U.S. DEPARTMENT OF ENERGY | Nuclear Energy

Office Of Nuclear Energy Materials Cross-Cut Meeting

Multiscale Magnetic Characterization of Reactor Structural Materials Degradation

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Project Overview

- **Goal: Develop tools & techniques to interpret state of irradiated materials degradation using magnetic NDE measurements**

- **Participants:**
  - PNNL (Pradeep Ramuhalli, Brad Johnson, Danny Edwards, Weilin Jiang, Jon Suter)
  - Washington State University (John McCloy, Ke Xu, Yue Cao, Muad Saleh)

- **Schedule**
  - Three years (FY 2014 – FY 2016)

Objectives

- **Develop tools & techniques to interpret state of irradiated materials degradation using magnetic NDE measurements**
  - Integrate microstructural metrology and meso-scale modeling
    - e.g., SEM, EBSD, EDS on FIB specimens
    - Phase field modeling at same length scales as metrology
    - Leverage magnetic signatures for NDE across multiple length scales: micro to macro
  - Use ion beam bombardment to simulate radiation damage

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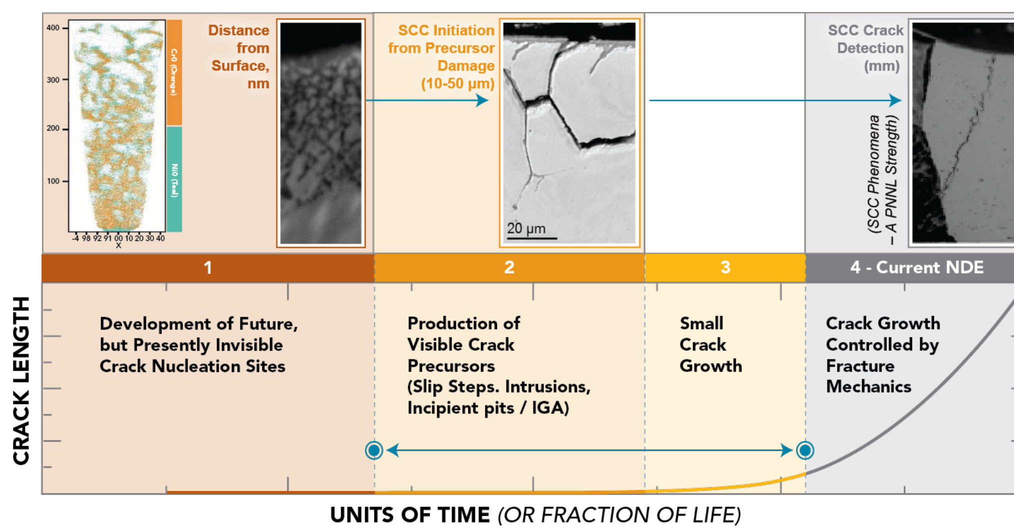
Background and Motivation

- **Neutron irradiation over long terms (40-80 years) likely to degrade mechanical properties of reactor materials**
- **Current NDE techniques generally incapable of characterizing state of material degradation (thermal, chemical, mechanical, radiation)**
  - Material changes due to irradiation embrittlement are at small length scales and potentially distributed over volume of material
  - Current NDE techniques geared to detecting mechanical cracking



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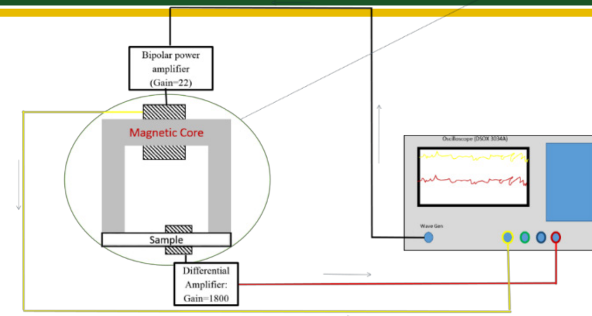
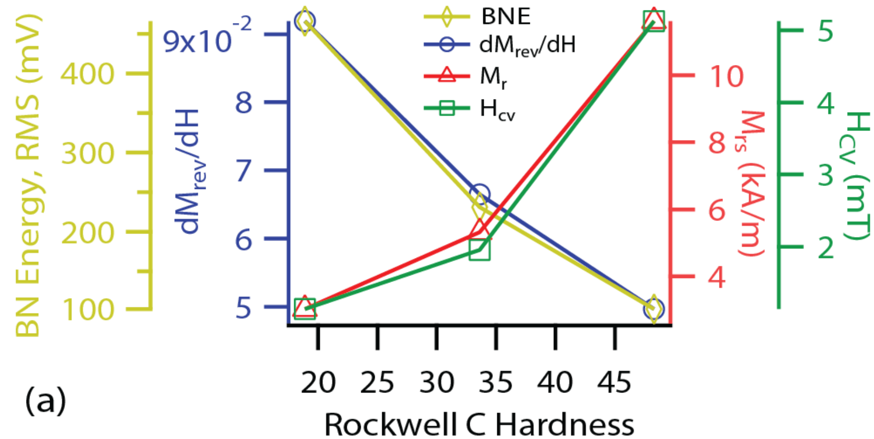
Problem Statement

- **Many studies show correlations between neutron damage and magnetic properties in RPV steel**
  - H_c, M_S, minor loops, ferromagnetic resonance, Magnetic Barkhausen Noise (MBN)
- **MBN used commercially for quantifying stresses in ferritic steels**
  - Recent work showed quantitative correlations between MBN micromagnetic measurements (first order reversal curves - FORC)
- **Gap: Quantifying level of degradation from magnetic measurements**



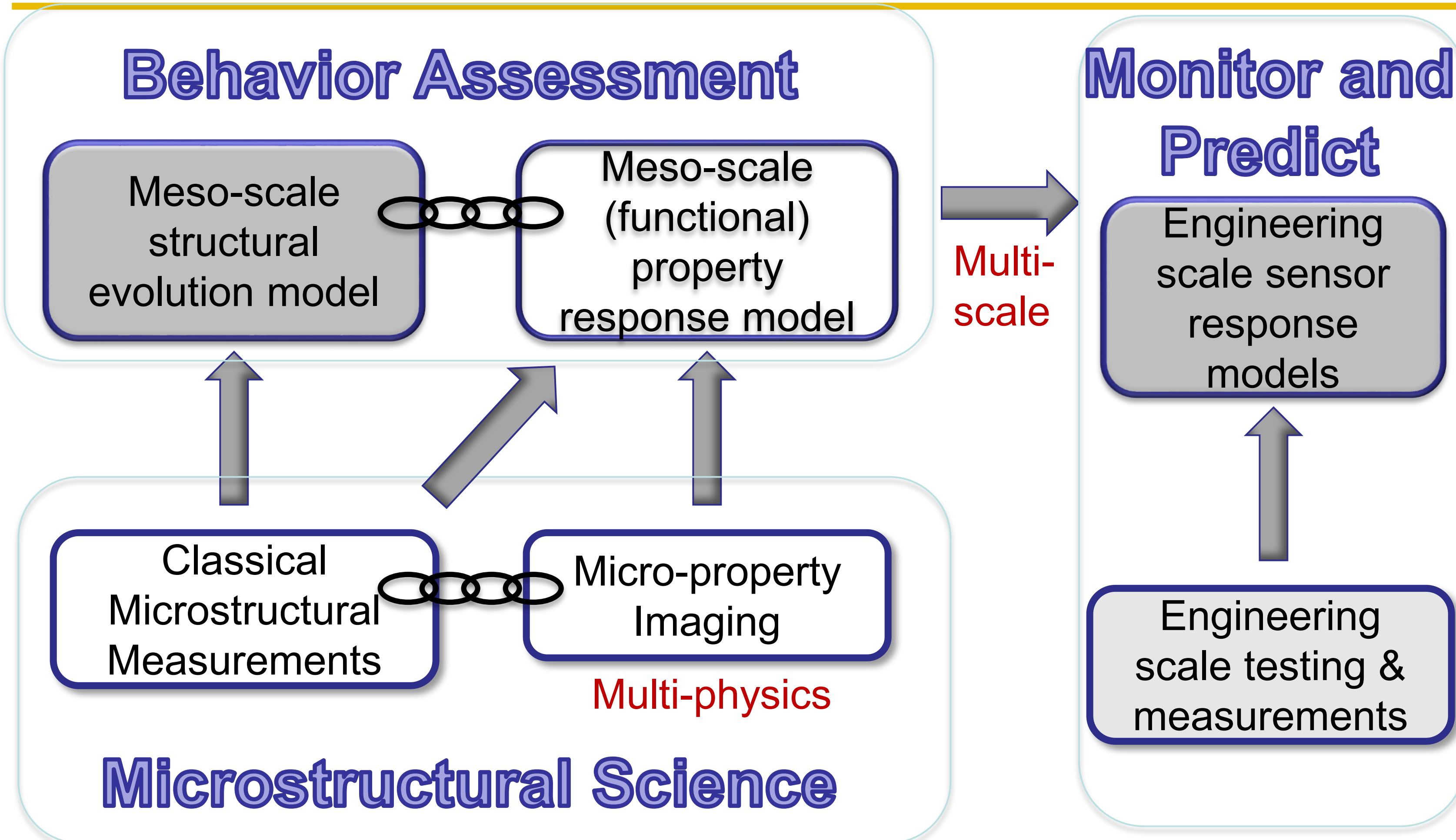
Lab MBN measurements



Correlations between MBN and dM_{rev}/dH (derived from FORC)

Can MBN be used quantitatively to monitor reactor steel degradation?

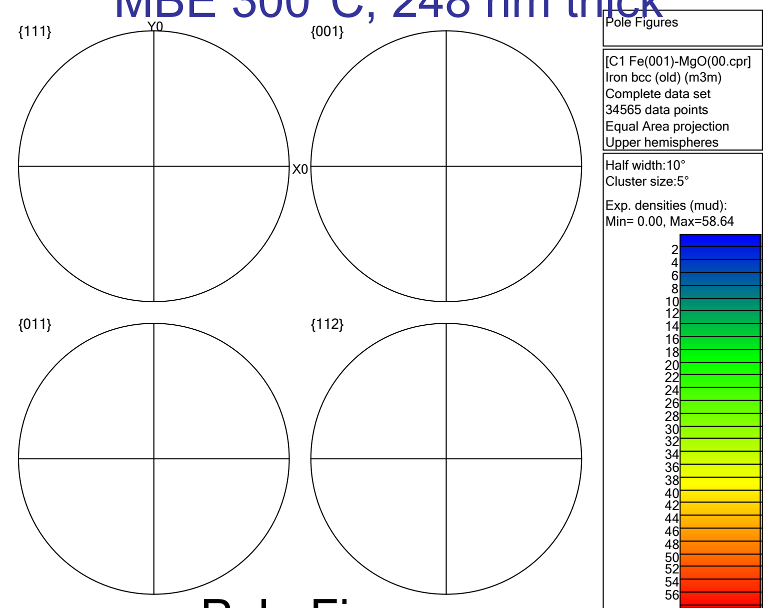
Approach


Behavior Assessment
Meso-scale structural evolution model
Meso-scale (functional) property response model
Multi-scale
Monitor and Predict
Engineering scale sensor response models
Classical Microstructural Measurements
Micro-property Imaging
Multi-physics
Engineering scale testing & measurements
Microstructural Science

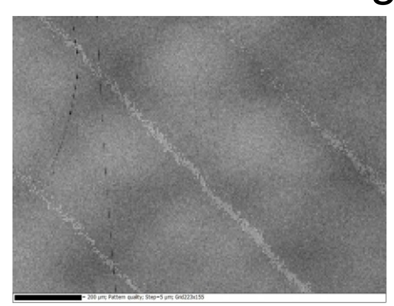
Experimental Plan

- **Sample Complexity Plan:**
  - Single crystal Fe on single crystal MgO
    - FIB'd regions same scale as models
  - Polycrystalline Fe on polycrystalline MgO
  - Fe 1% Cu thinned from bulk alloy
- **Thin films: Allow ion beam bombardment and deposition of atoms through film into the substrate**
  - Single crystal Fe
    - Fiducial marks to enable co-registration of different measurement types
    - Geometric structures using FIB

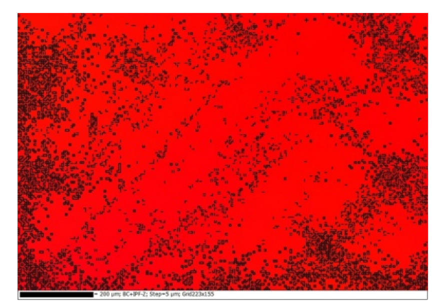
Fe(001)/MgO(001)
MBE 300°C, 248 nm thick



Pole Figure



Pattern Quality Map



IPF-Z Map (Normal to Surface)

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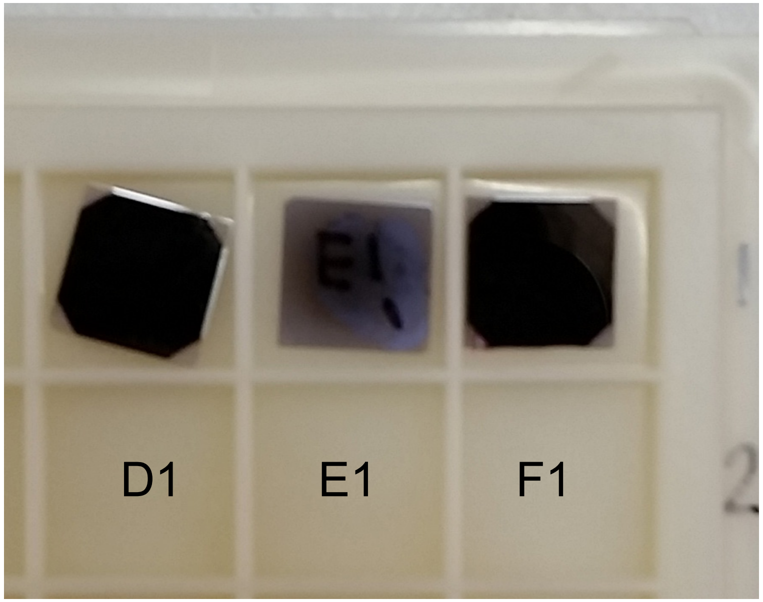
Materials and Methods

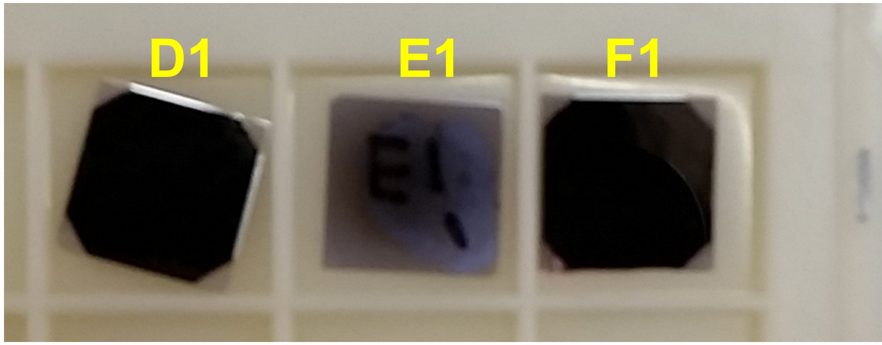
- **Focus of this presentation on single crystal thin film Fe**

Sample	Film/Substrate	Film Thickness (1E15 at./cm^2)	Grain Size (nm)	χ_{min}	T (°C)	Note
A1	Fe(001)/MgO(001)	2100 (248 nm)	HRXRD: Single Crystal	5.9%	300	Small peaks in GIXRD
B1	Fe(001)/MgO(001)	2130 (251 nm)	HRXRD: Single Crystal	3.5%	300	Very good
C1	Fe(001)/MgO(001)	2120 (250 nm)	HRXRD: Single Crystal	3.2%	300	Very good
D1	Fe(001)/MgO(001)	2100 (248 nm)	HRXRD: Single Crystal	6.2%	300	Good
E1	MgO(001)	---	---	---	---	Substrate
F1	Fe(001)/MgO(001)	2160 (255 nm)	HRXRD: Single Crystal	7.3%	300	Small peaks in GIXRD



Irradiation Conditions

- 2 MeV Fe^{+} ions at 24°C under a vacuum level of 7×10^{-8} Torr
- Beam rastered across the sample of a 10 mm x 10 mm area
- Dose
  - A1 (not shown): Unirradiated
  - D1: 10 dpa,
  - F1: 50 dpa
  - E1: MgO only, 50 dpa



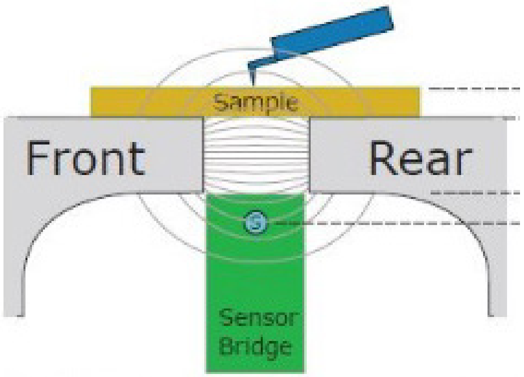
Measurement Capabilities Brought to Bear on Problem

Microscopy

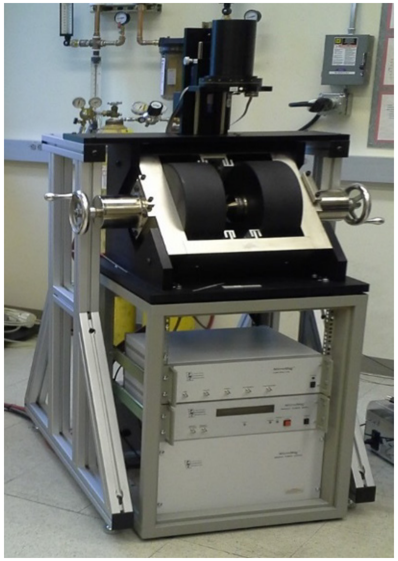
- Transmission Electron Microscopy: For TEM, FIB samples extracted from the center of the coupon in cross-section
  - FIB region was coated with a Pt cap, then milled down to capture the thin cross section, sample was mostly MgO
  - Could clearly see the damage profile through the Fe into the MgO, peak damage appears to be well into the MgO
- Variable field magnetic force microscopy (VFM)

Macroscopic measurements

- Positron annihilation
- Vibrating sample magnetometry (VSM)
  - Magnetic major and minor loop analysis
  - First order reversal curves
- Magnetic Barkhausen Noise



VFM Concept



VSM

Results

- Microstructural Characterization
- Variable field magnetic force microscopy
- Vibrating sample magnetometry

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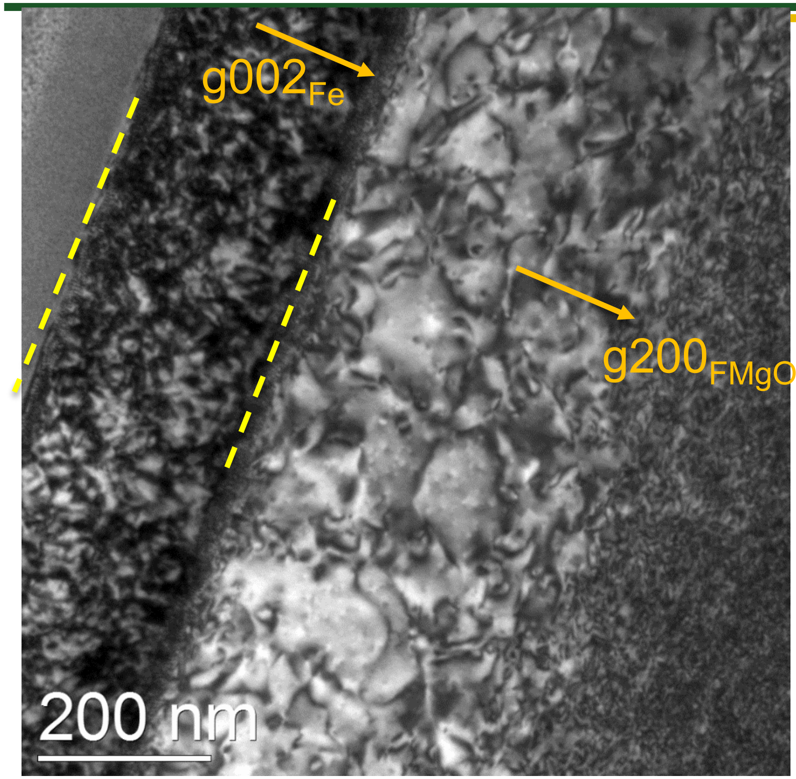
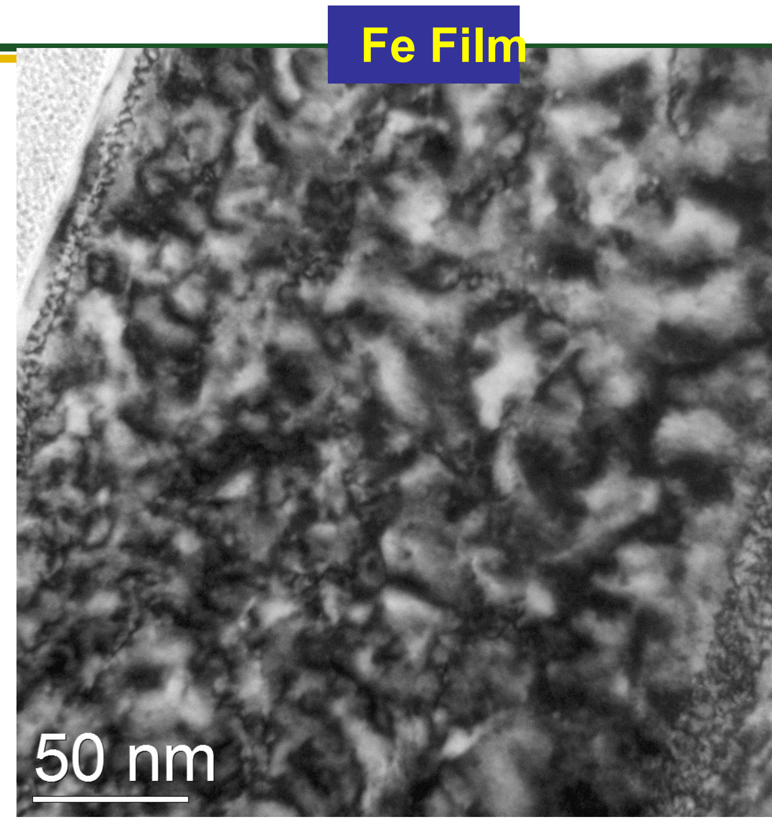
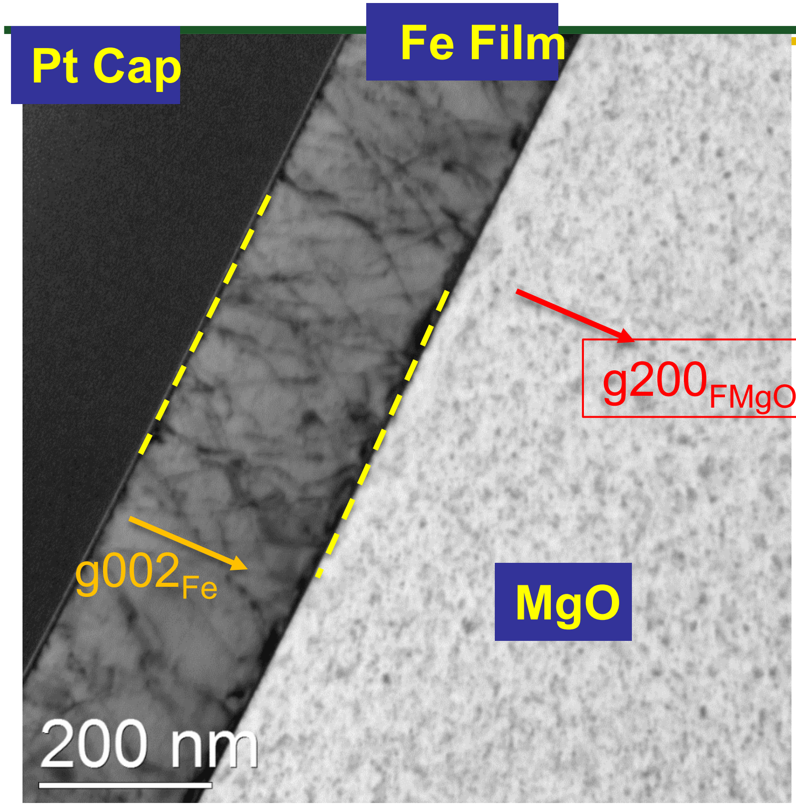
Sample F1: Overview TEM

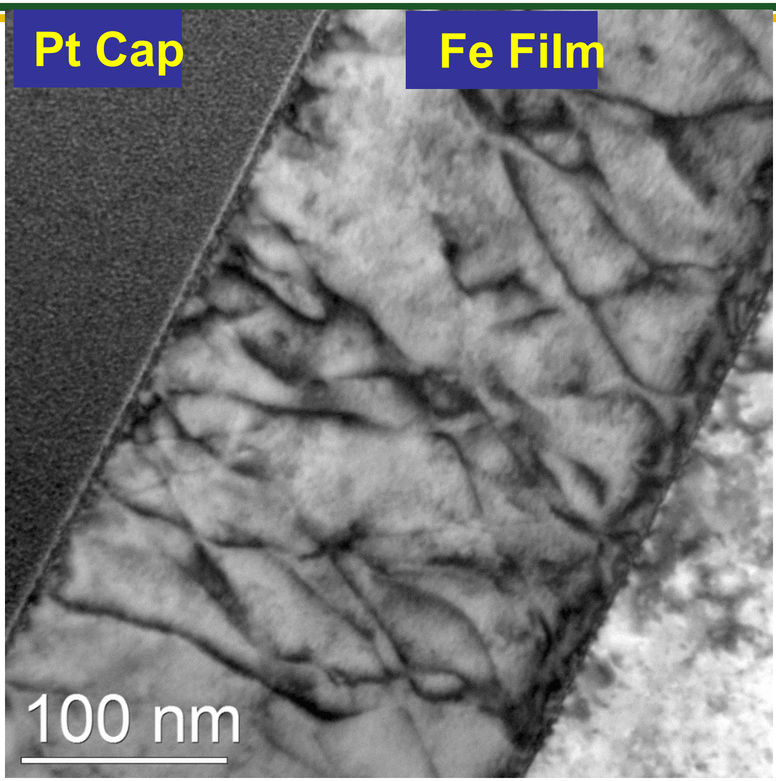




- Fe film was roughly 200 nm thick, ion damage extended up to over a micron past the Fe/MgO interface
- Damage appears uniform in the Fe thin film, but there is considerable differences in the adjacent MgO

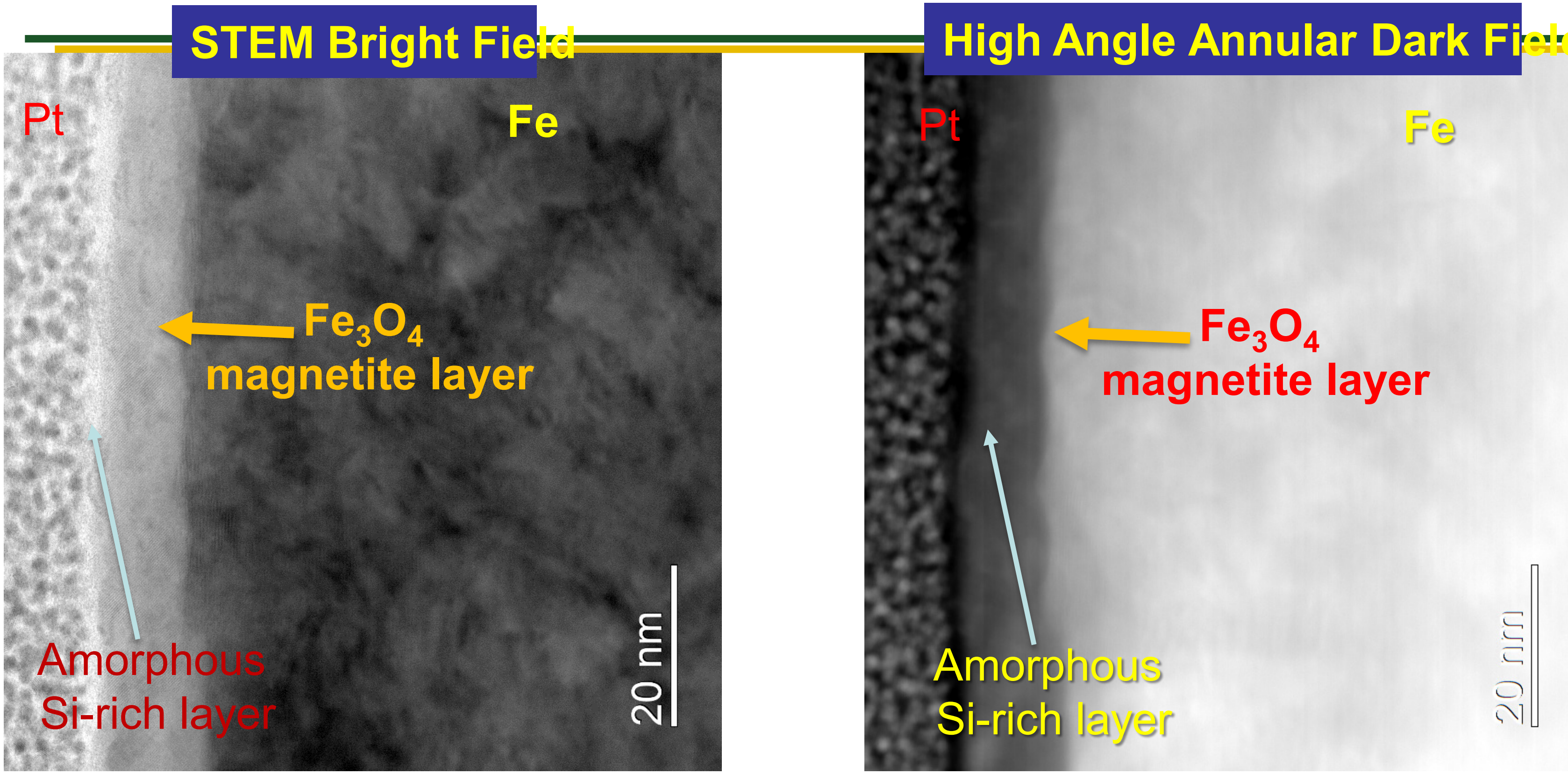
Unirradiated Fe Thin Film: Overview TEM





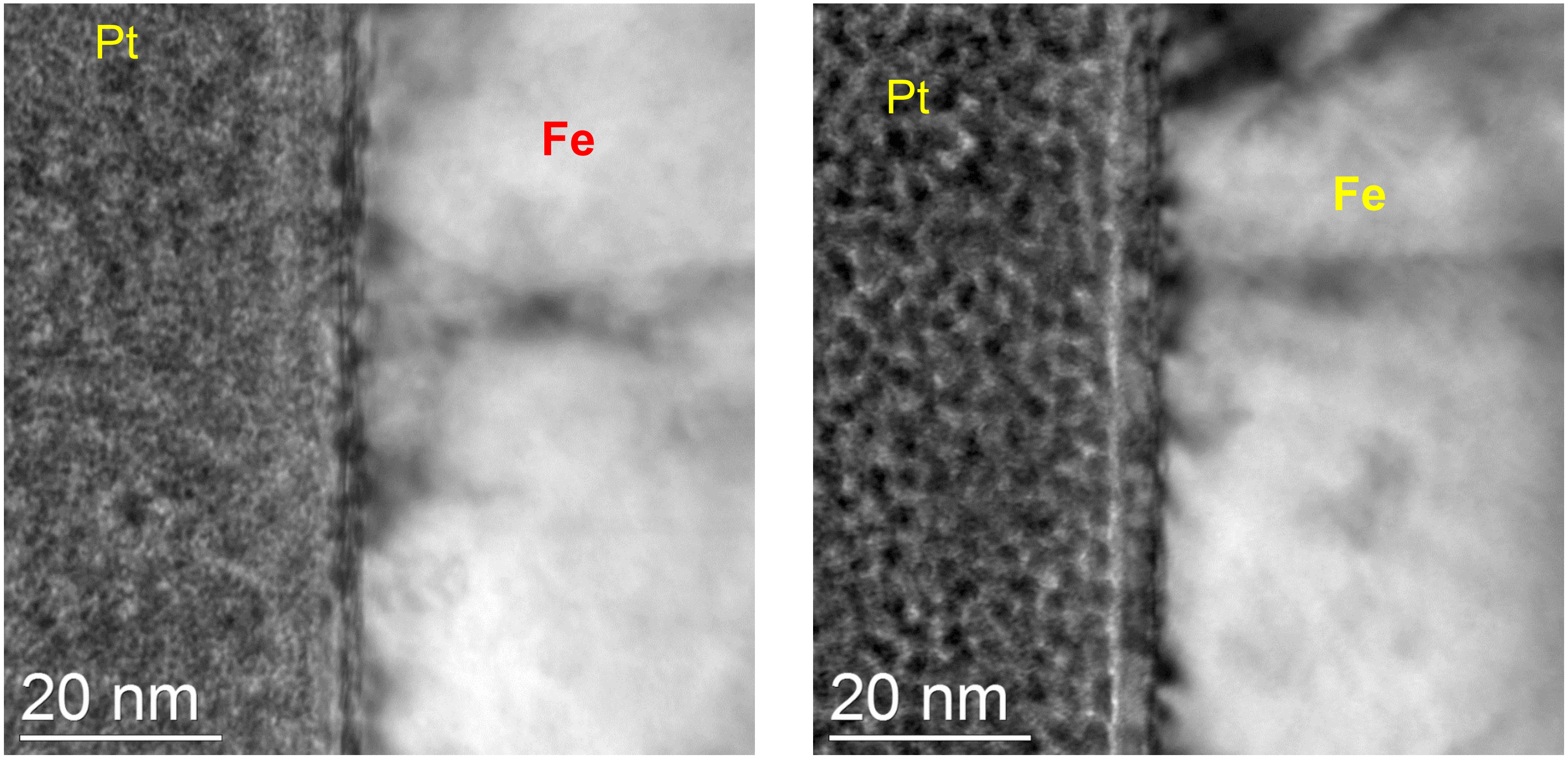
- Fe film was roughly 200 nm thick, line dislocations present throughout the film
- Black spot damage (small dislocation loops/clusters below 5 nm) are present in both the Fe and MgO from FIB damage

Sample F1: Surface of Fe Film



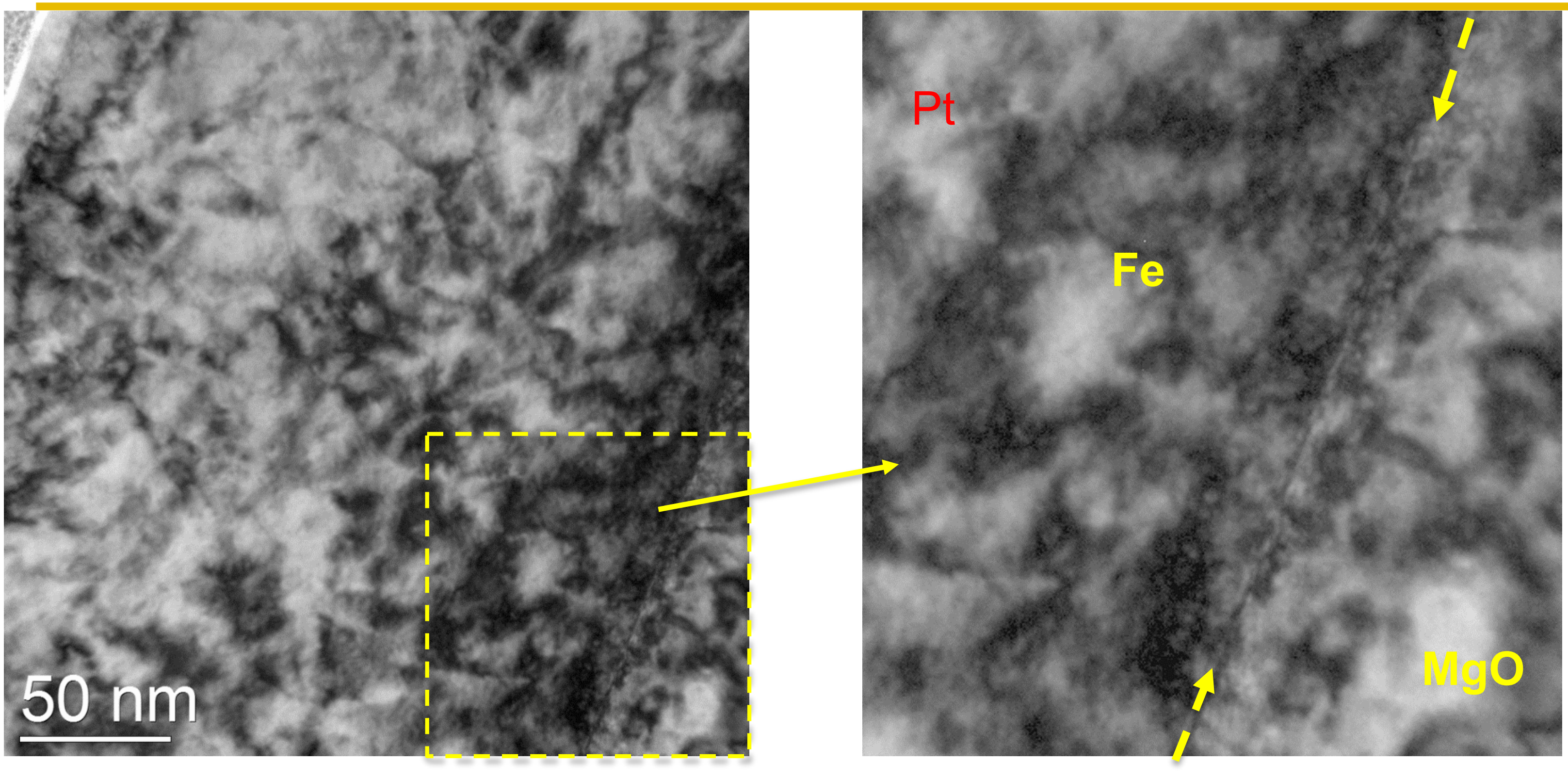
- Top surface of Fe film is mostly intact and protected by the Pt cap deposited during FIB preparation
- Amorphous Si-rich layer still present, only a few nanometers in width
- Fe_3O_4 magnetite film is thicker in this higher dose condition, to 12 nm in some places

Unirradiated Fe Film: Close-up of Surface



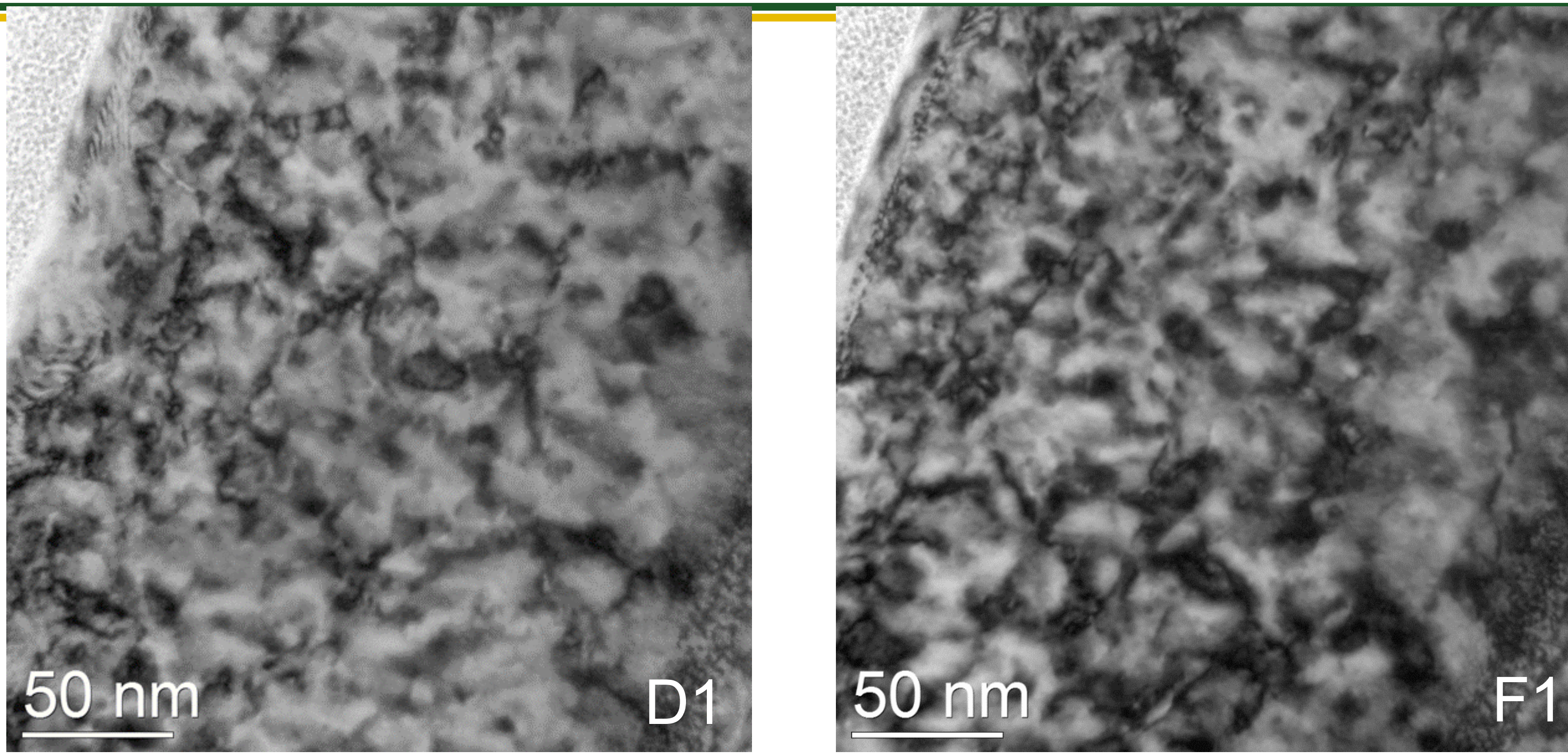
- Surface has a Si-rich layer according to EDS maps
- Magnetite film found in the irradiated samples doesn't appear to be developed as a crystalline phase at this point

Sample F1: Close-up of Damage Region



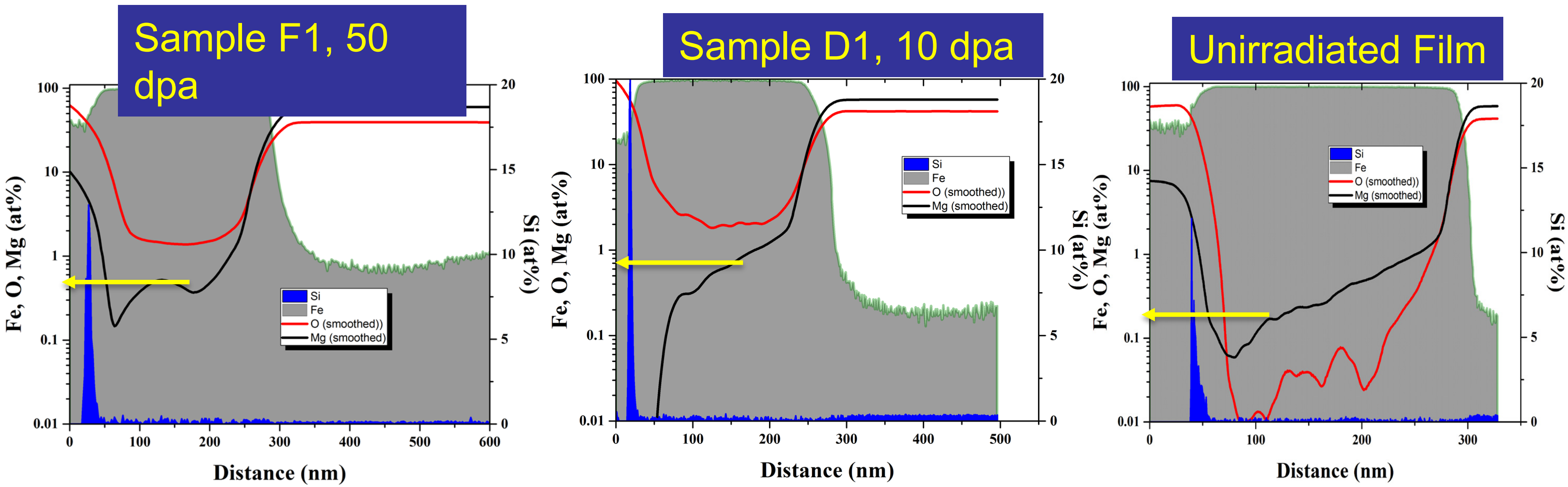
- Interface between the Fe and MgO fairly sharp, but the region is strained based on the changing diffraction contrast

Dislocation Structures



- TEM bright field shows larger loops have formed, line dislocation structure is similar to that observed in the 10 dpa D1 sample
- Loop analysis still ongoing to resolve the effects of irradiation

Compositional Profile Comparison



- Elemental profile shows the Si is still present, perhaps slightly thicker in the F1 sample
- The Mg appears to be present at higher levels in sample F1, indicating Mg ingress into the Fe
  - May be due to flux of defects to the surface, which brings along Mg

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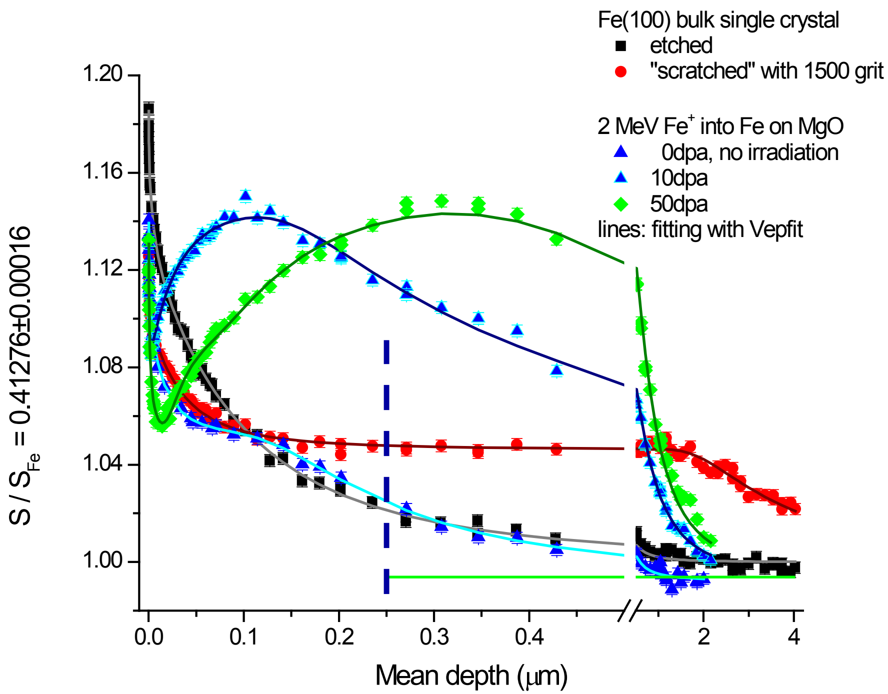
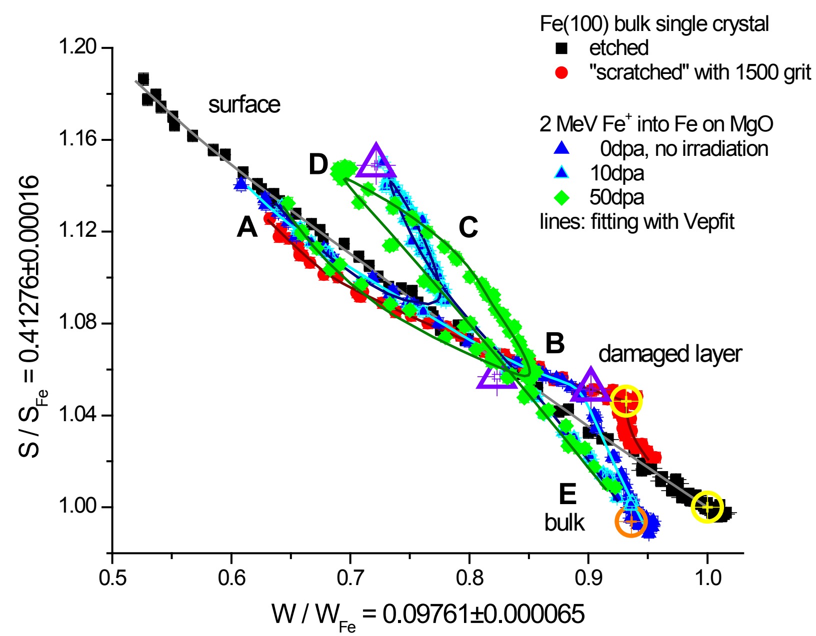
Positron Annihilation



S vs. Mean Depth



S vs. W

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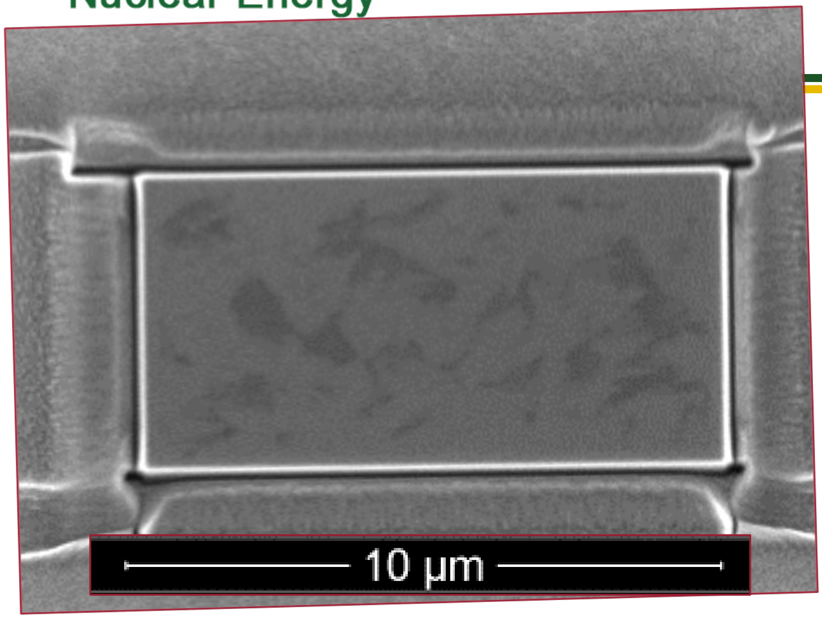
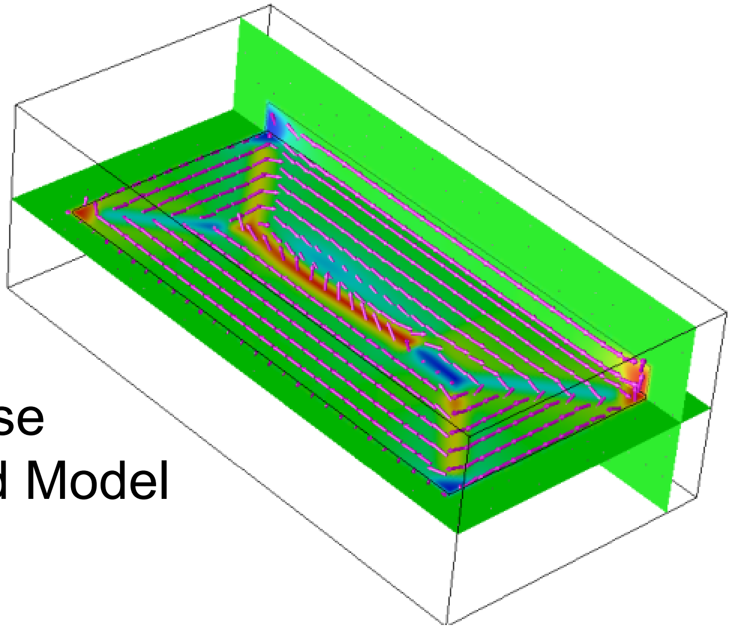
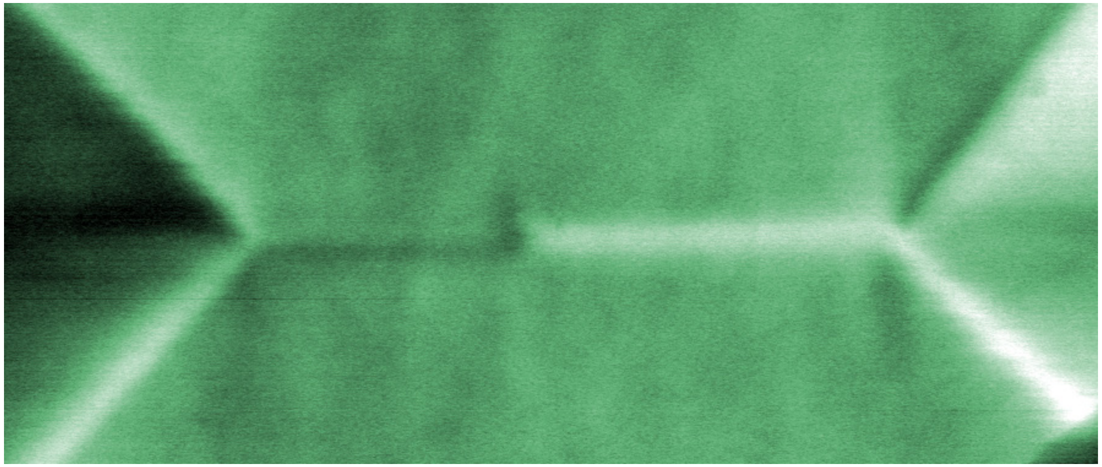
Single Crystal Fe Thin Film FIB Region: SEM, MFM & Modeling Results



SEM Micrograph of FIB region

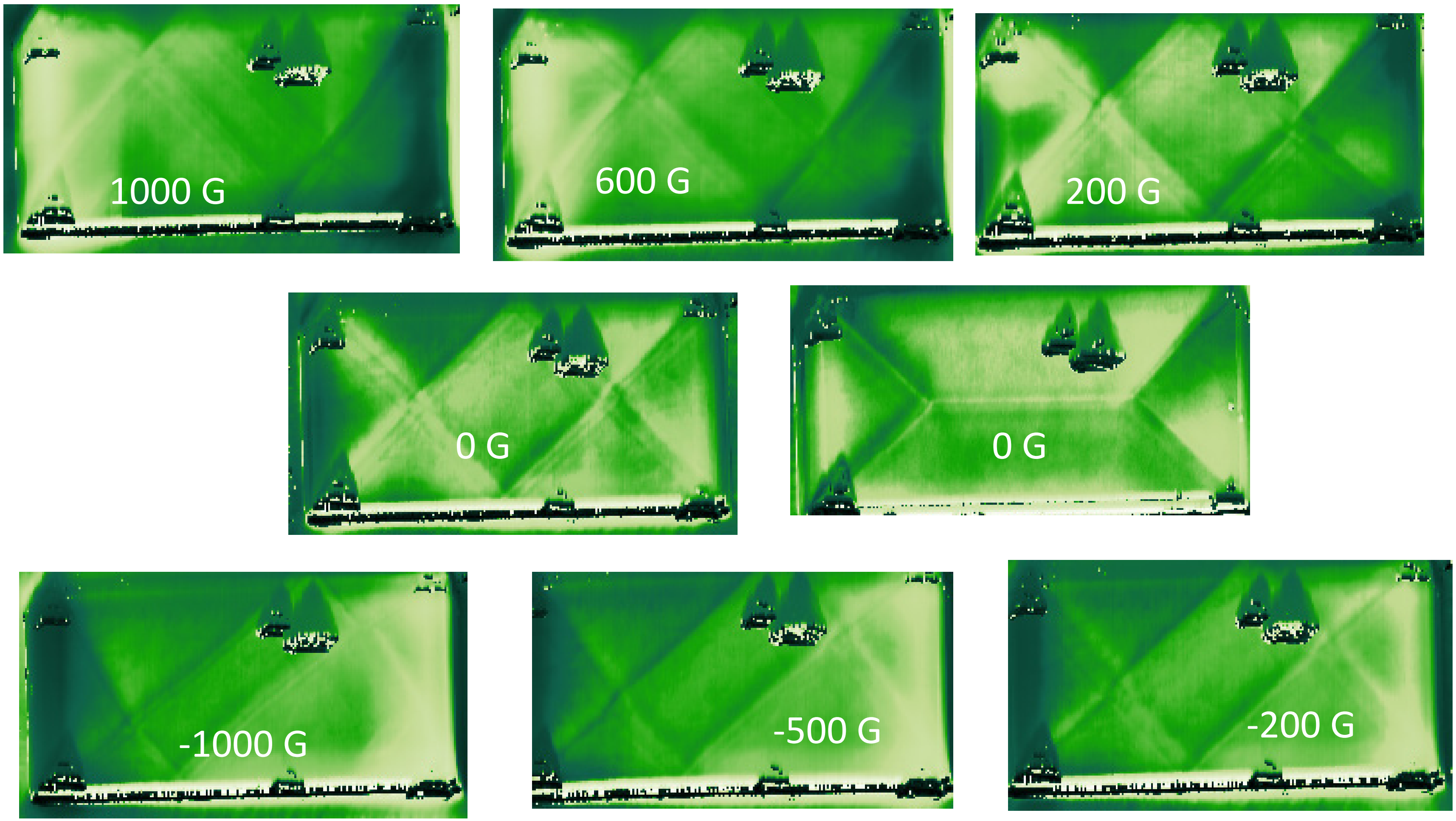


Phase Field Model



MFM of FIB region

Variable field MFM: FIB'd mini-regions



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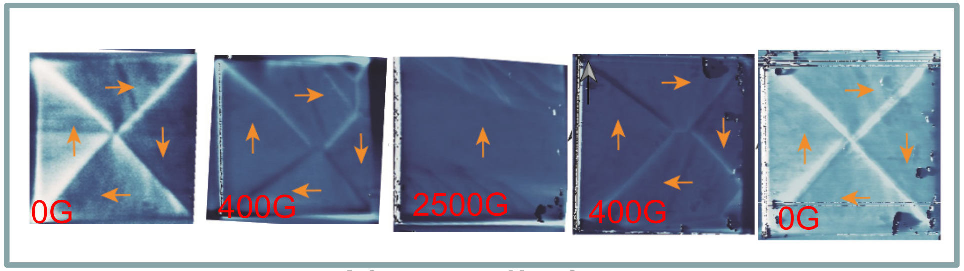
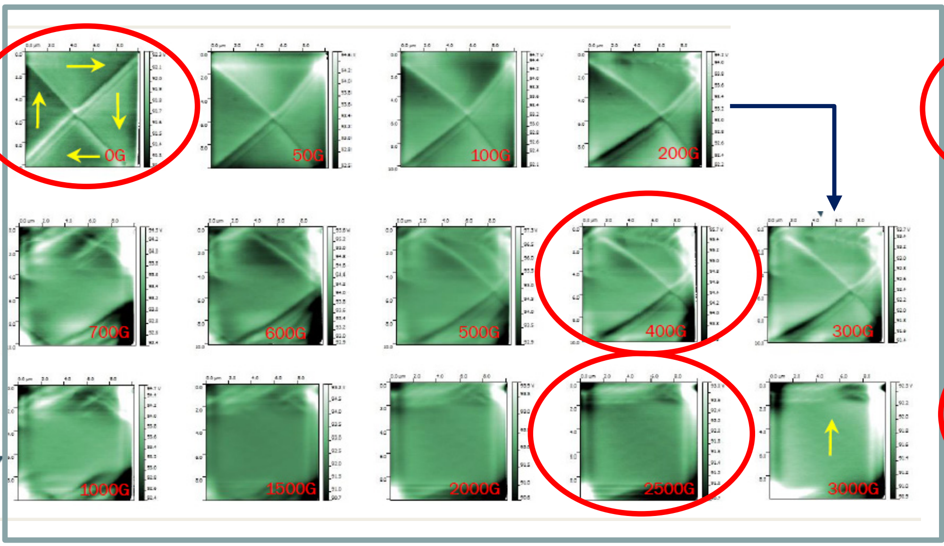
VFM Comparison on FIB structures: Unirradiated vs Irradiated

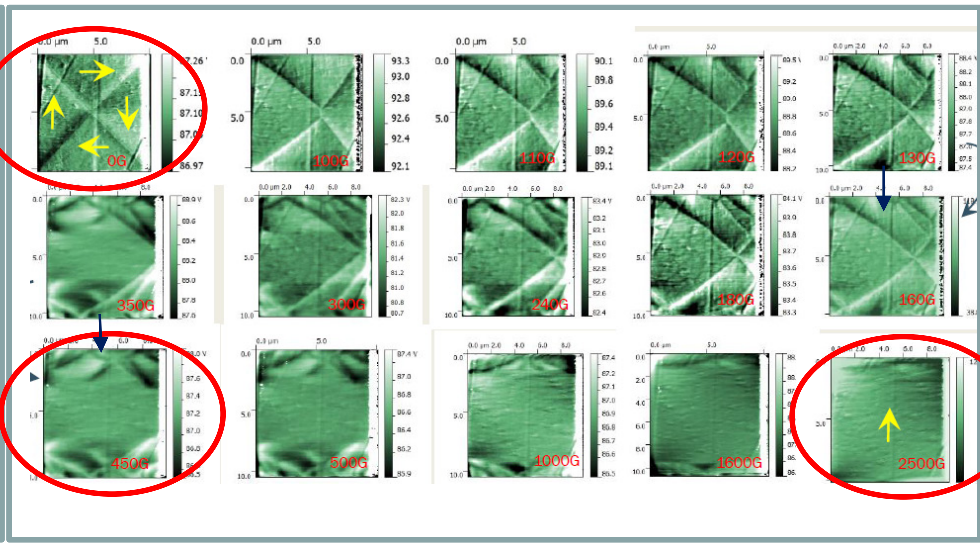
Applied Field Direction



No Irradiation



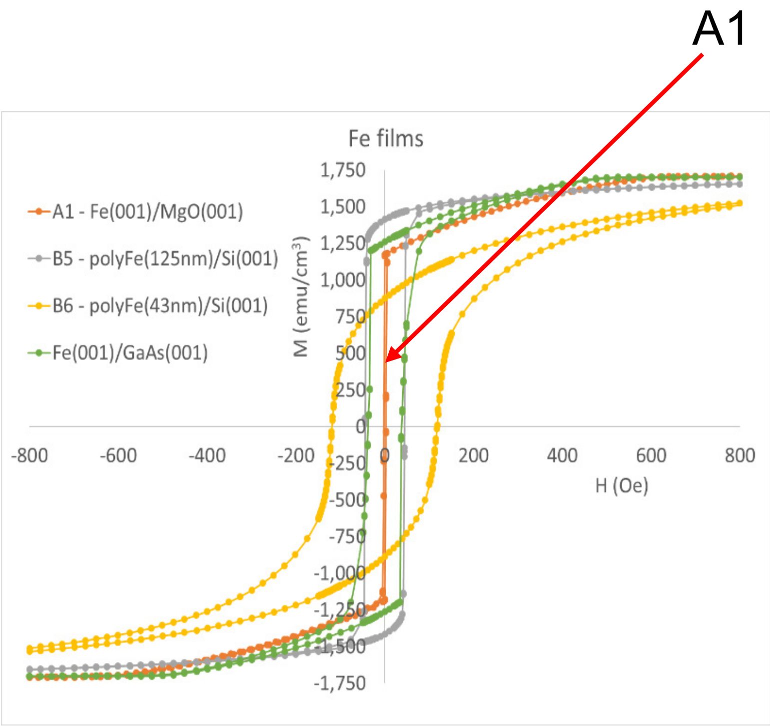
D1

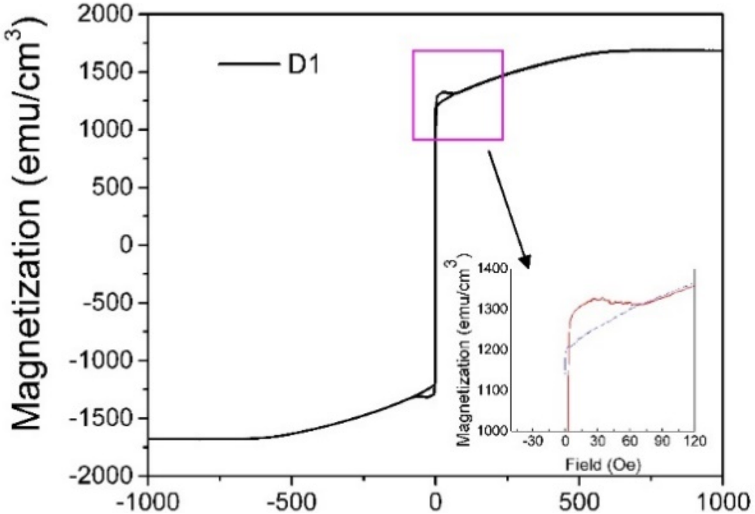


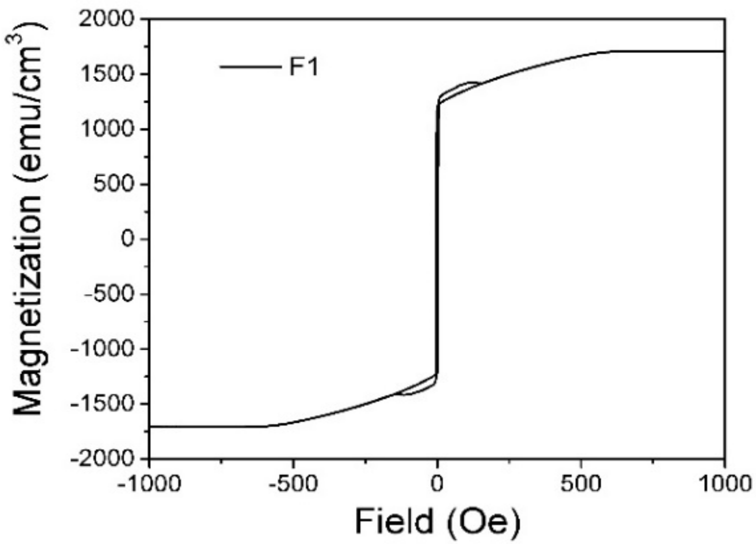
F1

All images are 10 μ x 10 μ

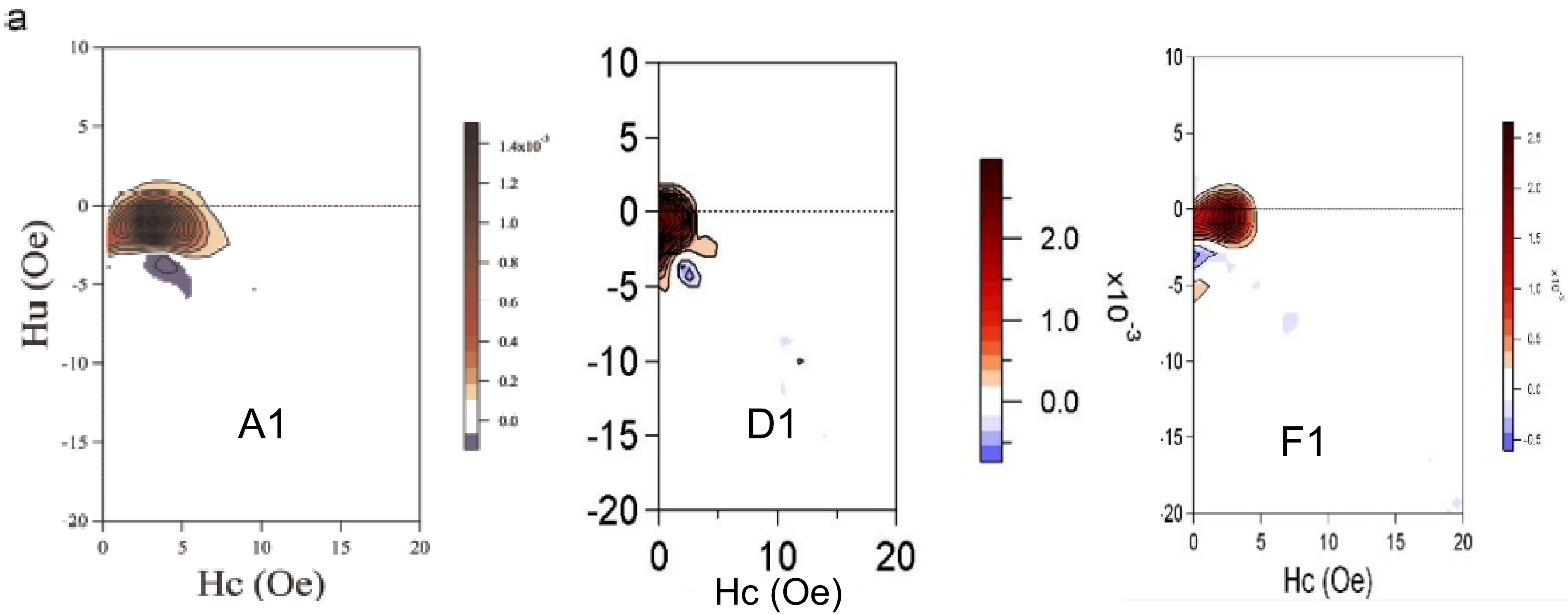
Magnetic Major Loop Analysis



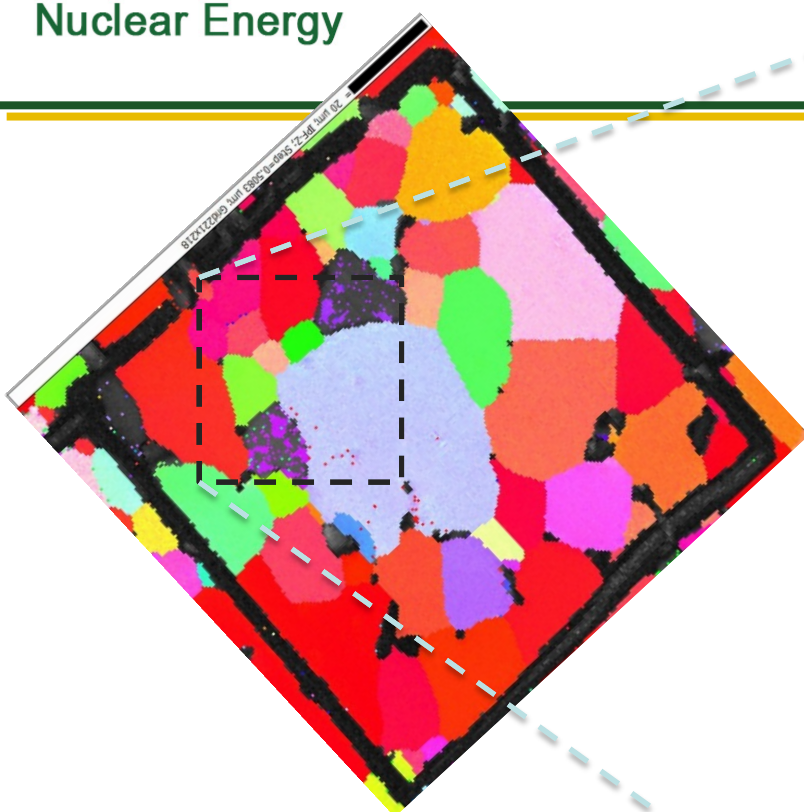




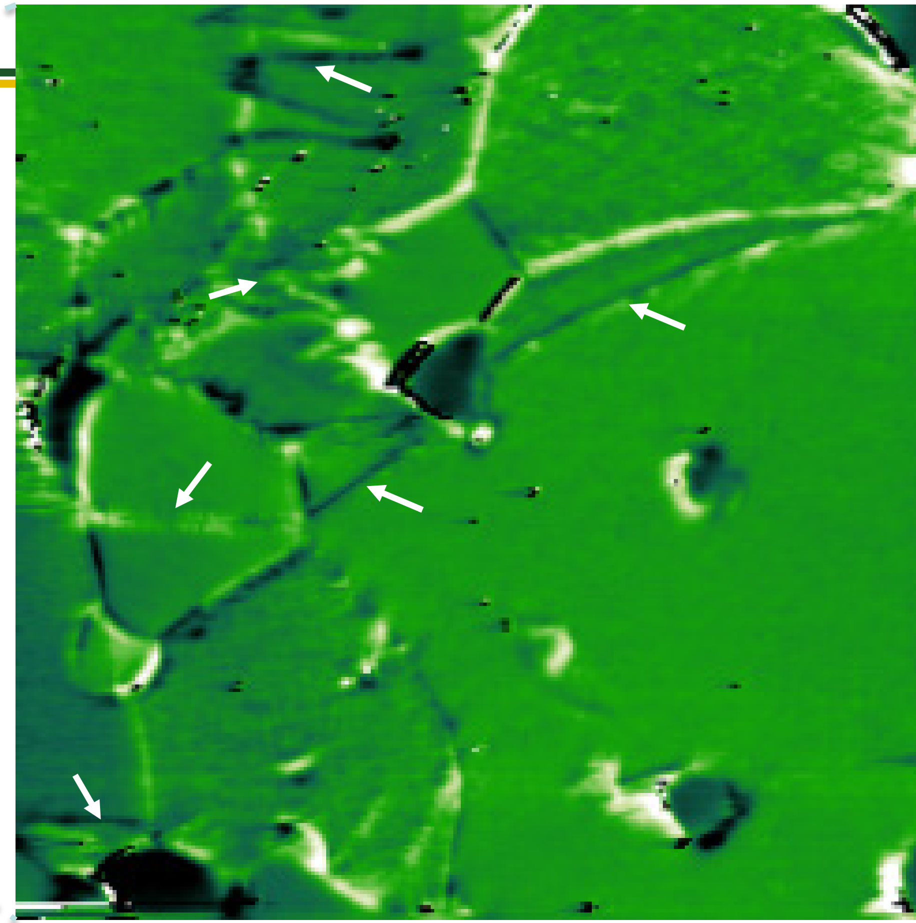
First Order Reversal Curve (FORC) Analysis



MFM Polycrystalline Fe Thin Film



EBSD map



40 x 40 µm MFM scan

Summary of Results

- **Experimental measurements (under unirradiated conditions) provide sufficient data to qualitatively validate phase field models**
  - Domain wall structures and domain wall movement under external fields
- **TEM data**
  - Mg ingress into Fe after irradiation (perhaps due to flux of defects to the surface, which brings along Mg)
  - Larger dislocation loops with irradiation
- **PA data indicate a higher defect density in irradiated specimens**
  - Data show some evidence of annealing, perhaps due to the irradiation conditions selected (room temperature)
- **VFM data show increased domain wall mobility with irradiation**
  - Results appear to show lower coercivity and need to be verified
- **VSM (major loop and FORC) show evidence of changes in magnetic properties**
  - Lower coercivity (which is in line with VFM data), but major loop shape changes
  - Changes in irreversible and reversible components of magnetization with irradiation – analysis ongoing

Key Findings to Date

- **Single crystal Fe, thin film**
  - Dislocation loops and defects affect the magnetic behavior of Fe (FORC, major loop analysis, VFM)
  - Some of the results need additional analysis
  - Ingress of Mg into the film with irradiation unexpected and its impact on magnetic behavior not fully accounted for
- **Polycrystalline Fe, thin film**
  - Grain boundaries play a role in magnetic behavior, may restrict domain wall movement
- **Fe-1% Cu (data not shown), bulk alloy**
  - Non-magnetic precipitates (from thermal treatment) show clear evidence of affecting FORC and MBN
  - Precipitate size and number density impact hardness of material (as measured by Vickers' hardness)
- ***Collectively, these data indicate a clear potential for using magnetic measurements at the bulk scale to quantify mechanical property changes due to embrittlement***

Summary

- **Micromagnetic measurements may provide a valuable tool to quantify level of damage in neutron-irradiated steels**
  - Improved understanding of **microstructure**, **damage**, and **magnetic** behavior required to develop quantitative tools, when coupled with advanced materials characterization tools
- **Meso-scale models can help explain physics of magnetic measurements in irradiated materials and provide bridge**
  - Effects of defects, finite thickness on domain wall movement
  - Impact on magnetic Barkhausen noise (MBN)
  - Model verification (& improvement) through coupling
    - Magnetic imaging
    - Meso-scale measurements

Next Steps

- **Complete analysis of bulk and meso-scale magnetic measurements**
  - Thin films and bulk alloys
- **Relationships between bulk and meso-scale magnetic measurements**
  - FORC and magnetic loop analysis
- **Apply meso-scale models to quantify impact of irradiation damage in model systems (thin films, Fe-1%Cu) and complex alloys on bulk magnetic measurements (VSM, MBN)**

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  - Tim Droubay
- WSU
  - David Field

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- Some of this research was partially supported under the **Laboratory-Directed Research and Development** program at PNNL. A portion of this work was supported by the **Sustainable Nuclear Power Initiative at PNNL.**
- Magnetometer was purchased as start-up incentive by the state of Washington for Prof. McCloy's research
- Current work is supported at WSU and PNNL by **DOE-Nuclear Energy Enabling Technology (NEET)** under the Reactor Materials technical area.

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Extra Slides

Background and Motivation

stresstechgroup.com

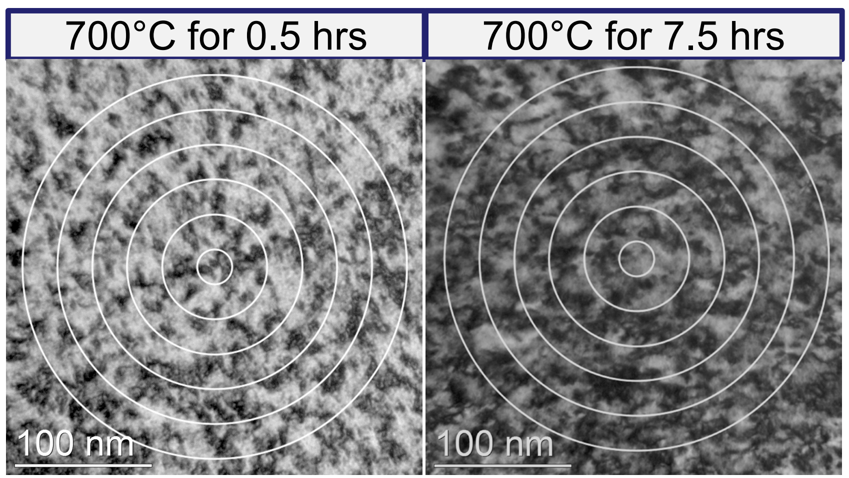
Irradiation & Temperature induce defects and microstructural changes.[1]

Microstructures of nuclear steel shows different magnetic signals [1].

Fe-1wt%Cu

BCC 9R FCC

Temperature/Irradiation

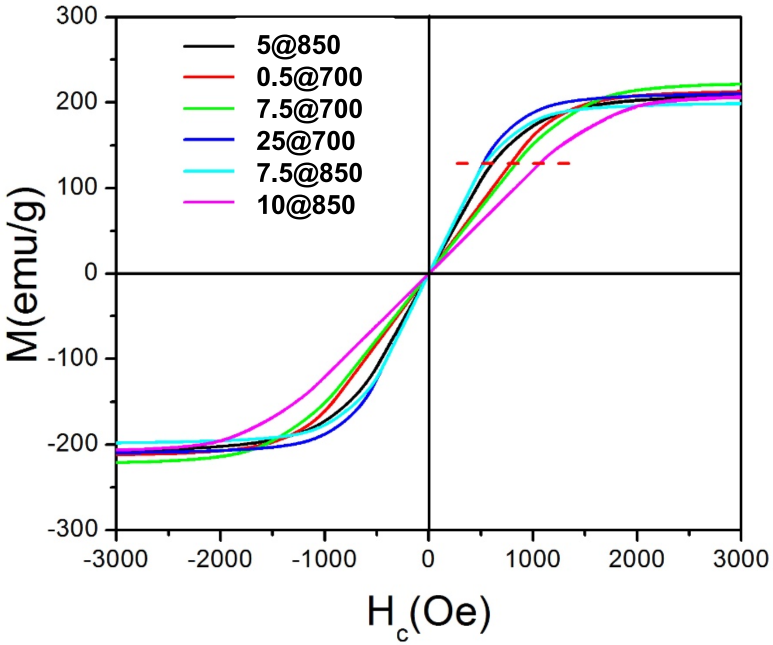


Dislocations?

TEM showing dislocations of Fe-1wt%Cu aged for different times

Measurements

- Vickers Microhardness
- Vibrating Sample Magnetometer (VSM)
  - Major Hysteresis loop
    - Coercivity (H_{cm})
    - Saturation M_s ~ 210 emu/g
- Transmission Electron Microscopy
  - Dislocation Structure and Density (~$10^{15}/m^3$)
  - Copper Precipitates Size and Number Density
- Magnetic Barkhausen Noise (MBN)

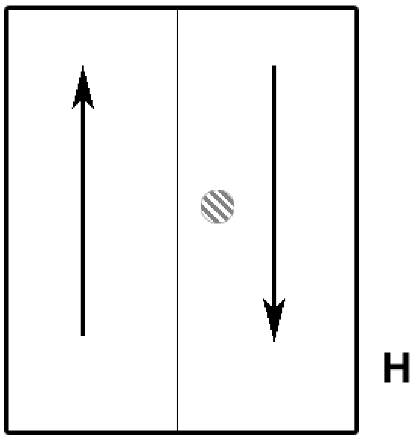


Sample	Heat treatment	Hardness (HV)	H_{cm} (Oe)	Copper precipitates average Diameter (nm)	Copper precipitates number density (×$10^{20}/m^3$)
5@850	5 h @ 850° C	104.5	1.109	0	0
7.5@850	7.5 h @ 850° C	103.4	1.098	0	0
10@850	10 h @ 850° C	105.8	1.032	0	0
0.5@700	5 h @ 850° C, 0.5 h @700° C	125.7 ↑	1.205 ↑	17.1 ↑	48 ↑
7.5@700	5 h @ 850° C, 7.5 h @700° C	104.1 ↓	1.164 ↓	37.2 ↑	2.9 ↓
25@700	5 h @ 850° C, 25 h @700° C	91.1 ↓	1.082 ↓	105.4 ↑	0.71 ↓

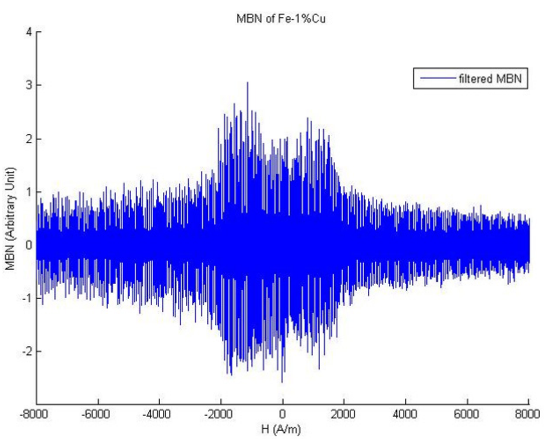
****The arrows indicate the changes compared to 5@850****

Magnetic Barkhausen Noise (MBN)

Theory



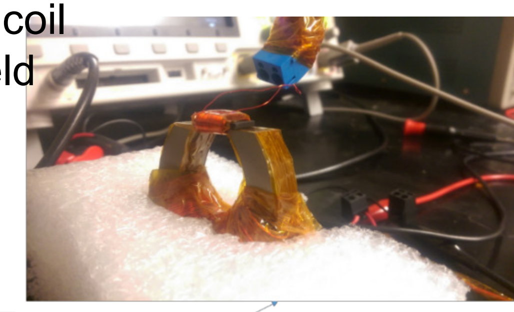
http://en.wikipedia.org/wiki/Barkhausen_effect

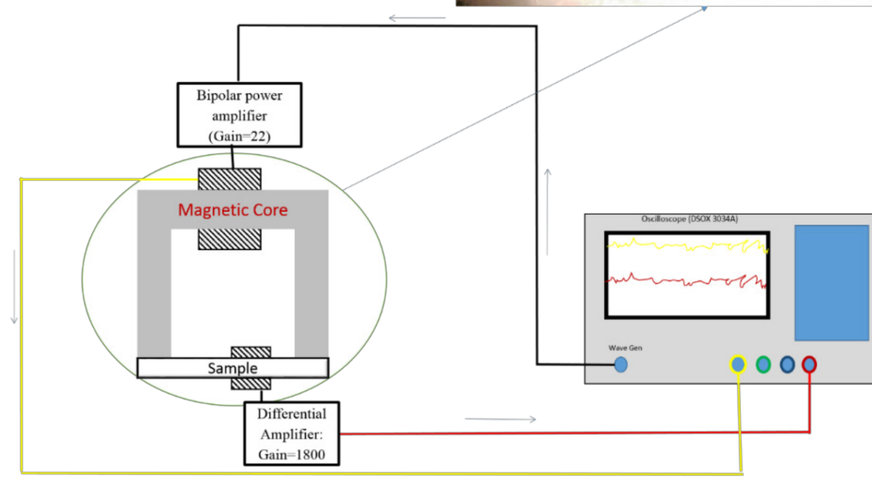


MBN Set-Up

MBN Measurement Parameters:

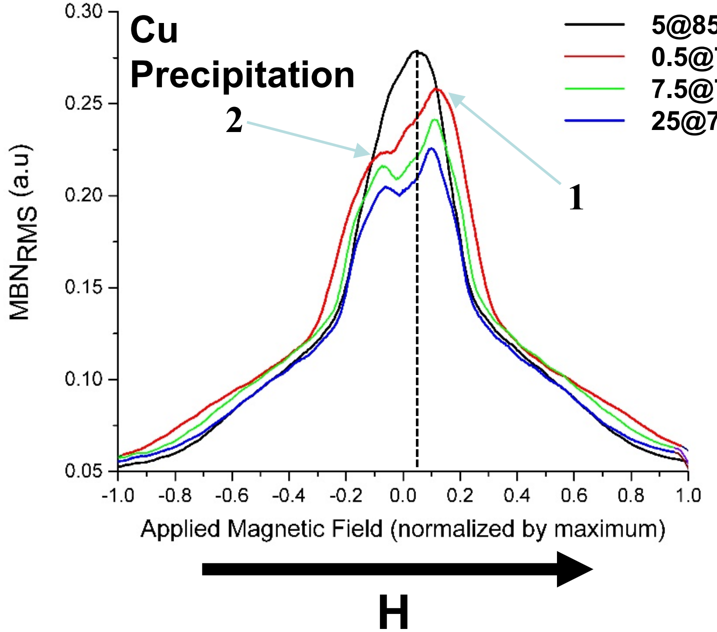
- Applied Field:
  - Triangular signal
  - ±2A Current to 500 turns coil
    - ±230 Oe magnetic field
  - 0.5Hz frequency



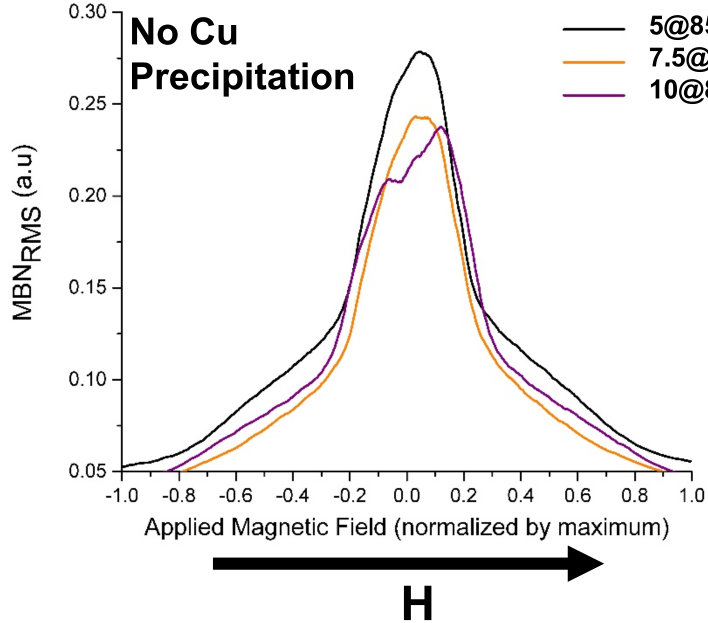


MBN Results

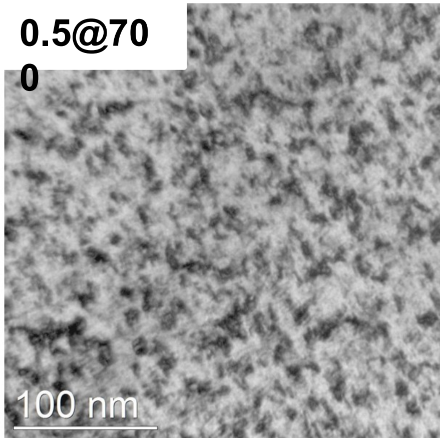
MBN RMS Envelope as a function of Applied Field

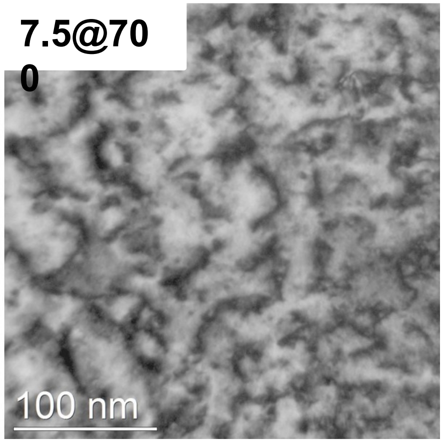


MBN RMS Envelope as a function of Applied Field



Sample	Cu precipitates average Diameter (nm)	Cu precipitates number density (×10²⁰/m³)
5@850	0	0
0.5@700	17.1 ↑	48 ↑
7.5@700	37.2 ↑	2.9 ↓
25@700	105.4 ↑	0.71 ↓





The arrows indicate the changes compared to 5@850

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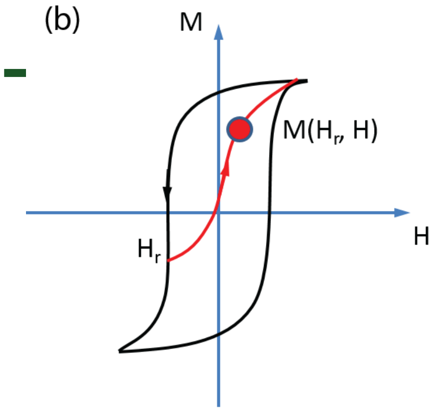
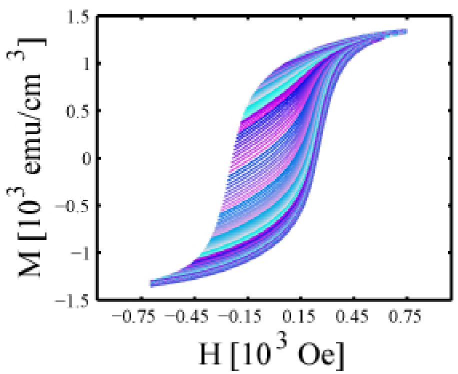
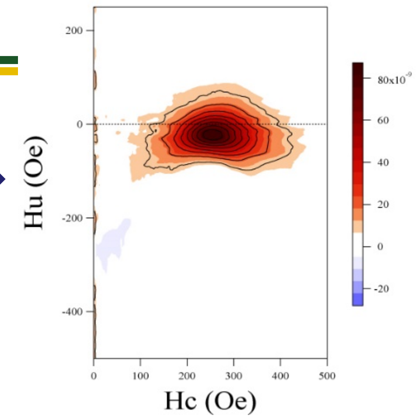
First order reversal curve (FORC)

FORC diagram of Fe thin film







FORC distribution density: $\rho(H_r, H) = -\frac{1}{2}\frac{\partial^2 M(H_r,H)}{\partial H_r \partial H}$

$$H_c = \frac{H - H_r}{2} \qquad H_u = \frac{H + H_r}{2}$$

Pike, et. al. (2000). J. Appl. Geophys 105(B12), 28461-28475.

Applications:

- Switching field distribution of magnetic (magnetic recording media)
- Magnetic phase identification and quantitative analysis
- Size distribution of magnetic particles
- Magnetic interaction analysis
- Reversible and irreversible magnetization
- Preisach model

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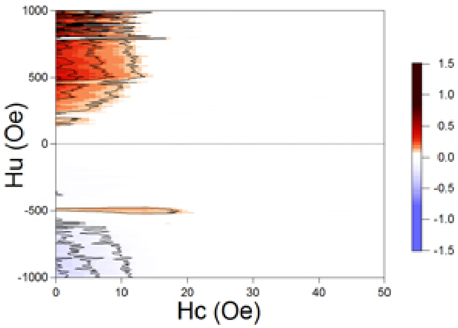
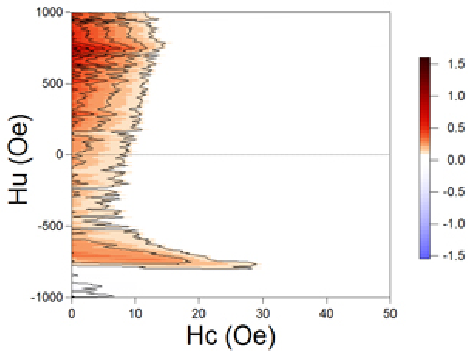
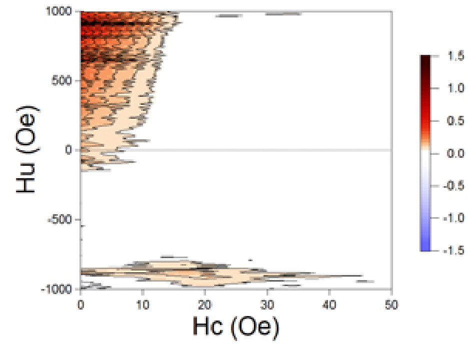
FORC of Fe-1%wt. Cu



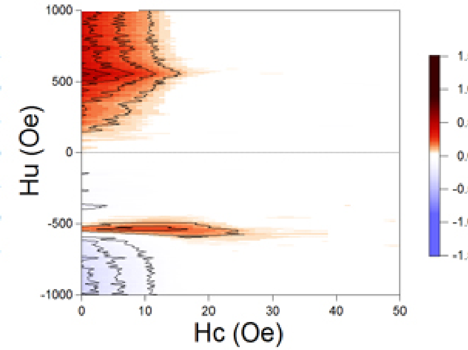
5@850



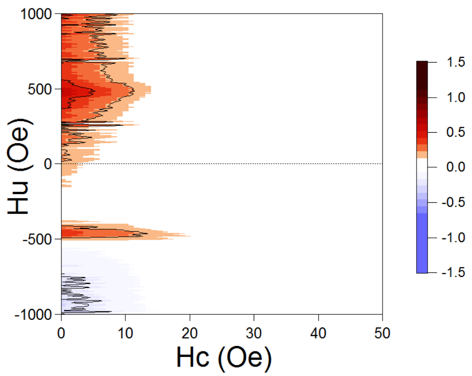
0.5@700



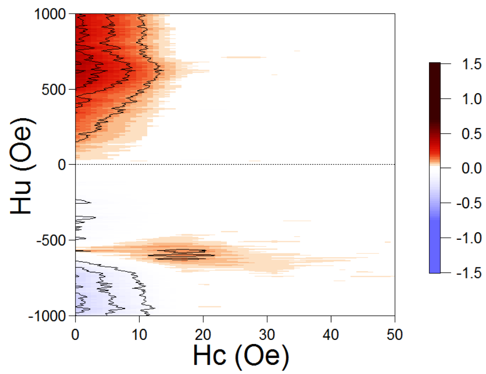
7.5@700



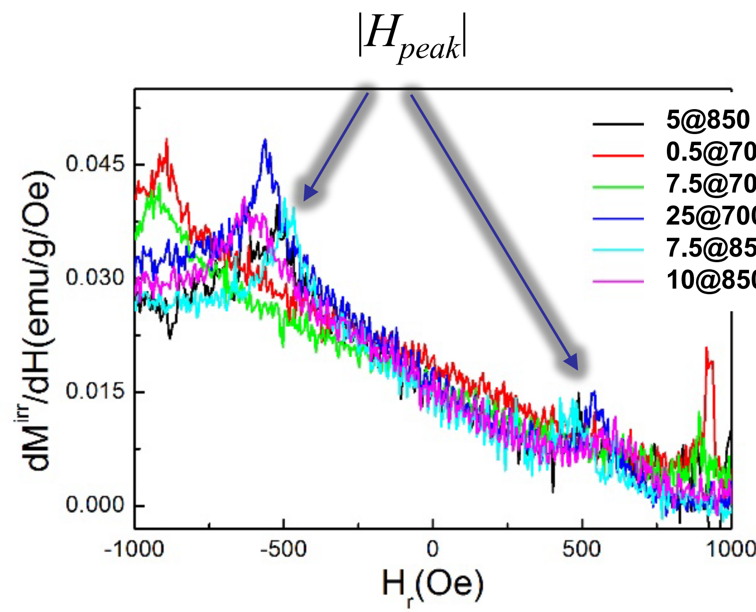
25@700



7.5@850



10@850



Irreverible

$$dM(H_r) = dM^{irr}(H_r) + dM^{rev}(H_r)$$

$$dM^{irr}(H_r)/dH = \lim_{H\to H_r} [M(H) - M(H_r, H)]/dH$$

$$dM^{rev}(H_r)/dH = \lim_{H\to H_r} [M(H_r, H) - M(H_r)]/dH$$

$$|H_{pos}| = |H_{neg}| = |H_{peak}|$$

M. Winklhofer, et, al.J. Appl. Phys. 103, 07C518 (2008).

Conclusion

- Cu precipitates
  - The H_{cm} and hardness increase, then decrease with further aging time.
  - The MBN_{RMS} keeps decreasing, and H_{RMS} is positively correlated with H_{cm} and hardness.
  - The mechanically harder sample has larger $|H_{peak}|$ in irreversible magnetization.
- No Cu precipitates
  - The H_{cm} and hardness of 5@850, 7.5@850 and 10@850 are similar.
  - The MBN_{RMS} is decreasing
  - The sample which has heat treated with longer time has a larger $|H_{peak}|$.

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