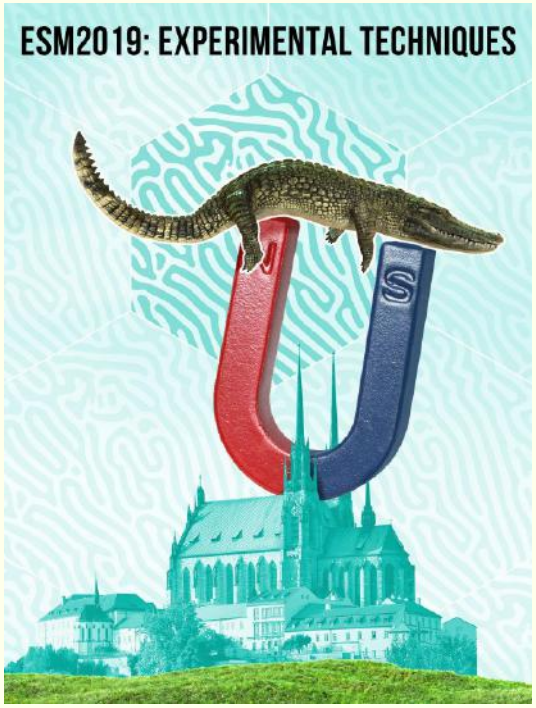
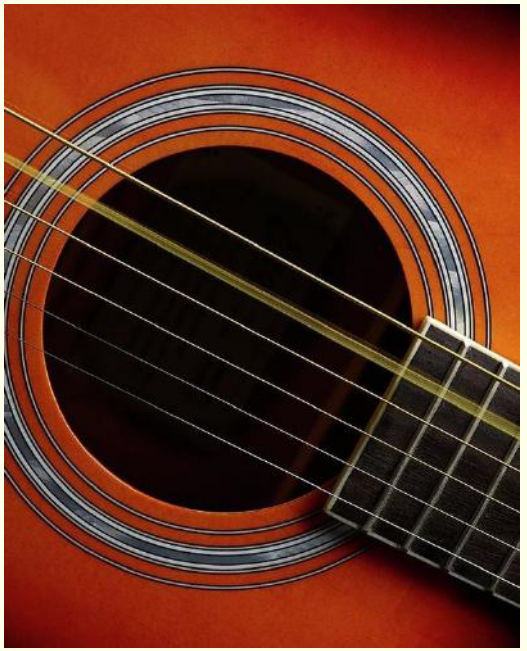
Vibrating sample magnetometry

Practical for the **European School on Magnetism 2019**, Brno (Czech Republic)





THE EUROPEAN SCHOOL ON MAGNETISM

CEITEC

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September 2-13, 2019

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Outline

- **Intro:** principle of operation, invention, SQUID-VSM systems, VSM system here in CEITEC, etc.
- Sample mounting techniques (films IP & OOP, powders, etc.)
- Experiments:
  - Case study I: AF-FM phase transition in FeRh films
  - Case study II: amorphous ferrimagnetic alloy films
- Notes on good practices during VSM measurements

VSM - Principle of operation

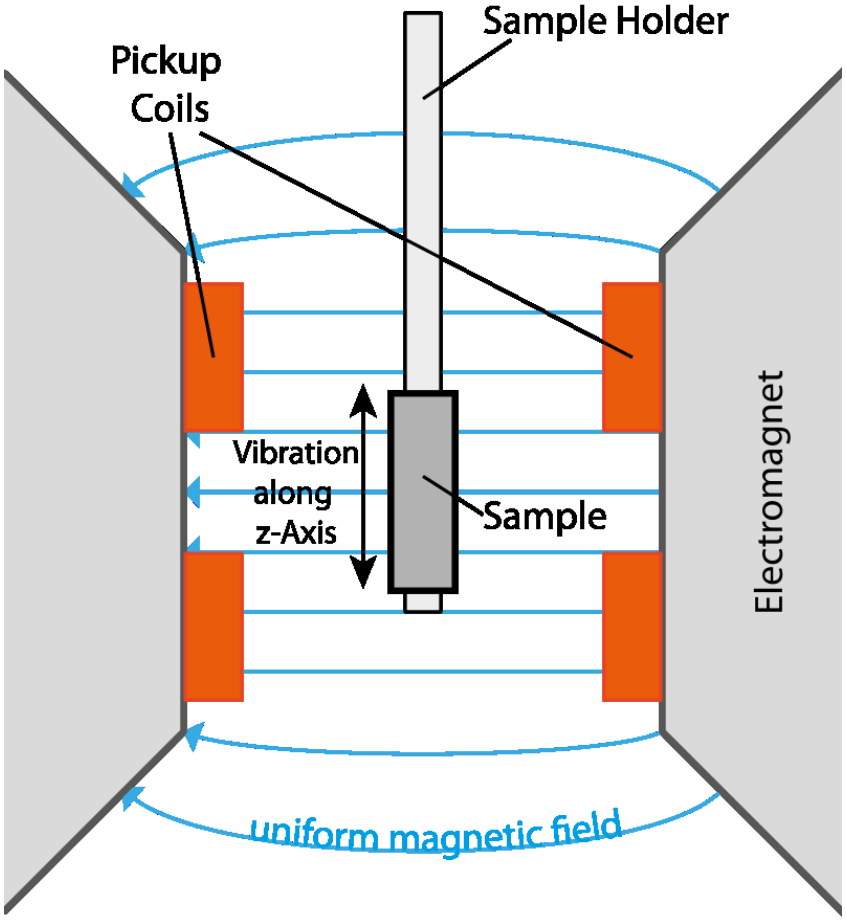


Image by R0oland, distributed under CC BY-SA 3.0 [link]

In vibrating sample magnetometry (VSM) the sample is attached to a nonmagnetic rod, which is oscillates or vibrates in a gap between (pairs of) fixed coils (***pick-up coils***)

The idea behind this procedure is that the **stray magnetic field** arising from the magnetized sample moves together with the sample, thus producing a **varying magnetic flux** in the coils. The way to read the magnetic moment of the sample consists in tracking the voltage generated by this varying magnetic flux in the coils, which is proportional to the magnetic moment.

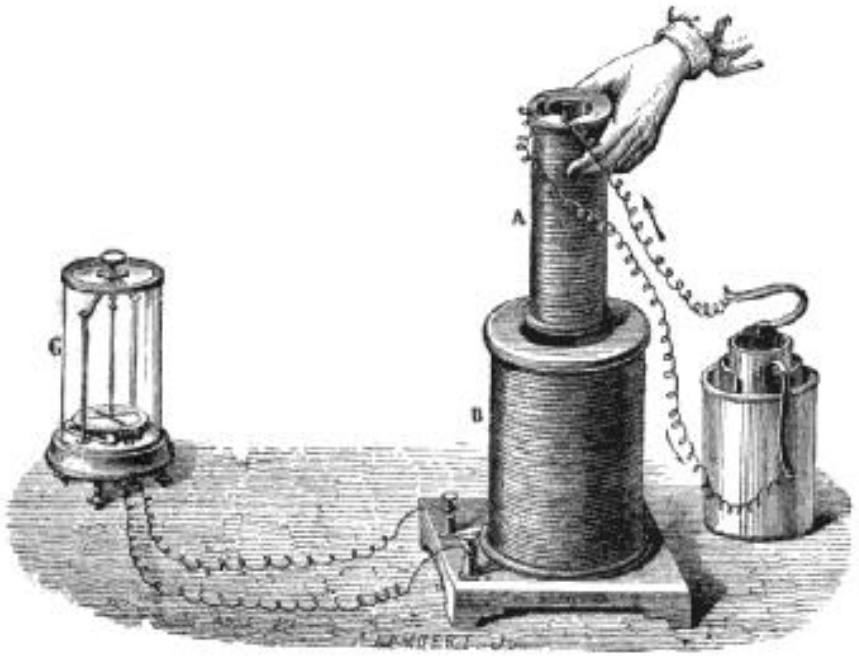
The absolute scale of magnetization and the corresponding voltage calibration is done by means of a reference sample.

VSM - Principle of operation → Electromagnetism!

How to measure the **magnetic moment** of a material?

One simple way consists on the **Faraday's law of induction**, in which a bar magnet/ dropped through a coil will generate a voltage in the latter.

Drawing of Michael Faraday's 1831 experiment showing electromagnetic induction between coils of wire, using 19th century apparatus, from an 1892 textbook on electricity. On the right is a liquid battery that provides a current that flows through the small coil of wire *(A)* creating a magnetic field. When the small coil is stationary, no current is induced. However, when the small coil is moved in or out of the large coil *(B)*, the change in magnetic flux induces a current in the large coil. This is detected by the deflection of the needle in the galvanometer instrument *(G)* on the left.



Author: J. Lambert (1892) [link]

VSM - Invention

Simon Foner
Lincoln labs @ MIT (1955)

VSM was invented in 1955 and presented to the public in in 1959

In 1959, he reported the measurement of **magnetic moment variations** as small as 10^{-5} and 10^{-6} emu

Inspired by D. O. Smith's **vibrating coil magnetometer**

Rev. Sci. Instr. 27, 261 (1956)

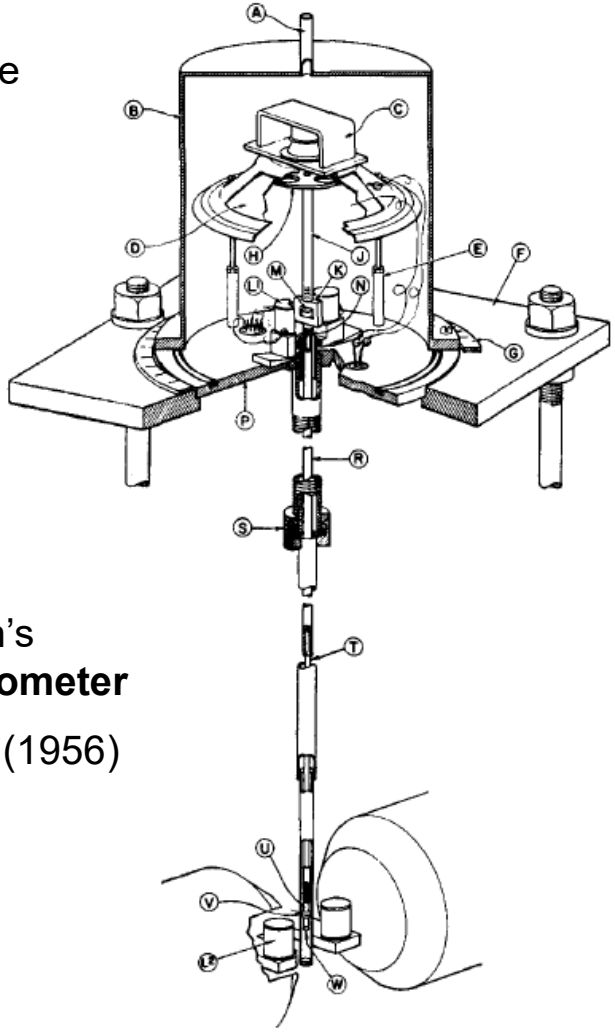


FIG. 2. Detailed mechanical construction of vibrating-sample magnetometer. The various parts are described in the text.

-S. Foner, Versatile and Sensitive Vibrating-Sample Magnetometer, Rev. Sci. Instrum. 30, 548 (1959) [link]
-S. Foner, The vibrating sample magnetometer: Experiences of a volunteer, J. Appl. Phys. 79, 4740 (1996) [link]
-A. Zieba, and S. Foner, Detection coil, sensitivity function, and sample geometry effects for vibrating sample magnetometers, Rev. Sci. Instrum. 53, 1344 (1982) [link]

How does it work in practice?

Electromagnetic induction + lock-in detection principle

The sample vibrates with frequency ω, such that the signal of interest has also this frequency, being characterized by an **amplitude A** in the pick-up coils (magnetic induction)

The signal from the pick-up coils can be interfered by external sources of electromagnetic radiation (50 Hz and its harmonics from power lines, etc.)

The measured signal is multiplied with the reference signal (ω_1) defined by the vibration driving the sample (a certain phase difference φ may exist).

Using the trigonometric identity: $$\cos(\alpha)\cos(\beta)=\frac{1}{2}\cos(\alpha-\beta)+\frac{1}{2}\cos(\alpha+\beta)$$

We have:

$$A\cos(\omega t)B\cos(\omega_1 t+\varphi)=\frac{1}{2}AB\cos(\omega t-\omega_1 t-\varphi)+\frac{1}{2}AB\cos(\omega t+\omega_1 t+\varphi)$$

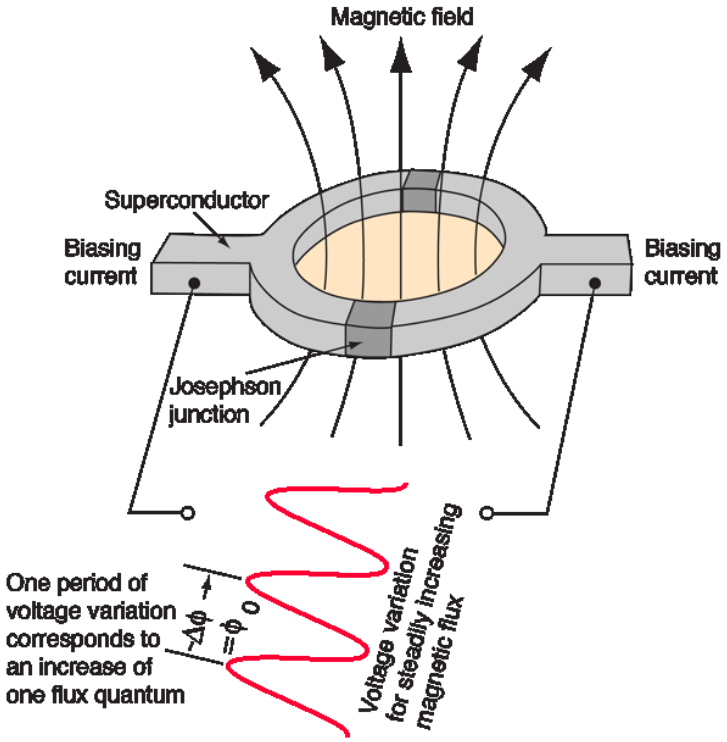
Constant signal ∝ A Time varying voltage

But since $\omega = \omega 1$

$$A\cos(\omega t)B\cos(\omega_1 t+\varphi)=\frac{1}{2}AB\cos(\varphi)+\frac{1}{2}AB\cos(2\omega t+\varphi)$$

And we get a **constant voltage which is proportional to the signal of interest A**

VSM and SQUID-VSM magnetometers



SQUID sensitivity	10^{-14} T
Magnetic field of heart	10^{-10} T
Magnetic field of brain	10^{-13} T

The superconducting quantum interference device (SQUID) consists of two superconductors separated by thin insulating layers to form two parallel Josephson junctions. The device may be configured as a magnetometer to detect extremely weak magnetic fields.

One of the discoveries associated with Josephson junctions was that flux is quantized in units of

$$\Phi_0 = \frac{2\pi\hbar}{2e} \cong 2.0678x10^{-15}\, tesla \cdot m^2$$

If a constant biasing current is maintained in the SQUID device, the measured voltage oscillates with the changes in phase at the two junctions, which depends upon the change in the magnetic flux. Counting the oscillations allows evaluating the flux change.

The sensitivity of the device allow the measurement of **hysteresis loops of single particles** [4]

[1] http://hyperphysics.phy-astr.gsu.edu/hbase/Solids/Squid.html
[2] C. D. Graham, High-Sensitivity Magnetization Measurements, J. Mater. Sci. Technol. 16, 97 (2000)
[3] R. L. Fagaly, Superconducting quantum interference device instruments and applications, Rev. Sci. Instrum. 77, 101101 (2006)
[4] W. Wernsdofer et al., DC-SQUID magnetization measurements of single magnetic particles, J. Magn. Magn. Mater. 145,33 (1995)

Versalab system in CEITEC

The VersaLab (Quantum Design Inc.) is a cryogen-free physical property measurement system, suitable for magnetic and electrical characterization.

Temperature range: 50-400 K

Max field: 3 Tesla

-Vibrating sample magnetometer (VSM)

-Electrical transport option (ETO)

-Oven option for the VSM (400-1000 K)

VSM

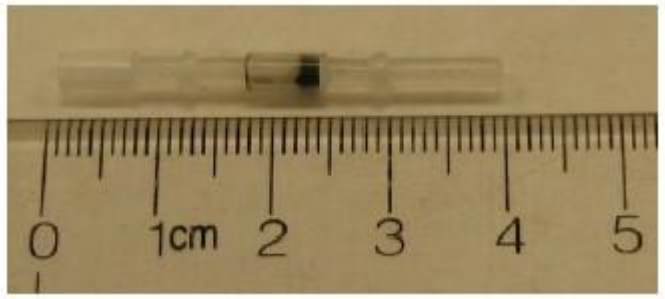
- Oscillation amplitude: 1-3 mm (peak)
- Frequency: 40 Hz
- Sensitivity: <1 μemu magnetic moment changes with 1 s data averaging

https://www.qdusa.com/products/versalab.html

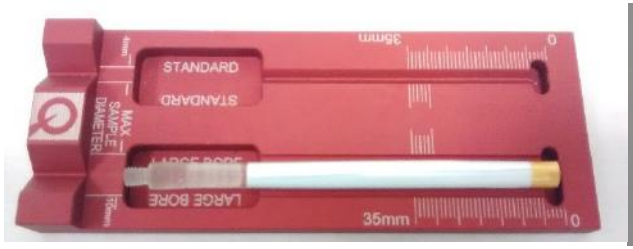
Sample mounting techniques

Quartz (best sensitivity) and brass holders

Capsule (powder, particles)



Straw (in-plane field)



Straw (out-of-plane field)

Always use transparent straws!

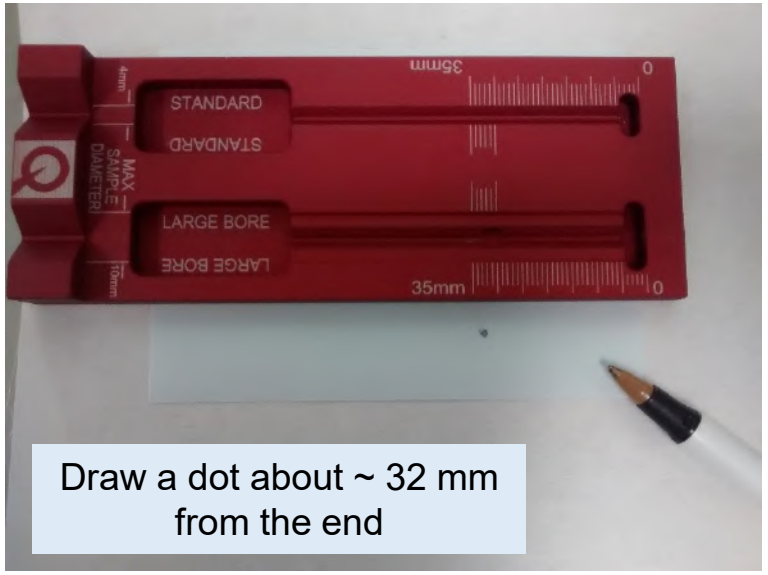
Clear plastic such as polycarbonate, polypropylene, Delrin (acetal copolymer), and Kel-F (PCTFE) have low background moments (also cryogenic compatible)

The **dyes used to color the plastics are generally magnetic (!!!)**

(1) Sample mounting for oven option (Quantum Design Inc.)
https://www.youtube.com/playlist?list=PLuI5kHh9kg1Z8TNTa8tLs9PsMrQJ_2Oko

(2) How to load powder samples (Quantum Design Inc.)
https://www.youtube.com/playlist?list=PLuI5kHh9kg1b2Xc1ZVB5Raq7C-NZYDEuc

Sample mounting 1 (straw, in-plane field)

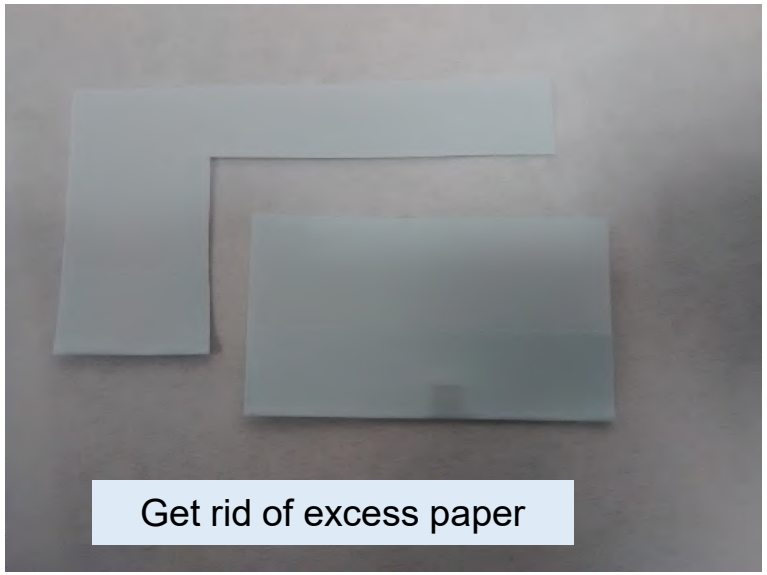


Draw a dot about ~ 32 mm from the end

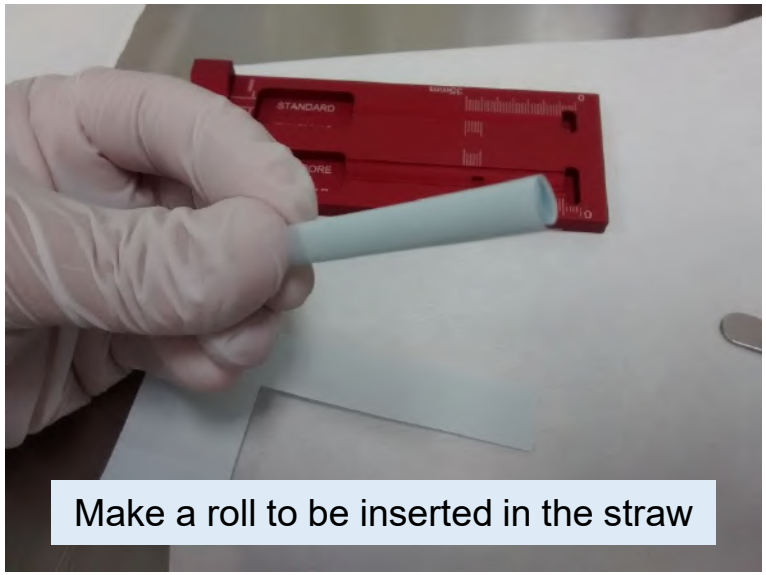
The sample will be place here (back side on sticky part)

Wrap the sample with the paper

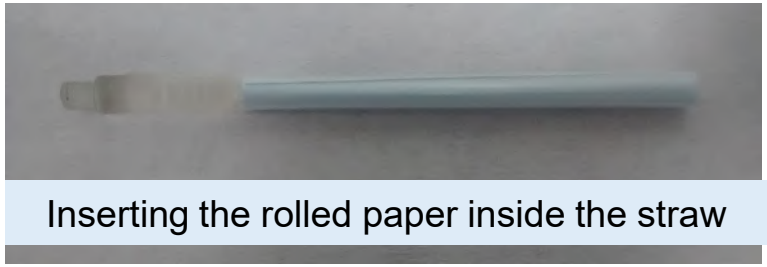
Sample mounting 1 (straw, in-plane field)



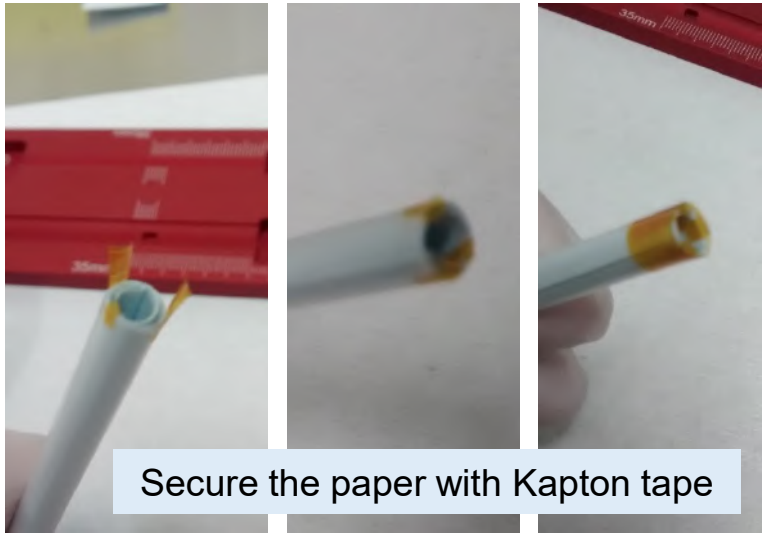
Get rid of excess paper



Make a roll to be inserted in the straw

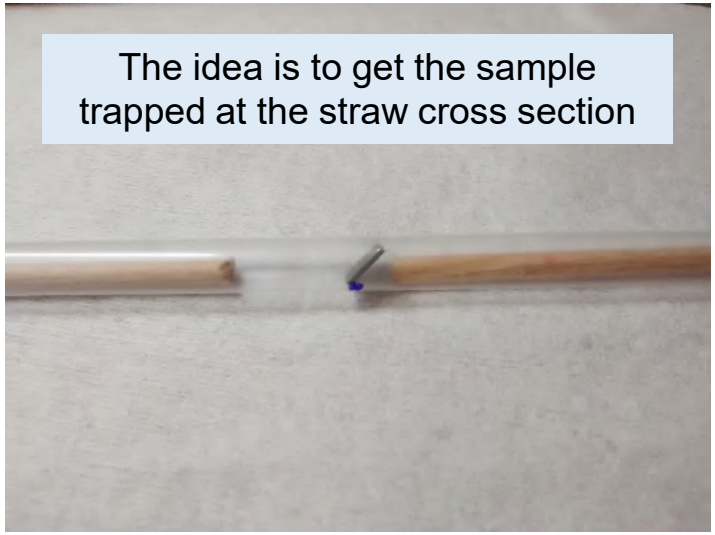


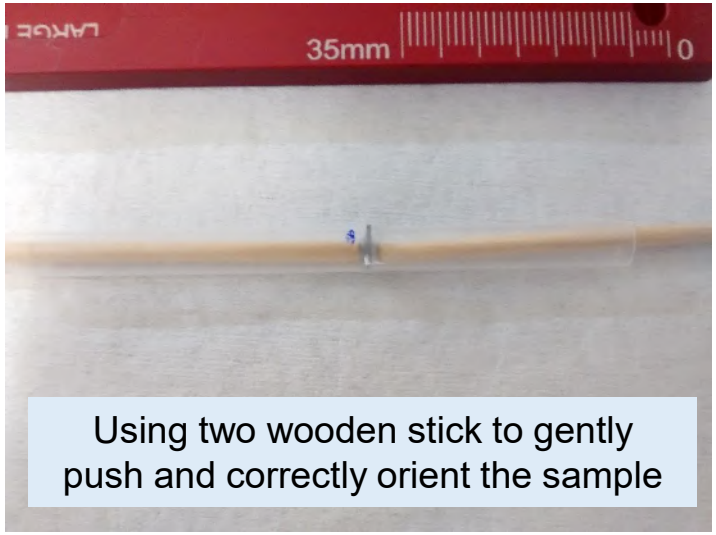
Inserting the rolled paper inside the straw

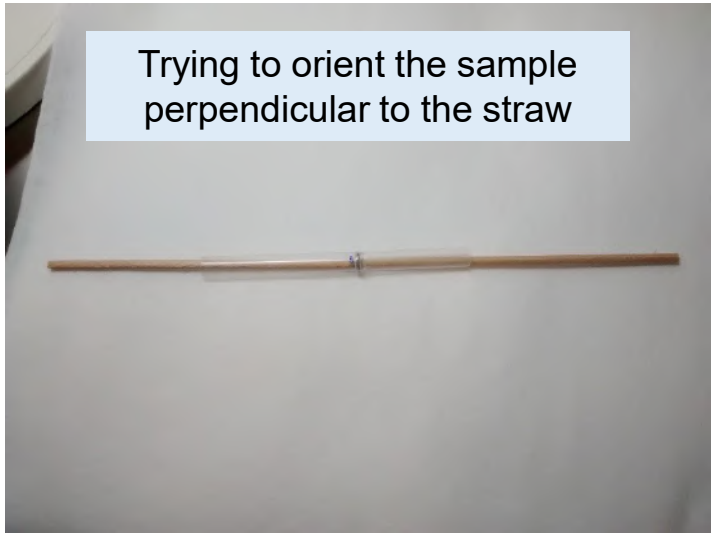


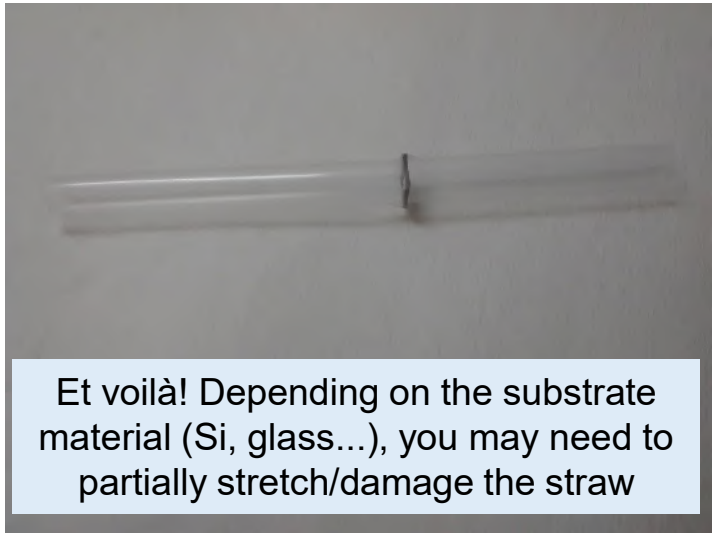
Secure the paper with Kapton tape

Sample mounting 2 (straw, out-of-plane field)



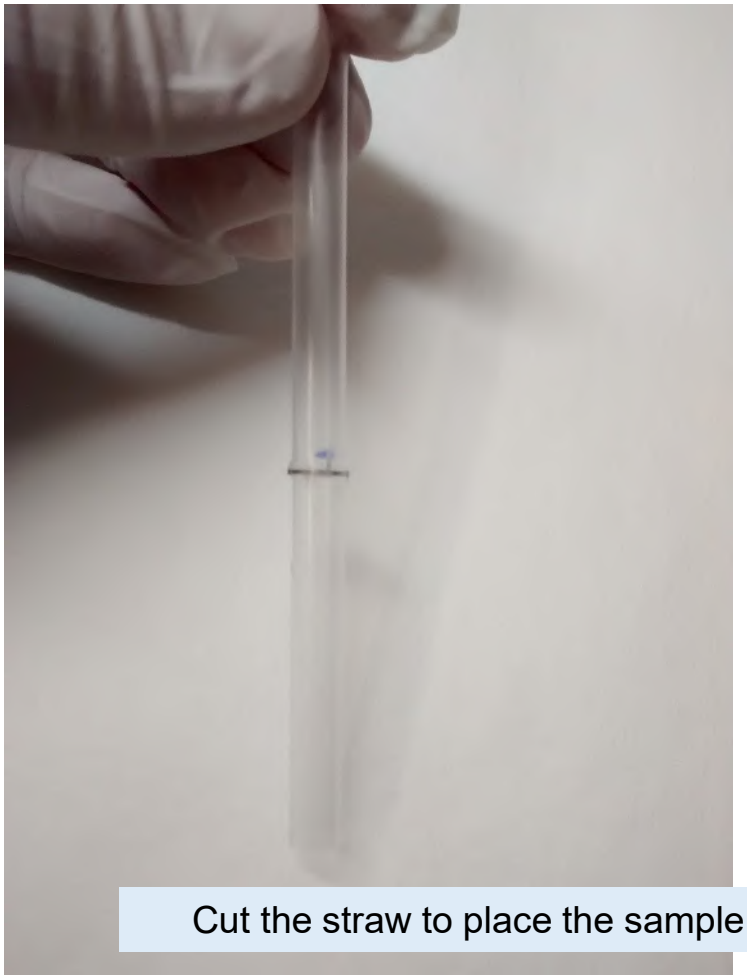


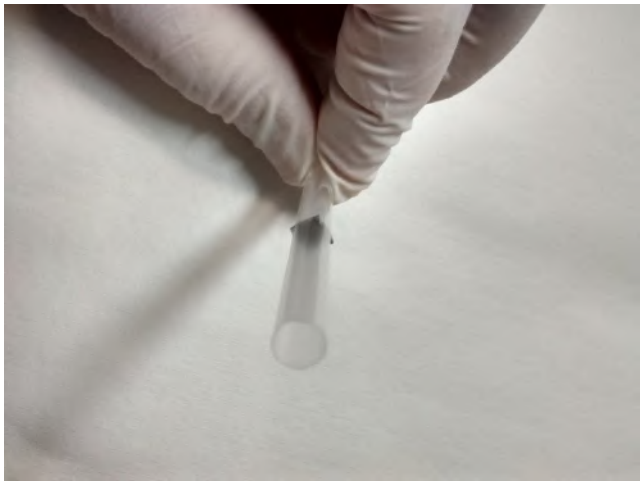




Appropriate sample size depending on straw diameter (here, < 5 x 5 mm2)

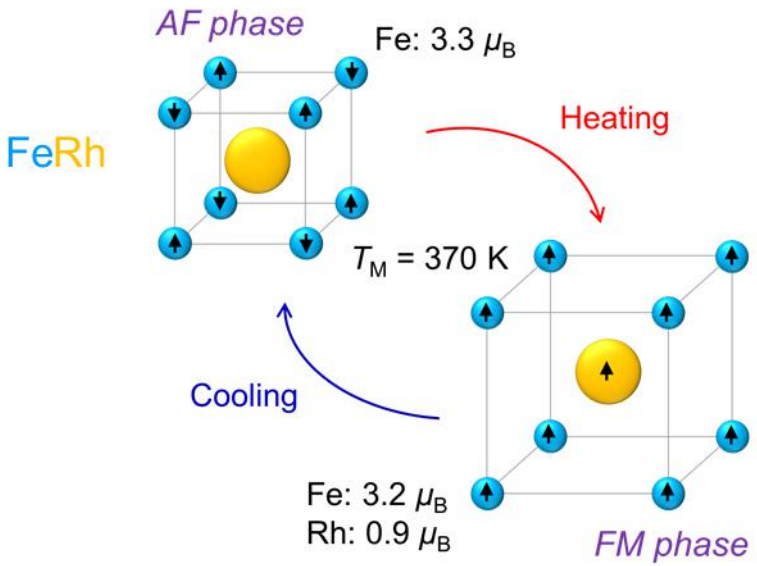
Sample mounting 2 (straw, out-of-plane field)





Cut the straw to place the sample at the right distance from the end

I. Metamagnetic first-order phase transition in FeRh



Antiferromagnetic (AF) below 370 K

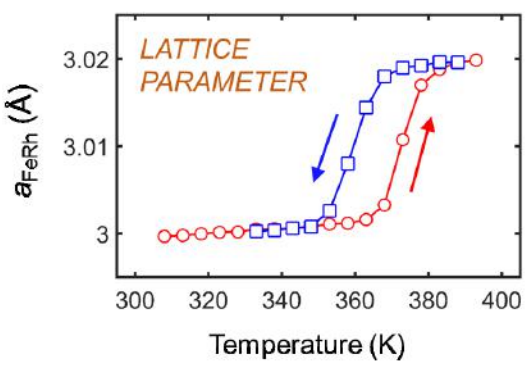
Ferromagnetic (FM) above 370 K

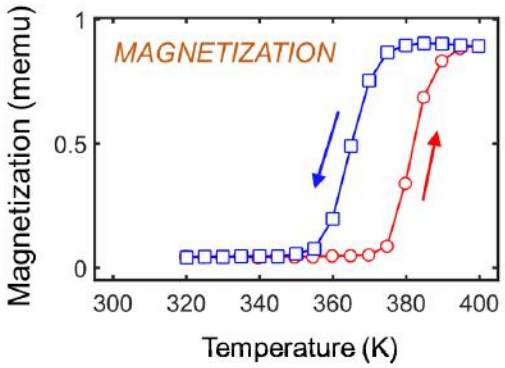
- Volume expansion (1%)
- Reduction in resistivity (50%)
- ❖ Doping:

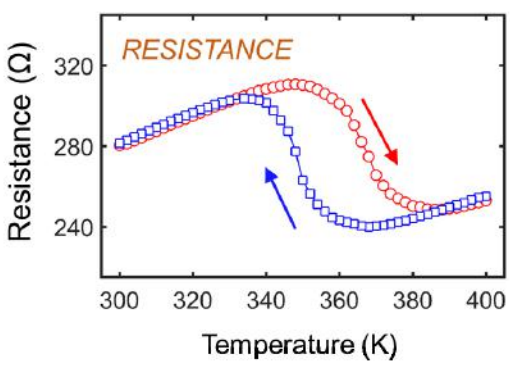
  (Pt, Ir) increase T_M

  (Ni, Pd) decrease T_M

Interplay of **structural**, **electronic** and **magnetic** order parameters in a metallic system



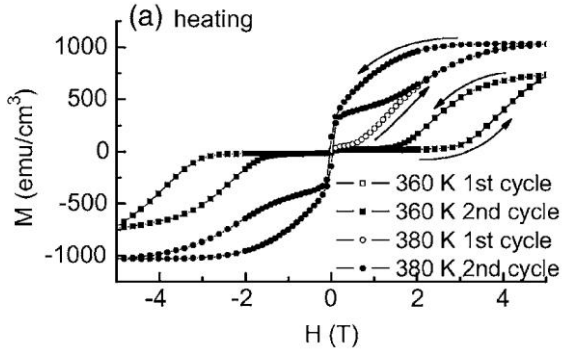




Maat, Thiele and Fullerton, Phys. Rev. B **72**, 214432 (2005); Lewis, Marrows and Langridge, *J. Phys. D: Appl. Phys.* **49**, 323002 (2016)

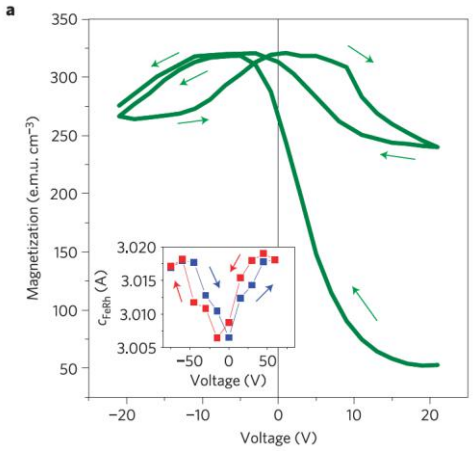
I. Metamagnetic first-order phase transition in FeRh

MAGNETIC FIELD



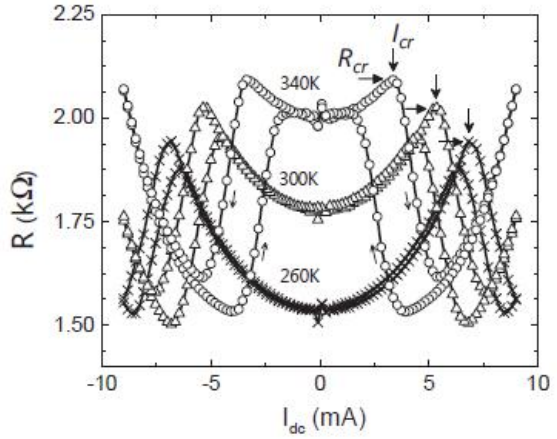
Maat, Thiele and Fullerton, Phys. Rev. B **72**, 214432 (2005)

STRAIN



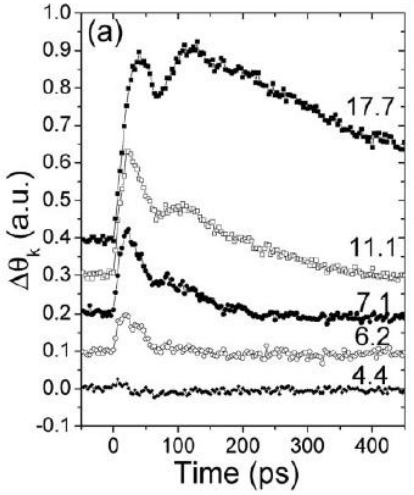
Cherifi et al., Nat. Mater. **13**, 345 (2014)

ELECTRICAL CURRENT



Matsuzaki et al., Jpn. J. Appl. Phys. **54**, 073002 (2015)

ULTRAFAST LASER PULSES



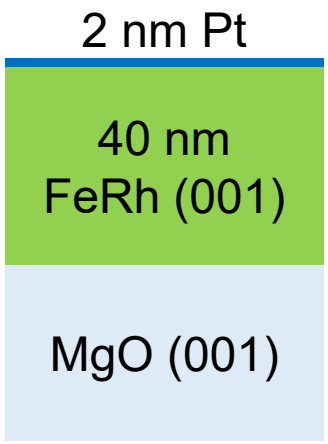
Thiele, Buess, and Back,
Appl. Phys. Lett. **85**, 2857 (2004)

Ju et al.,
Phys. Rev. Lett. **93**, 197403 (2004)

Mariager et al.,
Phys. Rev. Lett. 108, 087201 (2012)

Pressacco et al.,
Struct. Dyn. **5**, 034501 (2018)

I. Metamagnetic first-order phase transition in FeRh



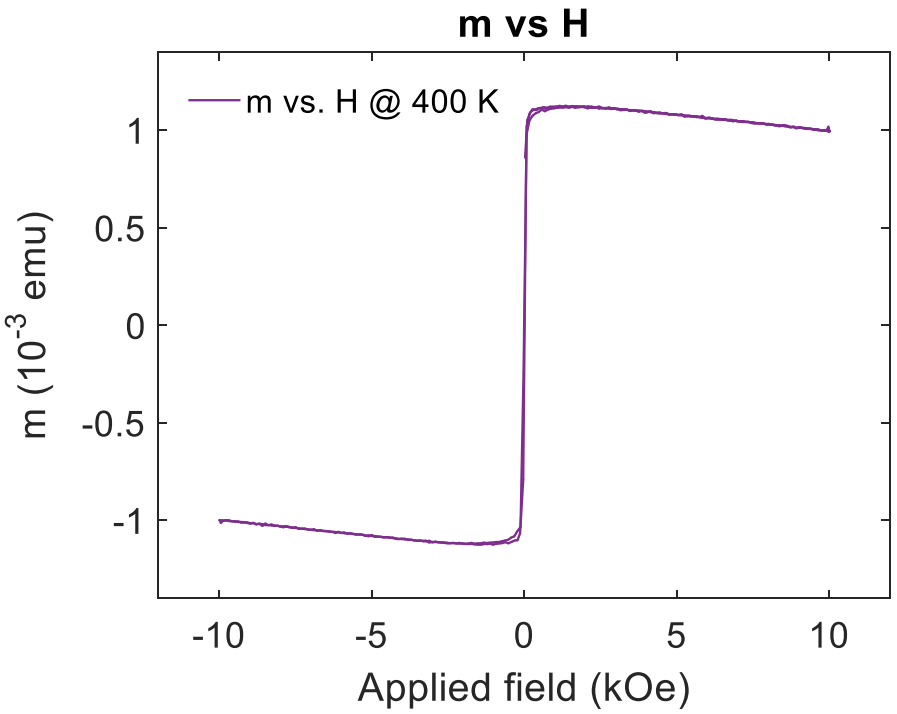
Epitaxial FeRh film on single-crystal MgO substrate

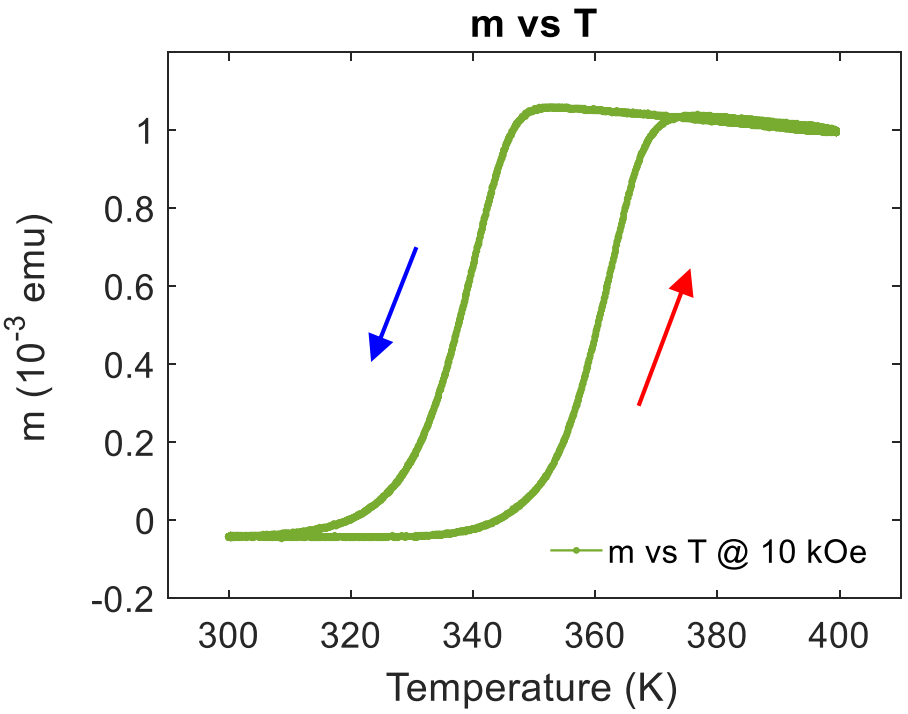
2-nm-thick Pt capping

We need to find out....

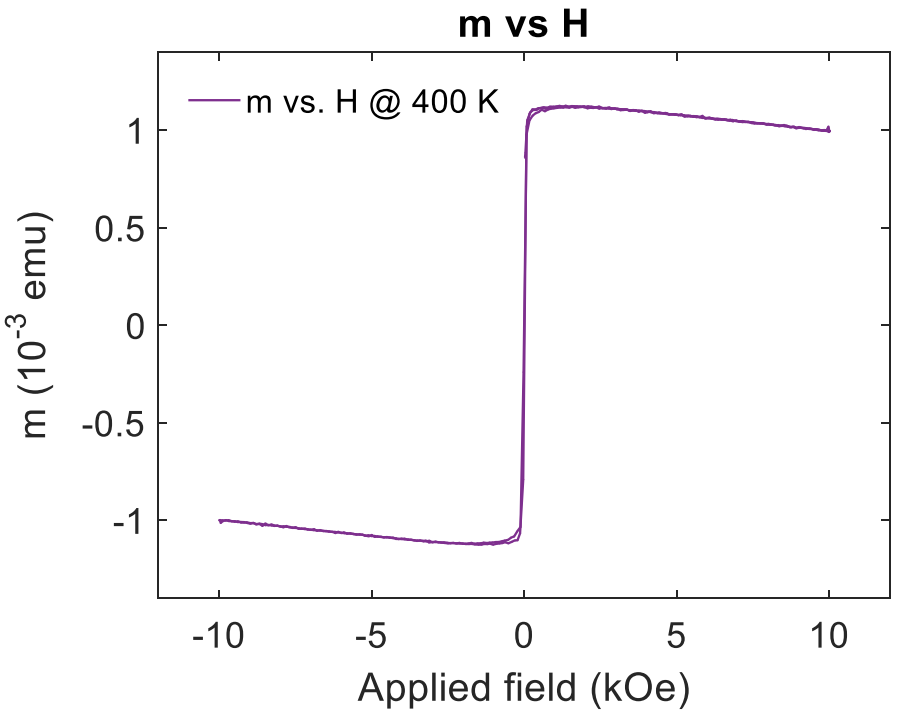
- ❑ Is the film ferromagnetic at 400 K?
- ❑ Is the film ferromagnetic at 300 K? (room temperature)
- ❑ Is there an AF-FM phase transition?

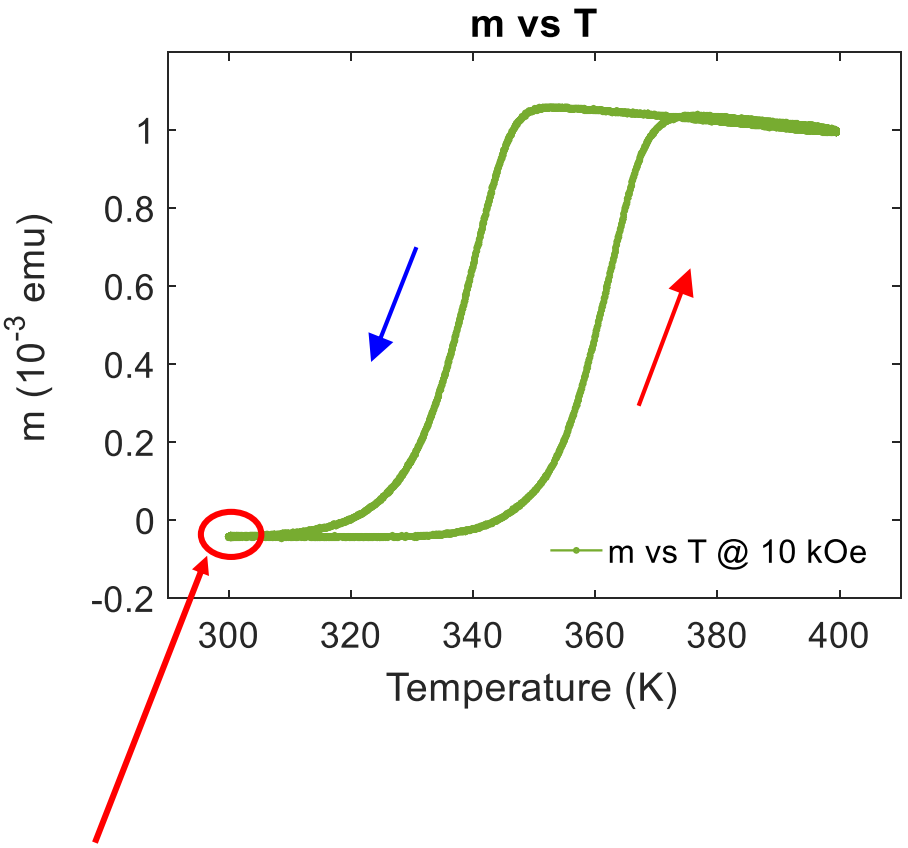
I. Metamagnetic first-order phase transition in FeRh





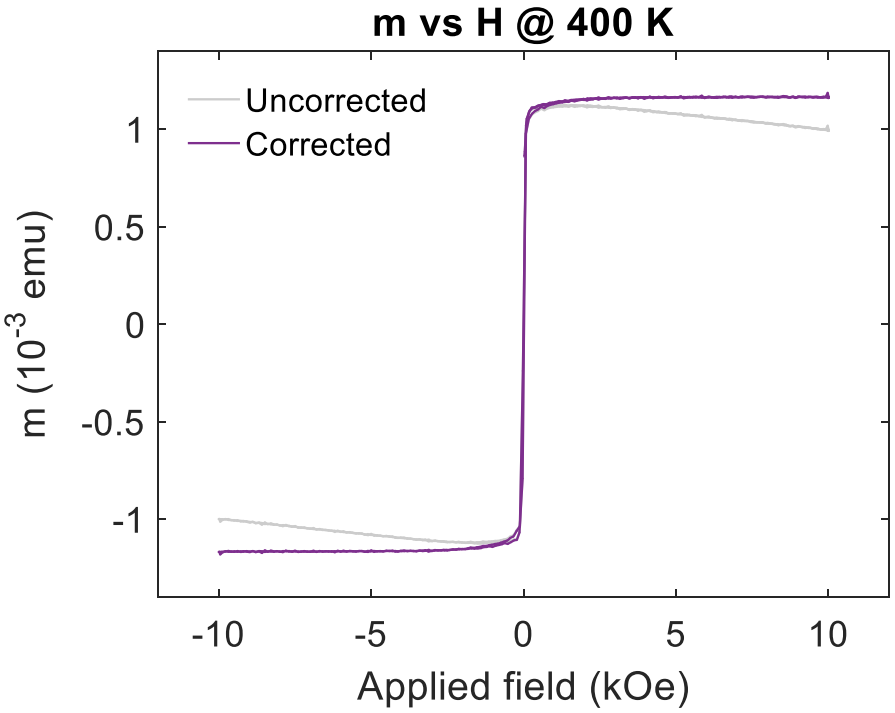
I. Metamagnetic first-order phase transition in FeRh

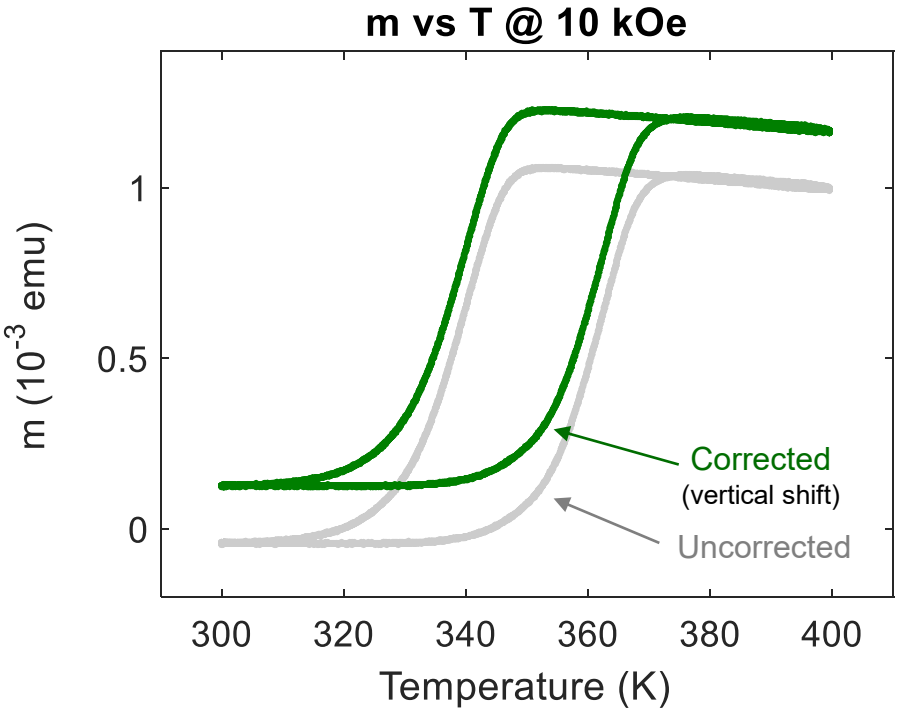




Why is the magnetic moment negative at 300 K?

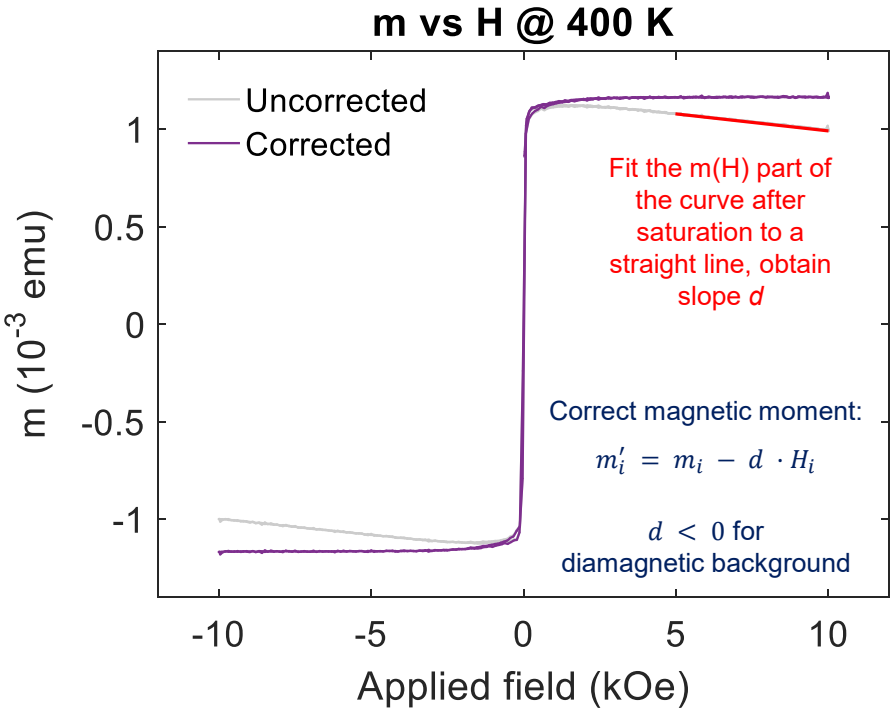
I. Metamagnetic first-order phase transition in FeRh

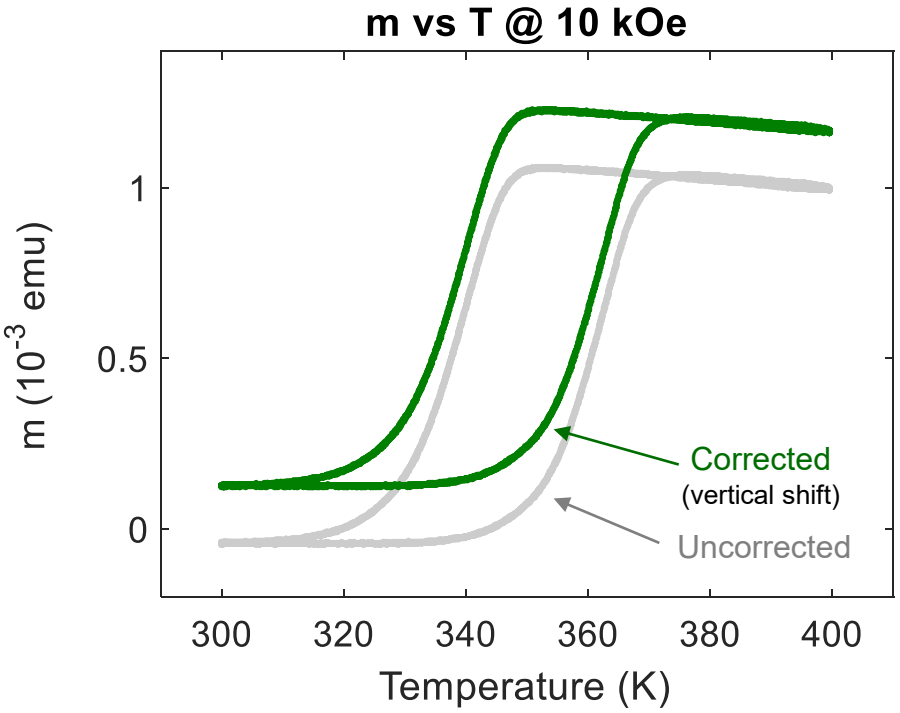




One needs to correct for the diamagnetic contribution of the substrate (/sample environment)

I. Metamagnetic first-order phase transition in FeRh





One needs to correct for the diamagnetic contribution of the substrate (/sample environment)

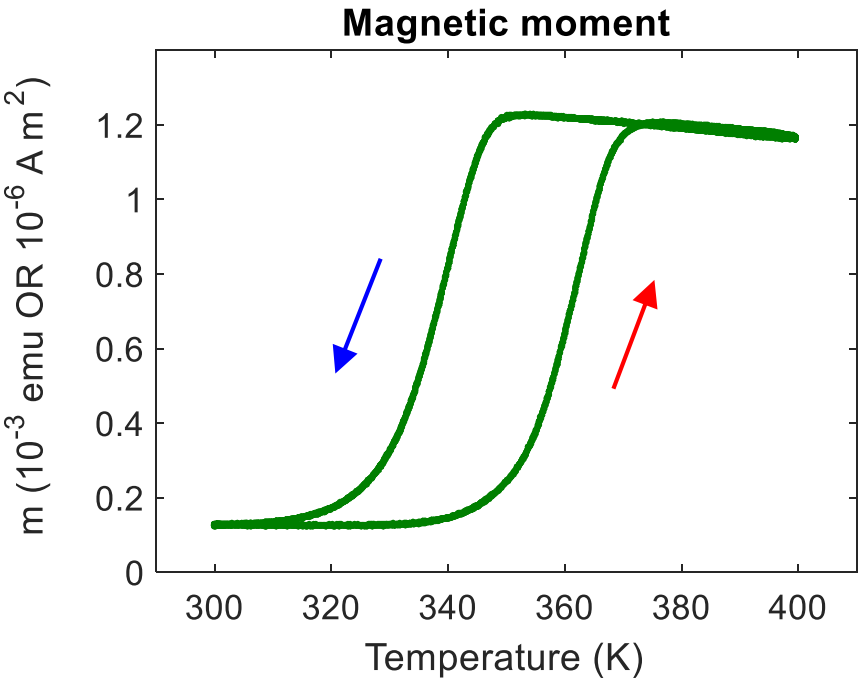
I. Metamagnetic first-order phase transition in FeRh

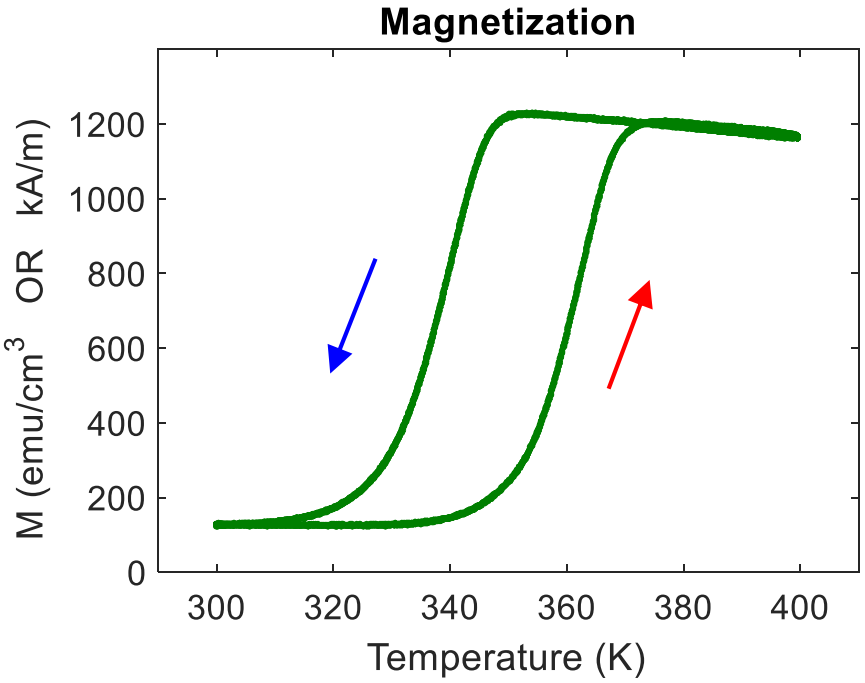
Converting from magnetic moment to magnetization, M = m/V

Our film volume = 5 mm x 5 mm x 40 nm = 10^{-12} m^3 or 10^{-6} cm^3

gauss: 1 memu → M = m/V = (10^{-3} emu)/(10^{-6} cm^3) = 1000 emu/cm^3

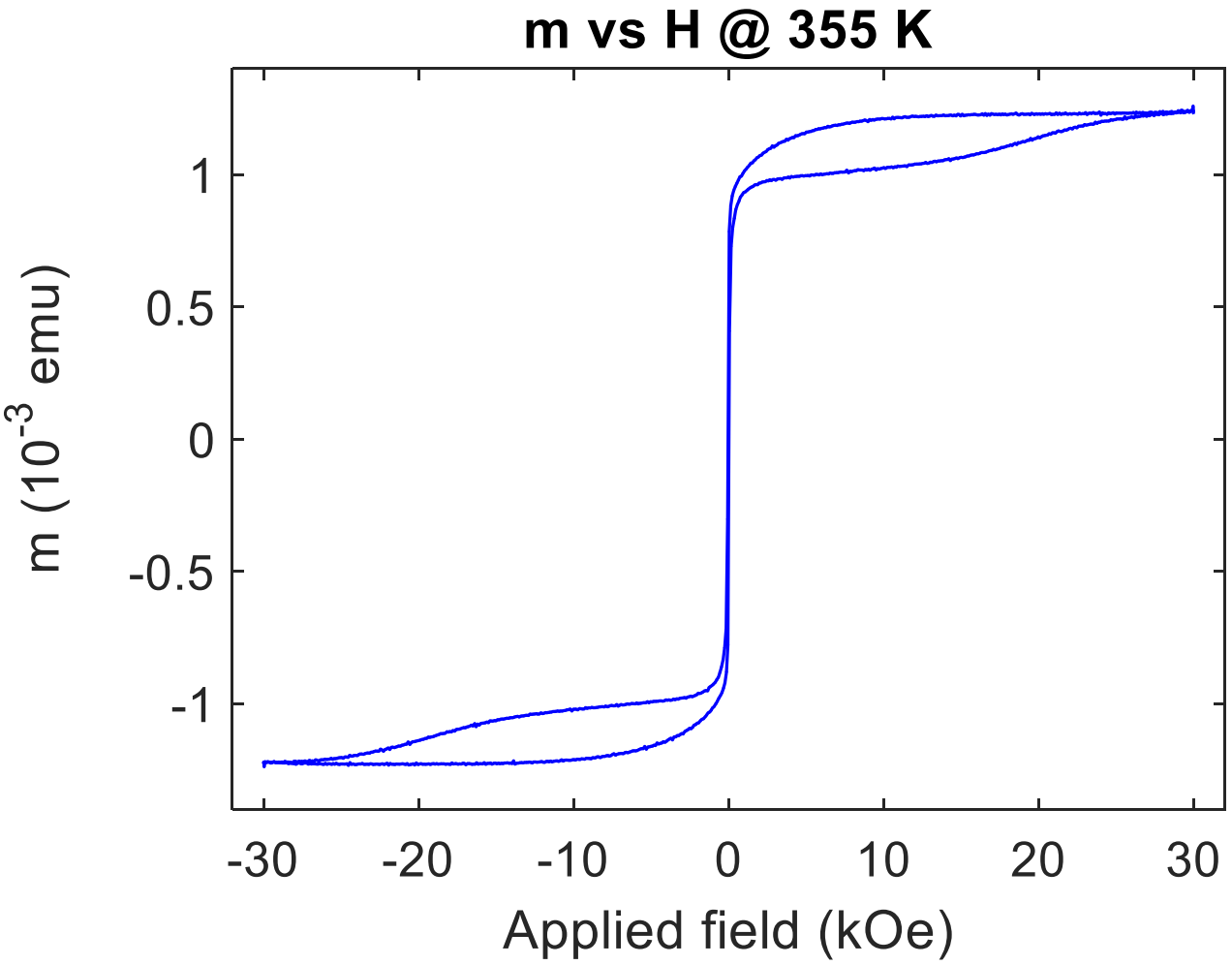
SI: 10^{-6} A·m^2 → M = m/V = (10^{-6} A·m^2)/(10^{-12} m^3) = 10^6 A/m = 1000 kA/m





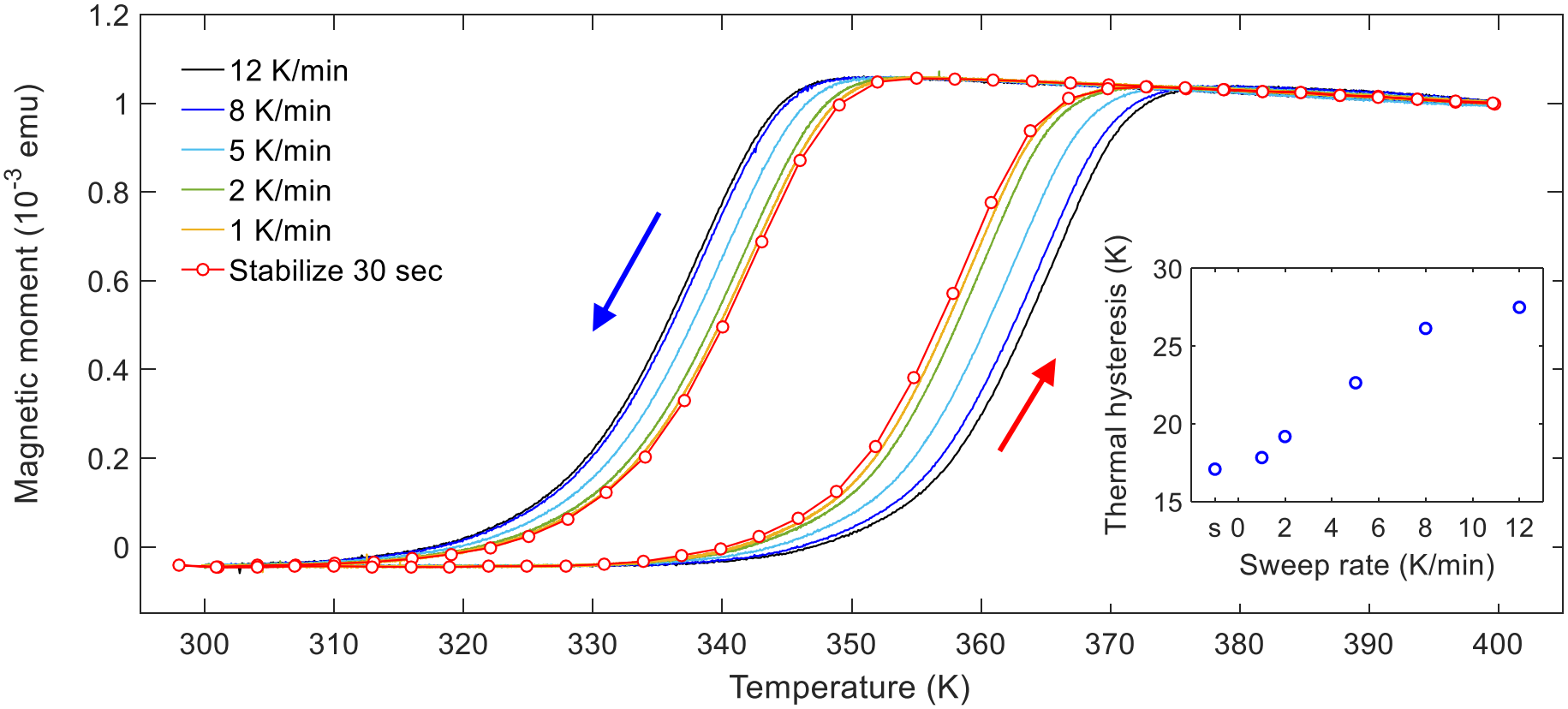
I. Metamagnetic first-order phase transition in FeRh

Field-driven phase transition



Effect of temperature sweep rate (sample thermalization)

*Thermal hysteresis in FeRh (40 nm film)

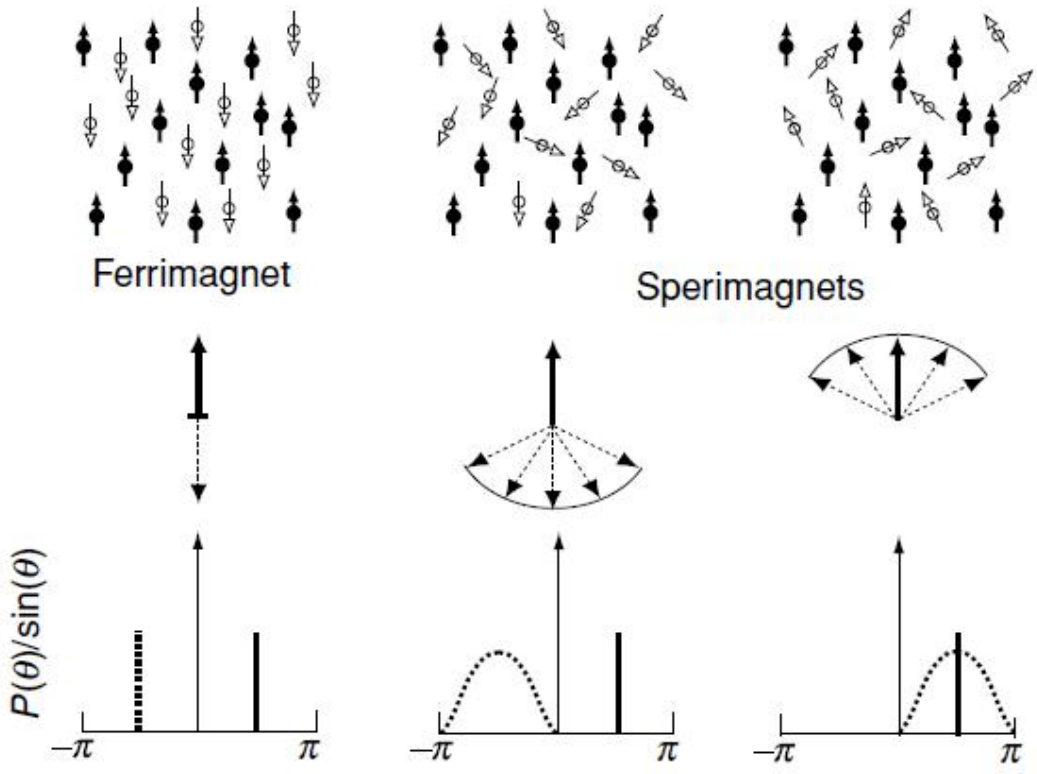


- There is a time delay in the thermalization of the sample!
- **Solutions:** (i) very low sweep rate (≤ 1 K/min)
  (ii) stabilize temperature at each acquisition

II. Amorphous ferrimagnetic RE-TM alloys

Figure 6.21

Possible two-subnetwork magnetic structures in amorphous binary alloys.



In RE-TM amorphous alloys, there are sublattices composed of 3*d* and 4*f* atoms

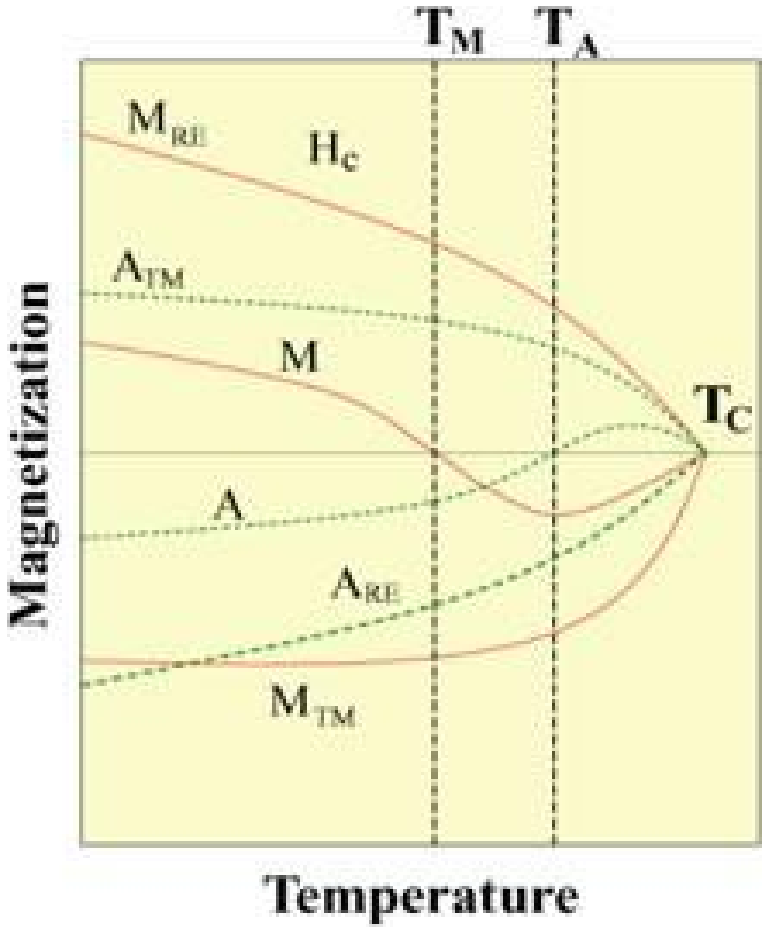
From: J. M. D. Coey, *Magnetism and Magnetic Materials*, Cambridge University Press (2010), pages 217-218

(i) d–d exchange is strongly ferromagnetic, defines a ferromagnetic 3d subnetwork,

(ii) 3d–4f interactions then tend to align the 4f spins antiparallel to the 3d spins

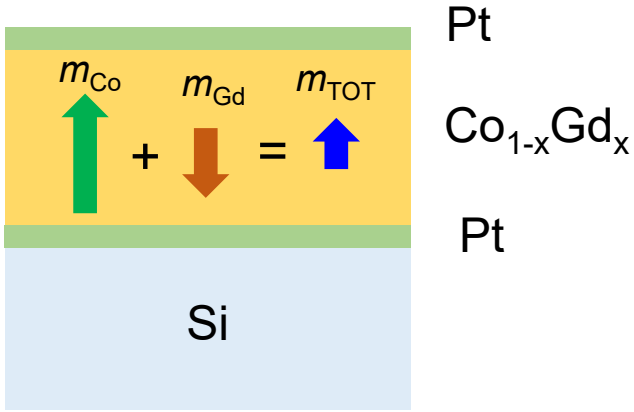
(iii) For RE with strong uniaxial anisotropy and weak exchange coupling to the 3d subnetwork, their local easy axes are defined by the local crystal-field interaction. Local easy axes are random, leading to the sperimagnetism

II. Amorphous ferrimagnetic RE-TM alloys



Magnetization (M) and angular momentum (A) of the sublattices versus temperature

Example: CoGd alloys



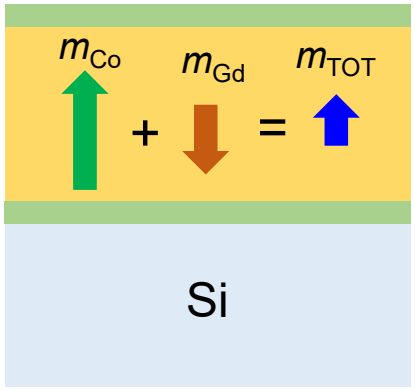
However, the temperature dependent magnetization dependence is not the same for Co and Gd. There is:

- A magnetic compensation point (T_M)
- An angular momentum compensation point (T_A)

*T_M and T_A may be different depending sublattice constituents of the alloy

II. Amorphous ferrimagnetic RE-TM alloys

Finding the compensation point in CoGd films



4 nm Pt

30 nm $Co_{78}Gd_{22}$

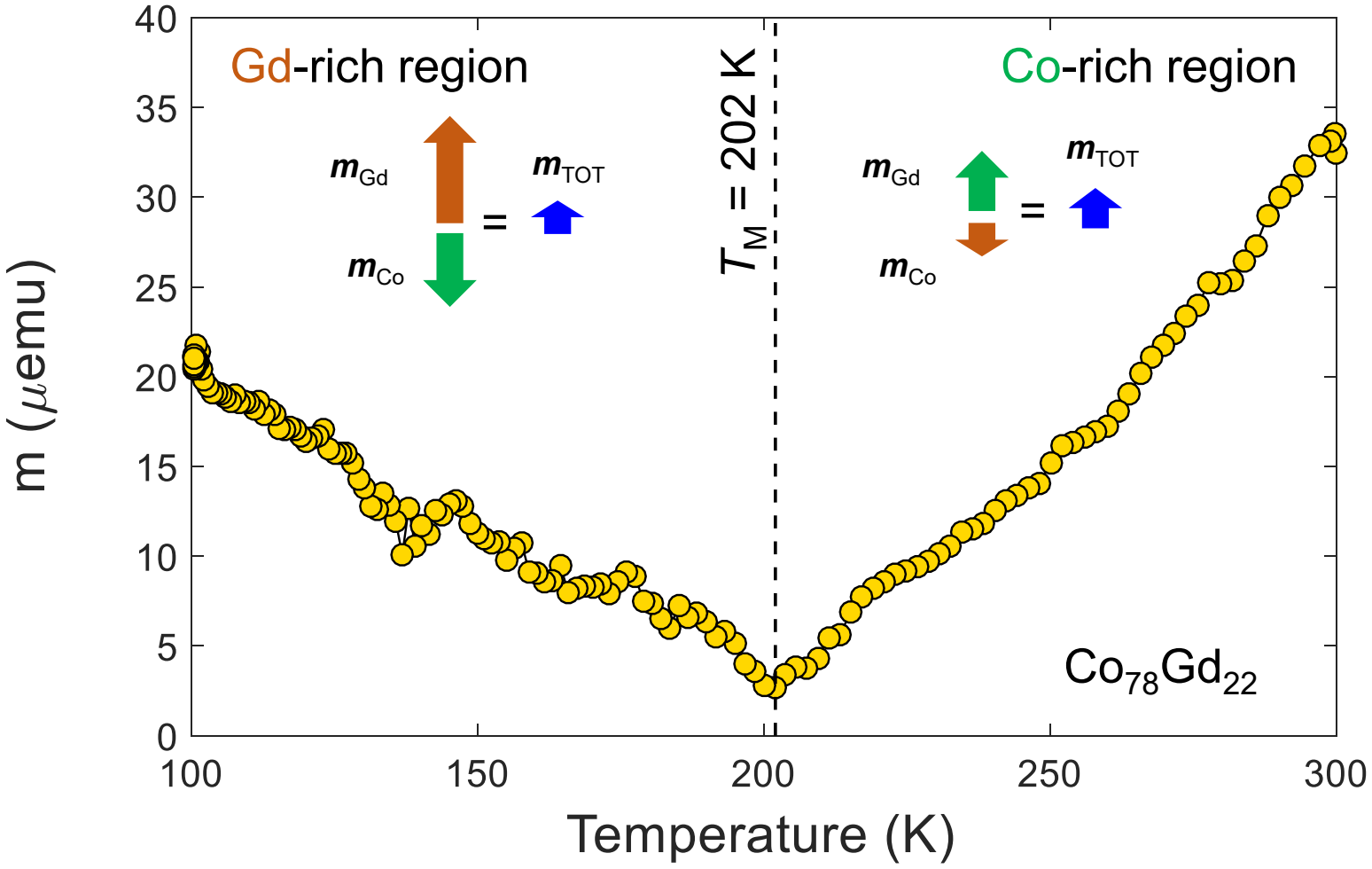
4 nm Pt

We need to find out....

- ❑ Do we have in-plane or out-of-plane anisotropy?
- ❑ Is there a compensation point in the range 50-300 K?

II. Amorphous ferrimagnetic RE-TM alloys

Finding the compensation point in CoGd films



m vs T @ 1.5 Tesla (out-of-plane) // corrected for diamagnetic contribution of the Si substrate

II. Amorphous ferrimagnetic RE-TM alloys

The m vs T curve can be fitted using a simple model*

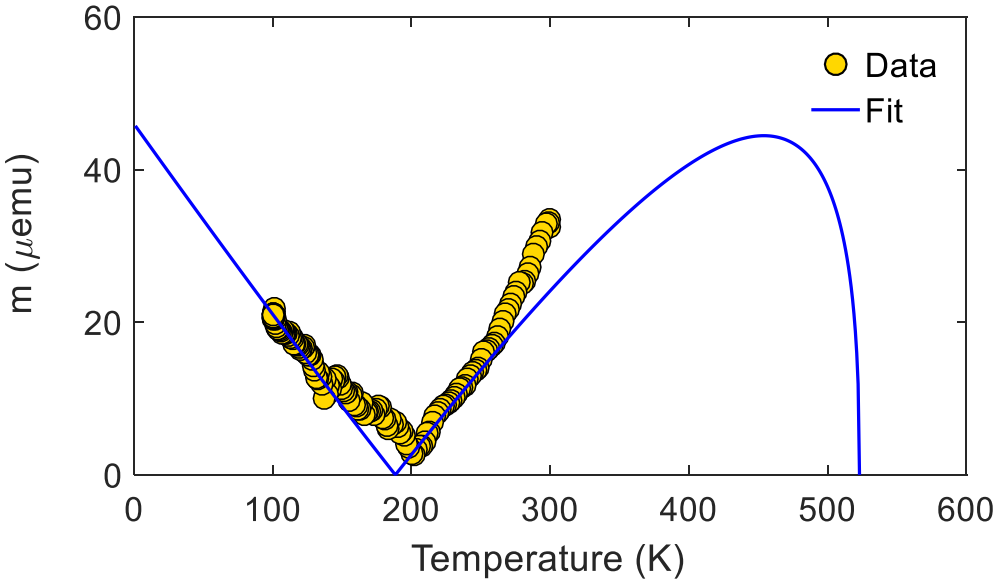
Sublattice magnetizations for Co, Gd (same T_C but different exponent β)

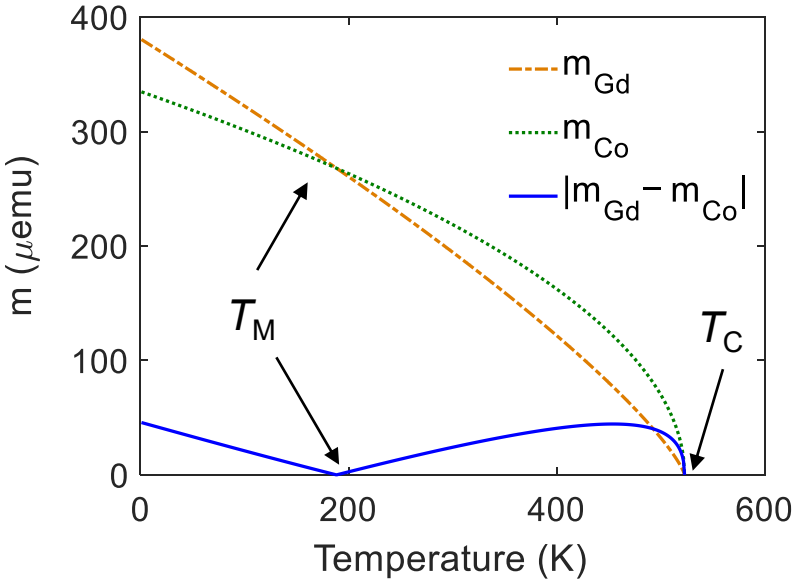
$$m_{Co} = A_{Co}\left(1 - \frac{T}{T_C}\right)^{\beta_{Co}}$$

$$m_{Gd} = A_{Gd}\left(1 - \frac{T}{T_C}\right)^{\beta_{Gd}}$$

Total magnetization

$$m(T) = |m_{Co} - m_{Gd}|$$





Here: T_C = 523 K, A_{Co} = 335 μemu, β_{Co} = 0.5, A_{Gd} = 381 μemu, β_{Gd} = 0.79

***Need to know T_C for obtaining reliable fit**
*In general, $\beta_{Co} < \beta_{Gd}$

(*) Kim et al., *Nat. Mater.* **16**, 1187 (2017) [supplementary, link]; Hirata et al., Phys. Rev. B **97**, 220403(R) (2018) [link]; Caretta et al., *Nat. Nanotechnol.* **13**, 1154 (2018) [supplementary, link]

Watch out the units!

Quantity	Gaussian & cgs	SI	Conversion
Magnetic flux density *B*	gauss (G)	Tesla (T)	1 G = 10^{-4} T
Magnetic field strength *H*	oersted (Oe)	A/m	1 Oe = $10^3/4\pi$ A/m
Magnetic moment *m*	emu, erg/G	A·m^2, J/T	1 emu = 10^{-3} A·m^2
Magnetization *M* (magnetic moment per unit volume)	emu, erg/G	A/m	1 emu = 10^3 A/m
Mass magnetization (magnetic moment per unit mass)	emu/g	A·m^2/kg	1 emu/g =1 A·m^2/kg

Find out more at:
http://www.ieeemagnetics.org/images/stories/magnetic_units.pdf
https://www.nist.gov/sites/default/files/documents/pml/electromagnetics/magnetics/magnetic_units.pdf

Magnetic unit converter:
http://www.magpar.net/static/magpar/doc/html/magconv.html

Low magnetic moments and spurious signals

is HfO_2 ferromagnetic or not? (D. W. Abraham et al., Appl. Phys. Lett. 87, 252502 (2005) [link])

APPLIED PHYSICS LETTERS **87**, 252502 (2005)

Absence of magnetism in hafnium oxide films

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We establish the limits of magnetism in thin, electronic grade, hafnium oxide, and hafnium silicate films deposited onto silicon wafers by chemical vapor deposition and atomic layer deposition. To the limits of sensitivity of our measurement techniques, no ferromagnetism occurs in these samples. Contamination by handling with stainless-steel tweezers leads to a measurable magnetic signal. The magnetic properties of this contamination are similar to those attributed to ferromagnetic HfO_2 in a recent report, including the magnitude of moment, magnetization field dependence, and spatial asymmetry. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2146057]

Si wafer!

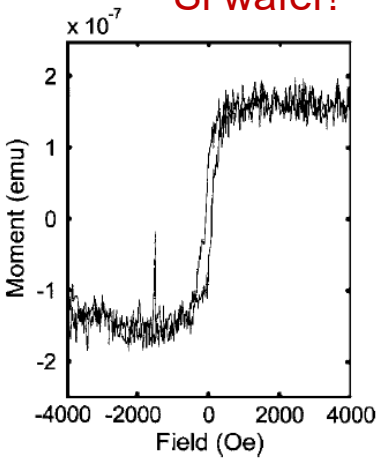

FIG. 4. Moment measured from silicon wafer after contamination by stainless-steel tweezers. Data were corrected for diamagnetic background.

*See also:

A. Ney et al., J. Magn. Magn. Mater. 320, 3341 (2008) [link]

"…**hysteresis** measurements are only a **necessary but not a sufficient** criterion to prove the **existence of ferromagnetism** if the size of the **signal is small**"

"...signals below 4×10^{-7} emu about are clearly in the range of possible artifacts and claims of ferromagnetism become questionable if no complementary techniques are used…"