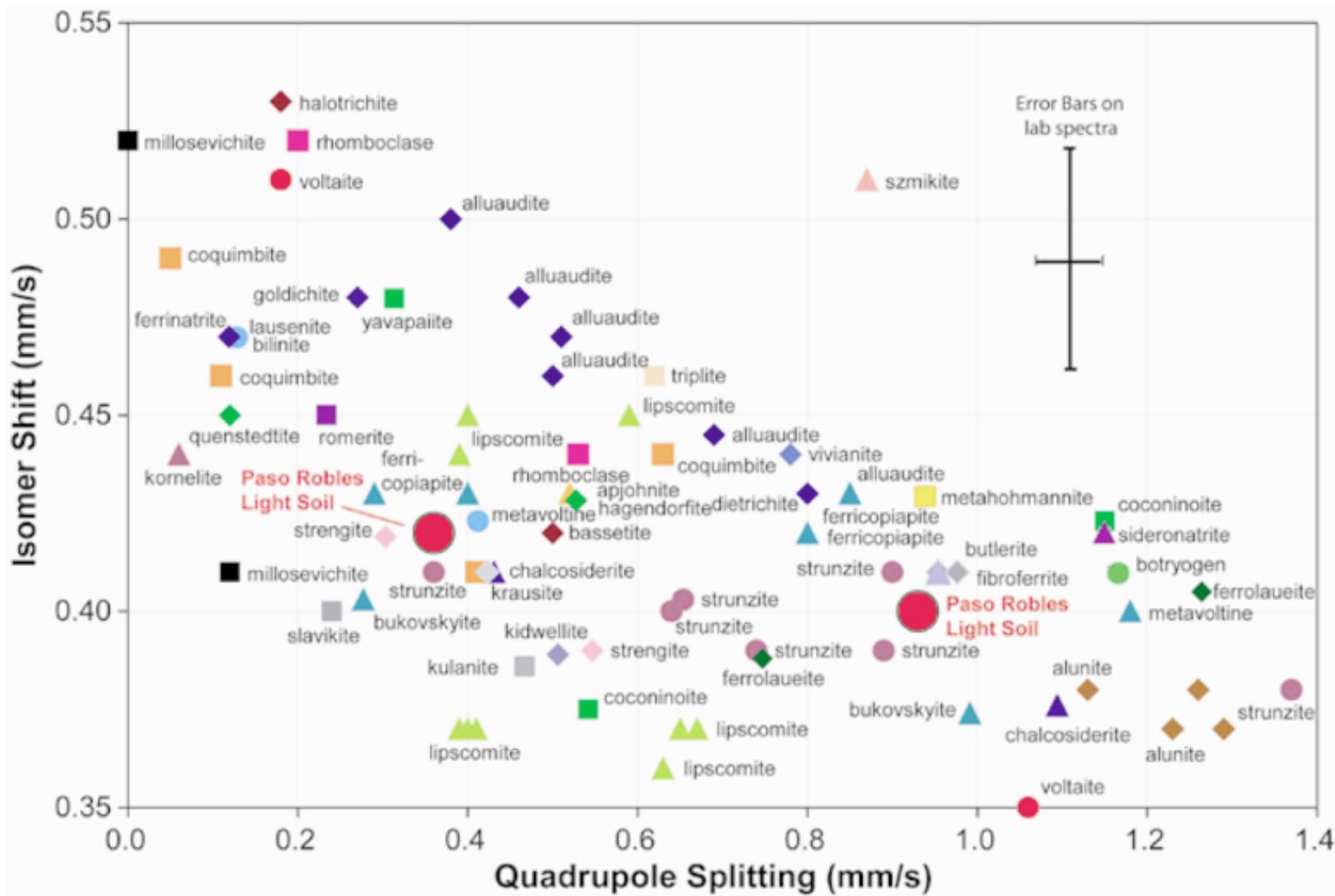


Minerals are important to understanding our planet.

To do anything quantitative with mineral samples you generally need reference materials. However, even this can be problematic.

And it can get worse...

If you add the sulphates...

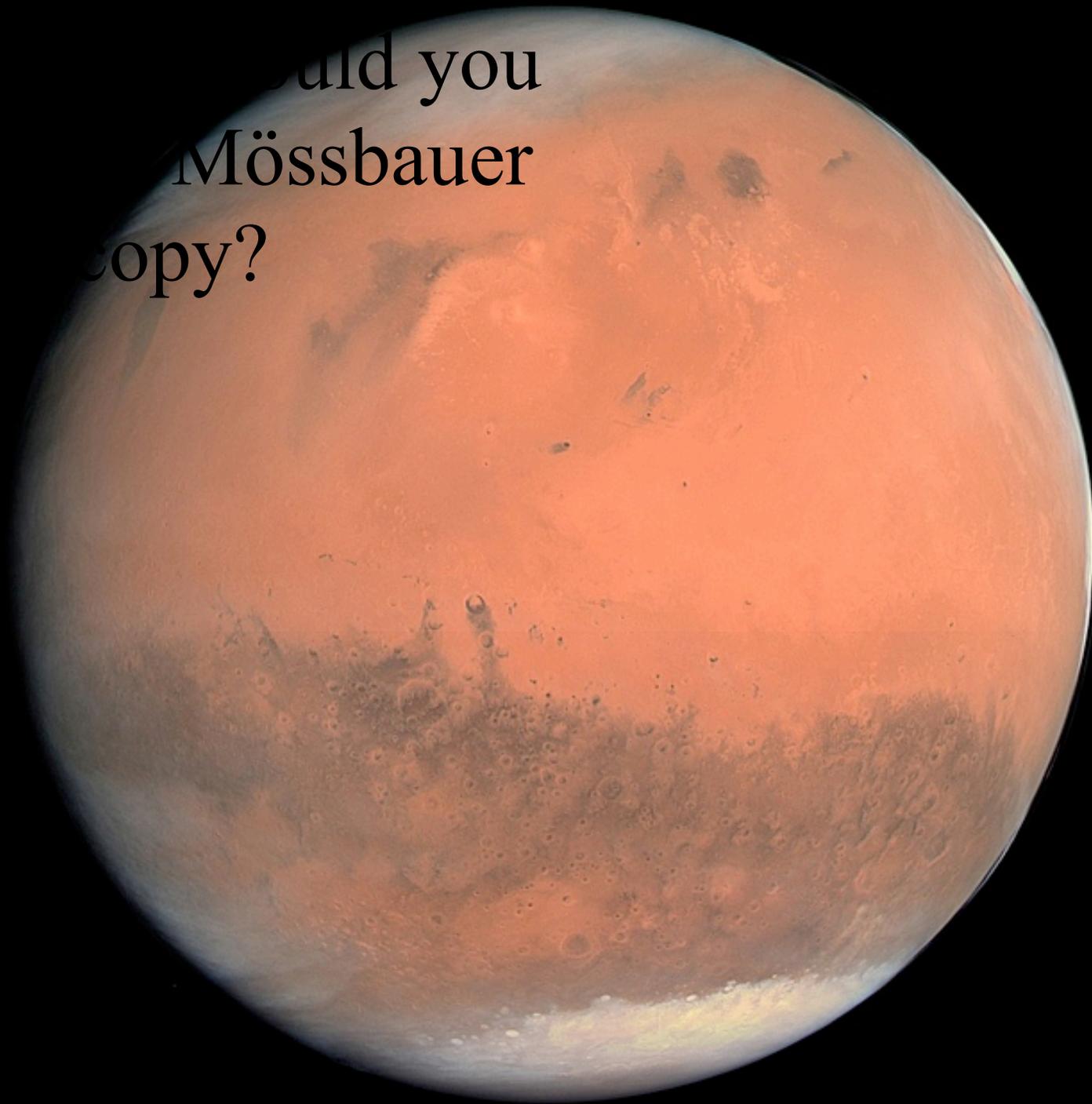


Seventh International Conference on Mars

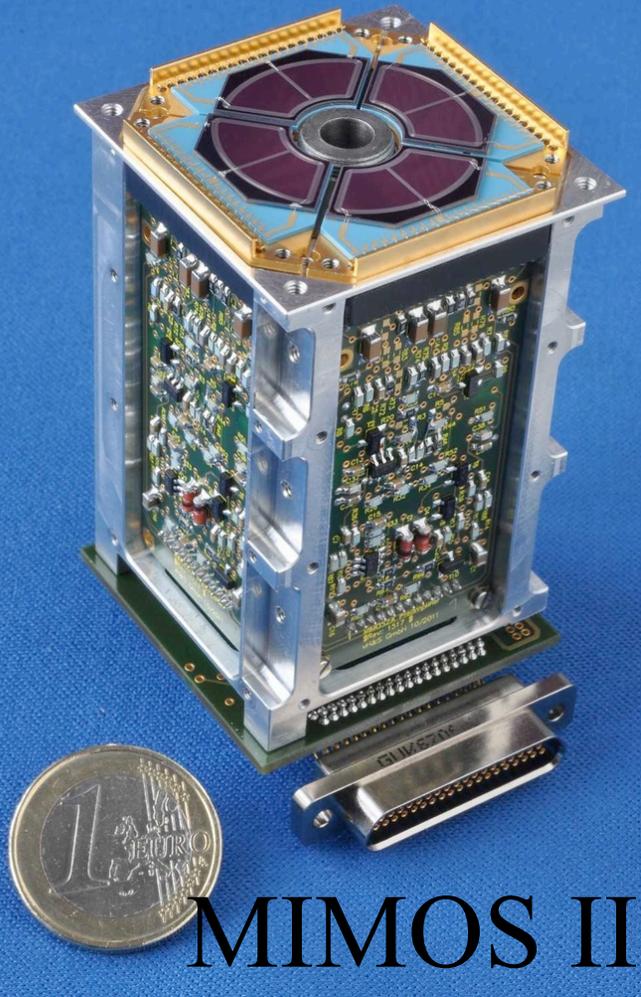
THE FERRIC SULFATE AND FERRIC PHOSPHATE MINERALS IN THE LIGHT-TONED PASO ROBLES ROVER TRACK SOILS: A MULTI-INSTRUMENT ANALYSIS. Melissa D.

Lane¹, Janice L. Bishop², M. Darby Dyar³, Mario Parente⁴, Penelope L. Kings⁵, and Brendt C. Hydes.

Why would you
want Mössbauer
spectroscopy?

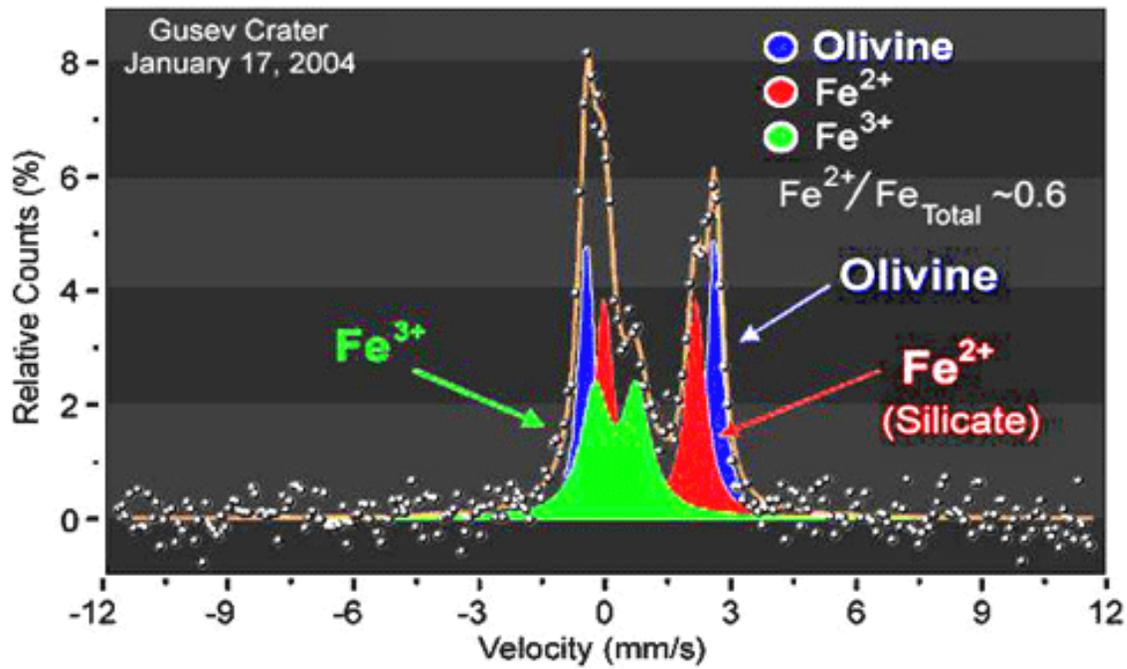


The Opportunity rover



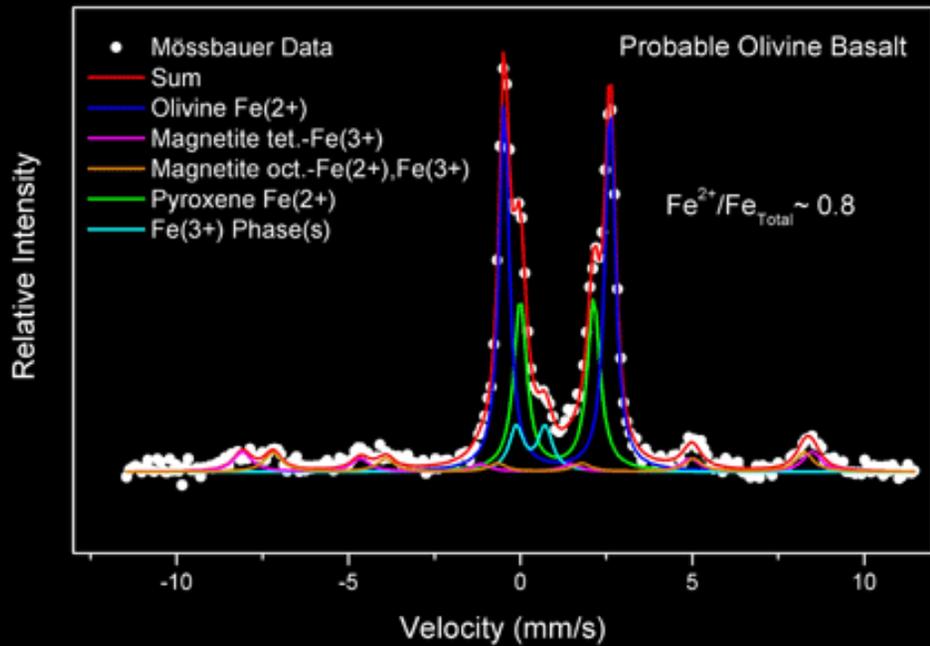
First Mössbauer Spectrum Recorded on Martian Surface

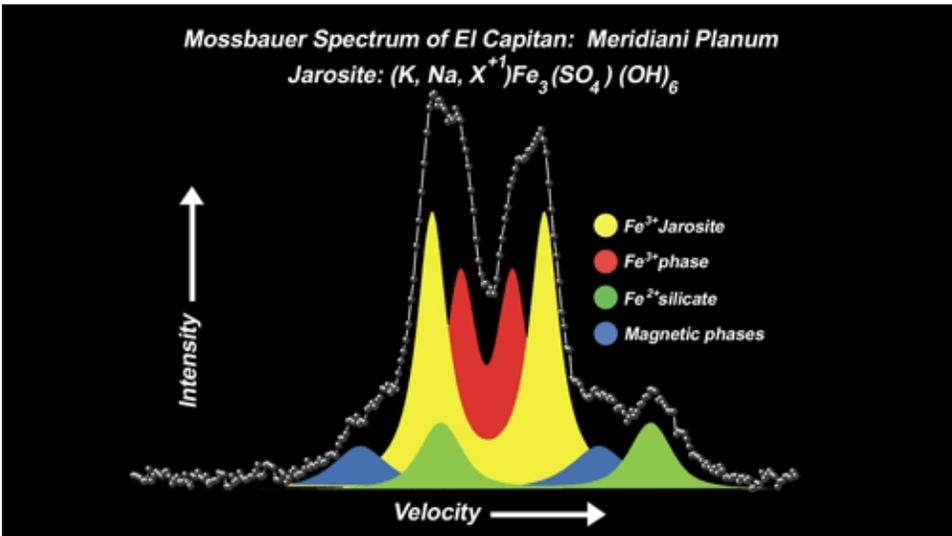
Image Credits: NASA/JPL/University of Mainz



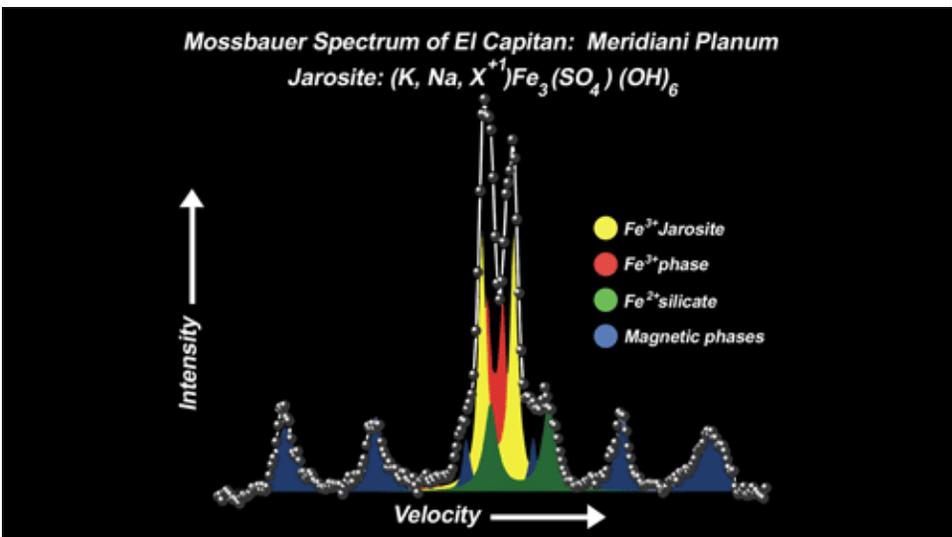
Göstar Klingelhöfer
2-Oct-1956 – 8-Jan-2019

Mössbauer Spectrum of Adirondack Rock
(Sol 18, Gusev Crater, Mars)



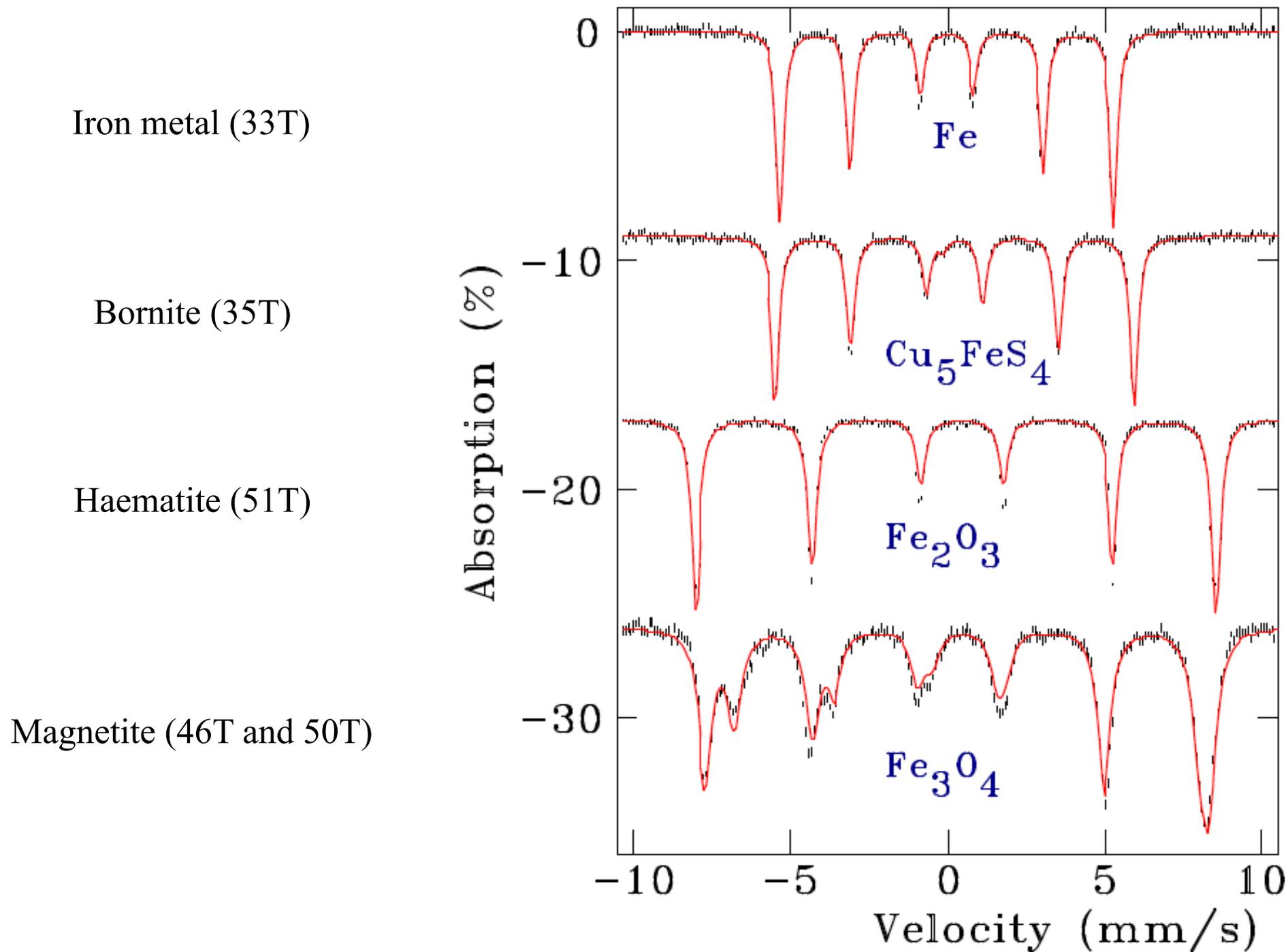


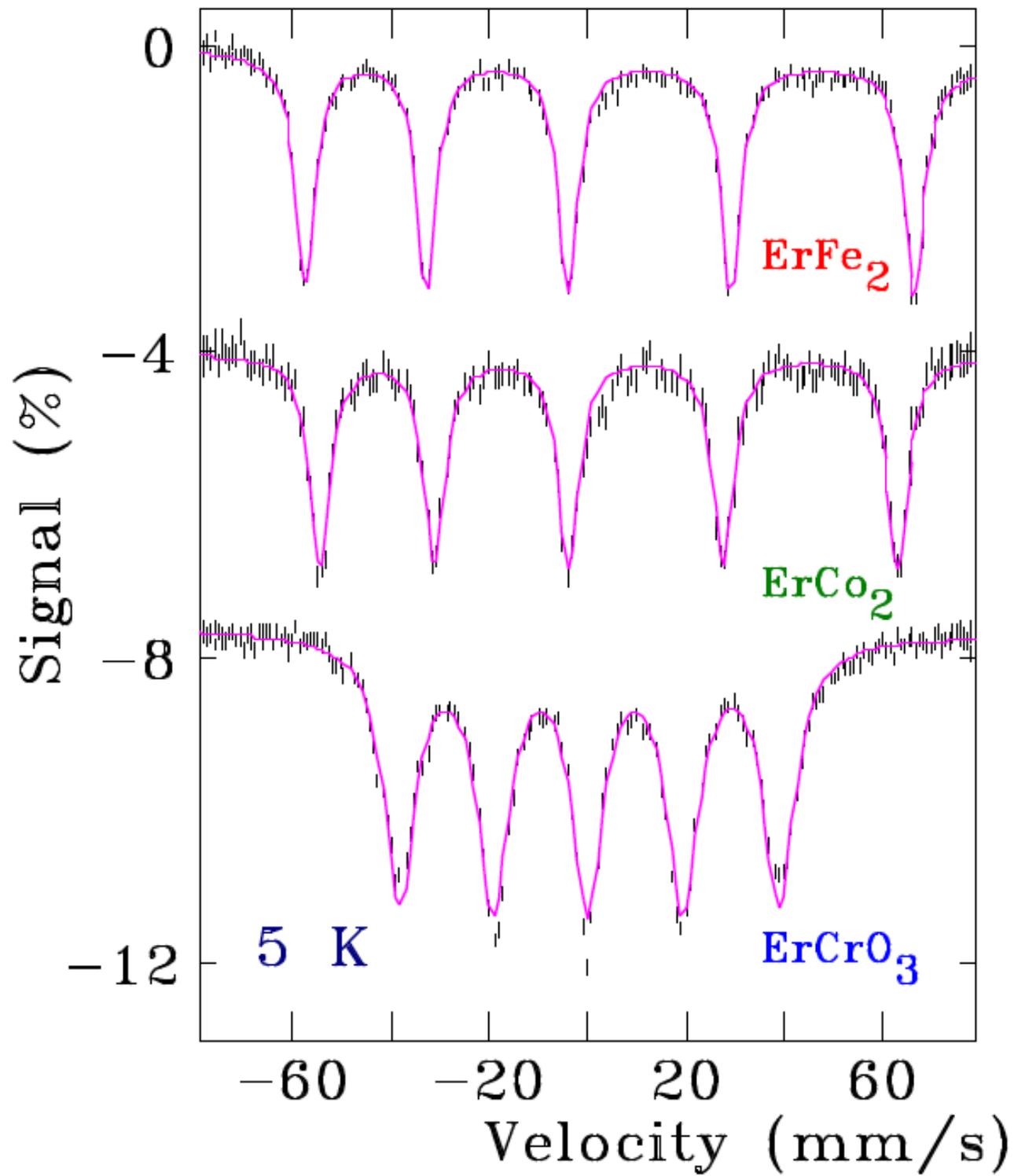
Sol 19



Sol 18

Image Credits: NASA/JPL/University of Mainz





B_{hf}

840 T

797 T

524 T

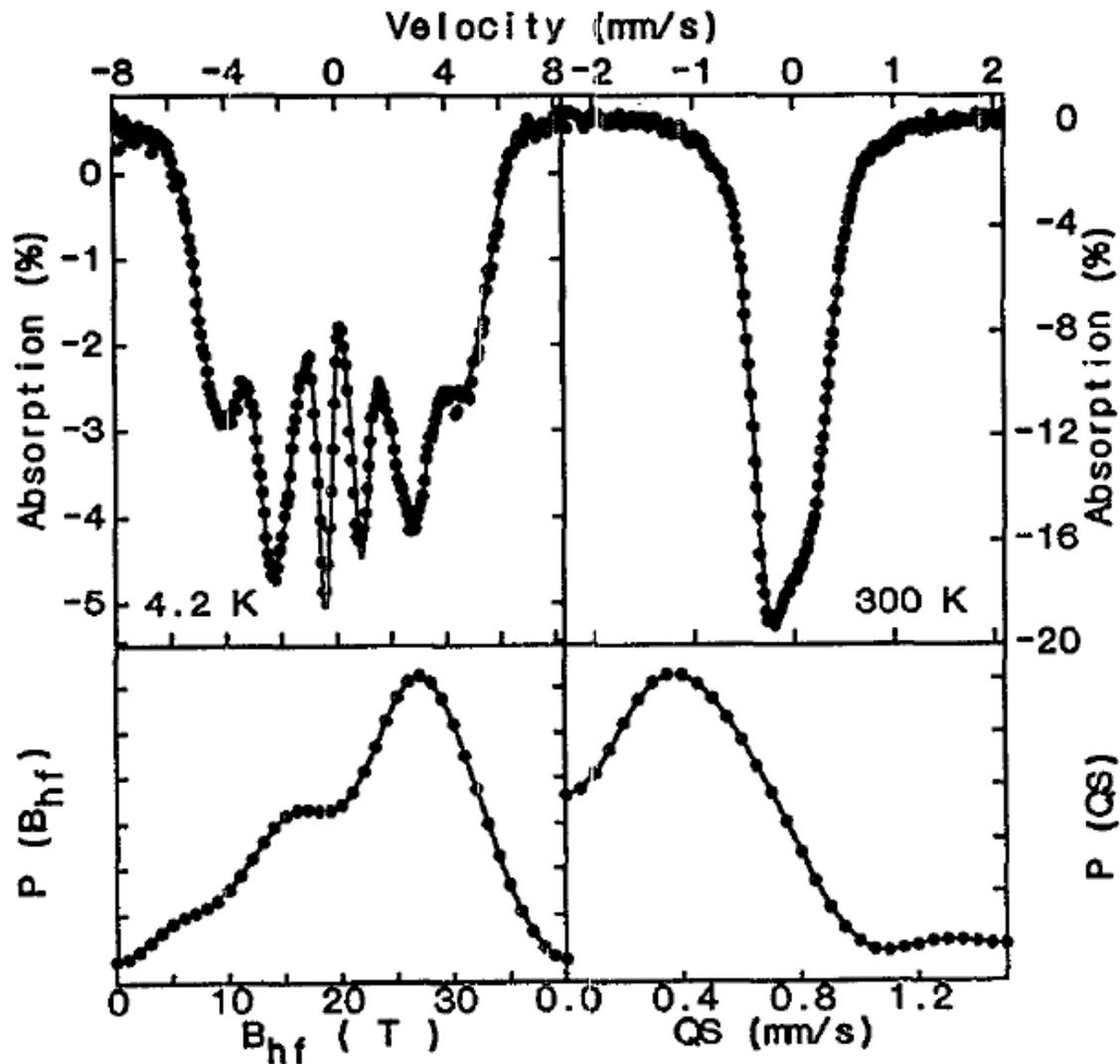
ErFe_2

ErCo_2

ErCrO_3

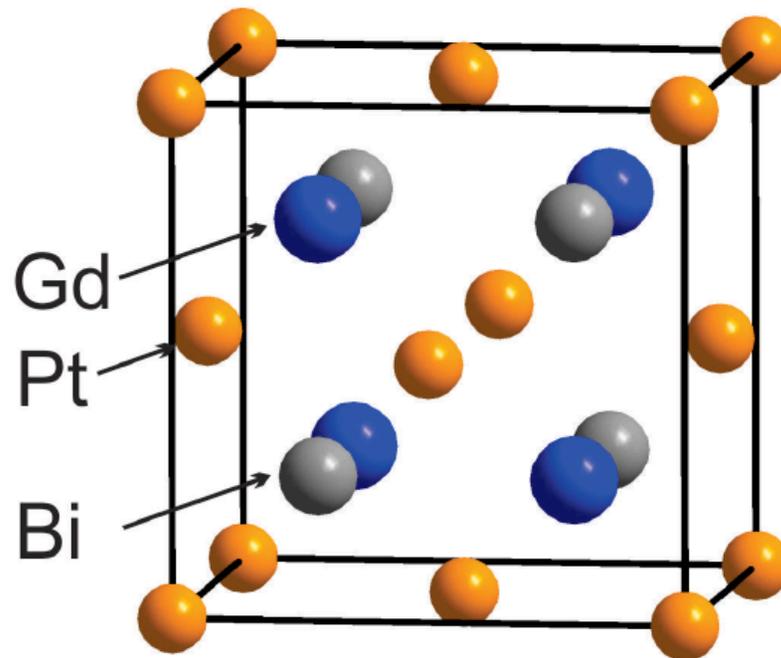
5 K

Amorphous materials exhibit a distribution of parameters

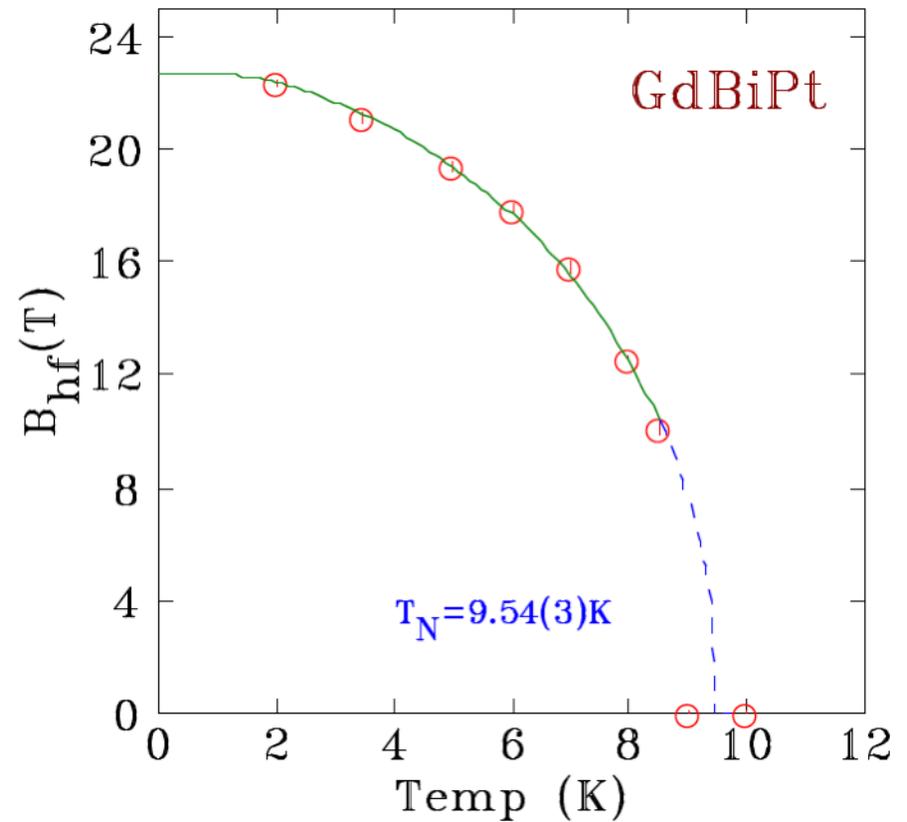
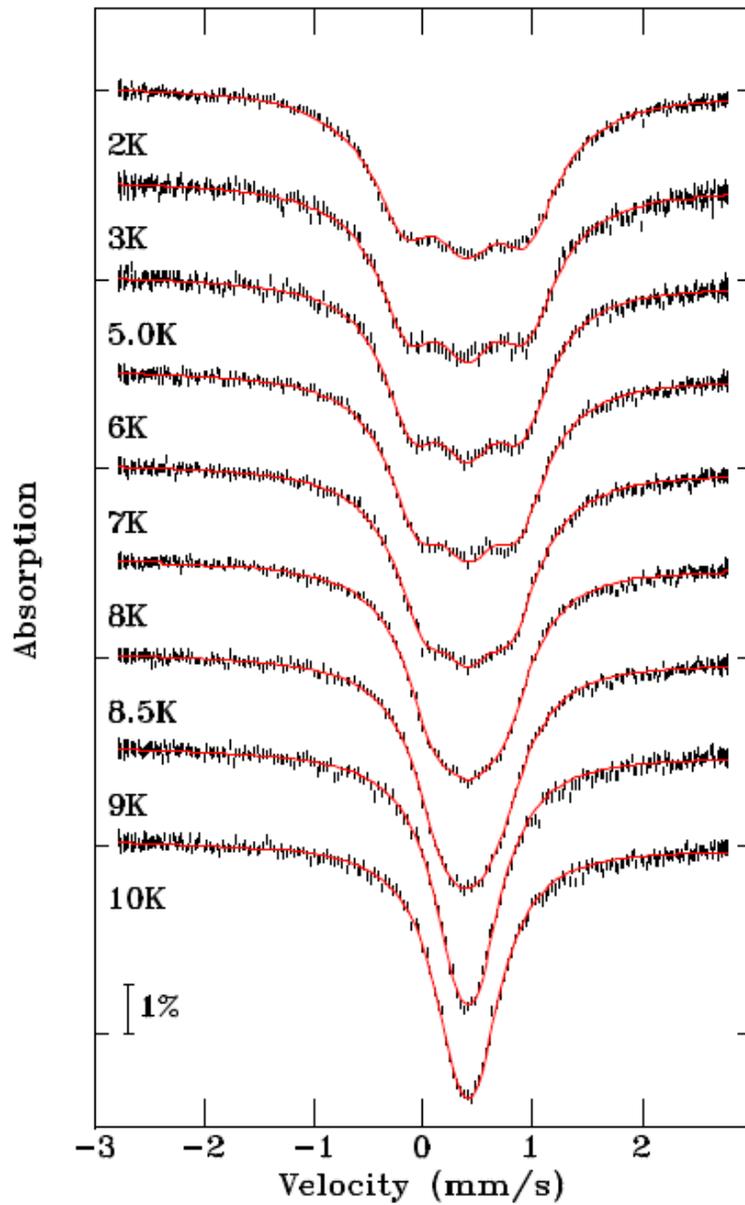


What can you learn about magnetic ordering?

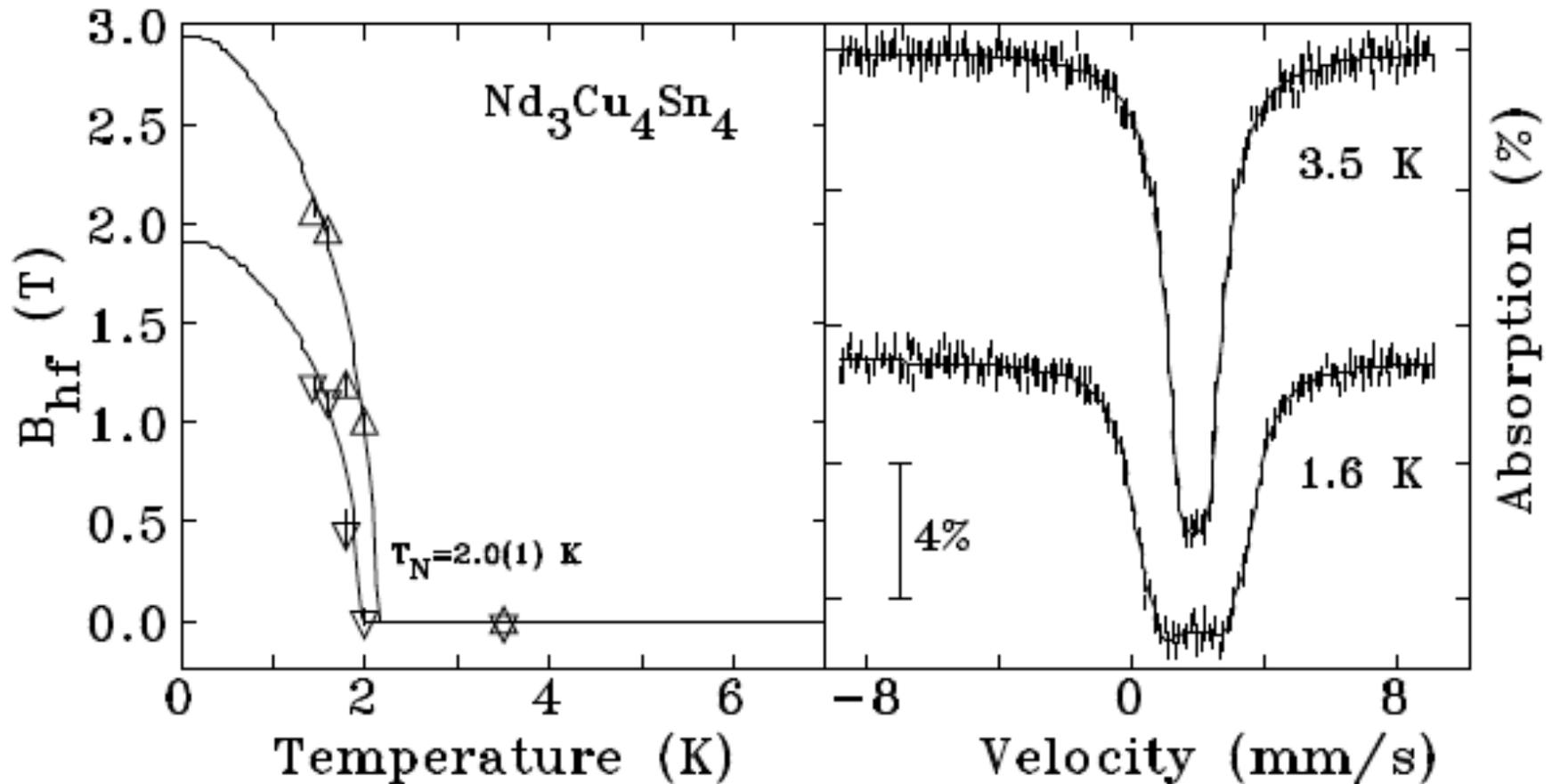
GdBiPt is a “half-Heusler” compound (four interpenetrating *fcc* lattices) and a candidate antiferromagnetic topological insulator, if it has the “correct” magnetic structure.



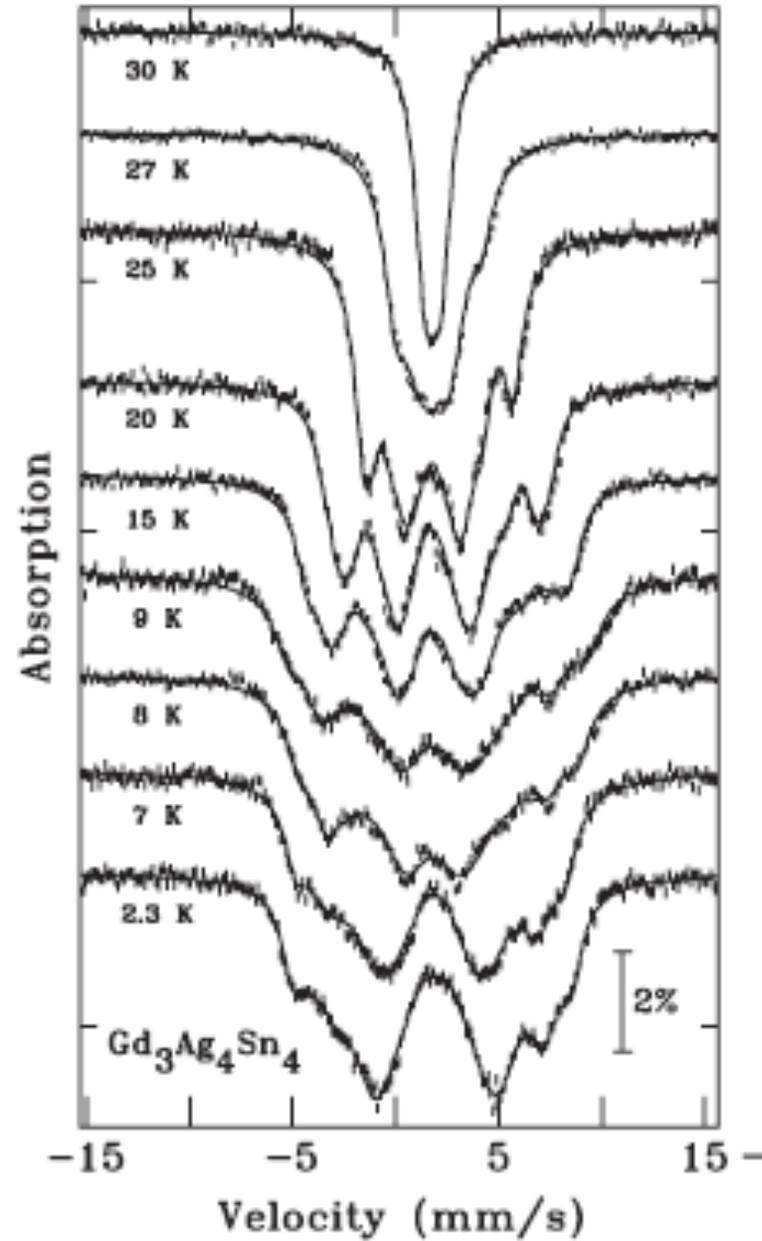
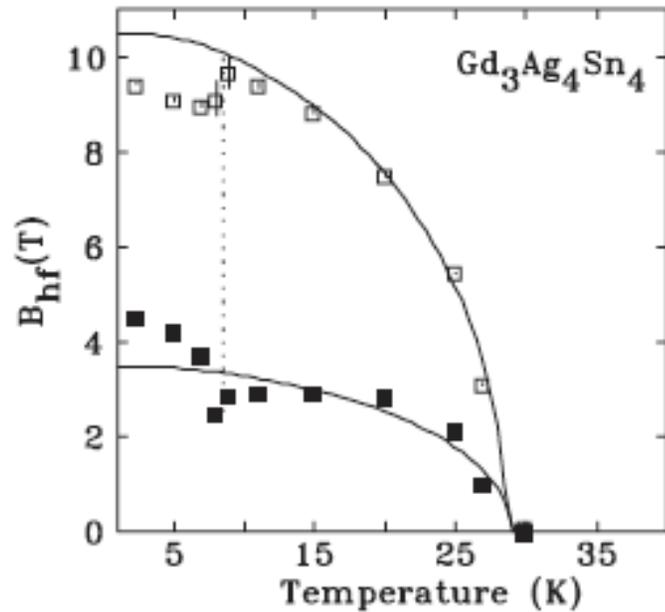
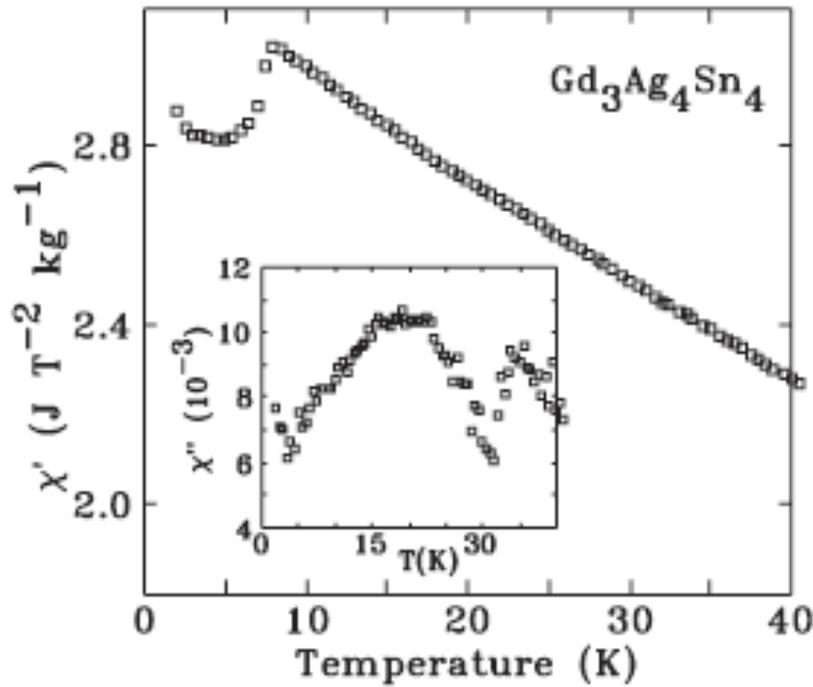
You can confirm *that* ordering occurs



This is not a trivial feature. The ordering of $\text{Nd}_3\text{Cu}_4\text{Sn}_4$ was *missed* in the original neutron work.

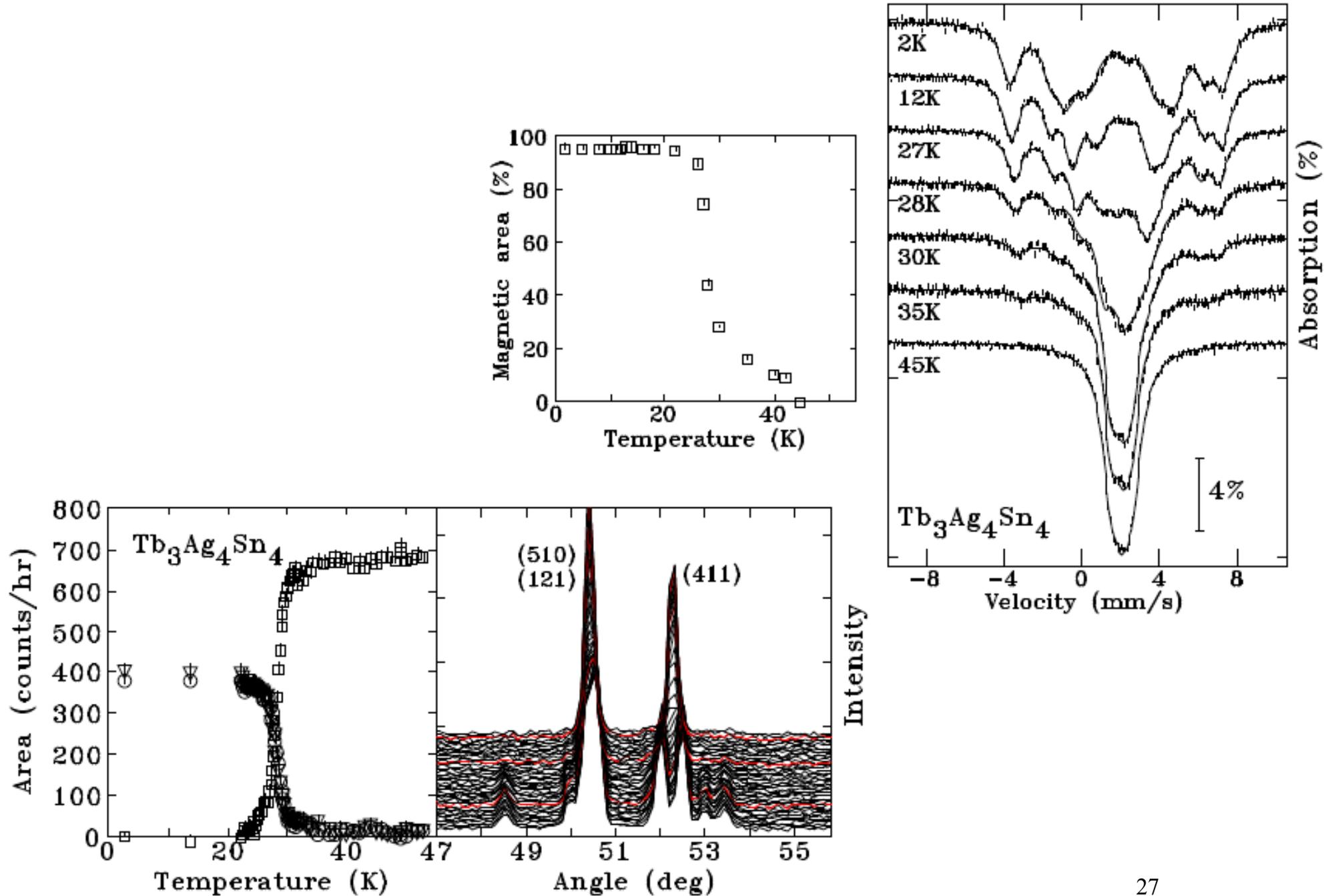


T_N for $Gd_3Ag_4Sn_4$ was *missed* by susceptibility

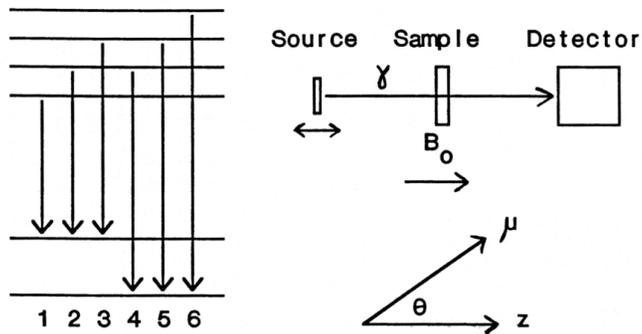
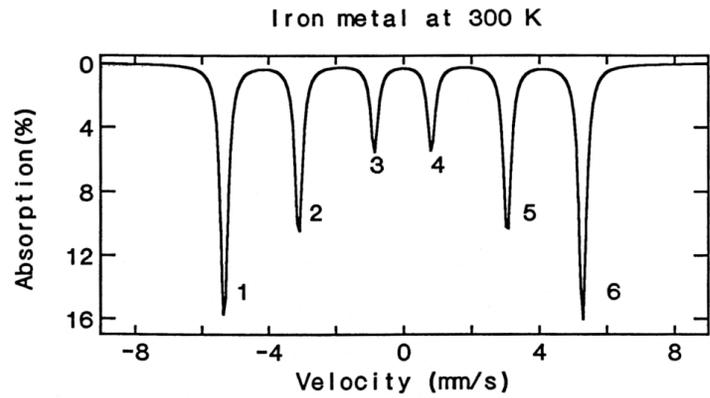


C J Voyer¹, D H Ryan^{1,4}, M Napolitano² and P Riani²
J. Phys.: Condens. Matter **19** (2007) 156209 (10pp)

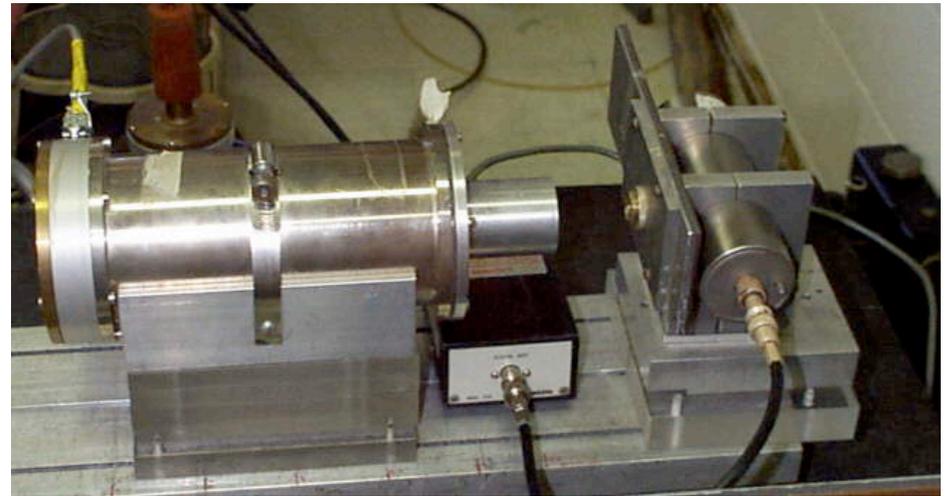
You can show that a transition is first-order



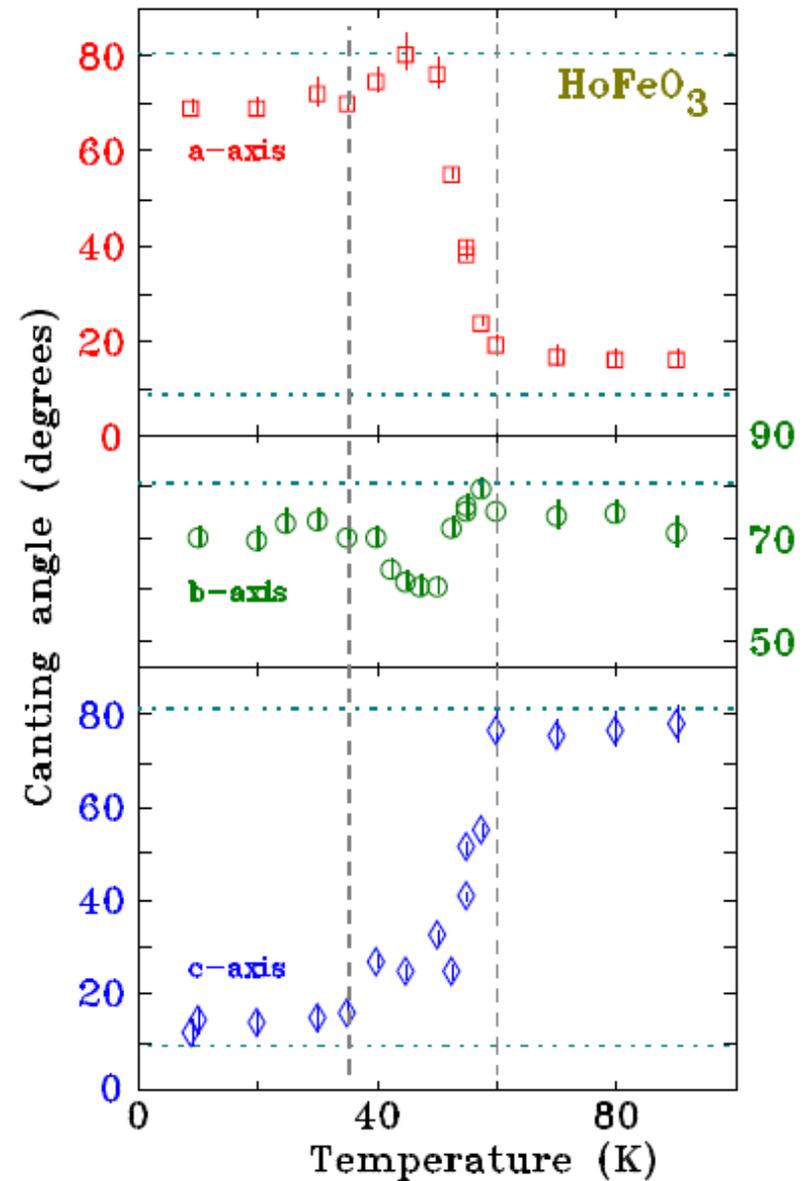
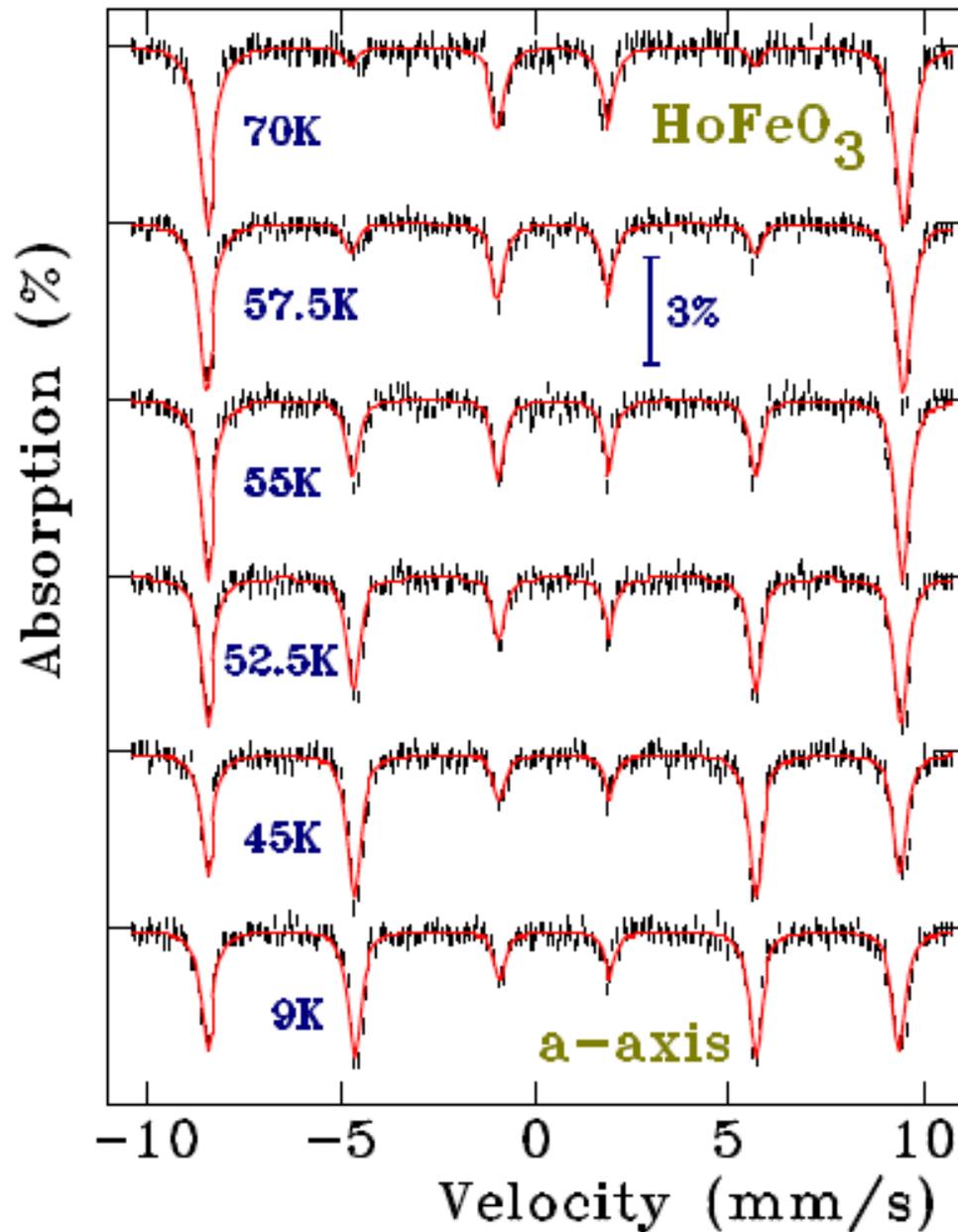
Instant Mössbauer (a reminder)



$$I_{2,5} = \frac{4\sin^2\vartheta}{1 + \cos^2\vartheta}$$



If you have single crystals, you can determine the ordering direction

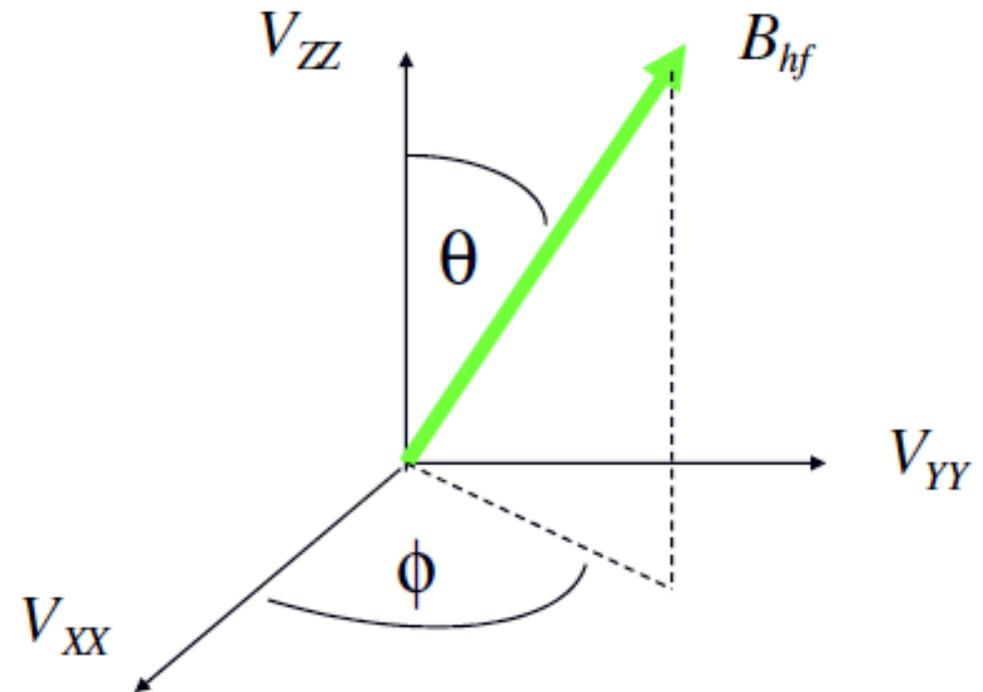


D. H. Ryan¹, Quentin Stoyel¹, Larissa Veryha¹, Kai Xu², Wei Ren²,
Shixun Cao², and Zahra Yamani³

IEEE TRANSACTIONS ON MAGNETICS, VOL. 53, NO. 11, NOVEMBER 2017

Combined interactions (a reminder)

If $B_{hf} \gg efg$ and $\eta=0$, then for the $3/2 \rightarrow 1/2$ transitions the effects are relatively simple, as are the angular effects.

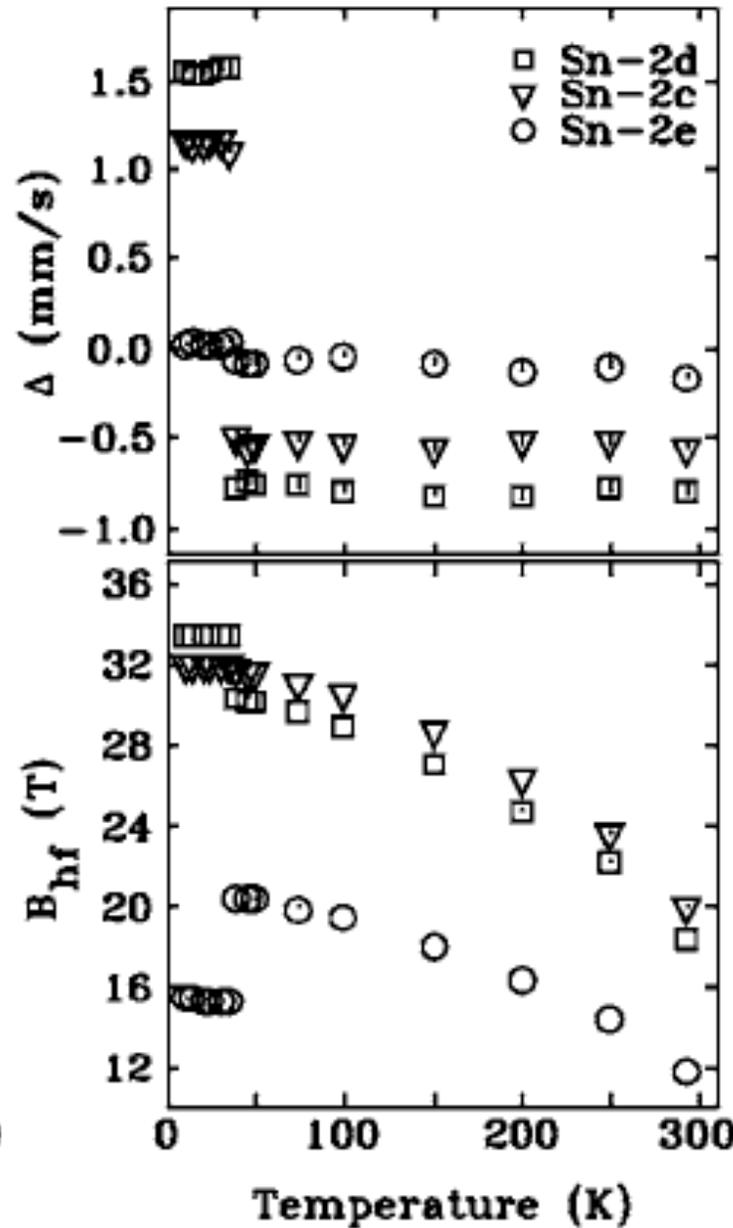
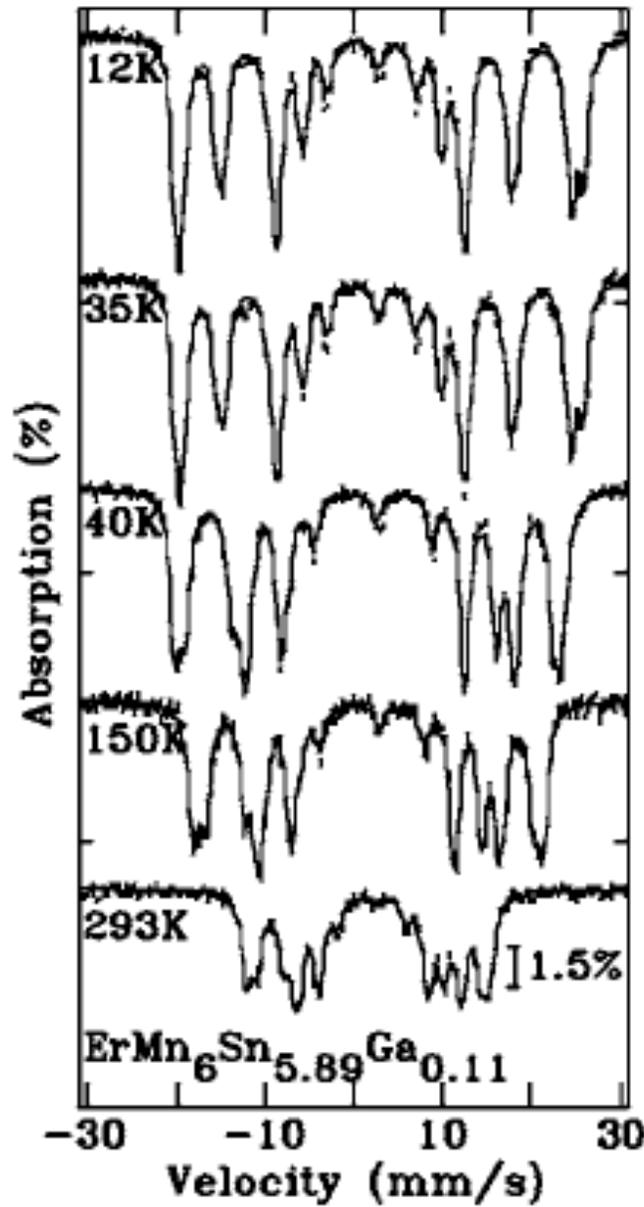


$$\Delta = \frac{eQV_{zz}}{4} (3 \cos^2 \theta - 1)$$

ϕ has no meaning for $\eta=0$

If θ changes by 90° , then Δ changes by a factor of -2

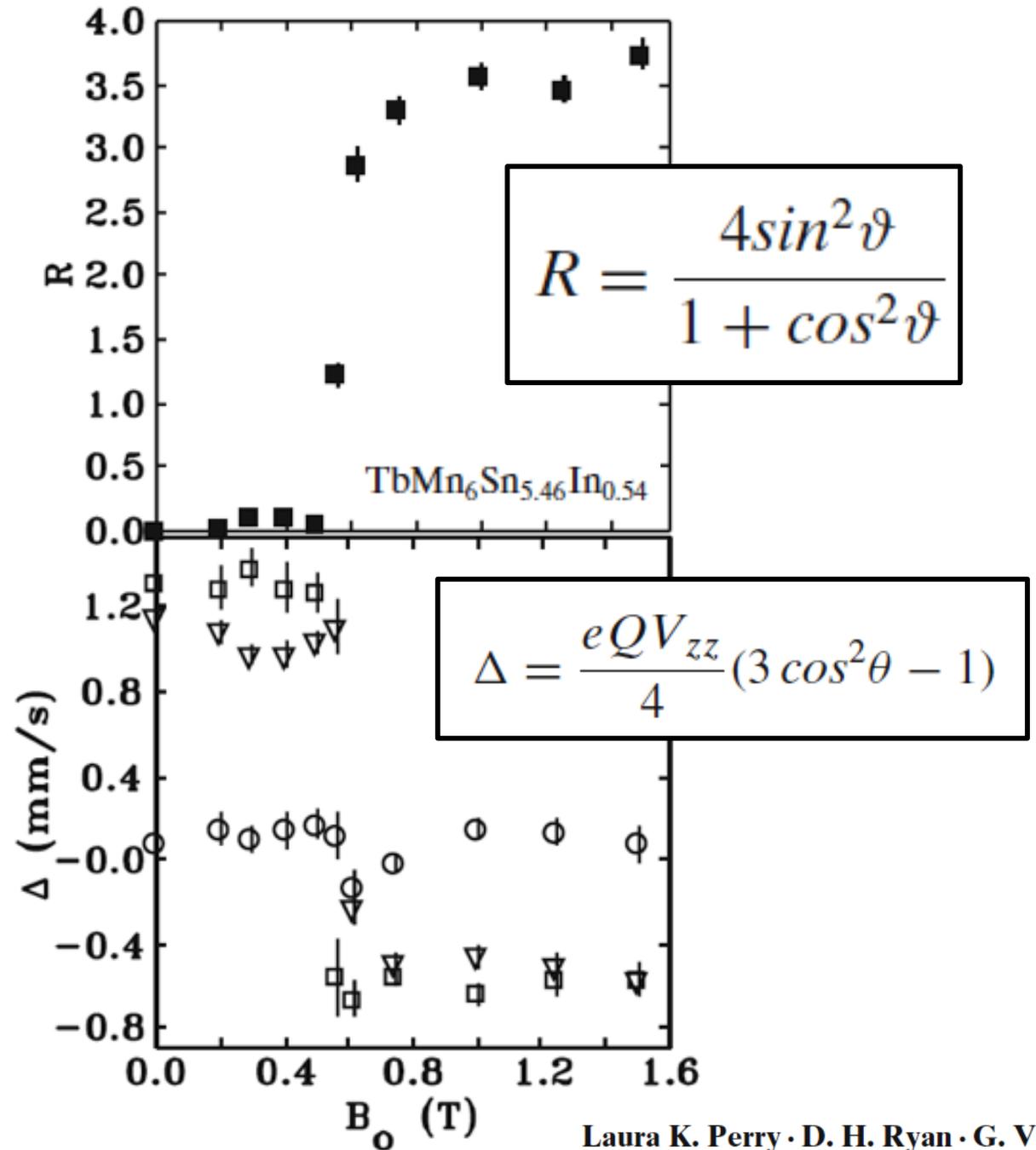
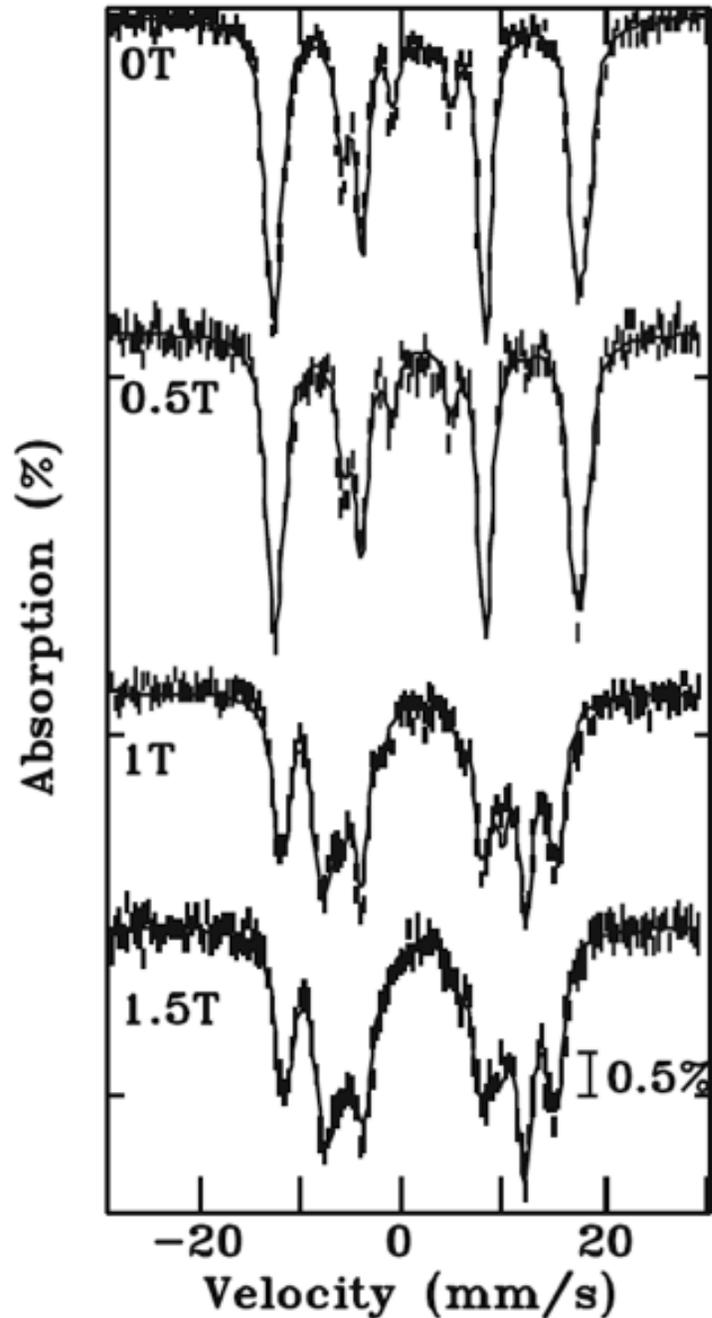
V_{ZZ} can provide the coordinate system for you in a powder



JOURNAL OF APPLIED PHYSICS 101, 09K504 (2007)

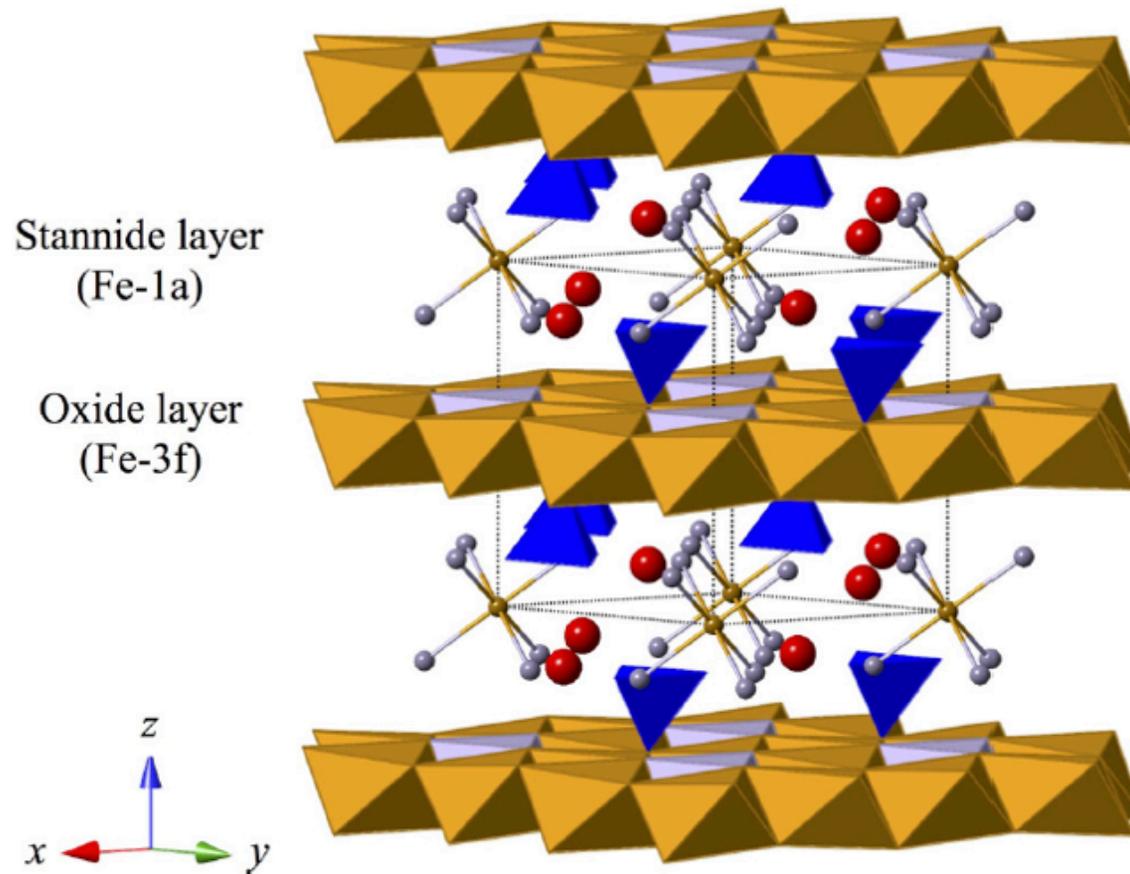
Laura K. Perry D. H. Ryan and G. Venturini

A field-driven spin-flop with a single crystal



Laura K. Perry · D. H. Ryan · G. Venturini
Hyperfine Interact (2006) 170:105–116

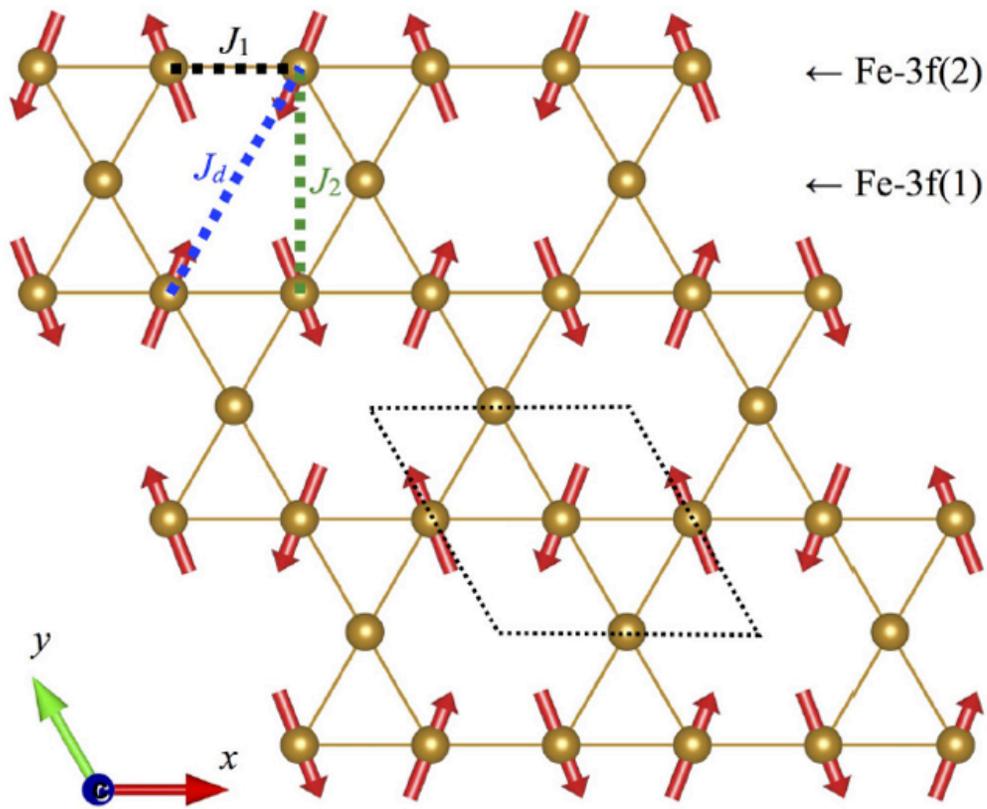
$\text{Fe}_4\text{Si}_2\text{Sn}_7\text{O}_{16}$



Kagome lattice of Fe moments – geometrically frustrated

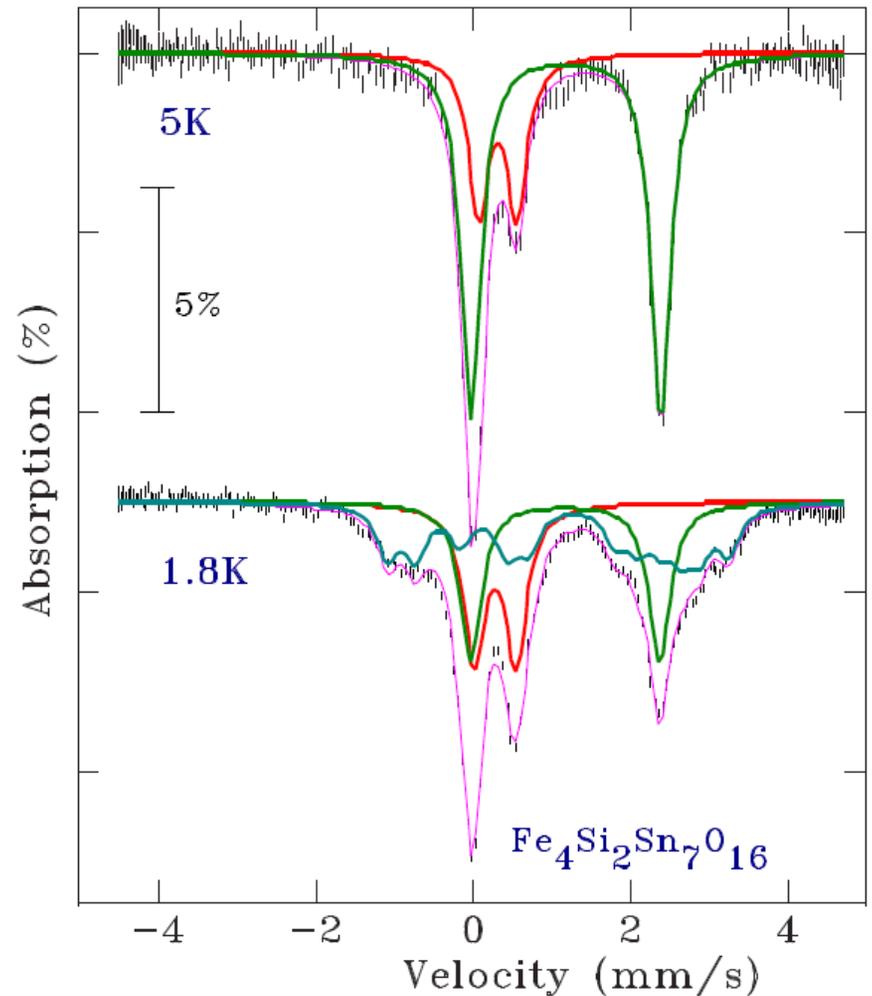
PHYSICAL REVIEW B **96**, 180410(R) (2017)

C.D. Ling, M.C. Allison, S.A. Schmid, T. Söhnel, M. Adveev, G.A. Stewart and D.H. Ryan³³



This was confirmed by Mössbauer spectroscopy

Fitting the neutron diffraction pattern yielded an unusual magnetic structure in which $\frac{1}{3}$ of the Fe-3f atoms did not order



PHYSICAL REVIEW B **96**, 180410(R) (2017)

C.D. Ling, M.C. Allison, S.A. Schmid, T. Söhnel, M. Adveev, G.A. Stewart and D.H. Ryan

Unconventional Mössbauer

Using the *physics* behind the effect to extend its reach.

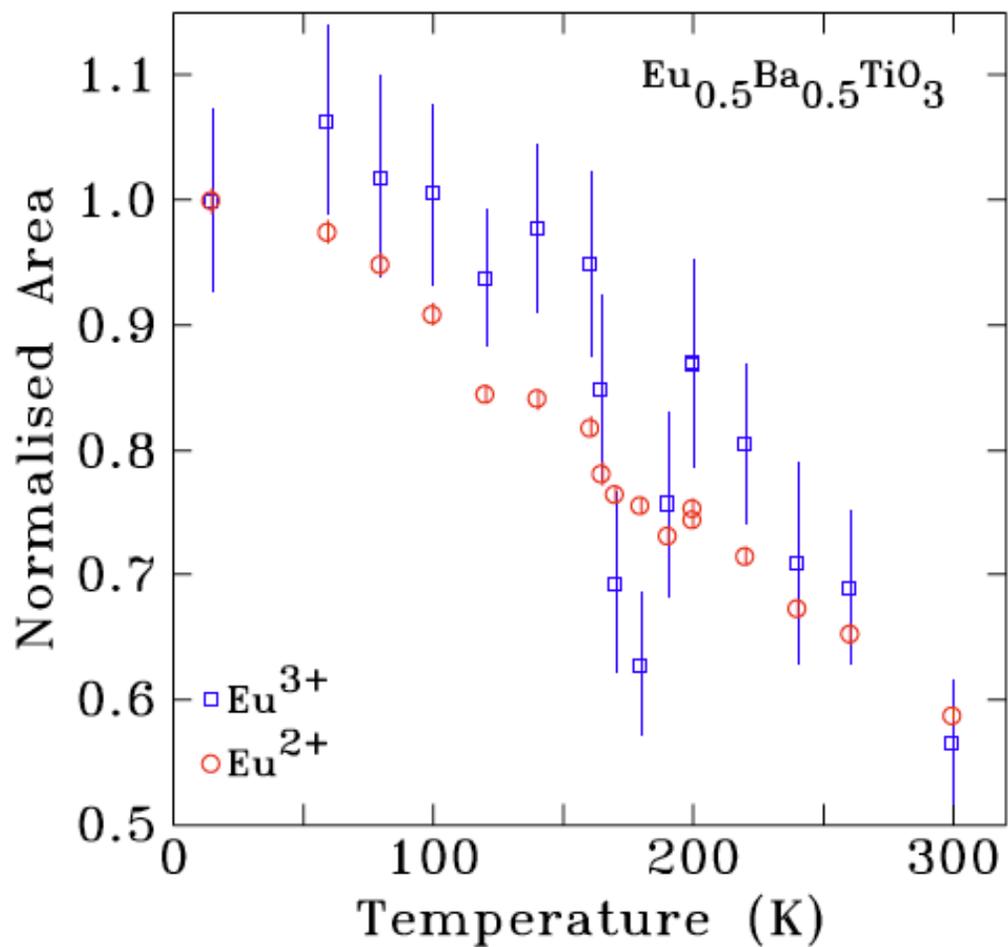
Lattice softening: a conventional measurement seeking a less common parameter

At a ferroelectric transition (or indeed any structural transition involving displacive motions), the energy of the phonon mode associated with the displacement goes to zero.

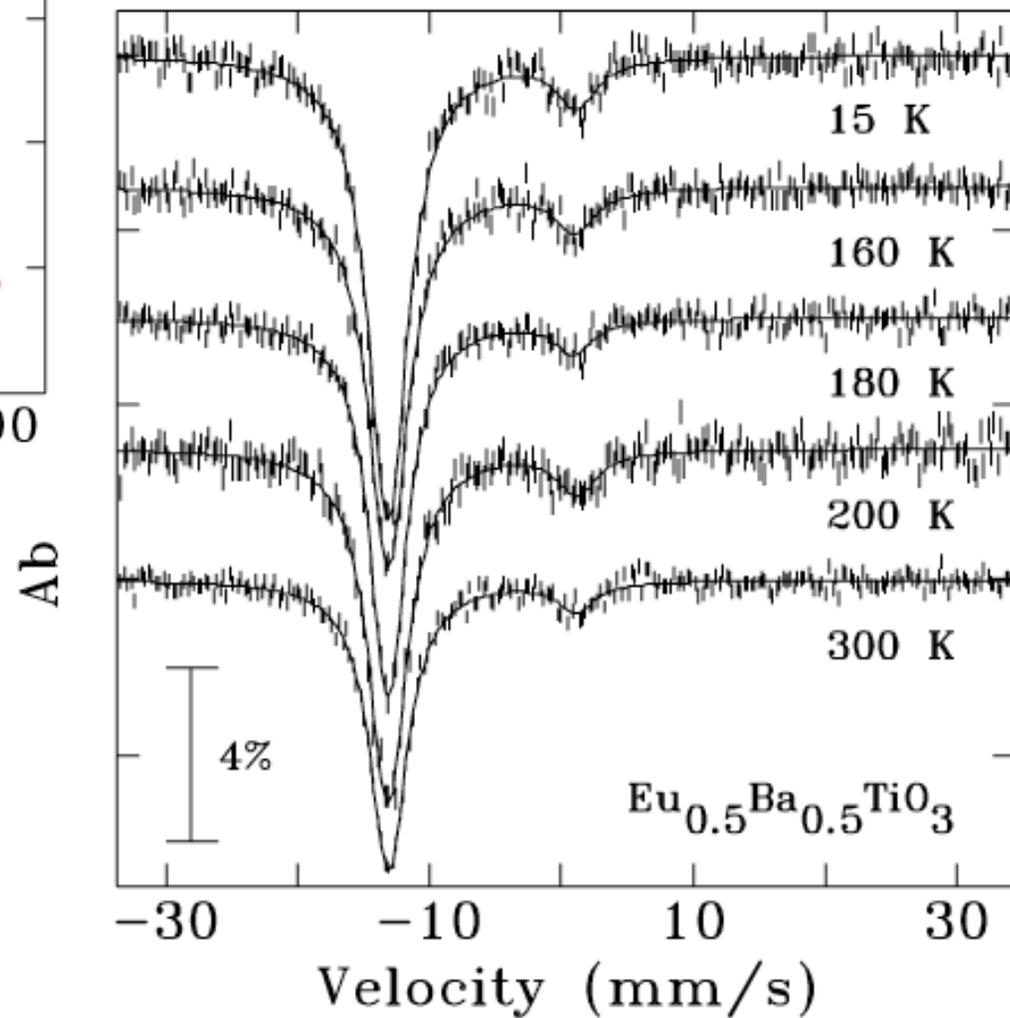
The zero energy cost means that the amplitude of the mode (in a linear approximation) diverges.

Large amplitude motions reduce the probability of observing a Mössbauer event and so the signal is reduced.

Once the structure has changed, the mode stiffens, the vibration amplitude falls and Mössbauer signal recovers.



The mode softening at the 170K ferroelectric transition in $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ is very clear.



Make the “sample” the source

I : Emission spectroscopy

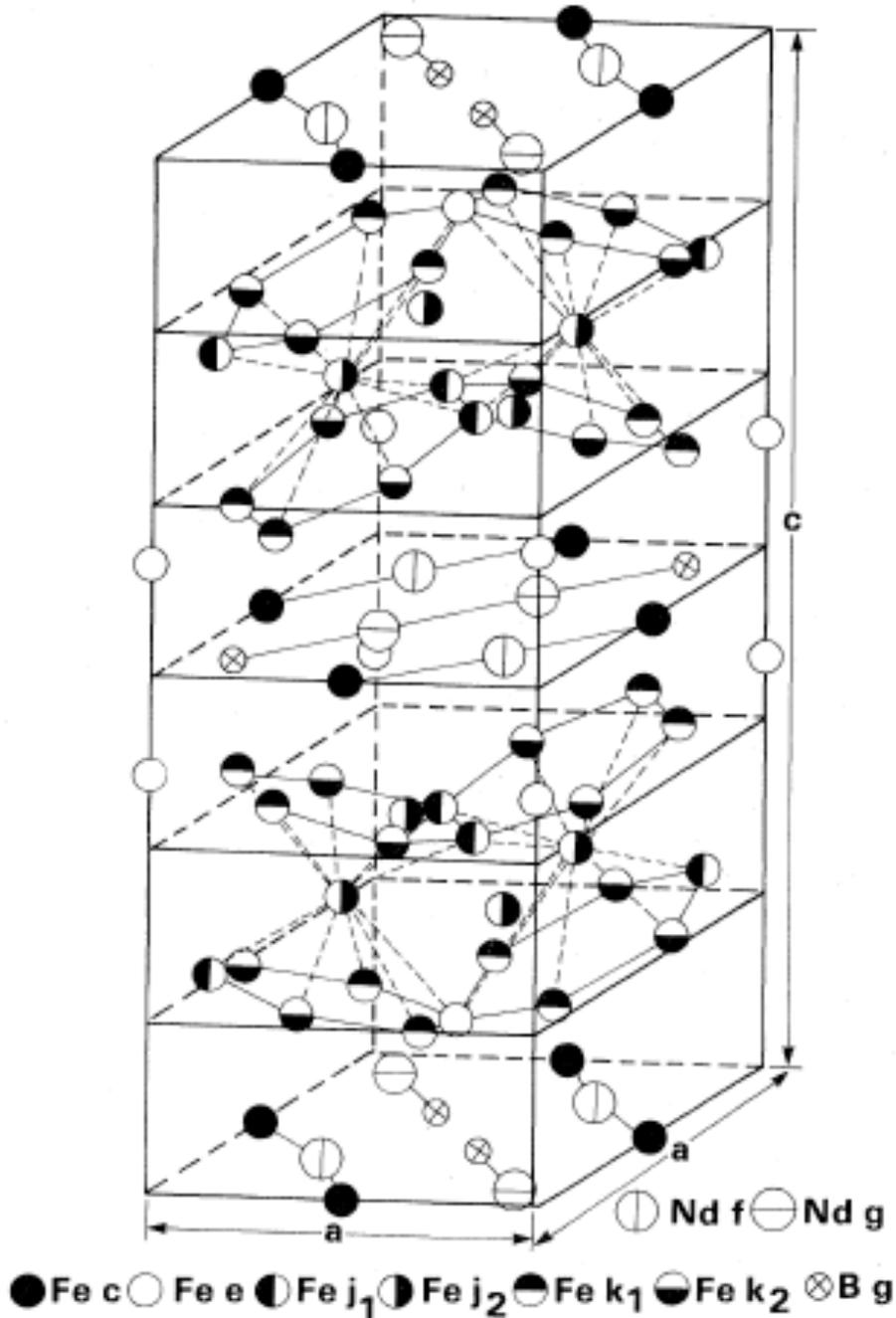
Dope ^{57}Co into the “sample” — the easy way to make your sample into a source

Cobalt site preferences in $\text{Nd}_2\text{Fe}_{14}\text{B}$

Adding cobalt to $\text{Nd}_2\text{Fe}_{14}\text{B}$ raises T_c and (initially) improves the magnetisation.

How can replacing $2^+\mu_B$ iron with $1.6\mu_B$ cobalt lead to a net increase in the magnetisation?

With six iron sites in the structure, where does the cobalt go?



Atom	Site	Occupancy	x	y	z
Nd	f	4	0.266	0.266	0.0
Nd	g	4	0.139	-0.139	0.0
Fe	k_1	16	0.224	0.568	0.128
Fe	k_2	16	0.039	0.359	0.176
Fe	j_1	8	0.097	0.097	0.205
Fe	j_2	8	0.318	0.318	0.247
Fe	e	4	0.5	0.5	0.113
Fe	c	4	0.0	0.5	0.0
B	g	4	0.368	-0.368	0.0

Several attempts were made using NMR, Mössbauer spectroscopy and neutron diffraction.

All looked for changes associated with adding cobalt.

Sensitivity limitations meant that they had to add quite a lot of cobalt, and this also affected the properties.

All suffered from the same basic problem:

**They were all looking for where the iron *wasn't*,
and NOT for where the cobalt *was*.**

Want to know where the cobalt goes?

Ask the cobalt!

Prepare a sample of $\text{Nd}_2\text{Fe}_{14}\text{B}$ using ^{56}Fe

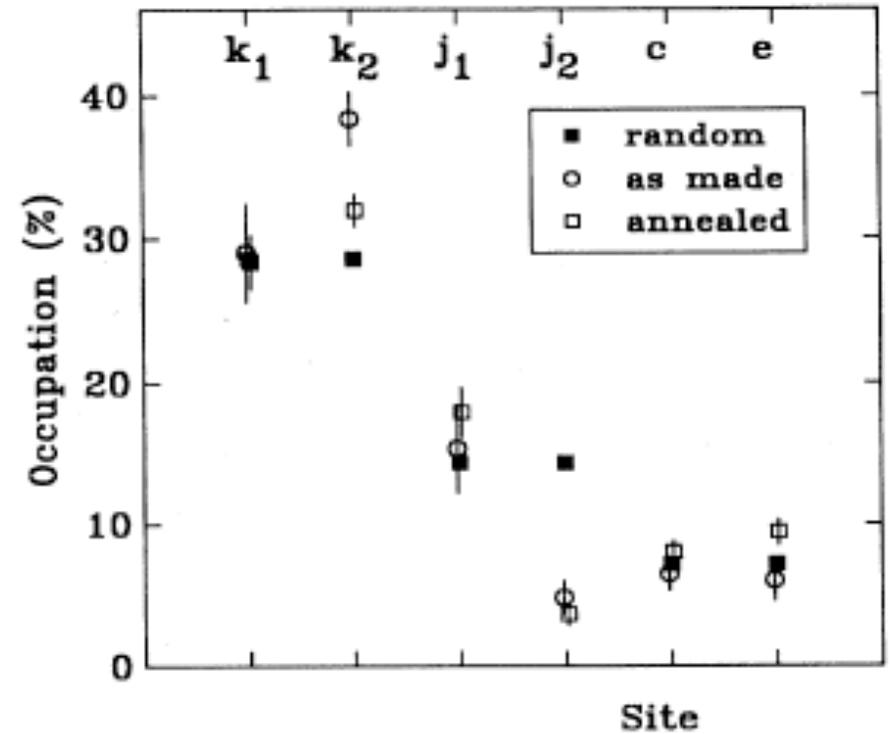
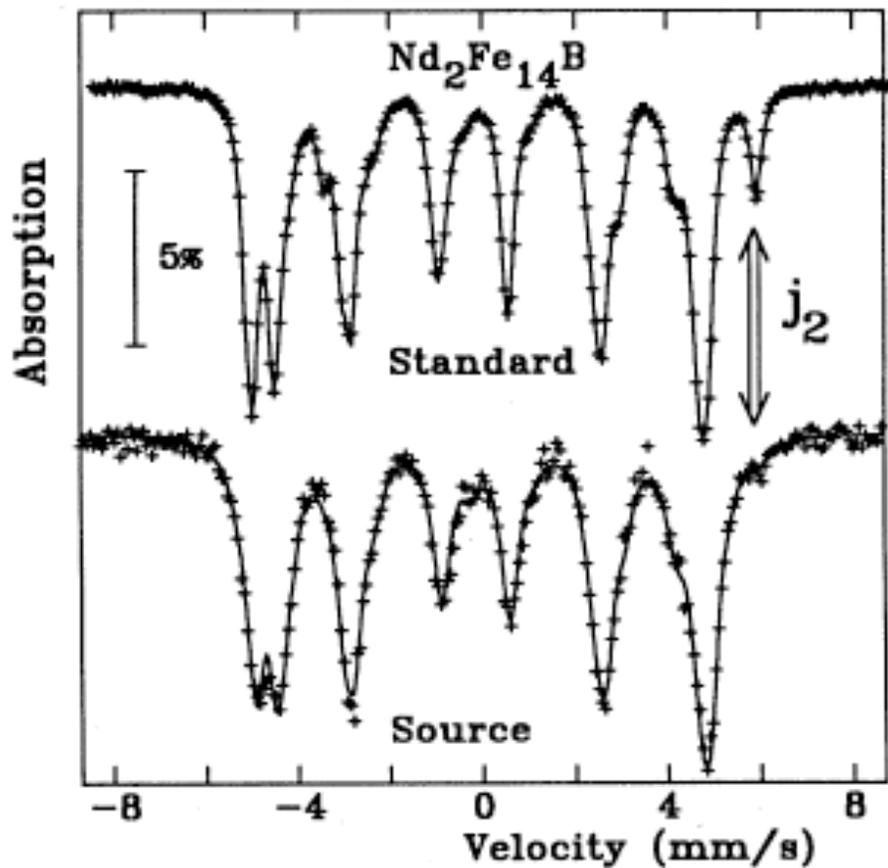
(learned that one the hard way!)

and dope it with ^{57}Co – making a Mössbauer source.

^{57}Co decays to ^{57}Fe *before* emitting the 14.4keV Mössbauer gamma, and the doping concentration needed is less than *1ppm*.

The emission comes from ^{57}Fe , in an effectively undoped sample, but from **sites** that were *selected* by ***cobalt*** atoms.

You don't even need to fit the spectrum to see that cobalt clearly avoids the j_2 site...



but if you feel the need, it is easy to show that cobalt avoids the j_2 and may prefer the k_2 .

Impact of the cobalt site preference in

$\text{Nd}_2\text{Fe}_{14}\text{B}$

The j_2 site in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ structure is important because it is the one in which the iron carries the *largest* moment.

By avoiding this site, cobalt reduces its impact on the magnetisation.

At the same time, it increases T_c so the net effect at room temperature is for the magnetisation to *increase* at low cobalt concentrations.

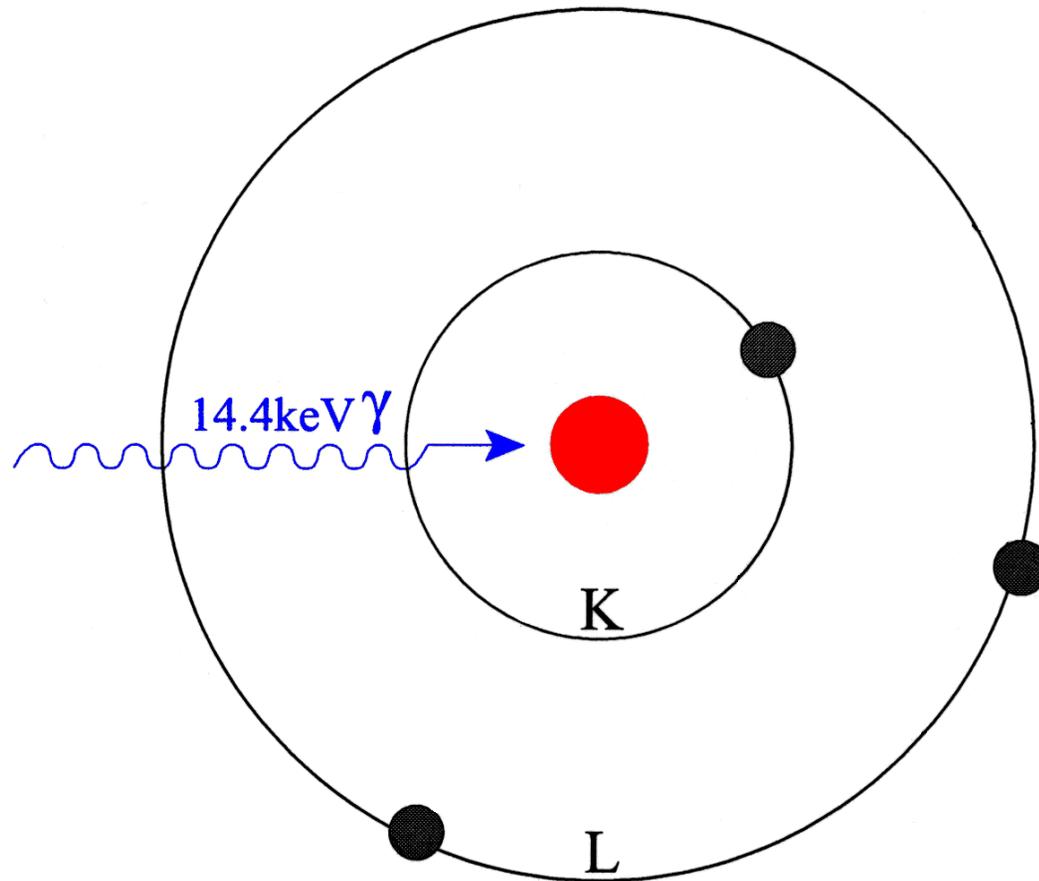
Make the “sample” the source

II : Backscattering

A harder way to make your sample into a source

- Each resonant absorption event creates an excited nucleus in the sample
- This nucleus *must* return to the ground state
- We normally rely on collimation to reduce the detection of the re-emitted radiation
- CEMS and XBS turn the whole problem around and *use* the re-emitted radiation
- To obtain a Mössbauer spectrum we must first *cause* resonant absorption events and then we must *detect* them

Resonant absorption

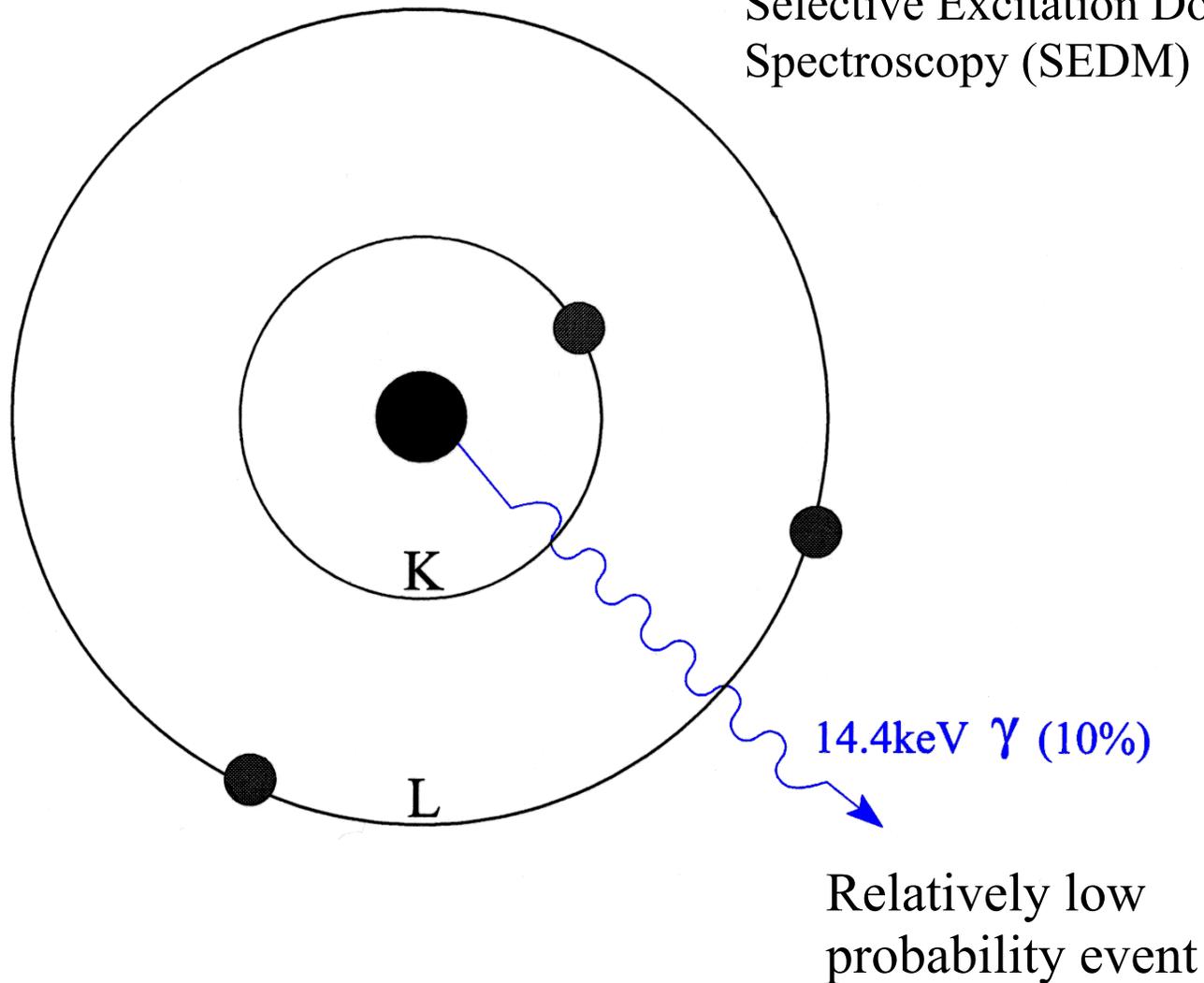


Creates a nucleus
in an excited state

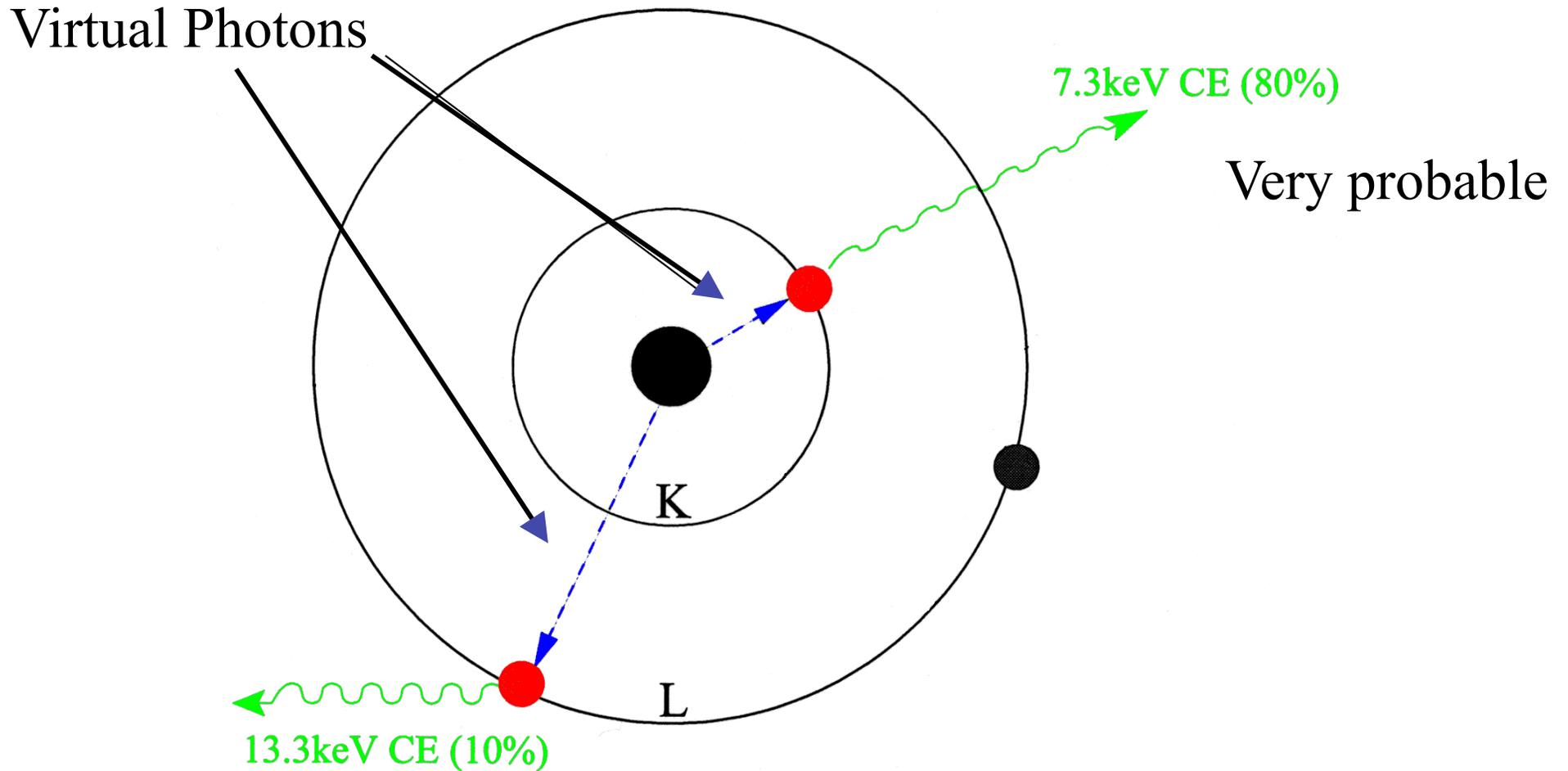
Conventional Mössbauer ends here

Re-emission of a γ

This process forms the basis for
Selective Excitation Double Mössbauer
Spectroscopy (SEDM)



Conversion Electrons

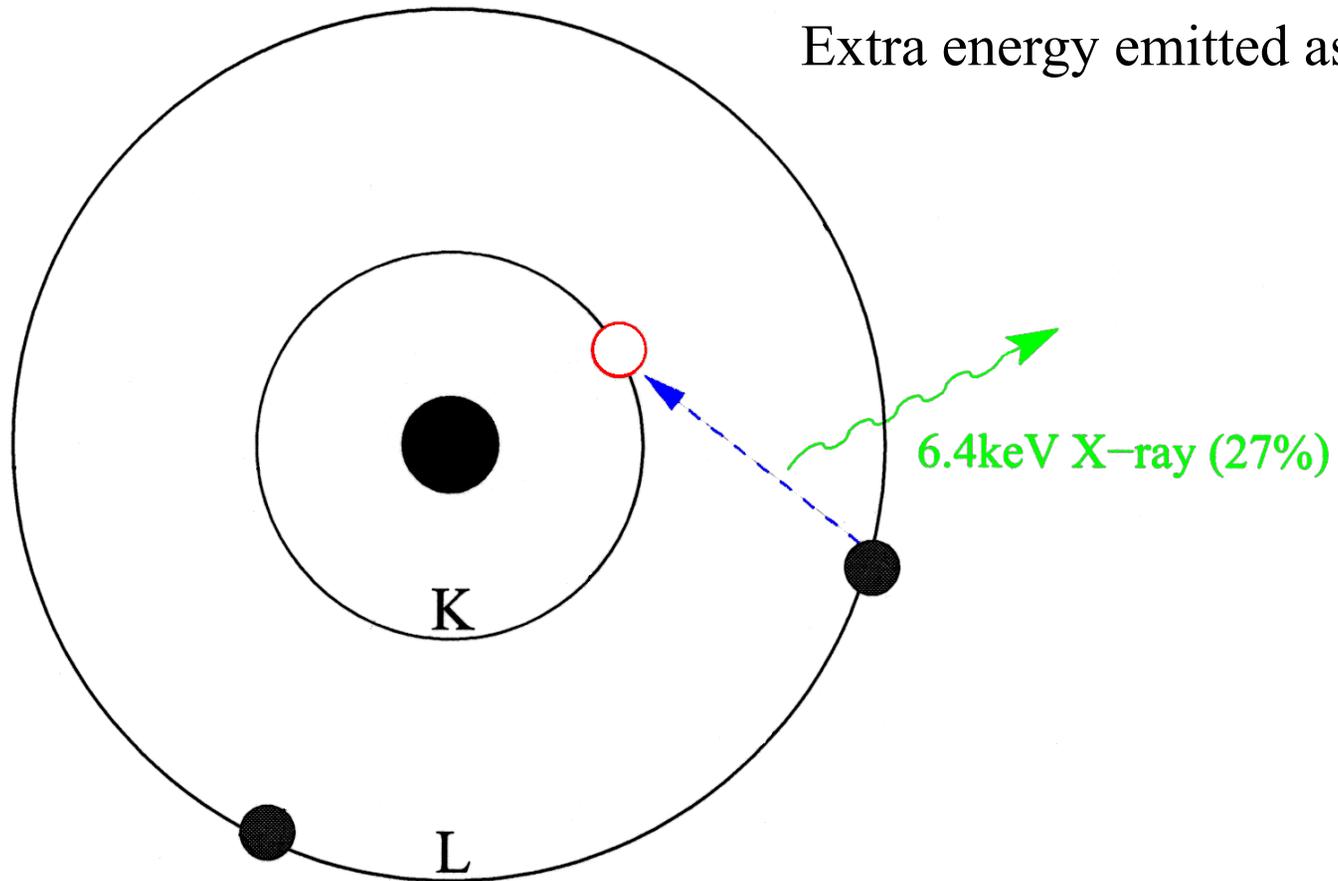


As likely as γ -emission

X-ray emission

L-electron replaces ejected
K-electron.

Extra energy emitted as a K_{α} x-ray



Many backscattered radiations

- 14.4 keV γ (10%)
Used for:
 γ -backscattering
and SEDM
 - 7.3 keV K-conversion electrons (80%)
 - 13.3 keV L-conversion electrons (10%)
 - 6.4 keV K_{α} x-rays (37%)
- CEMS
- XBS

Features of backscattering

- Detected signal comes from incident face of the sample (backscattering)
- Signal is “upside down” (emission)
- 4π emission pattern demands careful design of detector geometry
- Limited range of backscattered radiations forces a sample-in-detector design
- Limited sample environments

Advantages of backscattering

- Can work with very *thick* samples

Beam does not have to pass *through* the sample

- Can work with very *thin* samples

Only see the real events, not swamped by unaffected beam

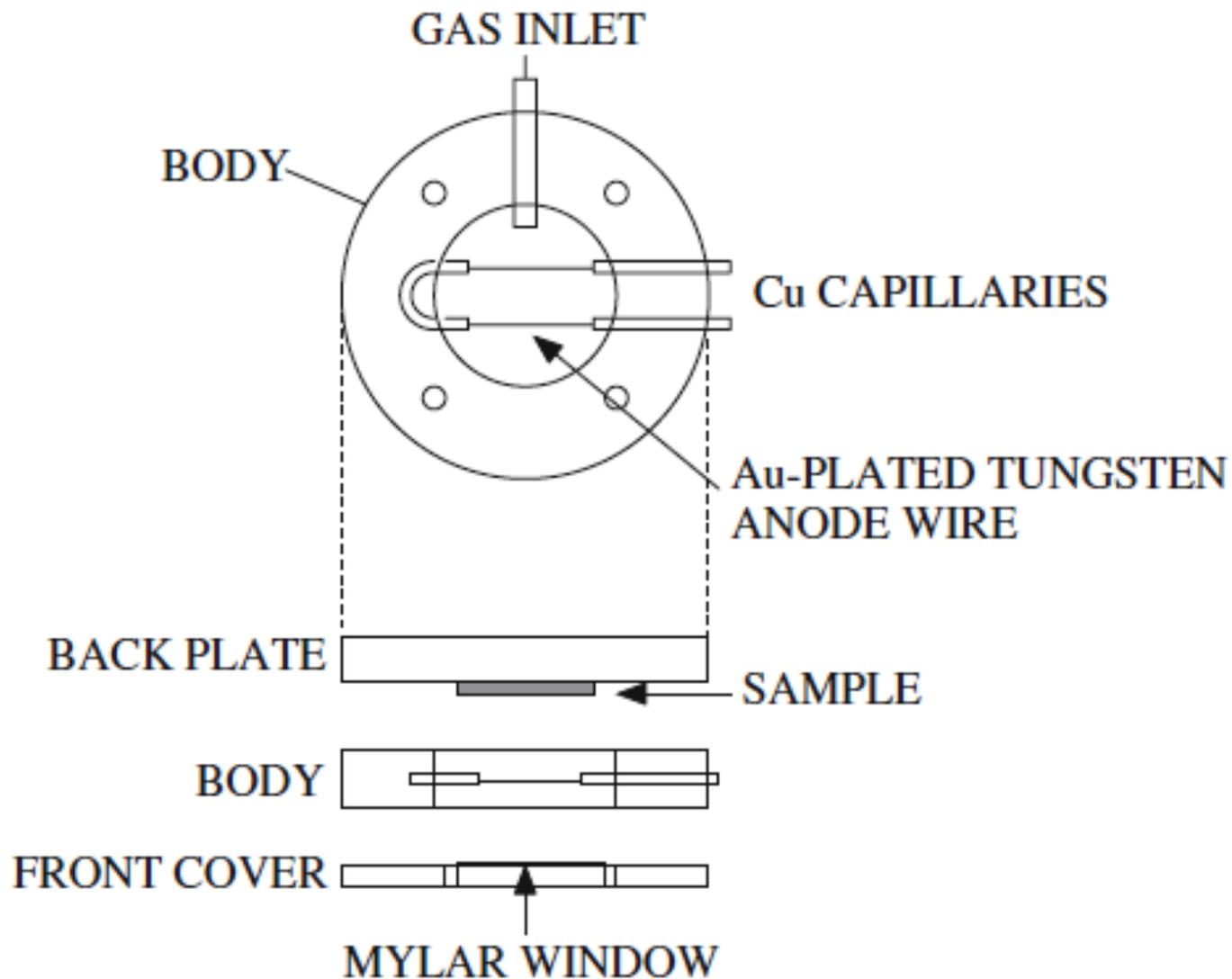
- Surface biased

Limited penetration means backscattered signal must come from events close to the surface

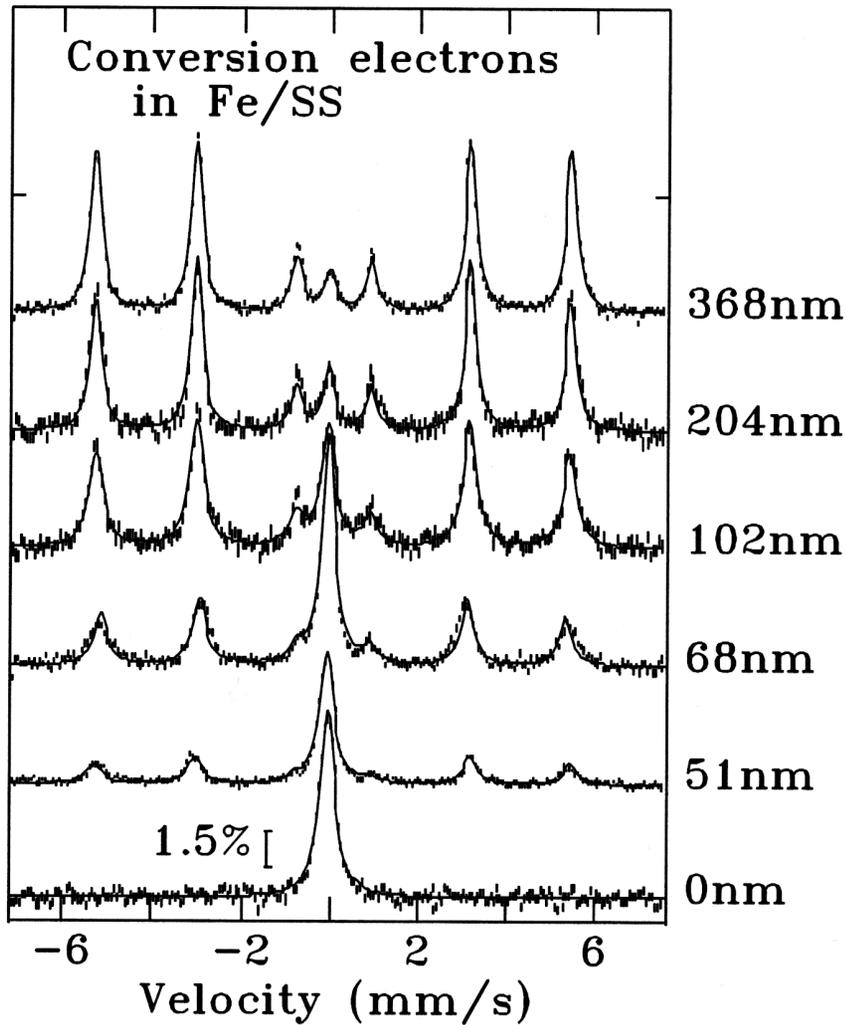
- Bias can be varied

CEMS: 100nm

XBS: 10 μ m

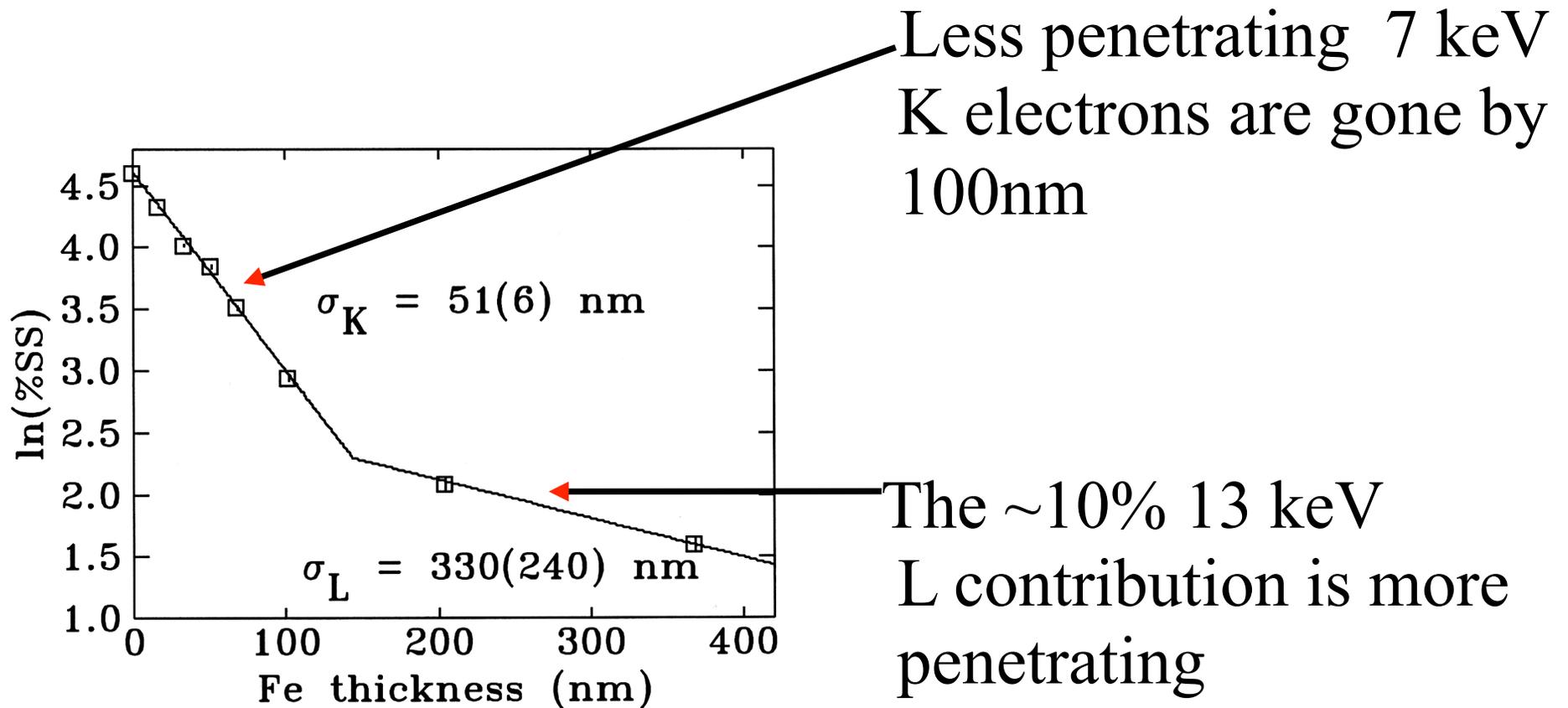


Use Fe over 304SS to measure escape depth of the conversion electrons

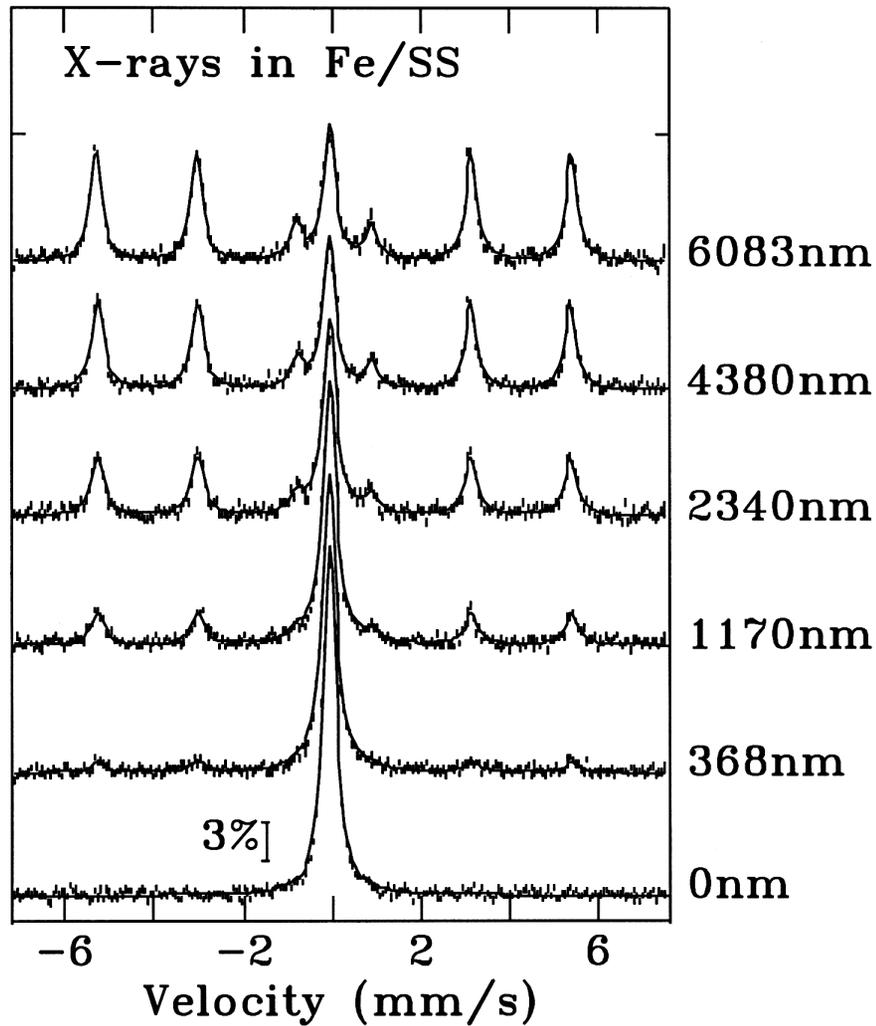


- Central peak from 304SS is rapidly attenuated
- 51nm of Fe is easily seen
- Some 304SS visible even with a 368nm overlayer

K and L conversion electrons

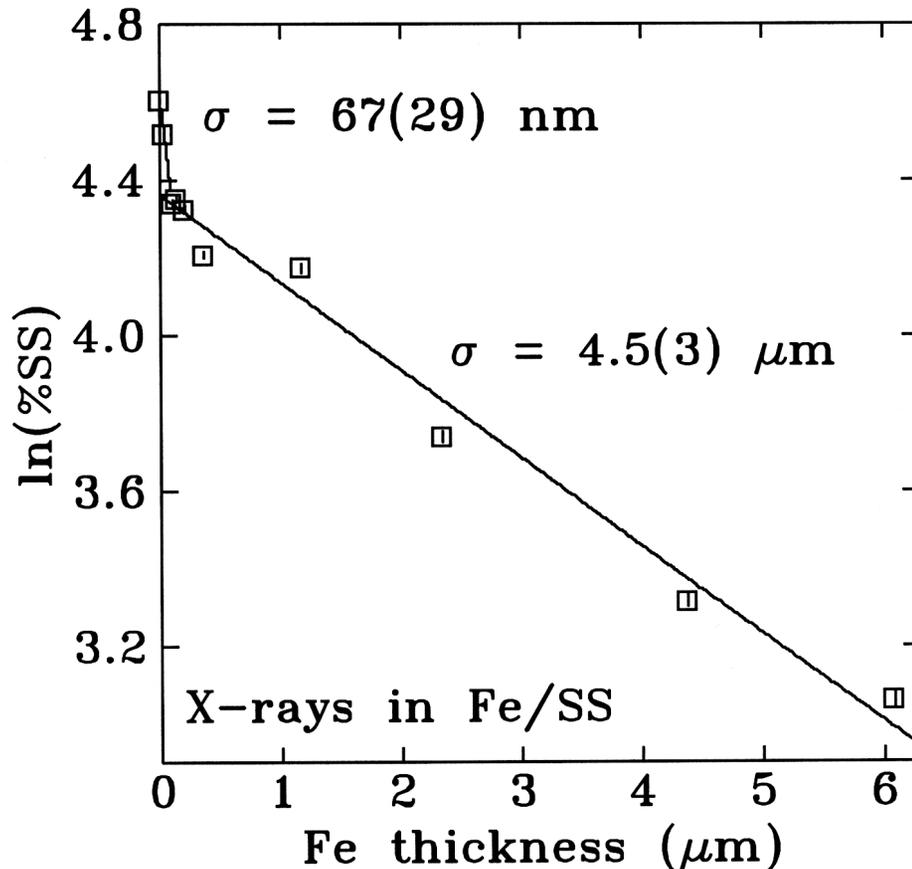


The 6.4 keV K_{α} x-rays are more penetrating



- Use the same Fe over 304SS method to measure the escape depth
- Even at 370nm we are only just starting to see the Fe

There is an electron contribution



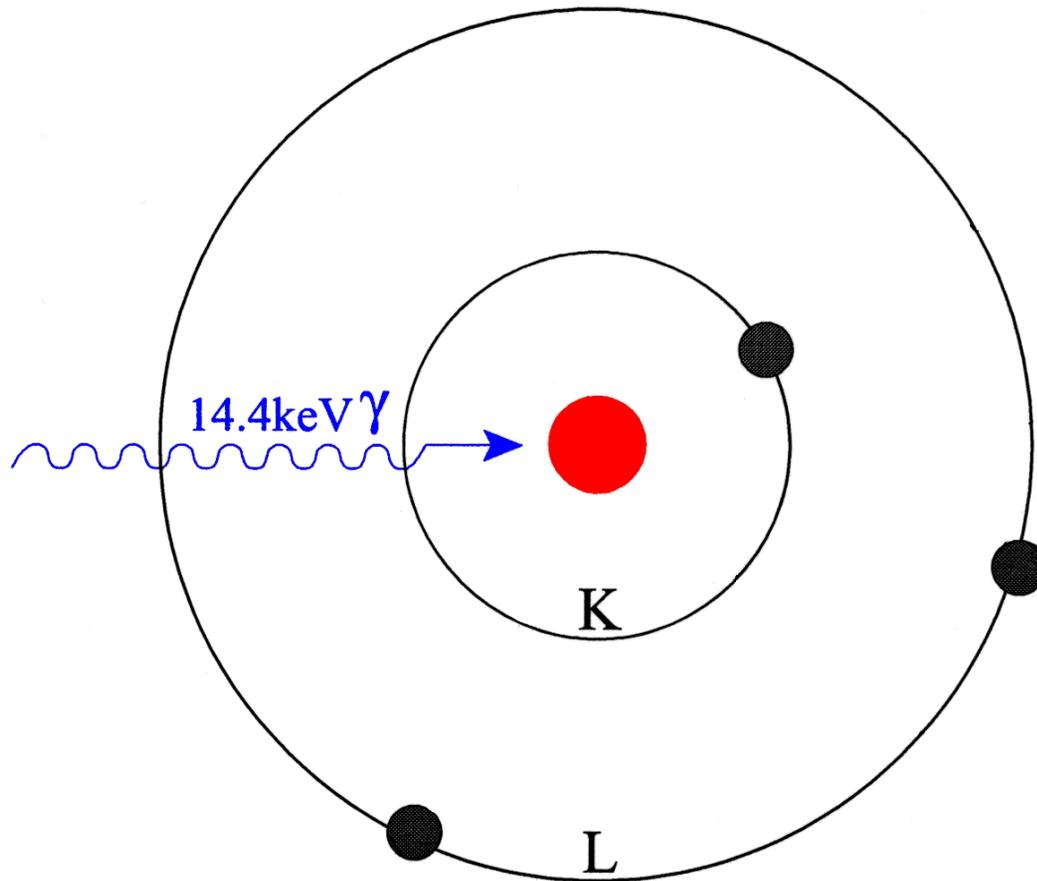
- With the sample inside the detector as with CEMS, we pick up some of the conversion electrons
- About 20% of the signal is a CEMS signal

Make the “sample” the source

III : Resonant γ -pumping

The *really hard* way to make your sample into a source

Resonant absorption

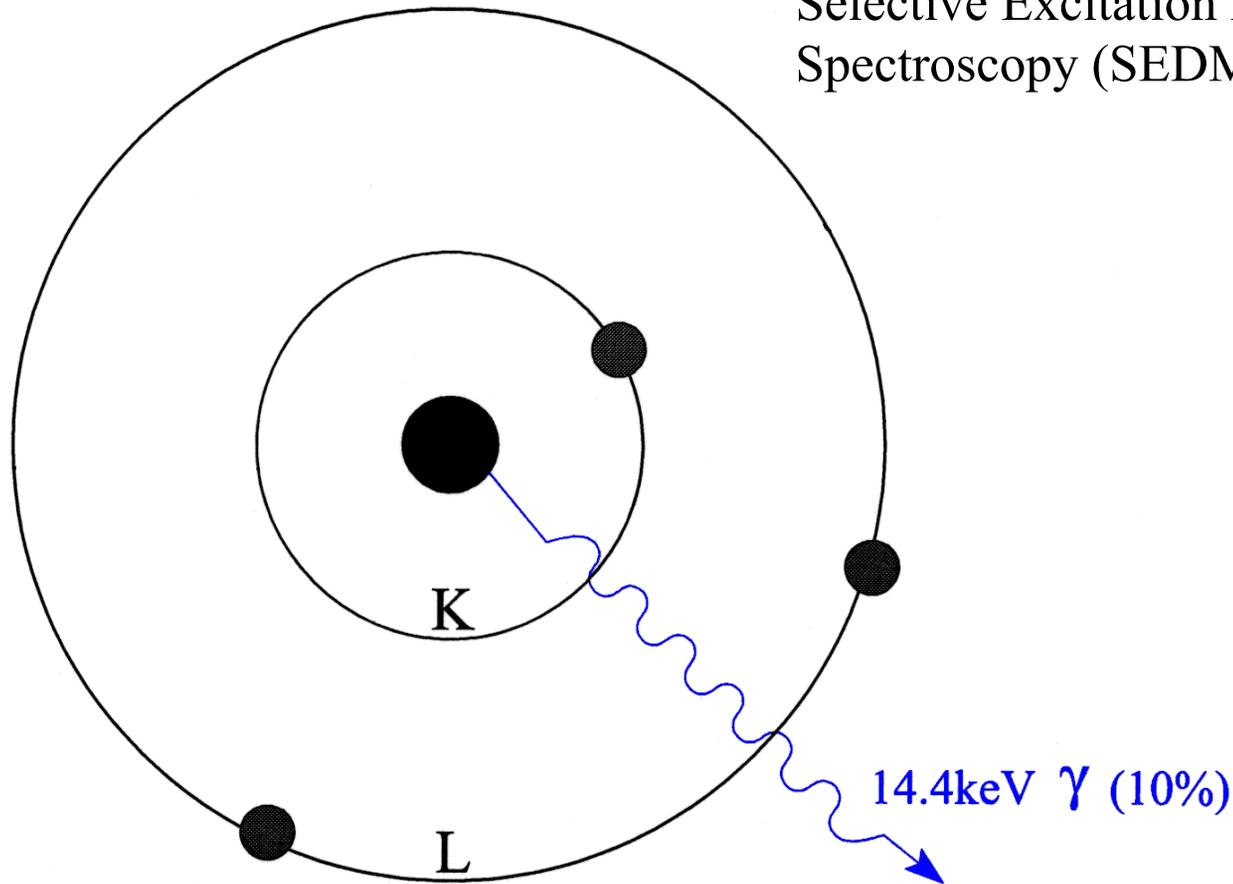


Creates a nucleus
in an excited state

Conventional Mössbauer ends here

Re-emission of a γ

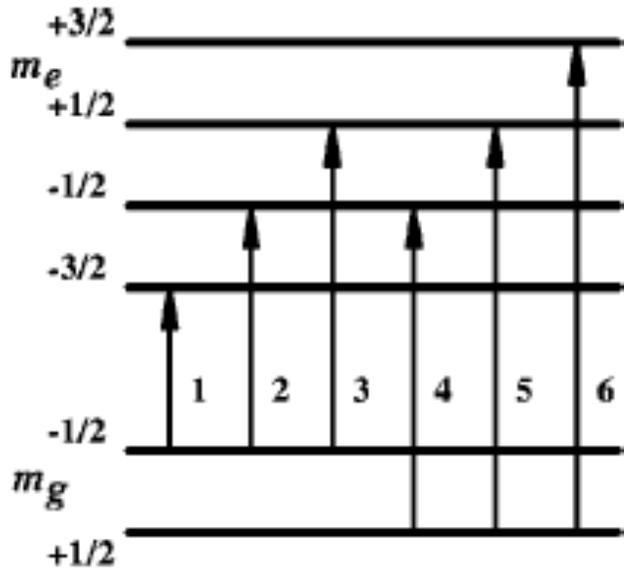
This process forms the basis for
Selective Excitation Double Mössbauer
Spectroscopy (SEDM)



Relatively low probability
event that carries a *lot* of
information

Selective Excitation Double Mössbauer Spectroscopy (SEDM)

Separating dynamics from disorder

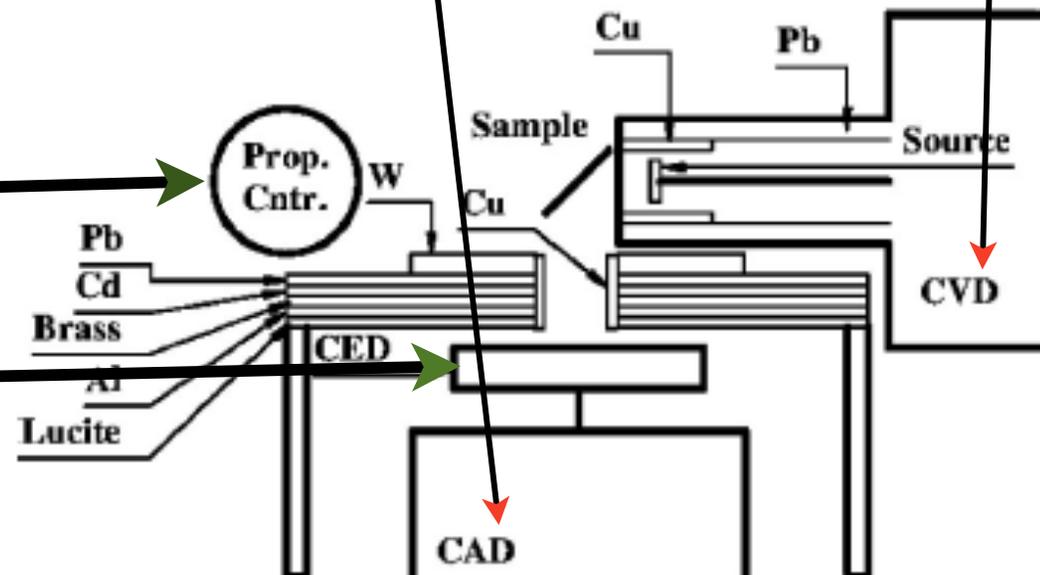


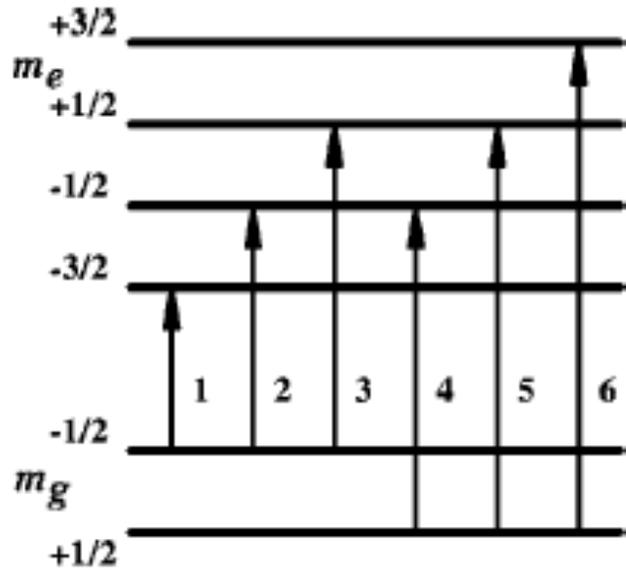
With the first drive (CVD) operating in “constant velocity” mode, tune the system to a transition in the sample.

The second drive (CAD) operates in a more conventional “constant acceleration” mode and is used to Mössbauer-analyse the emissions from the sample.

Standard detector for transmission work and tuning

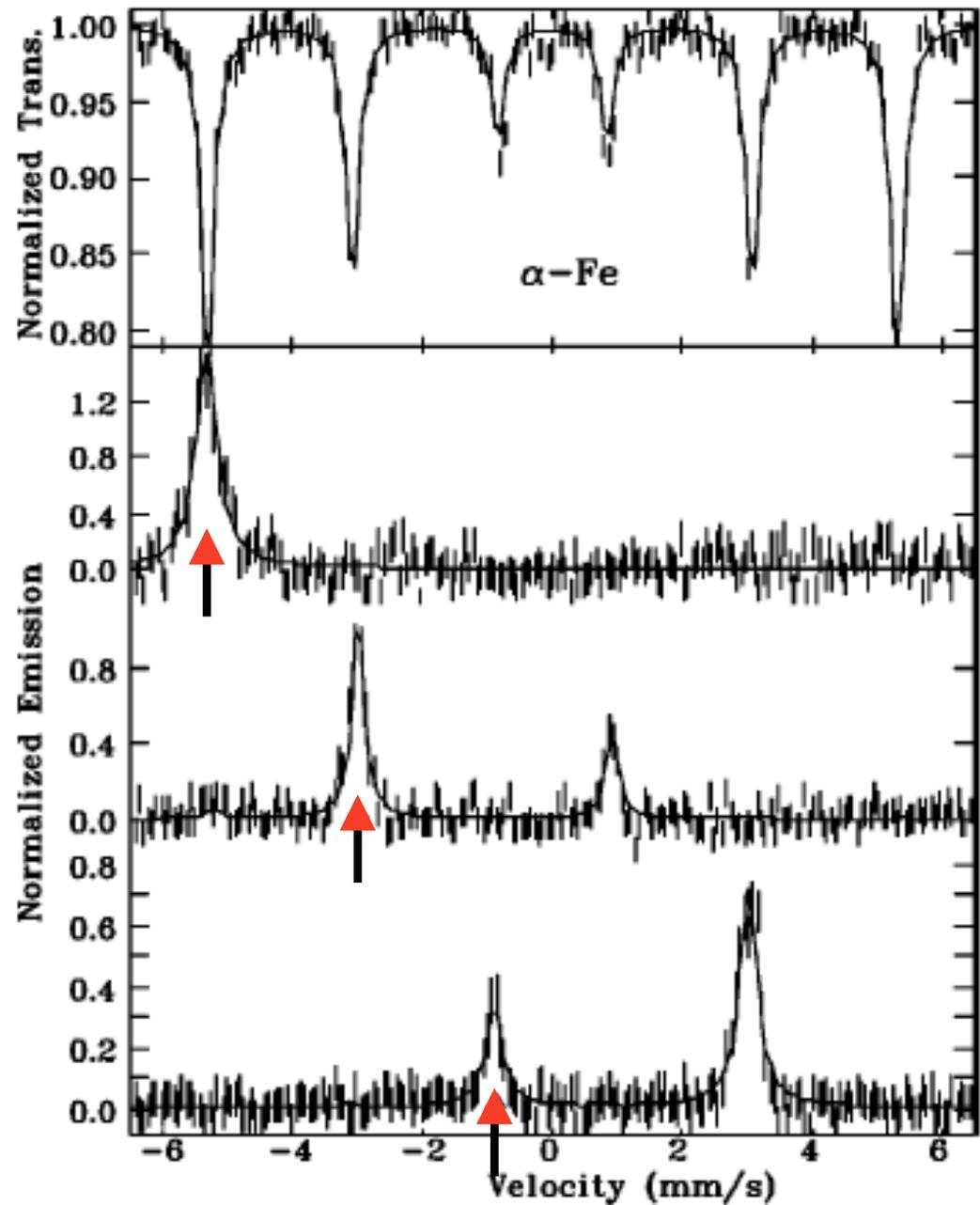
Resonant CEMS detector for SEDM analysis





Working our way across the transitions we pick up the allowed returns.

Notice that the observed intensities are set not by which transition we drove, but by the allowed return paths.



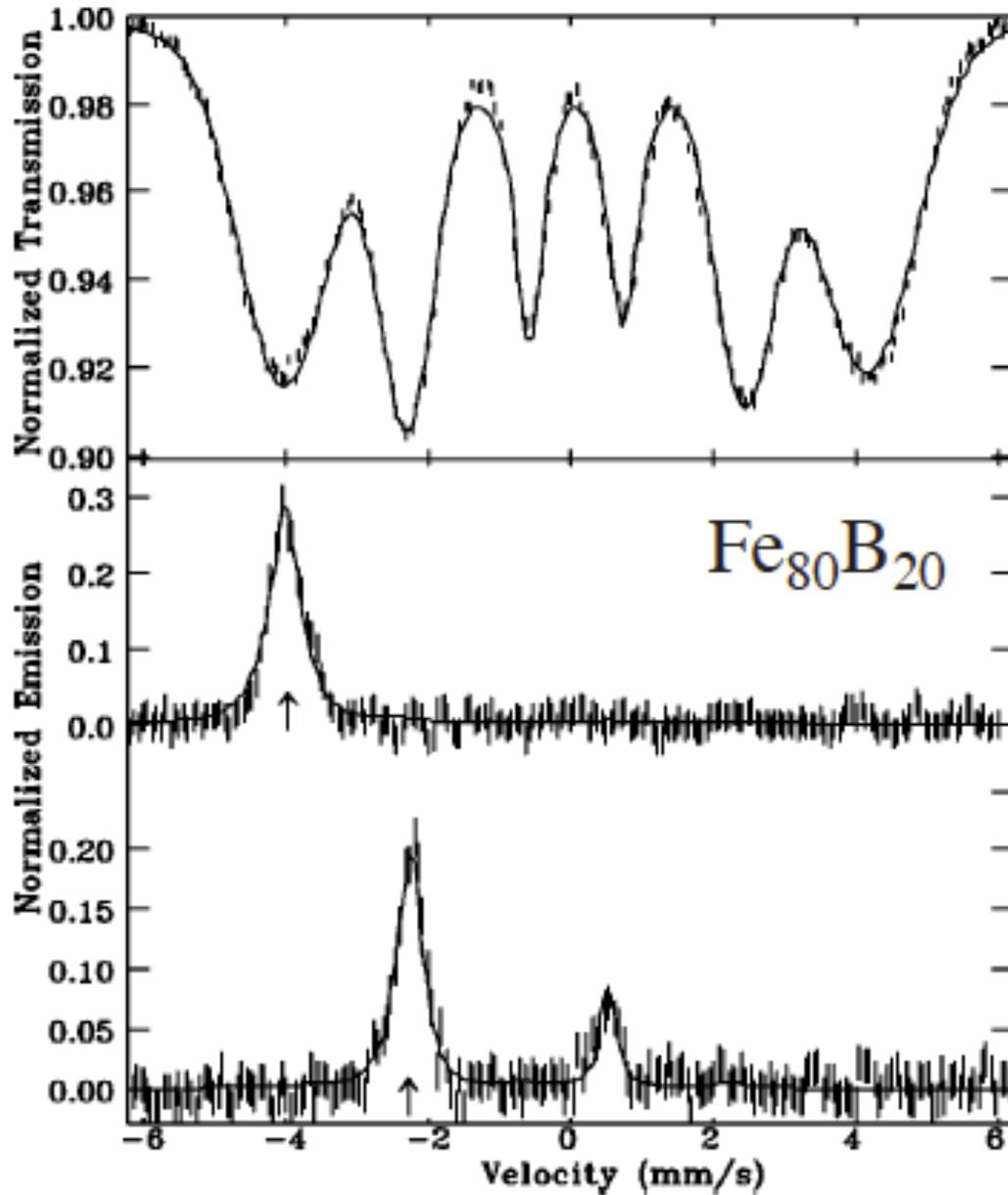
Separating dynamics from disorder

If your sample is chemically and/or structurally disordered, there will be a range of iron environments and the Mössbauer spectrum will exhibit broad lines.

If your sample exhibits time-dependent effects (e^- hopping, magnetic fluctuations) then it will exhibit broad lines.

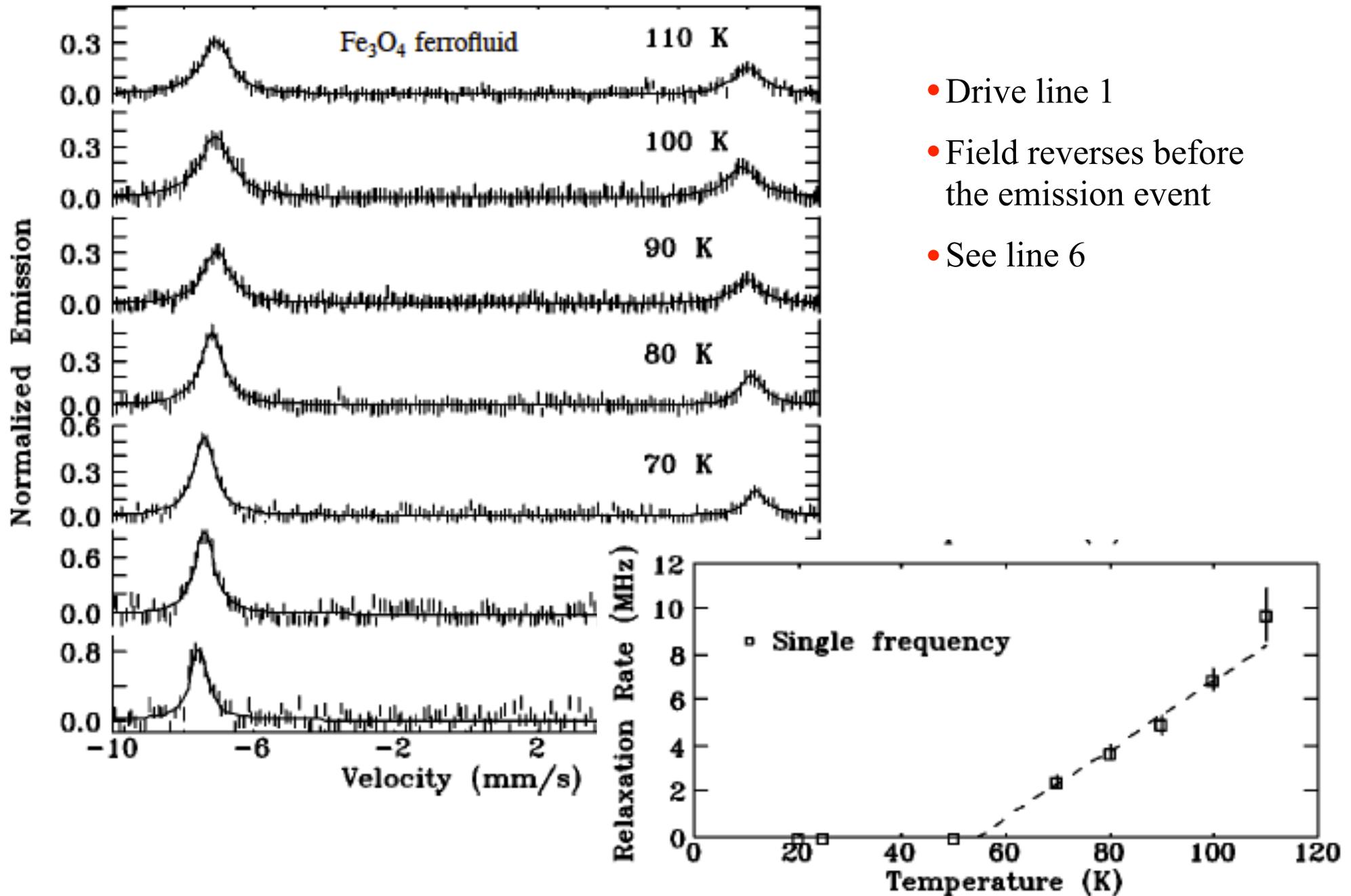
Often the temperature dependence of the spectral shape can be used to distinguish the effects, but if your sample is both *dynamic* and *disordered*...

Static disorder

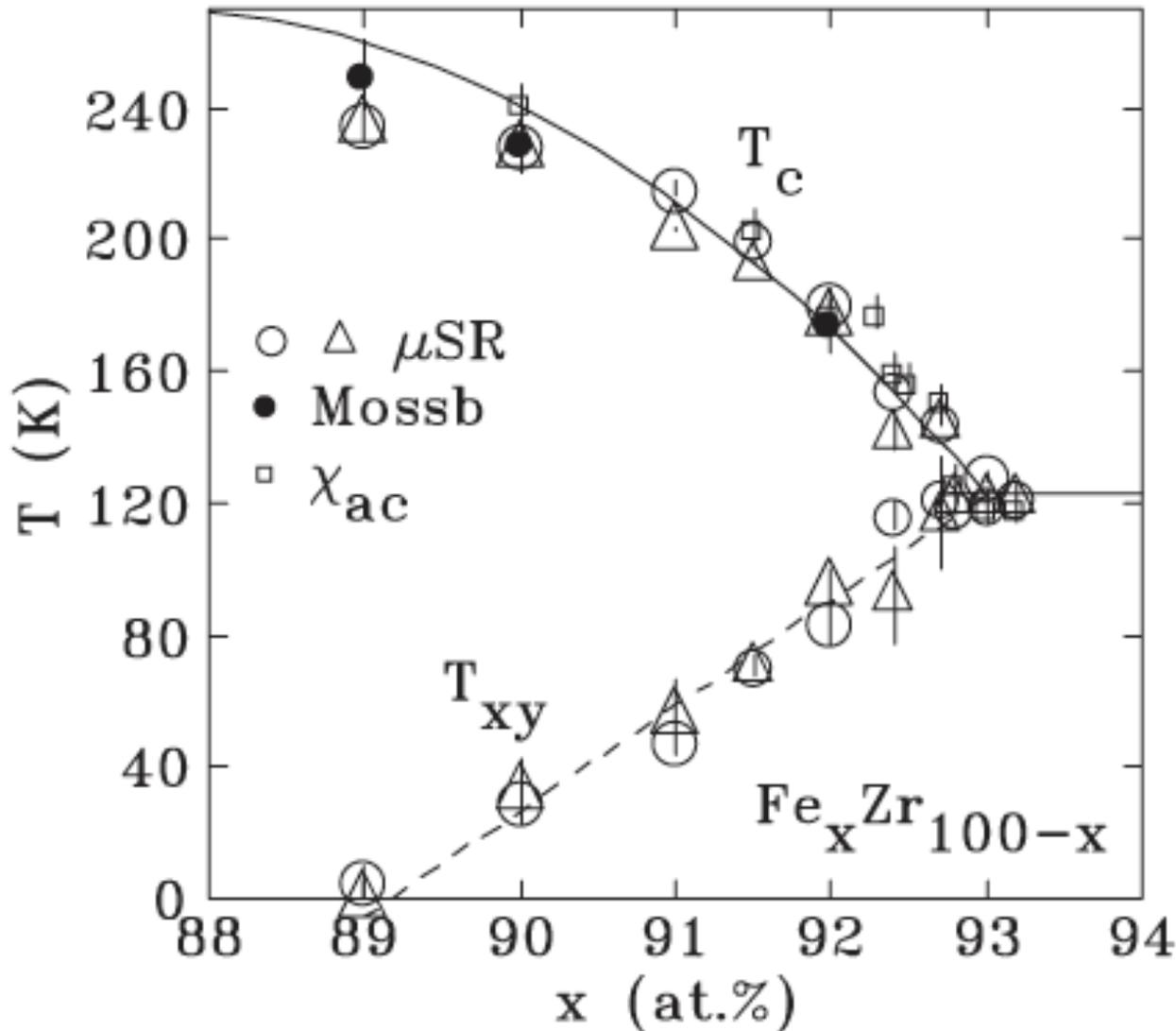


Notice how the emission line is sharper than that seen in transmission.

Simple dynamics

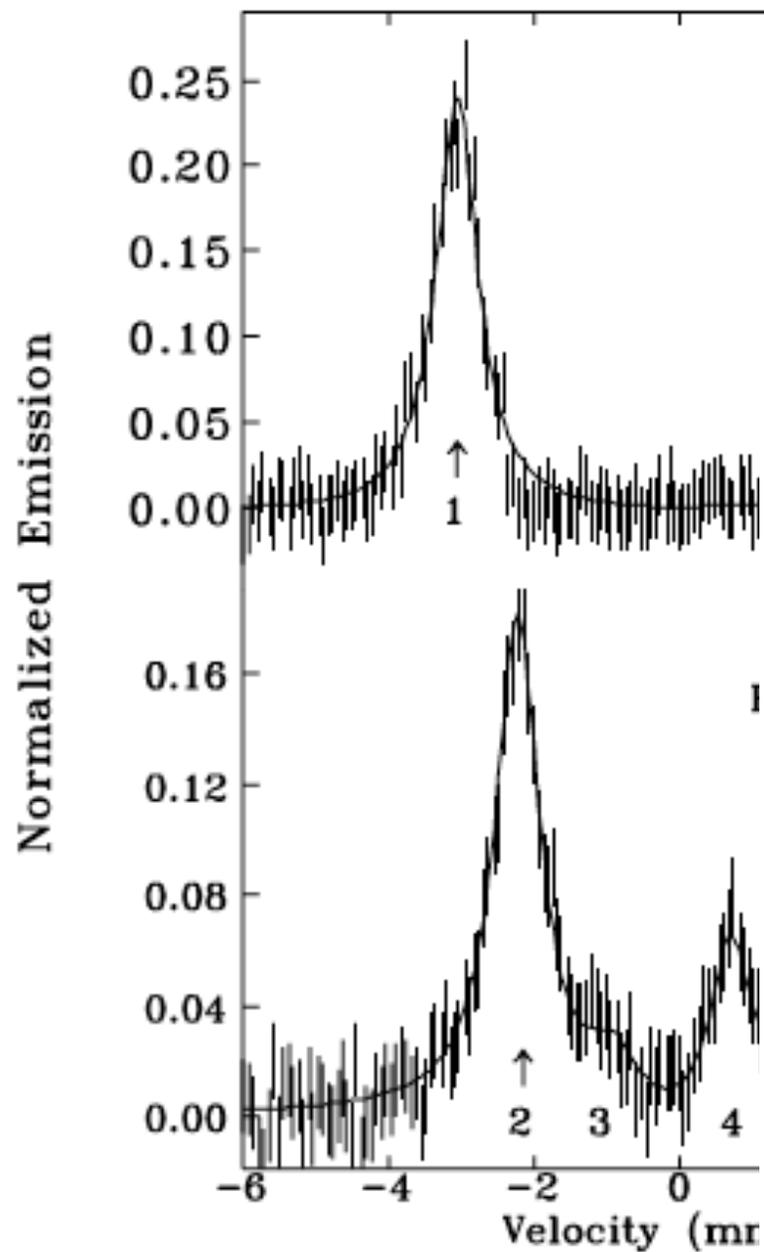


Dynamics *under* disorder



Adding enough bond frustration to a ferromagnetic will turn it into a spin-glass, but before it gets there, it passes through a more complex region where it exhibits both long-ranged FM order and xy-spin-glass order.

Numerical simulations predicted a fluctuation peak at T_{xy} . This has now been seen by μ SR and SEDM.



Drive lines 1 or 2 at T_{xy}

