2011.09.13
PF研究会「軟X線分光・散乱測定を用いた物性研究の現状と展望」

軟X線放射光を用いた顕微分光研究

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Photoelectron emission microscopy (PEEM)

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Scanning Transmission X-ray Microscopy (STXM)

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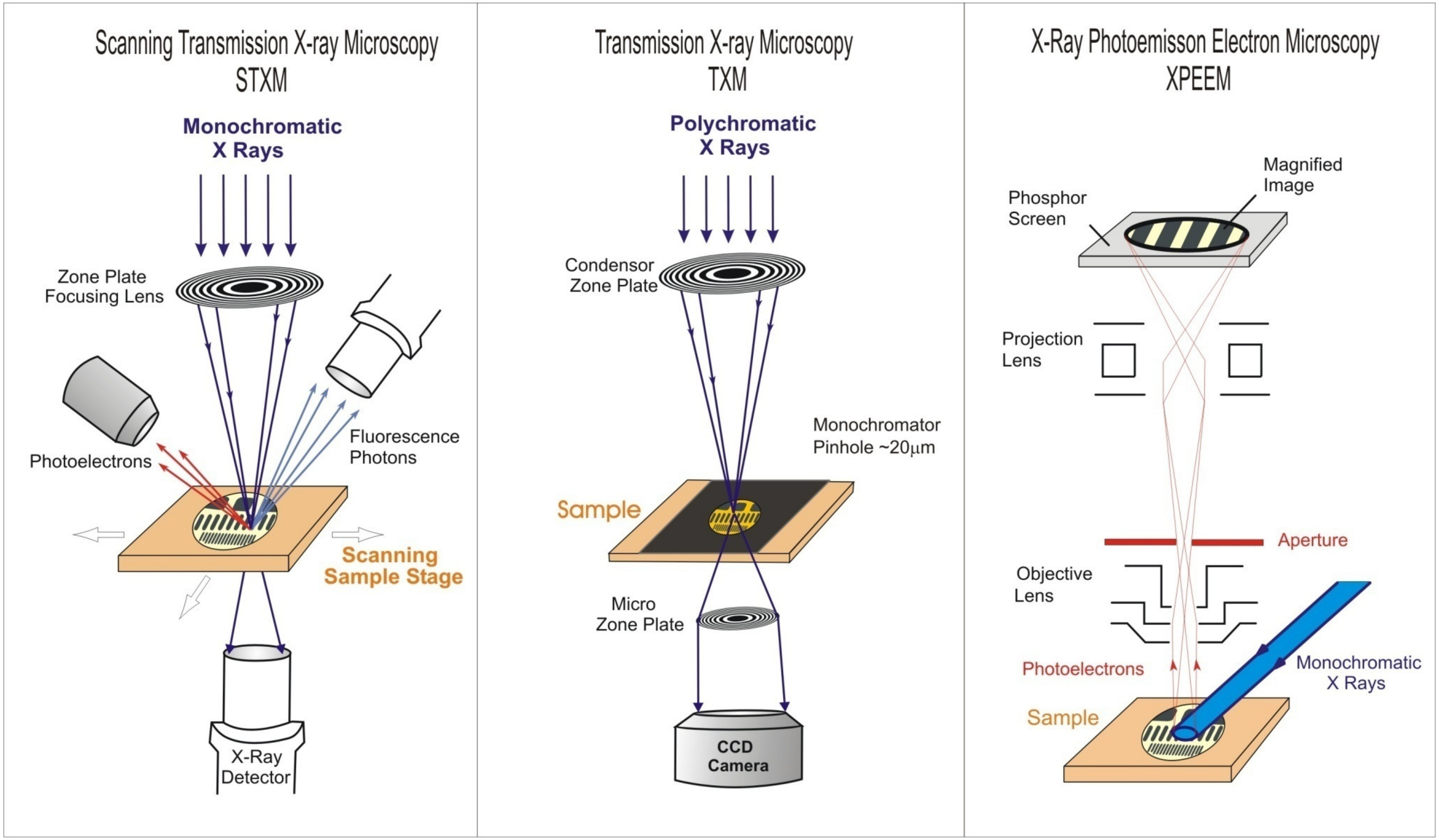
X-ray microscopy



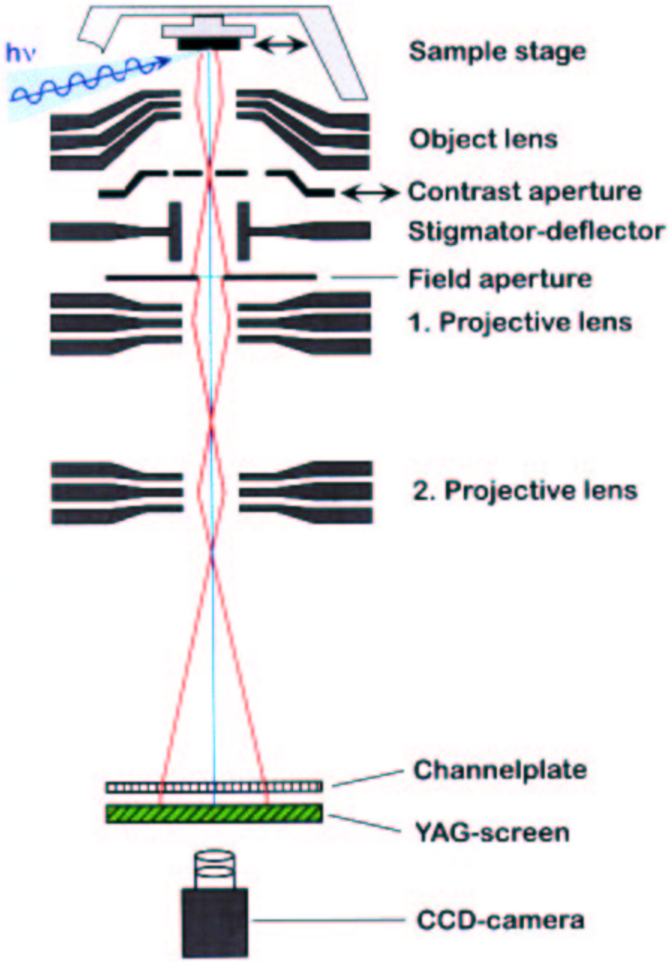
空間分解能は 10 ~ 20 nm

Soft x-ray imaging techniques

Methods	Spatial Resolution	Optics	Vibration	Mag. Field	Low Temp.
Photoelectron Emission Microscopy (PEEM)	15 nm	Electron Lens	×	×	△
Transmission X-ray Microscopy (TXM)	10 nm	FZP (Condenser + Objective)	△	○	△
Scanning Transmission X-ray Microscopy (STXM)	1 nm	FZP	△	△	△
X-ray Fourier Transform Holography	50 nm	Lensless (coherent x-ray)	◎	◎	◎
Coherent x-ray diffraction microscopy	< 10nm	Lensless (coherent x-ray)	◎	◎	◎

光電子顕微鏡

Photoelectron Emission Microscopy (PEEM)



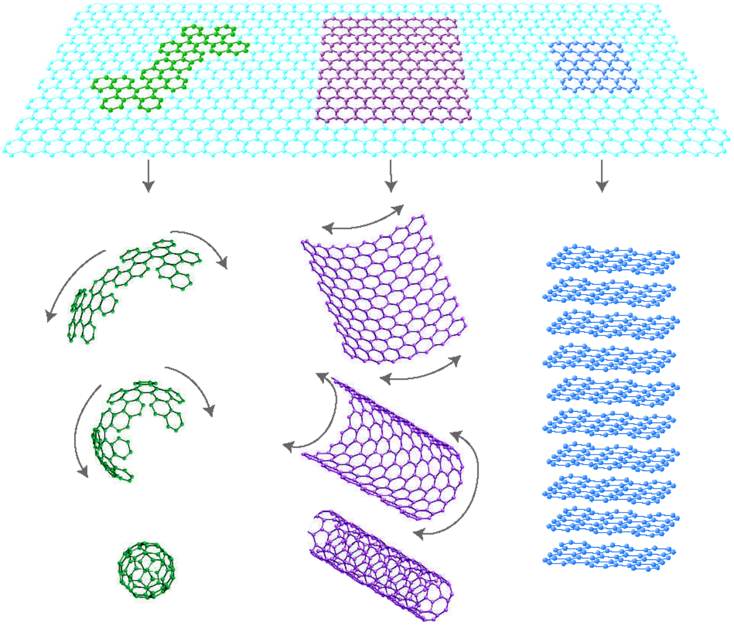
試料に光を照射したとき、試料から出る光電子を電子レンズにより拡大する。

1.Sample stage
2.Object lens
3.Projective lens
4.MCP
5.YAG screen
6.CCD camera

PEEM 像のコントラストは光の吸収強度に比例する。

PEEMを用いたアトグラム分光

2次元ナノ材料の電子状態を解明するために光電子顕微鏡（PEEM）を用いたX線ナノスペクトロスコピー手法を開発する



光電子顕微鏡

- ・ 高い空間分解能 (<30 nm)
- ・ 表面敏感 (< 数 nm)

2次元ナノ材料の研究に最適

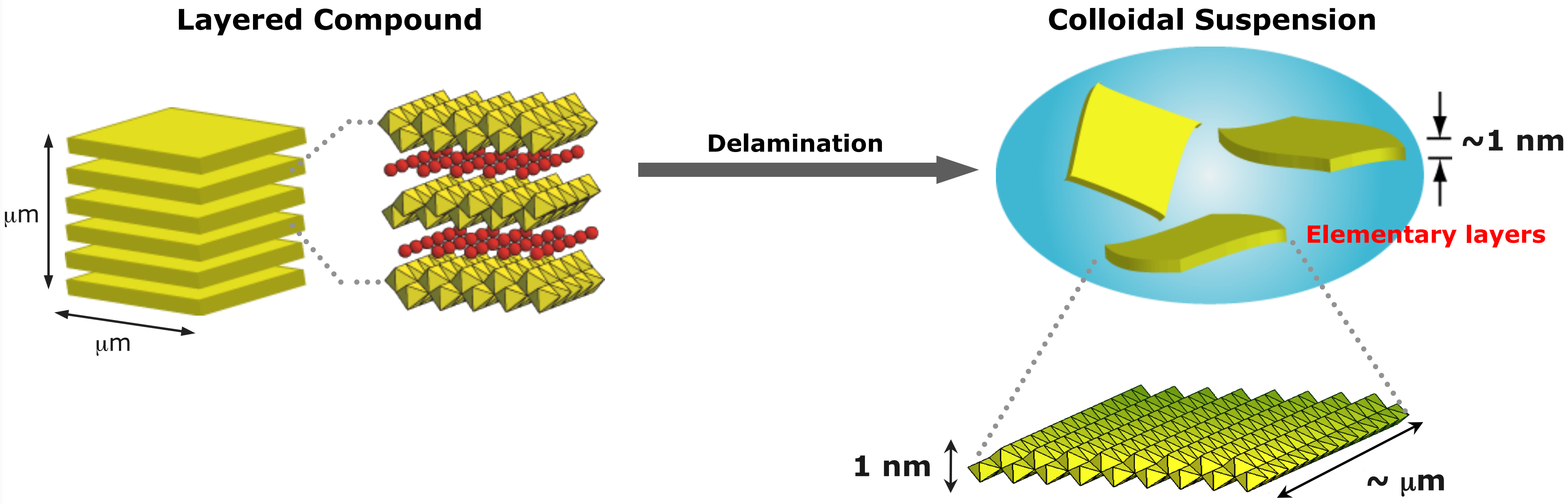
目標

アトグラム (10^{-18} g)

~ 15 nm x 15 nm x 0.5 nm 試料の測定

Oxide Nanosheets - A new class of 2D nanomaterials! -

Derived from Layered Host Materials *via* Exfoliation

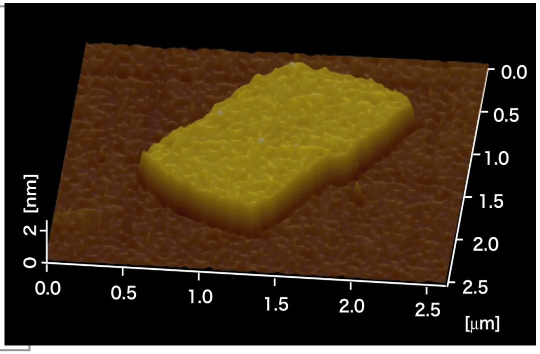


Nanosheet
(Functional nanoblock)

Sasaki *et al*., *JACS.* 120, 4682 (1998)

■ Unique features of Nanosheets

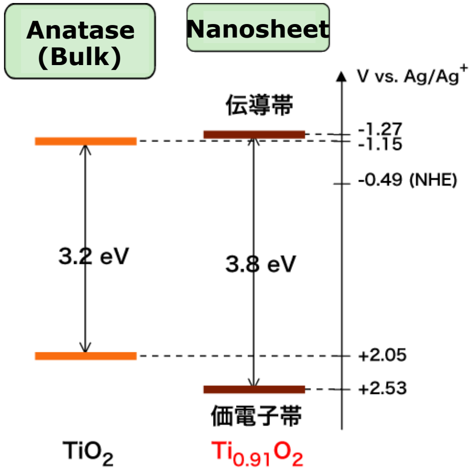
- **Ultimate 2D nature (Thickness ~nm, Lateral size ~µm)**
- **2D single molecule/crystal with well-defined composition**
- **Novel physical properties in 2D System**
  substantially different from 3D bulk system



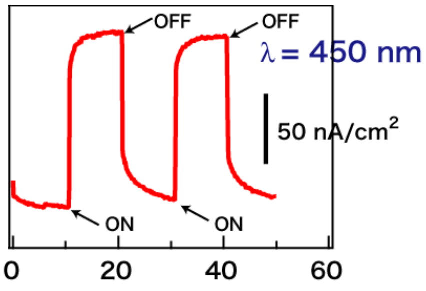
Physical Properties -Depending on nanosheets & film nanoarchitecture-

Optical

Wide gap ($Ti_{0.91}O_2$)



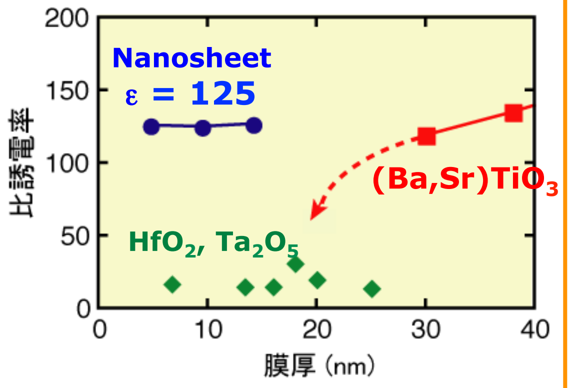
Photocurrent (MnO_2)



N. Sakai *et al.*, JACS (2004)

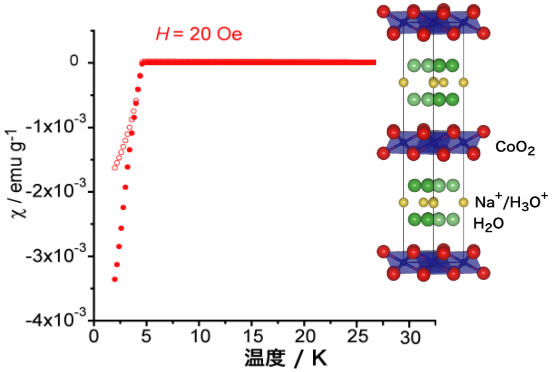
Electric

High-k dielectric ($Ti_{0.87}O_2$)



M. Osada *et al.*, Adv. Mater. (2006)

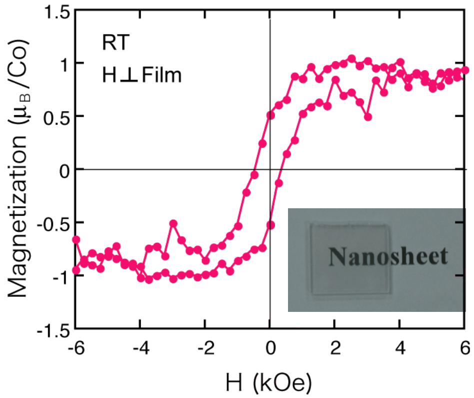
Superconductivity (CoO_2)



K Takda *et al.*, Nature (2003)

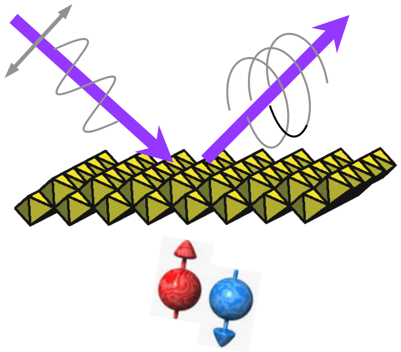
Magnetic

Ferromagnetic ($Ti_{0.8}Co_{0.2}O_2$)



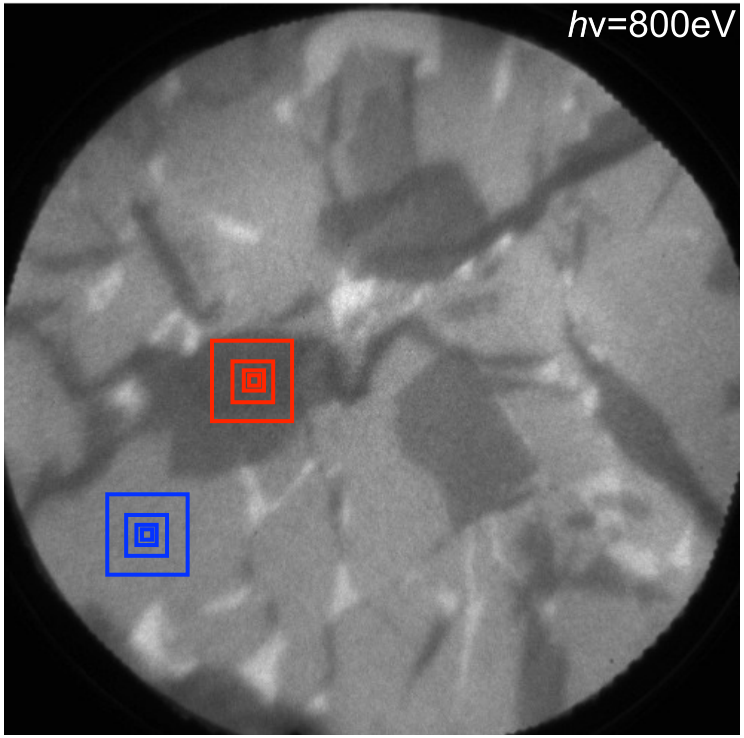
M. Osada *et al.*, Phys. Rev. B (2006)

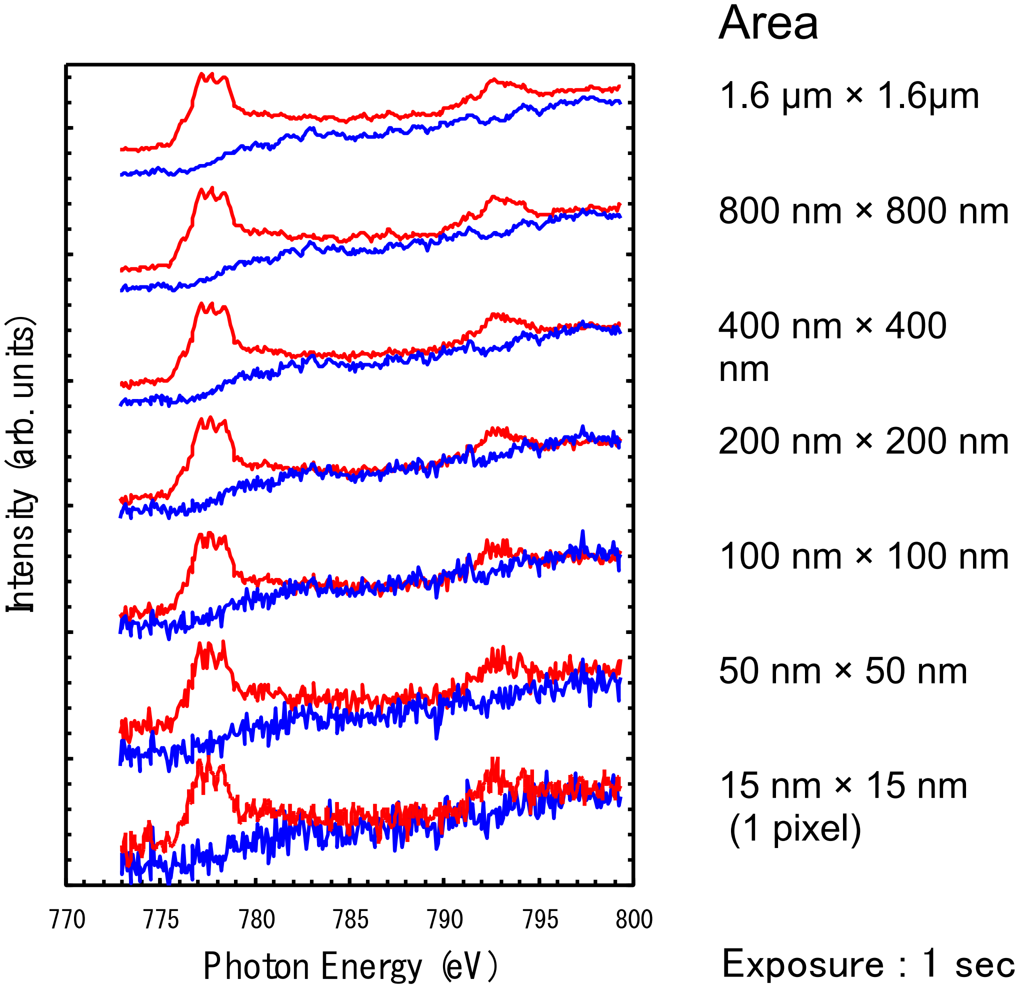
Magneto-optical



M. Osada *et al.*, Adv. Mater. (2006)

Attogram soft x-ray spectroscopy



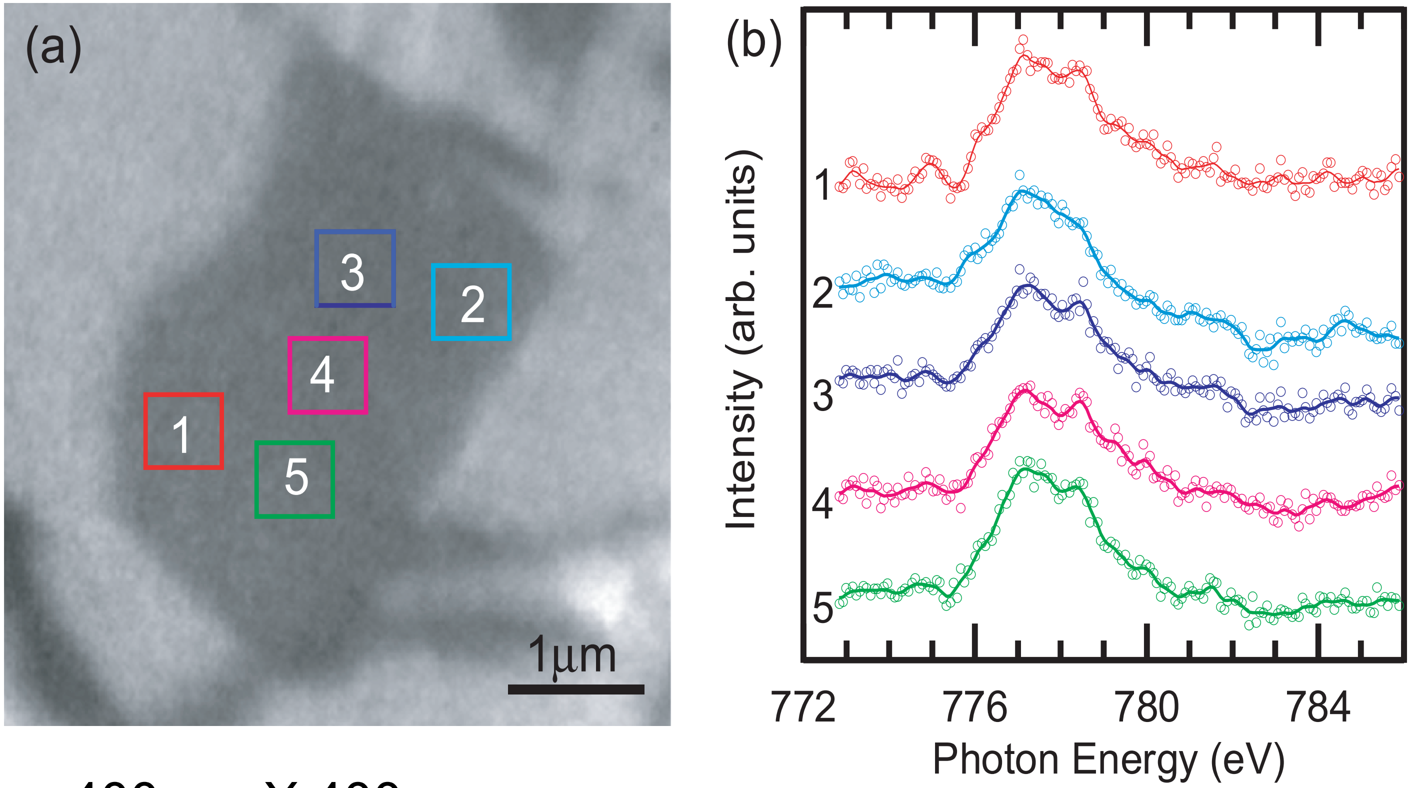


Exposure : 1 sec

Intensity is enough.
Spatial resolution of our PEEM is limited.

i.e. 10 nm x 10 nm x 1 nm sample
~ 10^{-18} g (= 1 atto gram)

Electronic structure distribution in a single molecular nanosheet



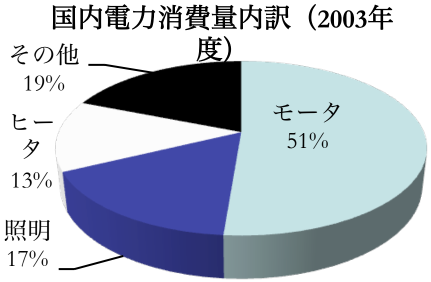
400 nm X 400 nm area

Y. Kotani, KO et al., Appl. Phys. Lett. 93 093112 (2008)

Chemical state of Co atom is Co^{2+} low spin state.
No significant change in the electronic structure and chemical structure distribution.

磁気構造可視化による高性能磁石の保磁力機構の解明

軟X線顕微鏡を用いてハイブリッド自動車用 (Nd,Dy)-Fe-B 磁石のナノスケールでの磁気構造を可視化することにより高保磁力発現メカニズムを解明し、レアアース使用量を低減した次世代高性能磁石の設計指針を与える。


国内電力消費量内訳（2003年度）

モータ性能向上は CO_2 排出量削減の鍵

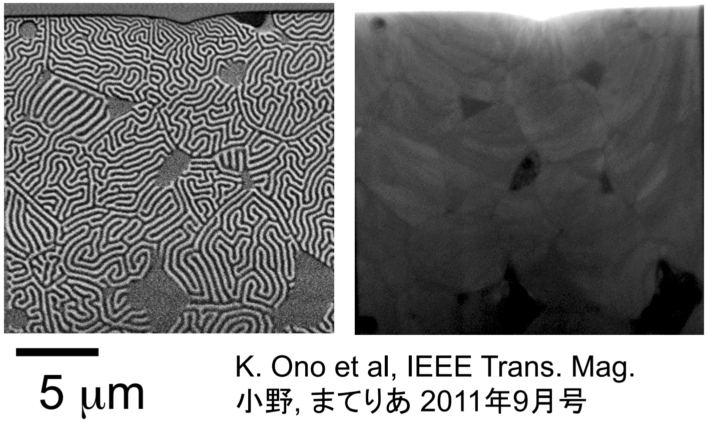
国内の電力消費量の 50% 以上をモータが消費している

モータ効率　1%　向上 ＝ 中規模の原子力発電所・火力発電所　1基

50 億kWh (50万kW) ＝ 50 億kWh (50万kW)

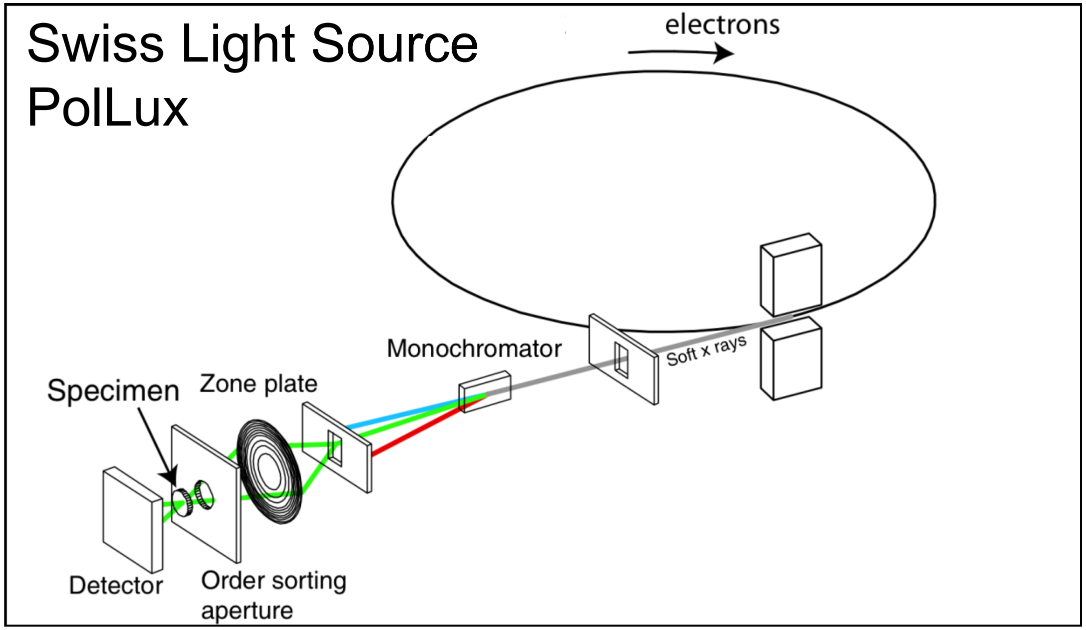
モータの効率向上のためには、永久磁石の性能向上が必須！
高性能化（高保磁力化）にはナノレベルでの磁気構造の可視化が必要。

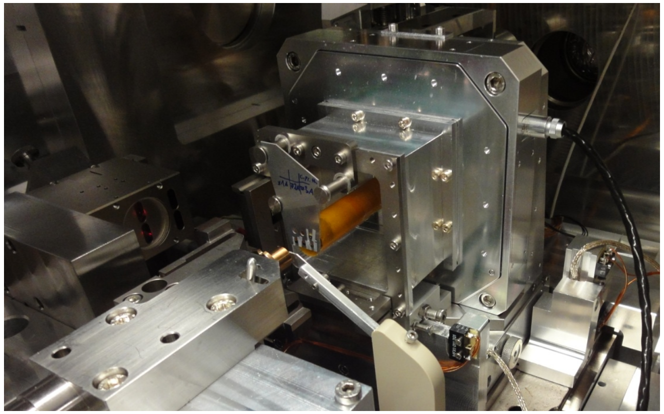
軟X線顕微鏡による磁気構造可視化



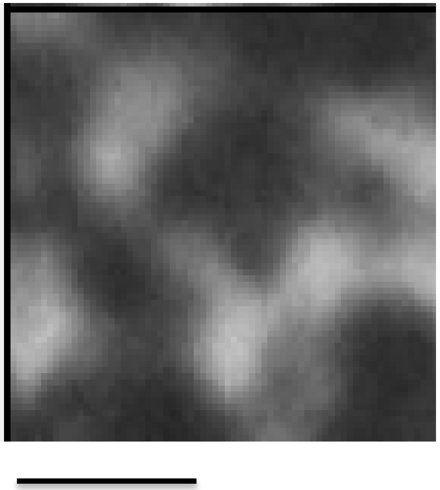
K. Ono et al, IEEE Trans. Mag.
小野, まてりあ 2011年9月号

Scanning Transmission X-ray Microscopy (STXM)





STXM magnetic image



10 nm spatial resolution !

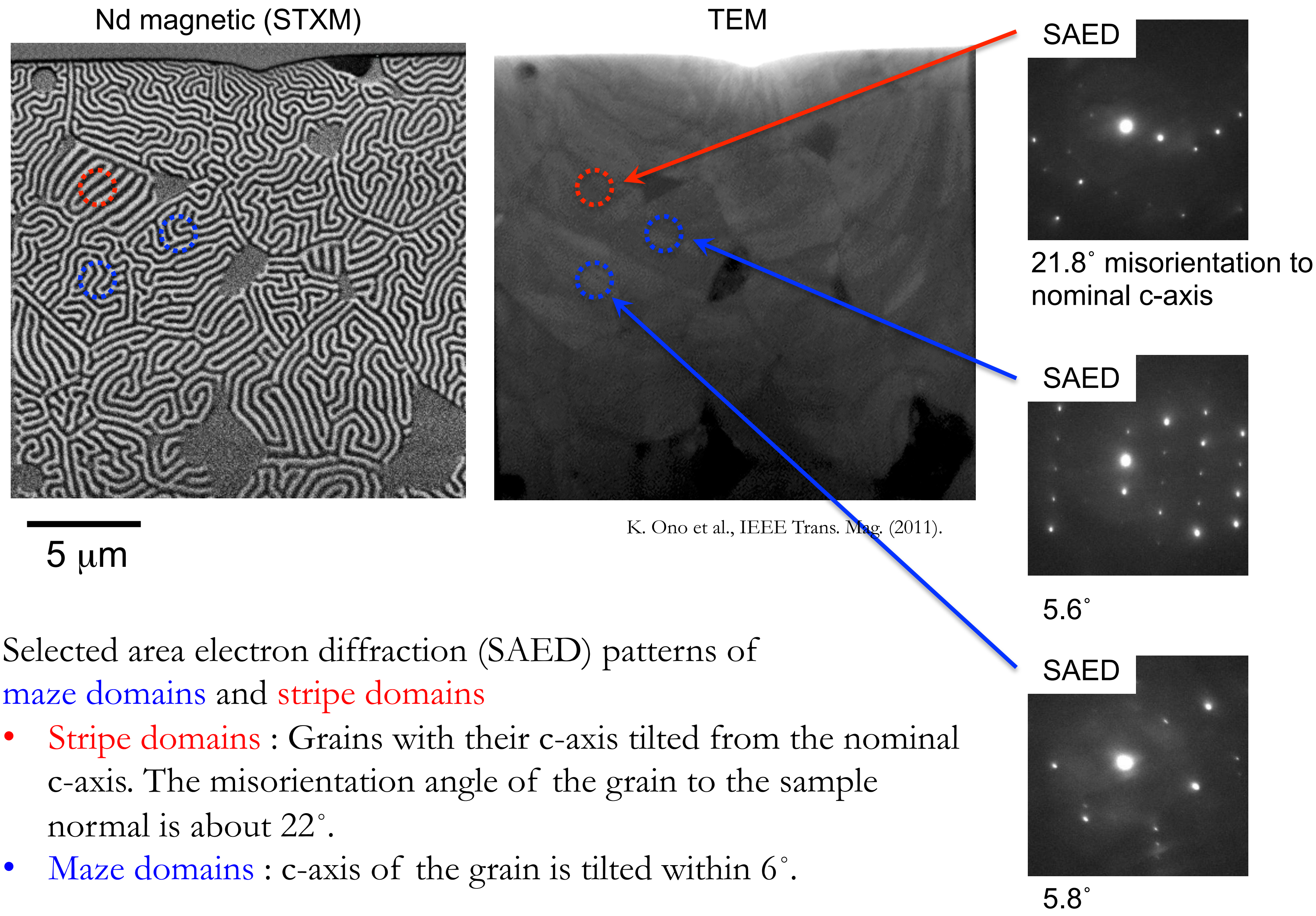
Spatial resolution depends on Fresnel Zone Plate (FZP) : 10 ~ 30 nm

Chemical imaging with tuning an x-ray energy

Magnetic imaging with the use of x-ray magnetic circular dichroism (XMCD)

TEM compatible sample

Maze domains and stripe domains

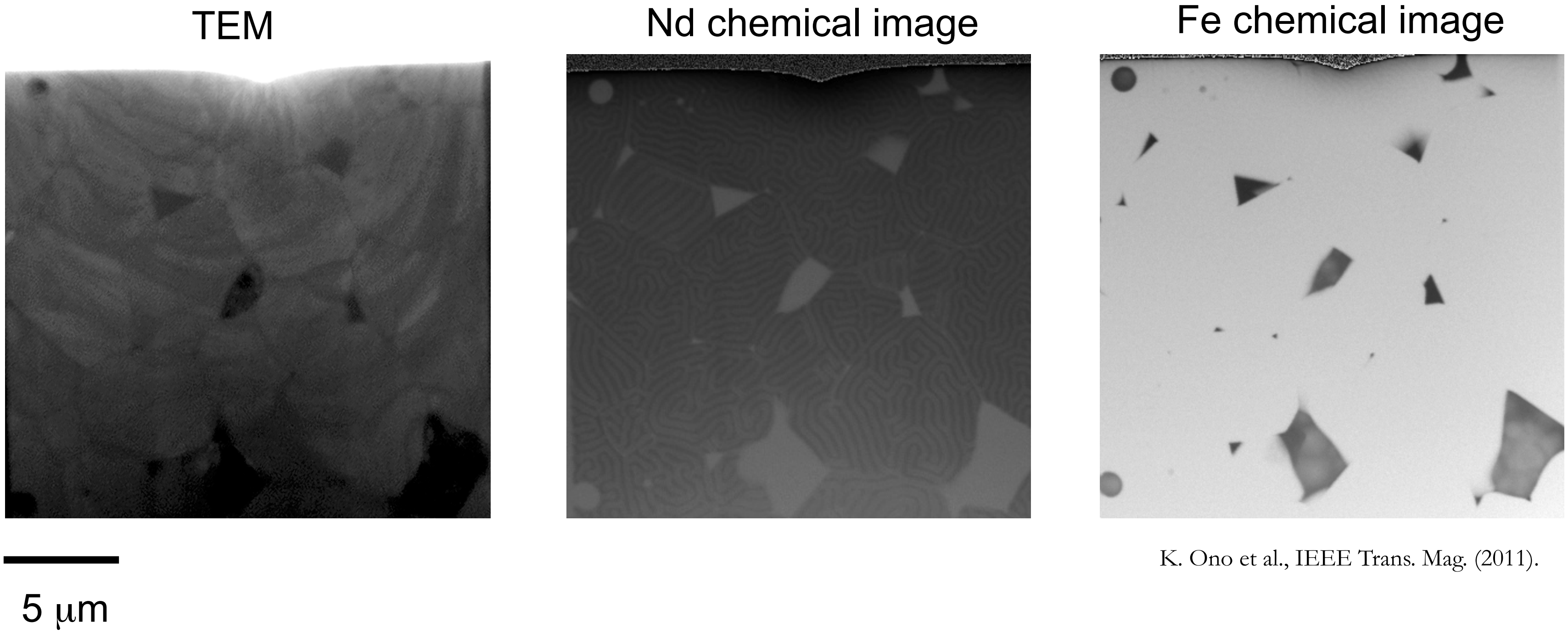


K. Ono et al., IEEE Trans. Mag. (2011).

Selected area electron diffraction (SAED) patterns of maze domains and stripe domains

- Stripe domains : Grains with their c-axis tilted from the nominal c-axis. The misorientation angle of the grain to the sample normal is about 22˚.
- Maze domains : c-axis of the grain is tilted within 6˚.

Grain boundary triple points and the interface

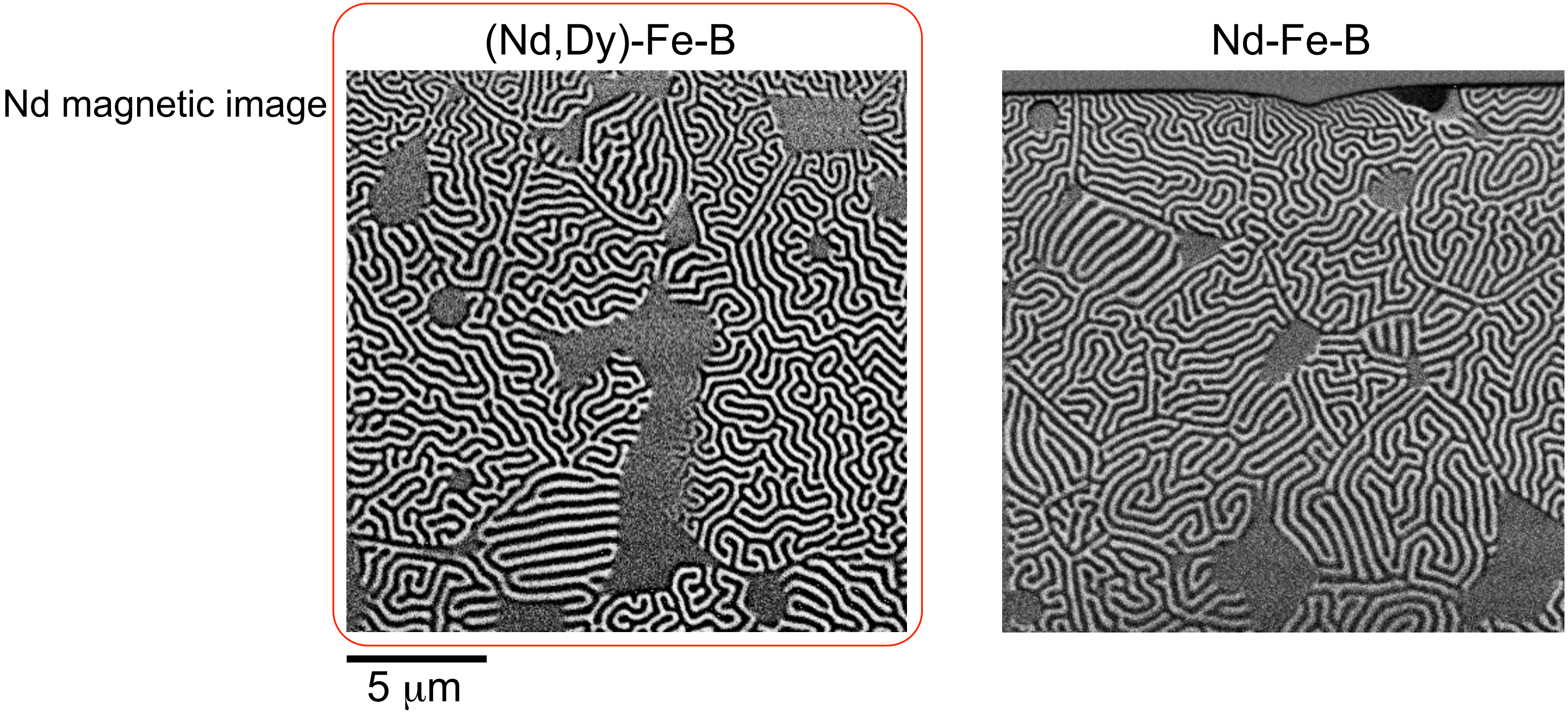


K. Ono et al., IEEE Trans. Mag. (2011).

Fe is poor in Nd-rich regions.
The Nd-rich regions are grain boundary triple points, not pores or cracks.

Sharp chemical contrast shows that the interfaces between $Nd_2Fe_{14}B$ grains and Nd-rich triple points are chemically abrupt without a prominent interdiffusion of Nd at the interface .

Magnetic image of (Nd,Dy)-Fe-B sintered magnet

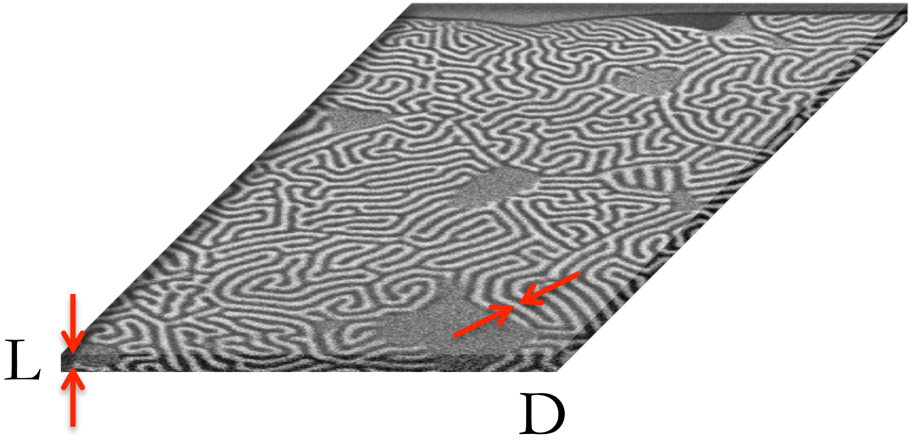


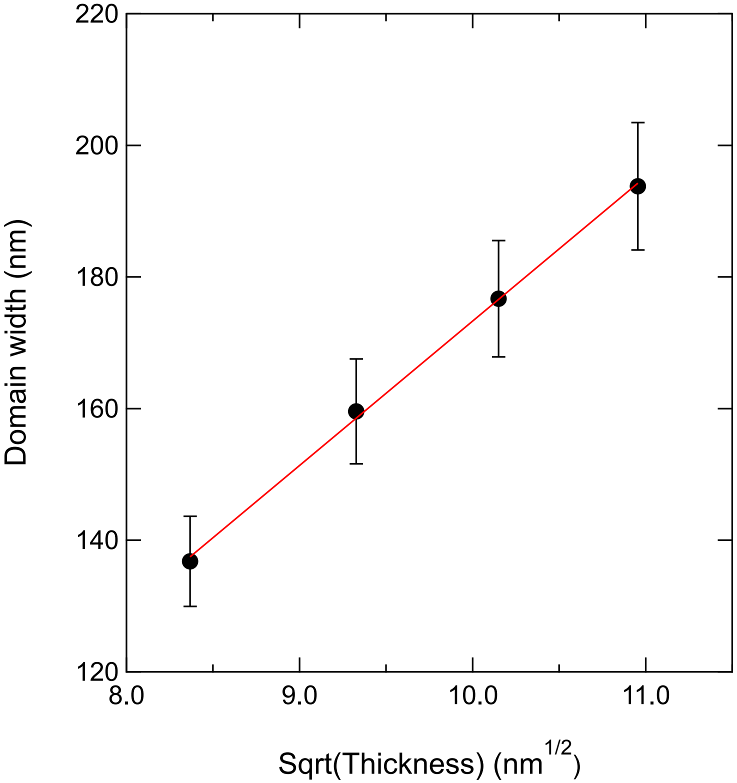
Overall features of magnetic domains in (Nd,Dy)-Fe-B are similar to these in Nd-Fe-B.

Maze and stripe domains

Magnetic domains seem to be terminated at grain boundaries

Domain-wall energy





$$\gamma = \frac{3.4 M_s^2}{1+\sqrt{\mu^*}} \frac{D^2}{L}$$

$$\gamma = 4\sqrt{AK}$$

D : domain width

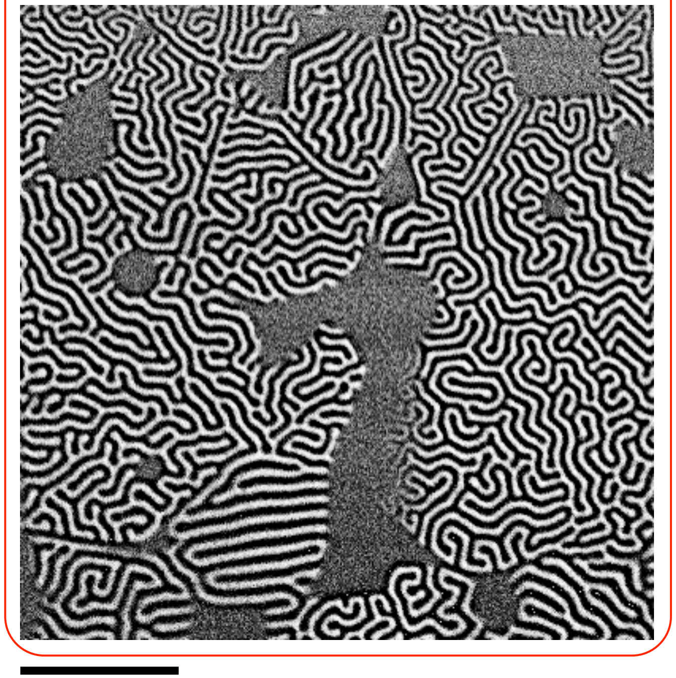
L : thickness

γ : domain-wall energy

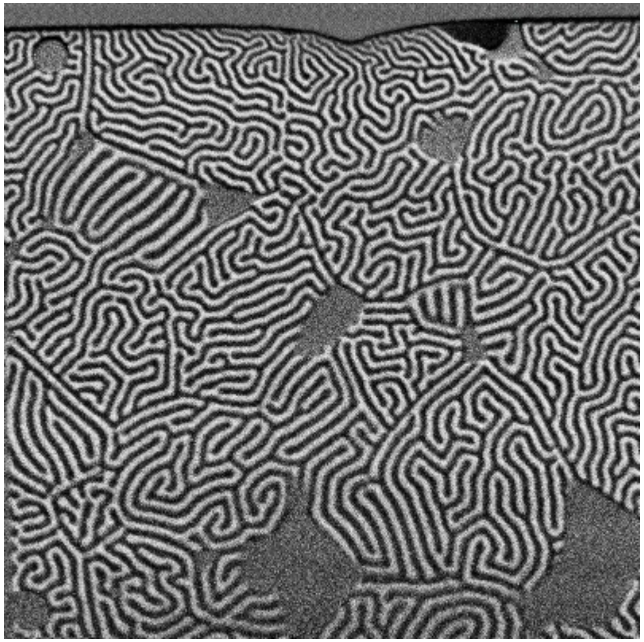
Domain-wall energy

Nd magnetic image

(Nd,Dy)-Fe-B



Nd-Fe-B



Domain width (D) of (Nd,Dy)-Fe-B is 5 % larger than that of Nd-Fe-B.

(Nd,Dy)-Fe-B : 10 % larger domain-wall energy (γ)

$$\gamma = \frac{3.4 M_s^2}{1+\sqrt{\mu^*}} \frac{D^2}{L}$$

20 % larger magnetocrystalline anisotropy

$$\gamma = 4\sqrt{AK}$$

Consistent with our small angle neutron scattering results of bulk sintered magnets

Summary

- 光電子顕微鏡 (PEEM) を用いて、室温強磁性を示す遷移金属酸化物ナノシートの電子状態の研究を行った。
  - 非常に少ない試料 (10^{-18} g) で X線吸収スペクトルをとることに成功した
- 走査型透過軟X線顕微鏡 (STXM) により、(Nd,Dy)-Fe-B 磁石の元素識別磁気イメージングを行った。

今後の展望

→ コヒーレント軟X線を利用したイメージング・顕微分光

時間がないので夜の部で話題提供したいと思います。