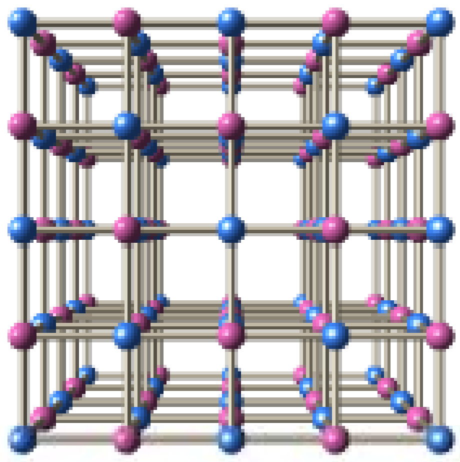
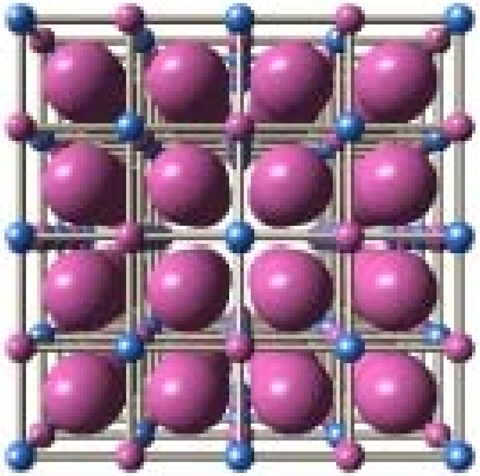
ポリマー型正極材料と界面状態の計測

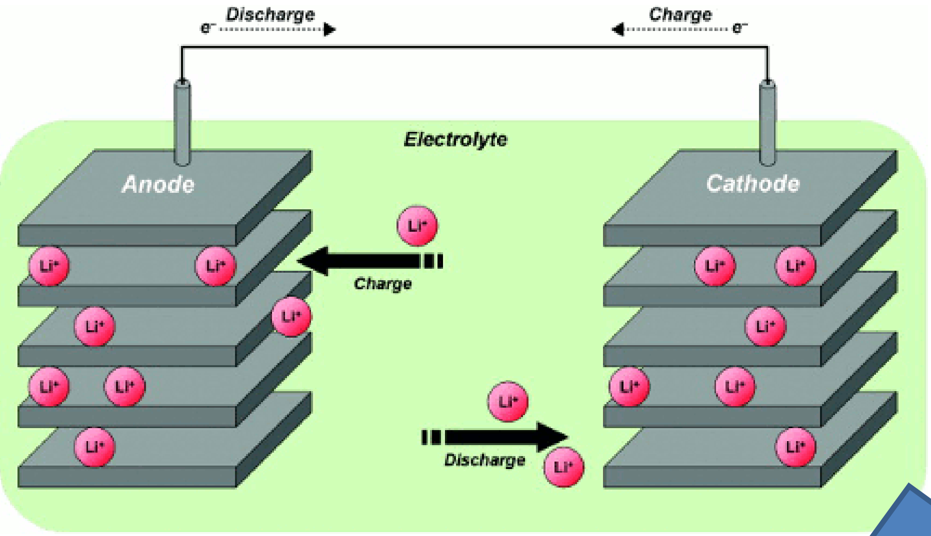


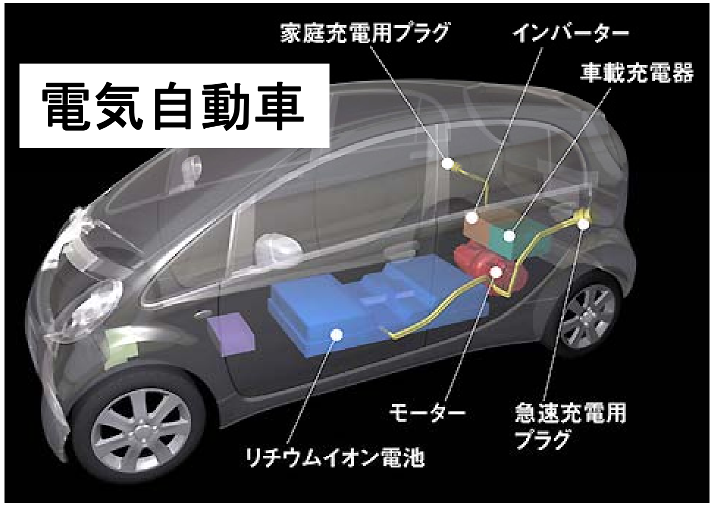


守友　浩

筑波大学

リチウムイオン電池



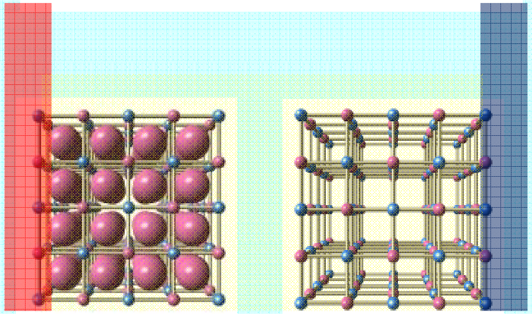


エネルギー貯蔵

↓

物性スイッチ

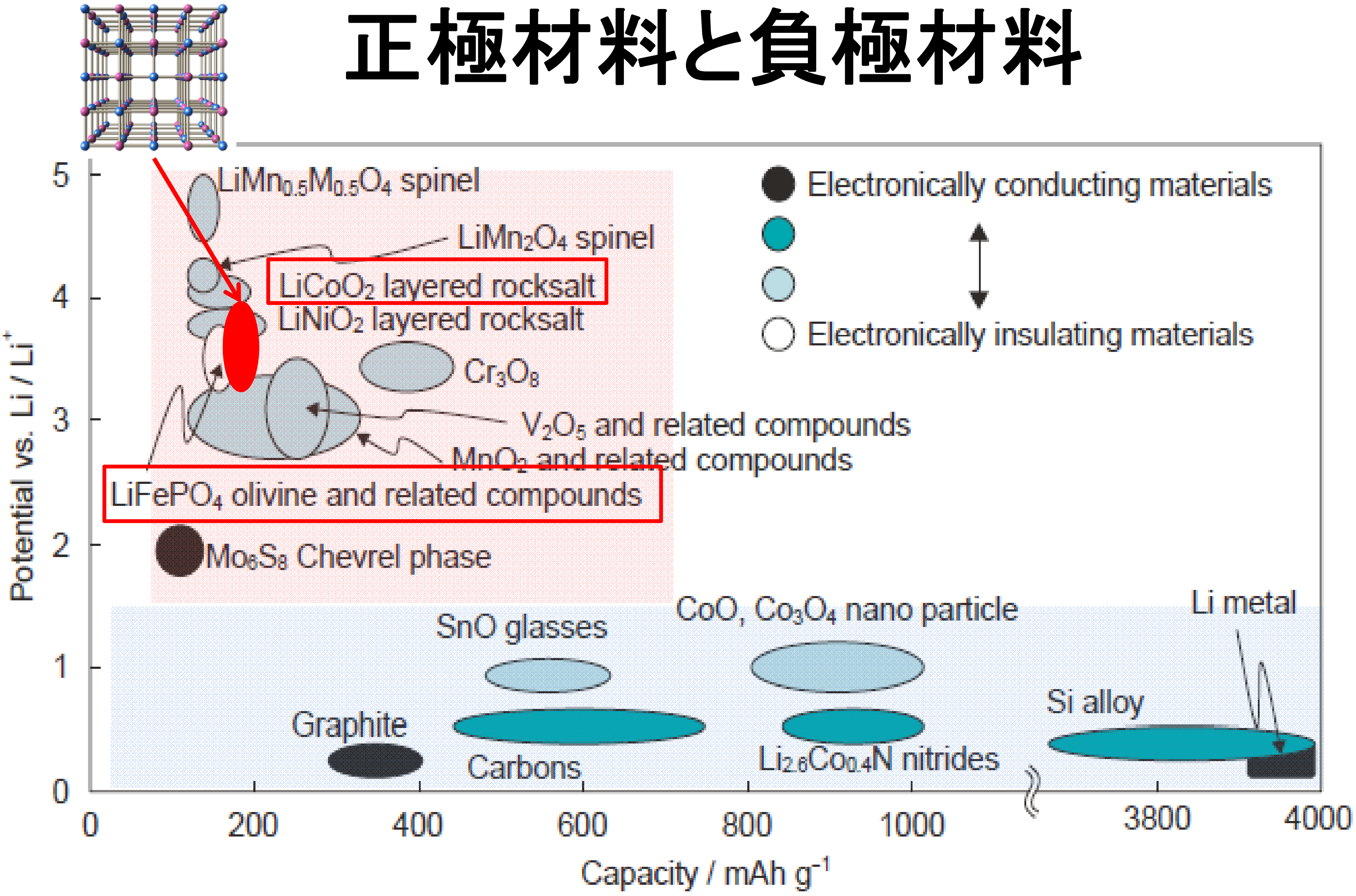
リチウムイオンメモリ



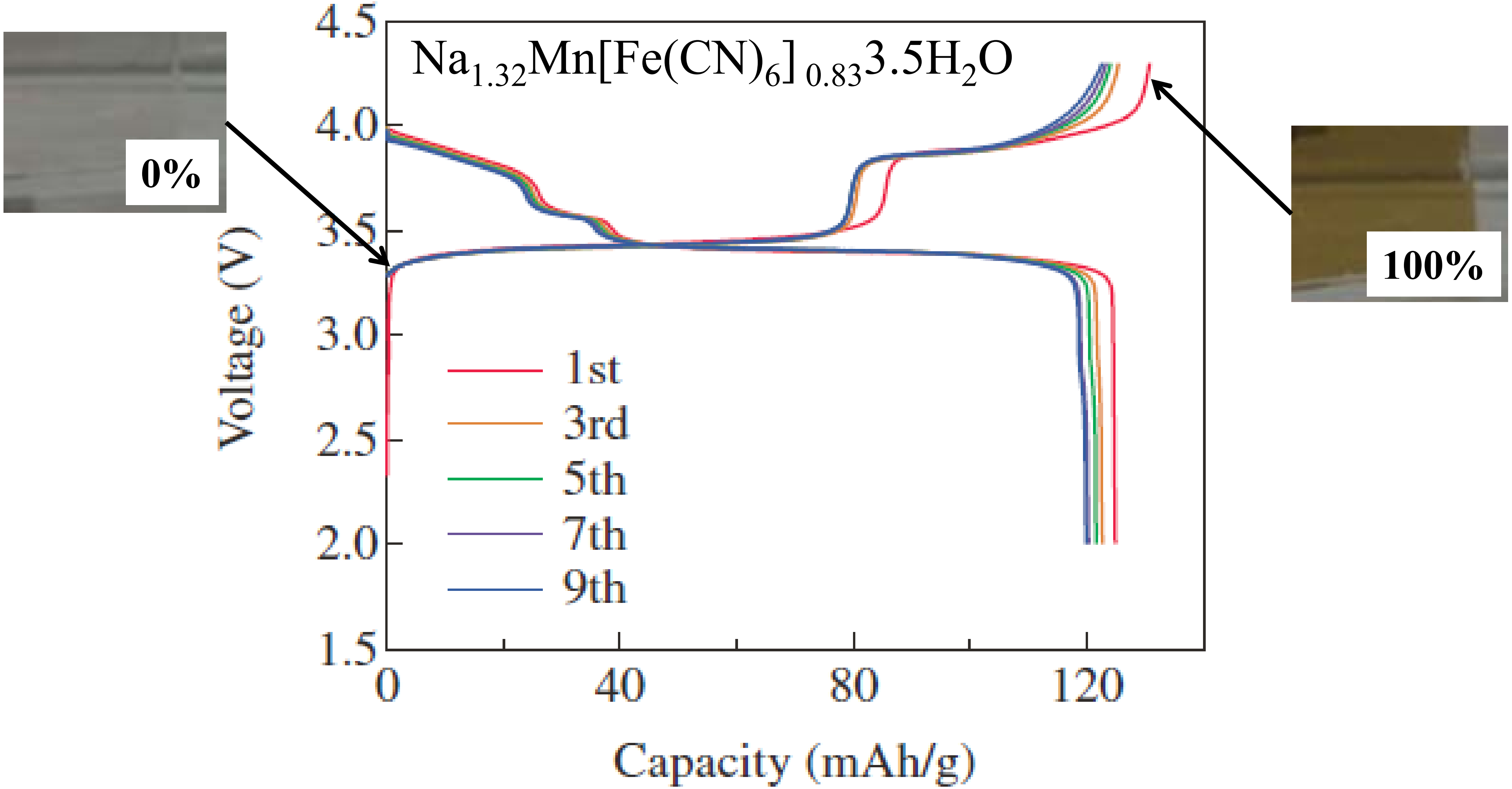
電圧印加で磁性･SHG活性･歪みの制御

Y. Moritomo, et al., APL94(2009)043502

正極材料と負極材料

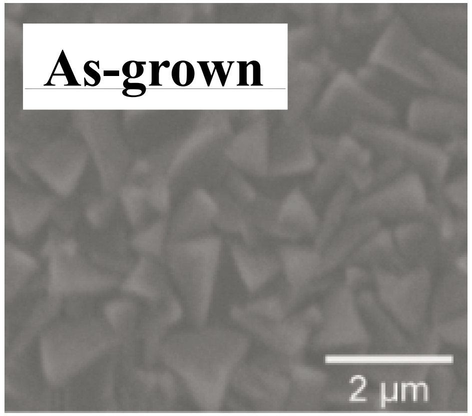

$LiMn_{0.5}M_{0.5}O_4$ spinel
$LiMn_2O_4$ spinel
$LiCoO_2$ layered rocksalt
$LiNiO_2$ layered rocksalt
Cr_3O_8
V_2O_5 and related compounds
MnO_2 and related compounds
$LiFePO_4$ olivine and related compounds
Mo_6S_8 Chevrel phase
Electronically conducting materials
Electronically insulating materials
SnO glasses
CoO, Co_3O_4 nano particle
Li metal
Si alloy
Graphite
Carbons
$Li_{2.6}Co_{0.4}N$ nitrides
Potential vs. Li / Li^+
5
4
3
2
1
0
0
200
400
600
800
1000
3800
4000
Capacity / mAh g^{-1}

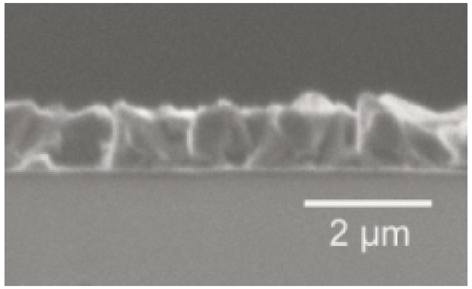
ポリマー型正極材料



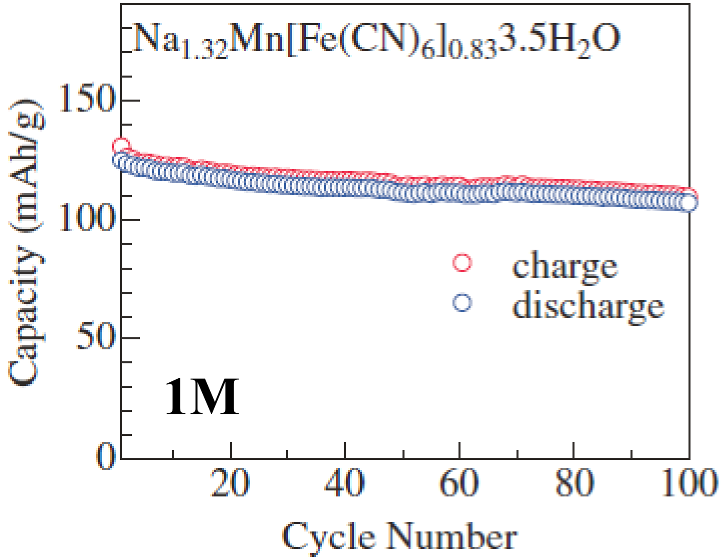
T. Matsuda, et al., APEX4(2011)047101

堅固なネットワークとグレイン

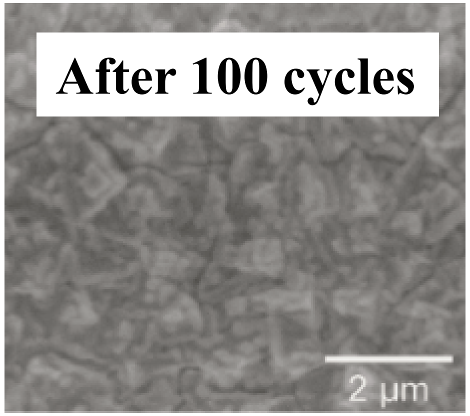


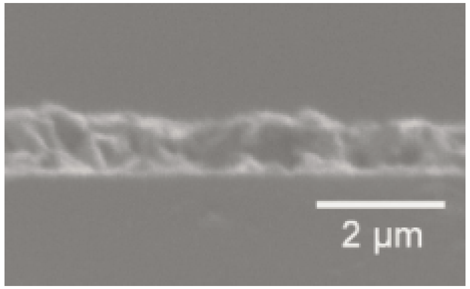


The Film consists of large crystalline grains (~1μm).



- **Large capacity (128mAh/g)**
- **Good cyclability (87% of the initial value after 100 cycles.**





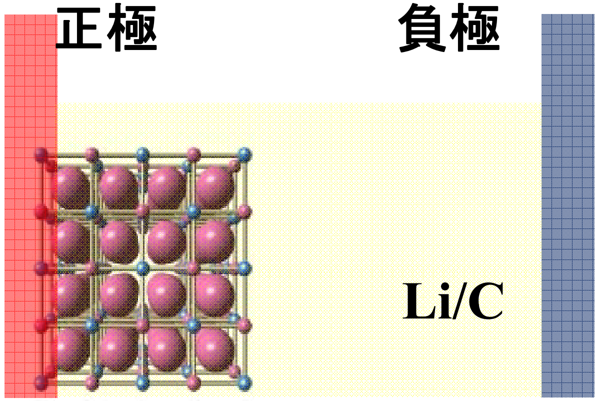
Overall grain structure is the same as the as-grown film. but edge regions are rounded and small **particles** are observed on the faces.

ポリマー型正極材料

1. 新しい材料系である。
2. 『カラー電池』という機能性を付加している。
3. 次世代正極材料としては、容量のインパクトにかける。
4. バインダーフリーであるので、リチウムイオン電池の精密科学には、貢献する。

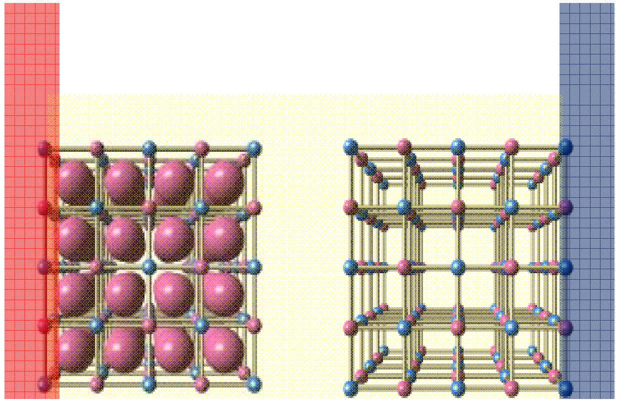
薄膜型電極の先にあるもの

(a) リチウムイオン電池



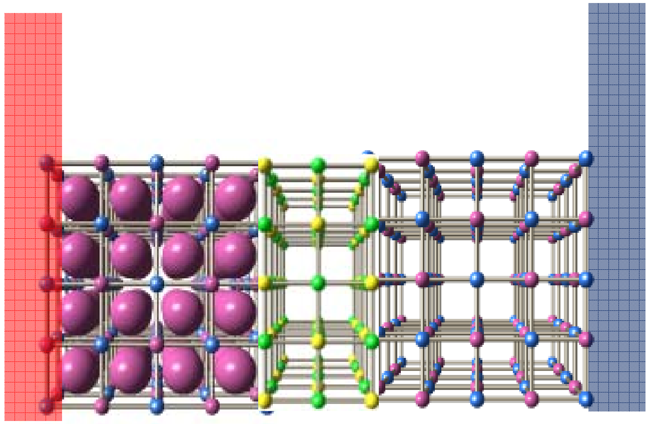
電解質溶液

(b) リチウムイオンメモリ



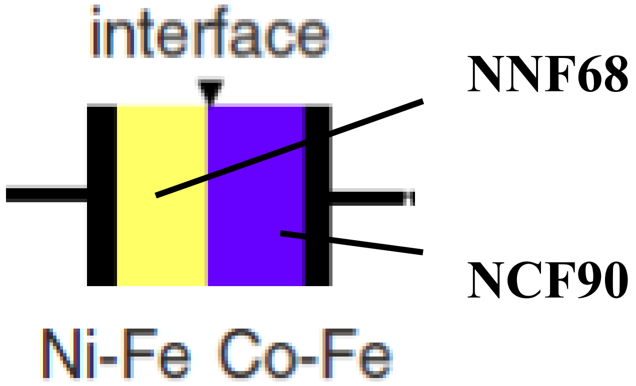
磁性スイッチ
SHGスイッチ
歪みスイッチ

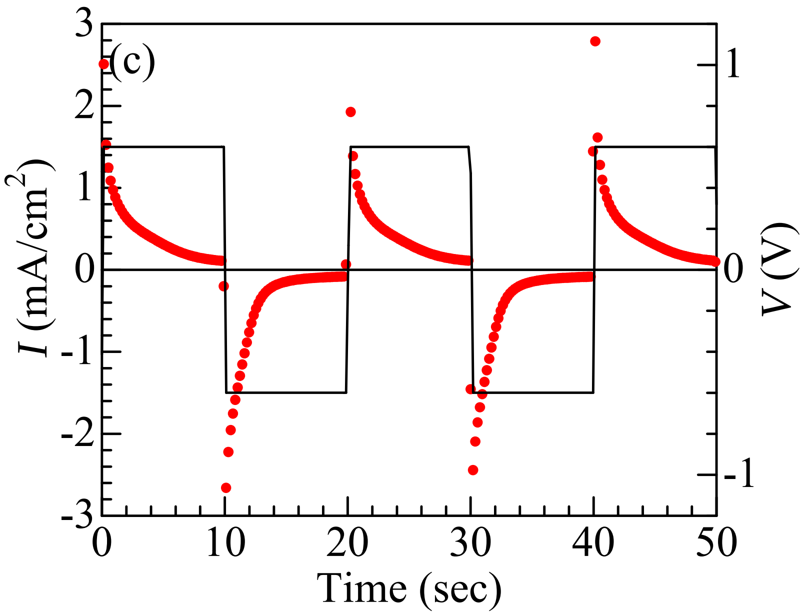
(c) 全固体イオンメモリ



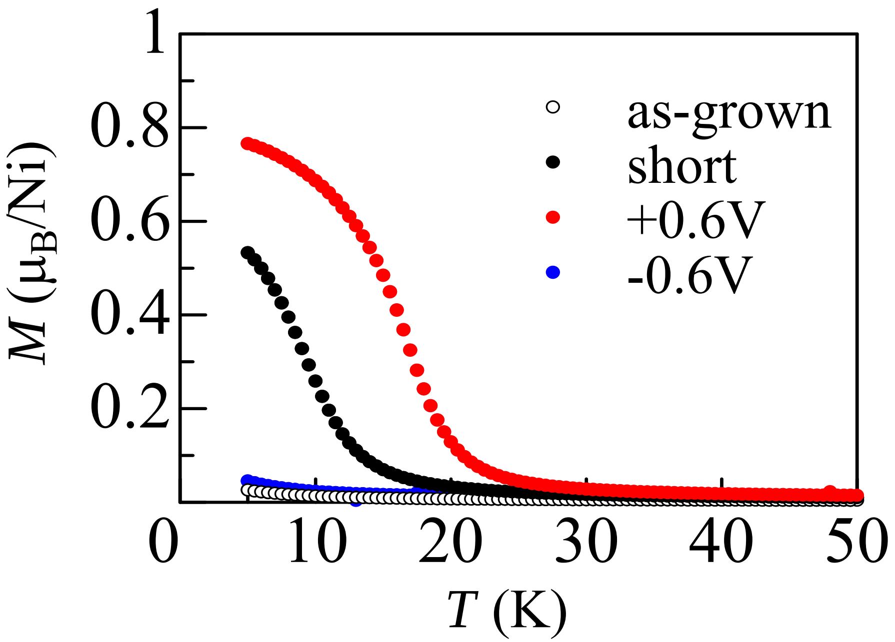
エピ界面の構築が不可欠

イオンメモリの例：磁性スイッチ





Ni^{2+}-$Fe^{2+\delta}$

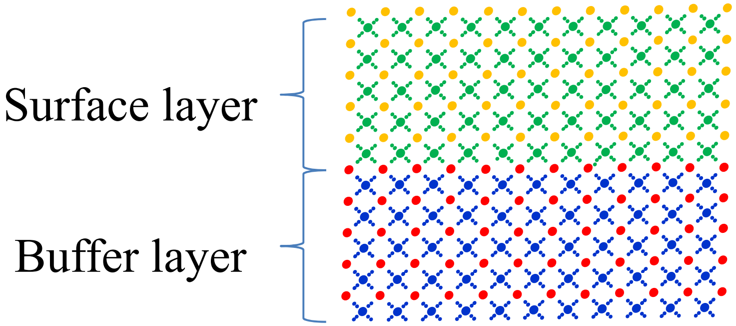


Y. Moritomo & T. Shibata, APL94(2009)043502

Epitaxial interface

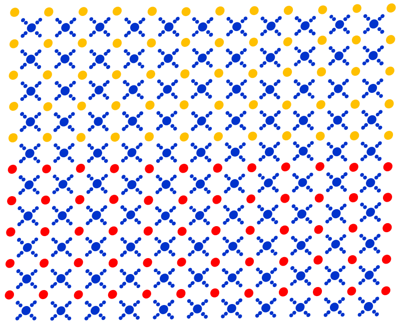
1. Epitaxial interface increases the contact area and reduces the response time.
2. Epitaxial interface causes a new electronics in molecular system.

$$A_x\, M_A\, [M_B\, (CN)_6]_y\, zH_2O$$

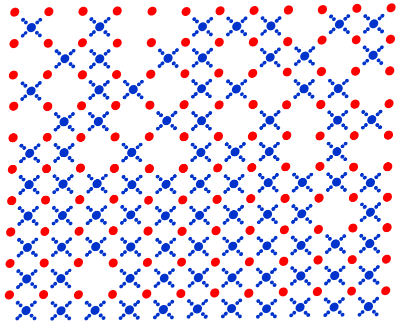


$M_A \neq M'_A$

$M_B \neq M'_B$



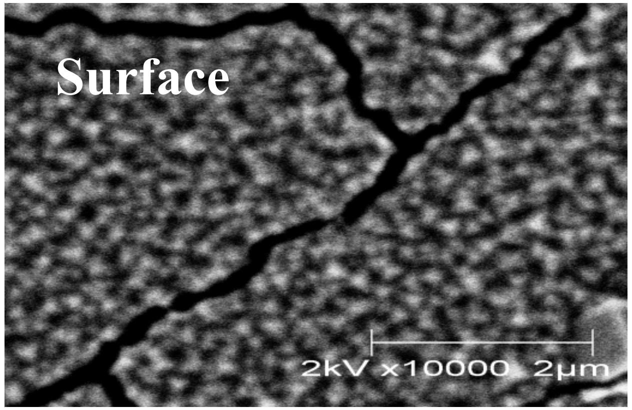
$M_A \neq M'_A$

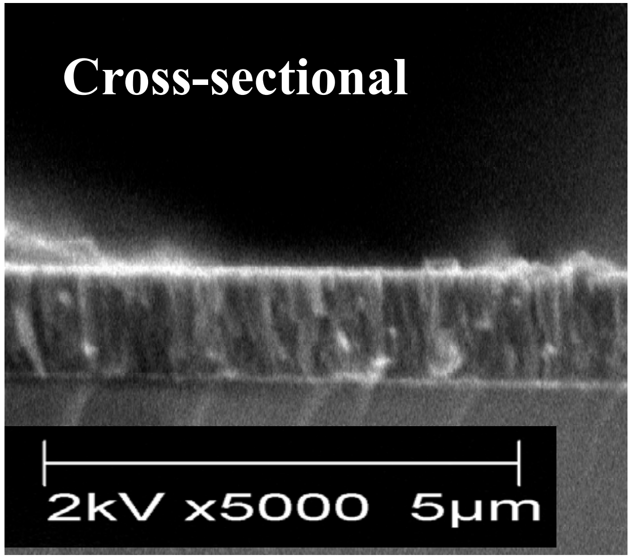


$y \neq y'$

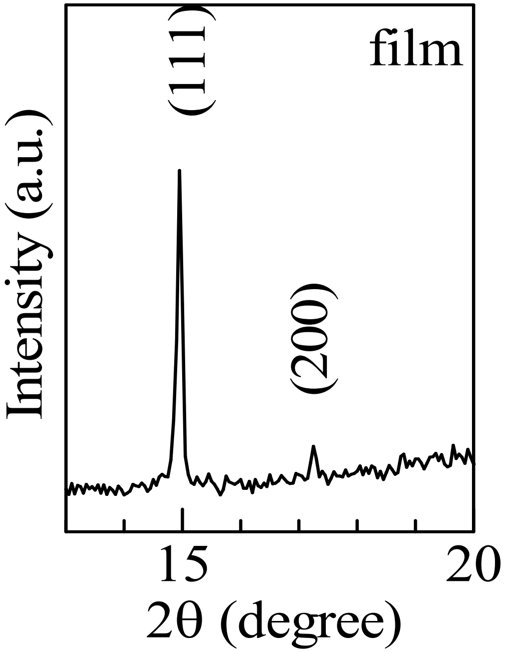
Structure of buffer layer

NCF71



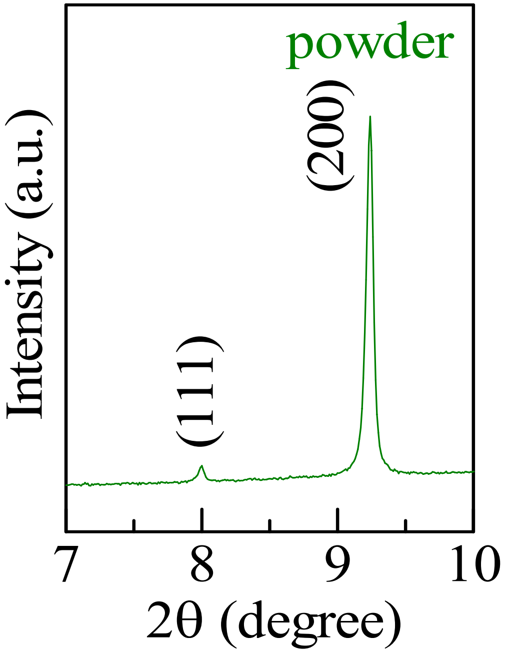


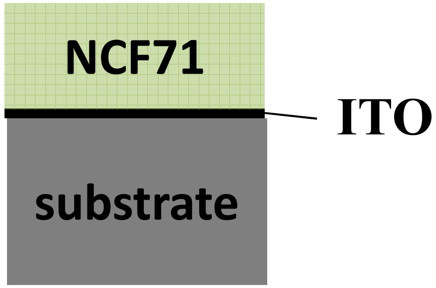
λ = 1.54 Å



Strong (111)-oriention

λ = 0.829 Å

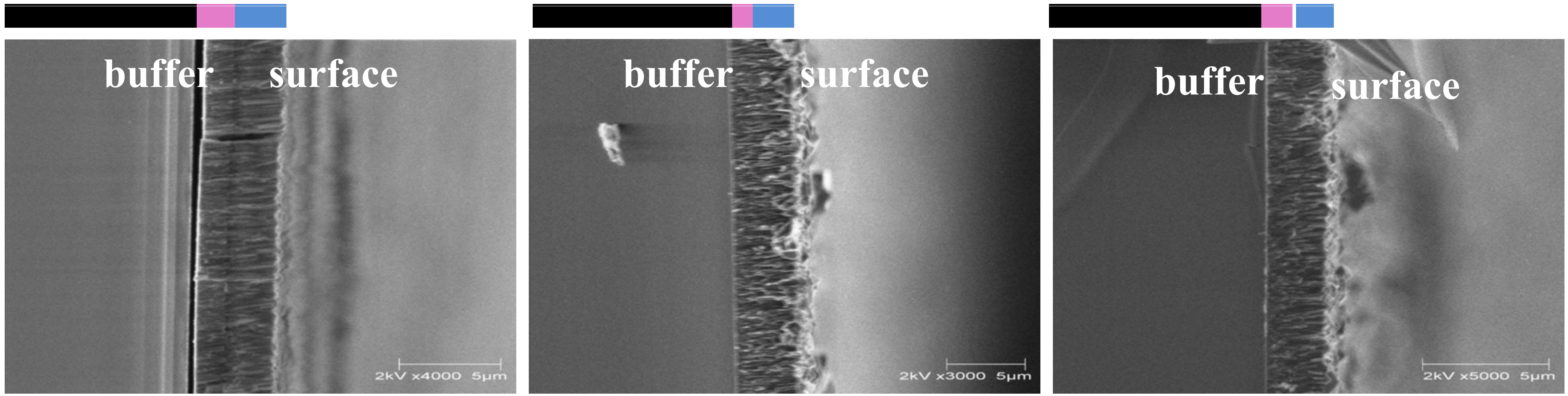




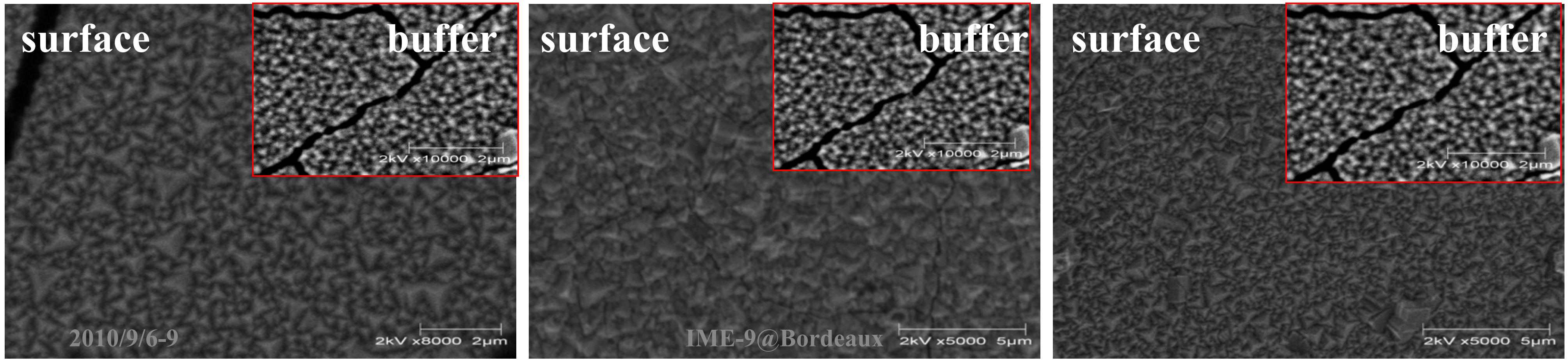
SEM image of by-layer film

NCF71/Fe-Cr **NCF71/Mn-Fe** **NCF71/NCF90**

Cross-sectional SEM

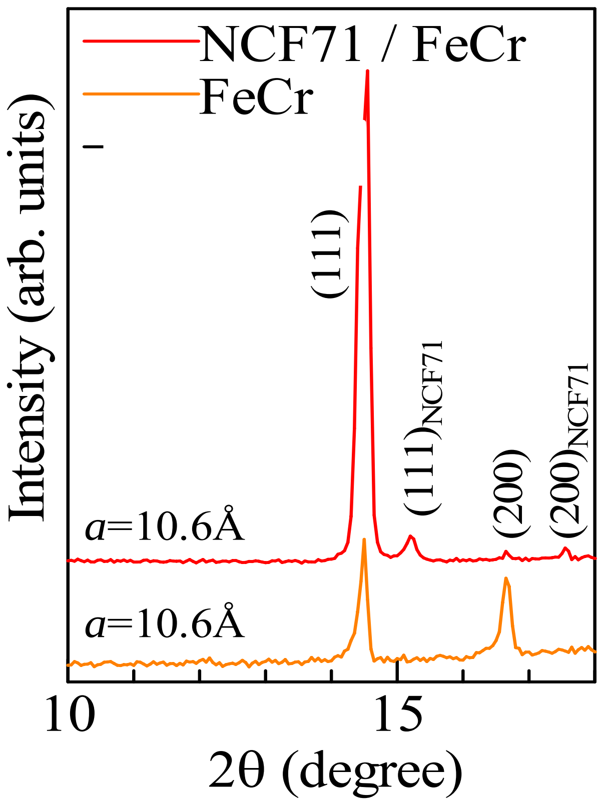


Surface SEM



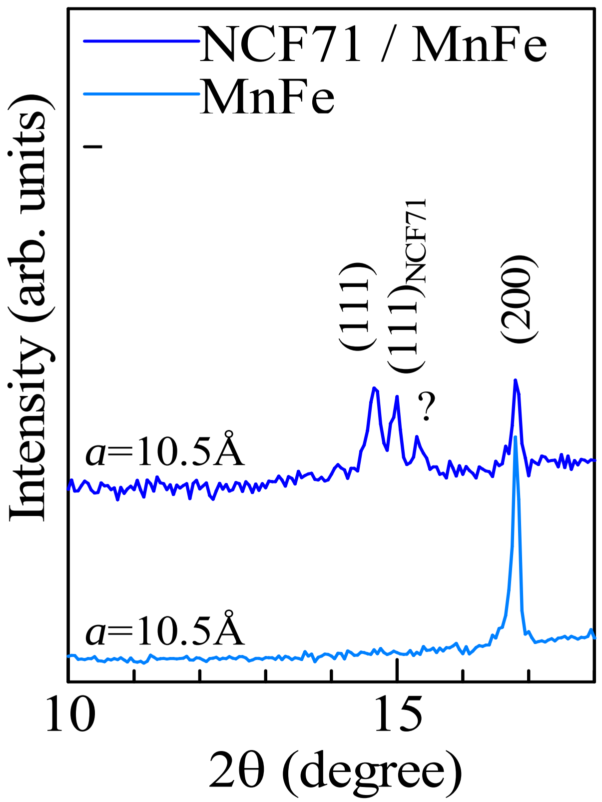
XRD pattern of mono-/bi-layer film

NCF71/Fe-Cr



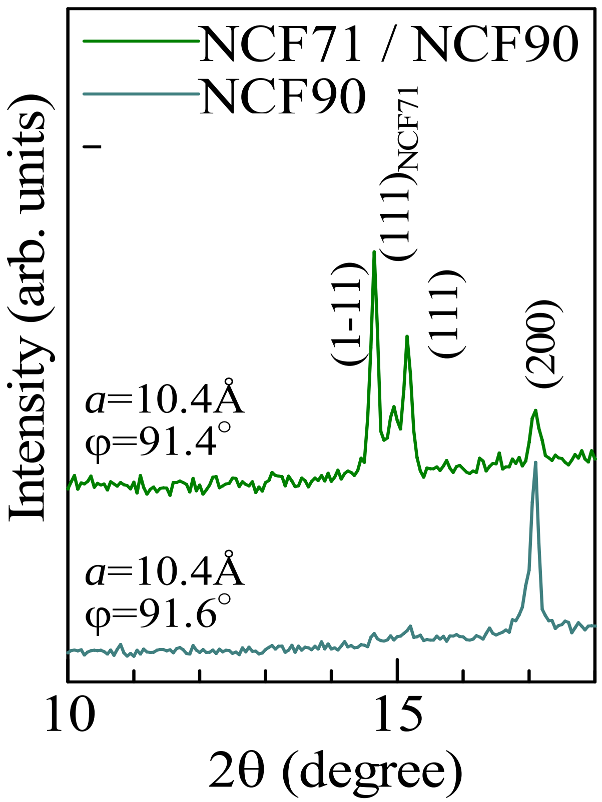
Cubic

NCF71/Mn-Fe



Cubic

NCF71/NCF90



Rhombohedral

Quantitative analysis of film orientation

Measure of orientation

$$S = \frac{v_{200}^{film}}{v_{111}^{film}}$$

v_{hkl}: **volume fraction**

The smaller S is, the higher the orientation is.

Intensity ration of Bragg reflection

$$\frac{I^{film}{}_{200}}{I^{film}{}_{111}} = S \cdot \frac{\left|F_{200}\right|^2 m_{200} \cdots}{\left|F_{111}\right|^2 m_{111} \cdots}$$

F_{hkl}: structure factor

m_{hkl}:degeneracy

For powder diffraction, ·····

$$\frac{\left|F_{200}\right|^2 m_{200} \cdots}{\left|F_{111}\right|^2 m_{111} \cdots} = \frac{I_{200}^{powder}}{I_{100}^{powder}}$$

$$\because) \; \frac{v_{200}^{powder}}{v_{111}^{powder}} = 1$$

$$\boxed{\therefore S = \frac{I_{200}^{film}}{I_{111}^{film}} \cdot \frac{\left|F_{111}\right|^2 m_{111} \cdots}{\left|F_{200}\right|^2 m_{200} \cdots} = \frac{I_{200}^{film}}{I_{111}^{film}} \Big/ \frac{I_{200}^{powder}}{I_{111}^{powder}}}$$

Results

	buffer layer	Surface layer		
	NCF71	Fe-Cr	Mn-Fe	NCF90
mono-layer film	200	17	5	5
bi-layer film	200	500	170	200

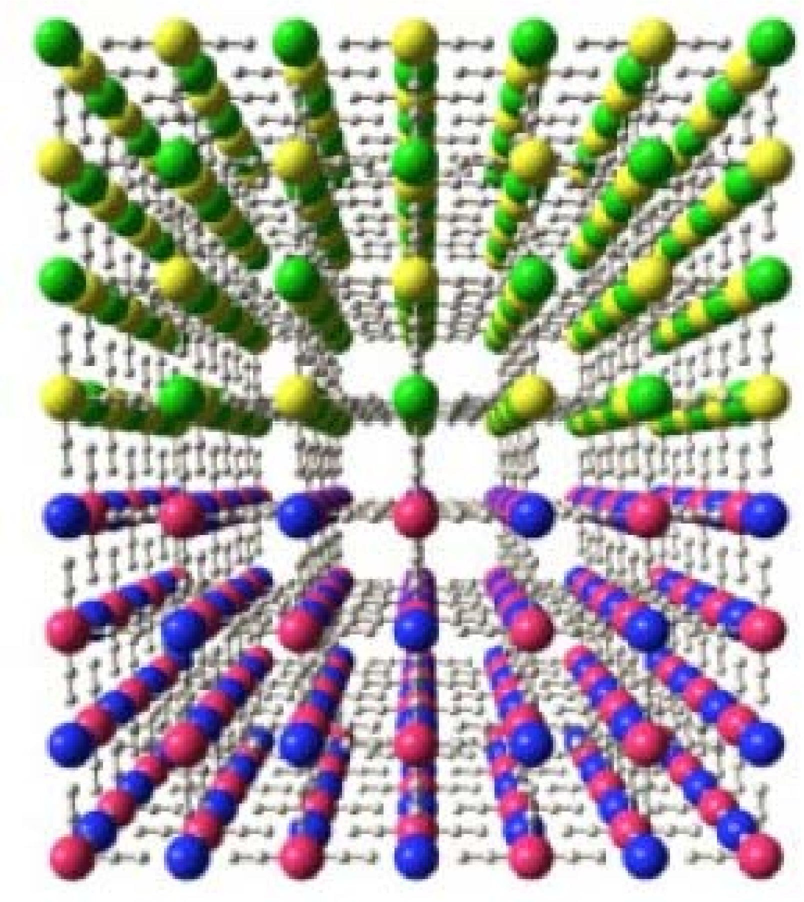
S-values of the surface layers are small as that of the buffer layer.

Epitaxial growth is successful!

Y. Kurihara, et al., JJAP50(2011)060201

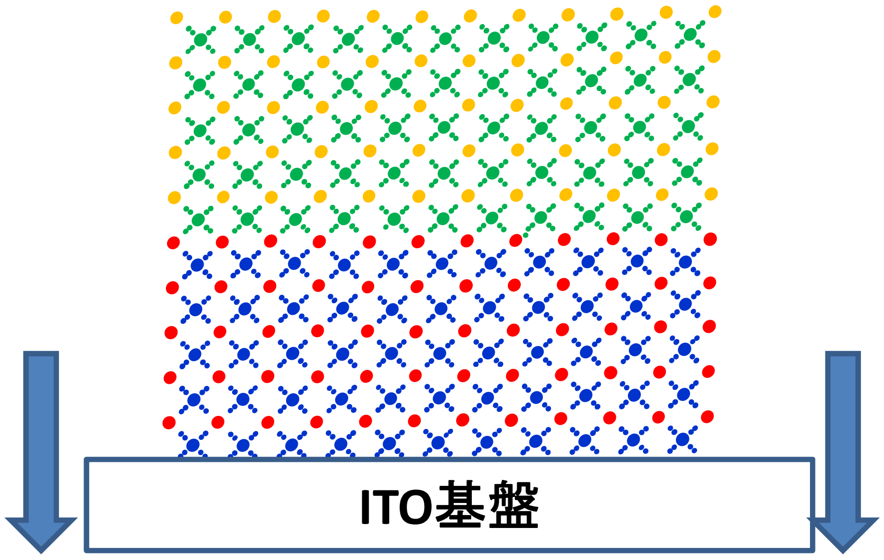
エピ界面

1. バッファーをかませて膜質向上
2. 膜形態の制御
3. 超格子の作製
4. 界面の電子状態の利用



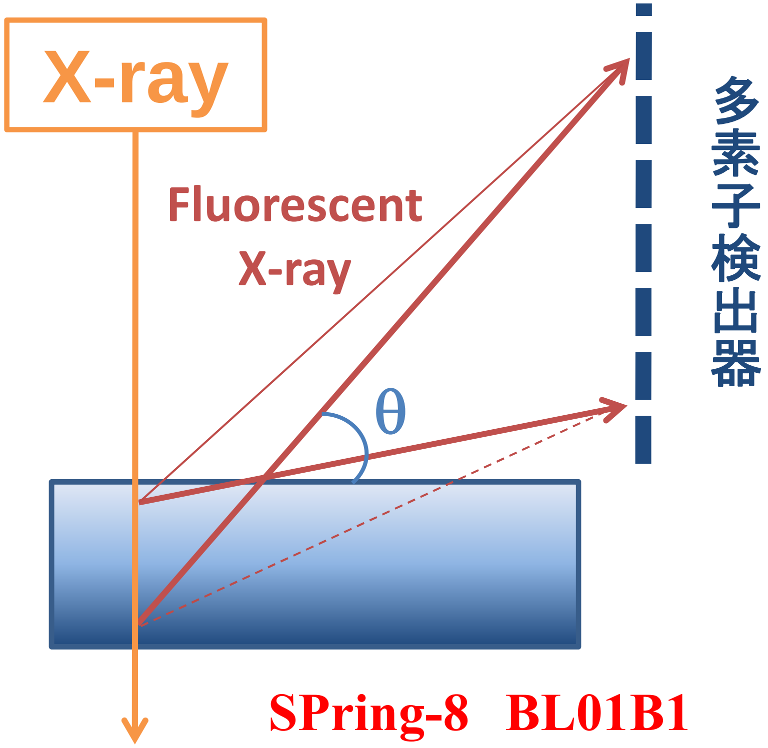
エピ膜の酸化プロセス

どちらの層から抜けるのか？



電子を引き抜く

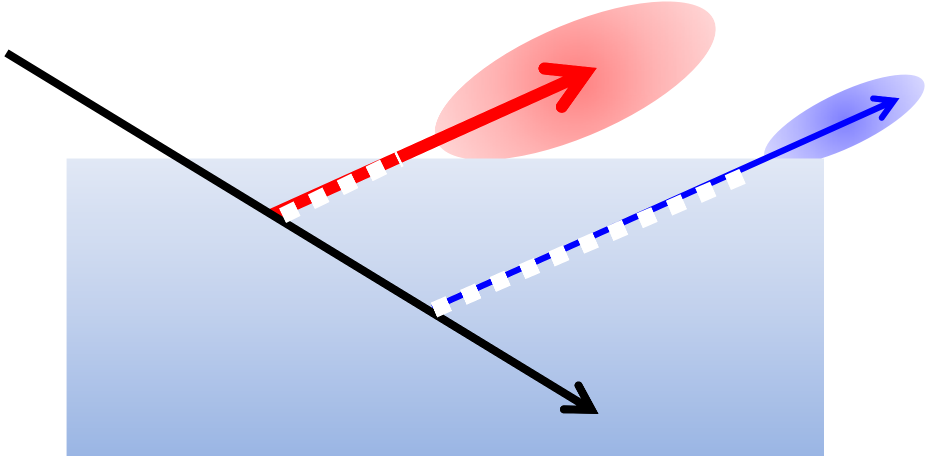
斜出射深さ分解XAFS法



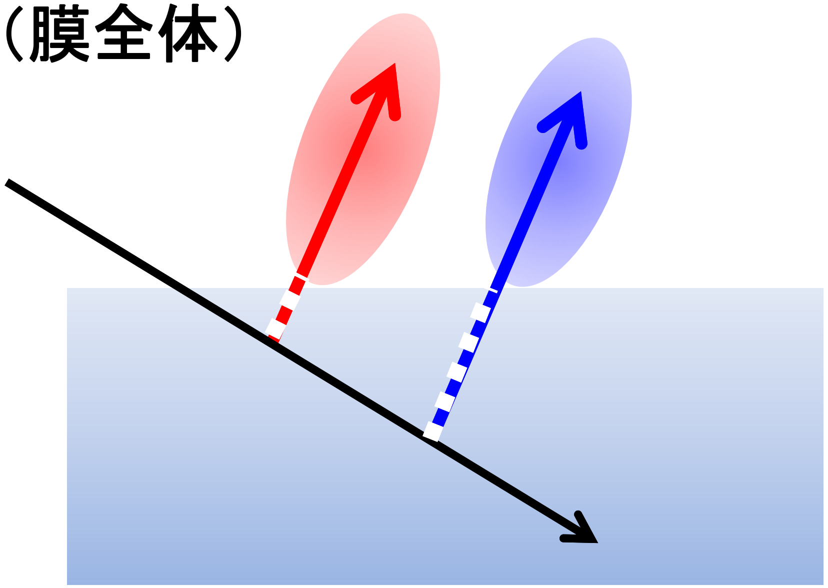
SPring-8　BL01B1

斜出射深さ分解XAFS

浅い角度
（表面成分）



深い角度
（膜全体）

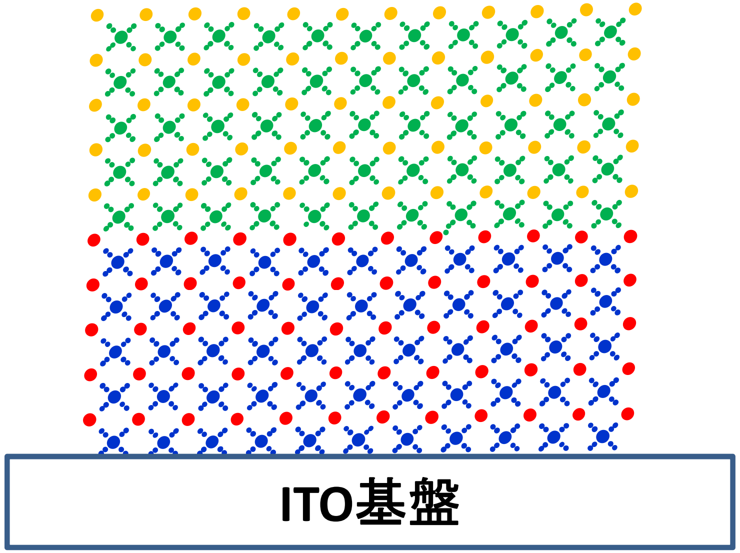


$$dI = I_z e^{-\mu z/\sin\theta} dz$$

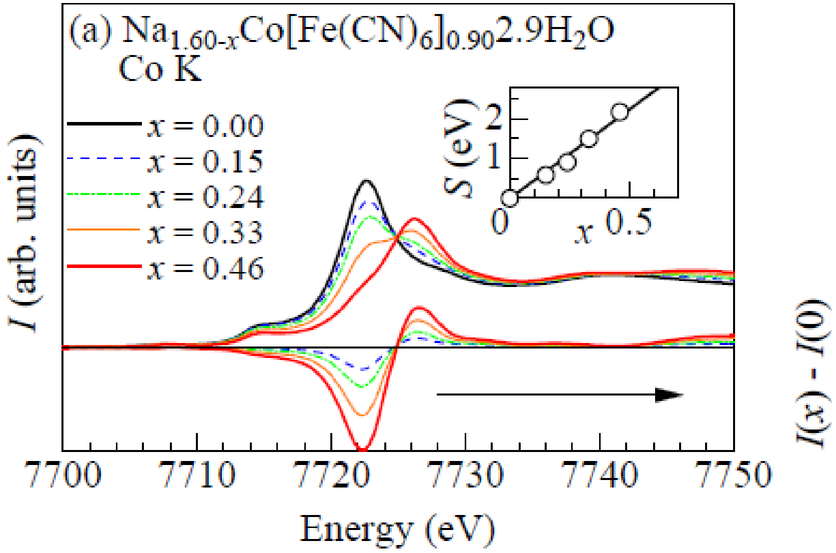
I_z：深さzにおける単位深さあたりの蛍光X線強度
μ：蛍光X線の吸収係数
θ：出射角度

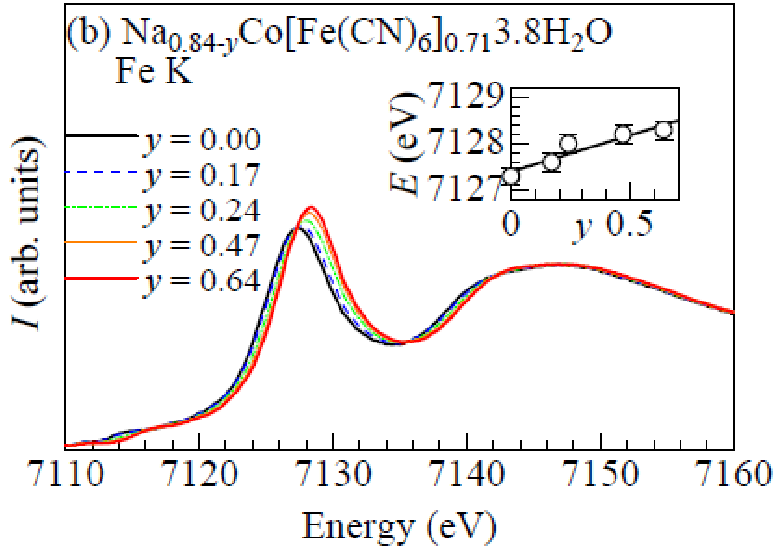
試料

Surface layer
NCF90 200nm $Co^{2+} \rightarrow Co^{3+}$



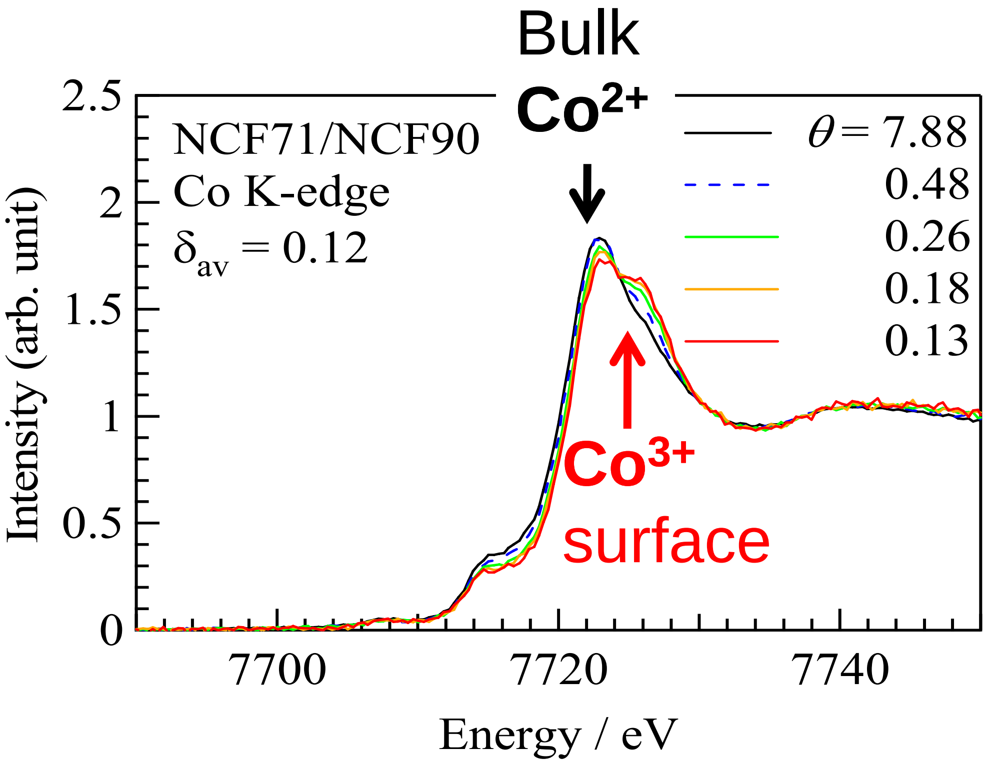
Buffer layer
NCF90 2200nm $Fe^{2+} \rightarrow Fe^{3+}$



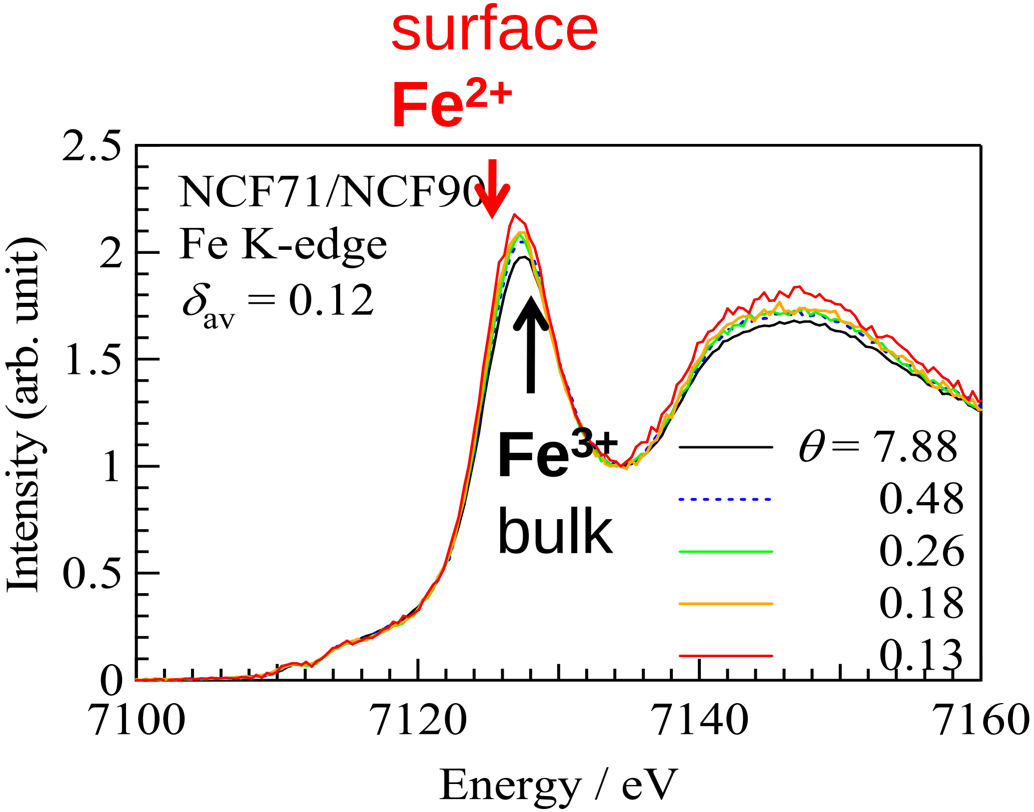


NCF71/NCF90の角度分解スペクトル

δ_{av}：膜全体のカチオンの平均濃度
θ：蛍光X線の出射角度

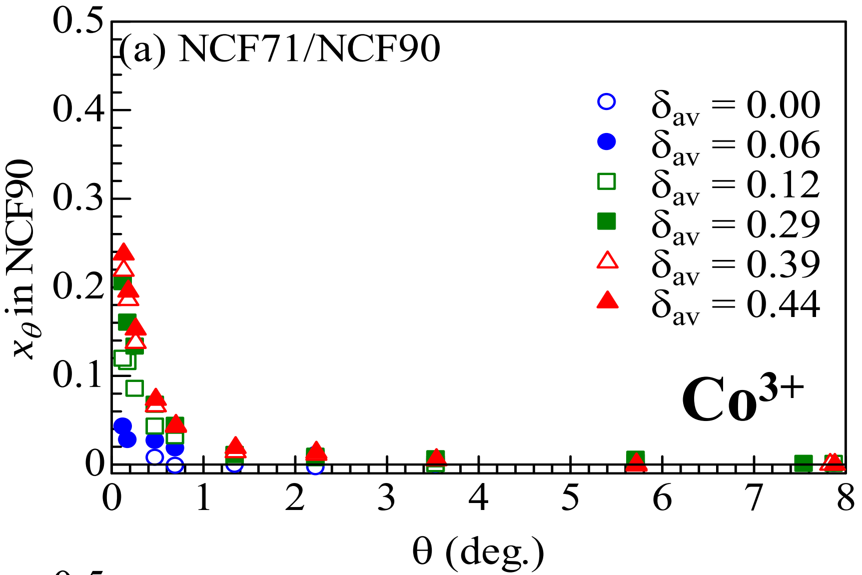

Bulk Co^{2+}

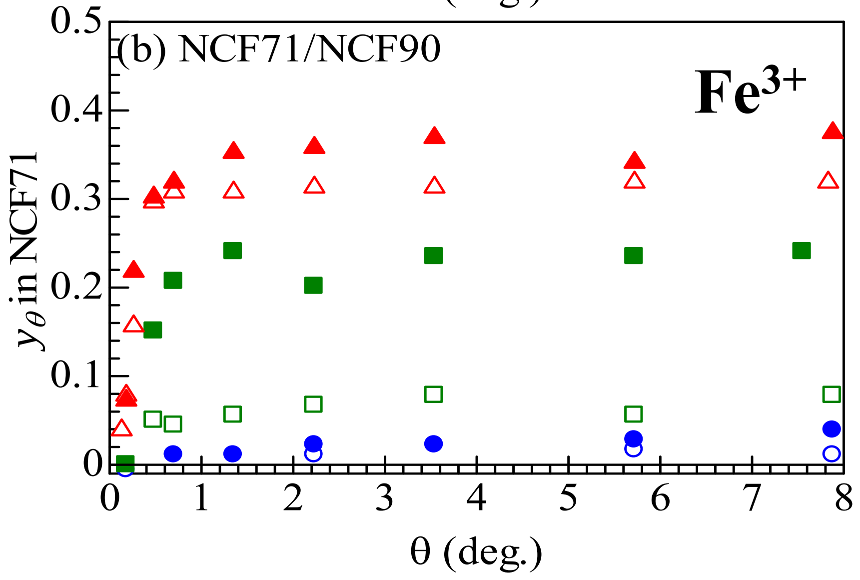
Co^{3+} surface


surface Fe^{2+}

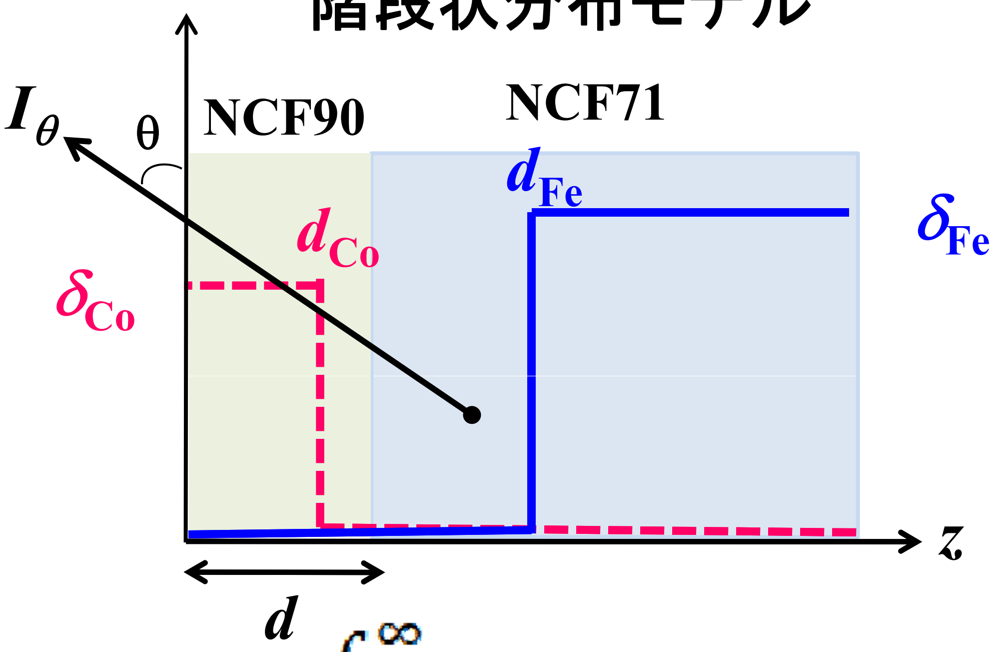
Fe^{3+} bulk

見かけの価数の角度依存性





階段状分布モデル



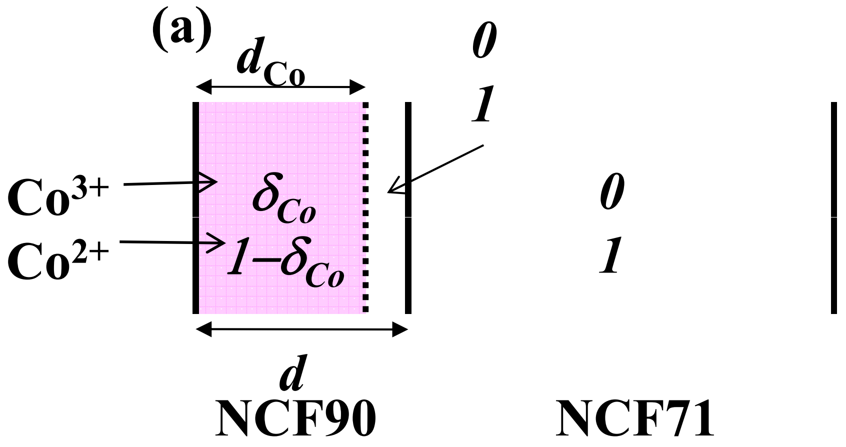
$$I_\theta = \int_0^\infty I_z \, e^{-\mu z/\sin\theta} \, dz$$

$$\mu = \rho \sum w_i (\mu/\rho)_i$$

< モデルの詳細 >

Co^{3+}の分布

d_{Co} : Co^{3+}の分布深さ


(a)

d_{Co}

0
1

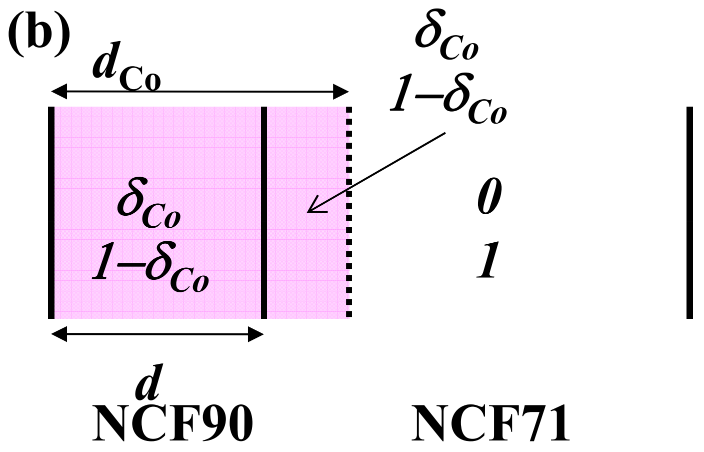
Co^{3+}
Co^{2+}

δ_{Co}
$1-\delta_{Co}$

0
1

d

NCF90 NCF71


(b)

d_{Co}

δ_{Co}
$1-\delta_{Co}$

δ_{Co}
$1-\delta_{Co}$

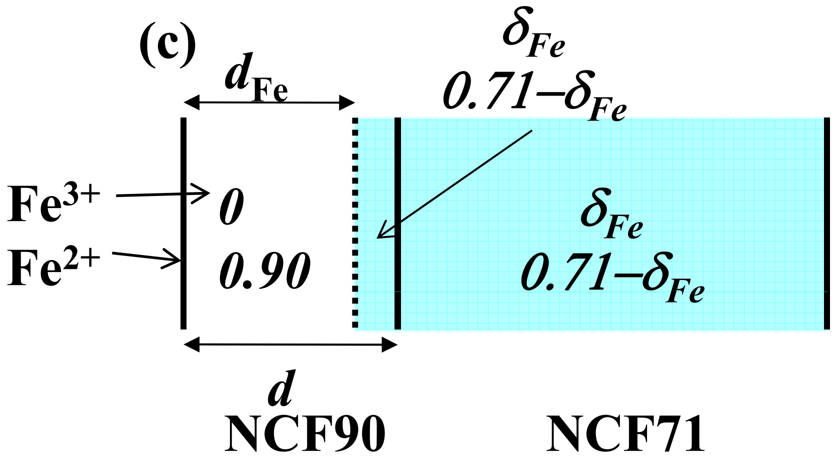
0
1

d

NCF90 NCF71

Fe^{3+}の分布

d_{Fe} : Fe^{3+}の分布深さ


(c)

d_{Fe}

δ_{Fe}
$0.71-\delta_{Fe}$

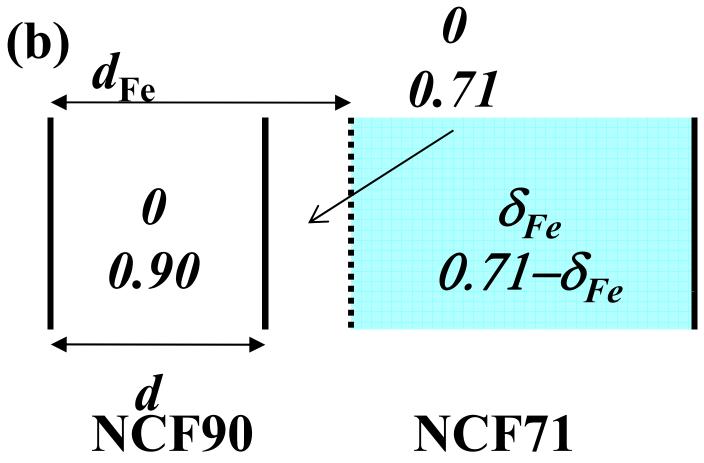
Fe^{3+}
Fe^{2+}

0
0.90

δ_{Fe}
$0.71-\delta_{Fe}$

d

NCF90 NCF71


(b)

d_{Fe}

0
0.71

0
0.90

δ_{Fe}
$0.71-\delta_{Fe}$

d

NCF90 NCF71

<モデルの詳細:Co価数の 角度依存性 >

$\boxed{I_{\mathrm{Co}^{3+}} = I_{\mathrm{Co}^{2+}}}$ **仮定**

$$\mu_z^{\mathrm{Co}} \equiv \frac{d\mu_s^{\mathrm{Co}} + (z-d)\mu_b^{\mathrm{Co}}}{z}$$

(a) $d_{\mathrm{Co}} \leq d$ のとき、

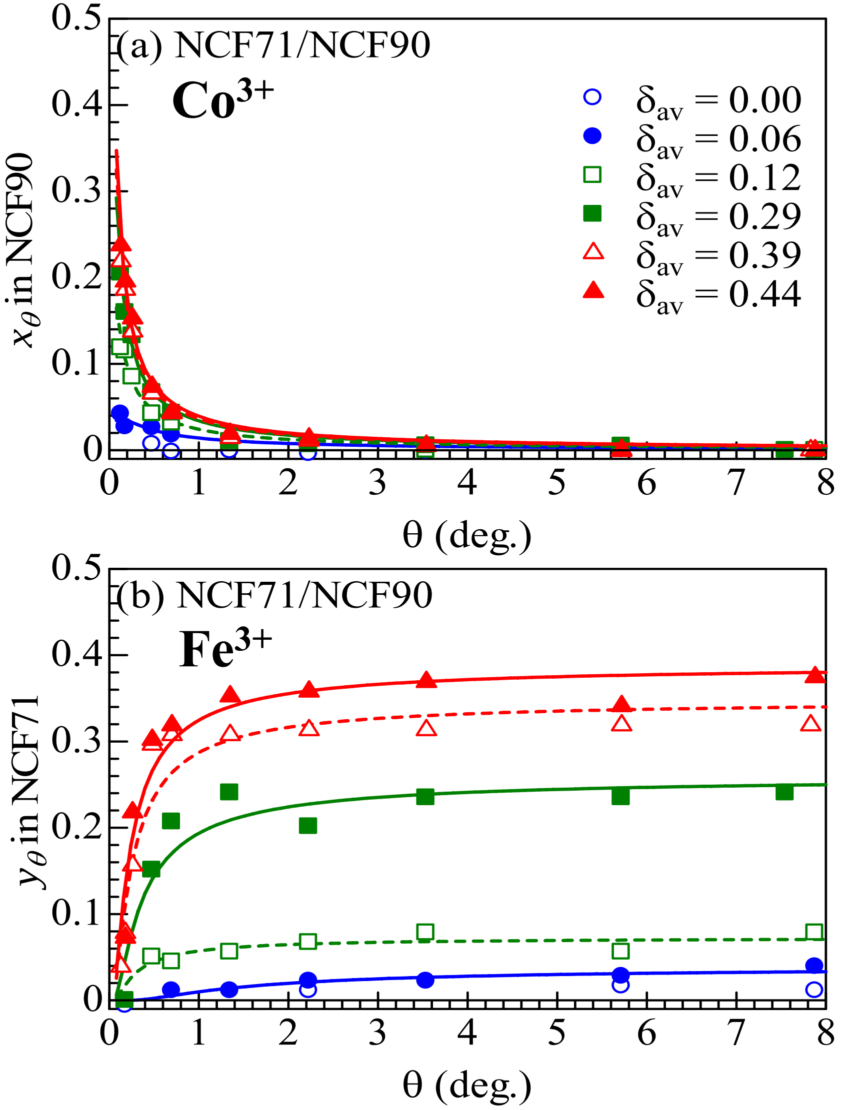
$$x_\theta = \boxed{\delta_{\mathrm{Co}}}\frac{1 - e^{-\mu_s^{\mathrm{Co}} \boxed{d_{Co}}/\sin\theta}}{1 - e^{-\mu_s^{\mathrm{Co}}\, d/\sin\theta} + (\mu_s^{\mathrm{Co}}/\mu_b^{\mathrm{Co}})e^{-\mu_b^{\mathrm{Co}} \boxed{d_{Co}}/\sin\theta}}$$

(b) $d_{\mathrm{Co}} \geq d$ のとき、

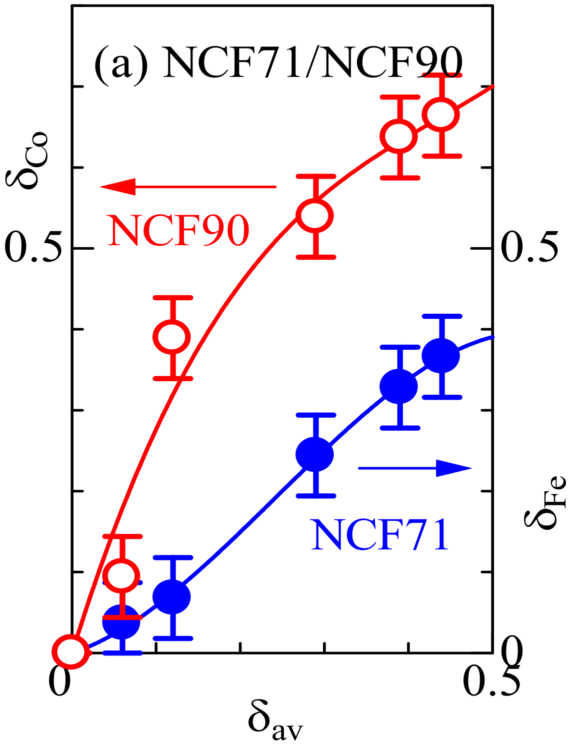
$$x_\theta = \boxed{\delta_{\mathrm{Co}}}\frac{1 - e^{-\mu_s^{\mathrm{Co}}\, d/\sin\theta} + \left(\mu_s^{\mathrm{Co}}/\mu_b^{\mathrm{Co}}\right)\left(e^{-\mu_b^{\mathrm{Co}}\, d/\sin\theta} - e^{-\mu_b^{\mathrm{Co}} \boxed{d_{Co}}/\sin\theta}\right)}{1 - e^{-\mu_s^{\mathrm{Co}}\, d/\sin\theta} + (\mu_s^{\mathrm{Co}}/\mu_b^{\mathrm{Co}})e^{-\mu_b^{\mathrm{Co}}\, d/\sin\theta}}$$

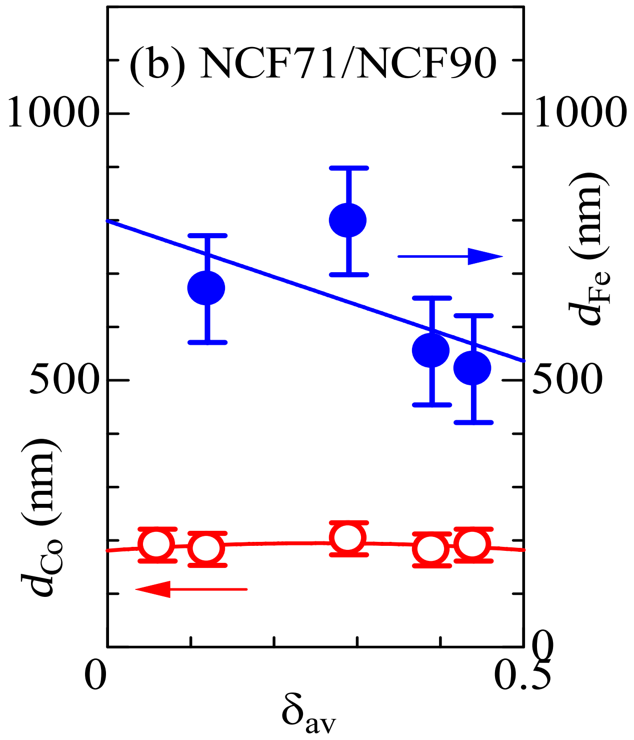
y_θについても同様に、$d_{\mathrm{Fe}} \leq d$ と$d_{\mathrm{Fe}} \geq d$で計算.

x_θ, y_θの角度依存性 +Fitting



結果





NCF90層の酸化が顕著

Co^{3+}の分布 ～200nm
Fe^{3+}の分布 ～600nm

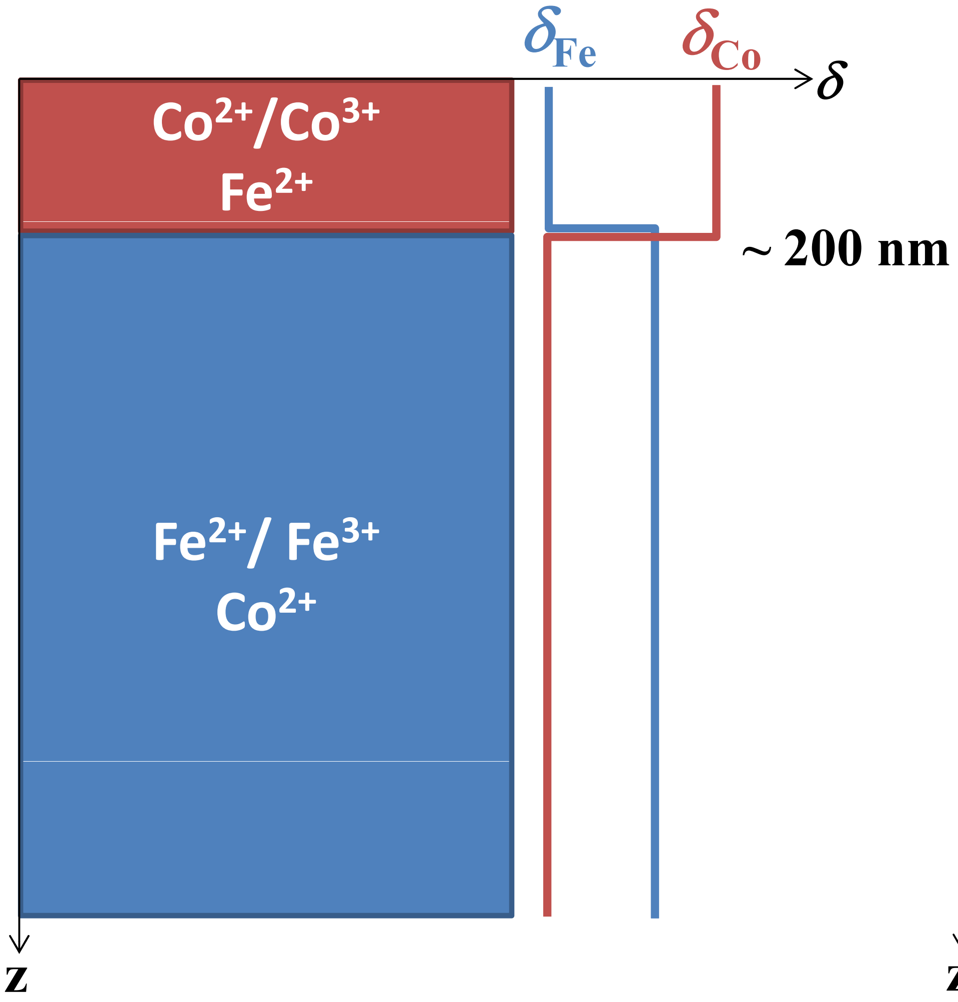
- 表面層が電解液と接している.
- 酸化還元電位 → NCF90 < NCF71

0.29eV　0.33eV
(vs Ag/AgCl標準電極)

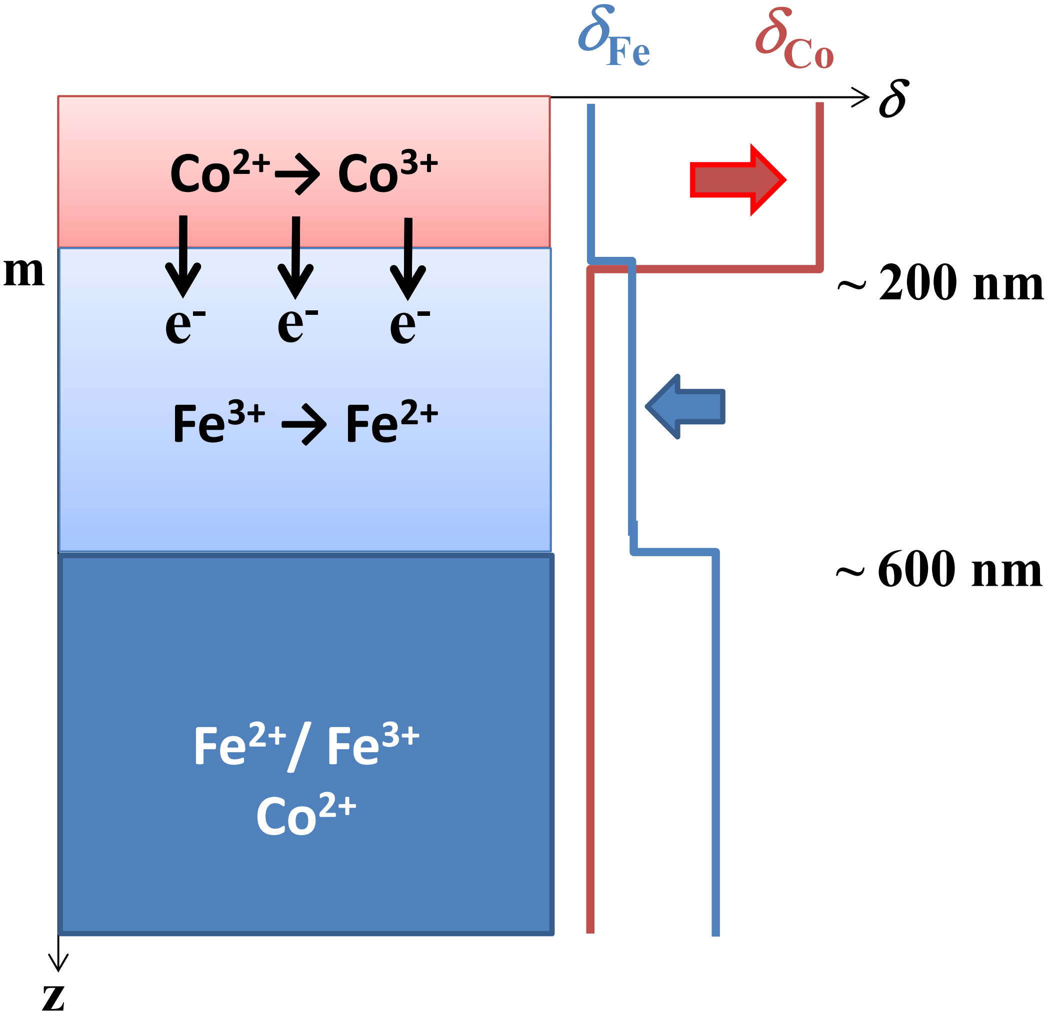
A. Oomura, et al., JJAP, in press.

エピ界面の電子状態

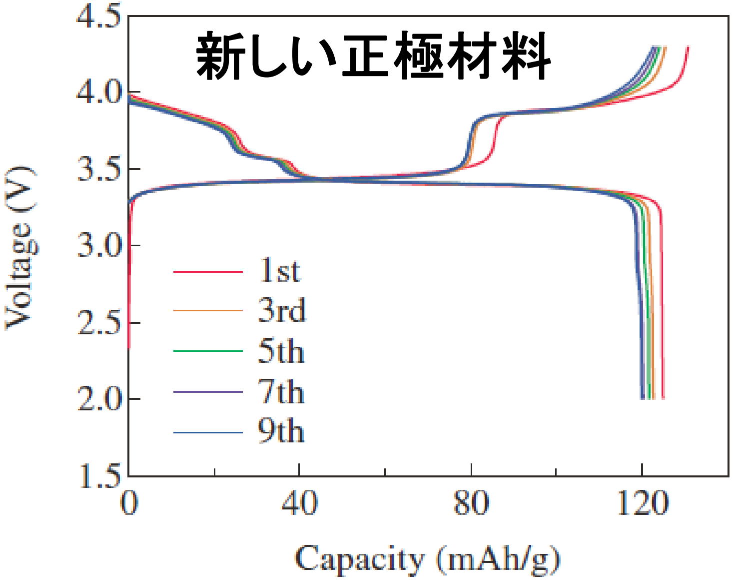
<界面で電子移動がない場合>

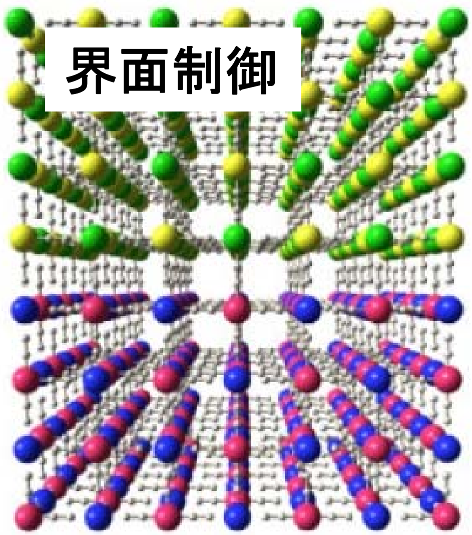


<界面で電子移動がある場合>

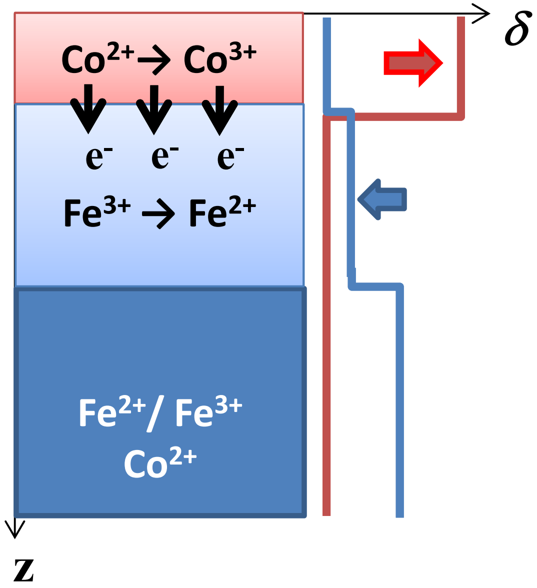


まとめと展望





界面の電子状態



① 時間分解XAFSによる深さ方向ダイナミクスの計測

② 界面の電子状態を積極的に利用した機能性発現

謝辞

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グリーン技術開発とサイエンスの掘り下げには、放射光は必須アイテムである。