



光電子顕微鏡でこんなことができる

鉄隕石の構造解析から金属材料への今後の展開

Principle

Application

百聞は一顕にしかず

財団法人 高輝度光科学研究センター
はやぶさサンプル初期分析チーム
JST-CREST

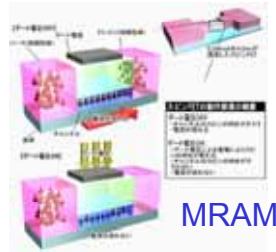
小嗣 真人 (Kotsugi Masato)

背景

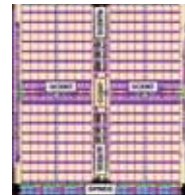
低炭素化社会へむけた材料開発が盛んに行われている

材料大国日本

スピントロニクス
MRAM
半導体
High-kゲート酸化膜
ReRAM
有機薄膜
カーボンナノチューブ
グラフェン
二次電池
触媒
鉄鋼材料
生体材料
土壌
隕石



MRAM



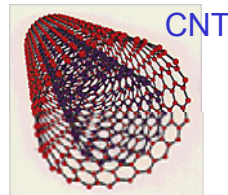
ReRAM



ハイブリッドカー



永久磁石



CNT



隕石



Li-ion電池



触媒

ナノスケールの状態分析

機能の解明

基礎科学から産業利用まで

PEEM

数十nmの分解能
表面/界面/バルク
時間分解測定

シーズ

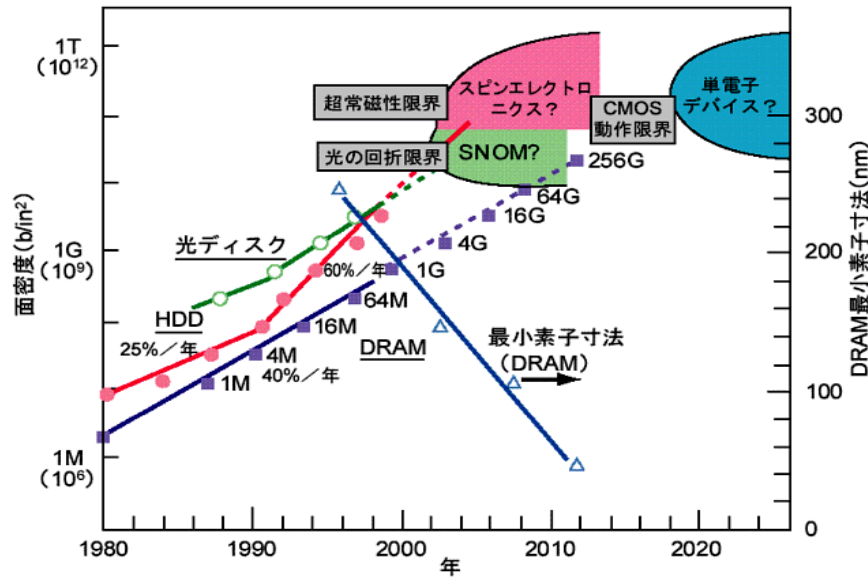
材料科学

各種ナノ材料のキャラクタリゼーション
省資源・省エネルギー
超高速動作

ニーズ

→ グリーンナノテクノロジーへの貢献

Rapid increase of areal density in electro-devices



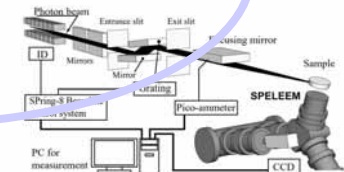
Scanning electron microscope

Spatial information
(several tens nm)



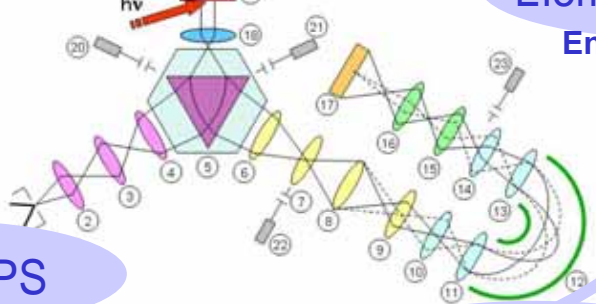
Synchrotron radiation

energy tunability
polarity
pulse



Magnetic imaging

MCD·MLD



Element specific
Energy tunability

Local XPS

dynamics
Time resolving

We can get these information directly

Microscopy + Spectroscopy

Seeing

knowing

Nanospectroscopy

ノーベル物理学賞
2007



Prof. Peter Grünberg

ノーベル化学賞
2007



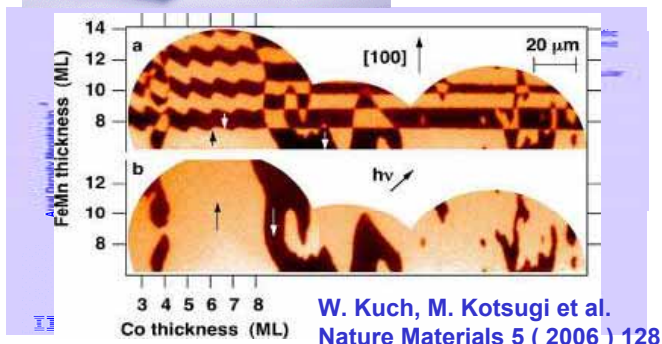
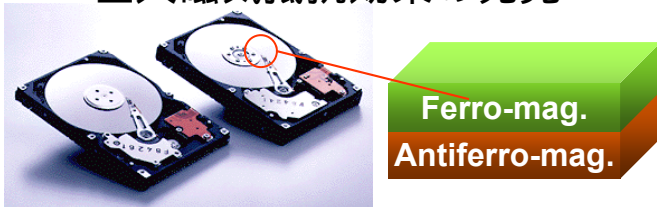
Prof. Gerhard Ertl

ノーベル物理学賞
2010

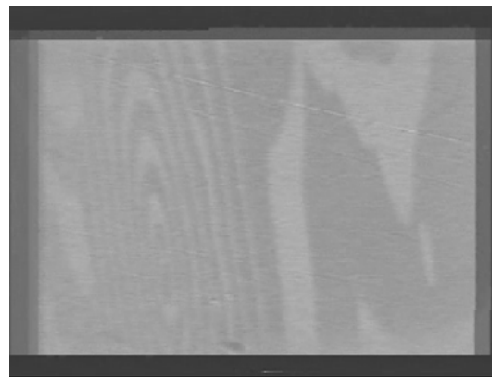


Prof. Andre Geim

巨大磁気抵抗効果の発見

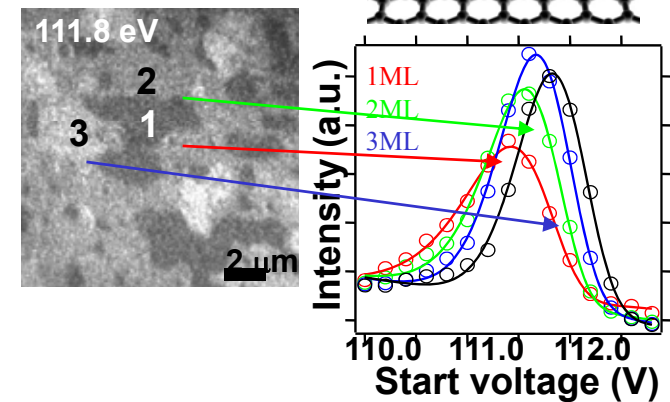
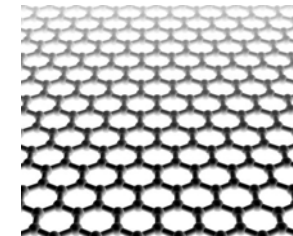


プラチナの触媒効果



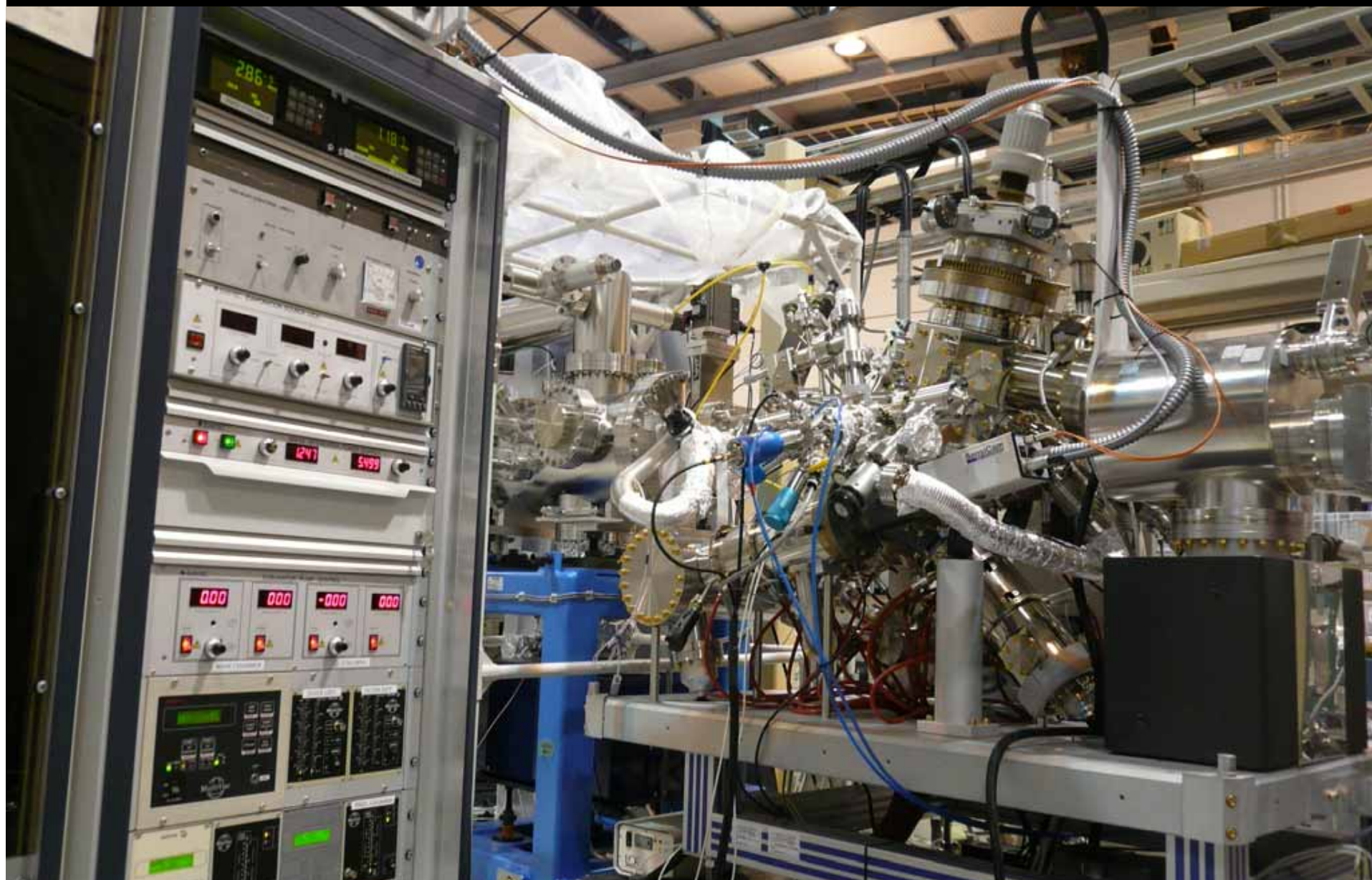
J. Chem. Phys. 98, 9977 (1993)

グラフェン



Phys. Rev. B 79 (2009) 125437

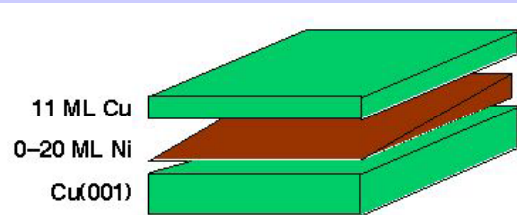
SPELEEM @ SPring-8 BL17SU



Tool for nanotechnology and related research field(s)

光電子顕微鏡(PEEM)の原理

磁性試料

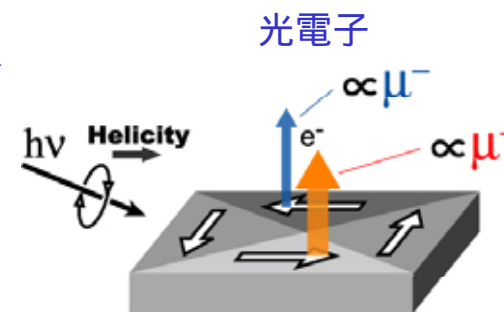
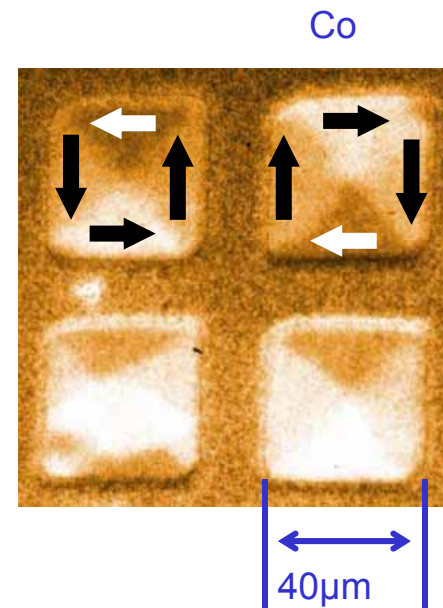
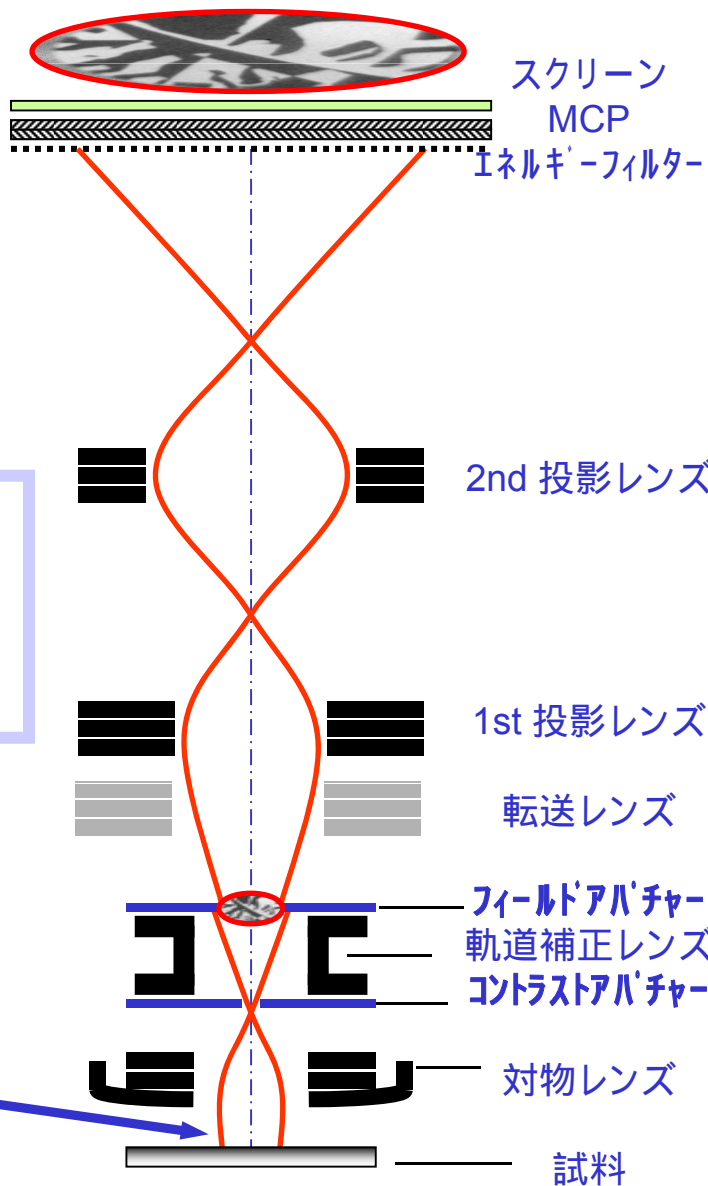


例) 磁性多層膜

磁区構造観察
 元素選択性
 画素毎のモーメントの議論
 表面界面の磁性

(円偏光)放射光

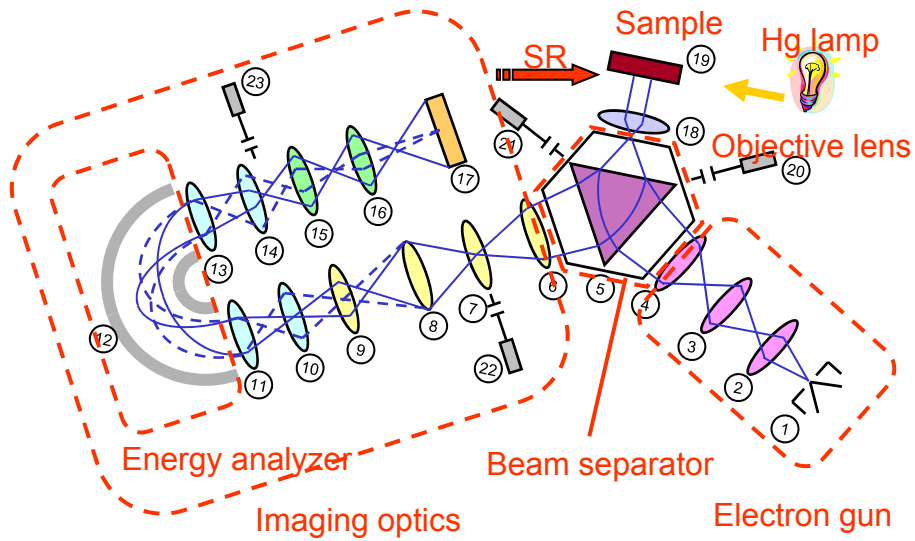
フォトン спин
 $\sigma^+ \sigma^-$



光電子の空間分布を測定する電子顕微鏡

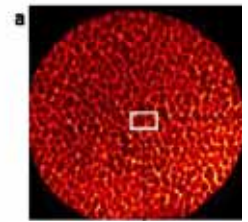
SPELEEM by Elmitec

BL scientists: M. Kotsugi and T. Ohkouchi



3 imaging mode
3 light source
High spatial resolution

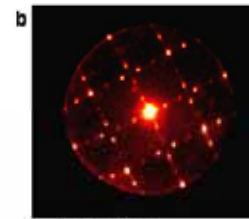
Imaging mode



FeO mirror image



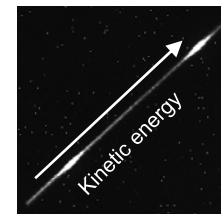
LEED mode



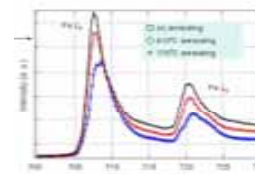
FeO LEED



Dispersion mode



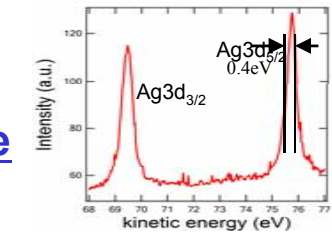
Ag/Si(111) $h\nu$: 530eV



NanoXAFS

Real space
Elemental mapping
Chemical mapping
Topology

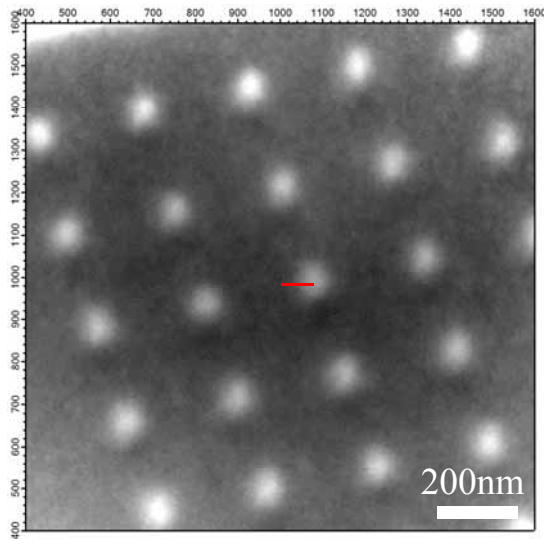
Reciprocal space
LEED pattern
 k -space mapping



Local XPS
Electronic state

Improvement in lateral resolution of SPELEEM

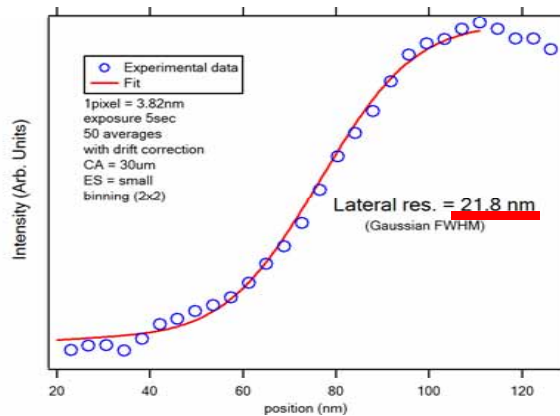
PEEM



Co₈₀Pt₂₀ nano dots
Width 50nm
Spacing 200nm
EB lithography

hν = 778.44eV
Field of view = 2μm
STV = 0 V

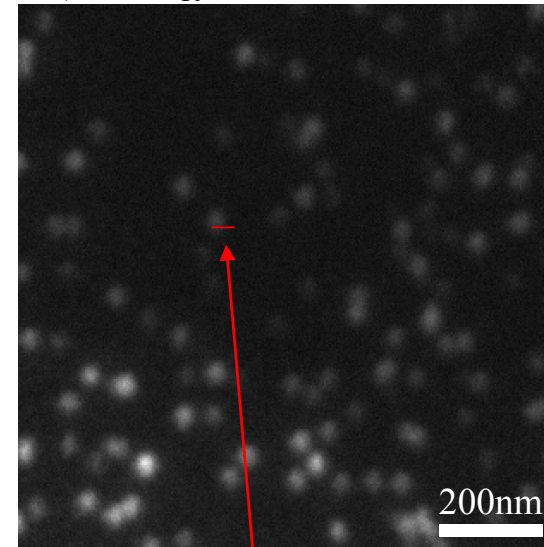
Magnetic domain investigation on CoPt dot using MCD-PEEM (Appl. No.:2008A1681)
Y. Kondo, T. Chiba, K. Taguchi (AIT), M. Kotsugi (SPring-8/JASRI)



Lateral resolution 85nm → 22nm

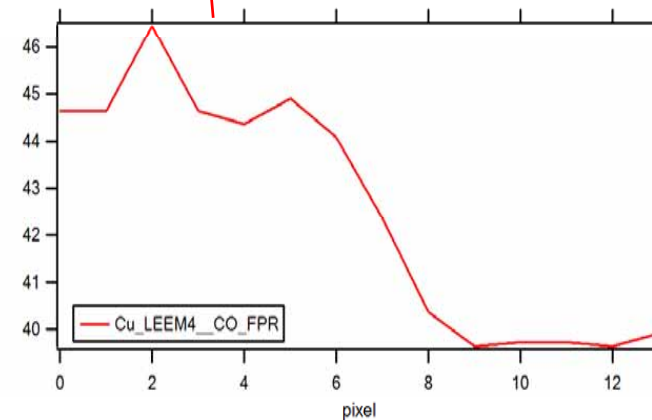
LEEM

(low energy electron emission microscopy)



Pb/Cu(111)
nano dots

FOV=1.86μm
STV=7.67V



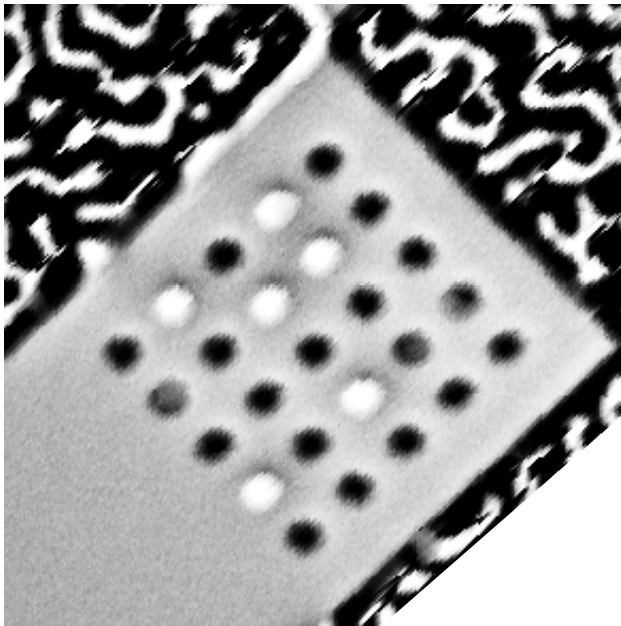
Lateral resolution : 7.6nm

Magnetic domain images of CoPt nanodots

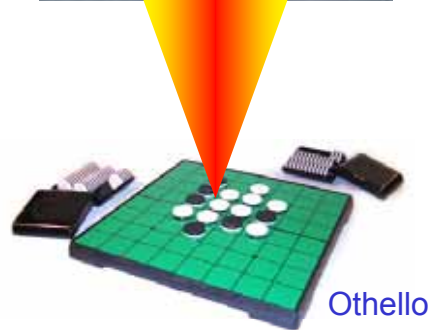
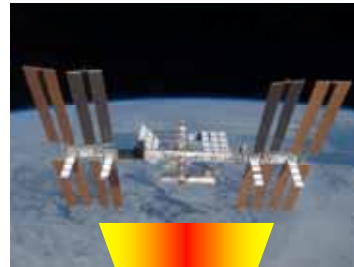
Magnetic domain investigation on CoPt dot using MCD-PEEM (Appl. No.: 2008A1681)
Y. Kondo, T. Chiba, K. Taguchi (AIT), M. Kotsugi (SPring-8/JASRI)

Dot width 100nm

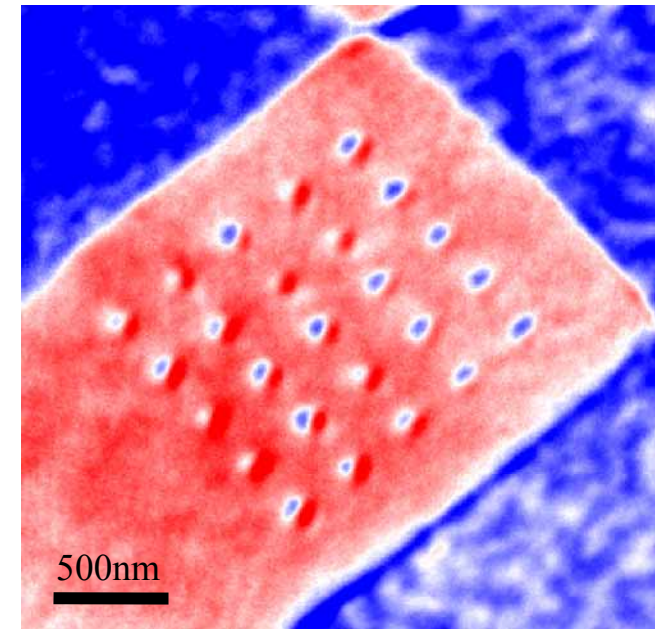
MFM



International Space station (ISS)

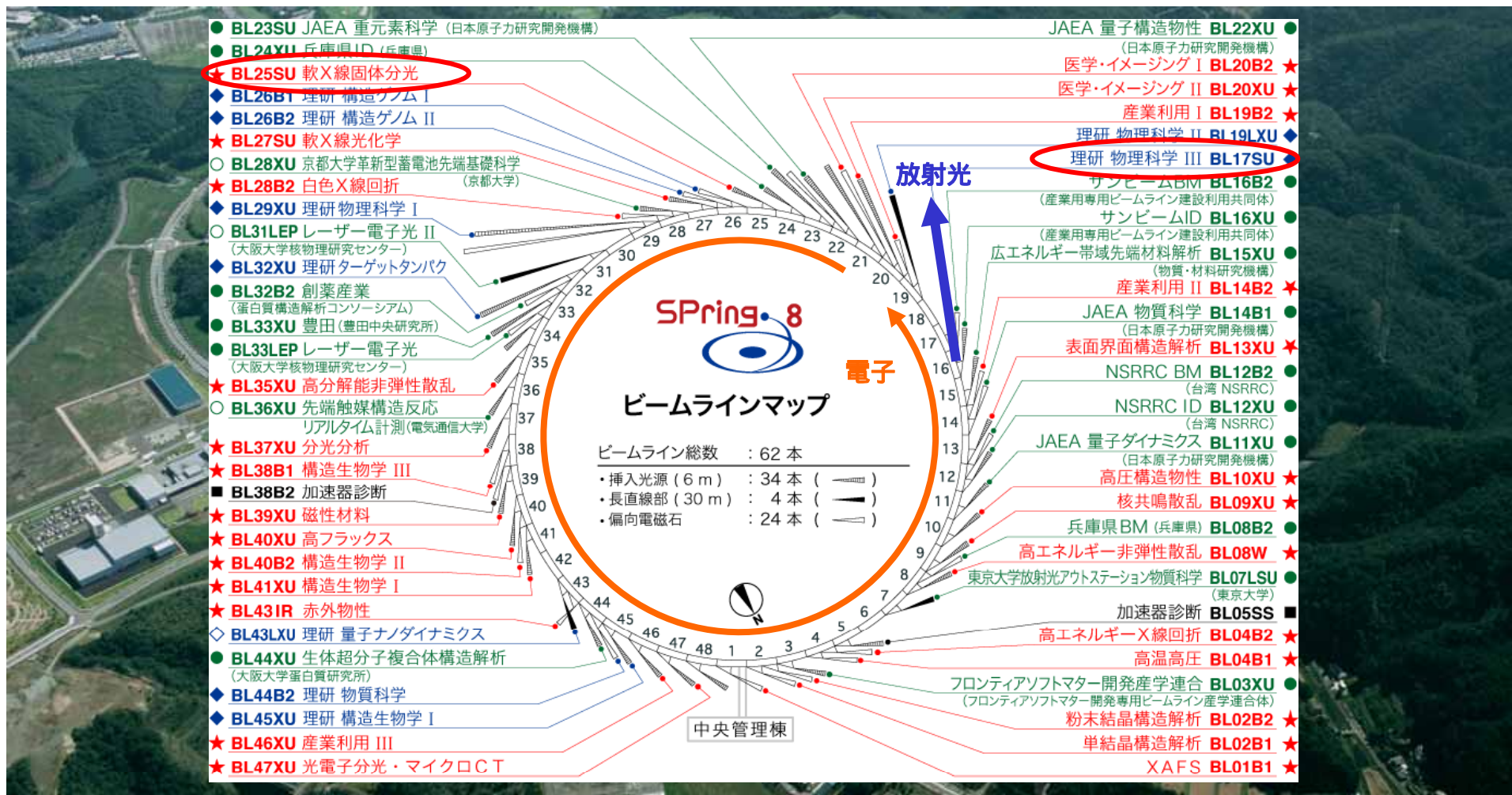


PEEM



Magnetic domain of 100nm CoPt dot is visible
(close to MFM)

SPring-8の紹介



放射光の特徴

- X線
- ・波長可変 — 元素選択性
 - ・高輝度 — 高分解能・高効率測定
 - ・偏光 — 磁気情報

Meteorite on PEEM

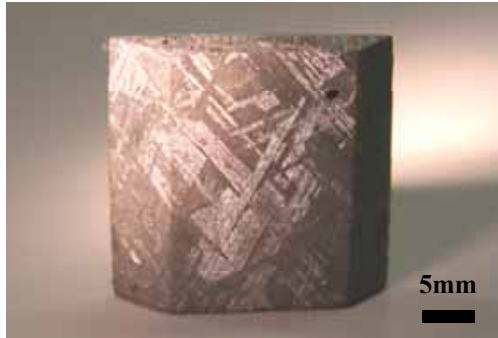
A new application to planetary science



Motivation

Iron meteorite is “ Extraterrestrial(ET) FeNi magnetic system “

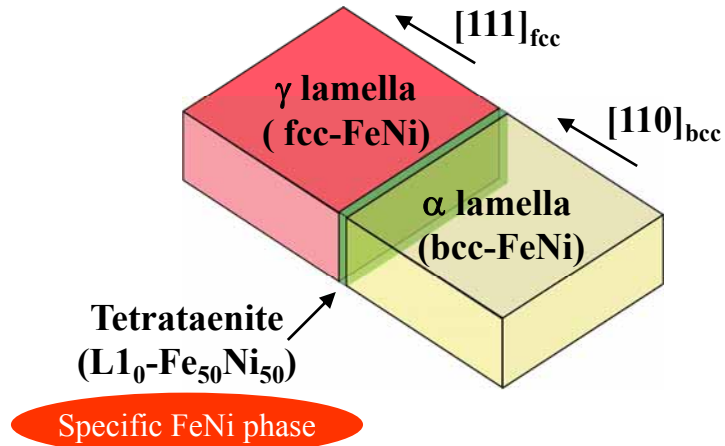
Iron Meteorite
Widmanstätten structure



Mixed crystal composed of α and γ -FeNi

Fine metallographic structure (4.6 billion years to produce)

Schematic view of interface region



Naturally fabricated magnetic multilayer

Magnetic recording medium



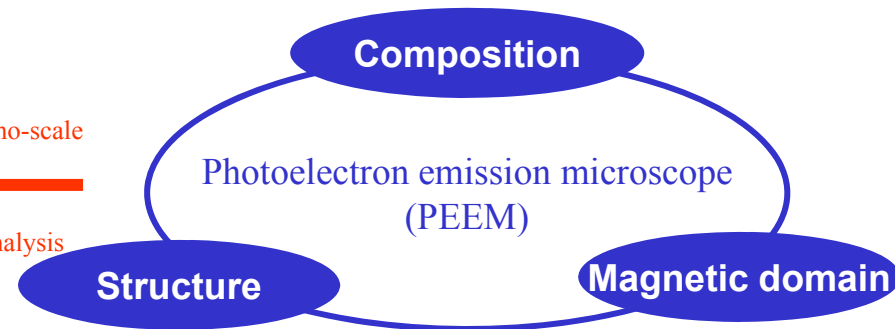
Magnetism

Large Magnetic anisotropy
Large coercivity
Tetrataenite($L1_0$ -FeNi)

Why?

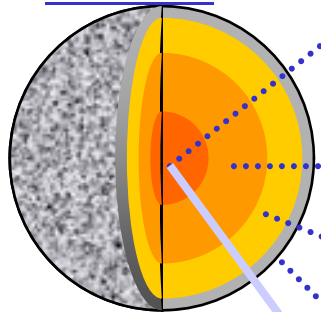
Significant difference from synthetic FeNi

Nano-scale
analysis

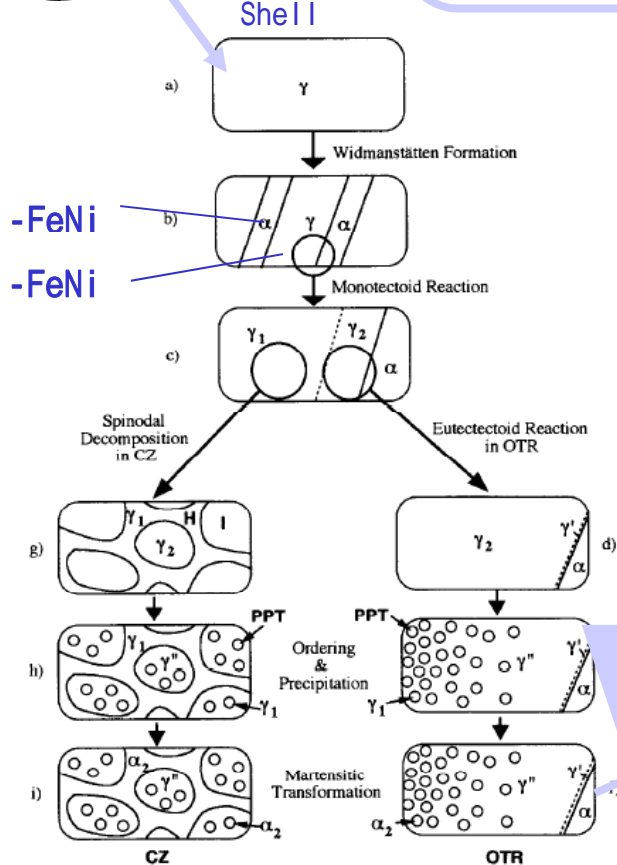


Iron Meteorite

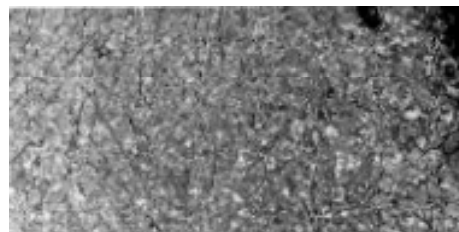
Asteroid



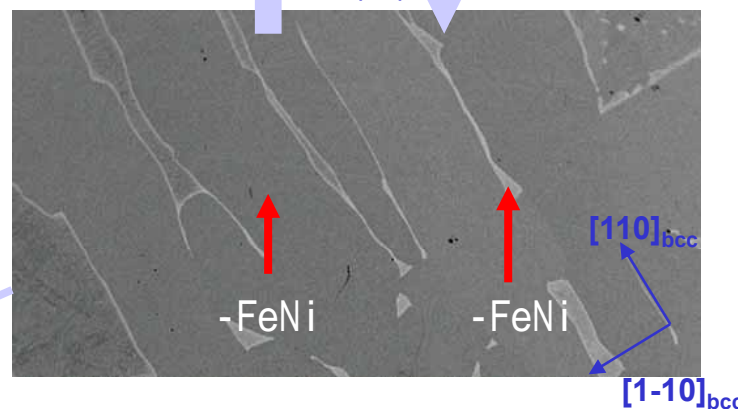
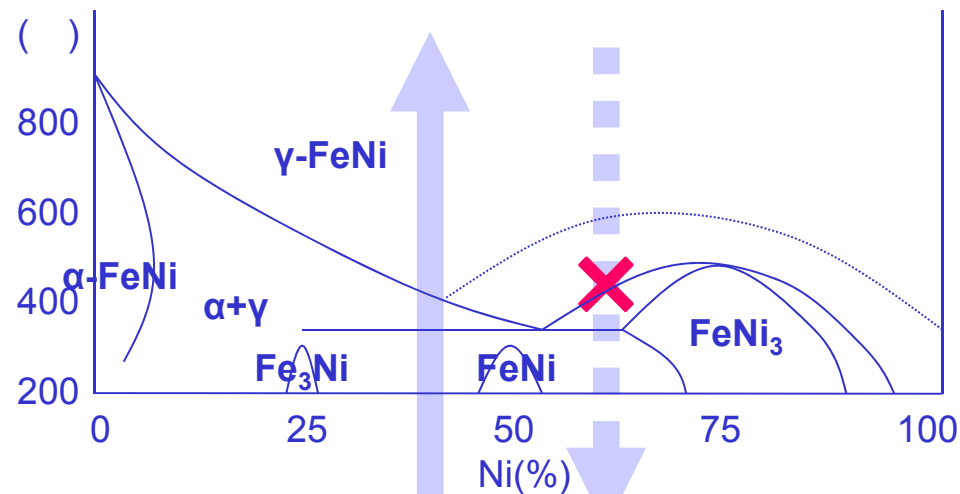
Gibeon iron meteorite
 90%: Fe
 7.93% Ni
 0.41% Co
 0.04% P
 2.0 ppm Ga
 0.12 ppm Ge
 2.3 ppm Ir



Cooling speed: 1 /1million year (4.6 billion years)



annealing(950)
destroys structure



Widmanstatten structure

FeNiの強磁性体

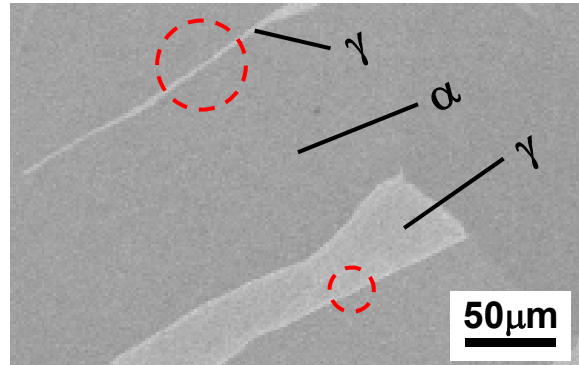
α相とγ相の混晶

L₁₀-FeNi

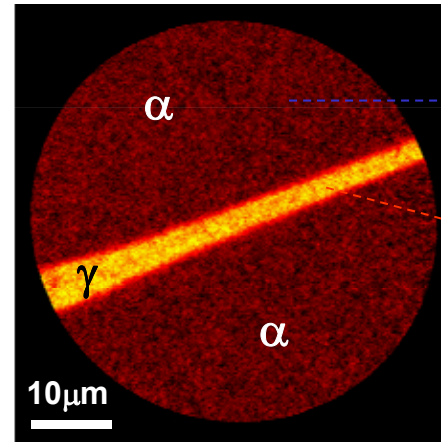
Geochimica et Cosmochimica Acta, Vol. 61, No. 14, pp. 2943-2956, 1997
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 0016-7037/97 \$17.00 + .00

Local structure analysis by PEEM(NanoXAFS)

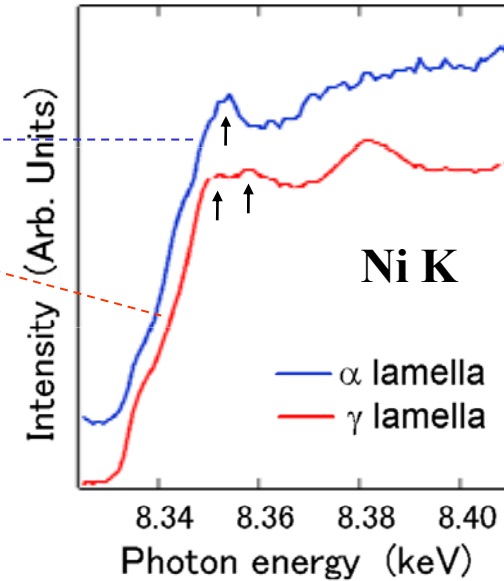
SEM image



PEEM image (composition)



XAFS

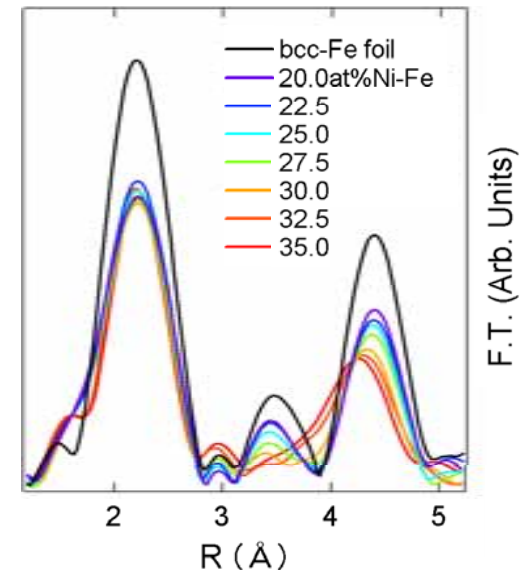
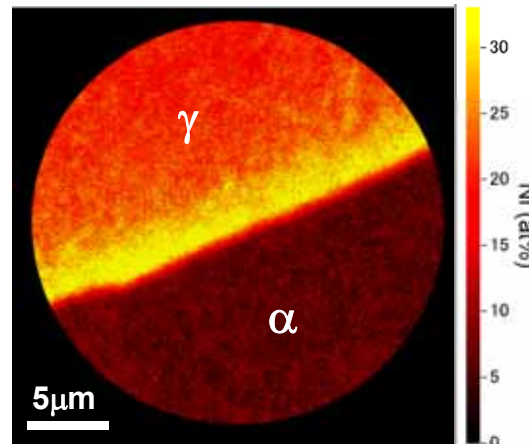


α : bcc structure (Ni=5at%)
 γ : fcc structure (Ni>25at%)

Rapid increasing of Ni composition
as close to the interface



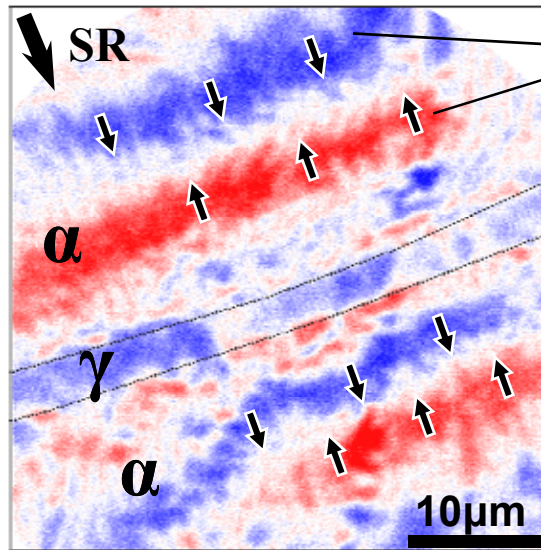
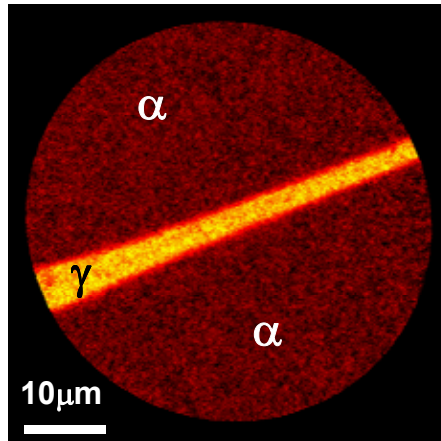
**$L1_0$ -FeNi phase is condensed
at the interface region**



EXAFS: Radial distribution function

Magnetic domain imaging by MCD-PEEM

Nano-XAFS

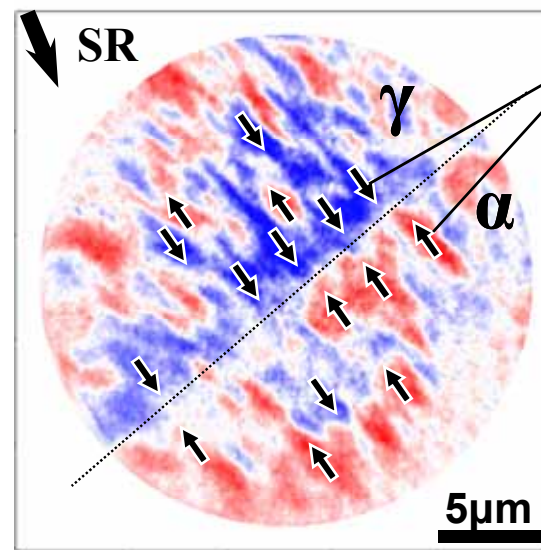
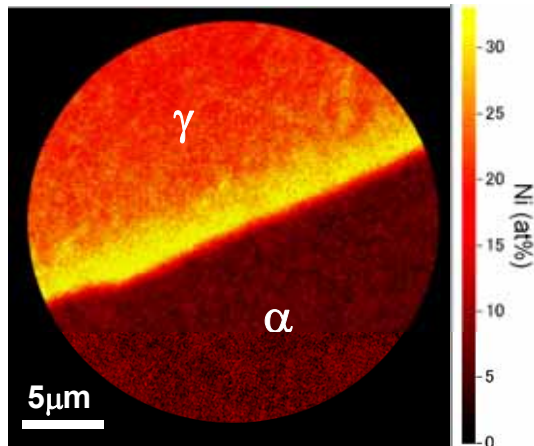


“Stripe” magnetic domain

Anisotropic shape

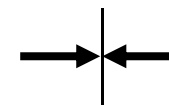
Stripe // interface(-110)_{bcc}

Related with interface?



“Head-on” magnetic domain

Head-to-head each other



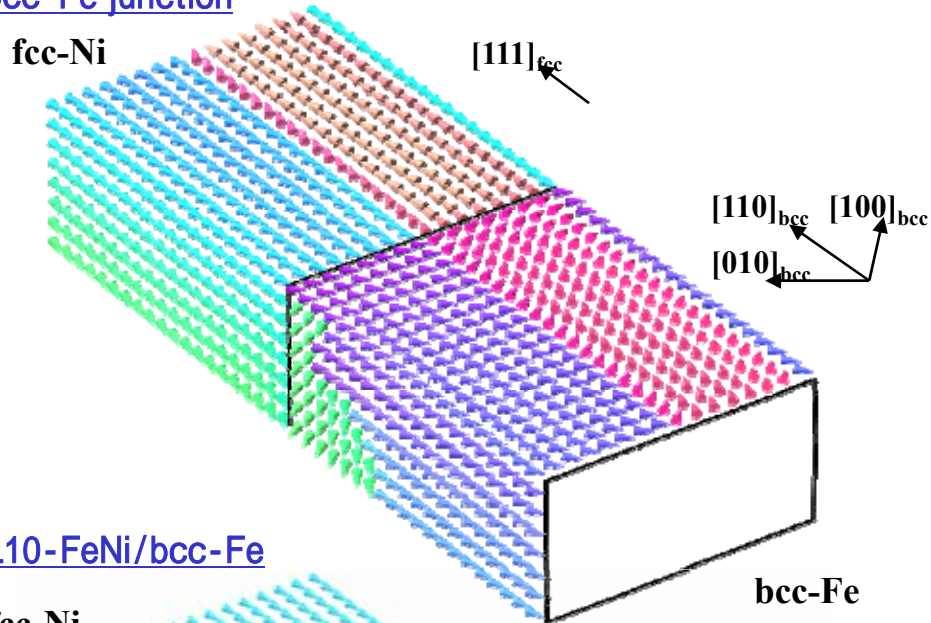
Huge loss of static magnetic energy over the interface

Why?

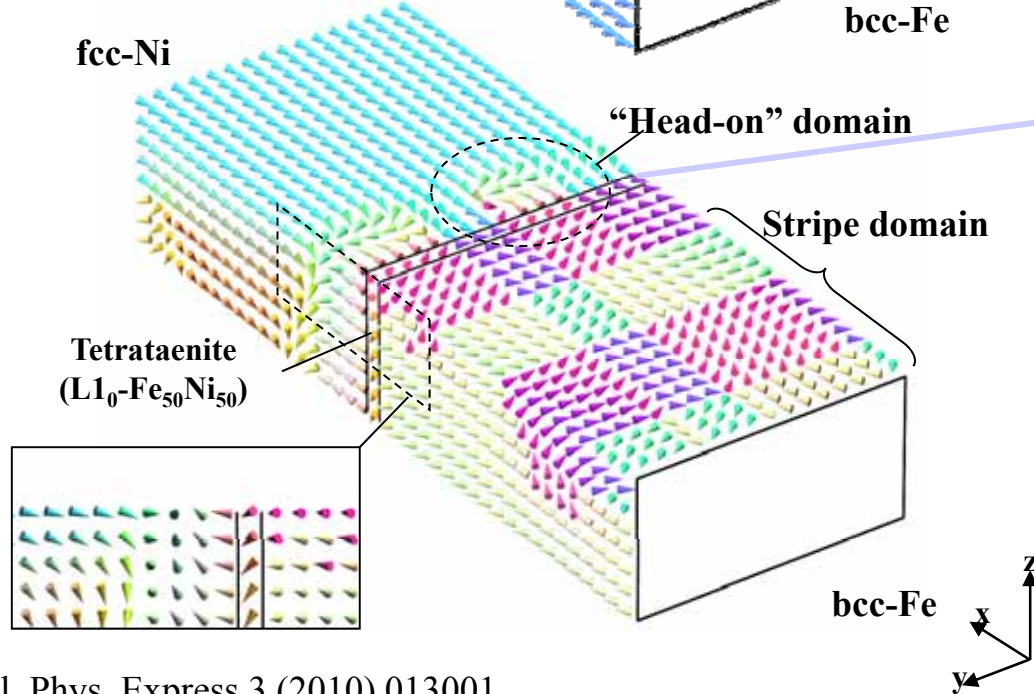
Non-expectable magnetic domain structure in common interface

Micromagnetics simulation

fcc-Ni/bcc-Fe junction



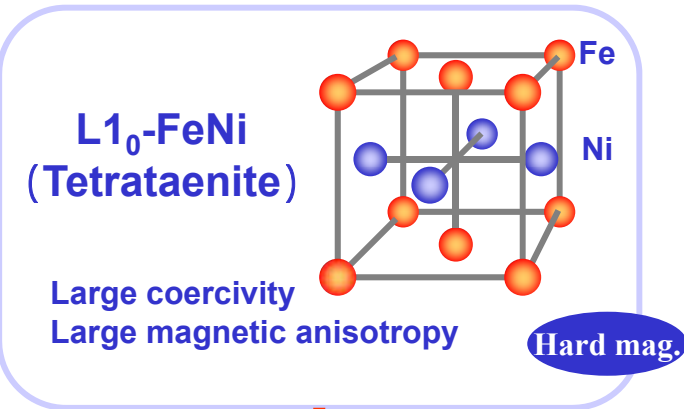
fcc-Ni/L10-FeNi/bcc-Fe



Magnetic property of FeNi

	Fe	L1 ₀ -FeNi	Ni
Coercivity(Oe)	0.05	4900	
MAE K ₁ (erg/cc)	3.8 × 10 ⁵	3.2 × 10 ⁶	-6 × 10 ⁴
Easy-axis	<001>	<001>	<111>
Periodicity	disorder	order	order
Lattice	bcc	fct	fcc

Neel et al. J. Appl. Phys. 35 (1964) 873
Handbook of magnetic materials by Chikazumi

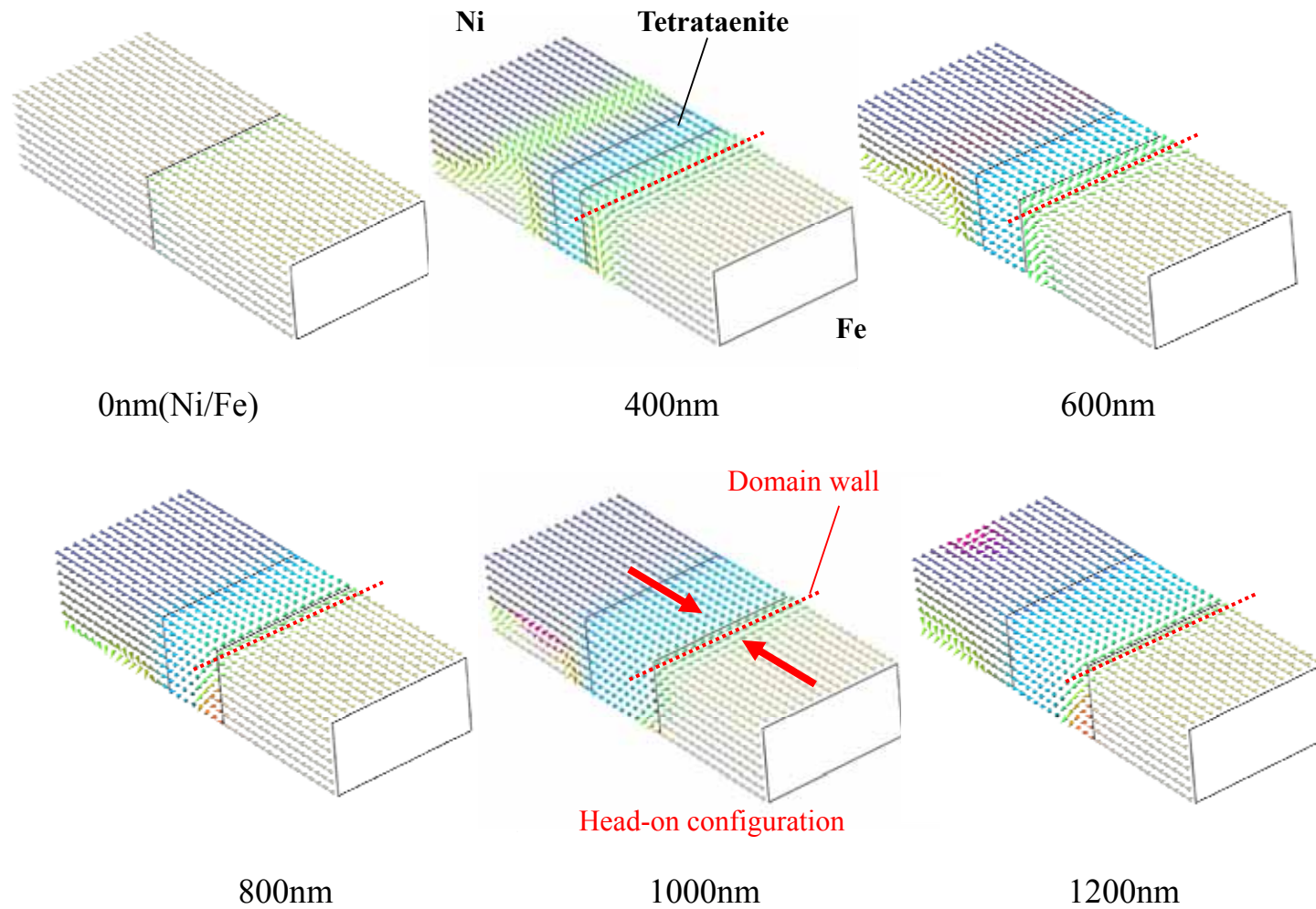


Affect the magnetization to surrounding Fe and Ni

Head-on domain
Stripe domain

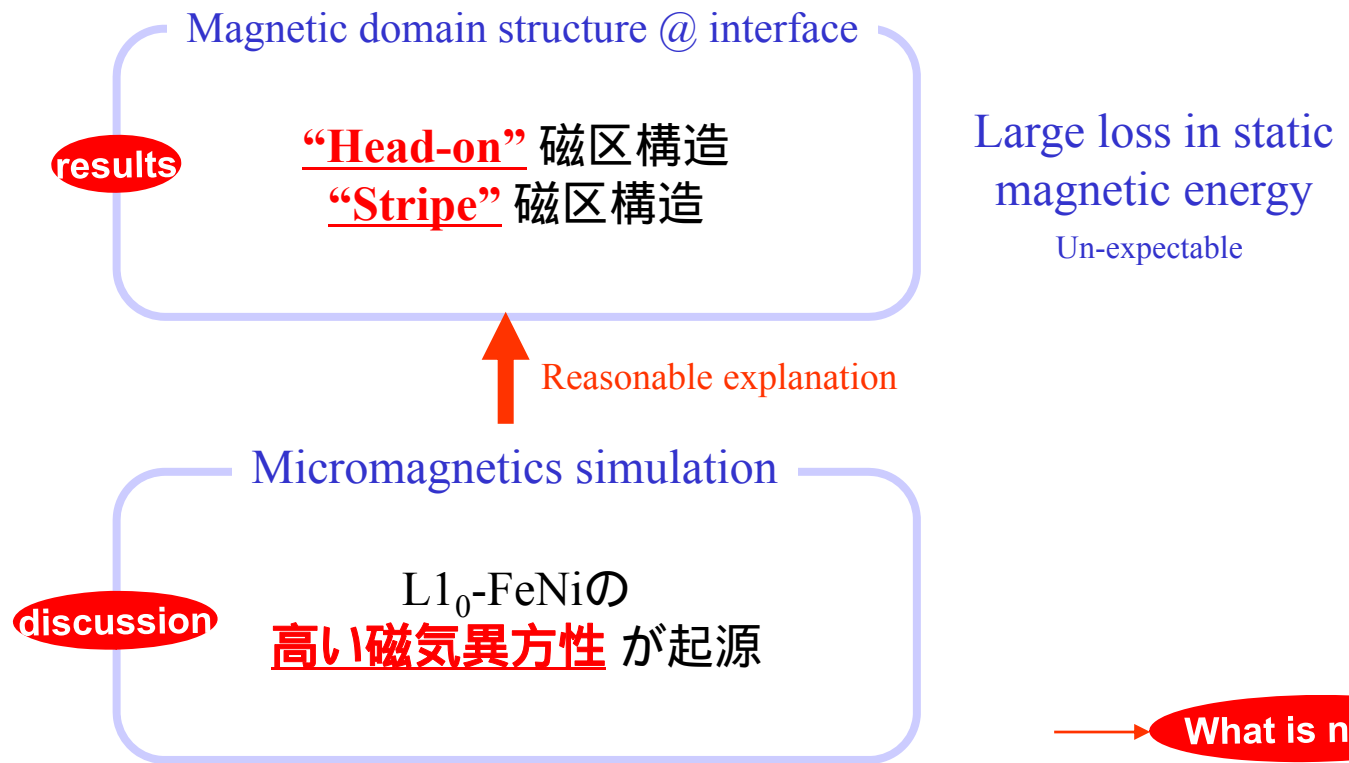
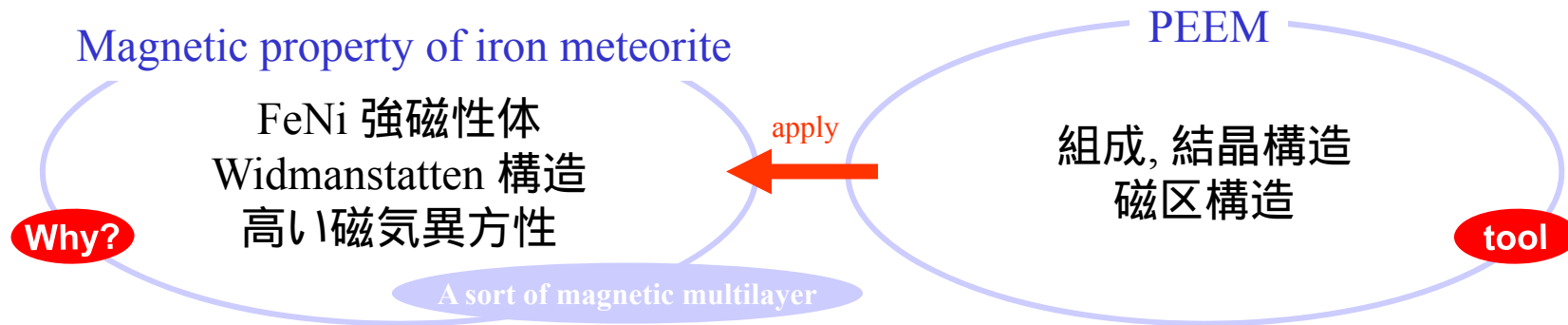
It is also correlated with whole magnetic anisotropy of iron meteorite.

Magnetic domain structure for various thickness of tetrataenite lamella



* Grid size is 100nm

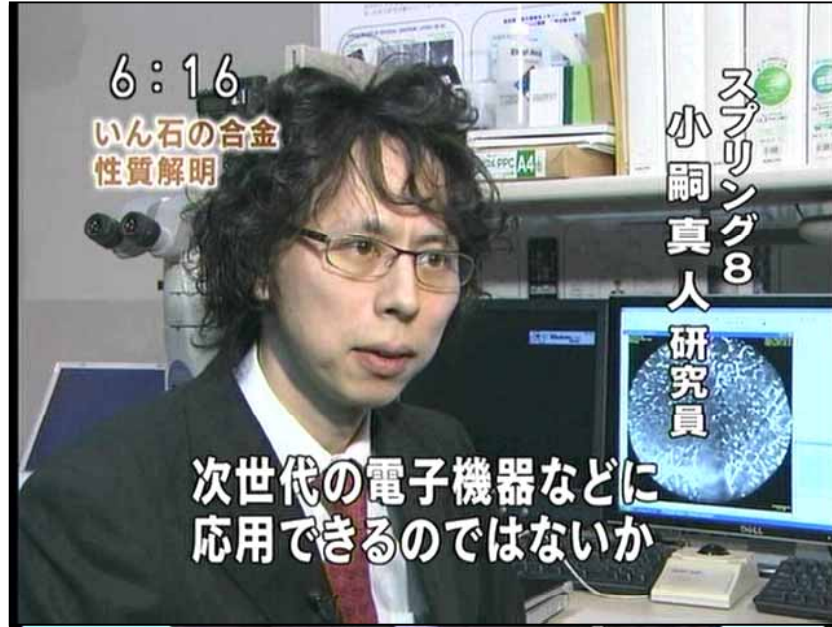
Summary



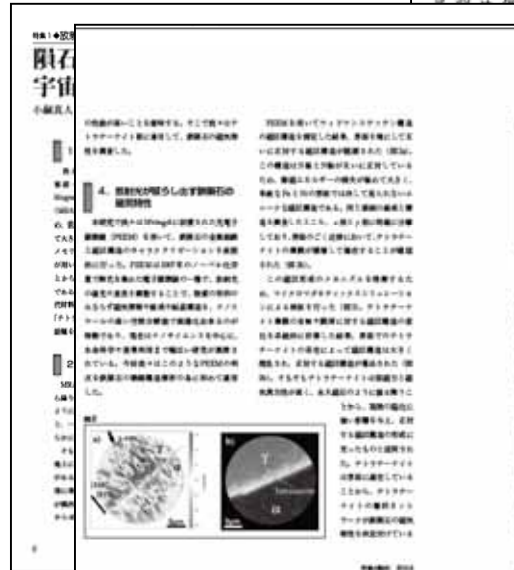
PEEM is spreading now

NHK news H21.12.16

朝日新聞(2009 12/17), 科学新聞(2010 1/1), 日経産業新聞(12/17)



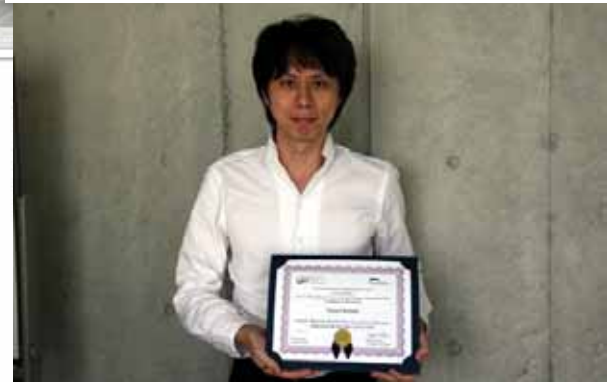
子供の科学(2010年3月号) 日本学術会議刊 学術の動向(2010年8月号)



日本金属学会 金属組織写真 最優秀賞



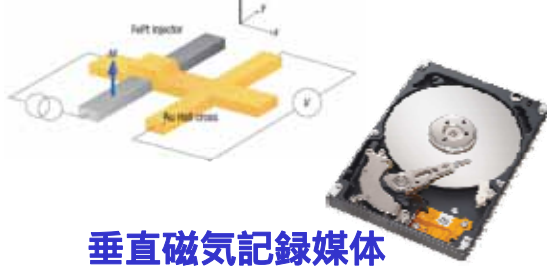
International Metallographic Society Dubose-Crouse Award



Current research

レアメタルフリーL1₀-FeNiのアプリケーションへの利用

スピントロニクス スピン源



垂直磁気記録媒体

L1₀型強磁性体 → 有望視

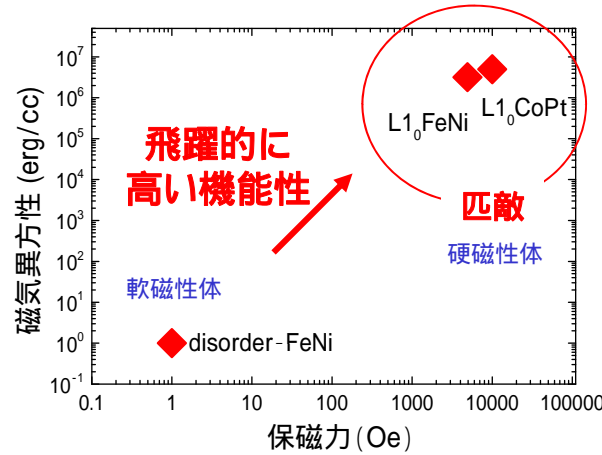
要求される機能性

高い磁気異方性
高い保磁力

L1₀-CoPt

価格の高騰・環境資源の枯渇

磁気特性の比較



飛躍的に
高い機能性

匹敵

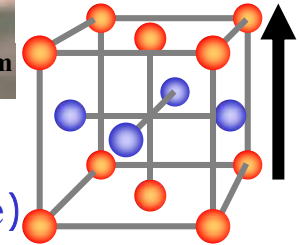
Comparable

鉄隕石 (隕鉄)

Widmanstätten structure



L1₀-FeNi
(Tetrataenite)

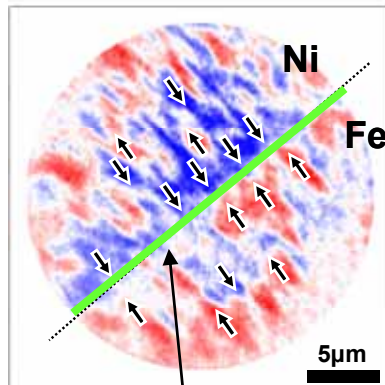


高い磁気異方性
高い保磁力

L1₀-FeNi

FeやNiは安価で潤沢な資源

鉄隕石の磁区像



L1₀-FeNi薄膜

Question

磁気異方性の獲得メカニズムの
微視的な振る舞い

規則性

外場

How?

Out-of-plane



In-plane

Experimental

Synthesis of L1₀-FeNi

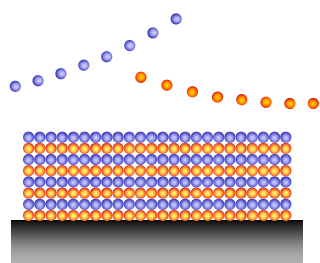
分子線エピタキシー(MBE)による試料創製

(Fe(001)/Ni(001))₅₀/Cu(001)/Au/Fe/MgO

JMMM 310 (2007) 2213

J. Appl. Phys. 107 (2010) 09A716

J. Phys.: Conf. Ser. 266 (2011) 012095



格子定数

a 3.65
c 3.59
c/a 0.984

$$K_u > 4.8 \times 10^6 \text{ erg/cm}^3$$

$$(4.8 \times 10^5 \text{ J/m}^3)$$

試料

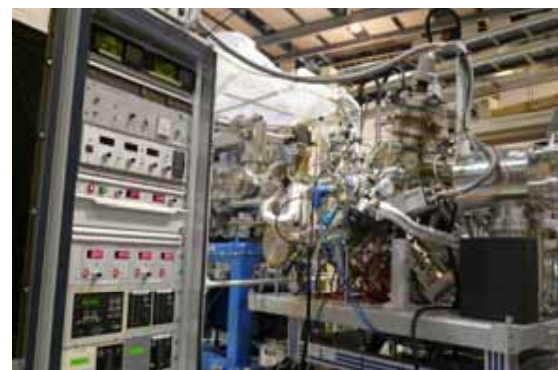
order / disorder

外場

消磁状態 / 着磁状態

(面直に1.1T、残留磁化で測定した)

SPELEEM@BL17SU SPring-8



国際宇宙ステーションISS



観戦



オセロ

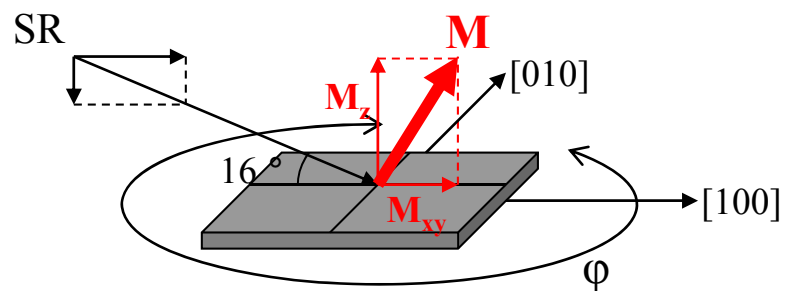
分解能: 22nm(PEEMモード)
7.8nm(LEEMモード)

磁区像測定: MCD@Fe-L3吸収端

測定時間: 数分 / 枚

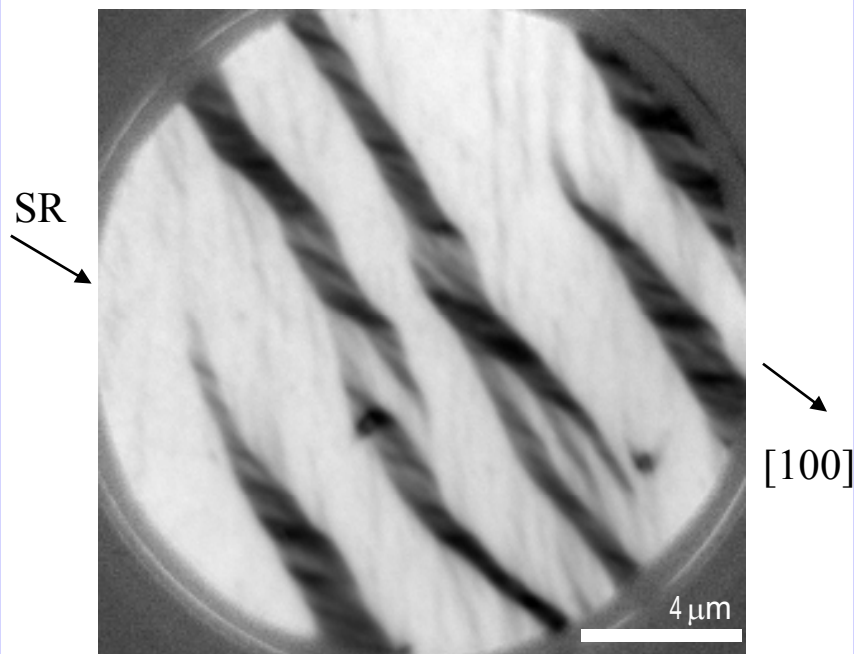
視野径: 30um 及び 20um

磁区測定 vs. ϕ → 面直磁化成分の観測



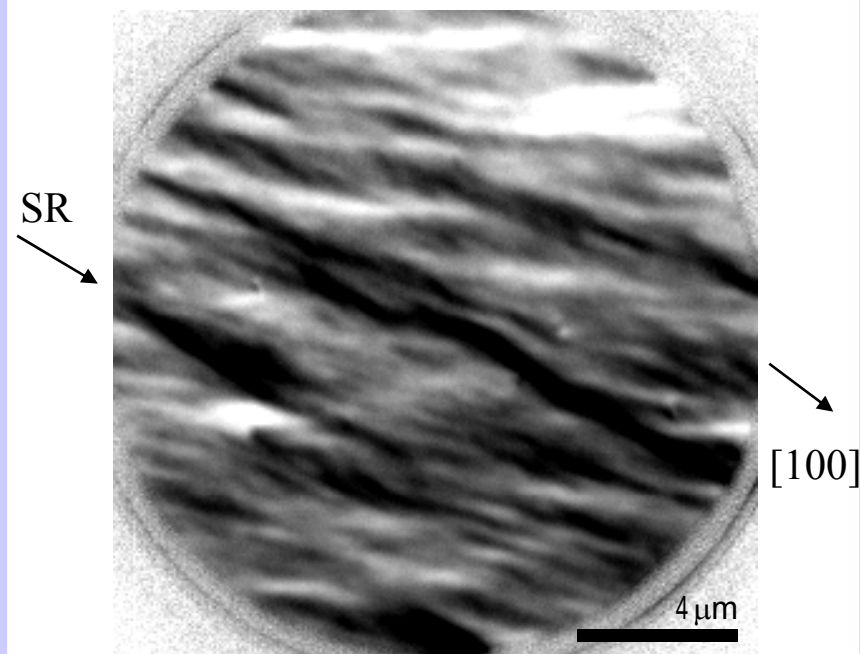
Magnetic domain of $L1_0$ -FeNi and FeNi

Disorder FeNi



面内磁区

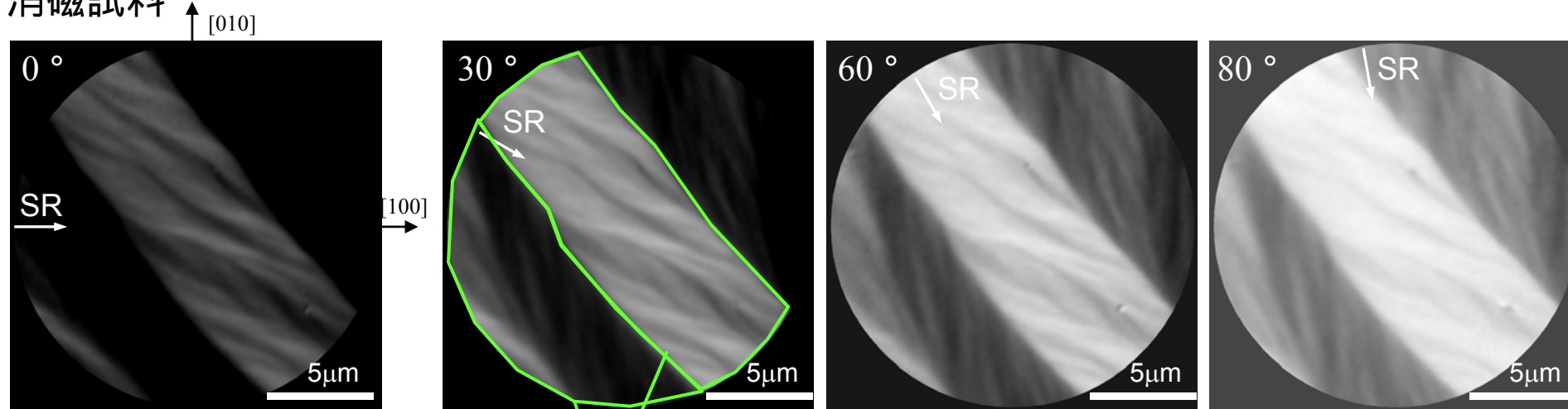
Order $L1_0$ -FeNi



→ 角度依存性測定へ

Magnetic domain of L1₀-FeNi vs. SR incident

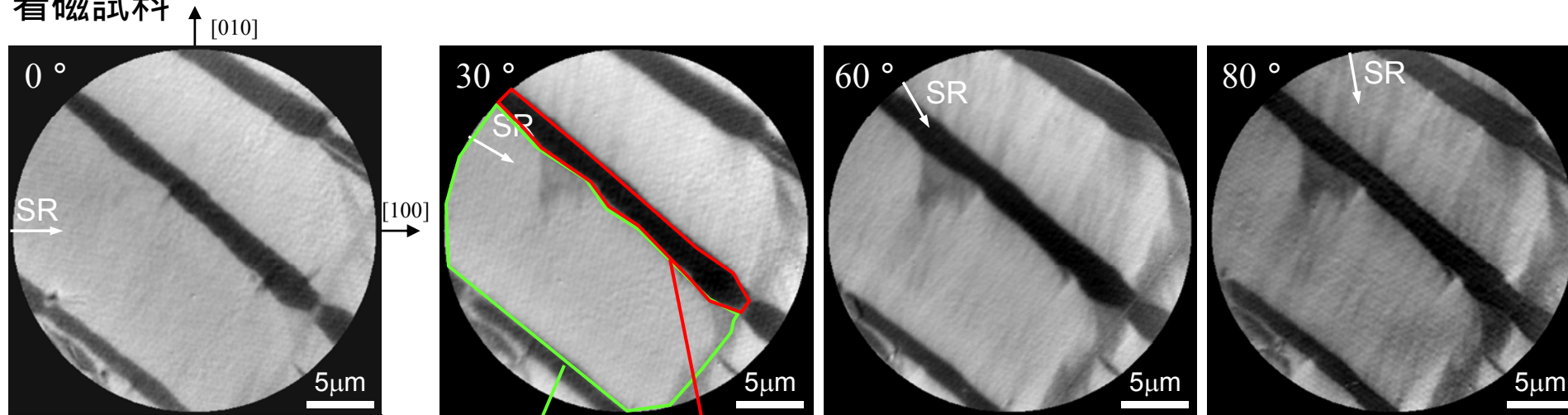
消磁試料



In-plane

→ 面内磁区と結論

着磁試料



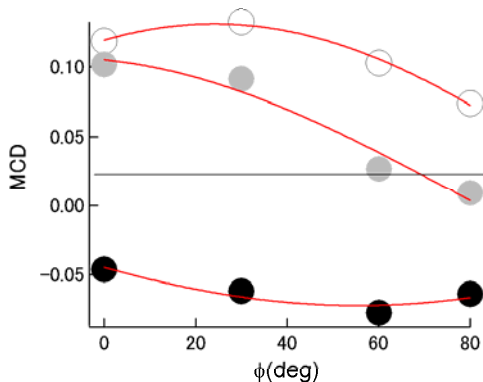
In-plane Out-of-plane?

→ 定量解析へ

面直1.1T
残留磁化で測定

In-plane and out-of-plane component

Pixel-by-pixel analysis



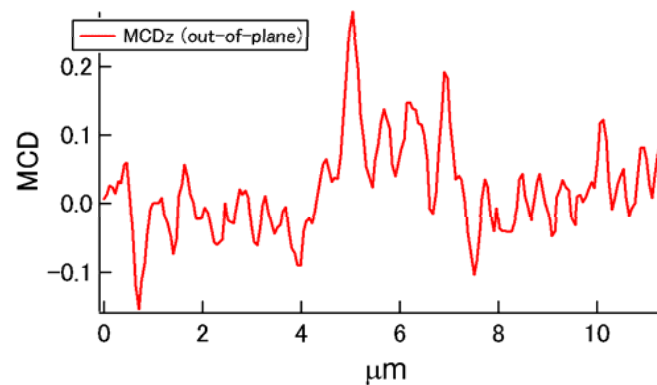
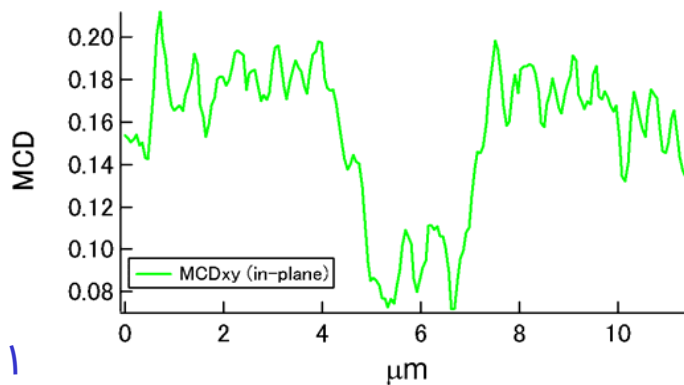
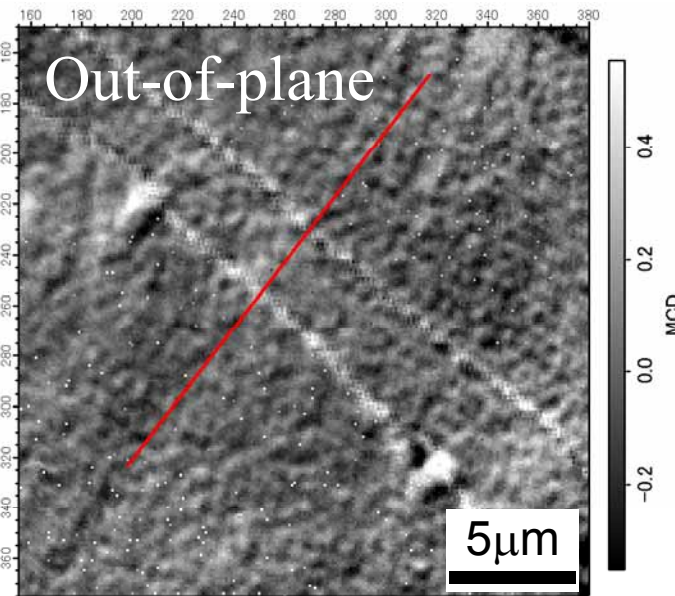
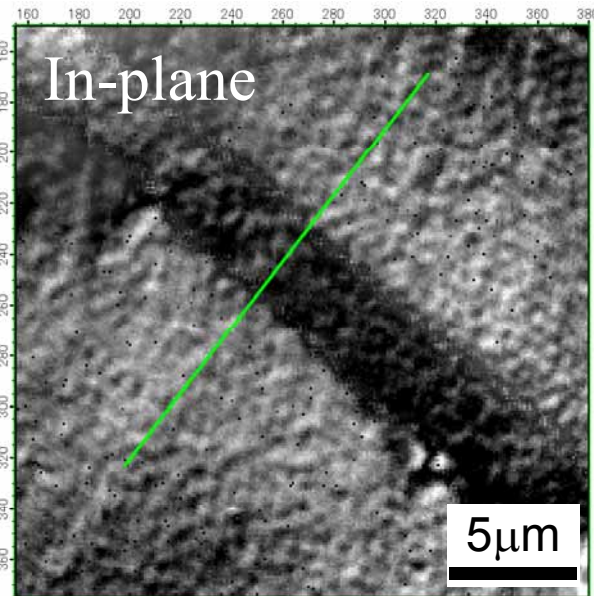
$$y = A_0 + A_1 \cos(\varphi + \delta)$$

$$MCD_{//} = A_1 / \cos 16$$

$$MCD_{\perp} = A_0 / \sin 16$$

面内磁化の向き = δ

各ピクセルに対して
フィッティングを行ない
面内、面直成分に分離する。



面直成分を確認

Summary

地球外物質である鉄隕石の磁気特性を
PEEMを用いてナノスケールで解析 & 議論した。

界面で互いに正対する新奇な磁区構造を発見した。

マイクロマグネティックスシミュレーションにより
界面に偏析した $L1_0$ -FeNiに起源する事が示唆された。

$L1_0$ -FeNiは通常のFeNiに比べて劇的に高い
磁気異方性を示す事に着目した。

MBEを用いて人工的に $L1_0$ -FeNiの創製を行なった。

$L1_0$ -FeNi人工膜における磁区構造で
面直成分を確認することができた。