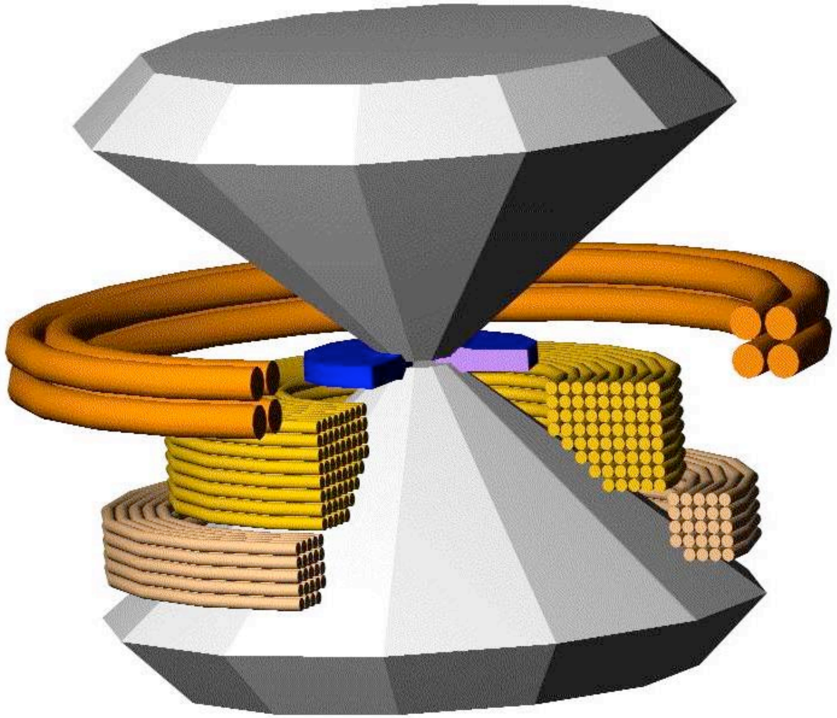

# Magnetism under high pressure

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**Ludwig Maximilians Universität Munich**

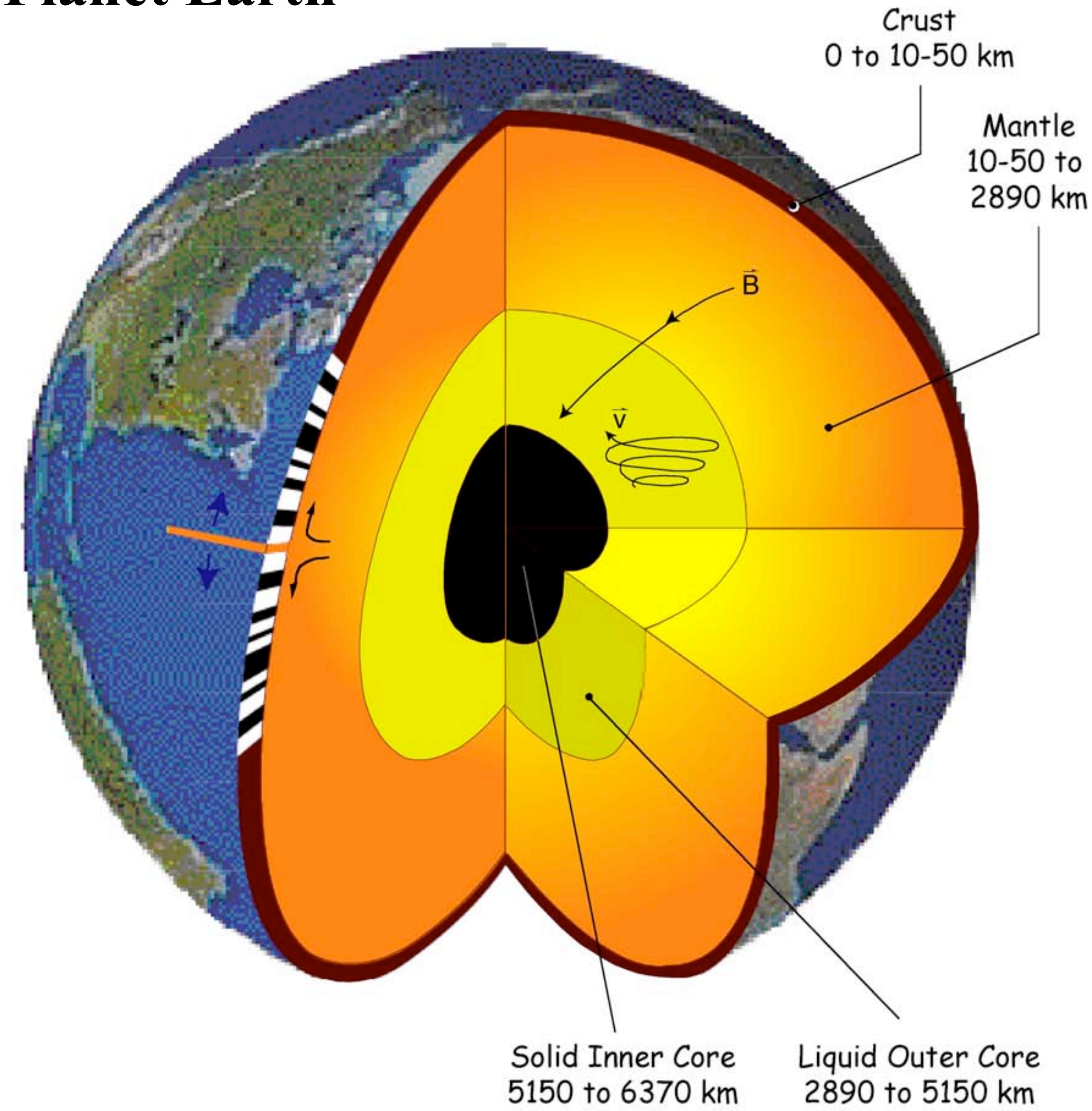
**04.04.2014**

Special thanks to:

Prof. Andrzej Kozlowski
and
Prof. Zbigniew Kakol

AGH
FACULTY OF PHYSICS AND APPLIED COMPUTER SCIENCE

# Role of Pressure and Temperature on Magnetization: Planet Earth




- *How does pressure influence magnetic anomalies?*
  *titanomagnetite*
- *Can we estimate pressure due to exhumation or shock?*
  *Verwey transition in magnetite*
  *Pyrrhotite inclusions in diamond*
- *Influence of the inner core on the geometry and stability of the magnetic field?*
  *iron*

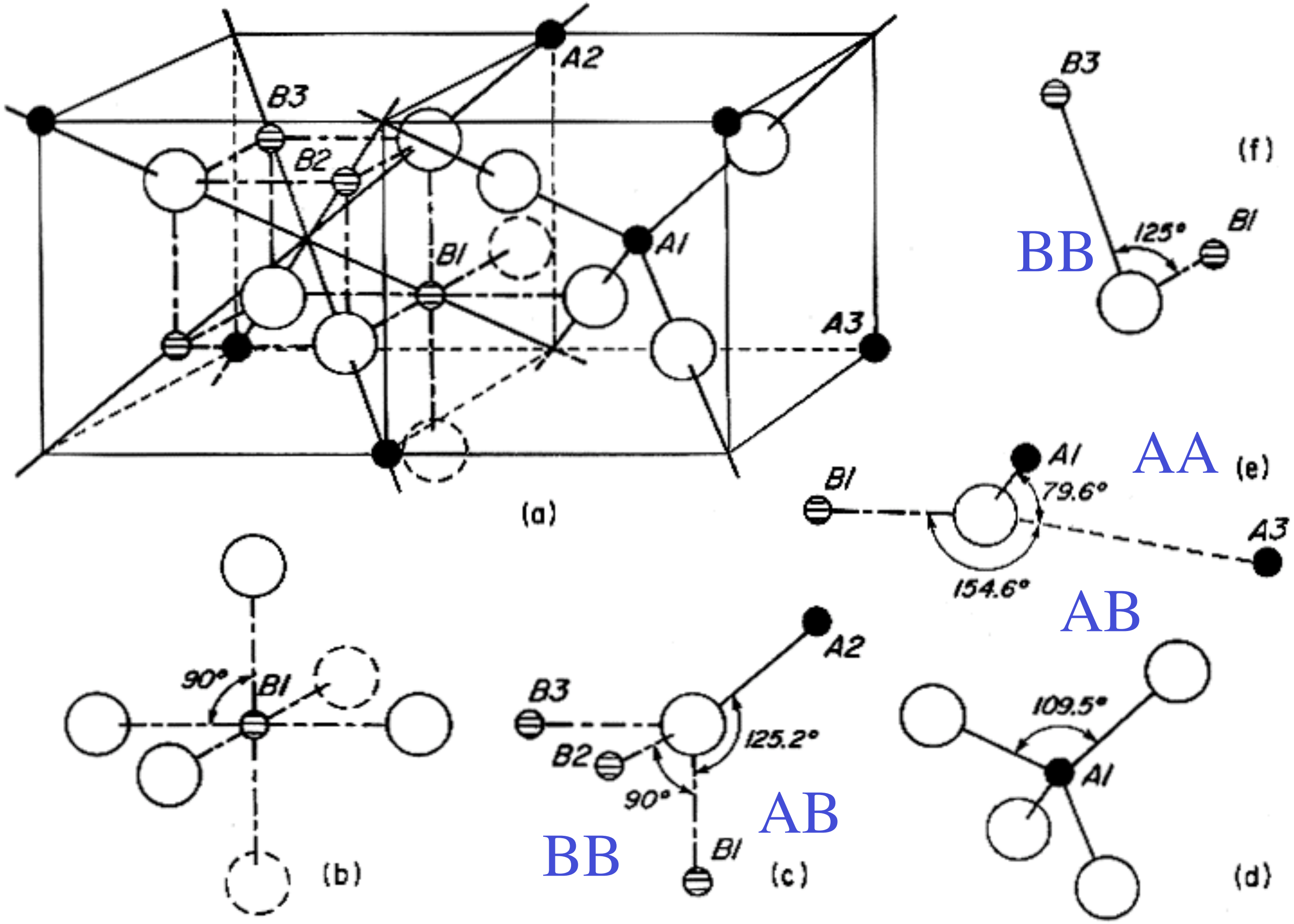



**Figure 3.4** (a) Sketch of $\frac{1}{4}$ of a unit cell of magnetite. The lattice parameter is *a*. Solid and hatched circles represent cations in tetrahedral (A-site) and octahedral (B-site) coordination, respectively, with $O^{2-}$ ions (large open circles). (b)–(f) Bond angles for specific cation pairs in (a). Bond angles near 90° are unfavourable for superexchange coupling. [After Gorter (1954), with the permission of the publisher, Philips Research, Eindhoven, The Netherlands.]

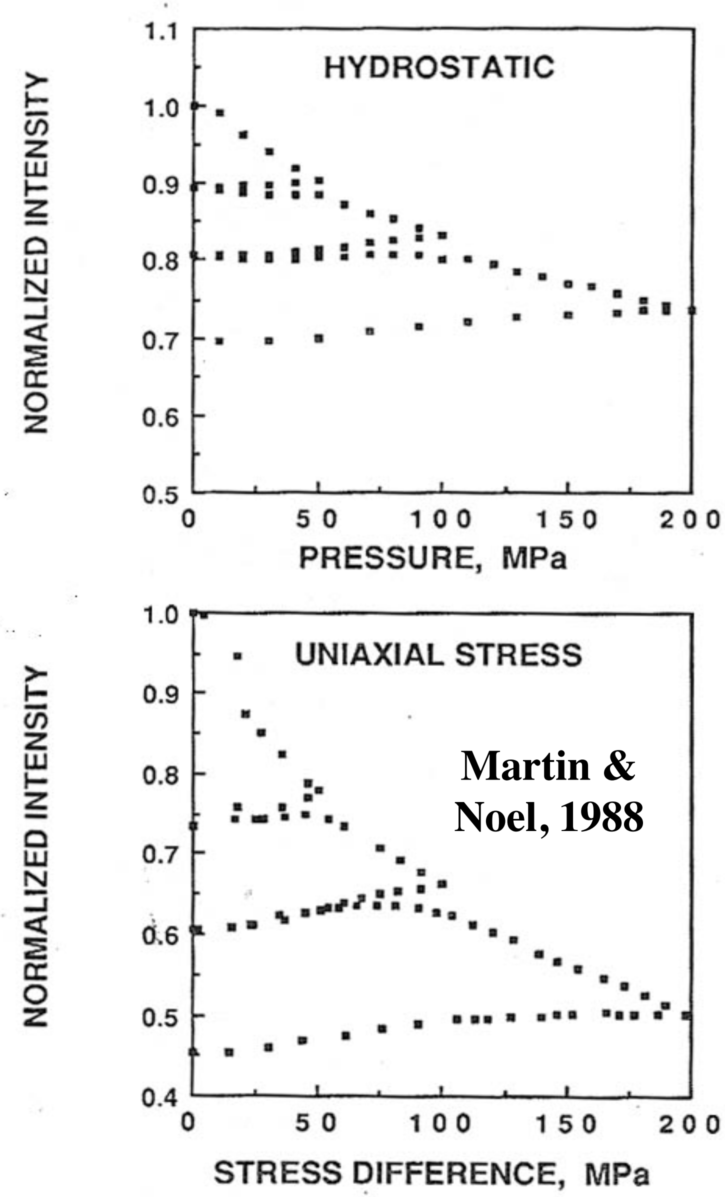
Dunlop and Özdemir (1997)

**The interactions of electrons between Fe-Fe give magnetite its remanence.**

**However, this interaction is indirect, passing through oxygen atoms.**

**Magnetite possesses three magnetic lattices which govern its magnetic characteristics.**

# Magnetism is very sensitive to the type and direction of applied stress




Martin & Noel, 1988

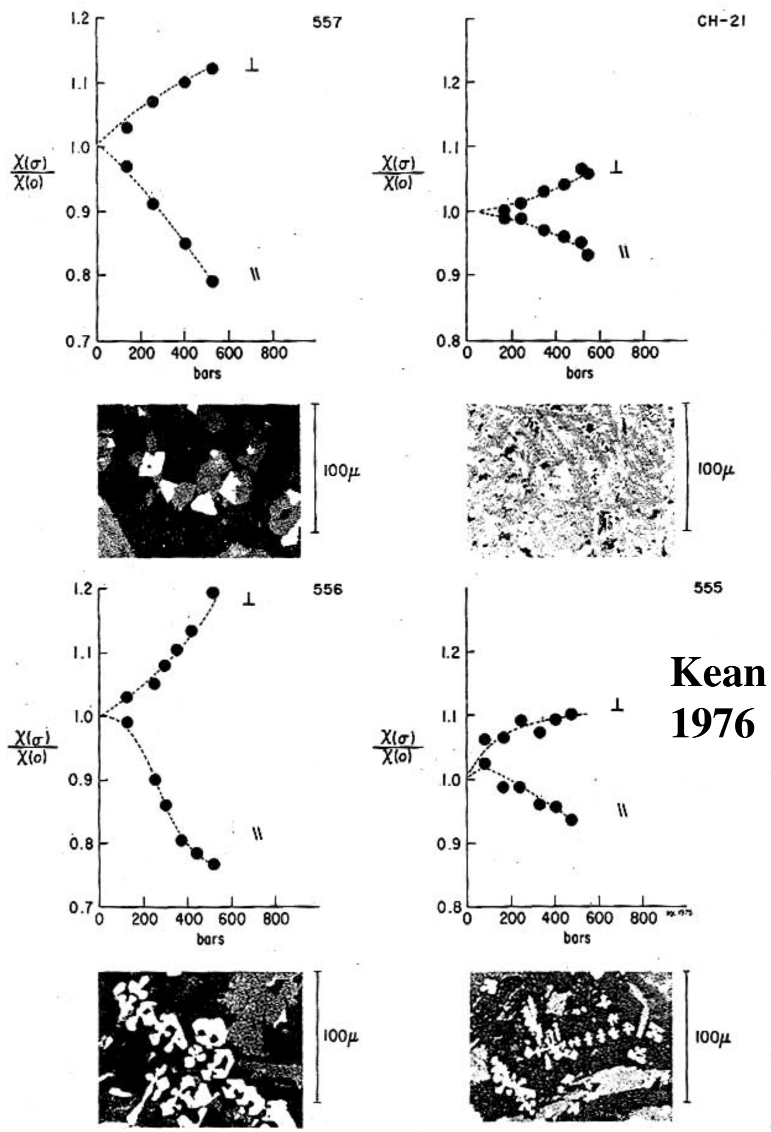
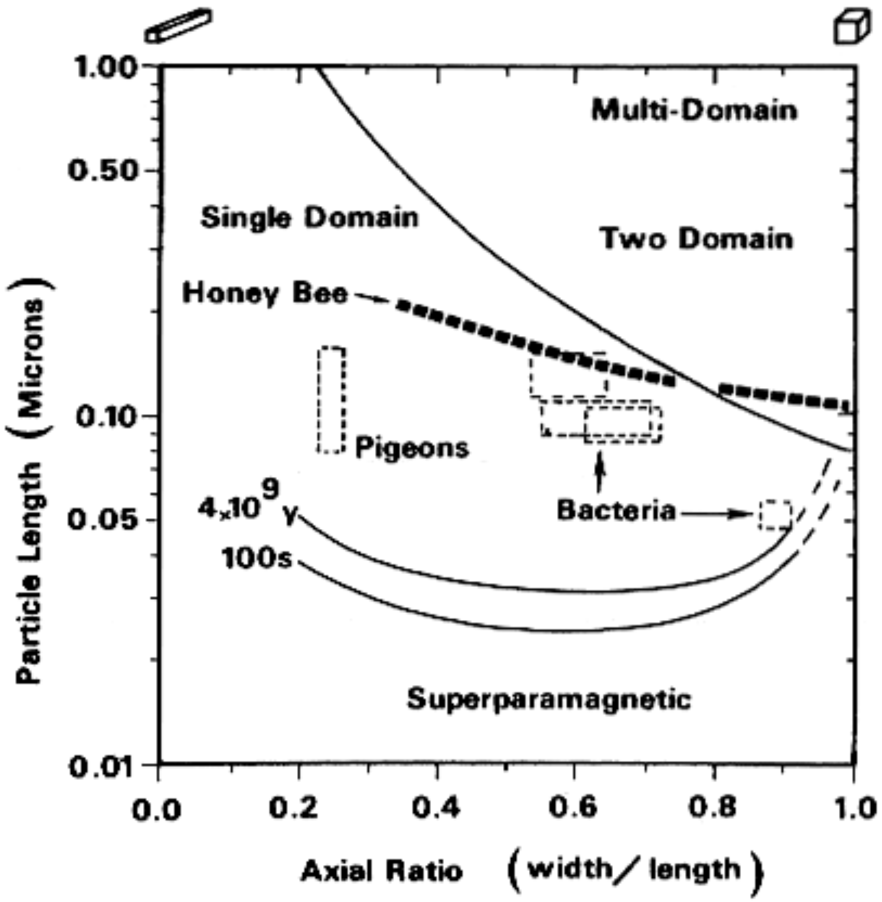
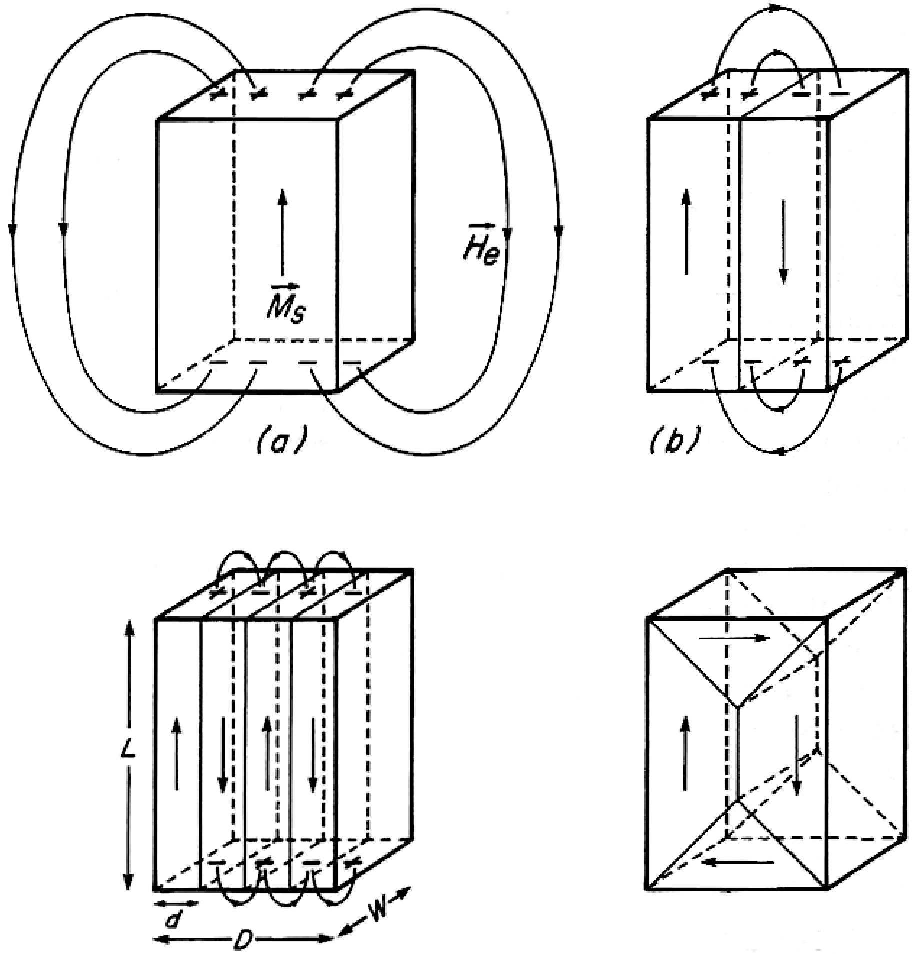



Fig. 3. Changes in susceptibility with stress for samples

Kean et al., 1976

# MAGNETITE



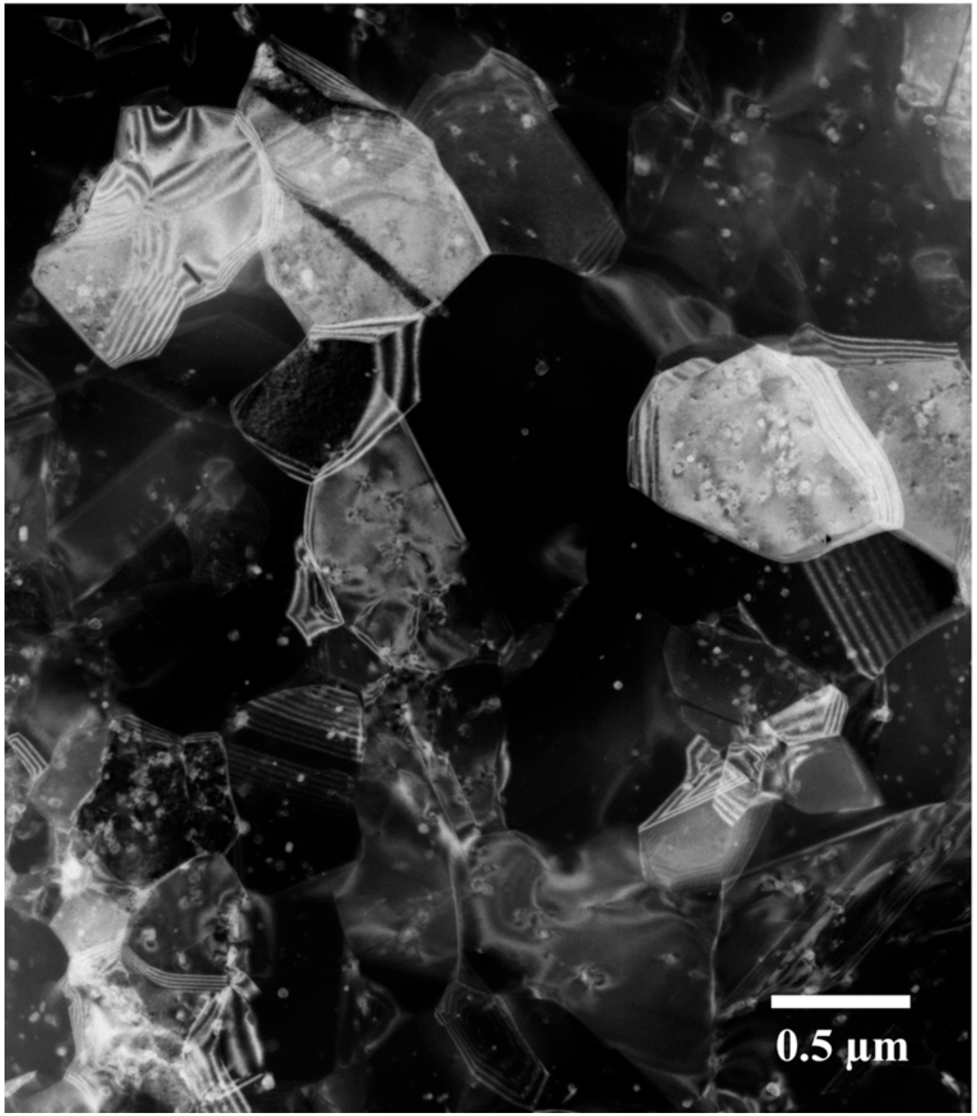

Magnetic properties are size and shape dependent

Superparamagnetic vs. Single domain vs. Multi-domain

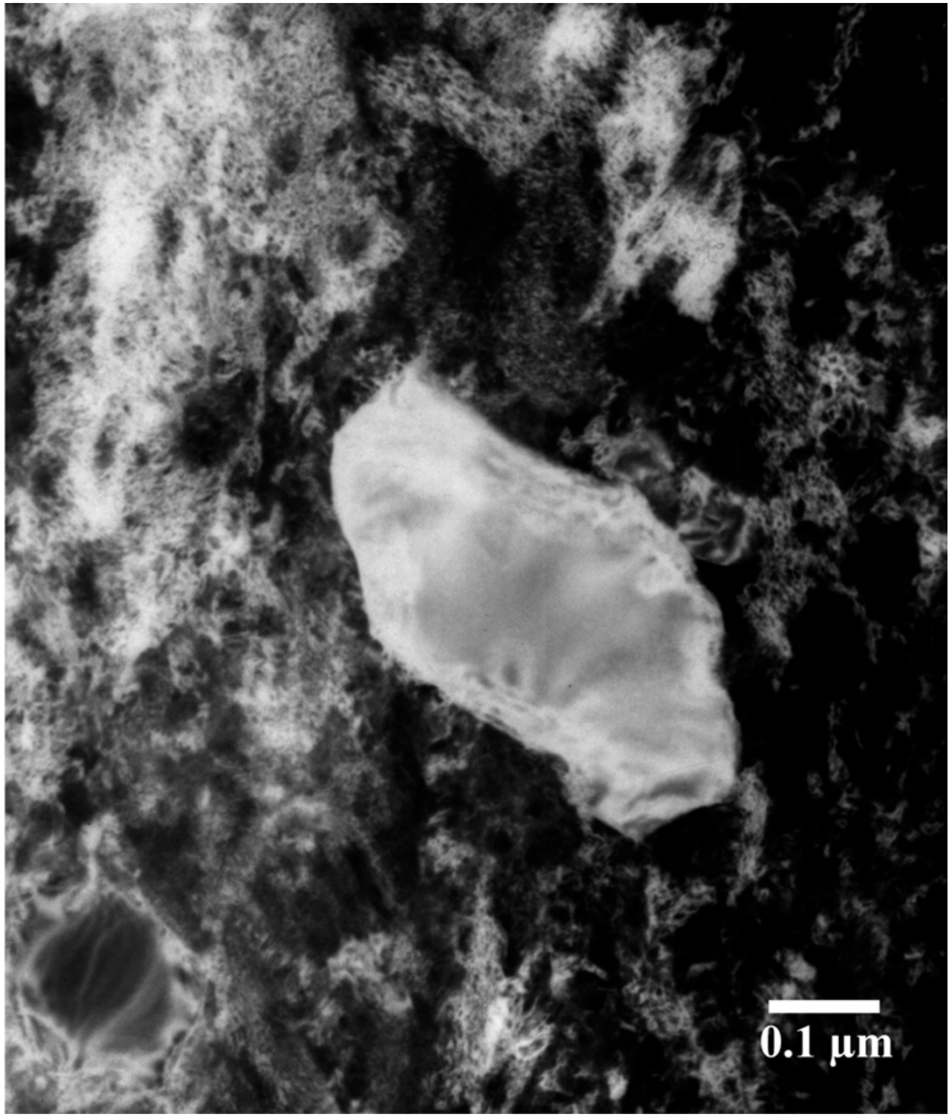
# TEM images of iron foil

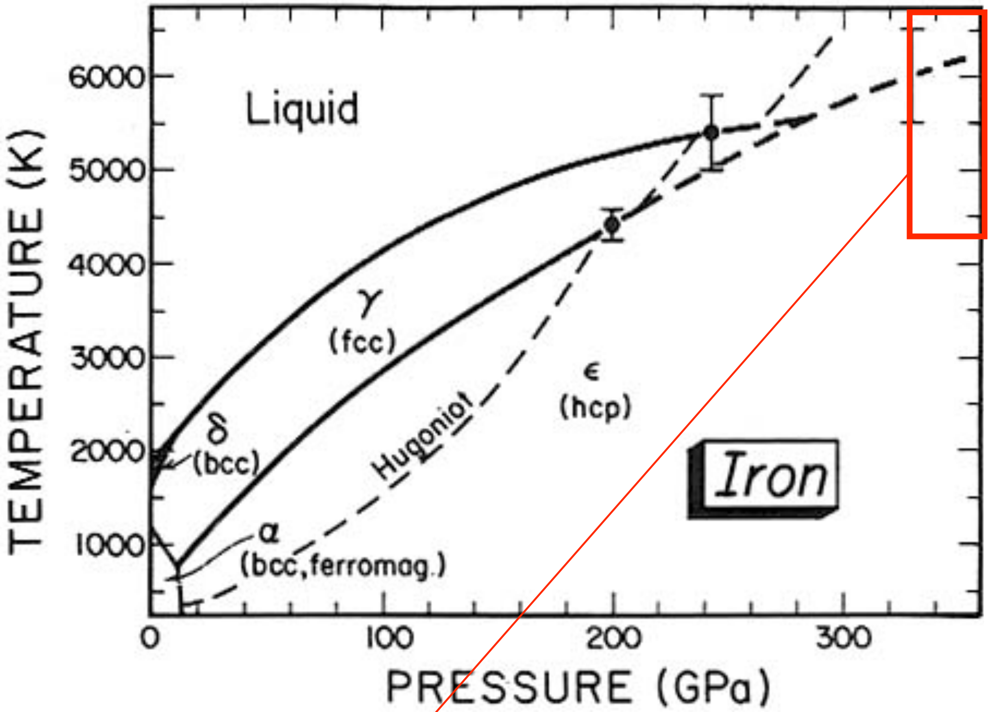
## bcc to hcp: a Martensitic phase transition

Non-compressed




Decompressed from 30 GPa






**The inner core probably consists of Fe in a hexagonal closed packed (hcp) phase.**

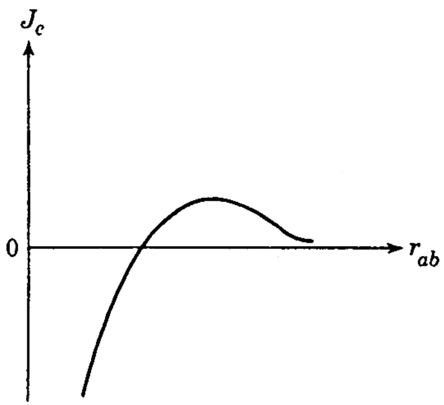



**Fig. 19-5.** Schematic representation of the behavior of the exchange integral as function of interatomic distance.



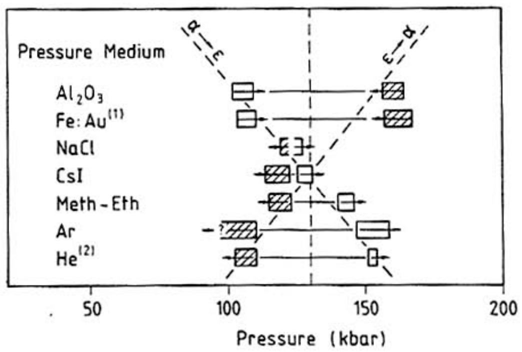



**Figure 4** Pressures of the onset of the $\alpha \rightarrow \varepsilon$ (open bars) and $\varepsilon \rightarrow \alpha$ transitions (filled bars) in different pressure media. The bars represents the uncertainty in pressure. (1) Huang *et al.*[10], (2) Zou *et al.*[11]

von Bargen and Boehler (1990)

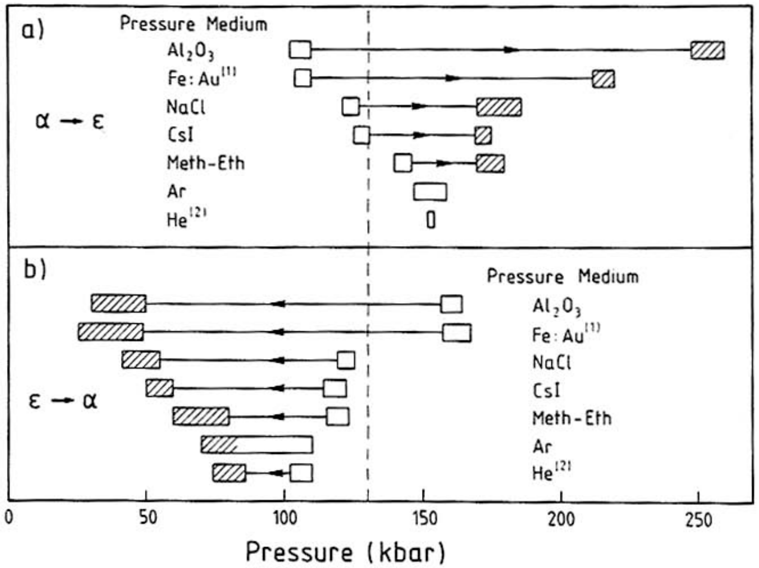
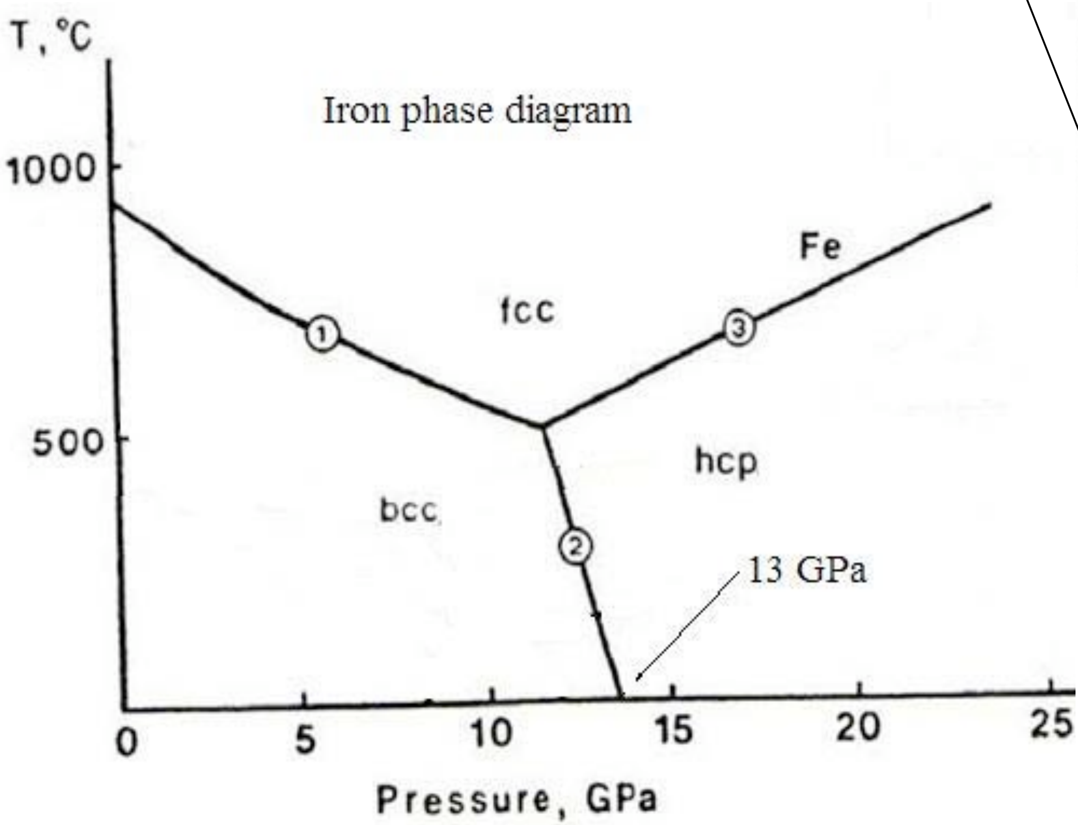


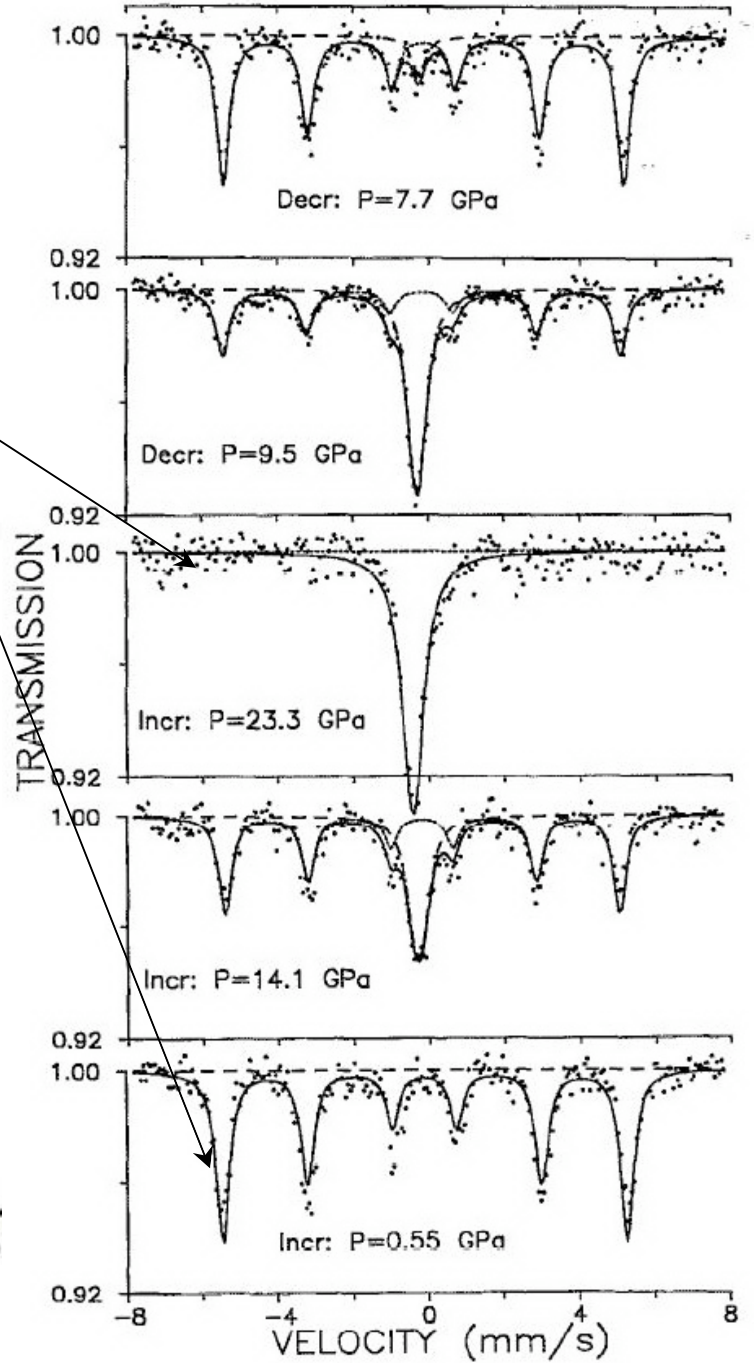

**Figure 5** Pressure ranges (solid lines) between the onset (open bars) and completion (filled bars) of (a) the $\alpha \rightarrow \varepsilon$ transition, (b) the $\varepsilon \rightarrow \alpha$ transition. The bars represent uncertainties in pressure. (1) Huang *et al.*[10], (2) Zou *et al.*[11]

# Magnetism of iron- prior work

Ferromagnetic Mössbauer spectra collapse to paramagnetic at high pressure

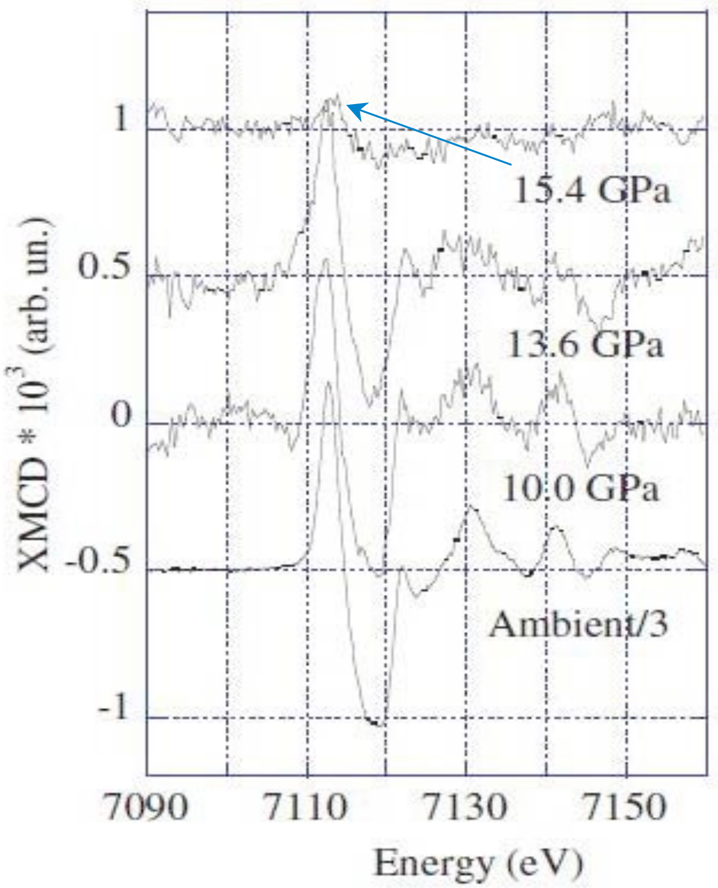



*Pure iron phase diagram*

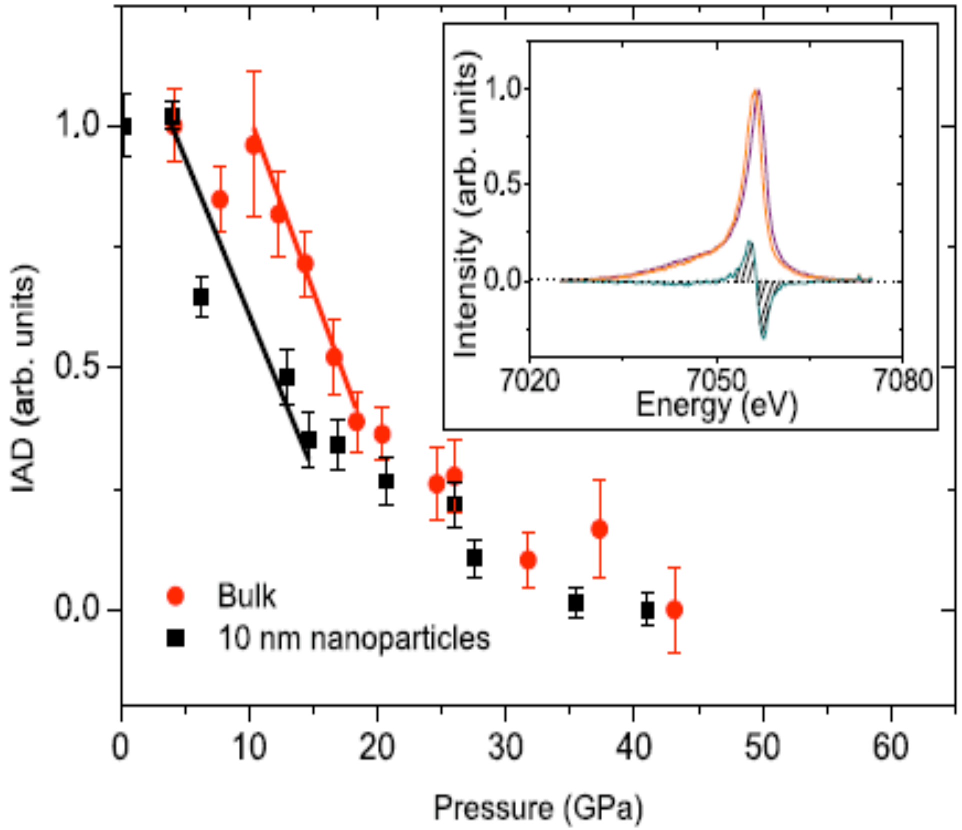



*Taylor et al., 1991*

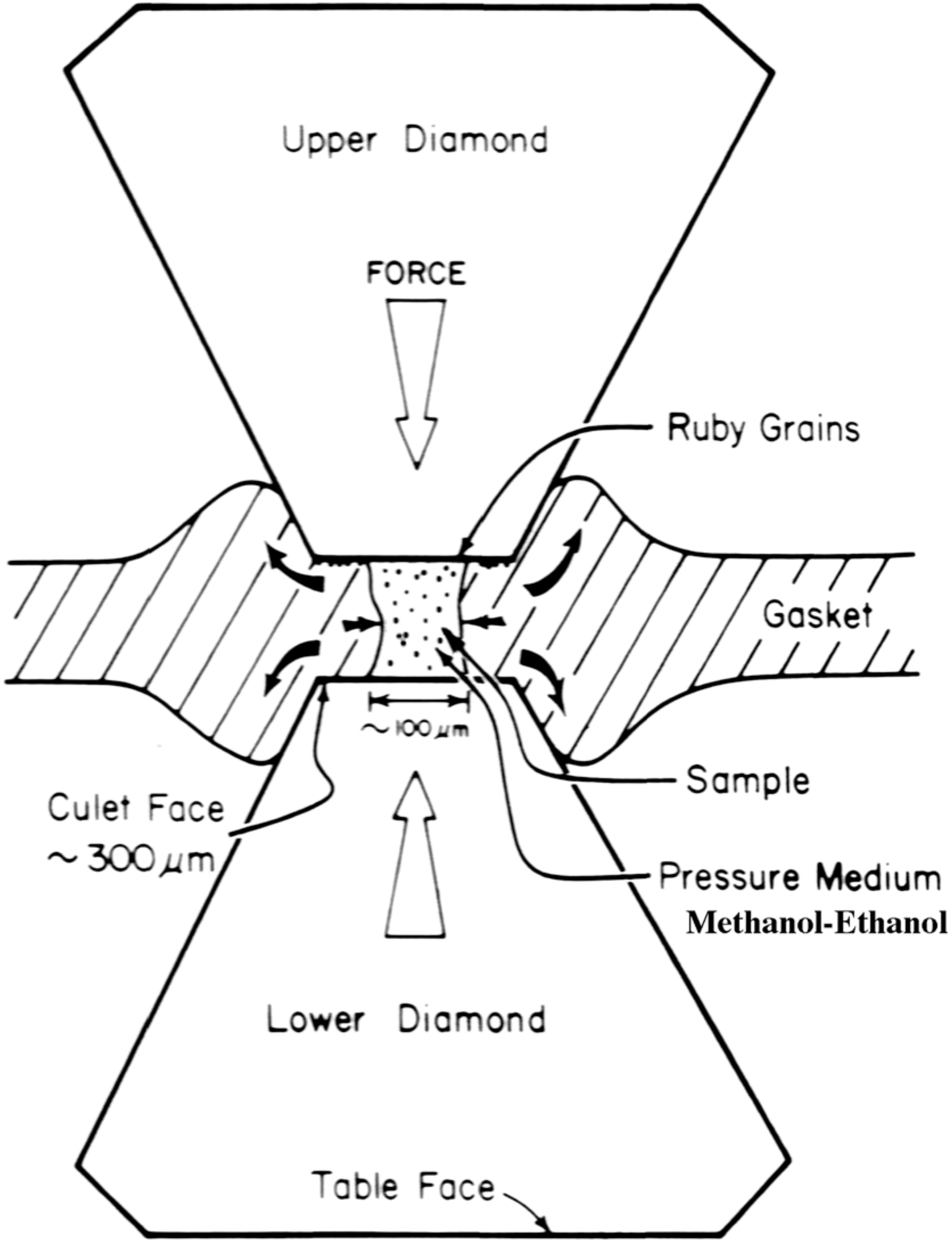
X-ray magnetic circular dichroism (*XMCD*) shows *hcp-Fe* is *non-magnetic* at ~ *16 GPa*
X-ray emission spectroscopy shows *hcp-Fe* is *magnetic* up to *40 GPa*



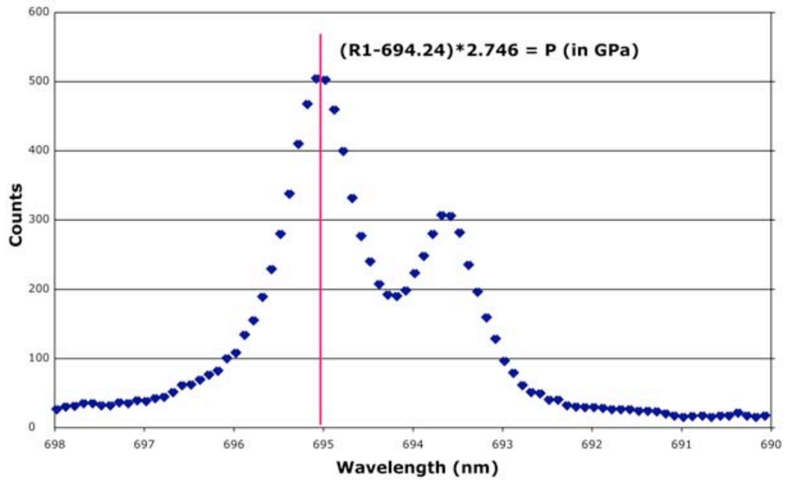

*X-ray magnetic circular dichroism (XMCD) of iron under pressure (Baudelet et al., 2005)*

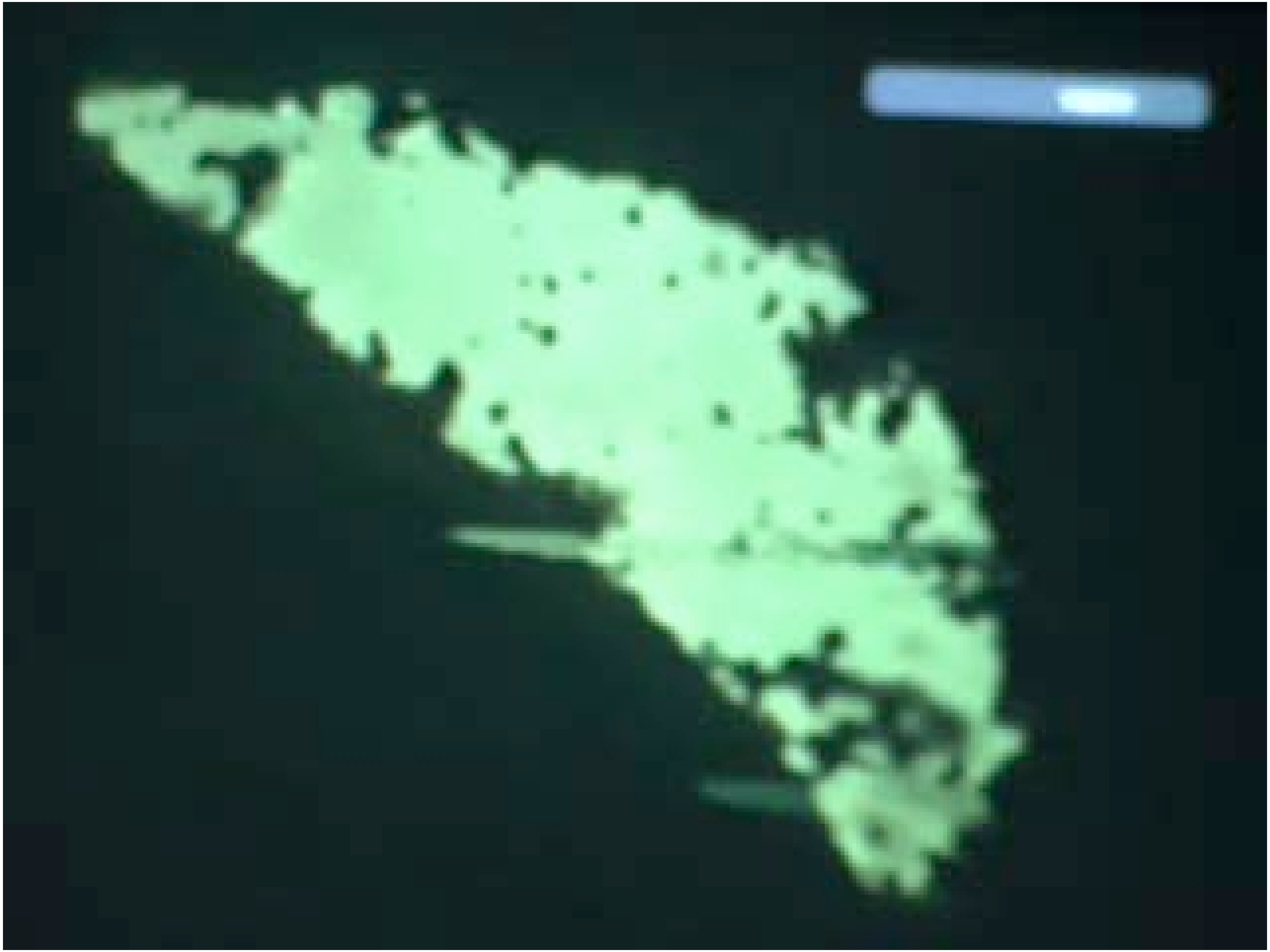



*X-ray emission vs pressure of iron at 300 K (Monza et al., 2011)*

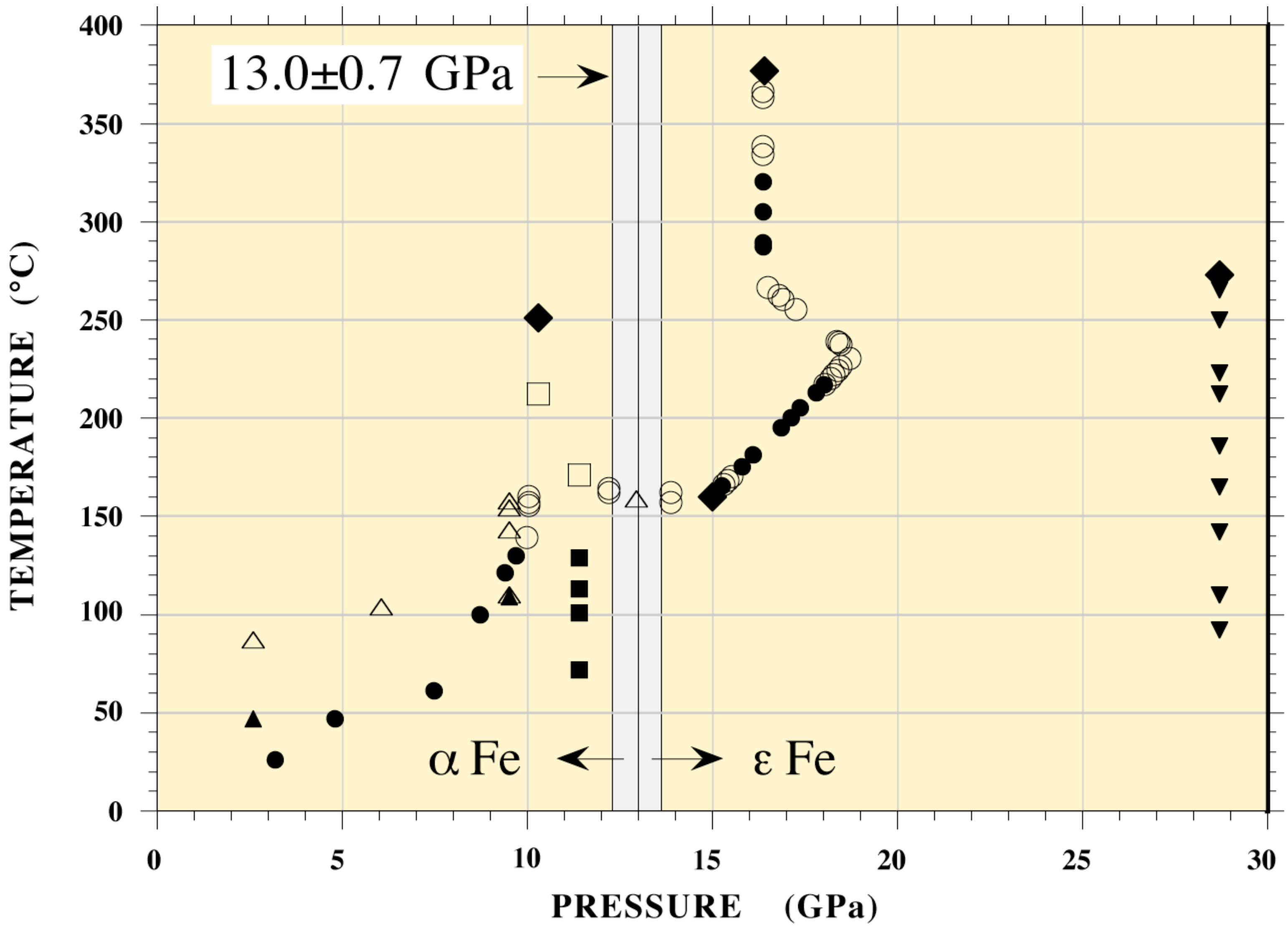



Spherical iron (>99.9%) particles with diameters of 1 to 5 μm were loaded together with ruby and a pressure medium into a ~100 μm sized hole formed in a Re gasket. Resistive heaters (not shown) surround the diamonds. The transparent pressure medium allows the iron particles to be imaged with a microscope.





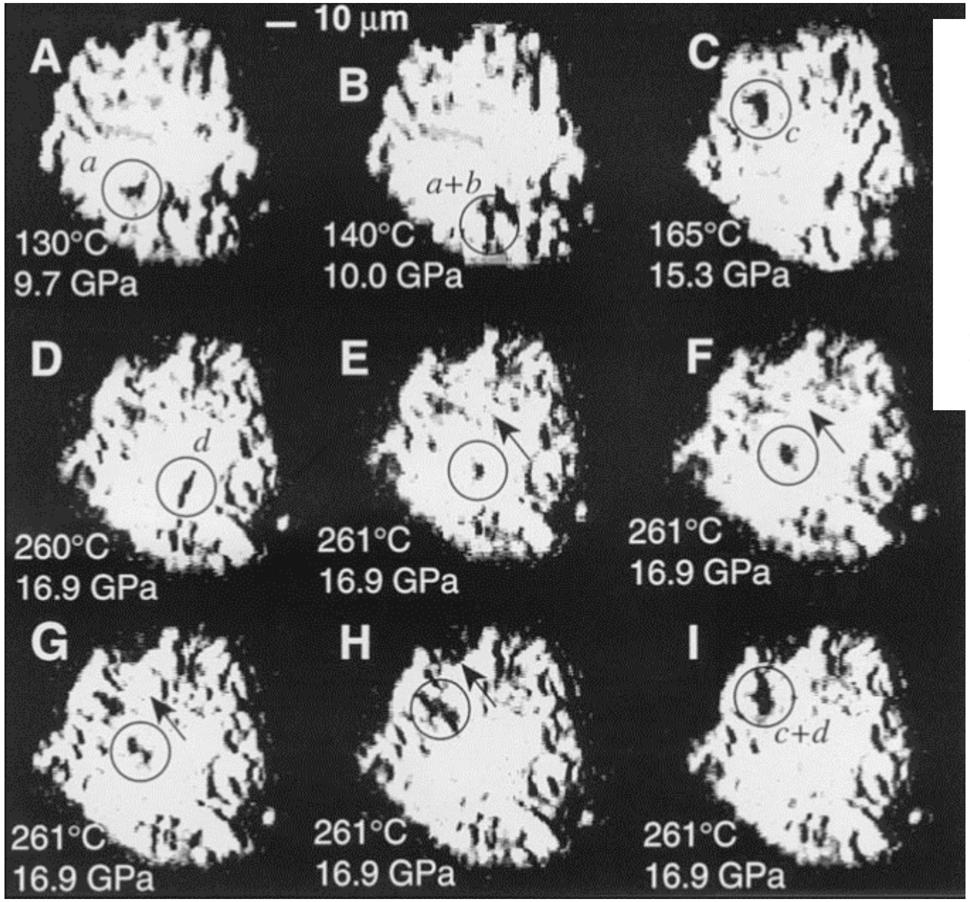
# Movement of iron induced by a magnet

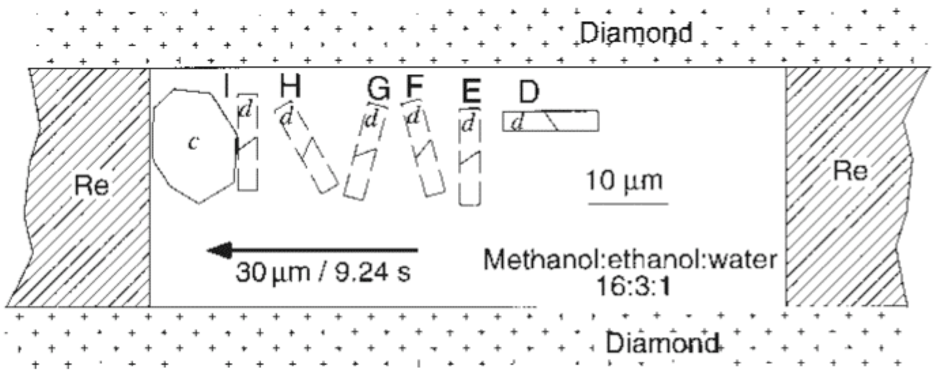



Open symbols = movement  Closed symbols = no movement

Diamonds = failure

Gilder and Glen (Science, 1998)

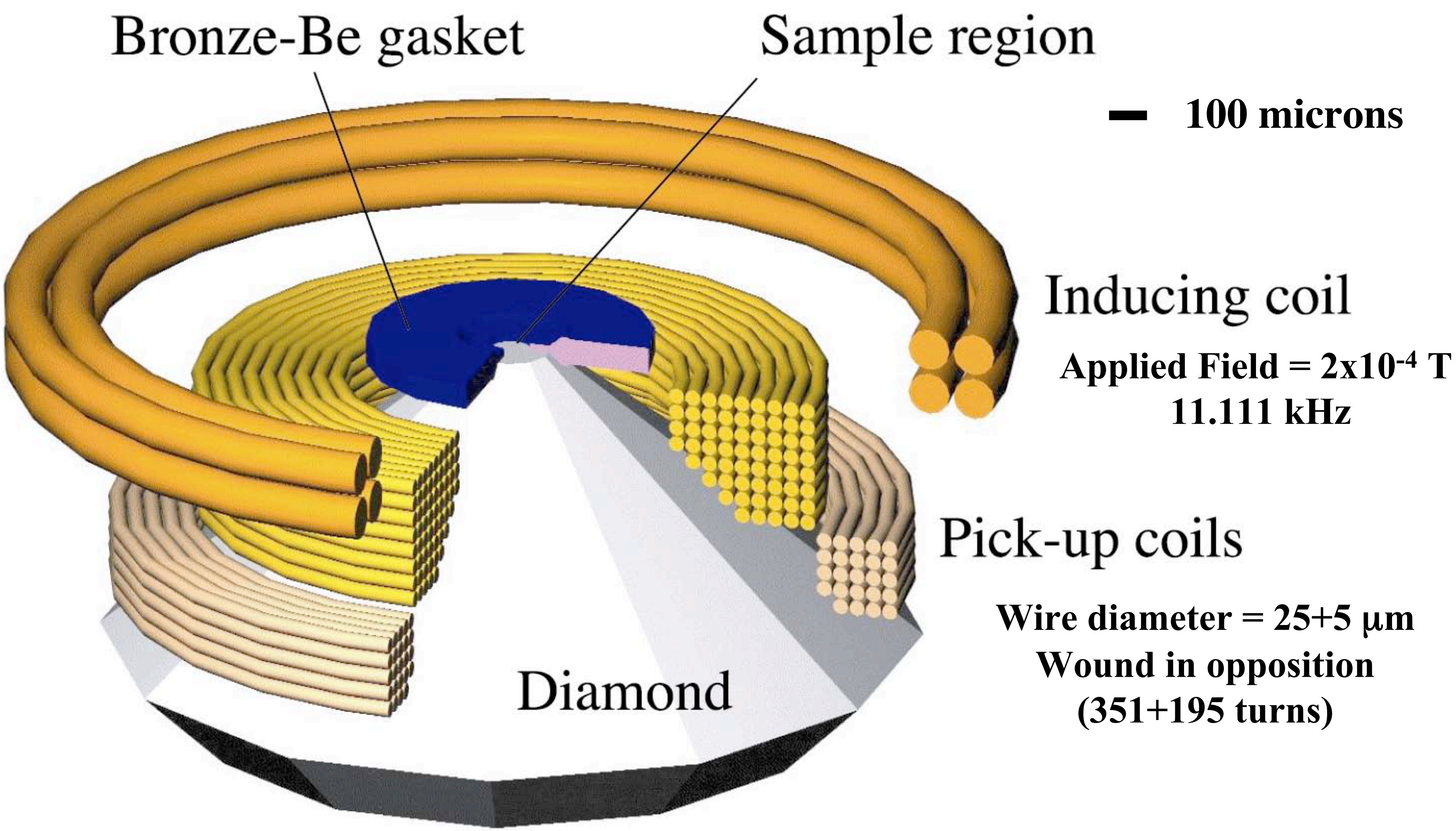



At 17 GPa and 260°C, we observed movement that allowed us to establish an equation of force couples between the magnetic attraction in one sense and viscosity in the opposite sense.

Two possibilities can explain the motion :

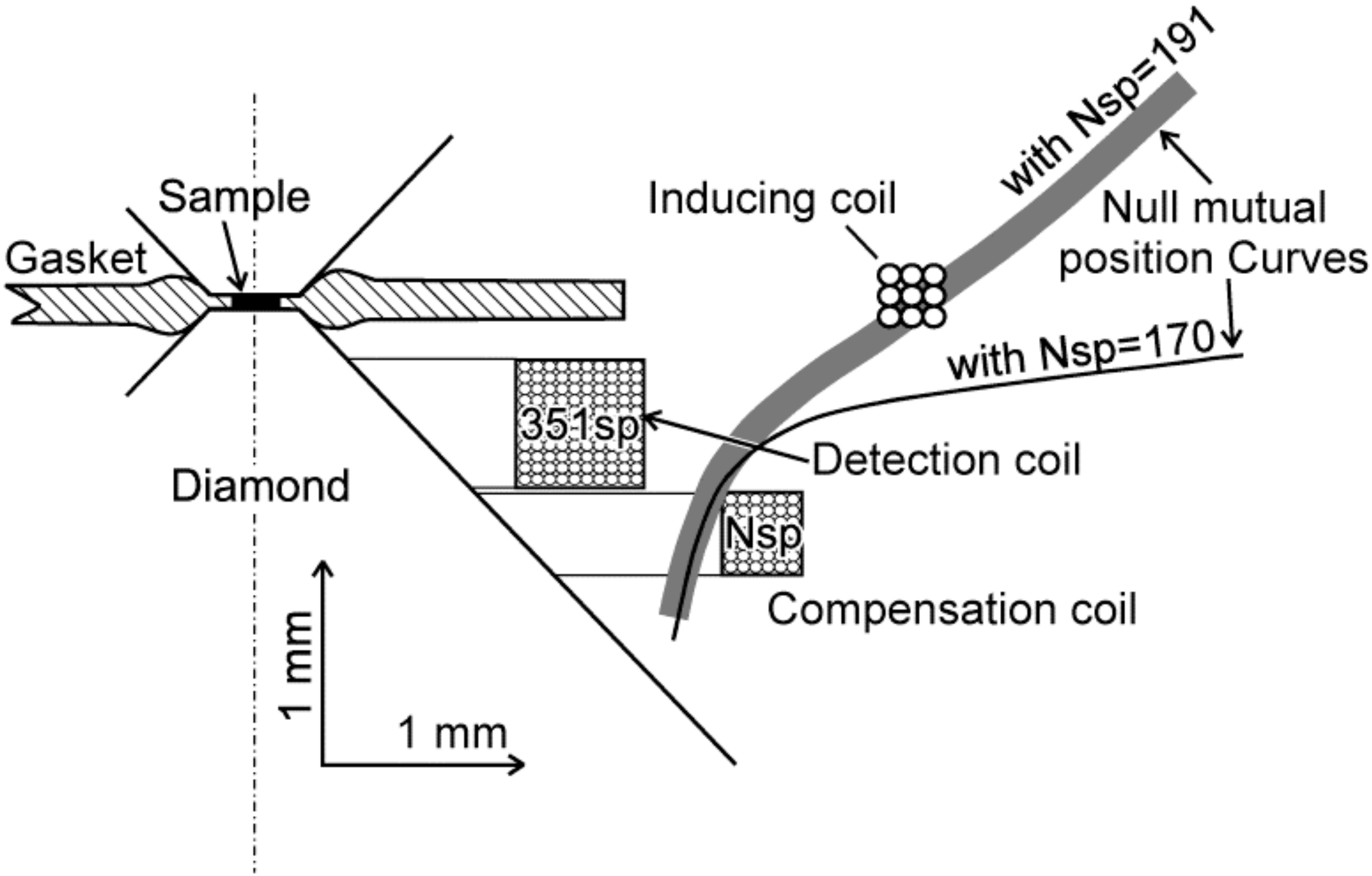
- Either hcp Fe is ferromagnetic.
- Or hcp Fe is paramagnetic with a very high bulk susceptibility with high crystalline anisotropy.

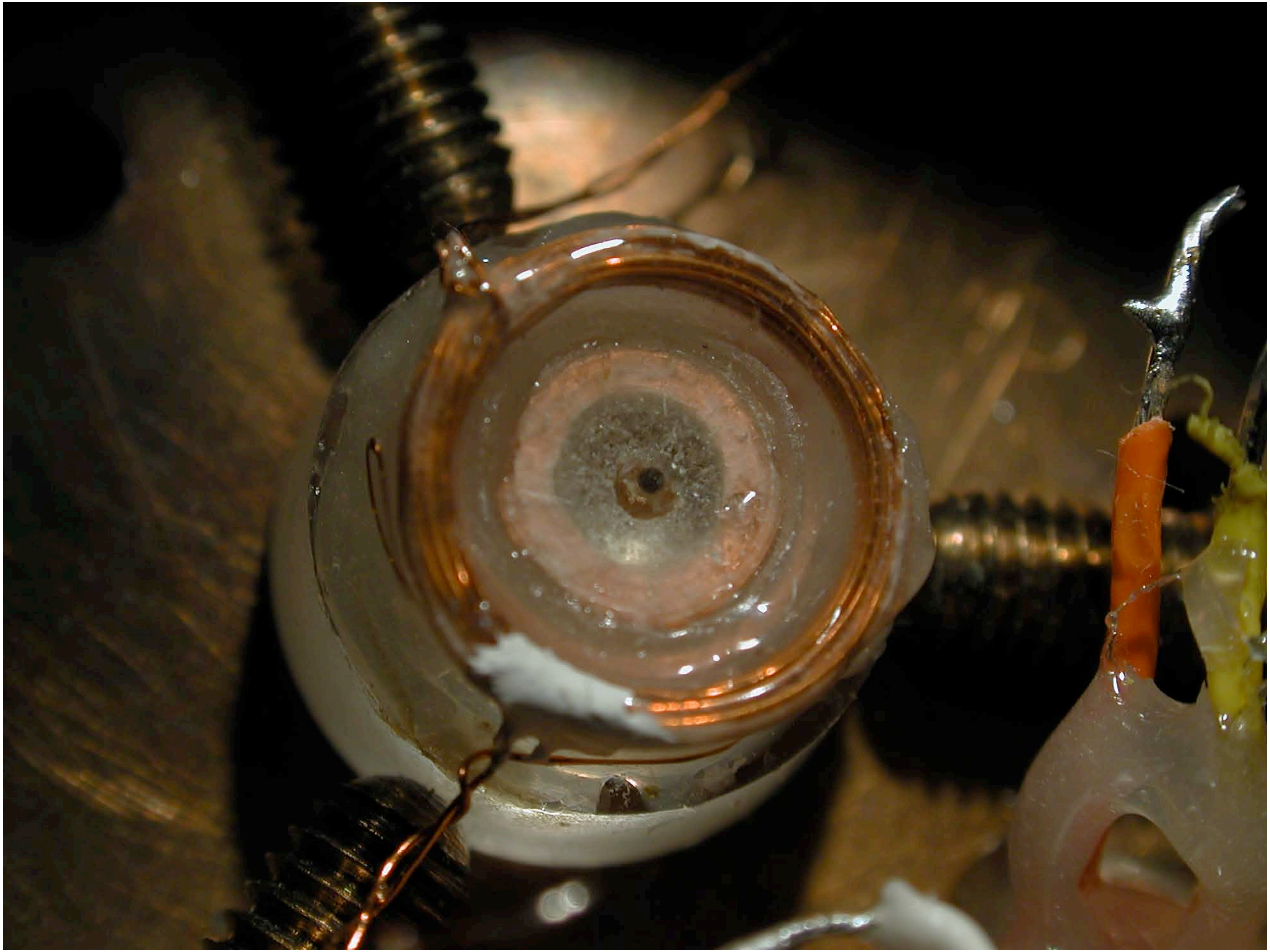



**When a sample is placed in the measure region, it induces :**

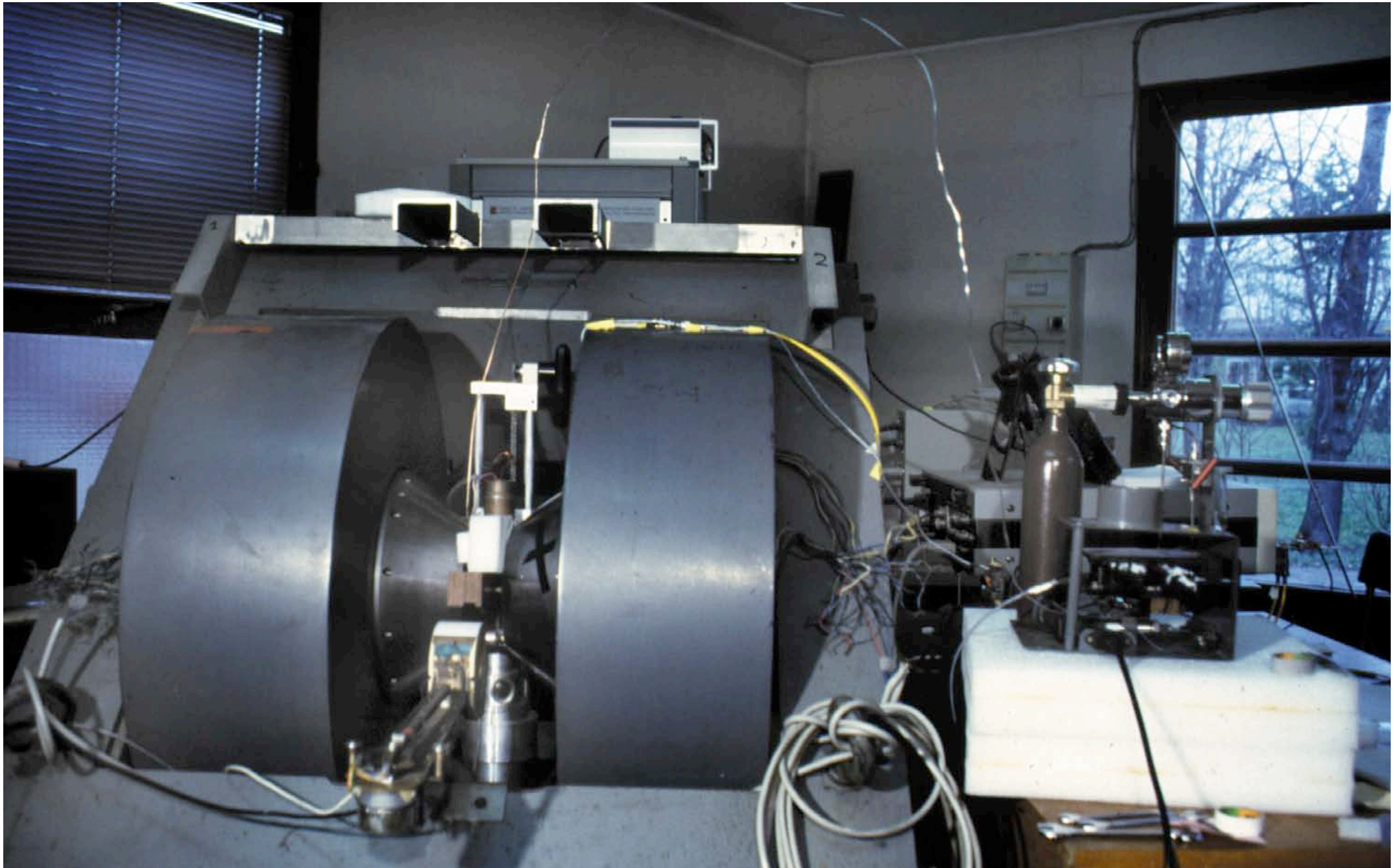
- **An in-phase alternating current proportional to its susceptibility.**
- **A quadrature voltage that depends on its electrical conductivity and on its magnetic viscosity.**

Studies on superconductivity detect changes on the order of millivolts. For our experiments, we needed to measure variations of micro- and nanovolts, so we had to significantly increase the number of windings.



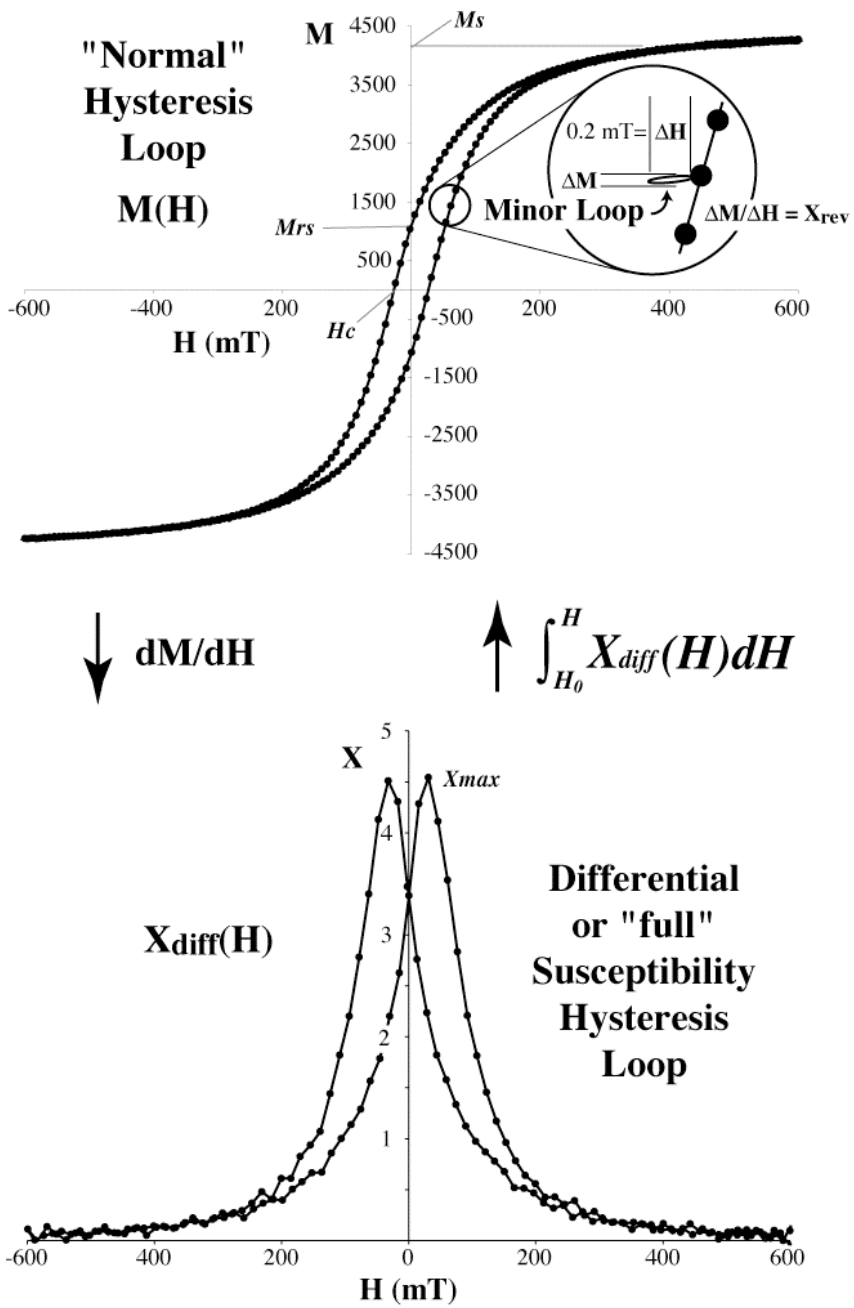


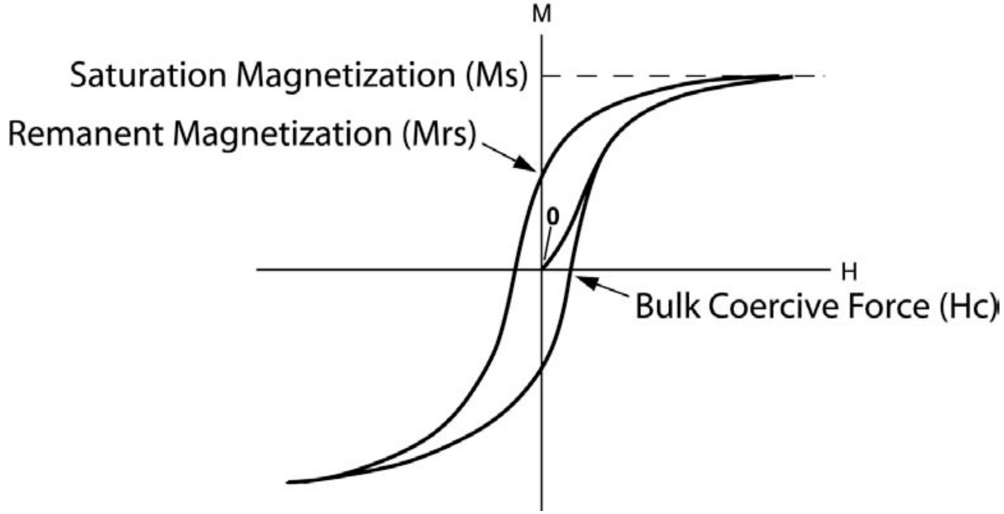
# BeCu Diamond Anvil Cell



**Electromagnet : maximum field = 1.4 T**

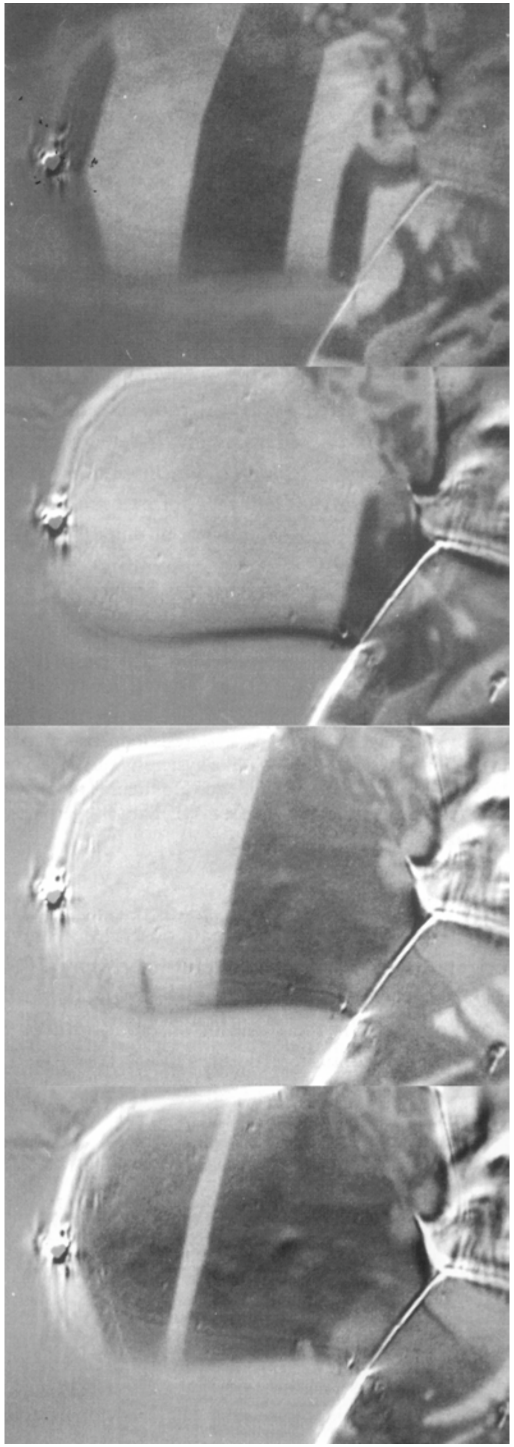
# Magnetic Hysteresis Loops

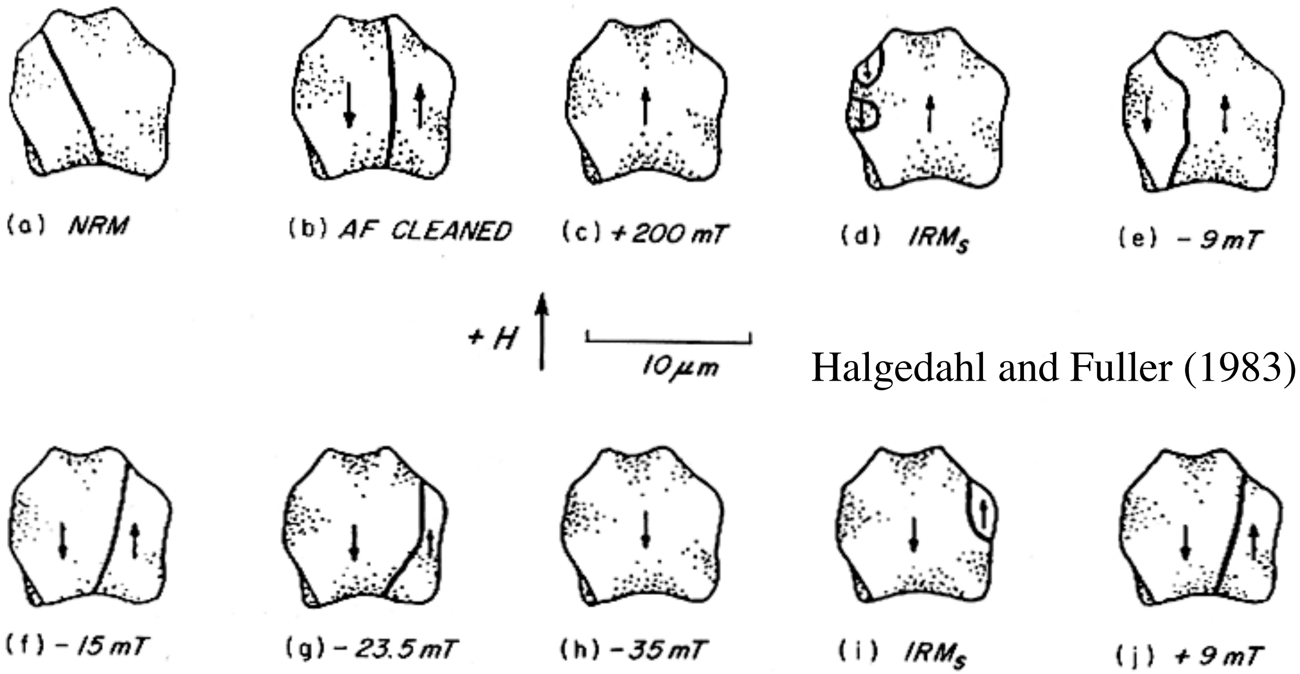



Strong magnets have high Mrs/Ms and high Hc

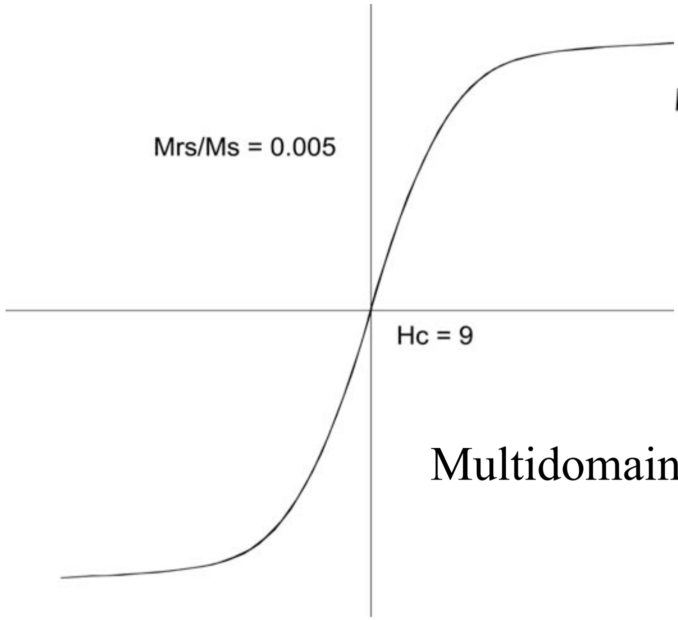
$$X_{diff} = X_{rev} + X_{irr}$$



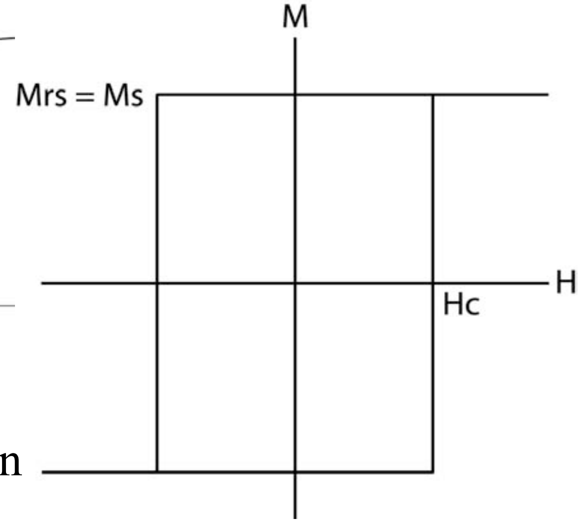



Halgedahl and Fuller (1983)

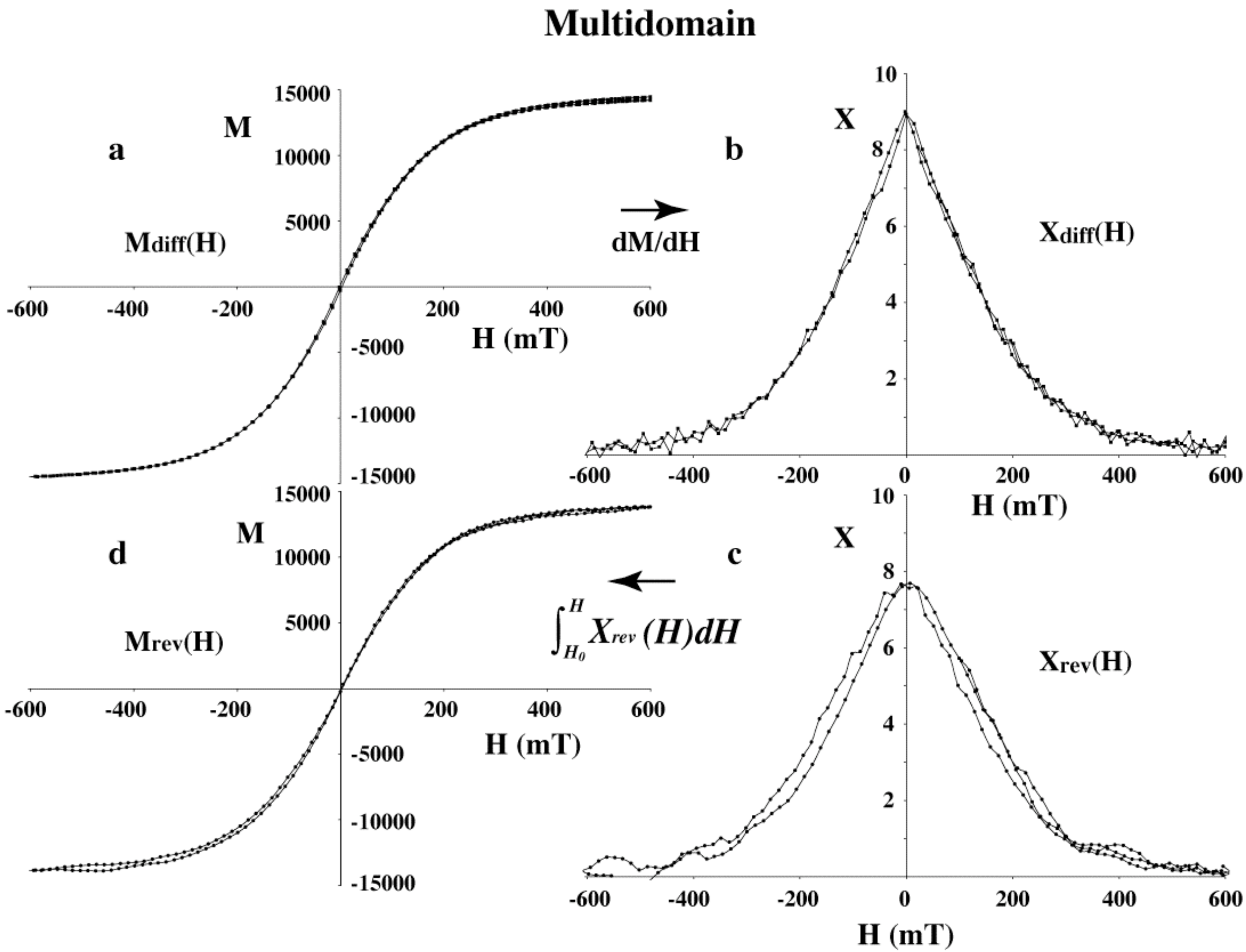
# Reversible vs. irreversible susceptibility

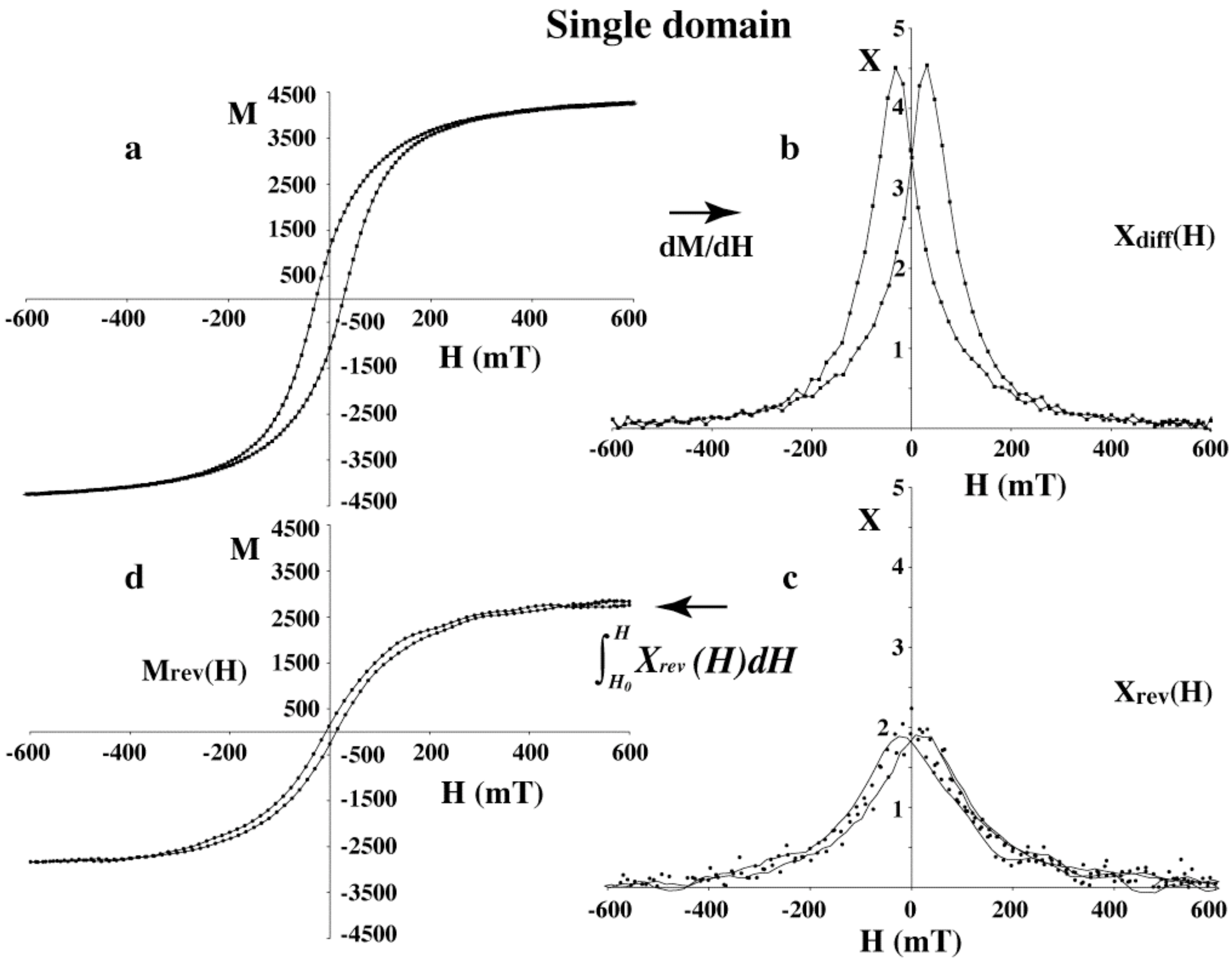



Multidomain

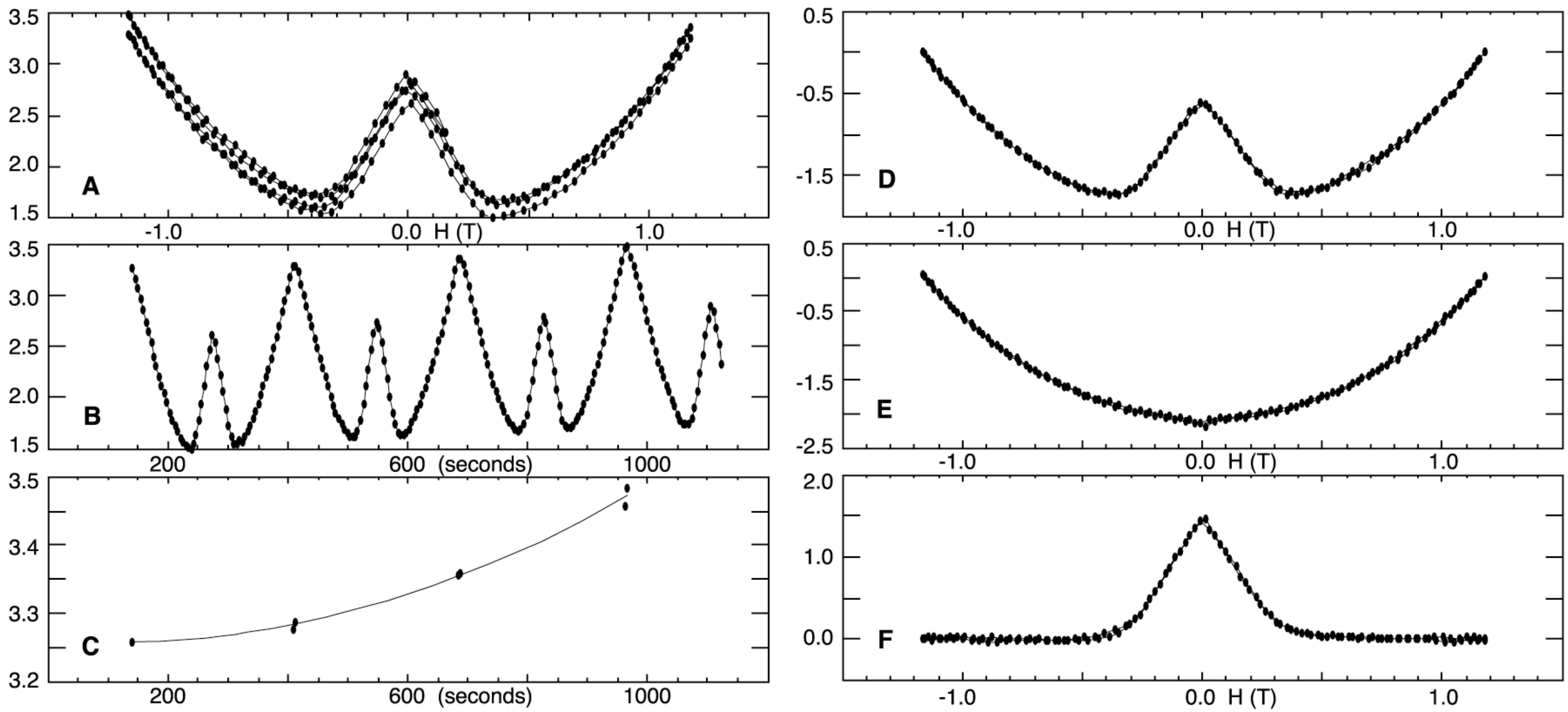



Single domain


Multidomain
a
M
Mdiff(H)
H (mT)
dM/dH
b
X
Xdiff(H)
H (mT)
c
X
Xrev(H)
H (mT)
d
M
Mrev(H)
H (mT)
$\int_{H_0}^{H} X_{rev}(H)dH$



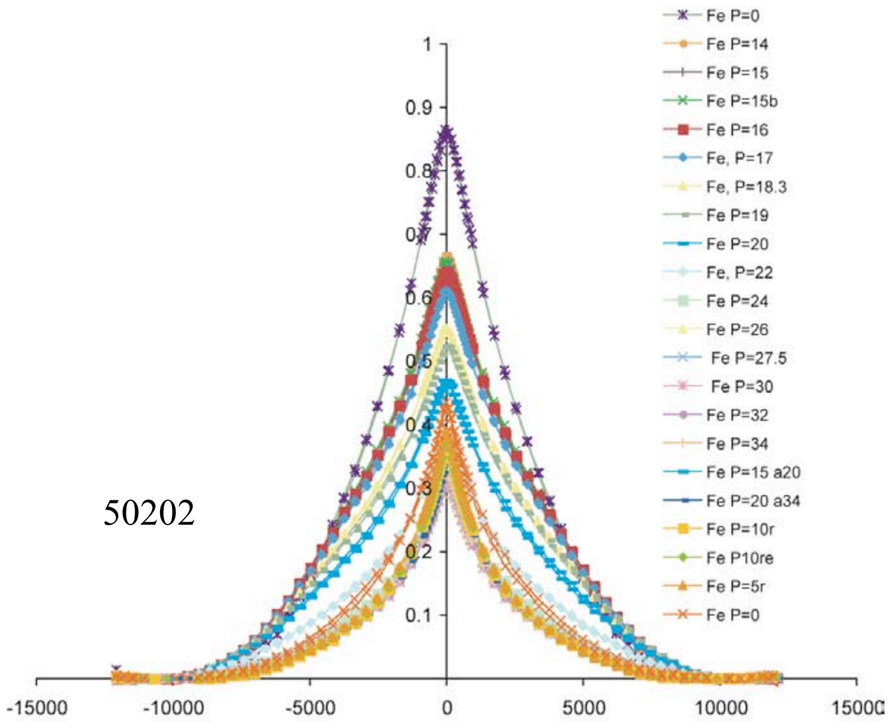
Single domain
a
b
c
d
M
X
H (mT)
dM/dH
$X_{diff}(H)$
$X_{rev}(H)$
$M_{rev}(H)$
$\int_{H_0}^{H} X_{rev}(H)dH$

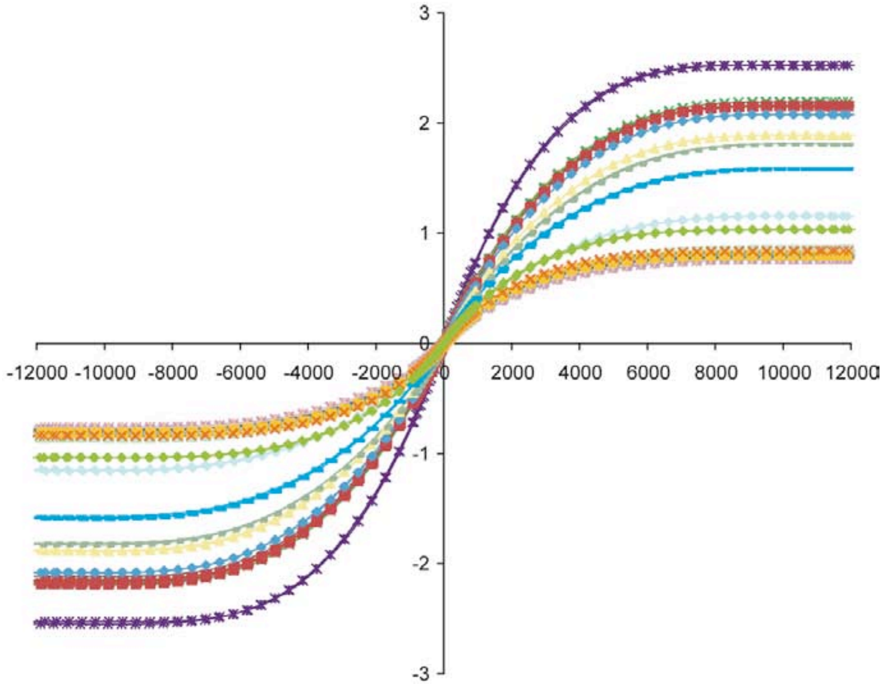


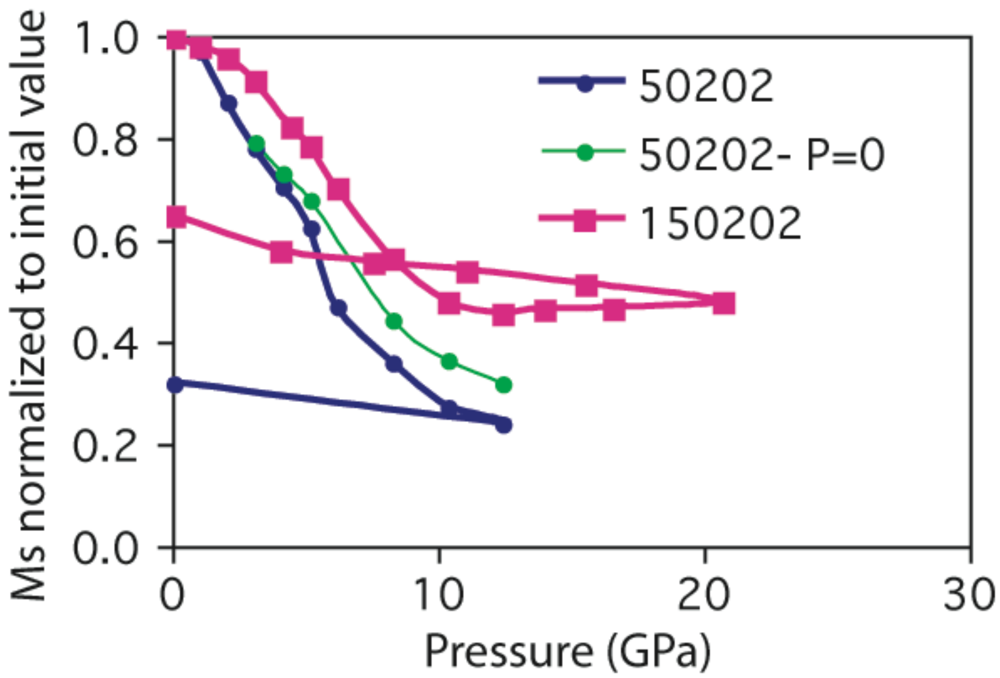

# Experiment on multi-domain magnetite

Two room-temperature AC susceptibility experiments on Fe powder show Ms decreases until ca. 13 GPa, consistent with a phase change at that pressure .

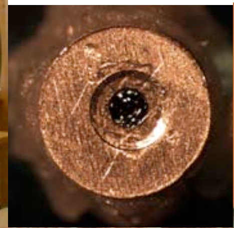
50202

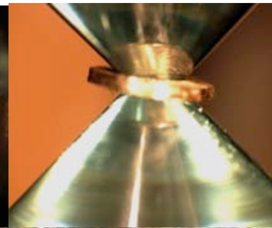


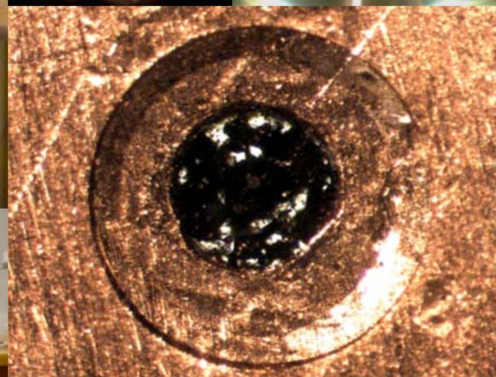



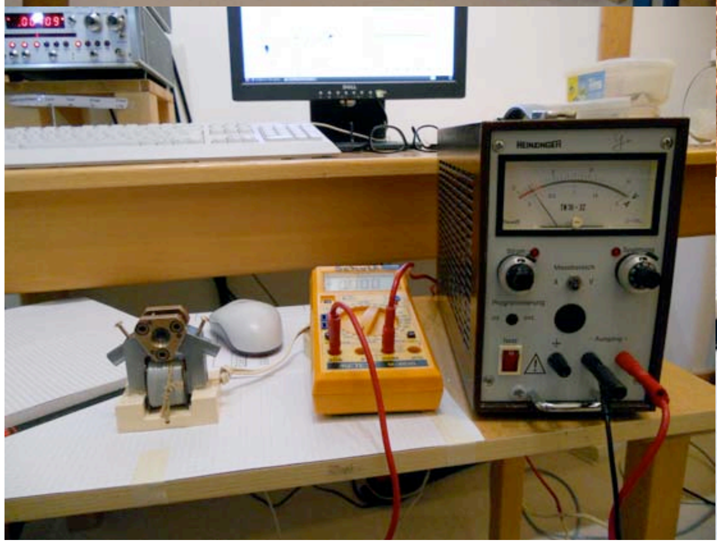


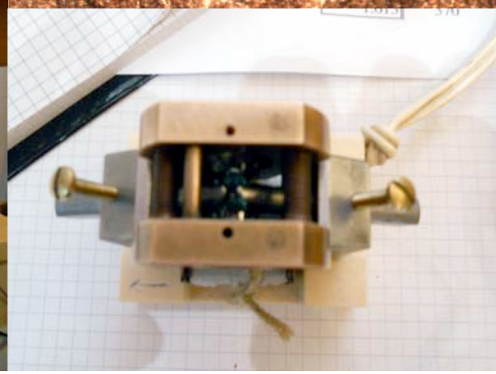
We now insert the diamond cell into a 3-axis, superconducting magnetometer to directly measure the full magnetic vector of material under pressure. Rubies placed in the center and edge allow us to directly measure the pressure gradient.





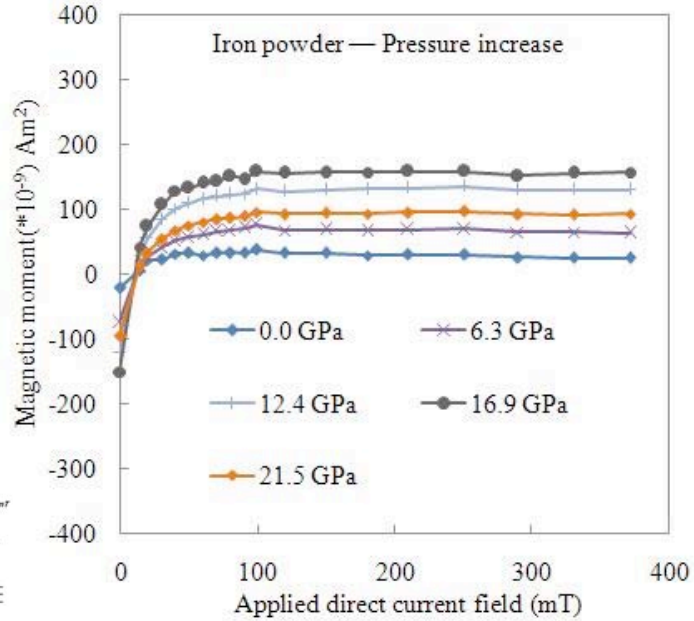


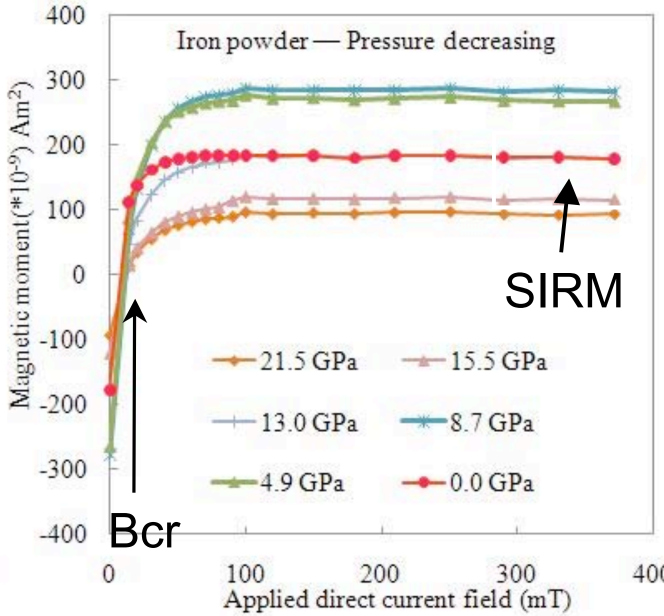


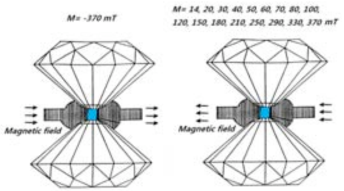


# Experimental data- Fe

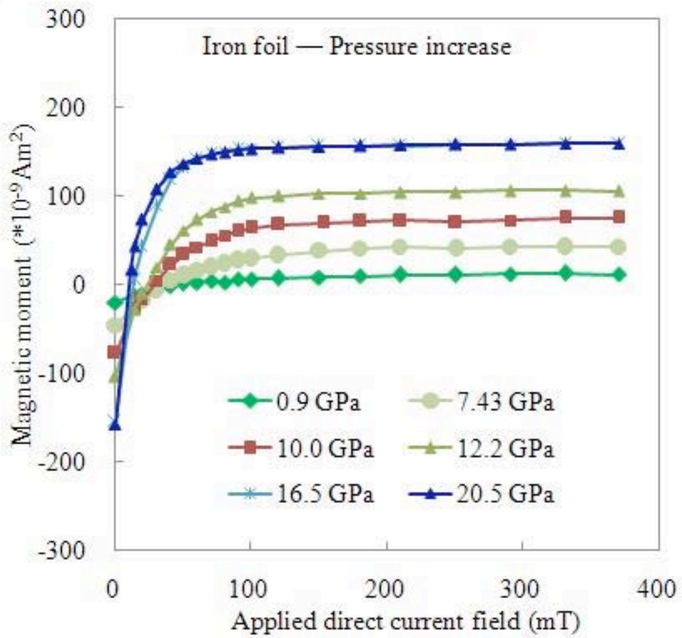
powder

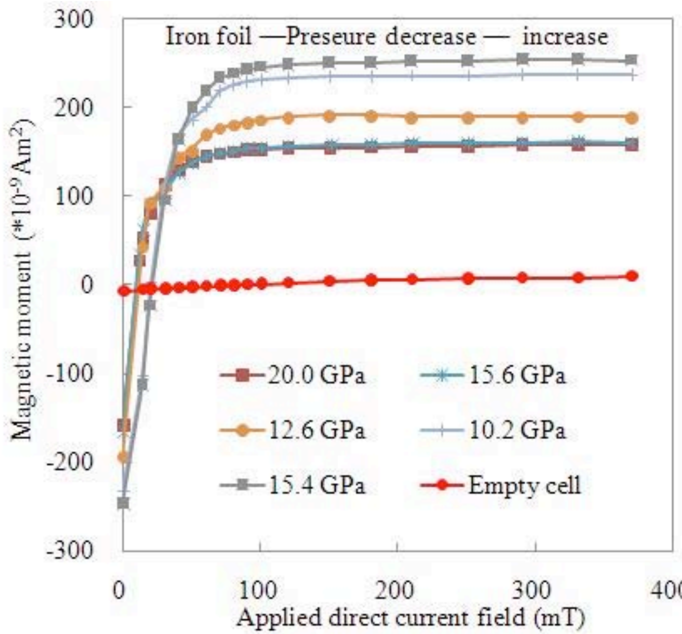


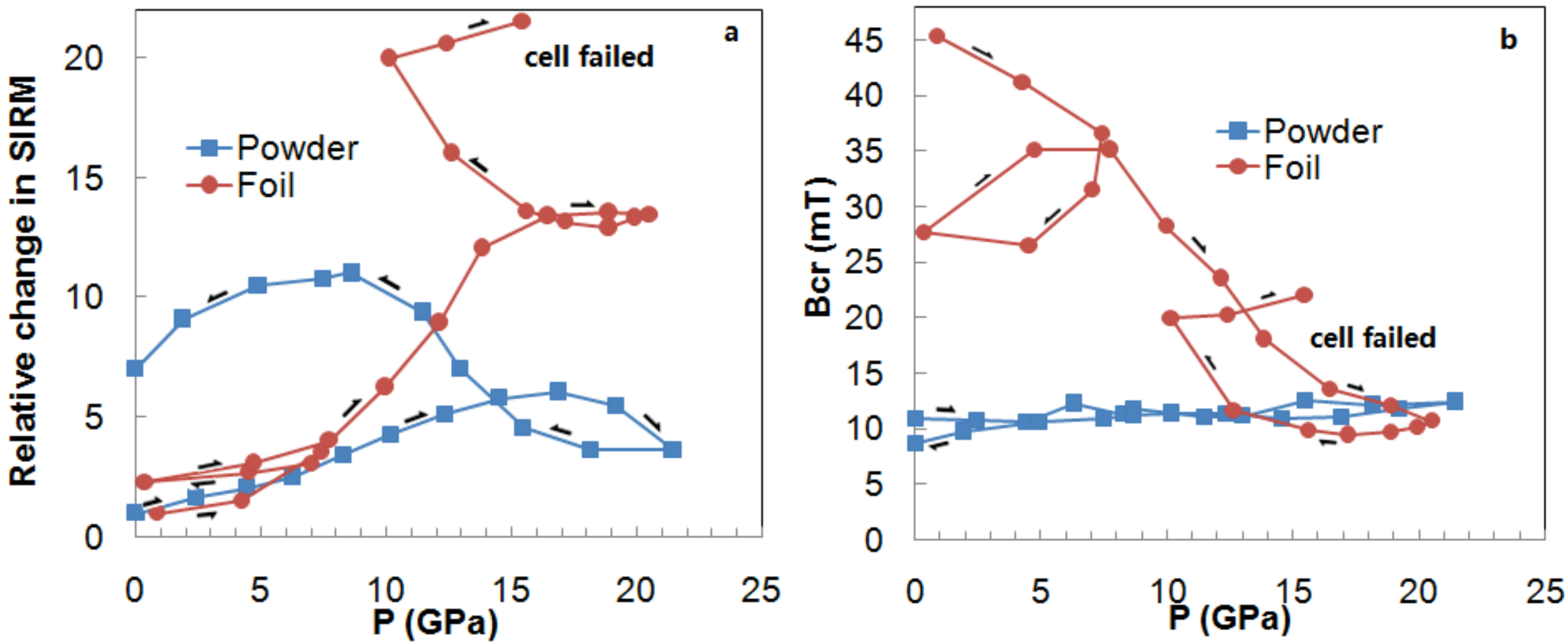



foil





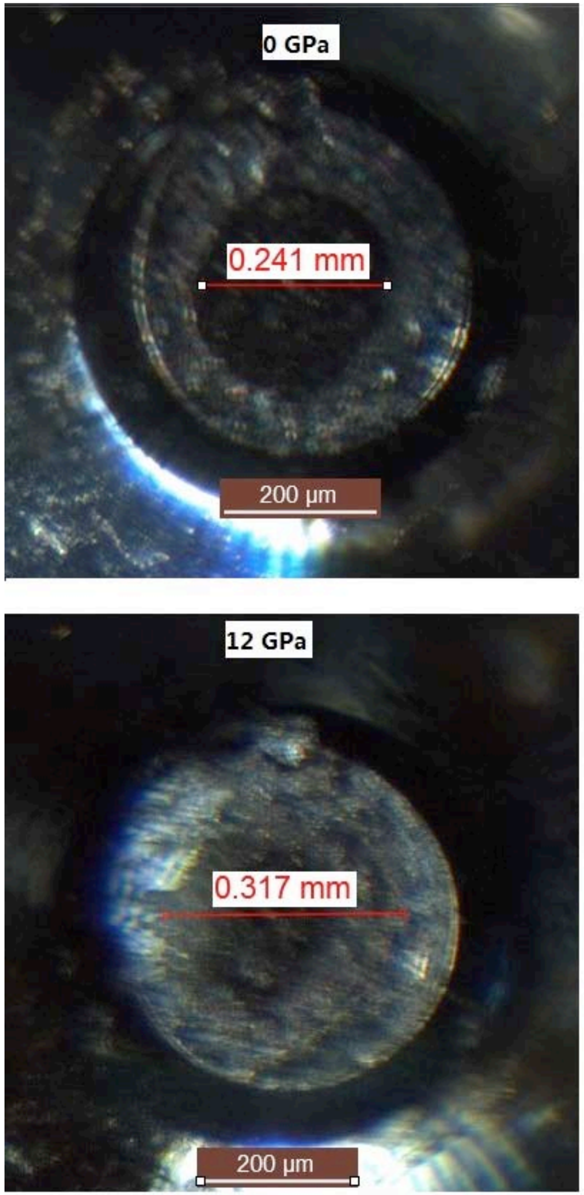

(a) *Saturation of isothermal remanent magnetization (SIRM) as a function of pressure.*

(b) *Coercivity of remanence (Bcr) as a function of pressure.*

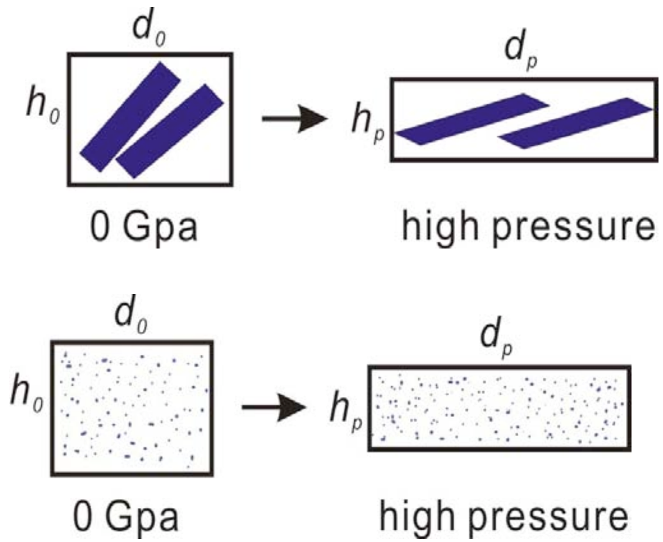
*Arrows show the pressure path*

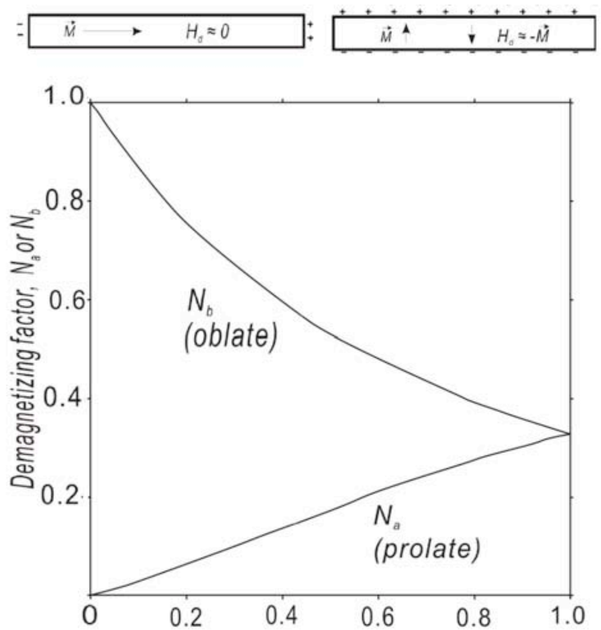
**Why are the results seemingly so different?**

# Shape anisotropy-demagnetization factor



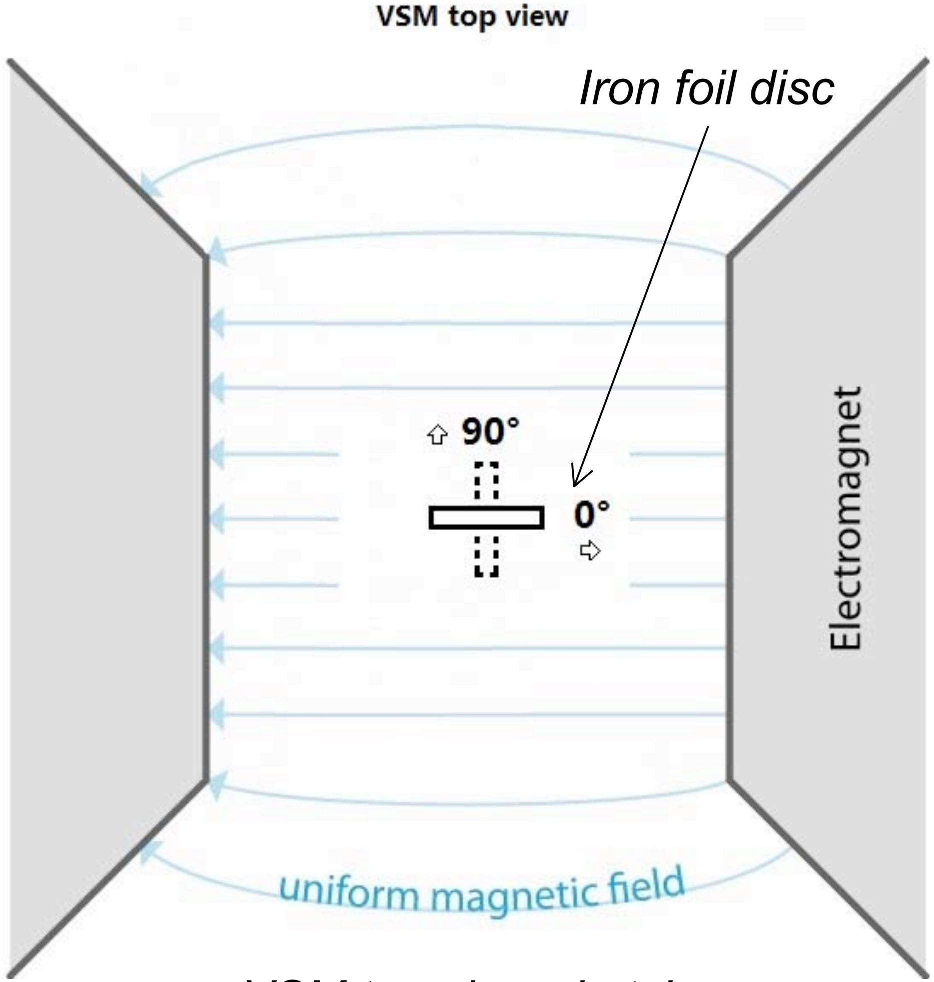

*Microscope top view*



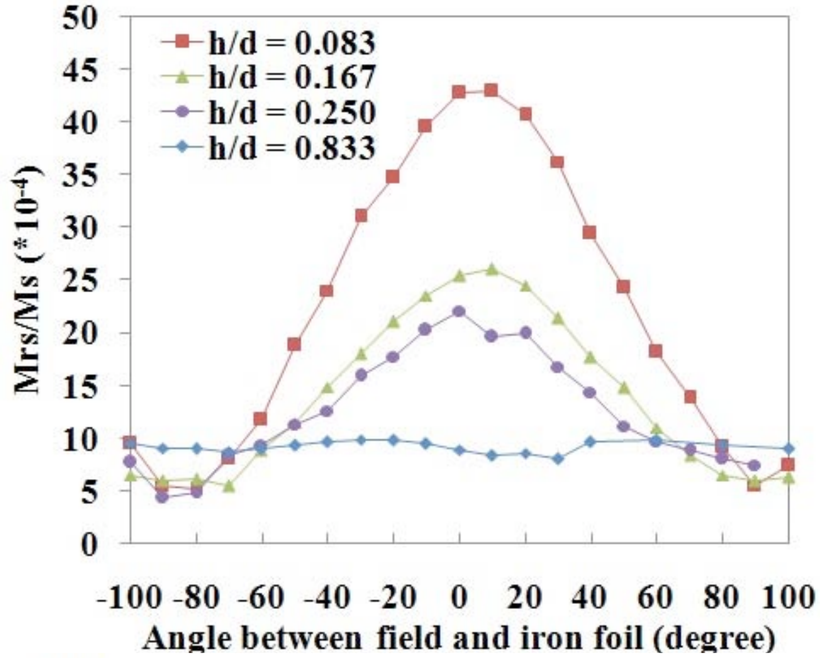



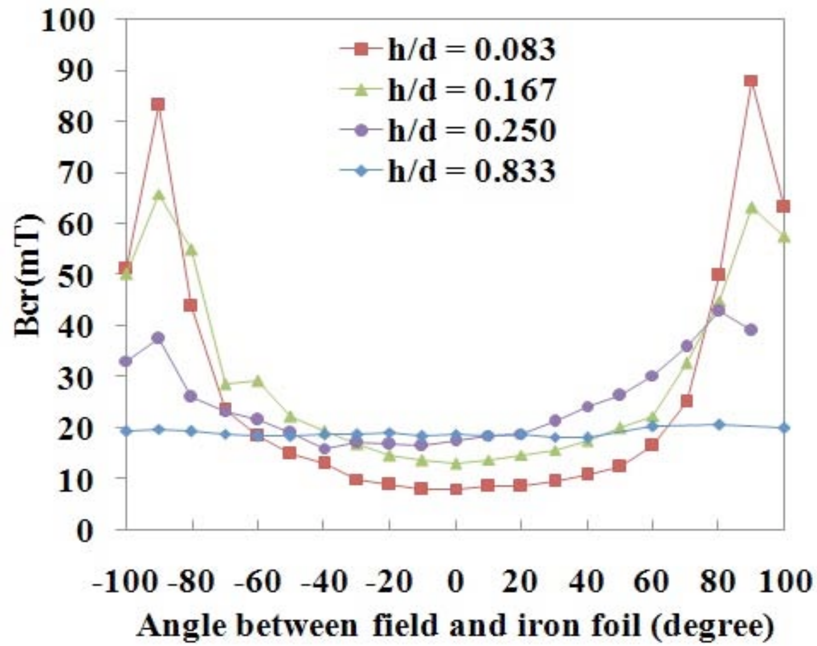

*Dunlop and Özdemir (1997)*

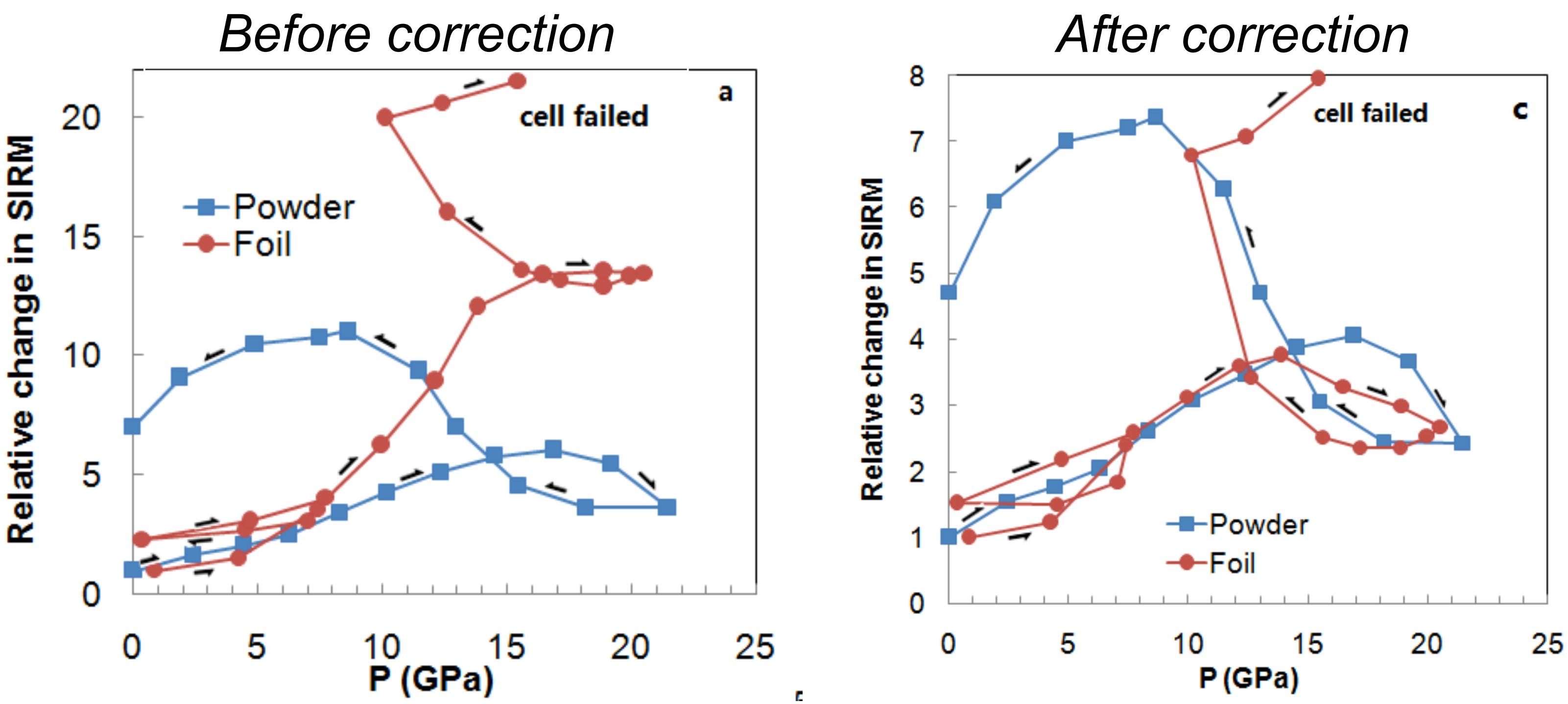
VSM (*Vibrating sample magnetometer*) measurements on iron foil discs
(*diameter 3 mm, height 0.25 - 2.5 mm*)




*VSM top view sketch*
*Iron disc at 0° = parallel to field,*
*at 90° = perpendicular to field*



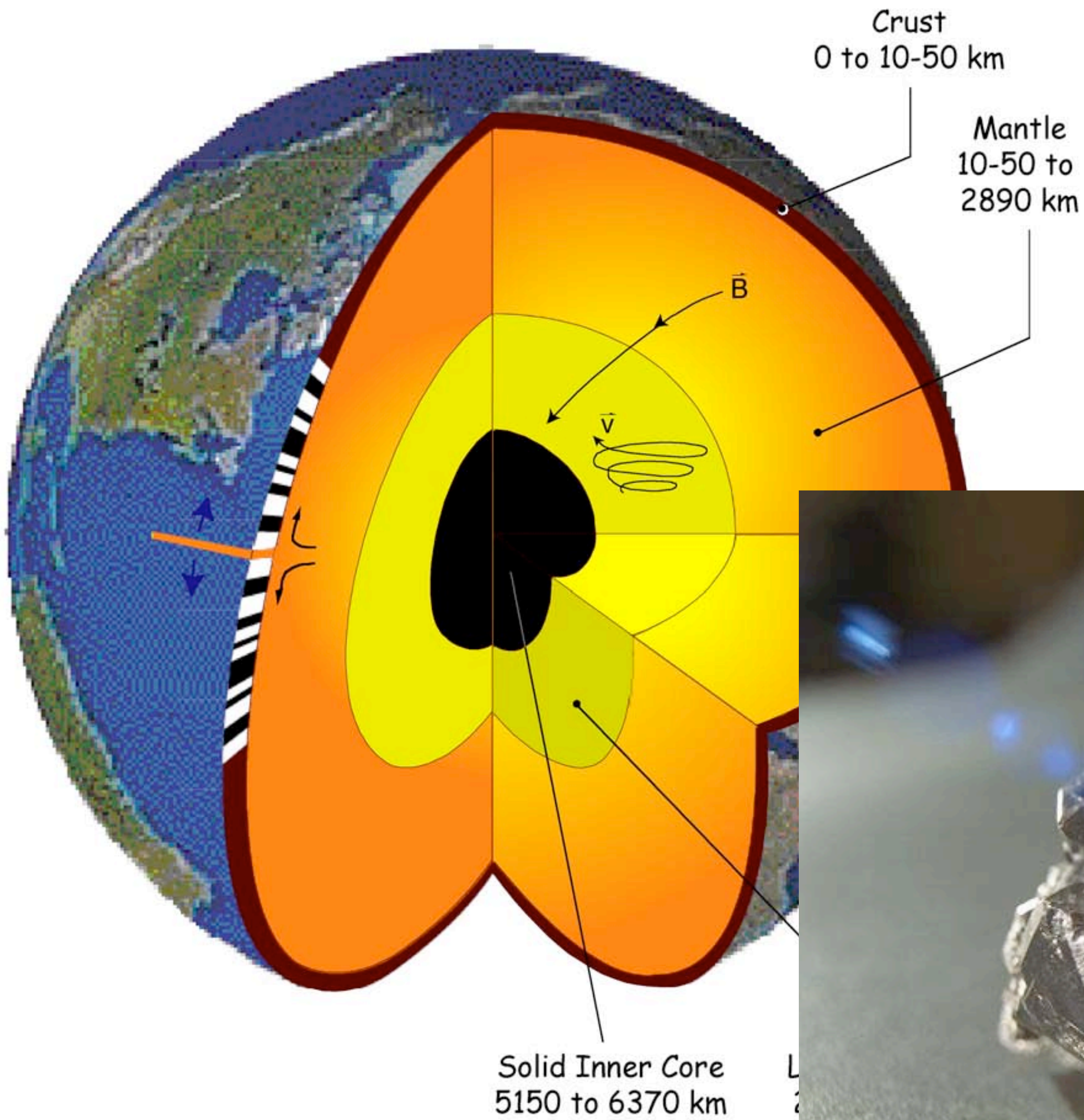






**The data become more consistent after correcting for shape anisotropy.**

- Iron has a higher remanent magnetization at *21.5 GPa* than at initial conditions.
- For NaCl pressure medium, the *bcc-hcp* transition starts at *12.4 ± 0.3 GPa*, with complete transformation to *hcp* at *17.8±0.8* GPa (*von Bargen and Boehler, 1990*), so <u>bcc Fe cannot account for the magnetization at the higher pressures</u>.
- We attribute the remanence to an "anomalous" phase with slightly different lattice constants than bcc or hcp-- this is the same conclusion we are also arriving at with the invar (FeNi) alloys.

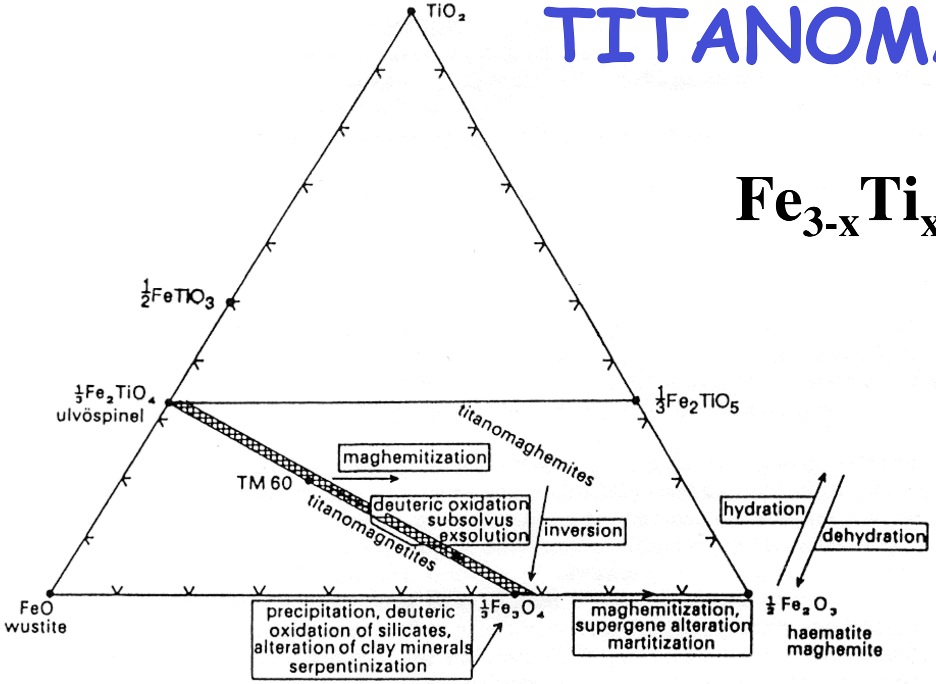
(Wei and Gilder, GRL 2013)




✹ ***Importance of induction in the crust ?***

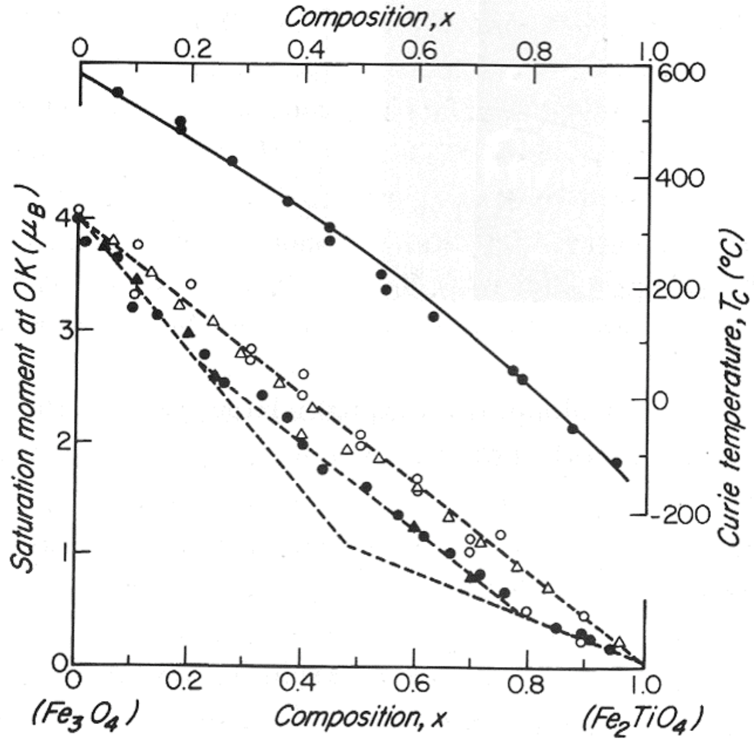
✹ ***Depth of magnetic anomalies ?***

# TITANOMAGNETITE

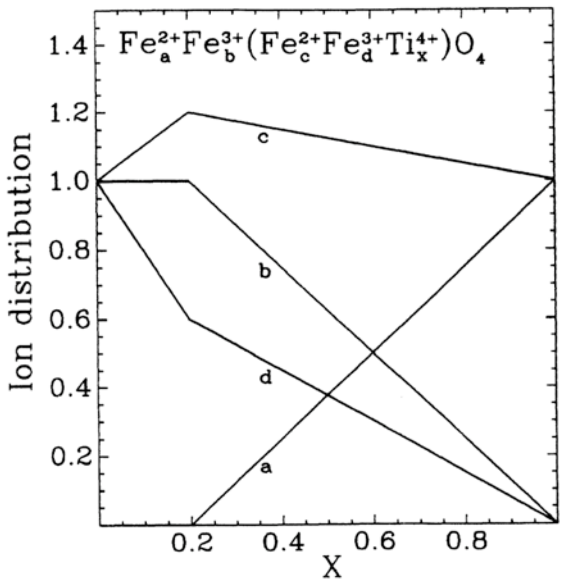



$$Fe_{3\text{-}x}Ti_xO_4 \;=\; xFe_2TiO_4(1\text{-}x)Fe_3O_4$$

$$(x = 0.6 \Rightarrow TM60)$$

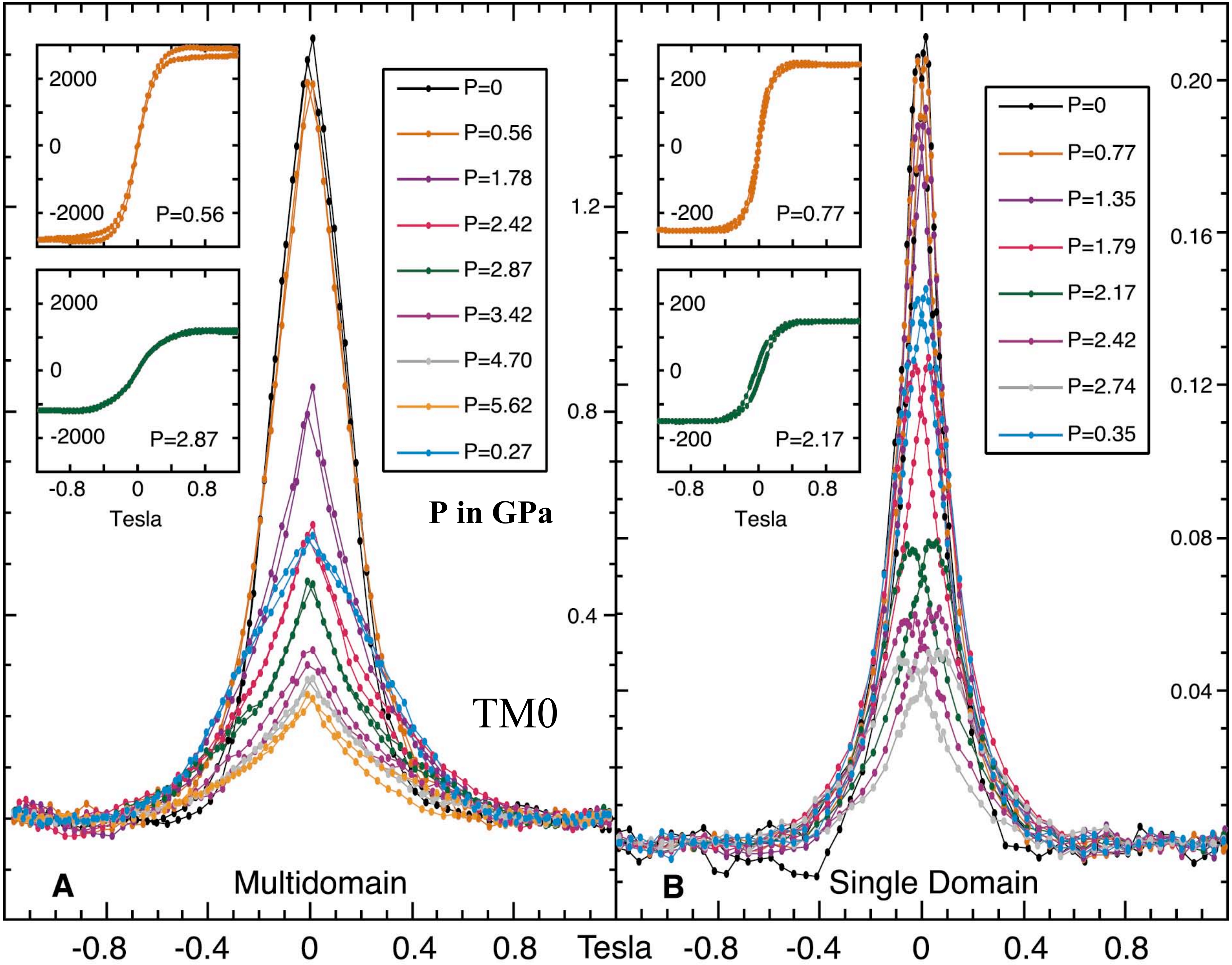



**Dunlop and Özdemir (1997)**

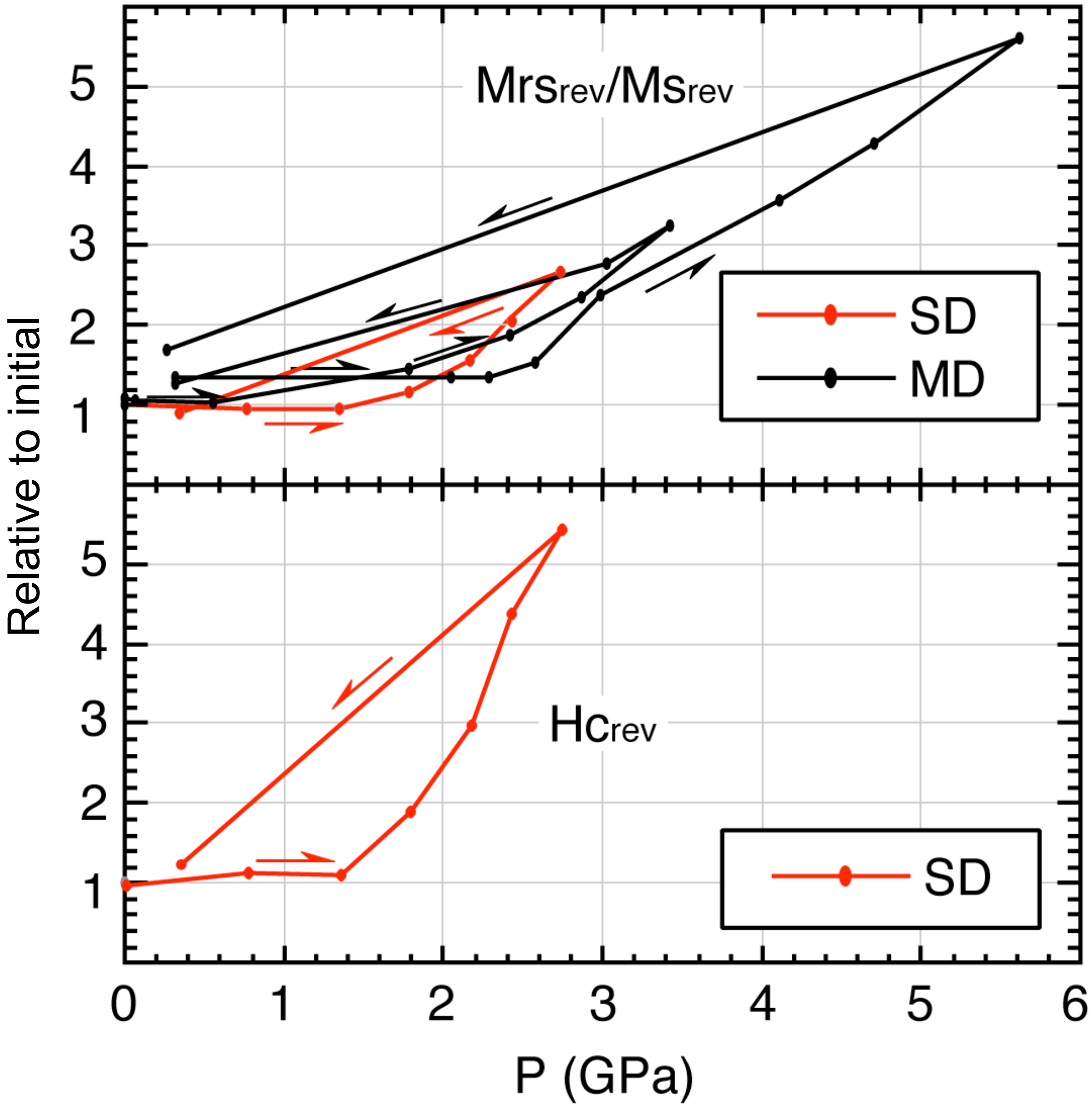



Ion distribution in the $Fe_{3-x}Ti_xO_4$ series

**Kakol et al. (1991)**



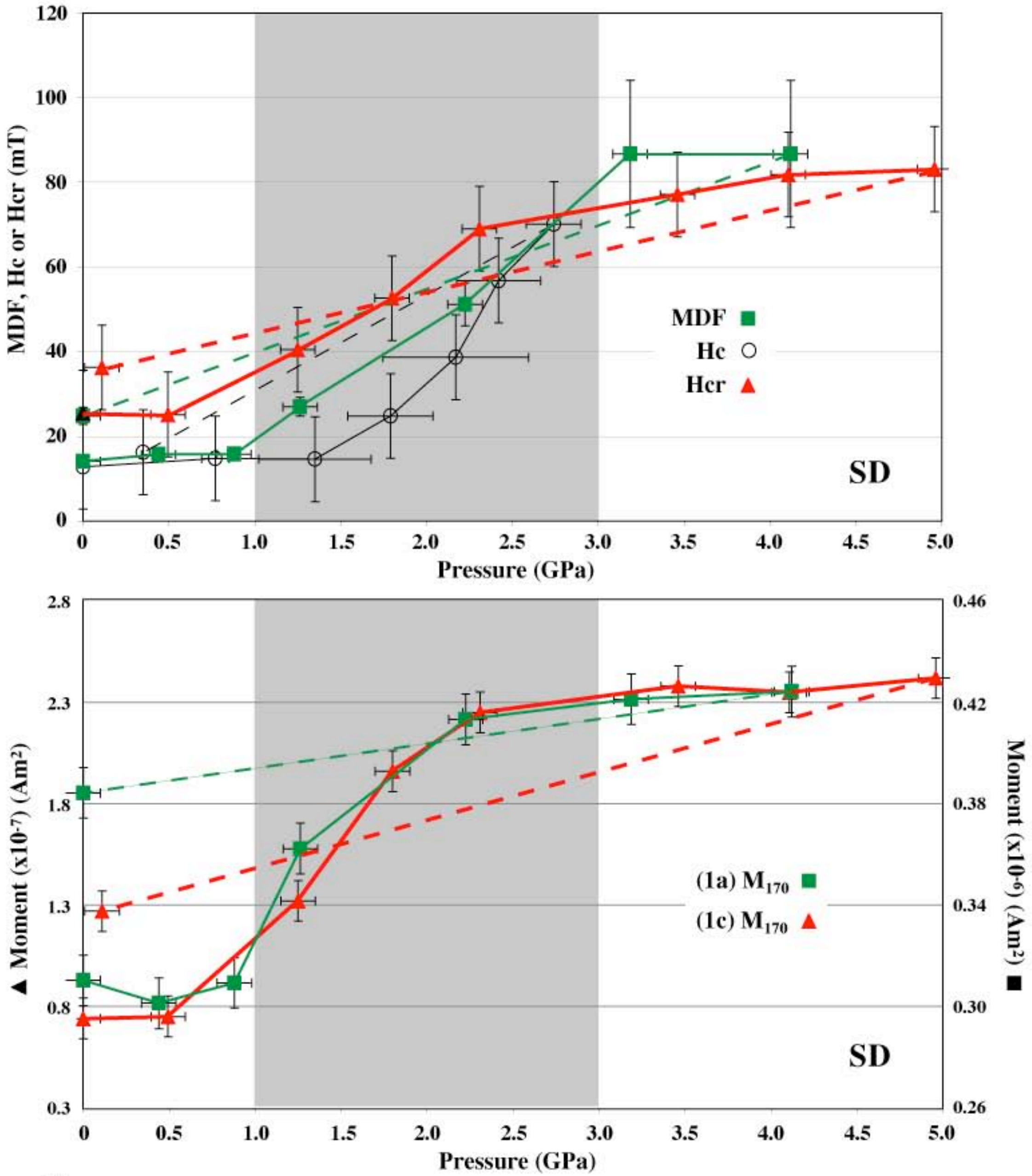
2000
0
-2000
P=0.56
2000
0
-2000
P=2.87
-0.8
0
0.8
Tesla
P=0
P=0.56
P=1.78
P=2.42
P=2.87
P=3.42
P=4.70
P=5.62
P=0.27
P in GPa
TM0
1.2
0.8
0.4
A
Multidomain
200
0
-200
P=0.77
200
0
-200
P=2.17
-0.8
0
0.8
Tesla
P=0
P=0.77
P=1.35
P=1.79
P=2.17
P=2.42
P=2.74
P=0.35
0.20
0.16
0.12
0.08
0.04
B
Single Domain
-0.8
-0.4
0
0.4
0.8
Tesla
-0.8
-0.4
0
0.4
0.8




From 1 to 3 GPa, Mrs/Ms in single domain magnetite increases three times and Hc increases five times.

Pressure transforms magnetite into a more perfect magnet.

Geophysical Research Letters, 2002



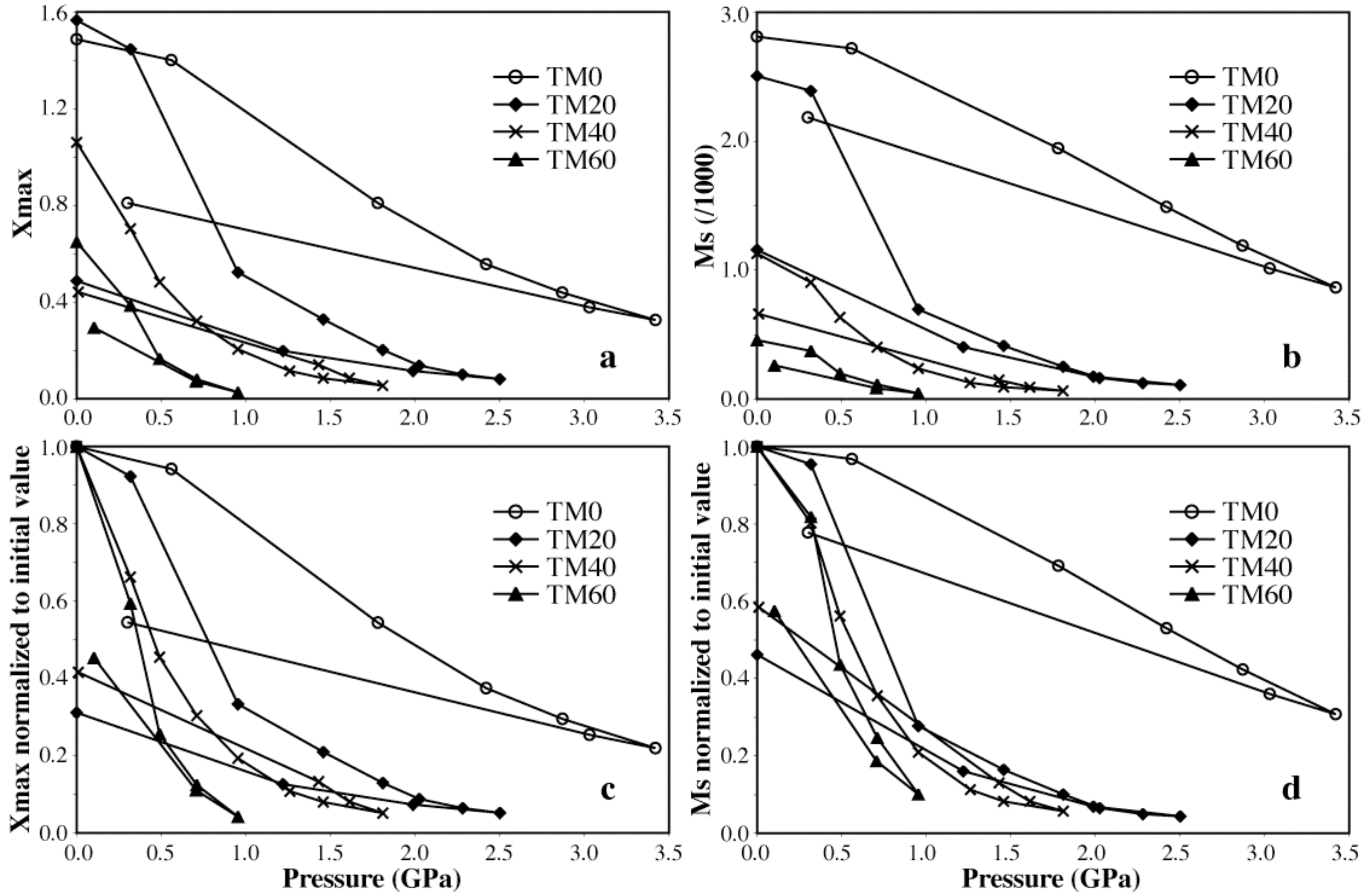

**Two independent experimental methods show that the magnetic properties of single domain magnetite (TM0) change significantly between 1 and 3 GPa.**

# Magnetic phase transition?

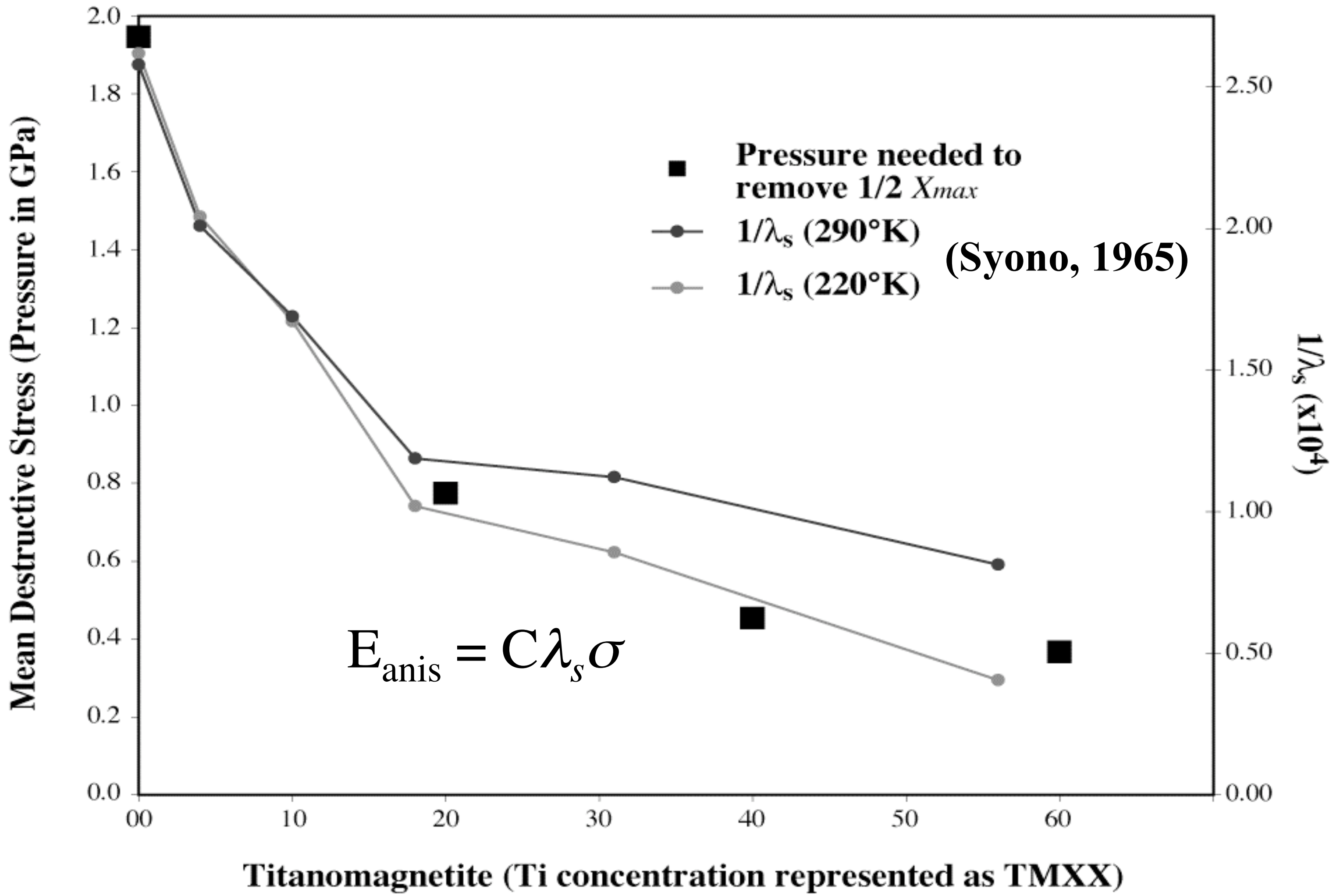
Geophysical Research Letters (2004)

# AC susceptibility of multidomain titanomagnetite

## As Ti increases, less pressure is needed to lower Xmax or Ms

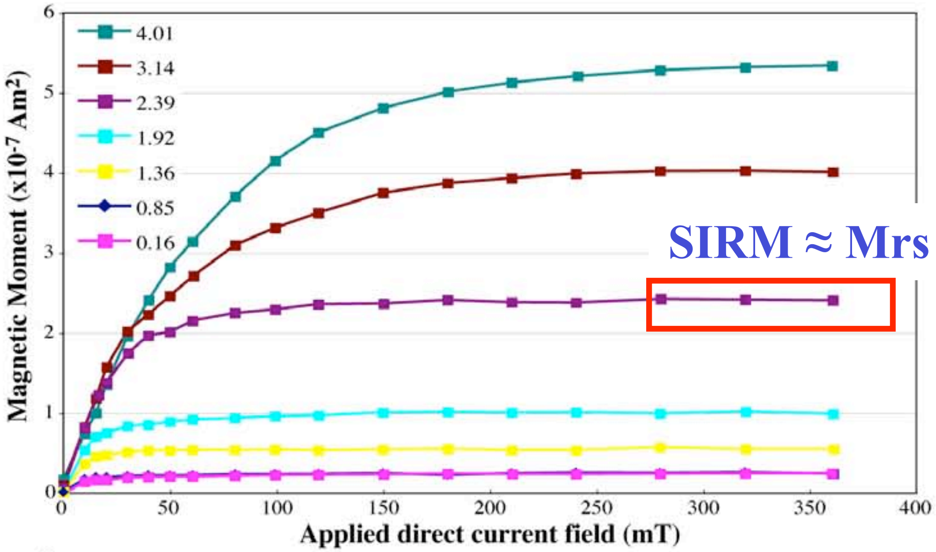


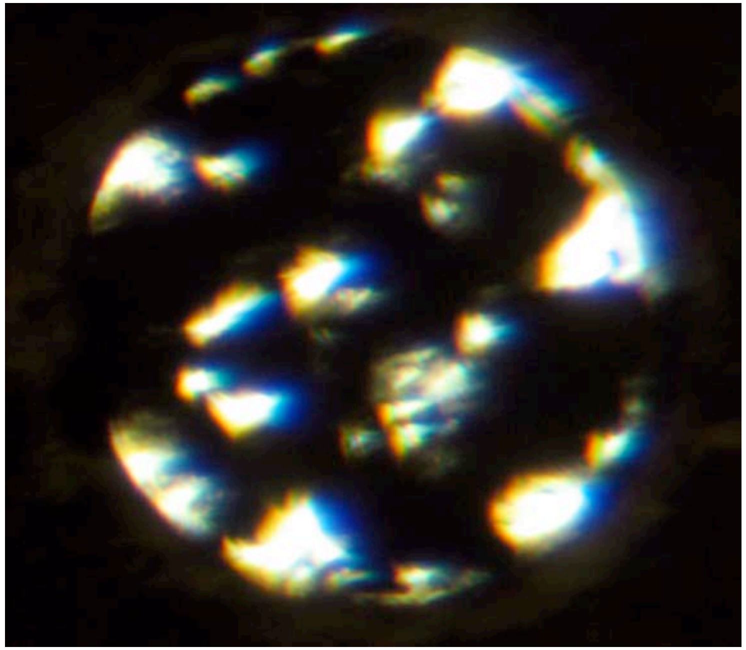
# Relationship between $\lambda_s$ and $\sigma$

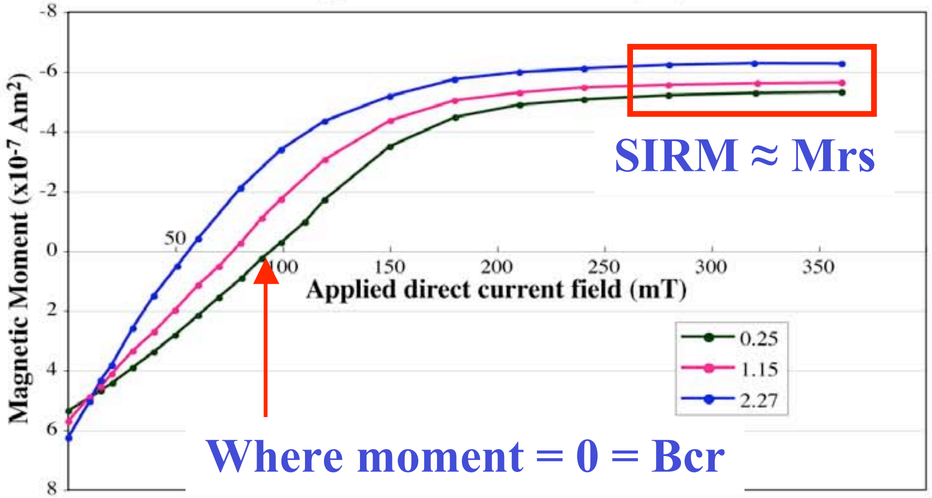


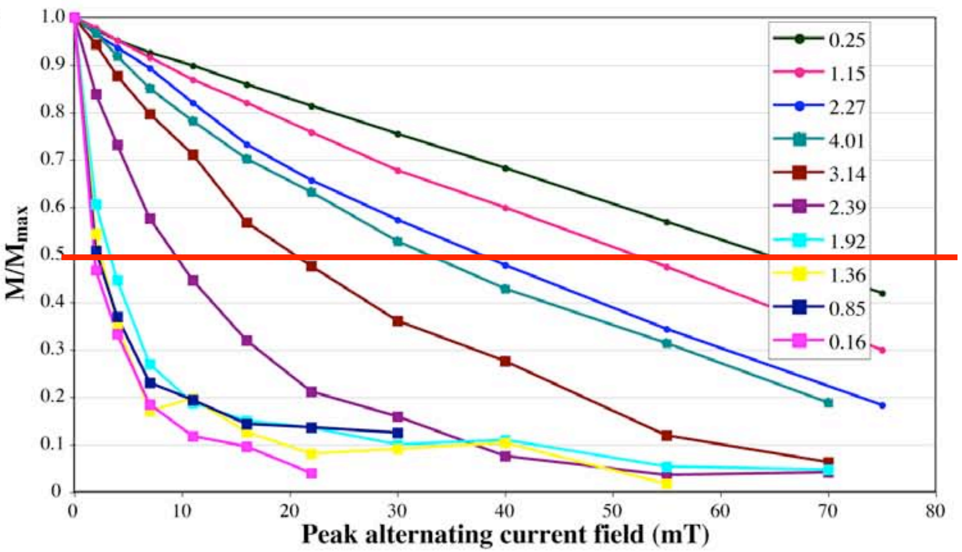

The higher the magnetostriction, the more sensitive magnetization becomes to an external stress.

# Full vector measurements: IRM acquisition and AF demagnetization

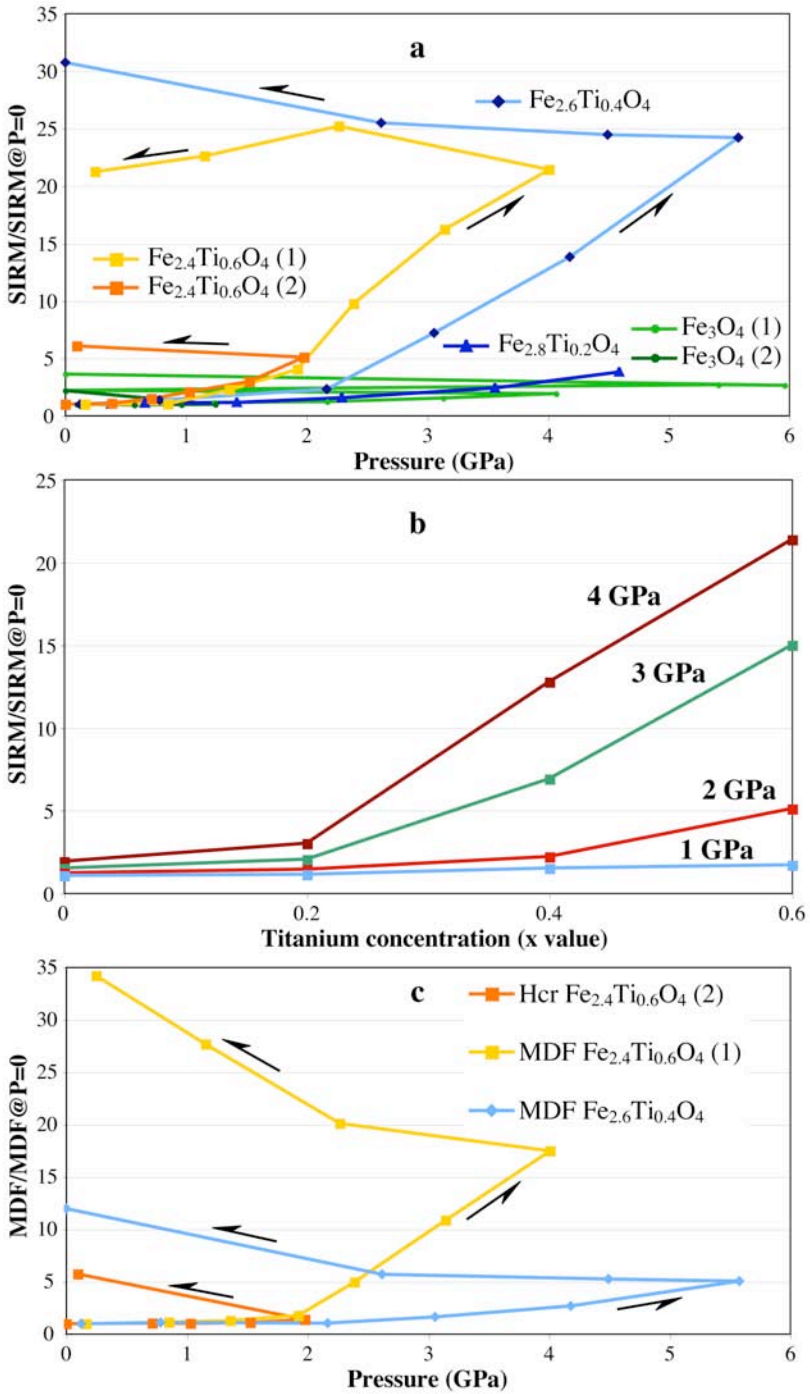





Median destructive field (MDF)

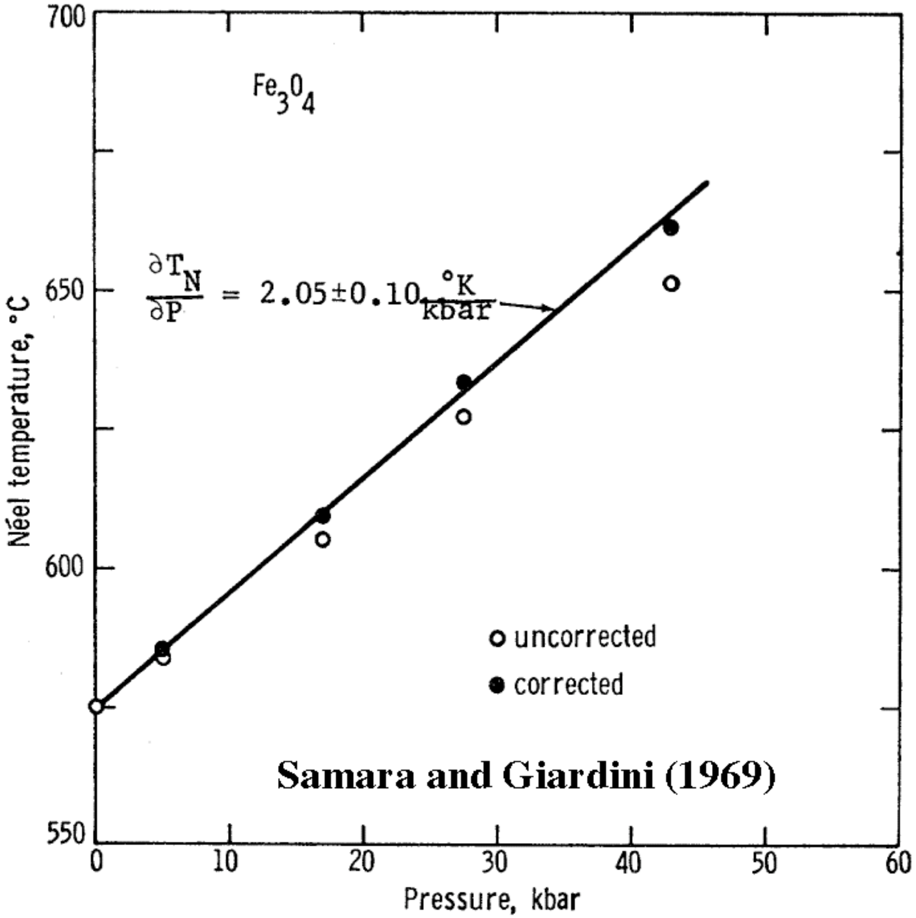


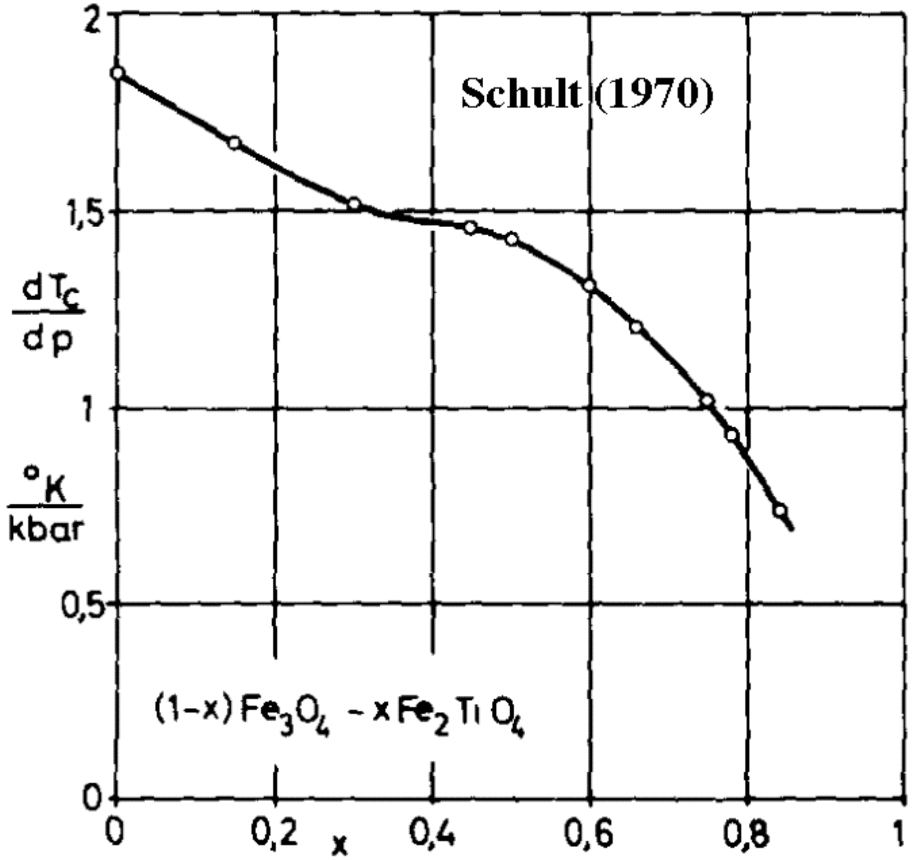

Pressure systematically enhances the magnetic properties of multidomain titanomagnetite, which are the principal carriers of magnetic remanence in nature.

Pressure makes multidomain titanomagnetite more single domain-like. This can potentially explain the origin of deeply rooted magnetic anomalies on Earth and other planets.

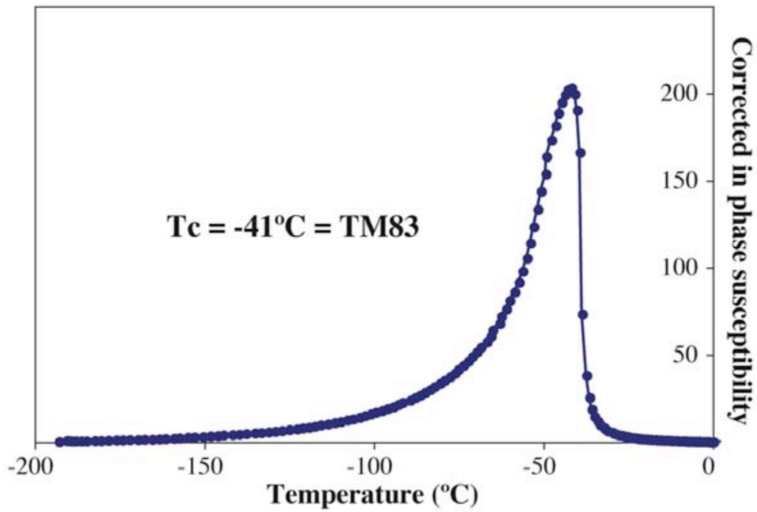
Gilder and Le Goff (GRL, 2008)

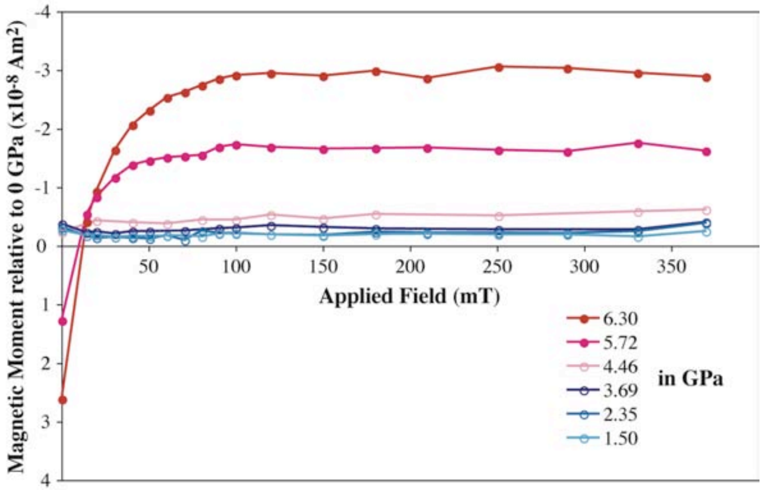
# The Curie points of pure magnetite and titanomagnetite increase by 10-20°C / GPa.

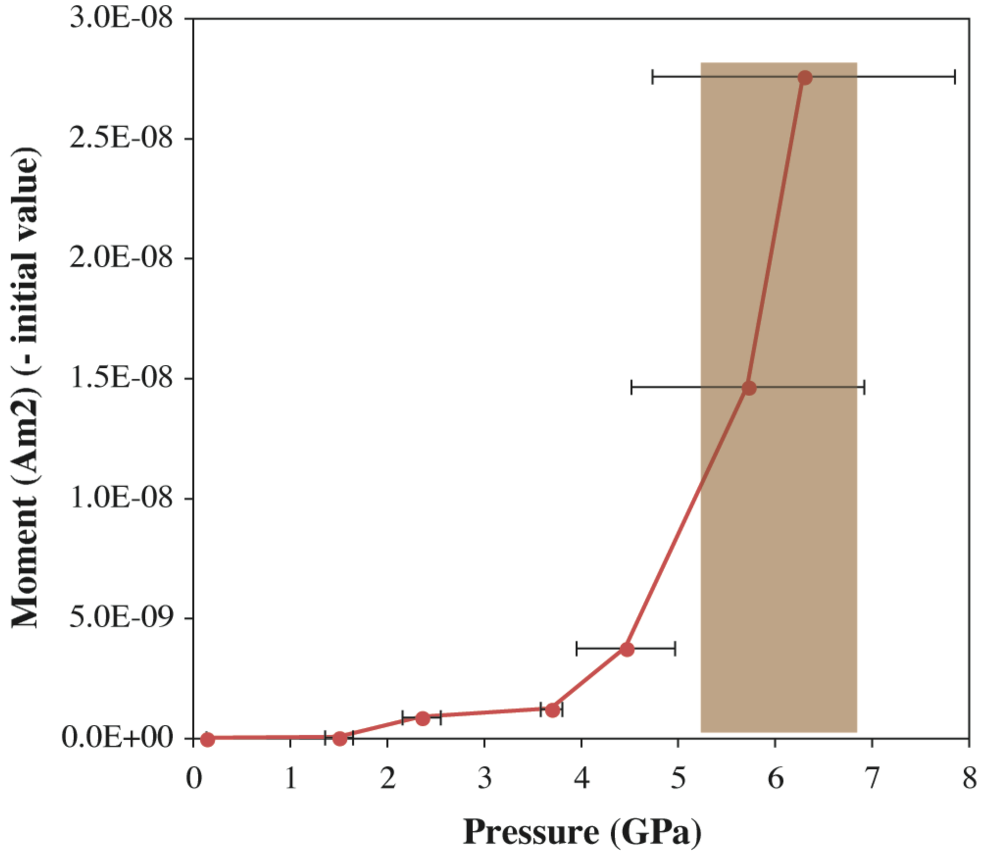


Paramagnetic TM83 becomes ferrimagnetic at ca. 6 GPa, suggesting that the Curie temperature increases by ca. 11°/GPa.

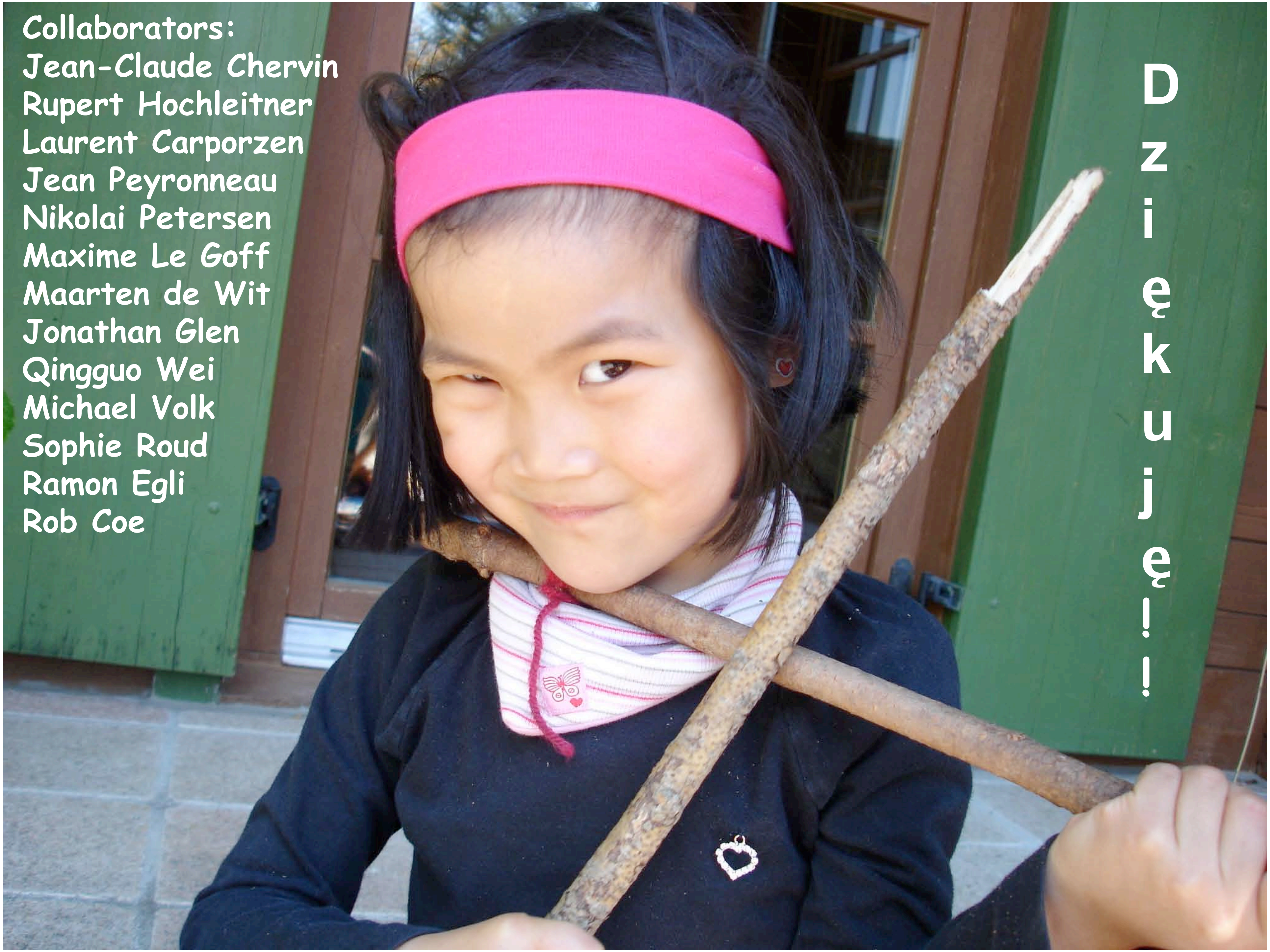


# Conclusions

1. The transition from bcc to hcp in Fe has an intermediate "anomalous" structural phase that is slightly more magnetic than the bcc phase. This is likely also true for the invar alloys.
2. Magnetite's magnetic properties are more stress-sensitive with increasing titanium concentration & non-reversible.
3. The shape effect has a non-negligible effect- especially on AC susceptibility measurements.
4. Future work will be at high P - low T: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Dziękuję!!