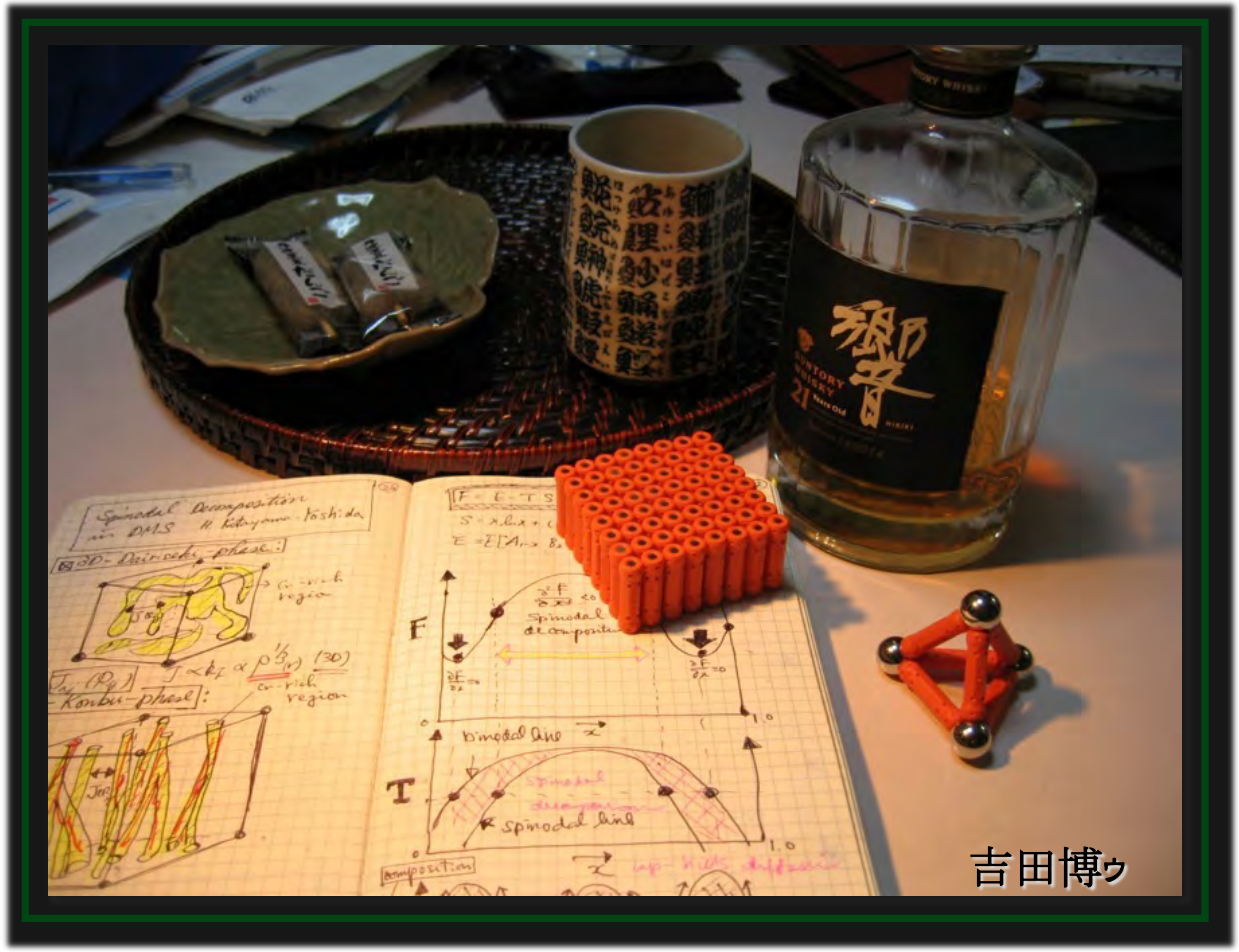
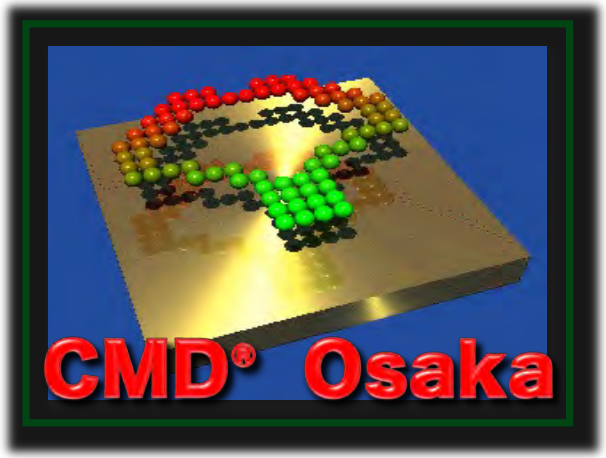
量子シミュレーションとデザイン

コース1 【1A-1-B: ナノマテリアル・ナノデバイスデザイン学】





東京大学大学院工学系研究科

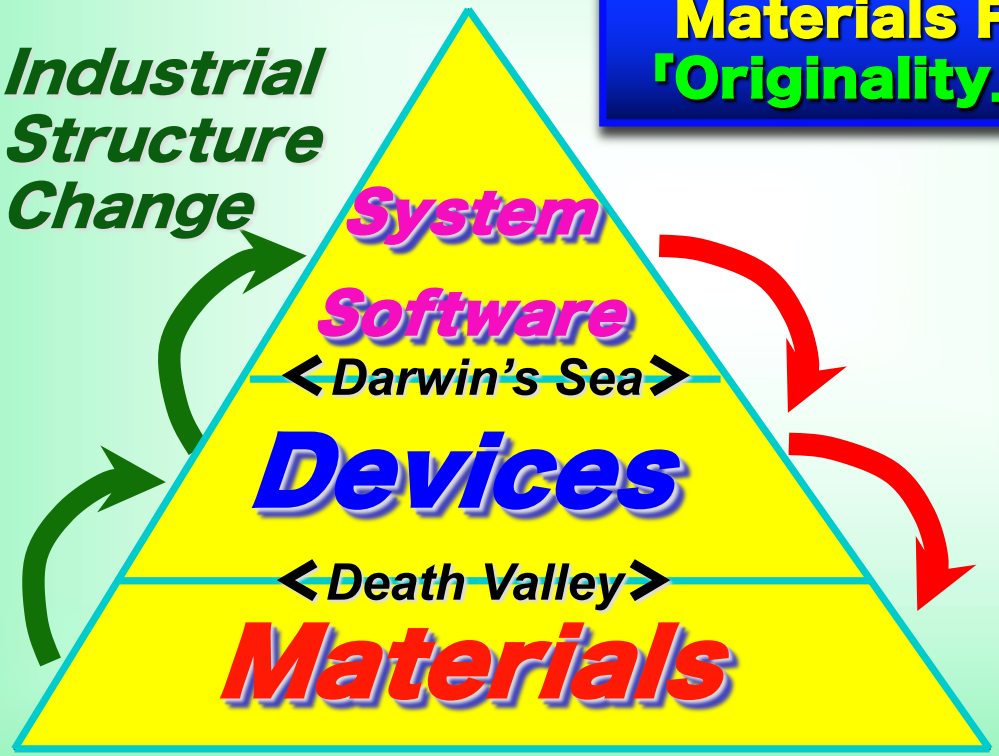
吉田　博

■Industrial-Structure Change
Industrial Society to Knowledge-based Society

Hierarchy of Industrial Structure

Progress

Industrial Structure Change

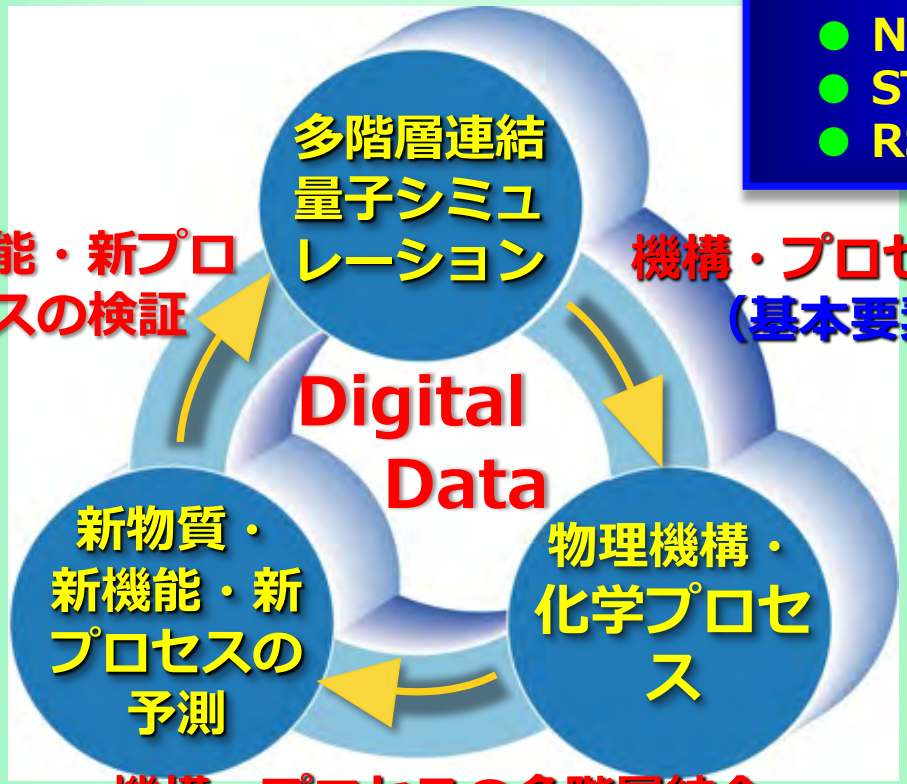


■Seamless Connection in the Hierarchy → Design-based Materials Fabrication
「Originality」 = 「Profitability」

吉田博©

計算機ナノマテリアルデザイン主導による実証実験 CMD®

ナノマテリアルデザインエンジン
(21世紀の賢者の石)



新機能・新プロセスの検証

機構・プロセスの解明
(基本要素還元)

機構・プロセスの多階層統合
(基本要素統合)

吉田博©

多階層連結シミュレーション・ソフト開発・
公開・登録・応用・普及活動・知財化

- OSAKA-2010 -nano
- MACHIKANEYAMA-2010
- KANSAI-2010 ●TSPACE ●ABCAP
- NANIWA-2010 ● HiLAPW-2010
- STATE-senri-2010● PSIC-Machi-2010
- RSPACE ● QSGW

実証実験
機能解析

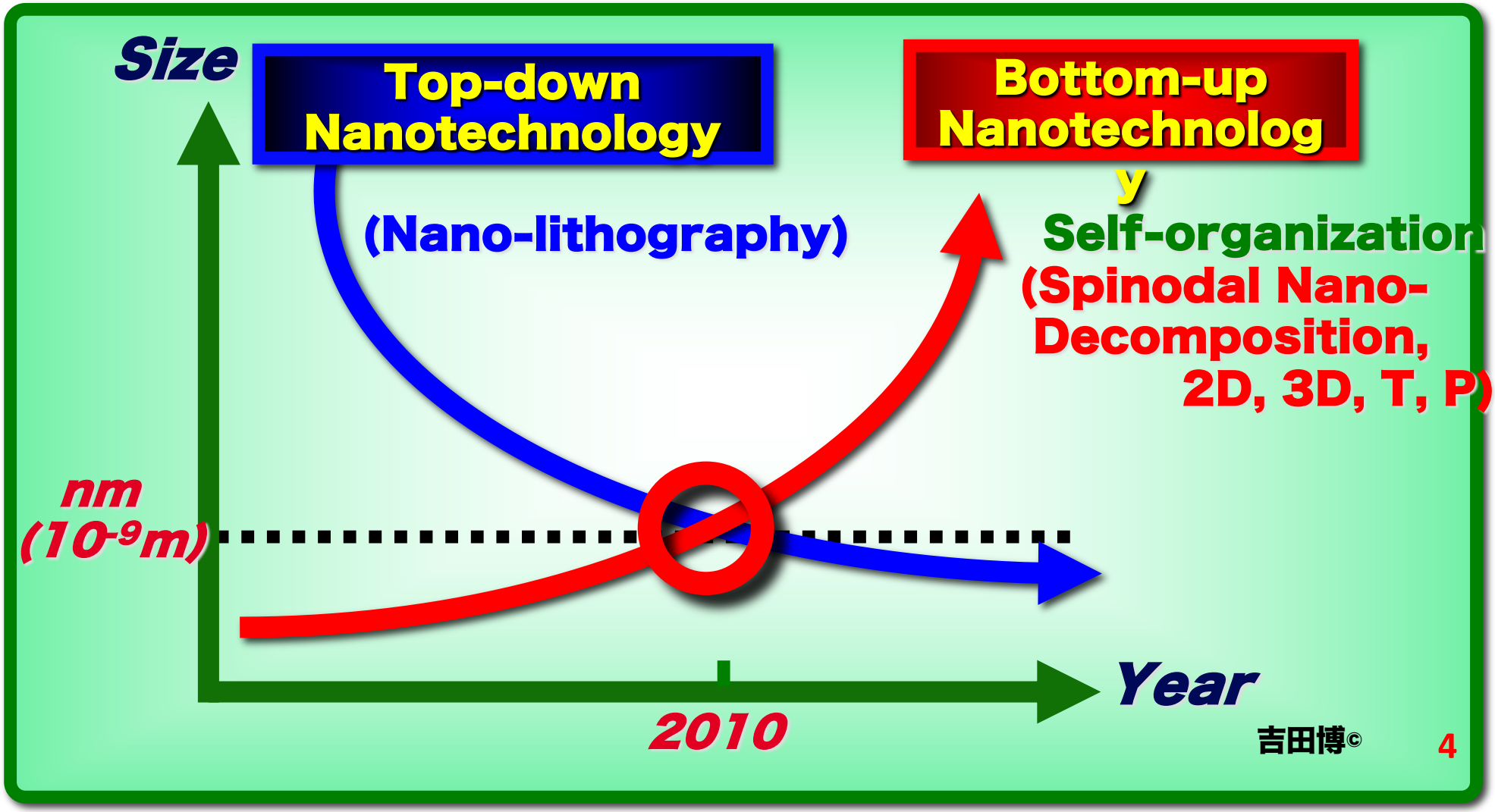
マテリアル
デバイス・システム
デザインの実証
と新機能解析

量子力学・量子化学に基づいた 21世紀の錬金術

■True Nanotechnology

"There's Plenty of Room at the Bottom", R. P. Feynman

"Father of Nanotechnology", APS, 12/29/1959 at CALTECH



■Katayama-Yoshida et al., phys. stat solidi a, 204 (2007) 15.
■Sato, Bergqvist et al., Rev. Mod. Phys. 82 (2010) 1633.
■Dietl, Sato, Fukushima et al., Rev. Mod. Phys. 87, (2015) 1131.

Part 【1】

半導体ナノスピントロニクス

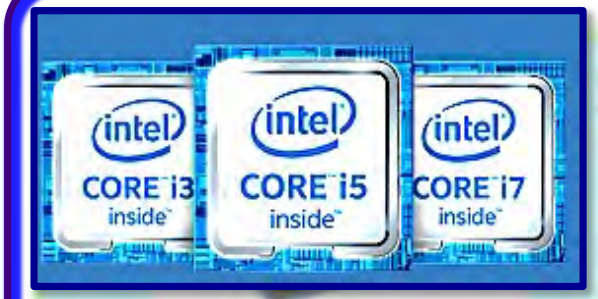
■新しいクラスのボトムアップ

ナノテクノロジー

スピノーダル・

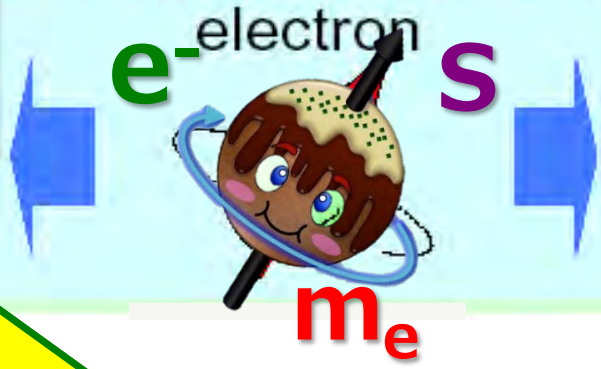
ナノテクノロジー

■半導体ナノスピントロニクス（超巨大物性応答のデザイン）



半導体デバイス
電荷の制御

Information Technology



磁気メモリ
スピンの制御

V_G 間相互作用のゲート制御

V_G

Nanospintronics
- ■スピントランジスタ
- ■超高温強磁性半導体
- ■脳型メモリ演算装置

Quantum IT
- ■量子計算
- ■量子暗号通信
- ■量子テレポーテーション

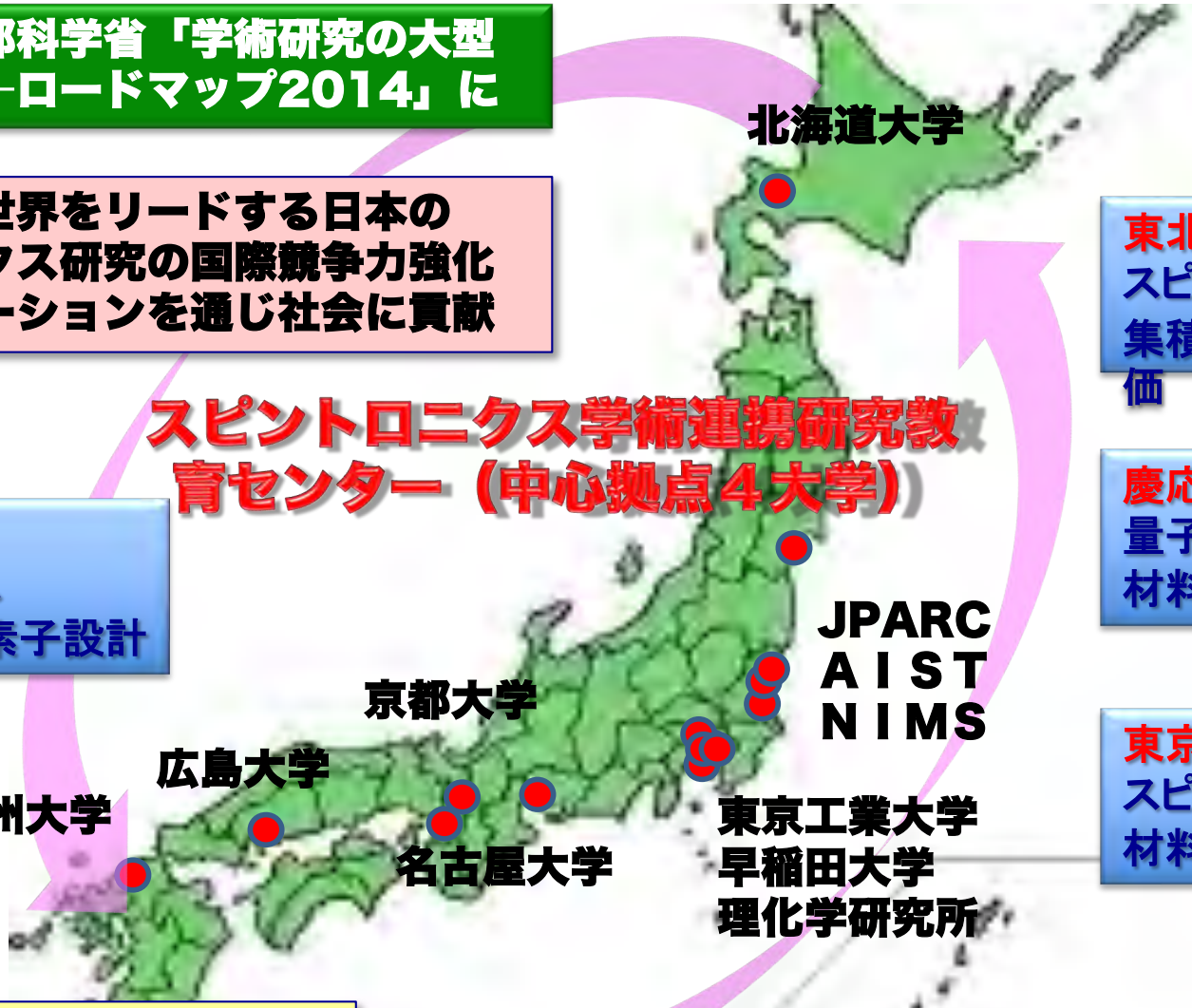
自己組織化ナノ超構造・超巨大物性応答

■高速（THz）　■高密度（Tbit/inch^2）　■省エネルギー(不揮発性)

「スピントロニクス学術研究基盤と連携ネットワーク」拠点整備

【背景】　文部科学省「学術研究の大型プロジェクト―ロードマップ2014」に採択

【必要性】　世界をリードする日本のスピントロニクス研究の国際競争力強化
⇒イノベーションを通じ社会に貢献



東北大学
スピントロニクス素子・集積システム製造・評価

慶応義塾大学
量子スピントロニクス材料・素子製造・評価

大阪大学
スピントロニクス材料デザイン・素子設計

東京大学
スピントロニクス材料・素子製造・評価

【目的】
①連携機関との共同研究の促進
②異分野横断型科学技術の創造
③イノベーションの創出
④国際的若手人材の育成

【波及効果】
・情報通信技術の革新
・現産業の強化と新産業の創成
・省エネルギー・環境調和型社会の実現

Ferromagnetic Mechanism, Electronic Structure and T_c in DMS

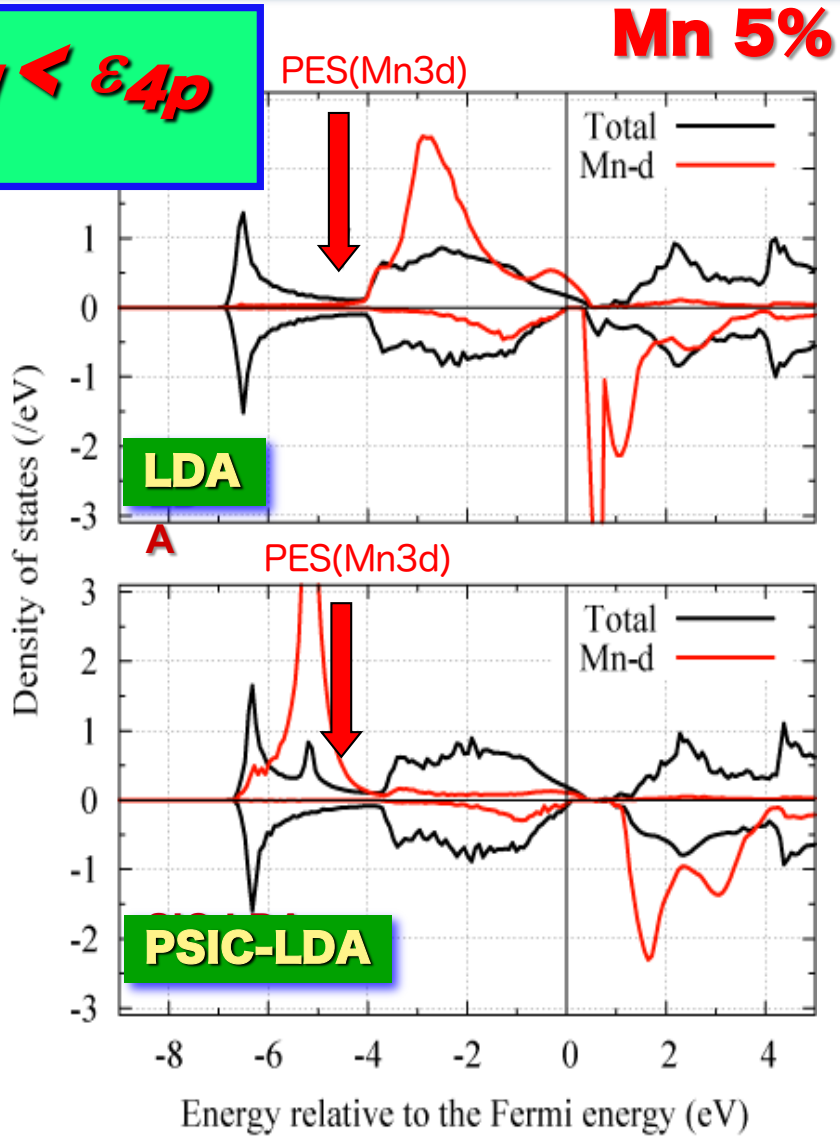
吉田博ゥ

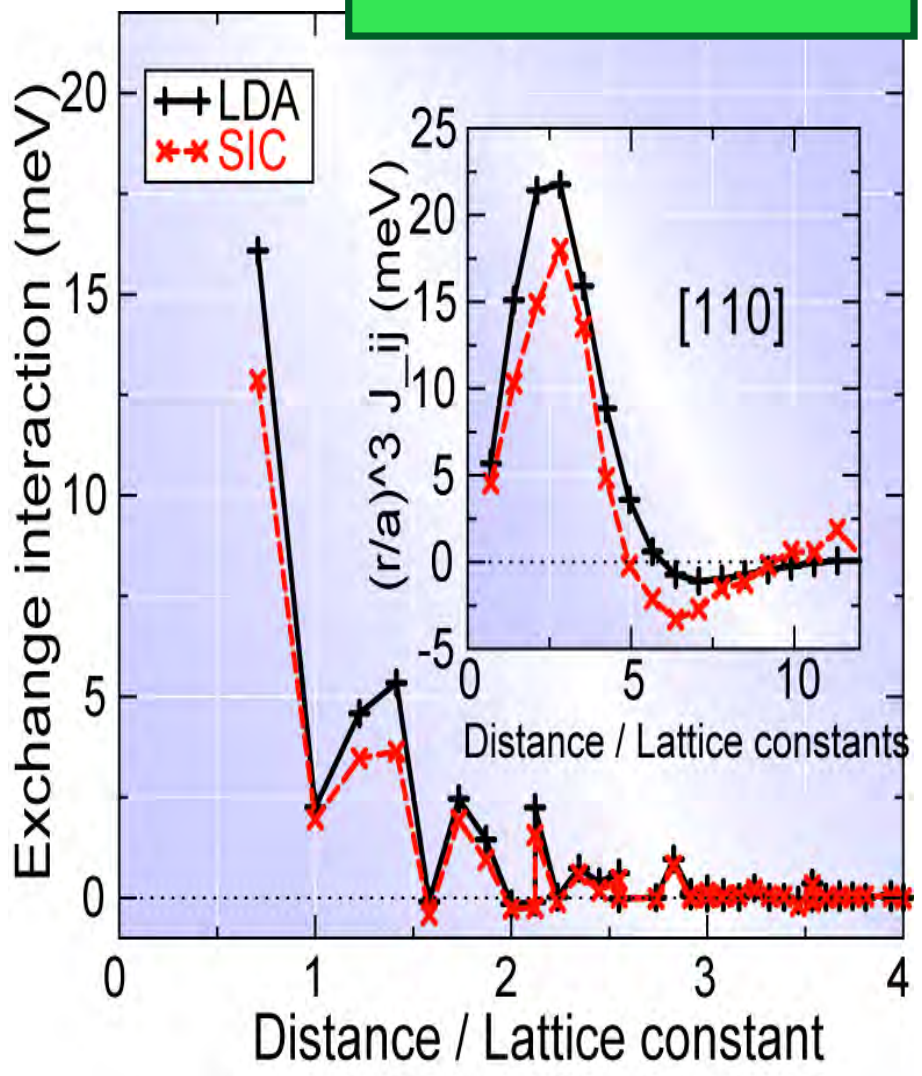
LDA vs. PSIC-LDA; (Ga,Mn)As

Zener's p-d exchange mechanism

$\varepsilon_{3d} < \varepsilon_{4p}$

$$\mathcal{H} = -\sum_{i \neq j} J_{ij}\, S_i \cdot S_j,$$





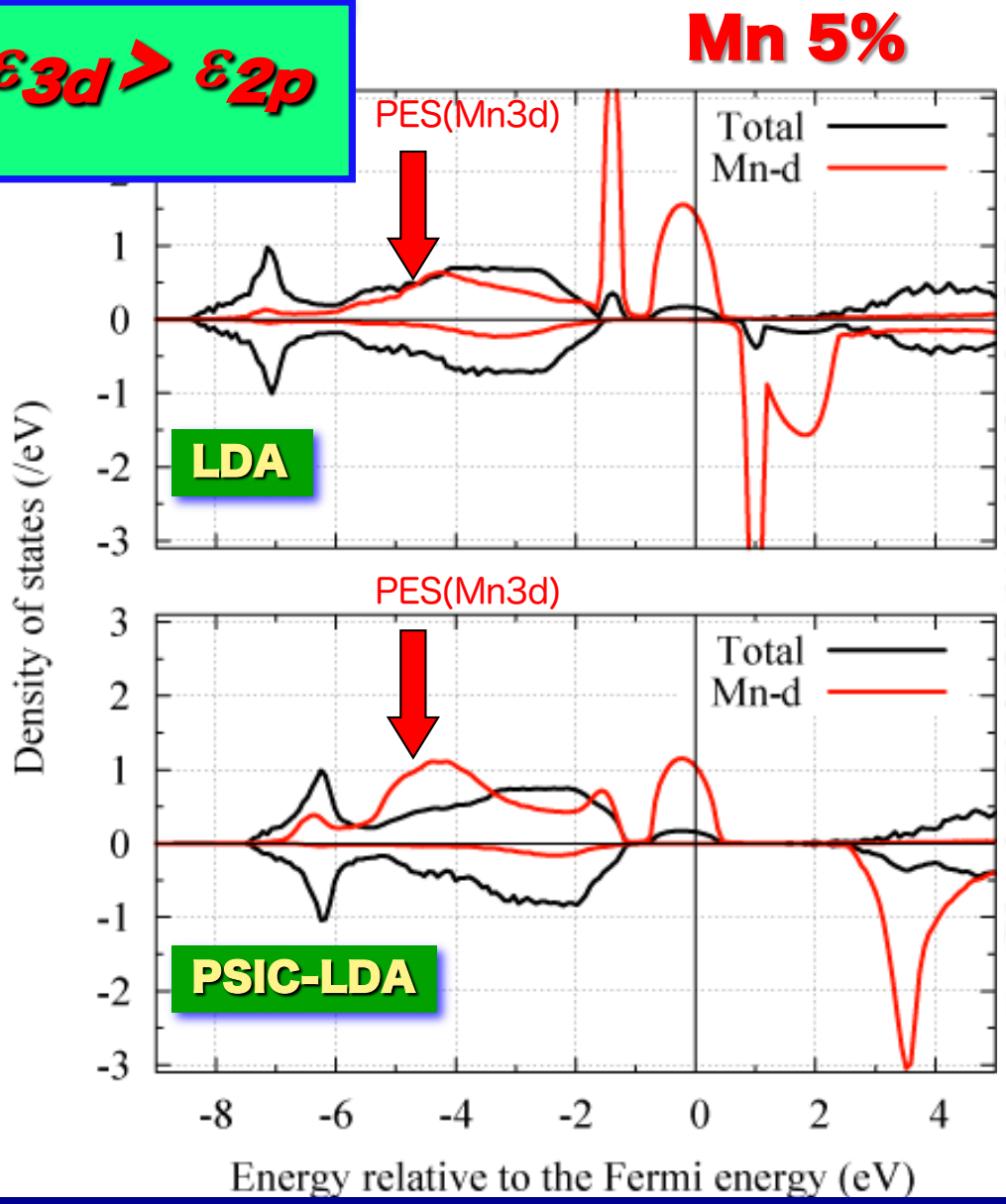
- M.Toyoda et al., Physica B, 376 (2006) 647.
- K. Sato et al., Rev. Mod. Phys. 82 (2010) 1633.

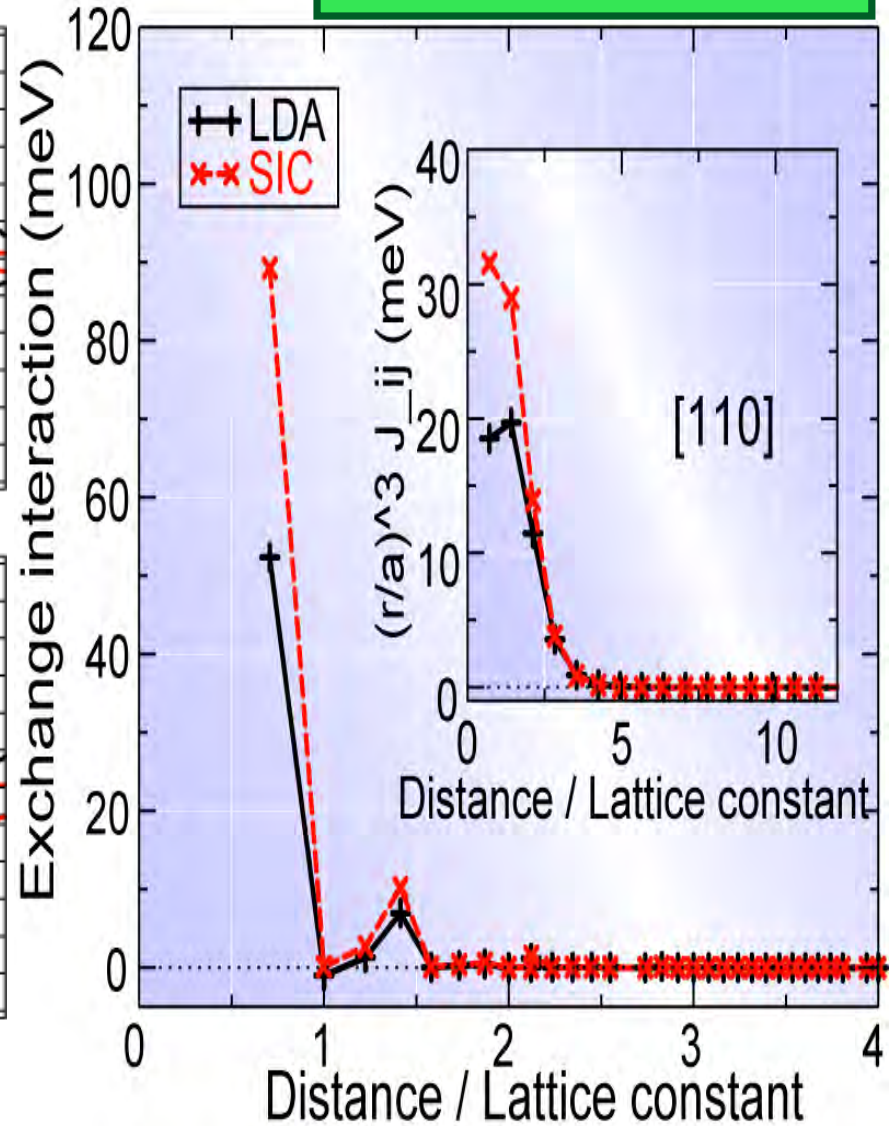
LDA vs. PSIC-LDA; (Ga,Mn)N

Zener's double exchange

$\varepsilon_{3d} > \varepsilon_{2p}$

$$\mathcal{H} = -\sum_{i \neq j} J_{ij}\, S_i \cdot S_j$$



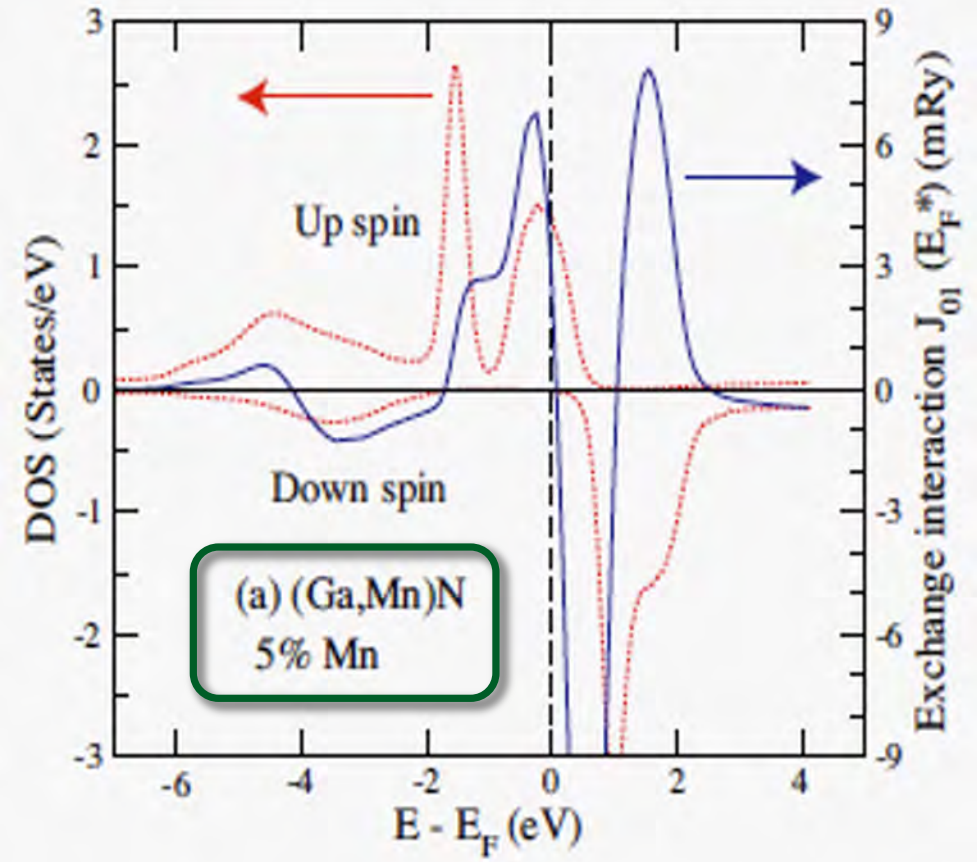


■ M.Toyoda et al., Physica B, 376 (2006) 647. ■ K.Sato et al., RMP, 2010

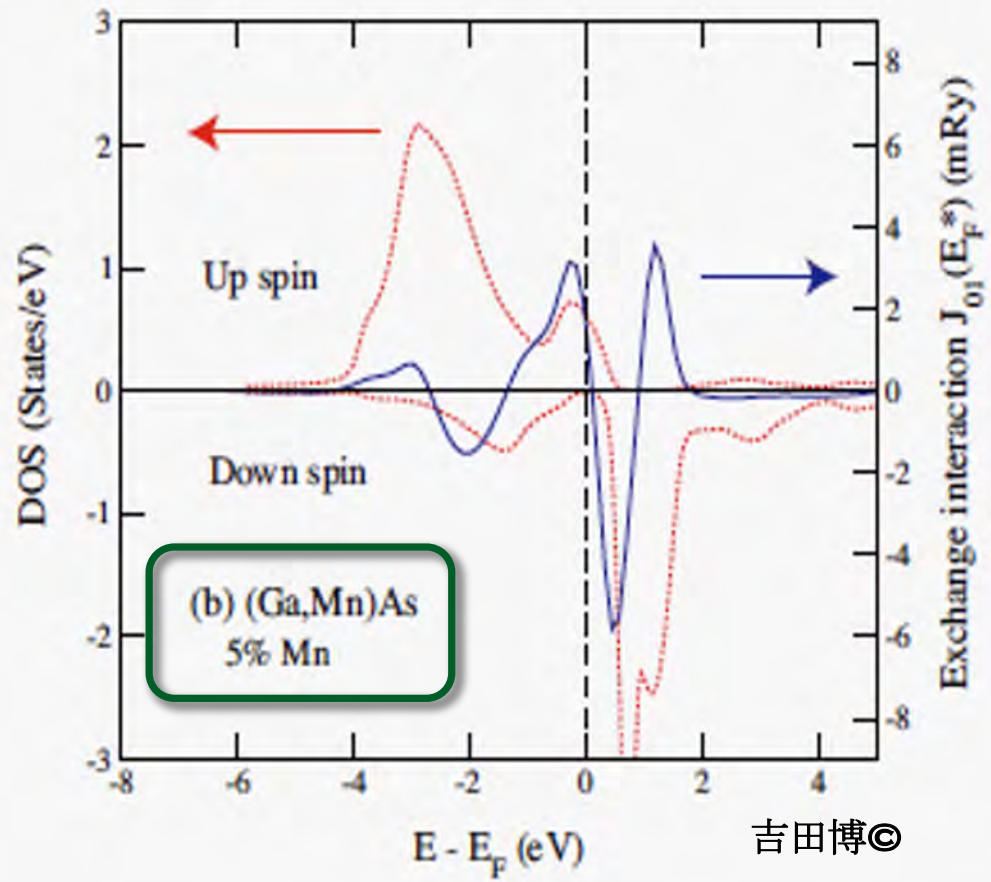
Universal Rule in Magnetism: $\mathcal{H} = -\sum_{i \neq j} J_{ij}(E)\, S_i \cdot S_j$

■*K. Sato et al., Rev. Mod. Phys., 82 (2010) 1633.*

(a) Zener's double exchange mechanism (Ferromagnetism)



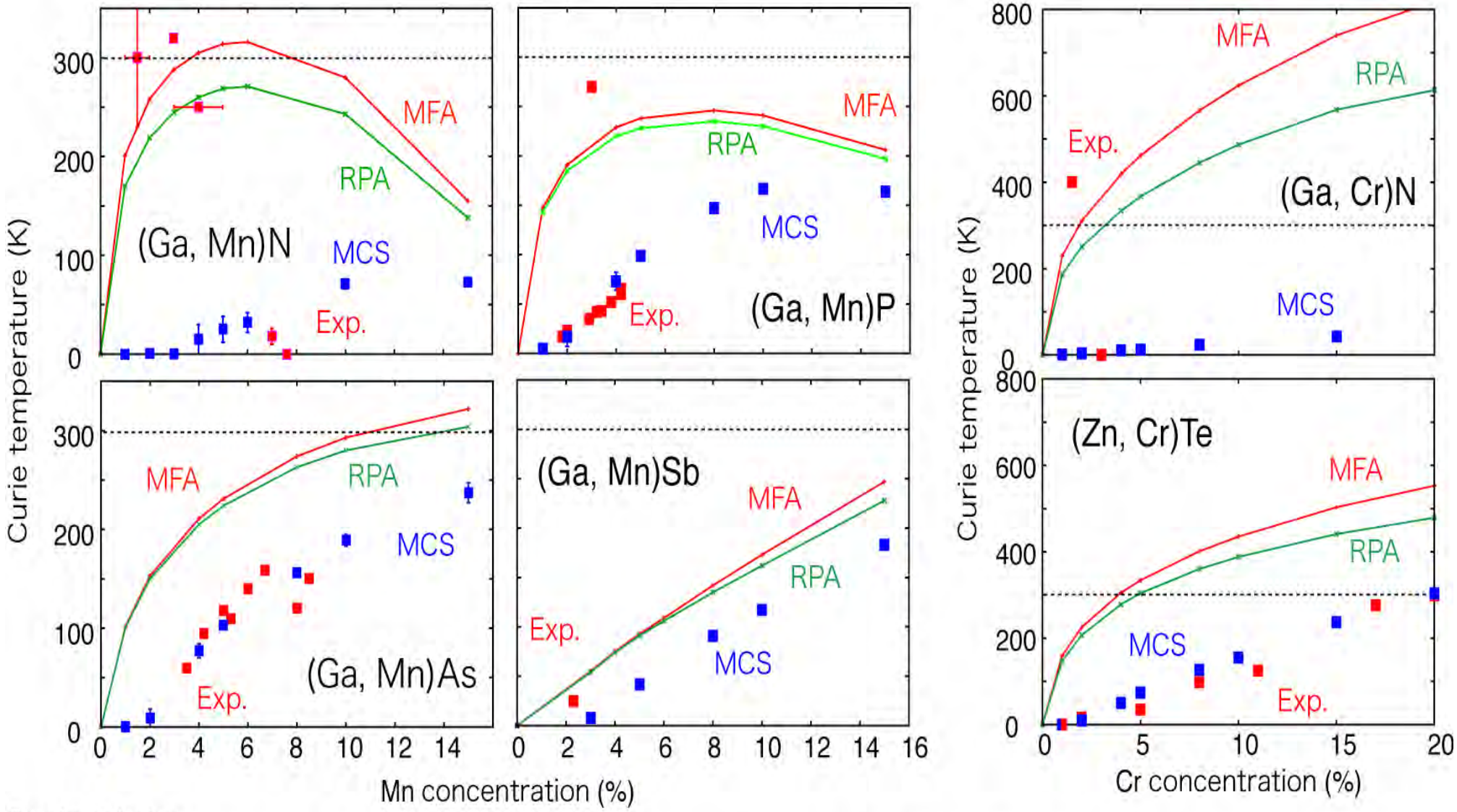
(b) Zener's p-d exchange mechanism (Ferromagnetism)



吉田博©

We can control $J_{ij}(E_F)$ by *p-*, *n*-doping or Gating.

Calculation of Tc: *K. Sato et al., Rev. Mod. Phys., 82 (2010) 1633.*
K. Sato et al., Phys. Rev. B 70 (2004) 201202.



- **MFA overestimates T_C for low concentrations (Need MCS)**
- **For higher concentrations (>30%), MFA is OK.**
- **MCS is in good agreement with the experiments.**

2006 E-MRS Fall Meeting, Symposium E Warsaw, Poland 4-8 September, 2006

- ***"Theory of Ferromagnetic Semiconductors"***

"Spinodal Nanotechnology as a New Class of Bottom-up Nanotechnology"

- ***H. Katayama-Yoshida, K. Sato, T. Fukushima, M. Toyoda, H. Kizaki, An van Dinh, P.H. Dederichs***

- ***phys. stat. sol. (a), 204 (2007) 15-32.***

2 次元スピノーダル・ナノ分解

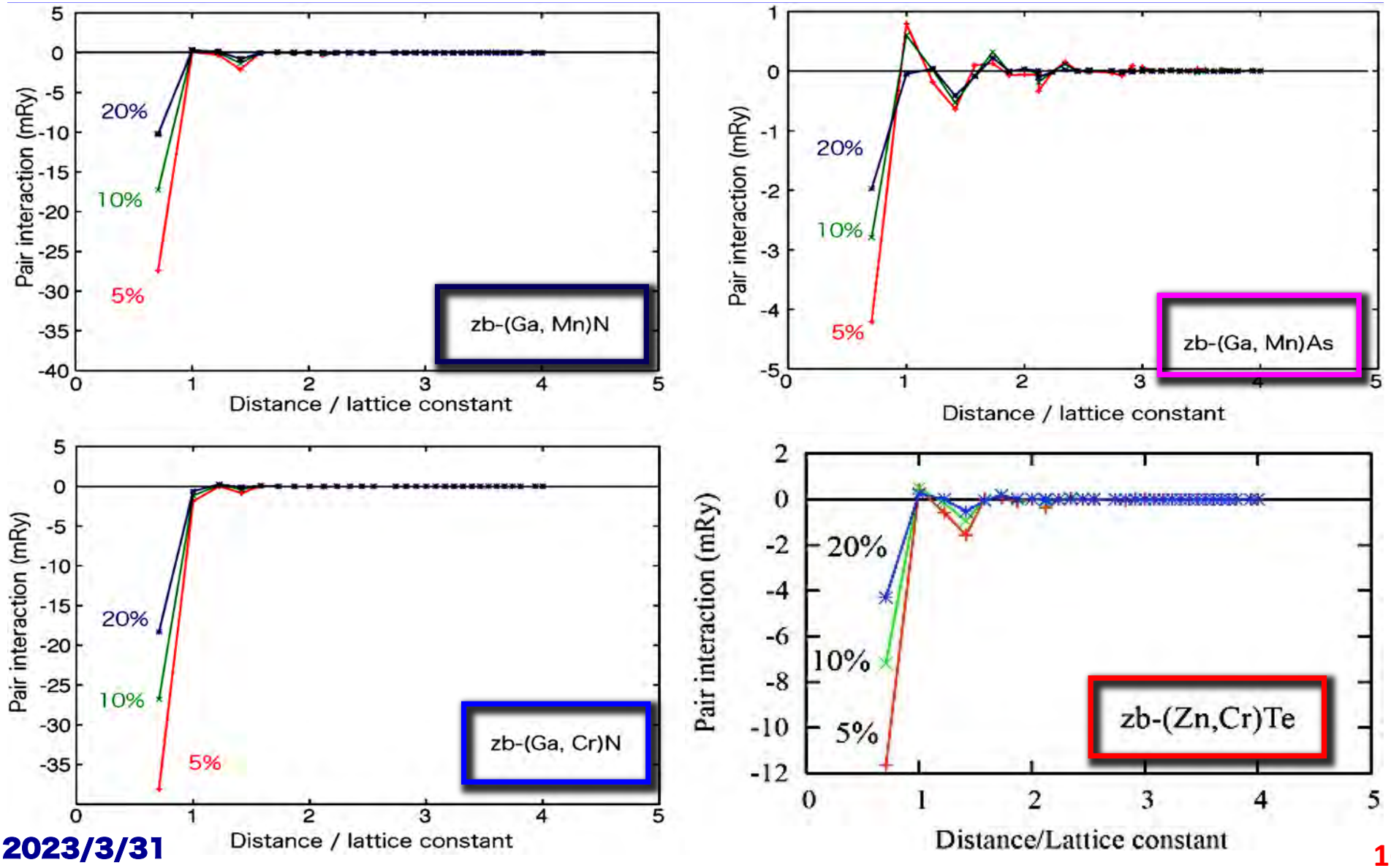
- Sato, et al., Jpn. J. Appl. Phys. 44 (2005) L945
- Fukushima, et al., Jpn. J. Appl. Phys. 45 (2006) L416
- Katayama-Yoshida et al., phys. stat. soli. (a), 204 (2007) 15.
- Dietl, Sato, Fukushima et al., Rev. Mod. Phys. 87 (2015) 1131.

Inhomogeneous DMS Fabricated by Spinodal Nano-Decomposition

有効化学対相互作用

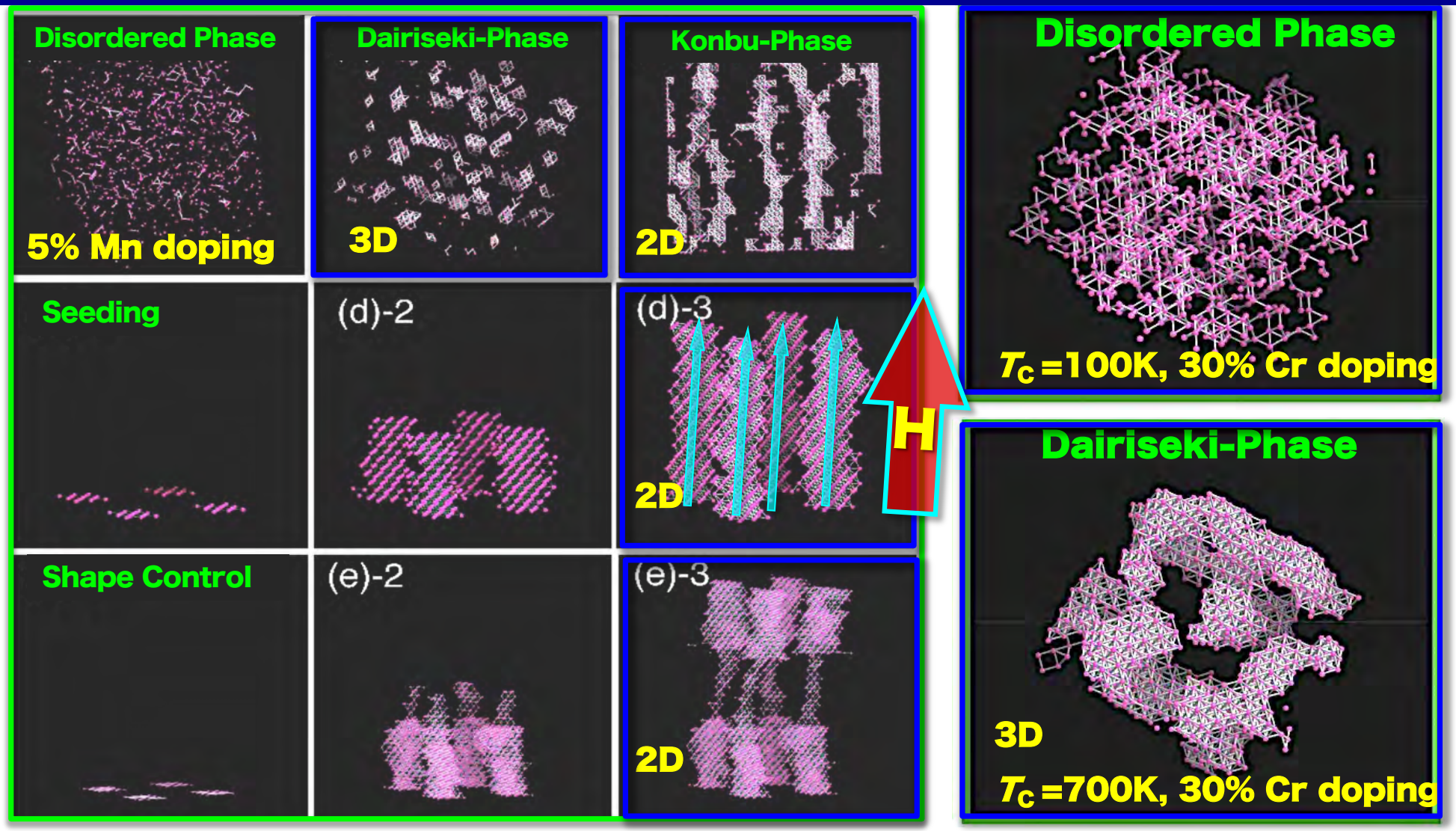
$$H = \sum_{i>j} V_{ij}\, \sigma_i \cdot \sigma_j \qquad V_{ij} = V_{ij}^{MnMn} + V_{ij}^{GaGa} - 2V_{ij}^{MnGa}$$

■Sato, Katayama-Yoshida, Dederichs., JJAP, 44 (2005) L948



スピノーダル・ナノ分解: $(Ga_{1-x}TM_x)$ N

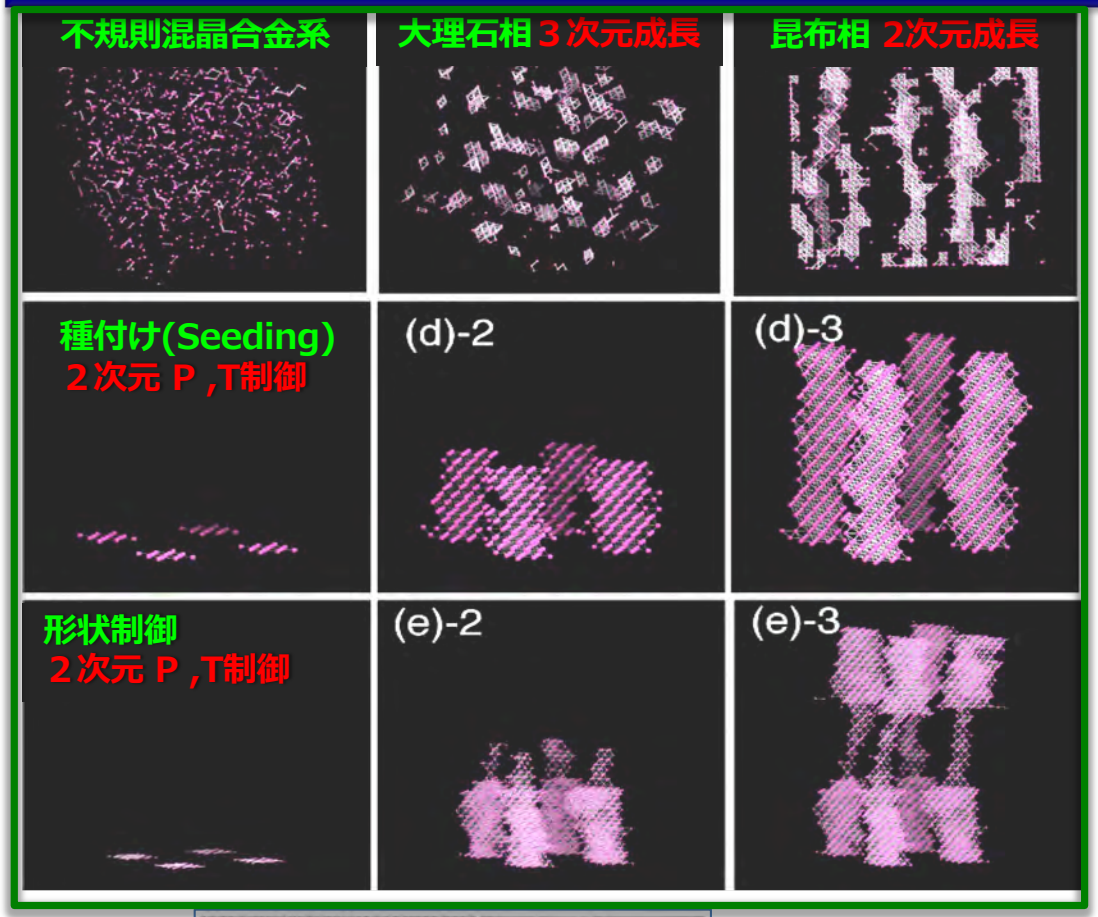
- *K. Sato et al., JJAP, 44 (2005) L948.*
- *T. Fukushima, et al., JJAP, 45 (2006) L416.*

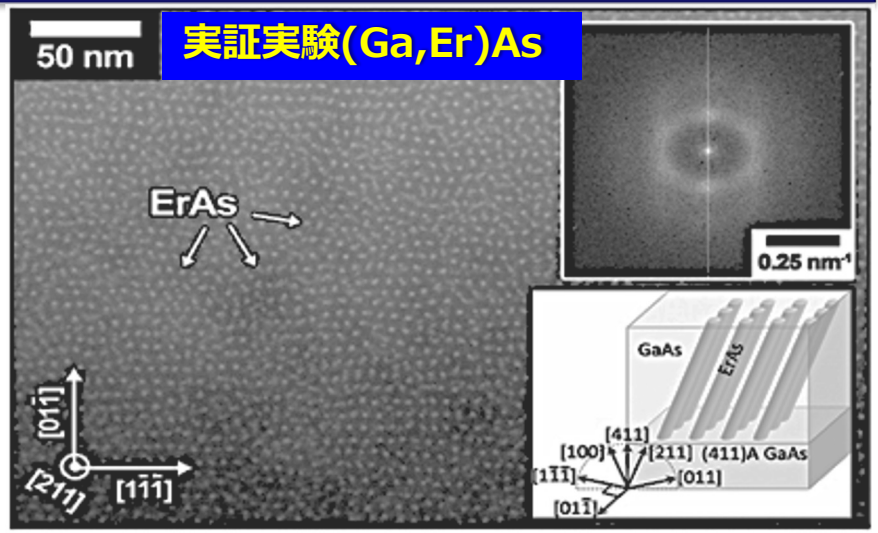


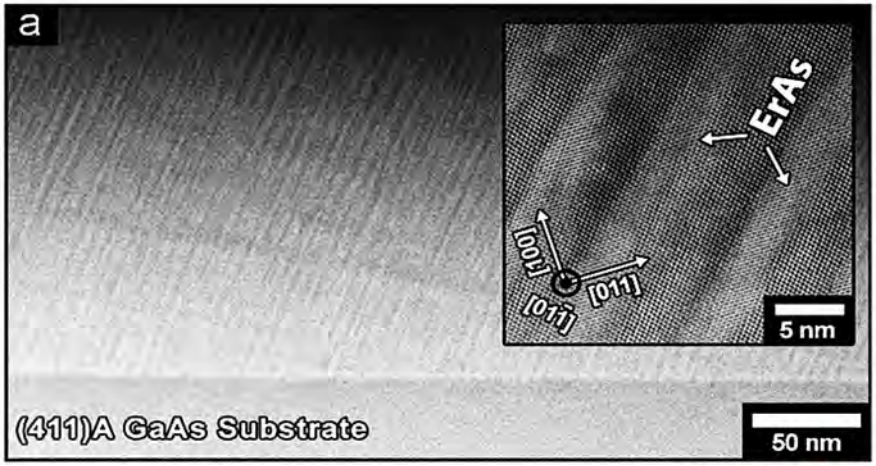
- *K. Sato, L. Bergqvist et al., Rev. Mod. Phys. 82, (2010) 1633.*
- *H. Katayama-Yoshida et al., phys. stat. soli. (a), 204 (2007) 15.*

スピノーダルナノ分解・自己組織化ナノ超構造：昆布相と大理石相

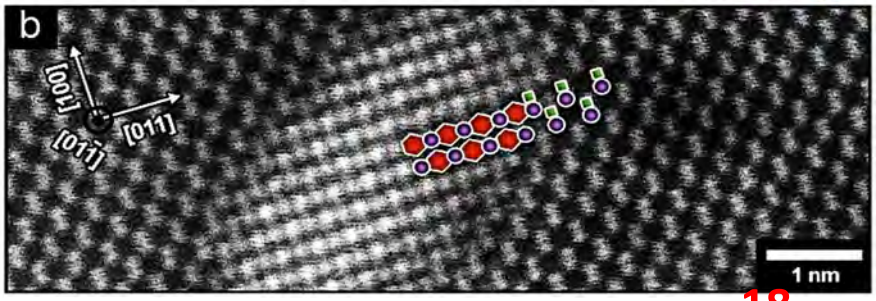
Fukushima, Sato, et al., JJAP, 45 (2006) L416.





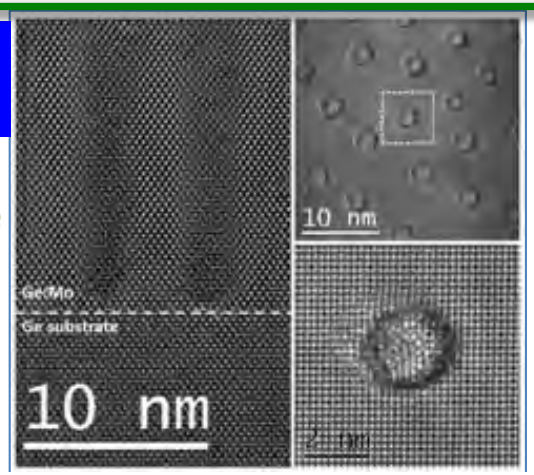


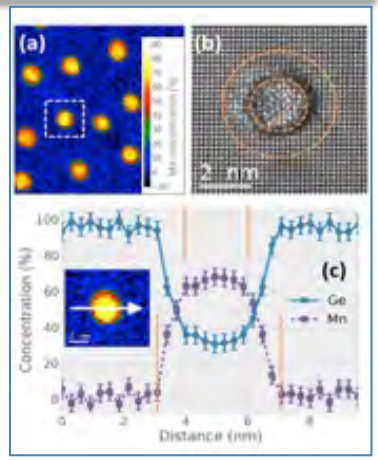
Ga As Er



実証実験 GeMn

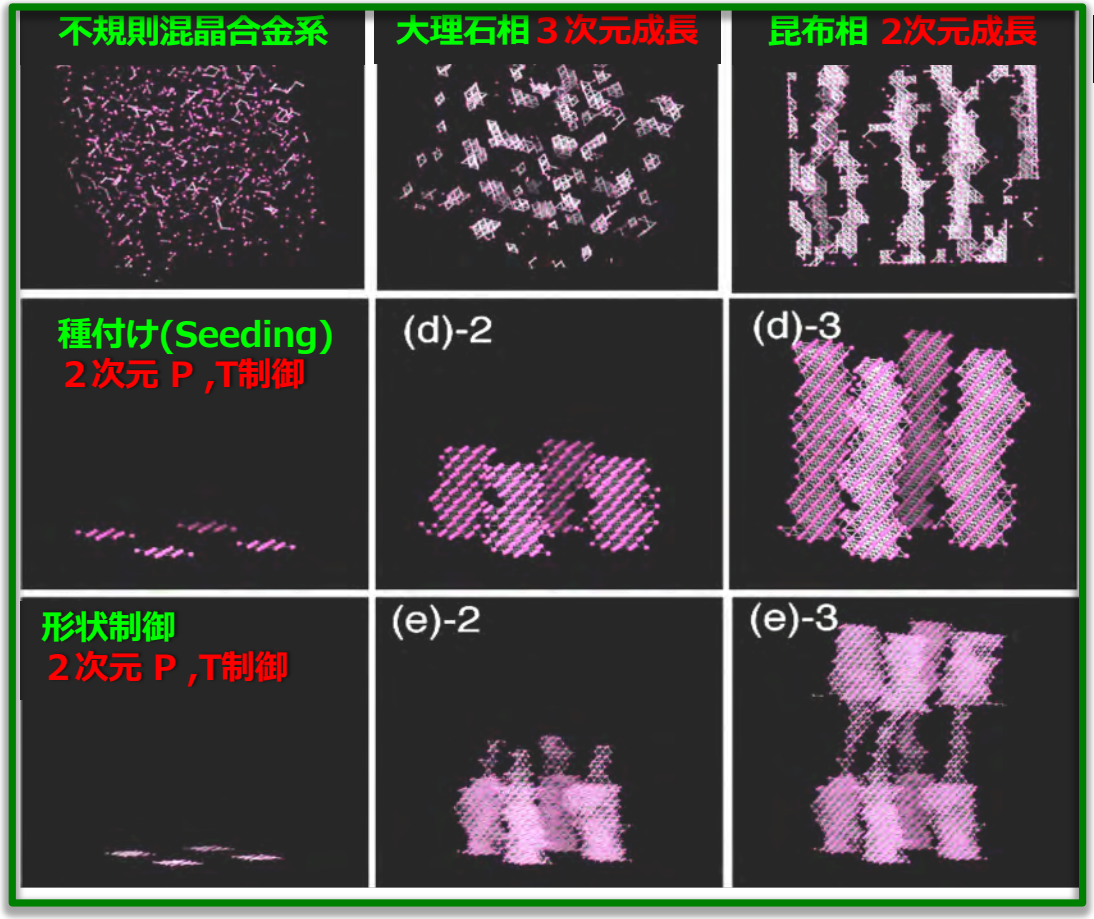
M.Jamet Grenoble JAP (2014).

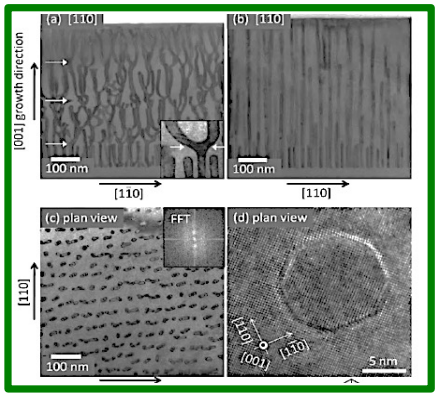


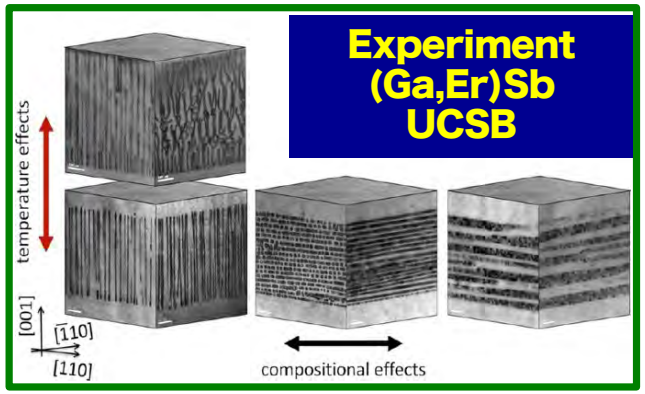


スピノーダル・ナノ分解による自己組織化ナノ超構造：大理石相と昆布相

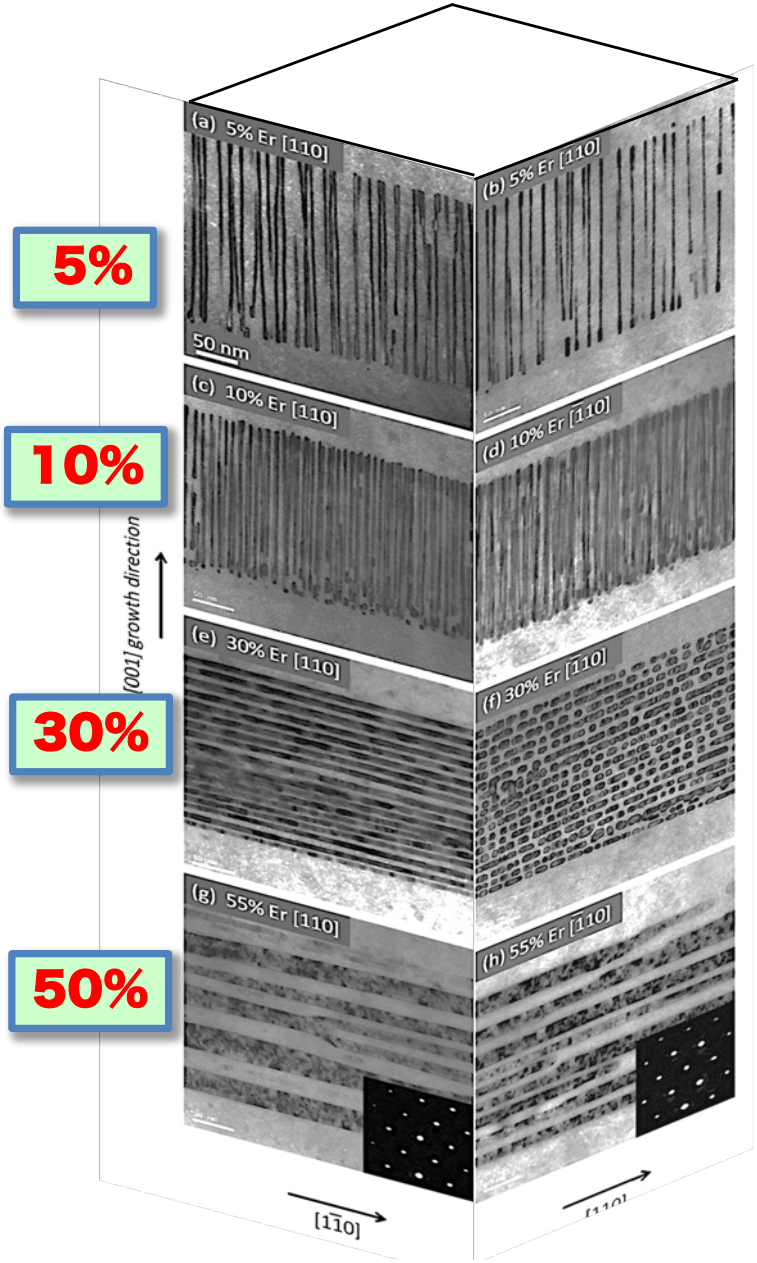
Sato et al., JJAP, 44 (2005) L948. *Fukushima et al., JJAP, 45 (2006) L416.*







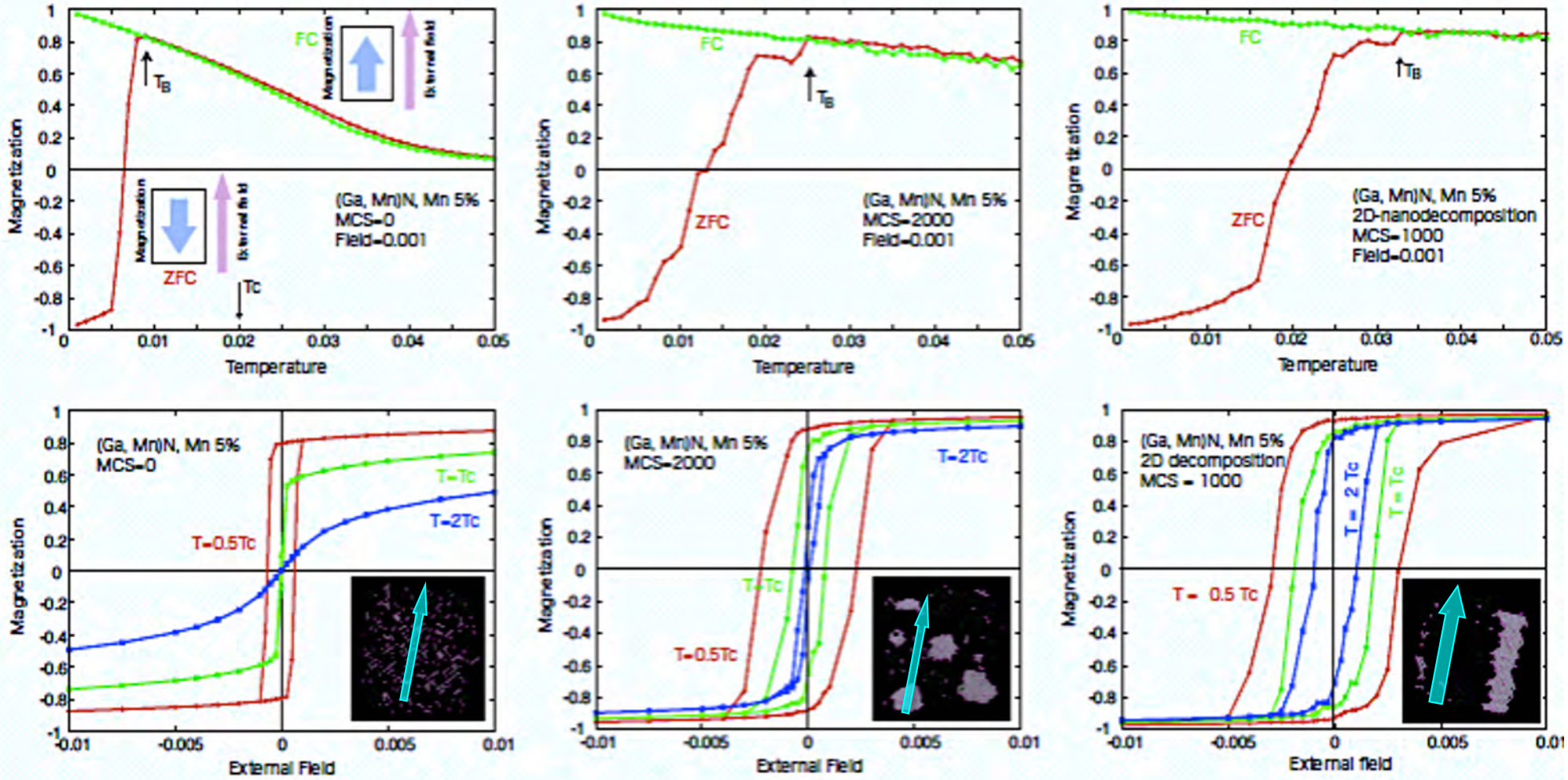
Christopher Palmstrom (UCSB), 2015



(Ga,Mn)N：スピノーダル・ナノ分解による超常磁性体の高いブロッキング温度 T_B

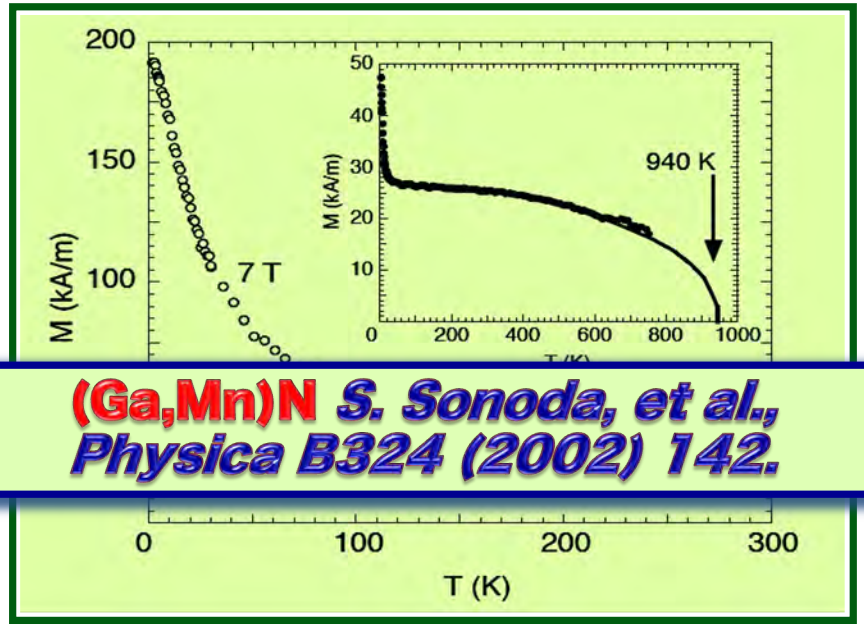
■*K. Sato et al., JJAP, 46, (2007) L682.*

■無秩序相　■大理石相(3D)　■曷布相(2D)

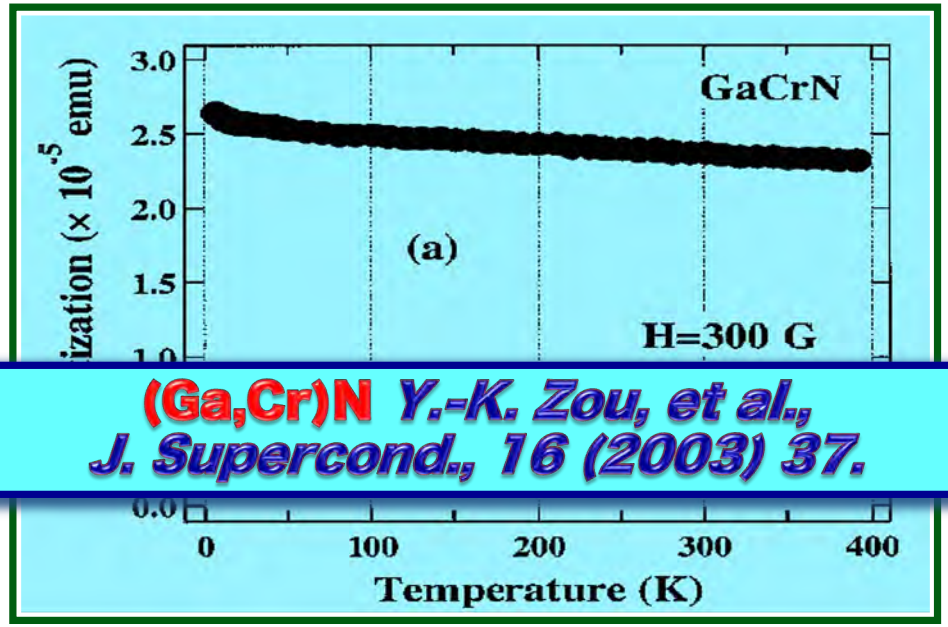


結晶磁気異方性と形状磁気異方性のナノ超構造による制御

■昆布相・大理石相における高いブロッキング温度：T_B

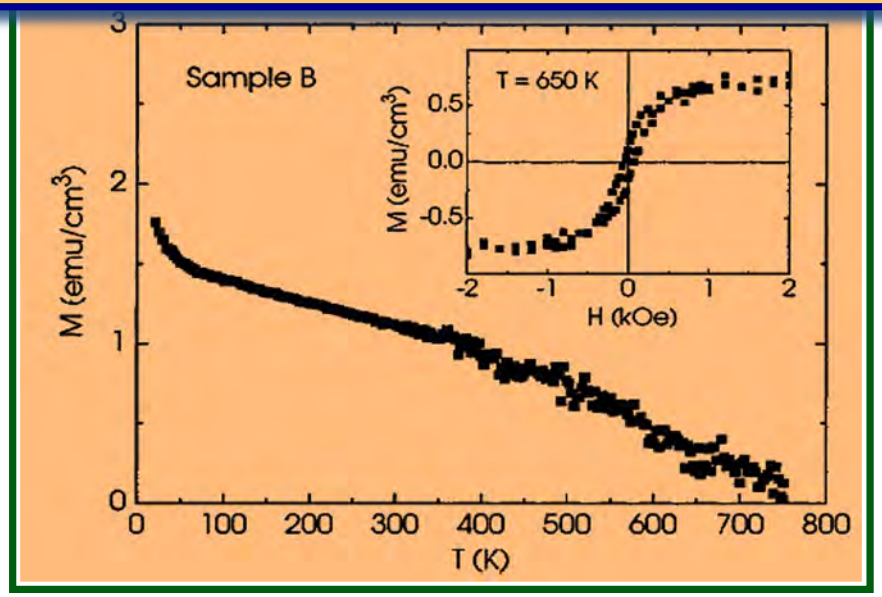


(Ga,Mn)N S. Sonoda, et al., Physica B324 (2002) 142.



(Ga,Cr)N Y.-K. Zou, et al., J. Supercond., 16 (2003) 37.

(Ga,Mn)N S. Dhar et al., APL 82 (2003) 2077.



(Ga,Cr)N N. Newman et al., (T_B) T_C=1,050K (Arizona)

基本特許(EU, USA, Japan)
H.Katayama-Yoshida, K. Sato
■EP-1219731B1,
■USP-0112278A1,
■EP-1367151A1
■JP2001-059195, 0593030

Alchemist's Materials Design for New Class of DMS without 3d Transition Metal

Materials Design for New Class of DMS without 3d Transition Metal : *2004*

Japanese Journal of Applied Physics
Vol. 43, No. 7A, 2004, pp. L934–L936

Express Letter

New Class of Diluted Ferromagnetic Semiconductors based on CaO without Transition Metal Elements

Kazuhide KENMOCHI*, Masayoshi SEIKE, Kazunori SATO, Akira YANASE and Hiroshi KATAYAMA-YOSHIDA
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
(Received April 26, 2004; accepted May 25, 2004; published June 18, 2004)

Journal of the Physical Society of Japan
Vol. 73, No. 11, November, 2004, pp. 2952–2954

LETTERS

Materials Design of Transparent and Half-Metallic Ferromagnets of MgO, SrO and BaO without Magnetic Elements

Kazuhide KENMOCHI*, Van Ann DINH, Kazunori SATO,
Akira YANASE and Hiroshi KATAYAMA-YOSHIDA

The Institute of Scientific and Industrial Research, Osaka University,
8-1 Mihogaoka, Ibaraki, Osaka 567-0047
(Received June 23, 2004)

N, C-doped alkaline-earth-metal-oxides were theoretically proposed as candidates of transparent ferromagnets without magnetic elements. *(Japn Patent : 2004-055017)*

Materials Design for New Class of DMS without 3d Transition Metal : *2004*

Journal of the Physical Society of Japan
Vol. 75, No. 9, September, 2006, 093705

LETTERS

Exchange Interaction and T_c in Alkaline-Earth-Metal-Oxide-Based DMS without Magnetic Impurities: First Principle Pseudo-SIC and Monte Carlo Calculation

Van An DINH[1,2*], Masayuki TOYODA[2], Kazunori SATO[2] and Hiroshi KATAYAMA-YOSHIDA[1,2]

[1]*Department of Condensed Matter Physics, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047*
[2]*Department of Computational Nanomaterials Design, Nanoscience and Nanotechnology Center, The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047*

(Received June 24, 2006; accepted July 31, 2006; published September 11, 2006)

The prospects of half-metallic ferromagnetism being induced by the incorporation of C atoms into alkaline-earth-metal-oxides are investigated by the first principle calculation. The origin of the ferromagnetism is discussed through the calculation of the electronic structure and exchange coupling constant by using the pseudo-potential-like self-interaction-corrected local spin density method. The Curie temperature (T_c) is also predicted by employing the Monte Carlo simulation. It is shown that by taking the electron self-interaction into account, the half-metallic ferromagnetism induced by C in the host materials is more stabilized in comparison with the standard local density approximation (LDA) case, and the C's $2p$ electron states in the bandgap become more localized resulting in the predominance of the short-ranged exchange interaction. While the ferromagnetism in $MgO_{1-x}C_x$ is stabilized due to the exchange interaction of the first-nearest neighbor pairs and might be suppressed by the anti-ferromagnetic super-exchange interaction at higher x, the ferromagnetism in $CaO_{1-x}C_x$, $SrO_{1-x}C_x$, and $BaO_{1-x}C_x$ is stabilized by both the first- and second-nearest neighbor pairs, and T_c monotonously increases with the C concentration.

KEYWORDS: *ab initio* calculation, pseudo-SIC, Monte Carlo simulation, dilute magnetic semiconductor, spintronics, alkaline earth metal oxide
DOI: 10.1143/JPSJ.75.093705

N, C-doped alkaline-earth-metal-oxides were theoretically proposed as candidates of transparent ferromagnets without magnetic elements. *(Japn Patent : 2004-055017)*

Experimental Verification : *2007, 2009*

Abstract Submitted
for the MAR09 Meeting of
The American Physical Society

Sorting Category: 06.14.6 (E)

Ferromagnetism in MgO by Nitrogen Doping CHENG-HAN YANG, MAHESH SAMANT, STUART PARKIN, IBM Almaden Research Center — The new group, dilute ferromagnetic oxide and nitride, provides a promising technology potential to combine the magnetic and electronic properties. Studies in creating ferromagnetism in

PRL 98, 137202 (2007) PHYSICAL REVIEW LETTERS week ending 30 MARCH 2007

Magnetizing Oxides by Substituting Nitrogen for Oxygen

I. S. Elfimov,[1] A. Rusydi,[2] S. I. Csiszar,[3] Z. Hu,[4] H. H. Hsieh,[5] H.-J. Lin,[5] C. T. Chen,[5] R. Liang,[1] and G. A. Sawatzky[1]

It was experimentally reported that local magnetic moments were formed in N-doped MgO (max 13 at.%) and SrO (max 25 at.%).

Approved & Registered Patent : *2011*

特　許　証
(CERTIFICATE OF PATENT)

特許第４７０８３３４号
(PATENT NUMBER)

発明の名称
(TITLE OF THE INVENTION)　透明強磁性単結晶化合物の製造方法

特許権者
(PATENTEE)　埼玉県川口市本町四丁目１番８号
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その他別紙記載

出願番号
(APPLICATION NUMBER)　特願２００６－５１０４８４

出願日
(FILING DATE)　平成１７年　２月２５日(February 25, 2005)

登録日
(REGISTRATION DATE)　平成２３年　３月２５日(March 25, 2011)

この発明は、特許するものと確定し、特許原簿に登録されたことを証する。
(THIS IS TO CERTIFY THAT THE PATENT IS REGISTERED ON THE REGISTER OF THE JAPAN PATENT OFFICE.)

平成２３年　３月２５日(March 25, 2011)

特許庁長官
(COMMISSIONER, JAPAN PATENT OFFICE)
岩井良行

JP 4708334 B2 2011.6.22

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H01F 1/00 (2006.01)　H01F 1/00　Z

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静岡県静岡市北１４６番地
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兵庫県明石市魚住町錦ヶ丘４丁目２－１８
(72)発明者　佐藤　和則
大阪府箕面市小野原東４丁目１６－３－２０１

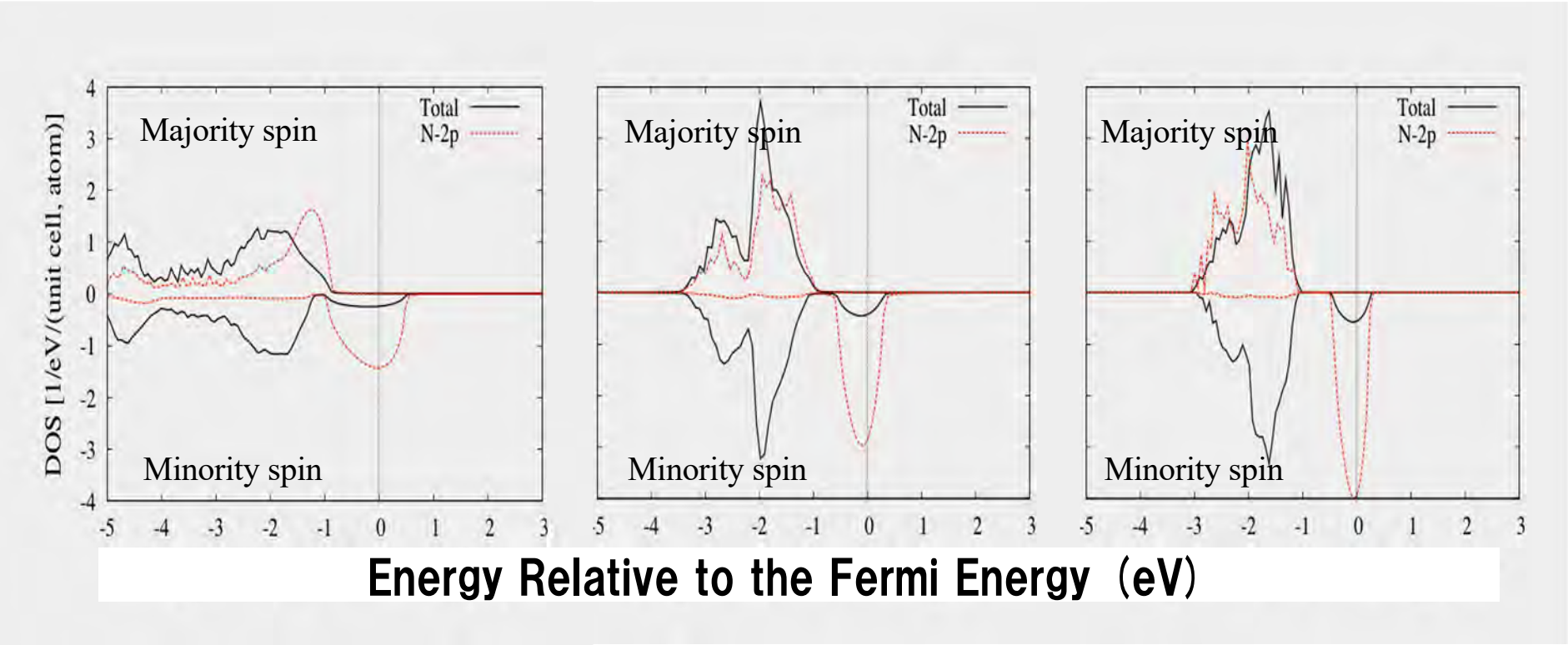
最終頁に続く

(54)【発明の名称】透明強磁性単結晶化合物の製造方法

(57)【特許請求の範囲】
【請求項１】
透明強磁性単結晶化合物を製造する方法において、
該化合物として、
アルカリ土類・カルコゲン化合物、アルカリ・カルコゲン化合物から選ばれる光を透過するワイドバンドギャップ化合物を用いること、
該化合物を基板上に成膜する方法として、MBE法を用いること、
該化合物の成膜時に、B,C,N,O,F,Si,Geから選ばれる最外殻に不完全なp電子殻をもつ少なくとも１種の元素を原子状に蒸発させて、成長した該化合物に１at%～２５at%固溶させることの組み合わせ
によって完全スピン分極した、強磁性転移温度が３００度K以上である単結晶化合物を成膜することを特徴とする透明強磁性単結晶化合物の製造方法。
【請求項２】
固溶させる元素の濃度の調整により強磁性特性を調整することを特徴とする請求項１記載の透明強磁性単結晶化合物の製造方法。
【請求項３】
成膜時にさらにn型ドーパント又はp型ドーパントの少なくとも一方を原子状に蒸発させて前記化合物に添加することによって強磁性特性を調整することを特徴とする請求項１記載の透明強磁性単結晶化合物の製造方法。
【発明の詳細な説明】

Zener's double exchange mechanism in Partially Occupied Deep Impurity Band : *U>W* (*PSIC-LDA*)

$Mg(O_{0.9}N_{0.1})$ **$Ca(O_{0.9}N_{0.1})$** **$Sr(O_{0.9}N_{0.1})$**

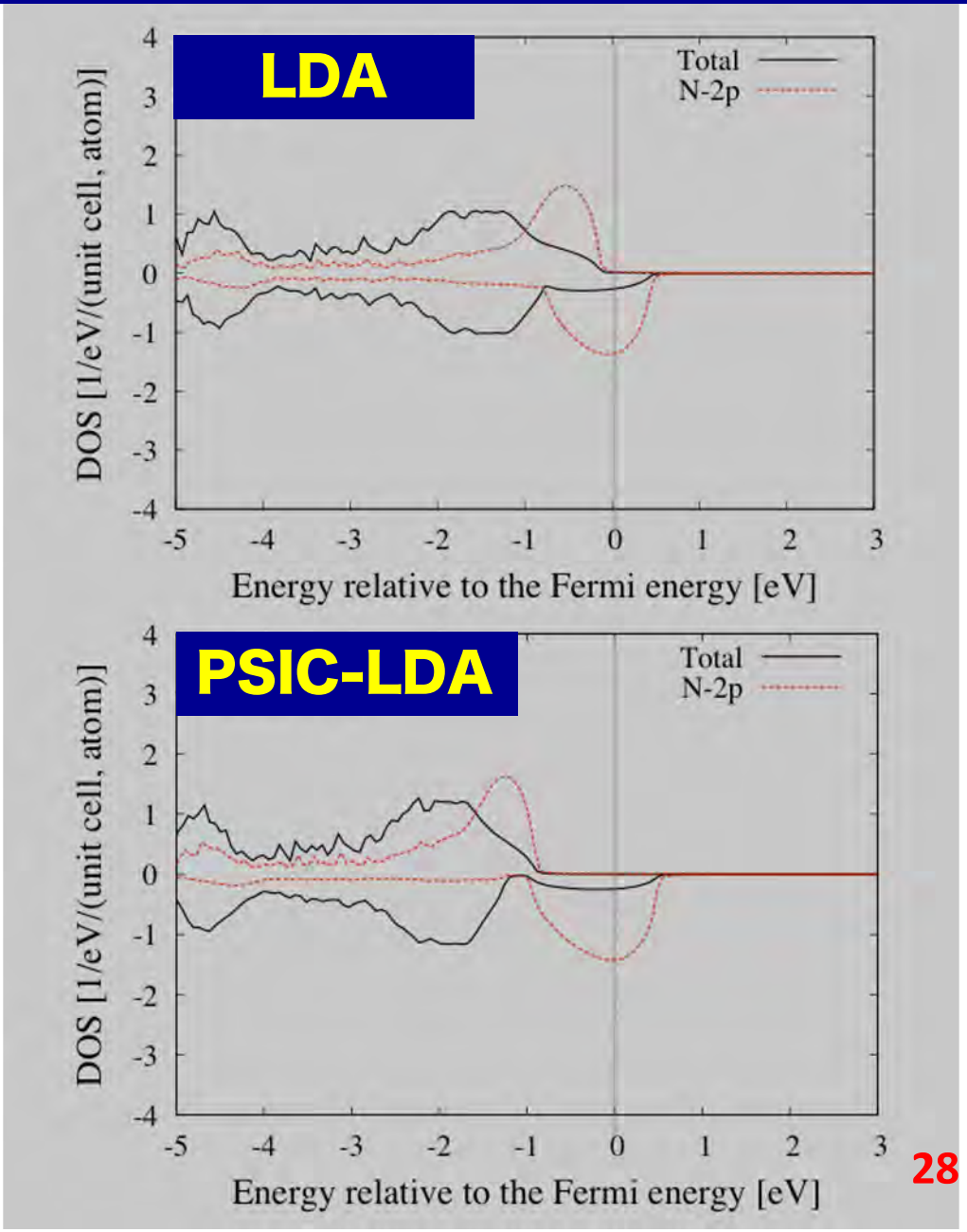


■*M. Seike, An Van Dinh, K. Sato, H. Katayama-Yoshida*

LDA vs. PSIC-LDA : U>W

Zener's Double Exchange Mechanism

$Mg(O_{0.9}N_{0.1})$

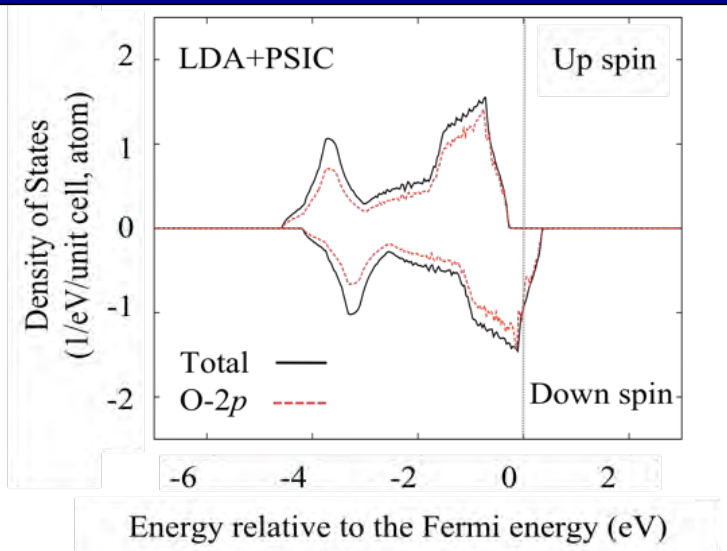


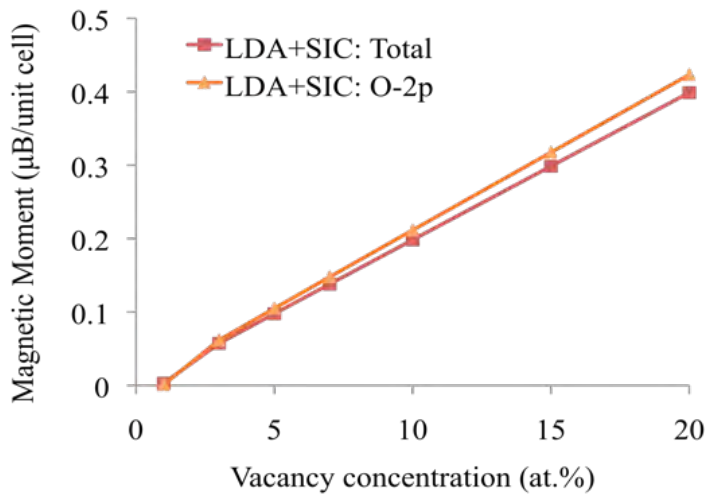
■ ***M. Seike, An Van Dinh, K. Sato, H. Katayama-Yoshida***

Narrow O_{2p} Band in $(Mg,V_{Mg})O$: U>W

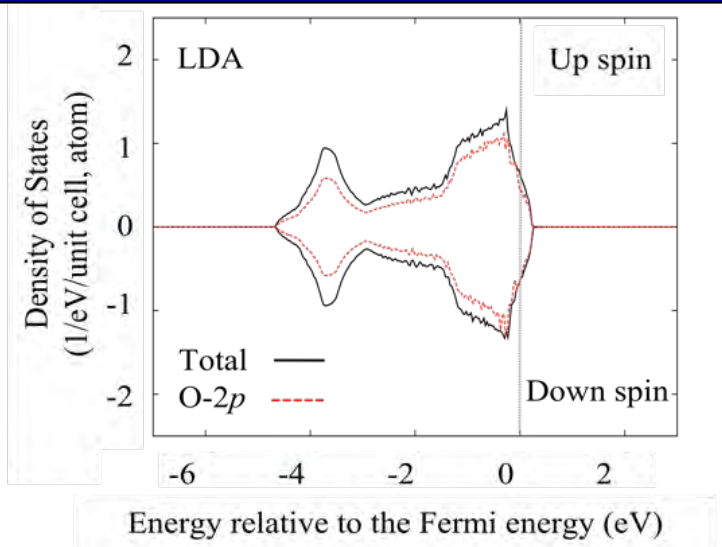
■*M. Seike, K. Sato, H. Katayama-Yoshida (2011)*

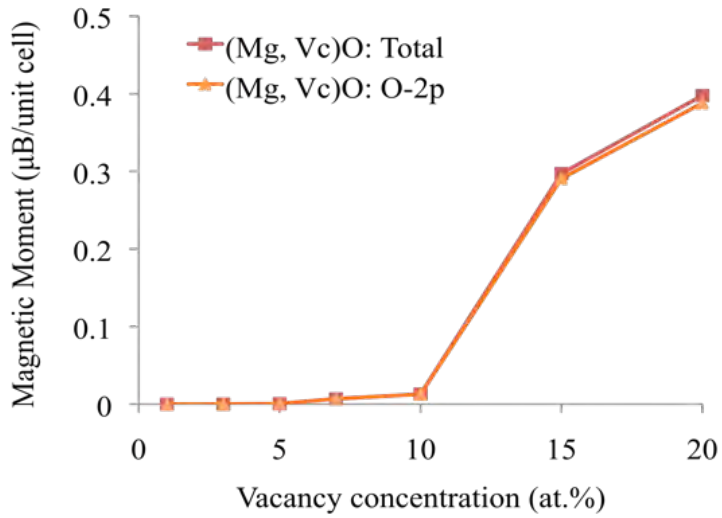
$(Mg_{0.9},V_{Mg0.1})O$: PSIC-LDA





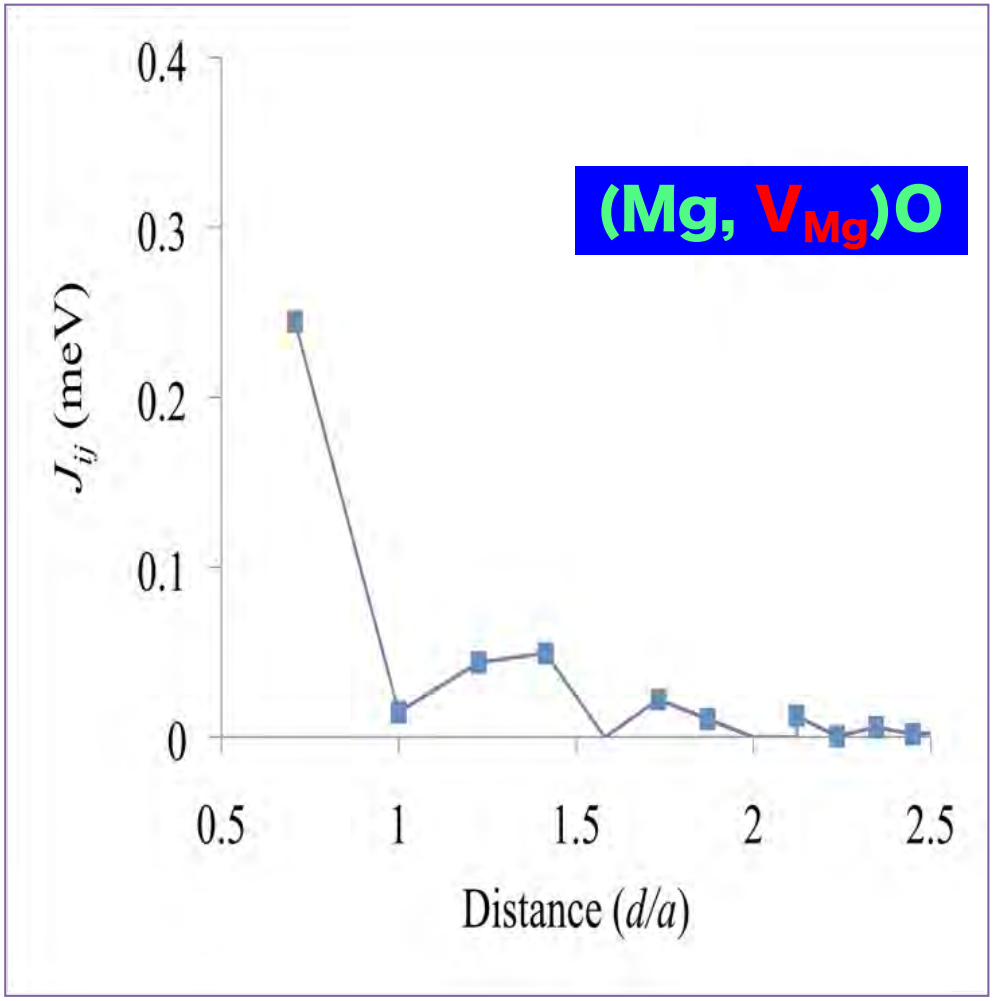
$(Mg_{0.9},V_{Mg0.1})O$: LDA



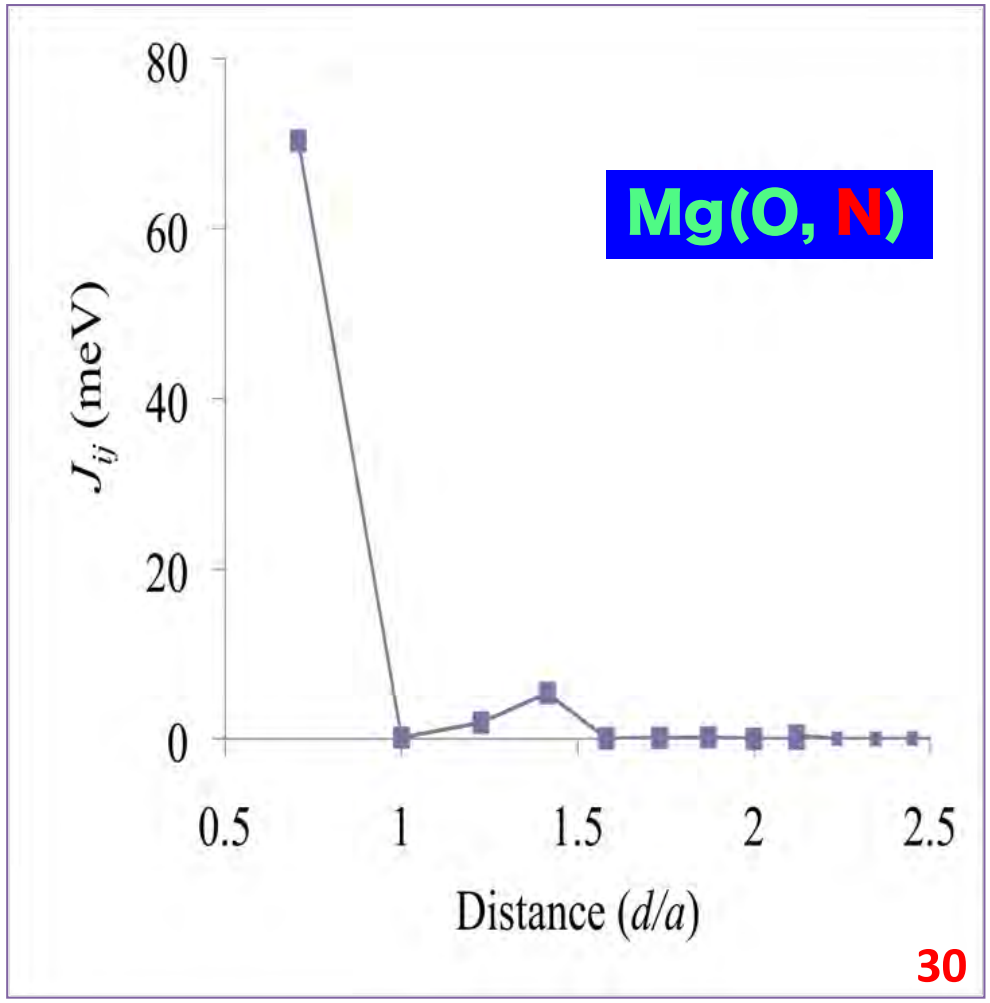


$$H = -\frac{1}{2}\sum_{i \neq j} J_{ij} \boldsymbol{e}_i \cdot \boldsymbol{e}_j$$

Exchange Coupling Constants between V_{Mg} in (Mg, V_{Mg})O

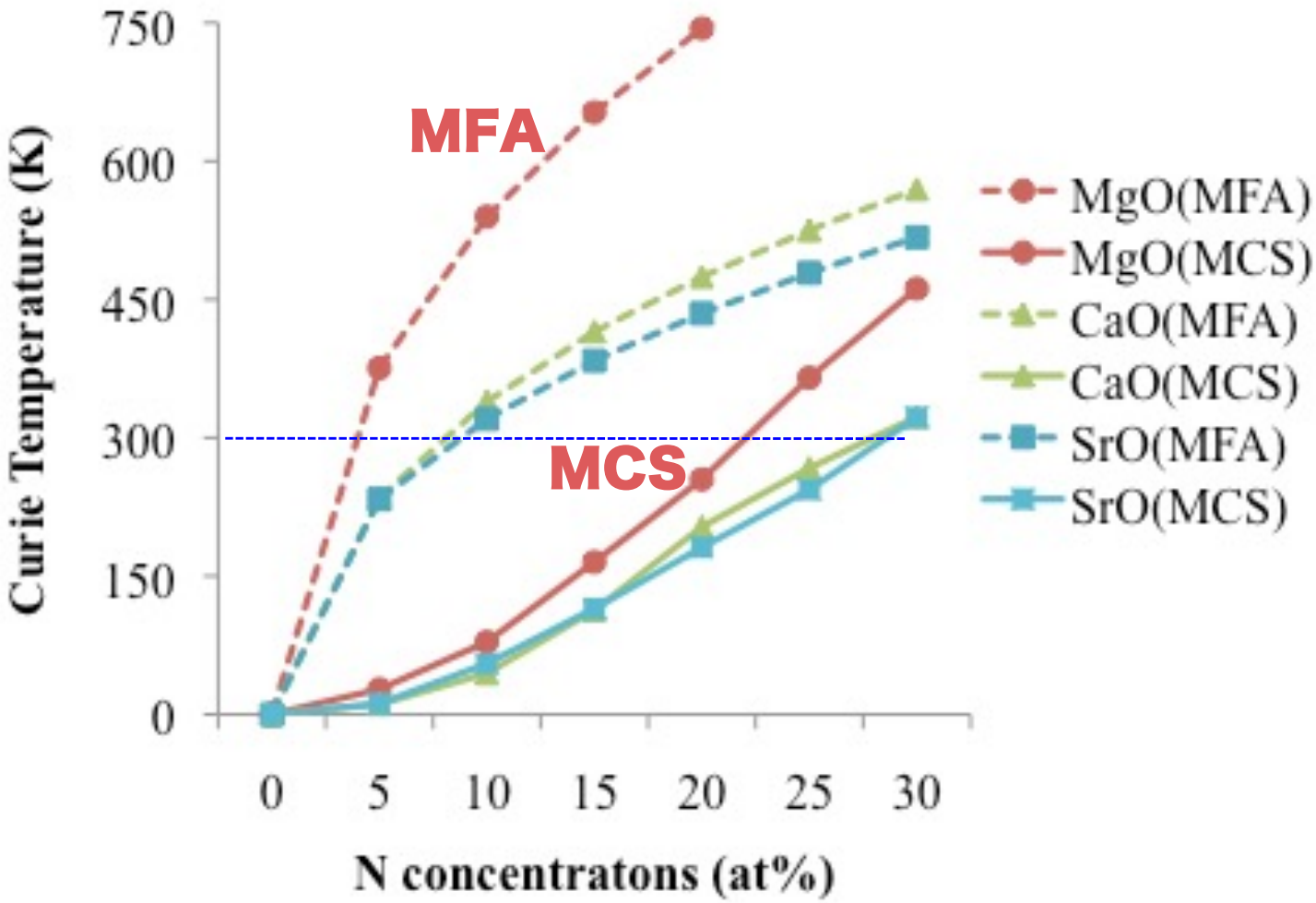


Exchange Coupling Constants between N in Mg(O, N)



MFA vs. MCS: Curie Temperature (T_c)

■ *M. Seike, An Van Dinh, K. Sato, H. Katayama-Yoshida*



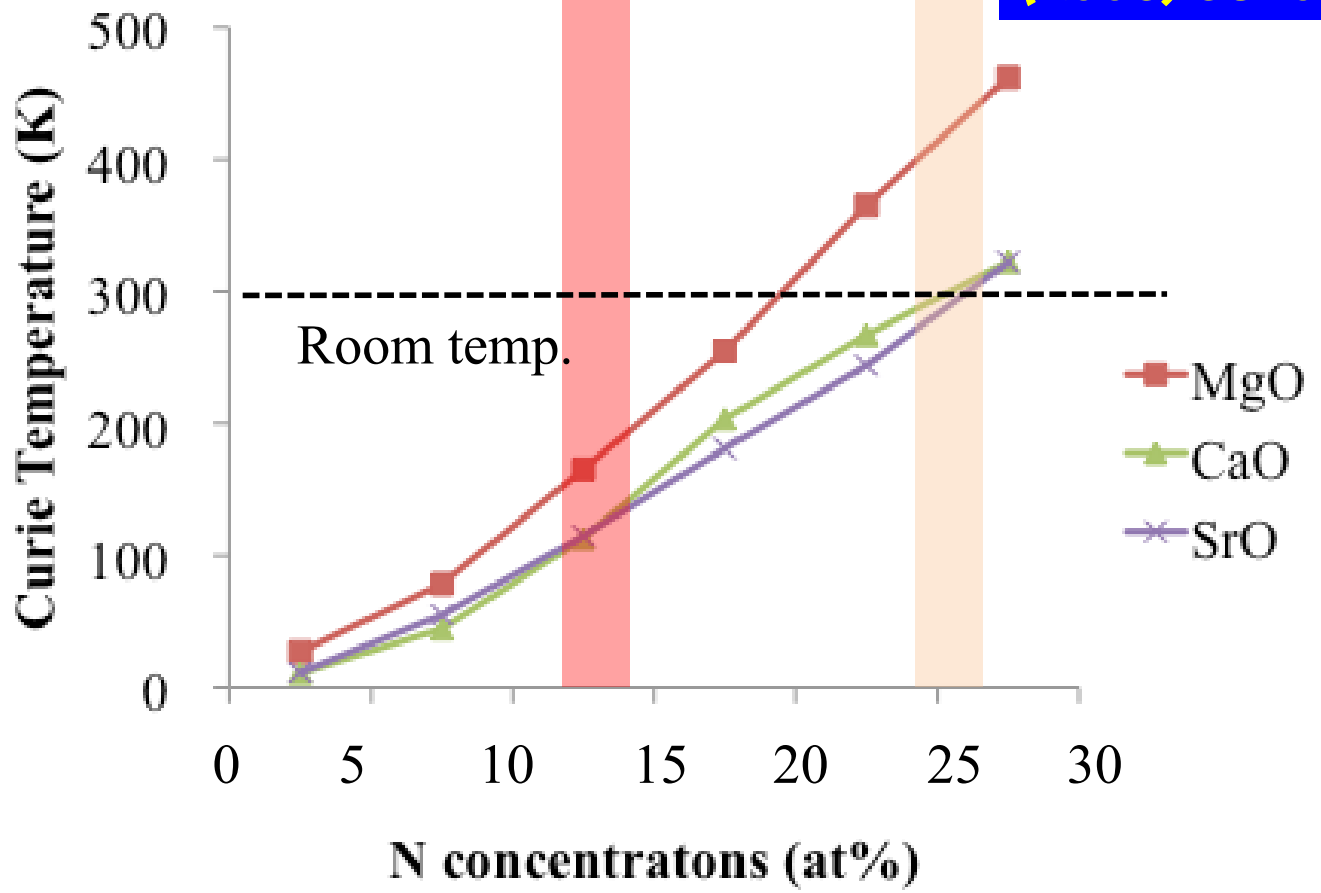
Curie Temperature (T_c) by MCS: PSIC-LDA

■ *M. Seike, An Van Dinh, K. Sato, H. Katayama-Yoshida*

Max doping conc. for SrO [2]

Max doping conc. for MgO [1]

Mg(O,C), Sr(O,C), Ba(O,C):
V. A. Dinh, M. Toyoda, K. Sato & H. Katayama-Yoshida, J. Phys. Soc. Jpn., 75 (2006) 93705



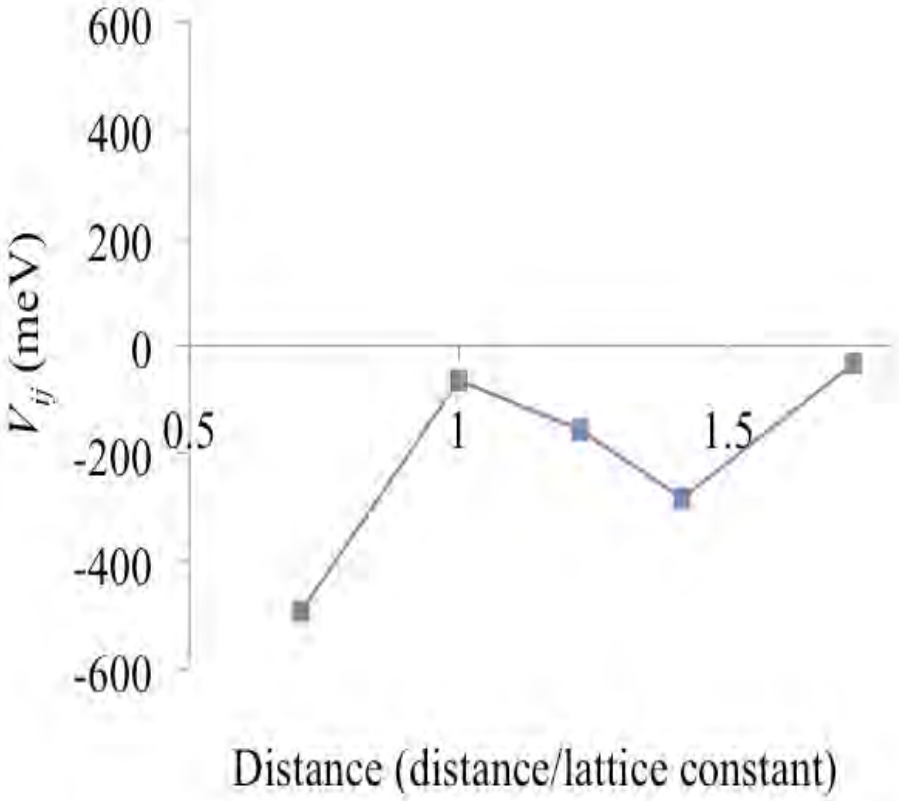
[1] *C. H. Yang et al., 2009 APS March Meeting, (2009).*
[2] *I. S. Elfimov et al., Phys. Rev. Lett. 98 (2007) 137202.*

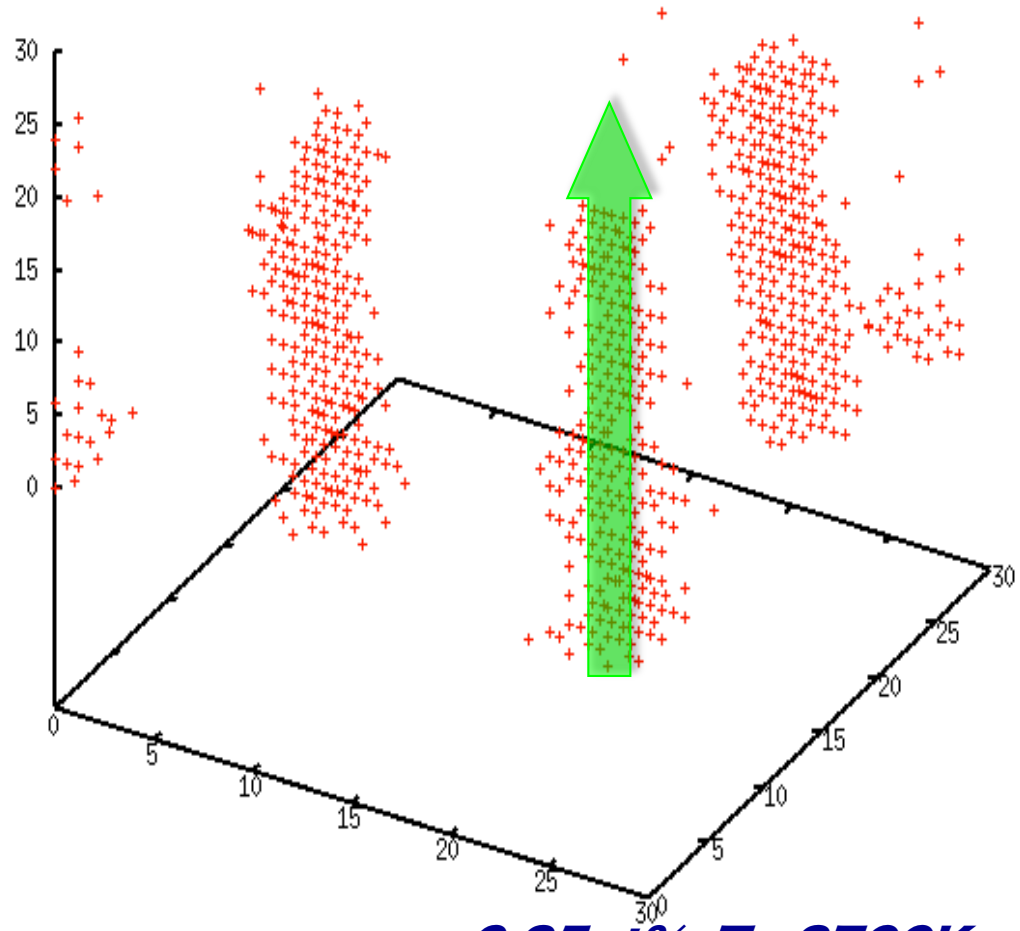
Konbu-Phase: 2D Spinodal Nano-Decomposition in Mg(O,N)

Effective Chemical Pair Interactions between N in MgO

$$V_{ij} = V_{ij}^{N\text{-}N} + V_{ij}^{O\text{-}O} - 2V_{ij}^{N\text{-}O}$$

$$\mathcal{H} = \sum_{i>j} V_{ij}\, \sigma_i \cdot \sigma_j$$





6.25at%, T~2700K, 1000 Steps

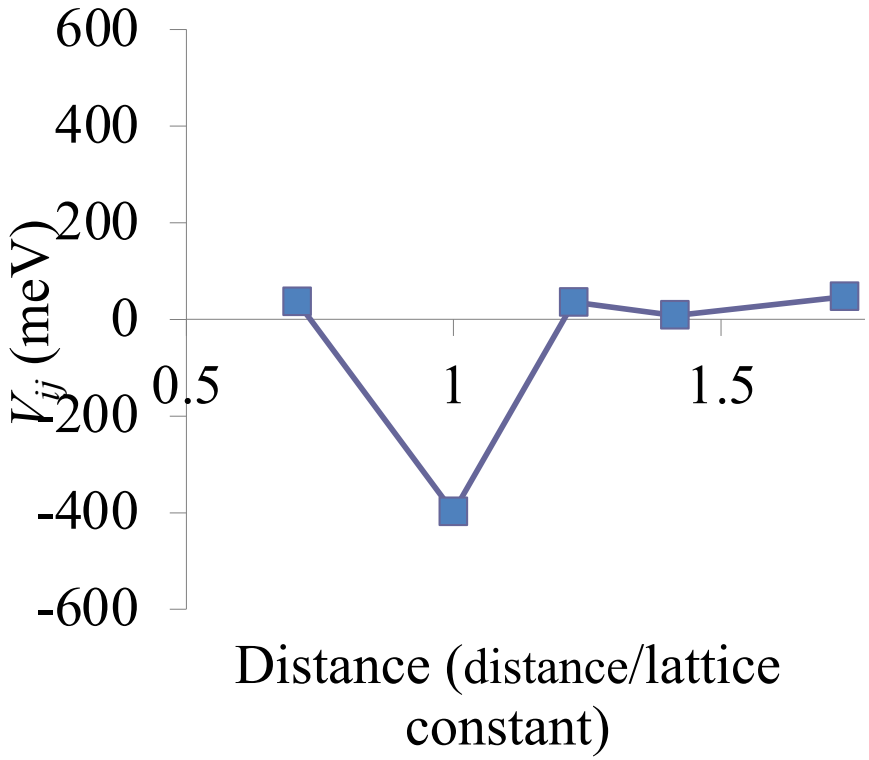
■ *M. Seike, K. Sato, H. Katayama-Yoshida (2011)*

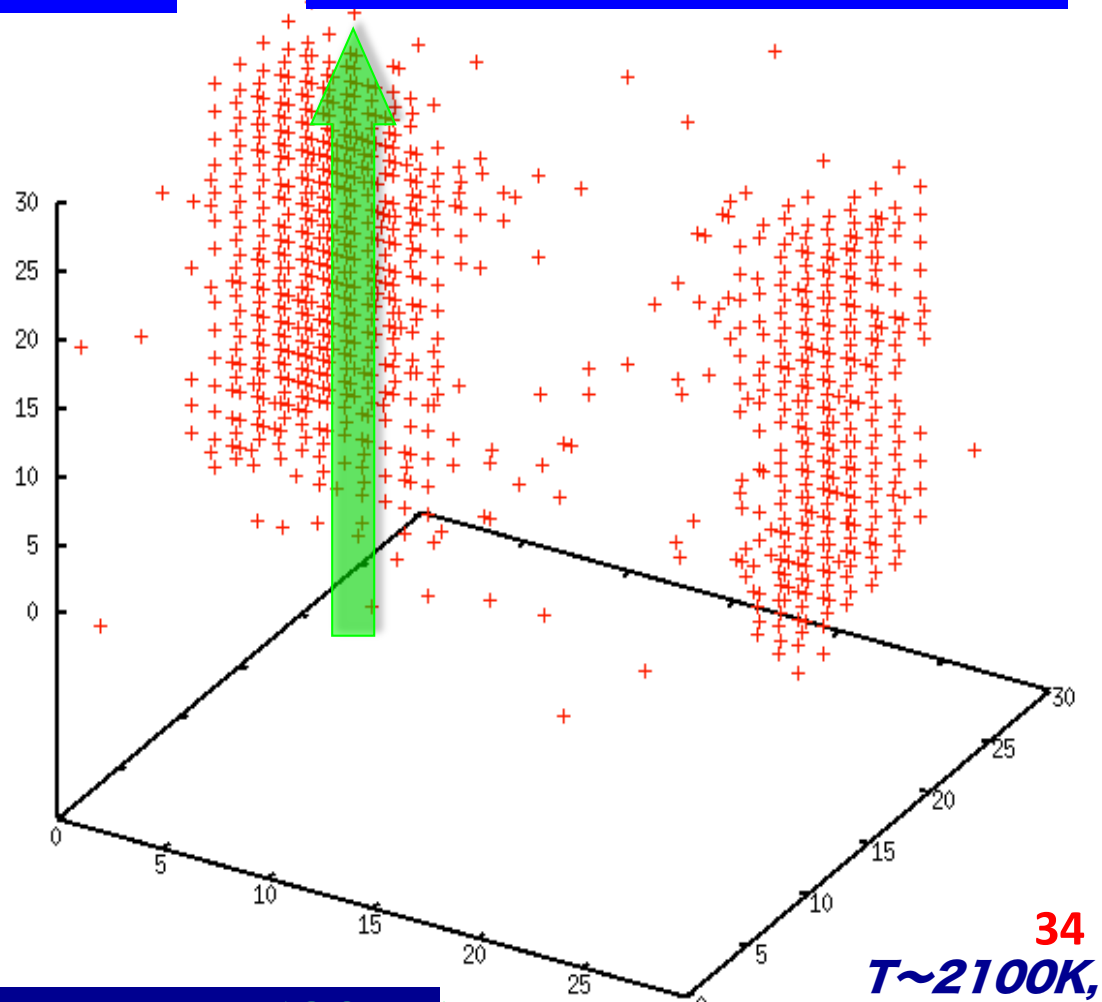
Konbu-Phase: 2D Spinodal Nano-Decomposition in $(Mg,V_{Mg})O$

Effective Chemical Pair Interactions between Mg Vacancies in MgO

$$V_{ij} = V_{ij}^{Mg\text{-}Mg} + V_{ij}^{V\text{-}V} - 2V_{ij}^{V\text{-}Mg}$$

$$\mathcal{H} = \sum_{i>j} V_{ij}\, \sigma_i \cdot \sigma_j$$





M. Seike, K. Sato, H. Katayama-Yoshida (2011)

T~2100K, MCS~10000 Steps

Experimental Verification : *2010*

PHYSICAL REVIEW B **82**, 024405 (2010)

Ferromagnetism in transparent thin films of MgO

C. Martínez-Boubeta,[1] J. I. Beltrán,[2] Ll. Balcells,[3] Z. Konstantinović,[3] S. Valencia,[4] D. Schmitz,[4] J. Arbiol,[3,5] S. Estrade,[1] J. Cornil,[2] and B. Martínez[3,*]

[1]*IN²UB and Departament d'Electrònica, Universitat de Barcelona, 08028 Barcelona, Spain*

[2]*Laboratory for Chemistry of Novel Materials, Université de Mons-Hainaut, 7000 Mons, Belgium*

[3]*Instituto de Ciencia de Materiales de Barcelona (ICMAB), CSIC, Campus UAB, 08193 Bellaterra, Spain*

APPLIED PHYSICS LETTERS **96**, 232505 (2010)

Room temperature ferromagnetism in pristine MgO thin films

C. Moyses Araujo,[1,2] Mukes Kapilashrami,[1] Xu Jun,[1,3] O. D. Jayakumar,[1,4] Sandeep Nagar,[1] Yan Wu,[1] Cecilia Århammar,[2,5] Börje Johansson,[2,5] Lyubov Belova,[1] Rajeev Ahuja,[2,5] Gillian A. Gehring,[6] and K. V. Rao[1,a)]

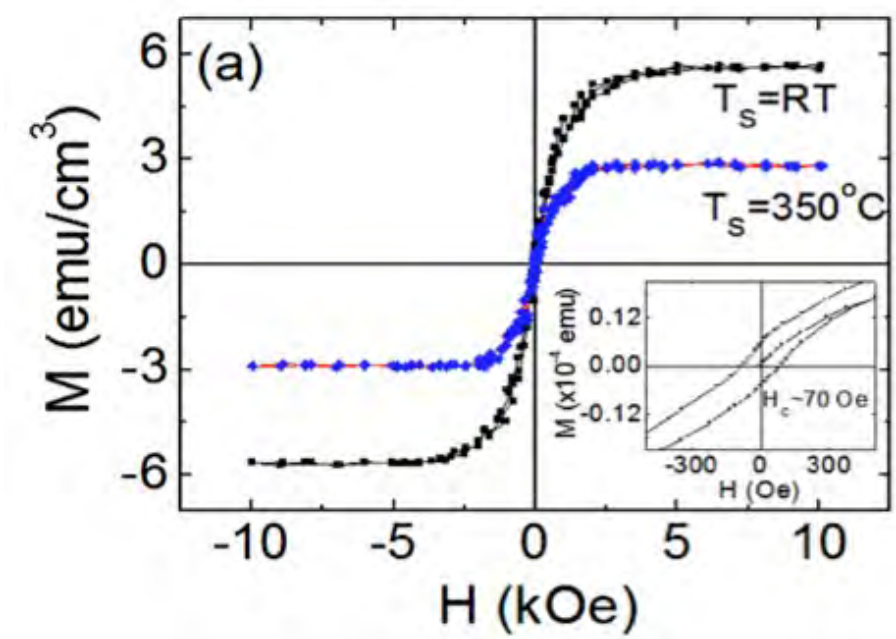
[1]*Department of Materials Science, Tmfy-MSE, Royal Institute of Technology, SE100 44 Stockholm, Sweden*

[2]*Department of Physics and Astronomy, Condensed Matter Theory Group, Uppsala University, Box 516, S-751 20 Uppsala, Sweden*

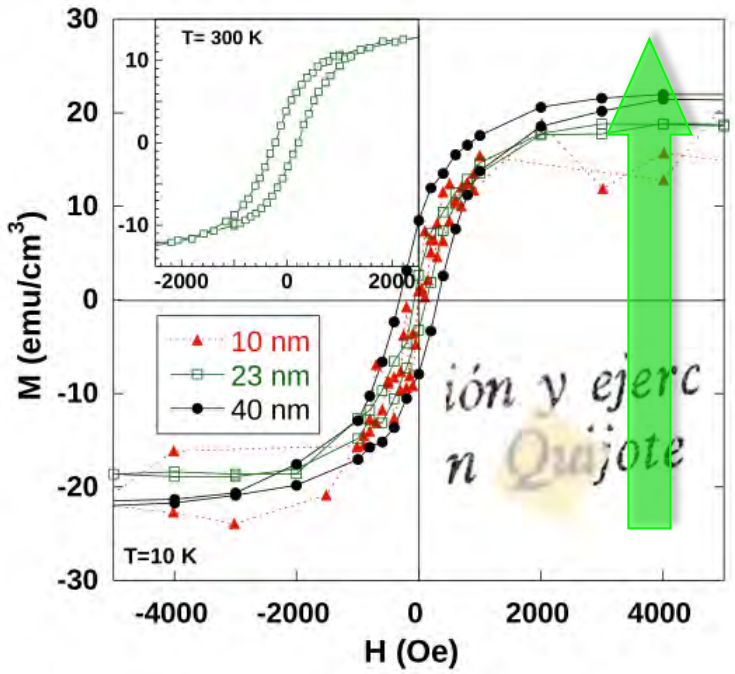
The existence of ferromagnetism has been experimentally reported in undoped (pristine) MgO with no magnetic elements.

Transparent & Super-paramagnetic pristine (Mg,V_{Mg})O thin films : *2010*

1 at.% V_{Mg} (T_s = RT)



4 at.% V_{Mg}



■ *C. Martínez-Boubeta, et al, Phys Rev B 82, 024405, (2010).*

A New Class of Bottom-up Nanotechnology

Spinodal Nanotechnology

- ☒ Semiconductor Nano-Spintronics
- ☐ Semiconductor Nano-Spincaloritronics
- ☐ Spinodal Thermoelectric-Power Materials
- ☐ High-efficient Nano-Spinodal LED & LASER
- ☐ Nanocatalyst for Automotive Gas-Emission
- ☐ Nano-Spinodal Photovoltaic Solar Cells
- ☐ Hydrogen Photosynthesis Nanocatalyst
- ☐ Semiconductor-DMS Hydrogen Storage
- ☐ High-T_c Nano-Superconductors
- ☐ Nanocatalyst for Fuel Cells
- ☐ Multi-ferroic Nanocomposites
- ☐ Spinodal Nano-Quantronics
- ☐ Spinodal Nano-Moltronics
- ☐ Spinodal Nano-Water-Splitting

吉田博ｳ

Part 【2】

■超高効率エネルギー変換スピノーダル・ナノテクノロジー

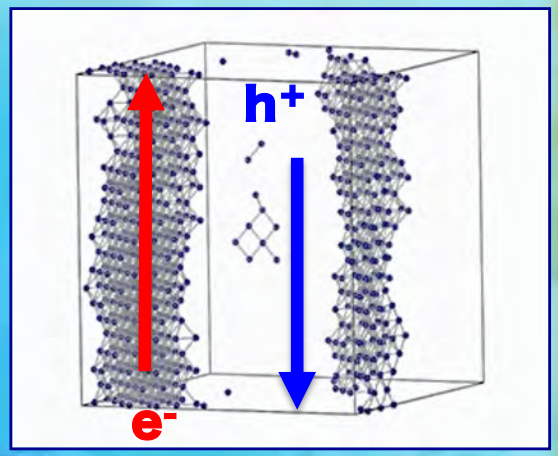
＜超低コスト・超高効率太陽電池＞

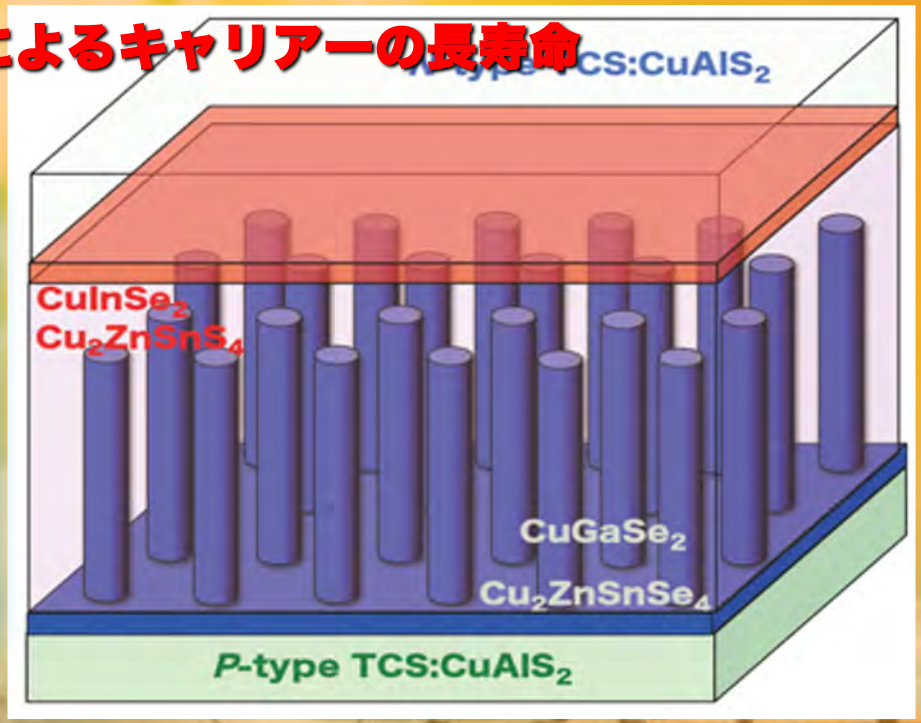
(1) 自己修復機構をビルト・インした不老不死の太陽電池

(2) スピノーダル・ナノ分解による自己組織化ナノ超構造

(3) 電子・正孔の超高速分離によるキャリアーの長寿命化

自己組織化ナノ超構造（昆布相）



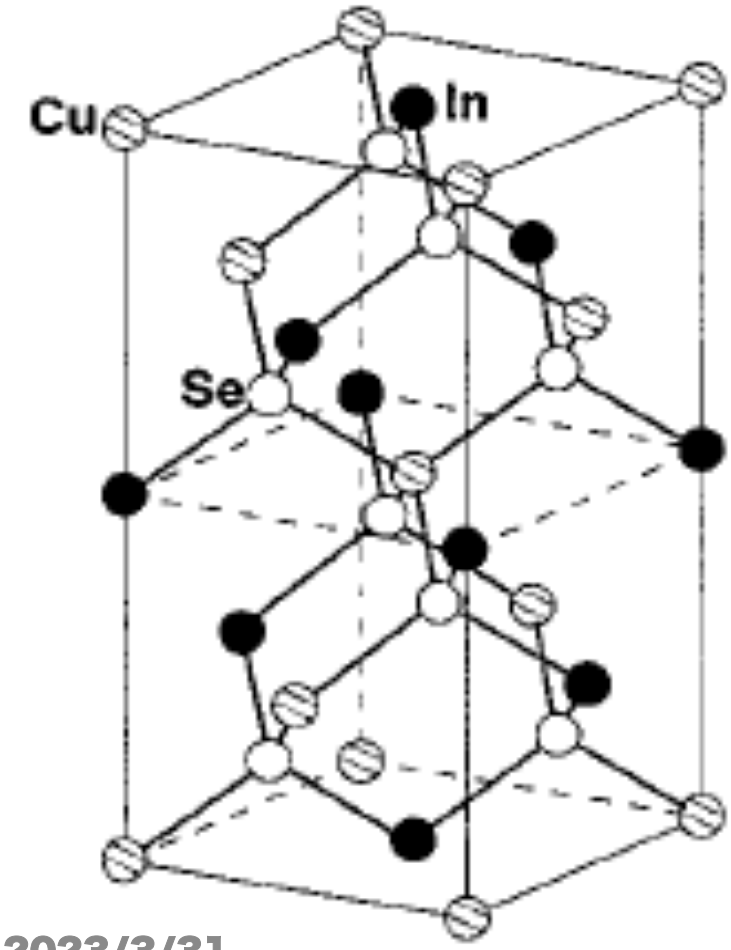


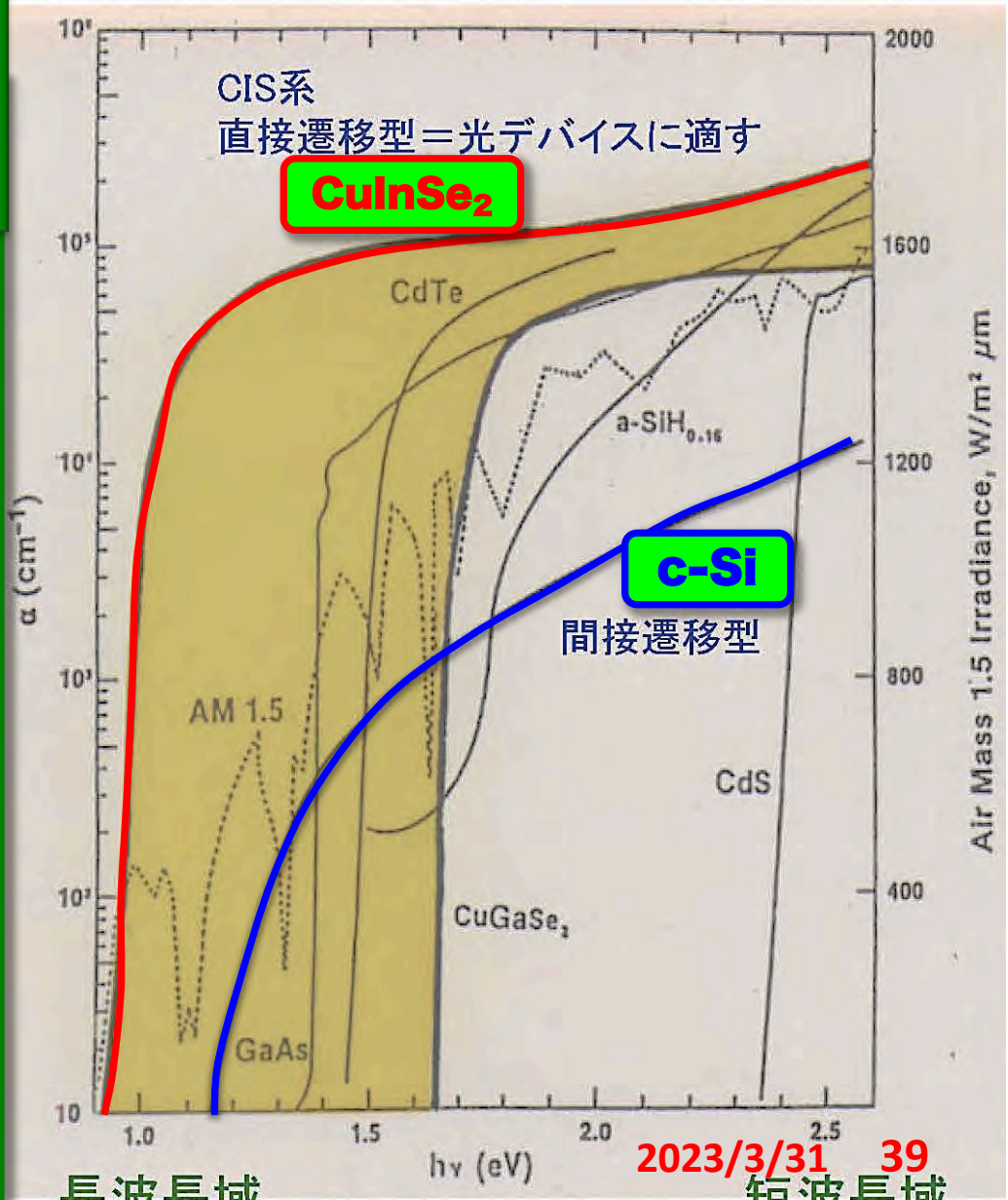
ダイヤモンド・ミューテーション：Chalcopyrite $CuInSe_2$

Diamond Mutation

Zn_2Se_2 ⇒ $CuInSe_2$

($2Zn^{2+}$ ⇒ Cu^{+} + In^{3+})

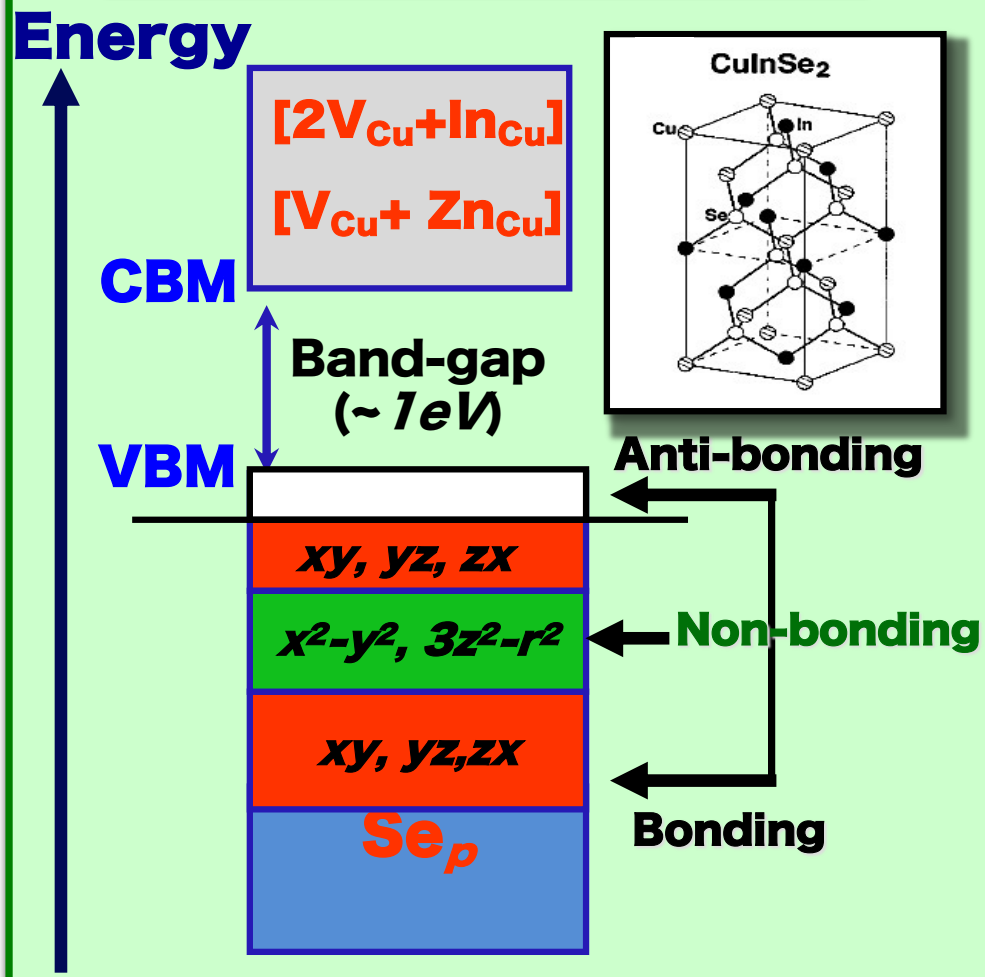


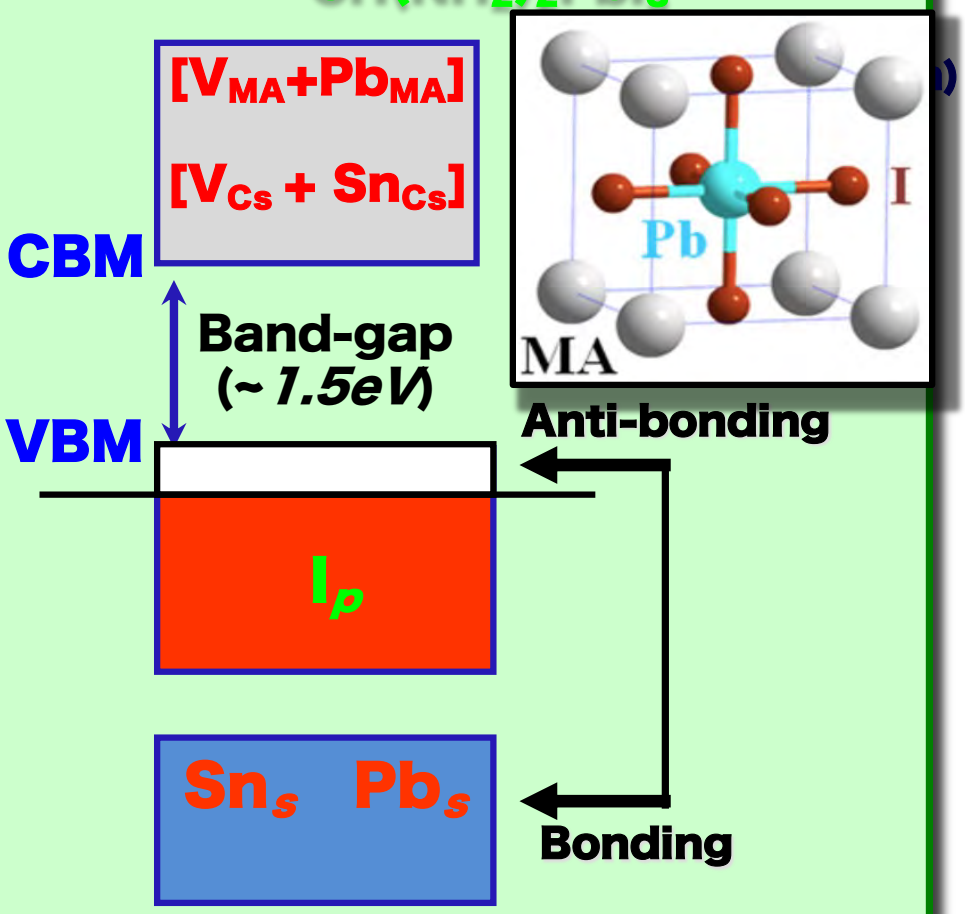


自己修復機構(Codoping)：反結合状態が電子で占有
チャルコパイライト, ケステライト, ペロブスカイト共通の電子状態

チャルコパイライト：$CuInSe_2$
ケステライト：$Cu_2ZnSnSe_4$

ペロブスカイト：$CsSnI_3$, $(CH_3NH_3)PbI_3$, $CH(NH_2)_2PbI_3$



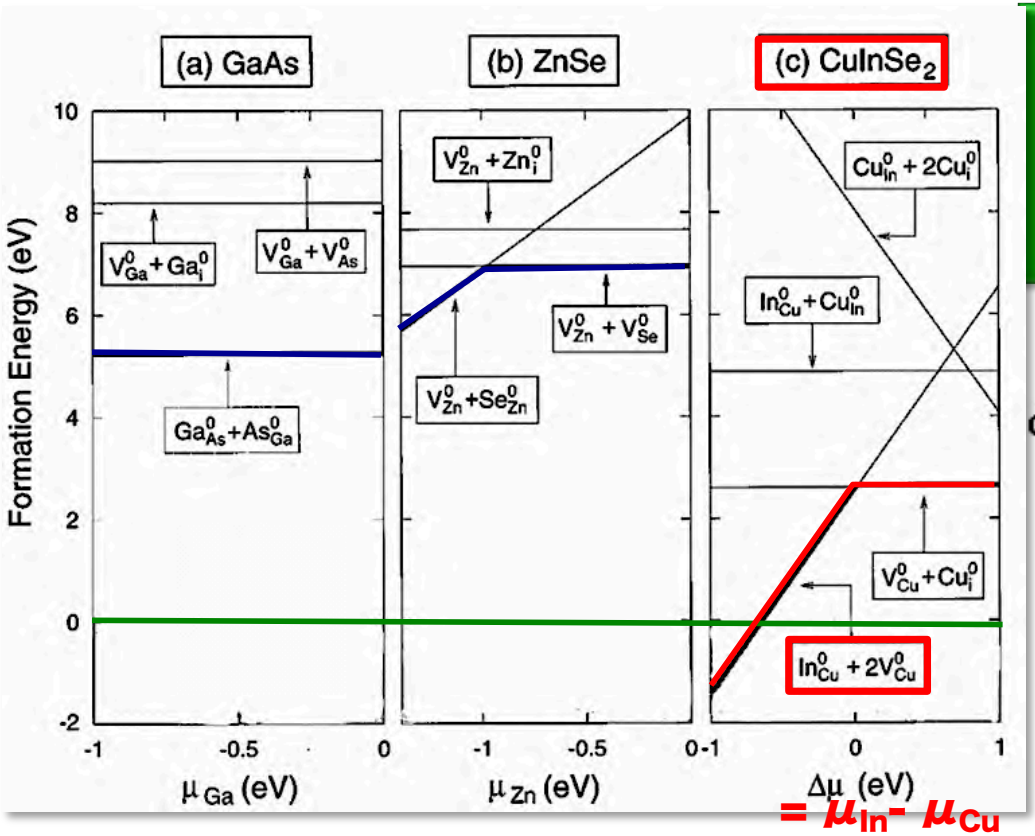


■Yamamoto, Katayama-Yoshida, *JJAP, 38 (1999) L166.* [ISI: 362]
■Zhang, Wei, Zunger, Katayama-Yoshida, *Phys. Rev. B57 (1998) 9642.* [ISI: 653]

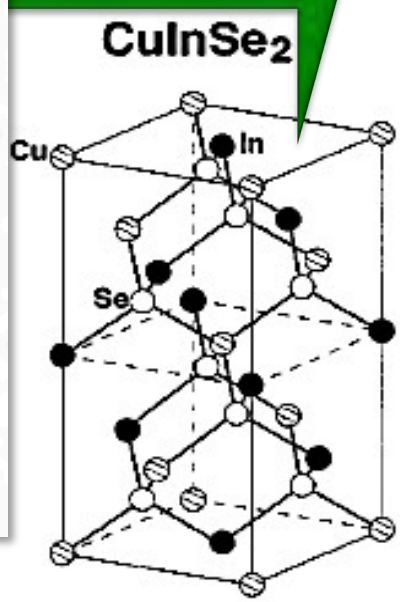
■$CuInSe_2$における自己修復機構[$2V_{Cu} + In_{Cu}$]のための結晶成長条件（Cu-poor & In-rich）

自己修復による低コスト化と高効率化のデザイン

η = 22.3%　（12/8/2015）

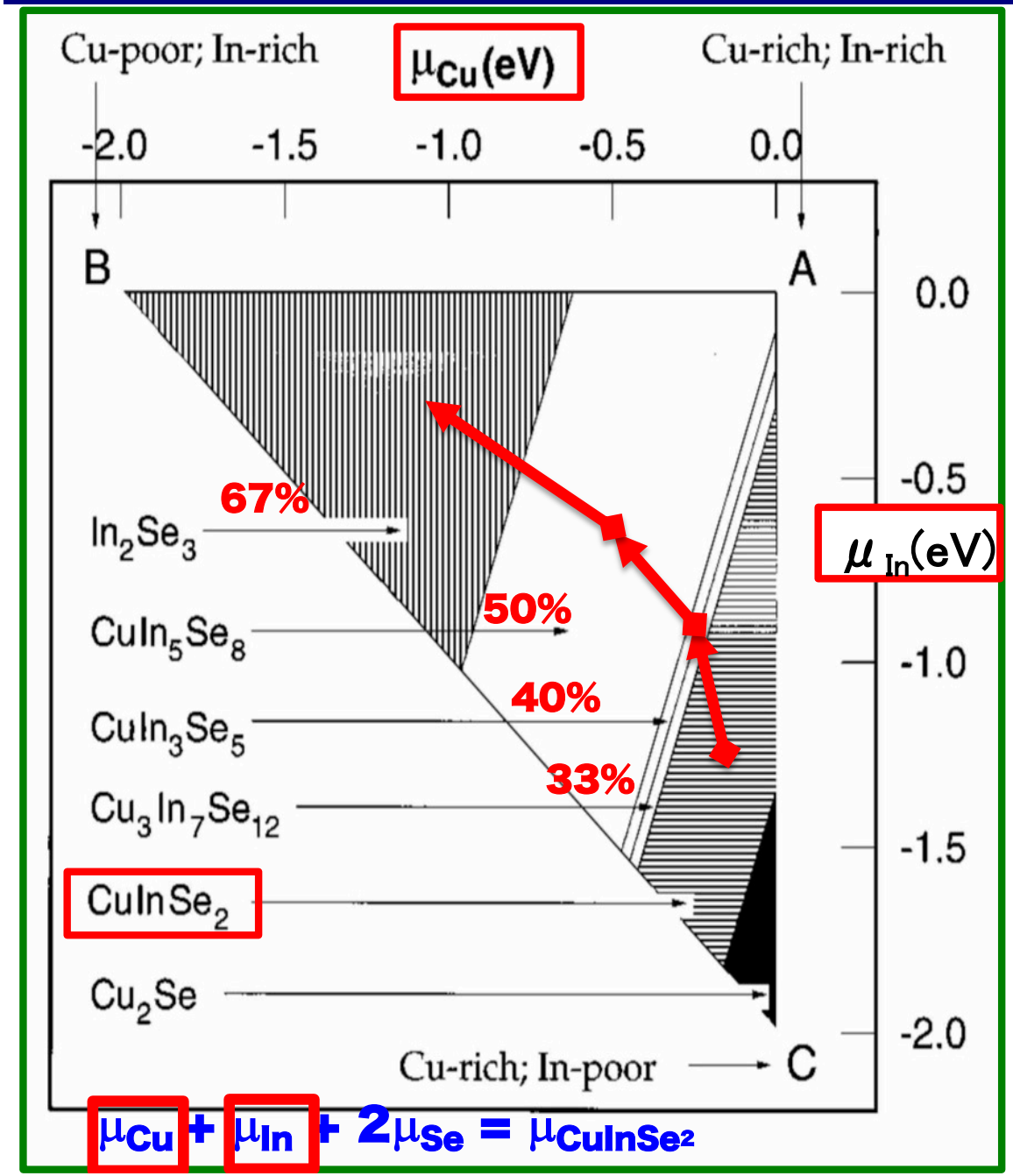


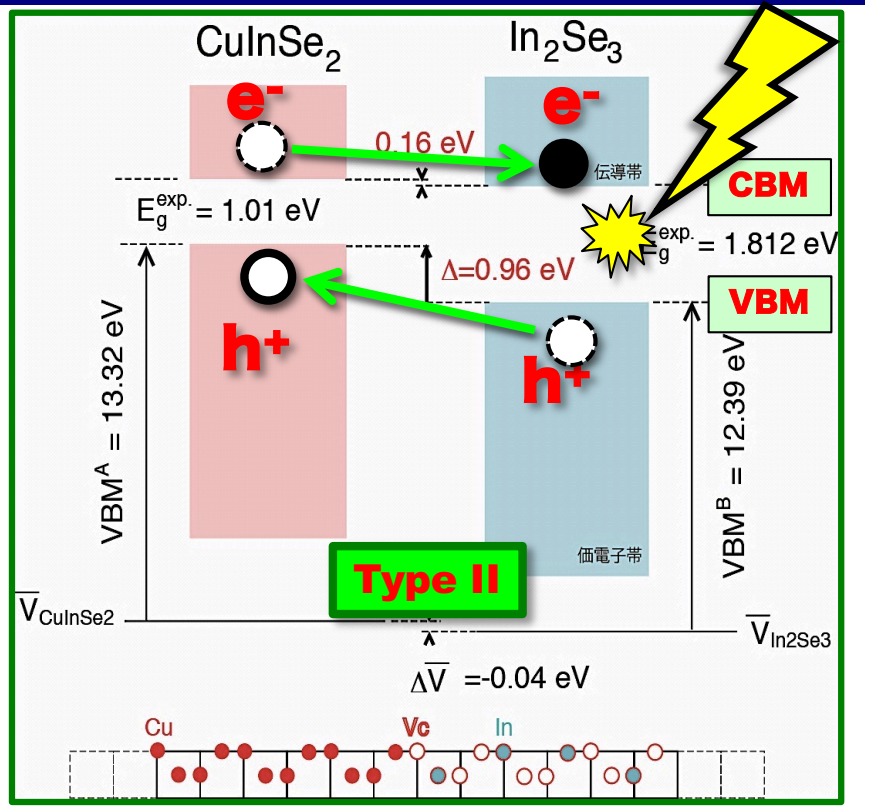
2007年
Honda Soltec
&
Solar Frontier

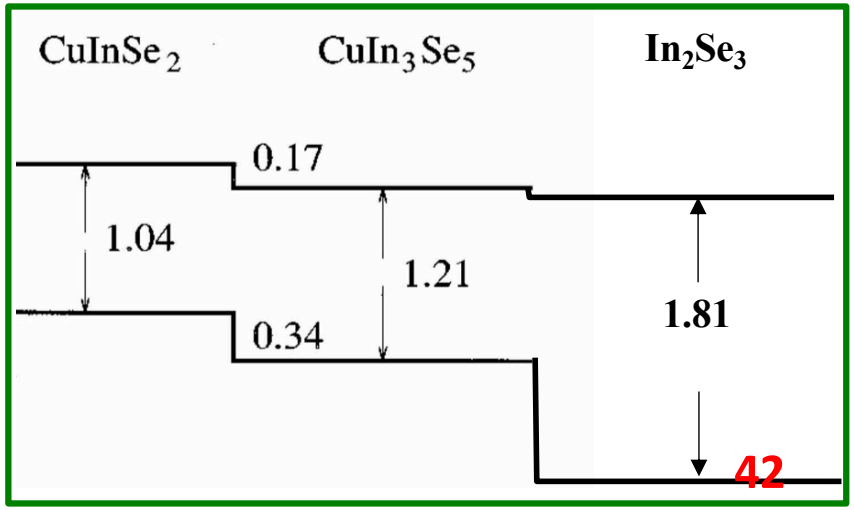


■*Zhang, Wei, Zunger, Katayama-Yoshida, Phys. Rev. B57 (1998) 9642.* [ISI: 731]
■*Yamamoto, Katayama-Yoshida, J. Crystal Growth, 214 (2000) 552.* [ISI: 88]
■*Yamamoto, Katayama-Yoshida, JJAP, 38 (1999) L166.* [ISI: 376]
■*Yamamoto, Katayama-Yoshida, PHYSICA B, 302 (2001) 115.* [ISI:129]

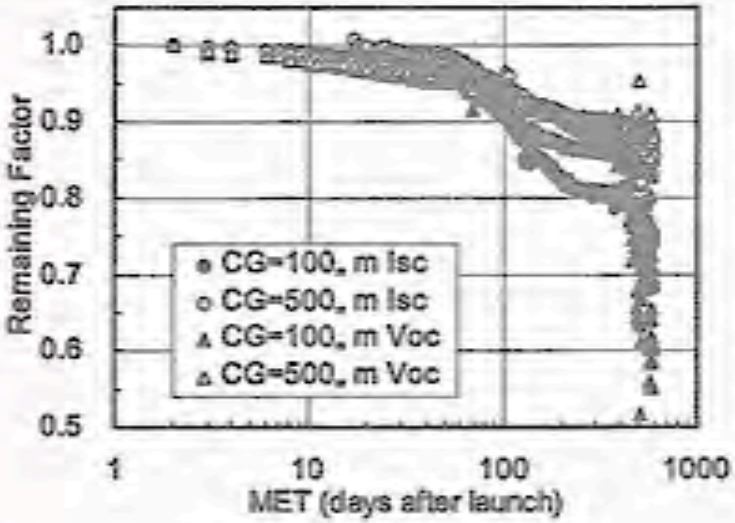
■自己修復機構：[$2V_{Cu}$+ In_{Cu}]
$CuInSe_2$, $Cu_3In_7Se_{12}$, $CuIn_3Se_5$, $CuIn_5Se_8$ & In_2Se_3



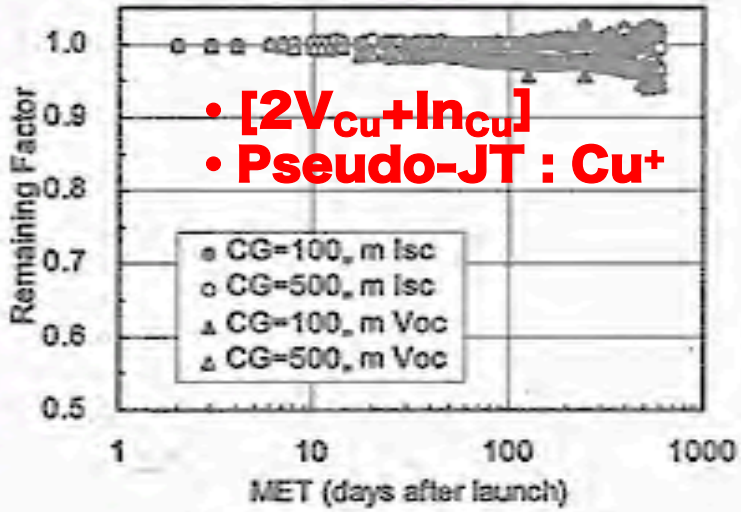




バン・アレン帯宇宙線放射損傷下での自己修復機構の実証実験
JAXA・「つばさ」： $Cu(In,Ga)Se_2$

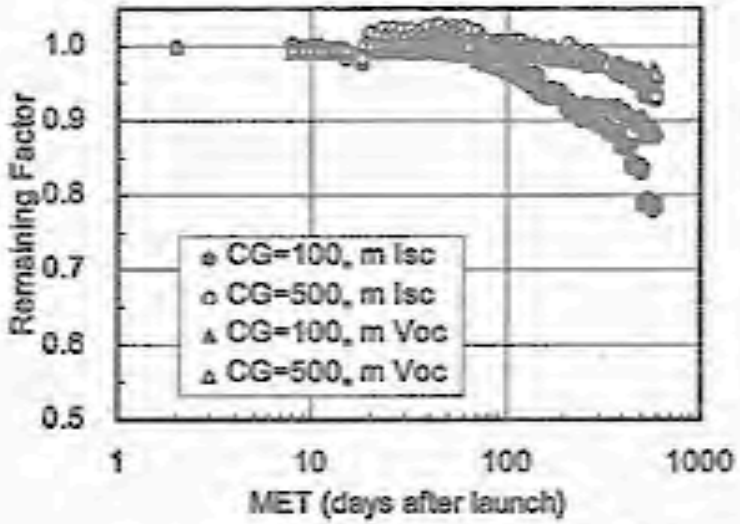


(b) バルク多結晶 Si 太陽電池

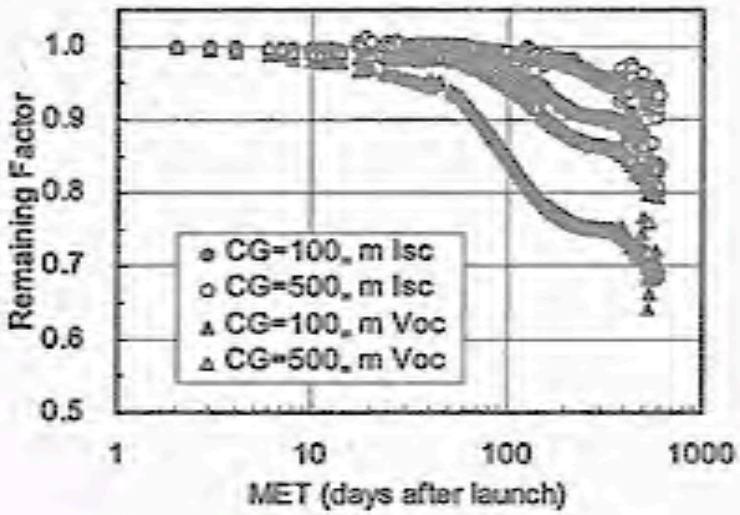


- $[2V_{Cu}+In_{Cu}]$
- Pseudo-JT : Cu^+

(e) 大面積 Cu(InGa)Se 太陽電池



(d) InGaP/GaAs タンデム２接合太陽電池



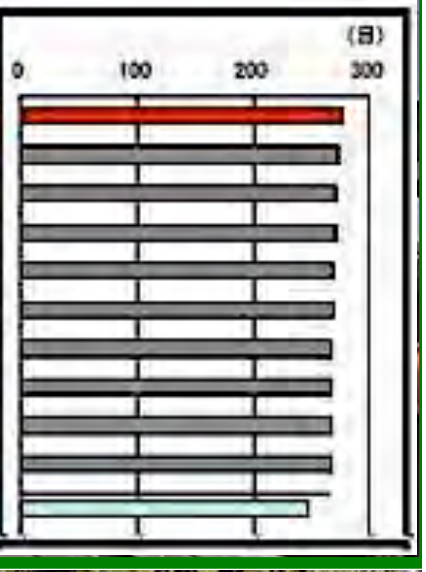
(g) 宇宙用単結晶 Si 太陽電池(10Ωcm)

M. Imaizumi et al (JAXA)., 2002.

My Parent's Country House（岡山吉備中央町・下加

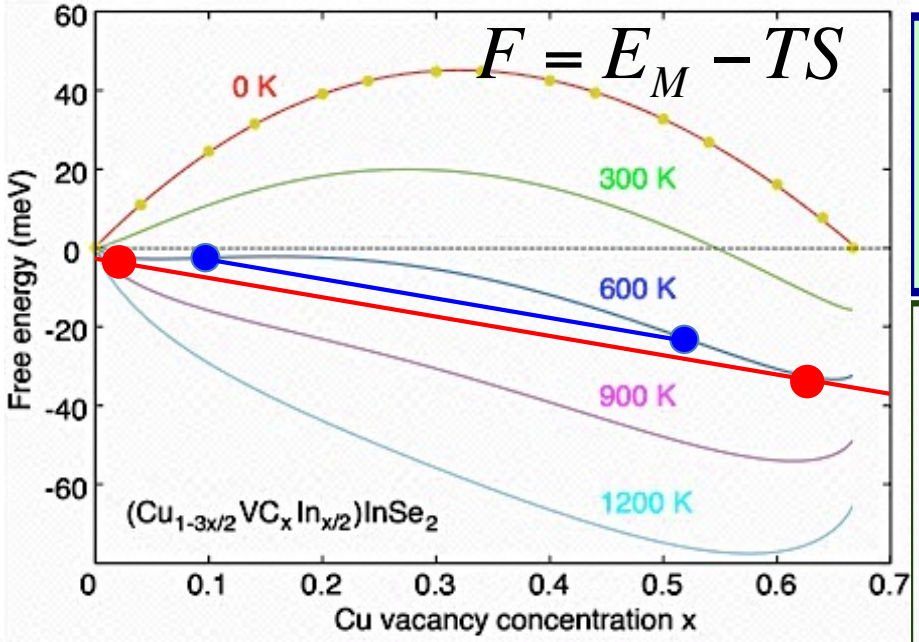
Buy : 7 Yen/kW・h
Sell : 42 Yen/kW・h

順位	都道府県名	降水量1mm未満の日数(日)
1	岡山	276.8
2	山梨	273.8
3	兵庫	271.6
4	広島	270.5
5	和歌山	269.0
6	埼玉	268.8
7	香川	267.8
8	大分	267.6
9	徳島	267.5
10	大阪	266.8
	全国平均	247.8

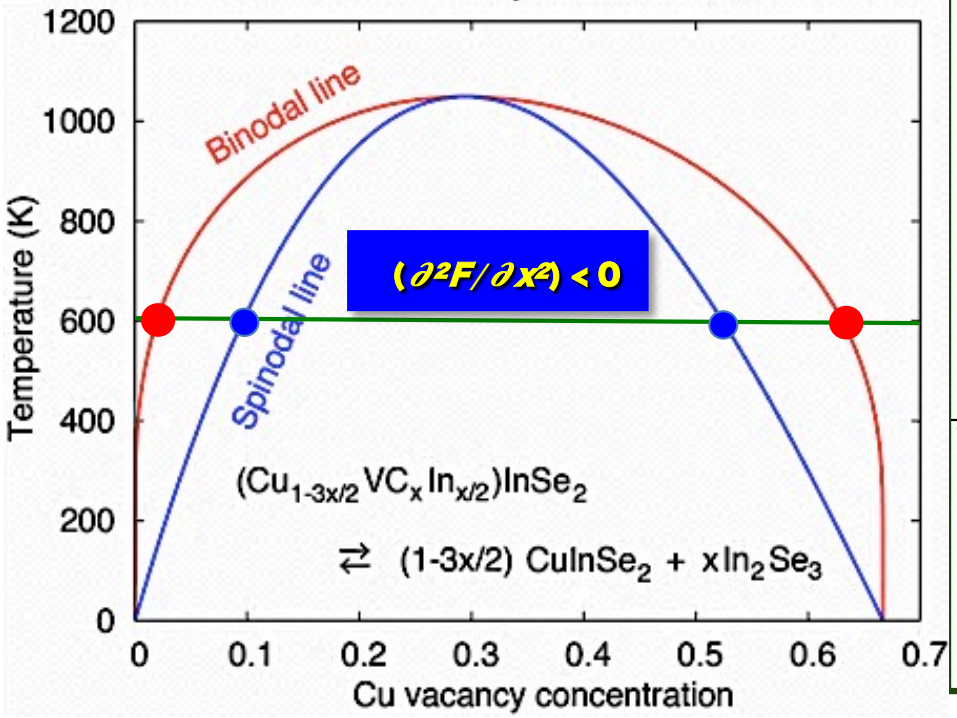


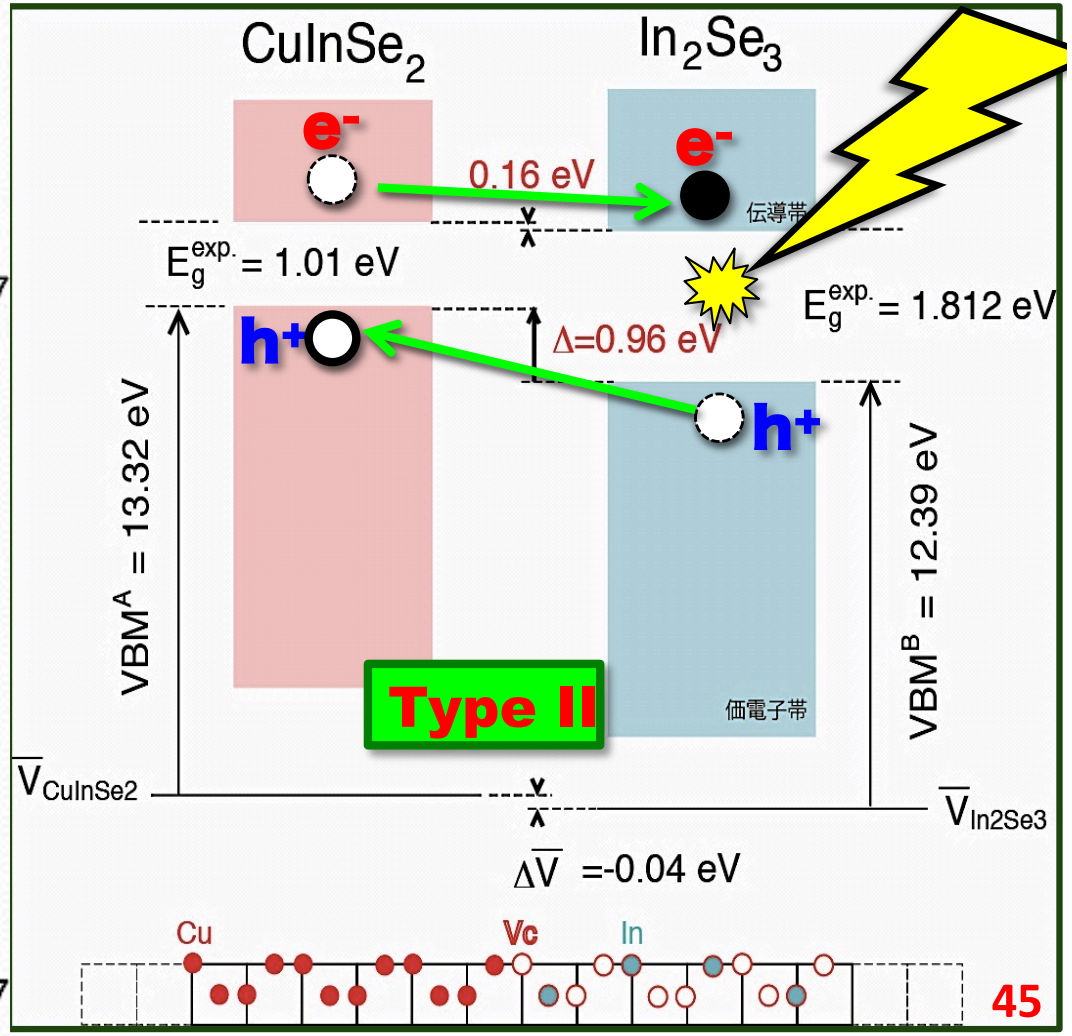
2023/3/31

$CuInSe_2$の自己修復とスピノーダル・ナノ分解の同時発現：[$2V_{Cu}$ + In_{Cu}]



$$E_M = E[Cu_{1-\frac{3}{2}x} Vc_x In_{\frac{x}{2}} InSe_2] - (1-\frac{3x}{2})E[CuInSe_2] - \frac{3x}{2}E[In_2Se_3]$$





スピノーダル・ナノ分解: *Tani et al.,(2010)* : $Cu(In,Ga)S_2$ & $Cu_2ZnSn(S,Se)_4$

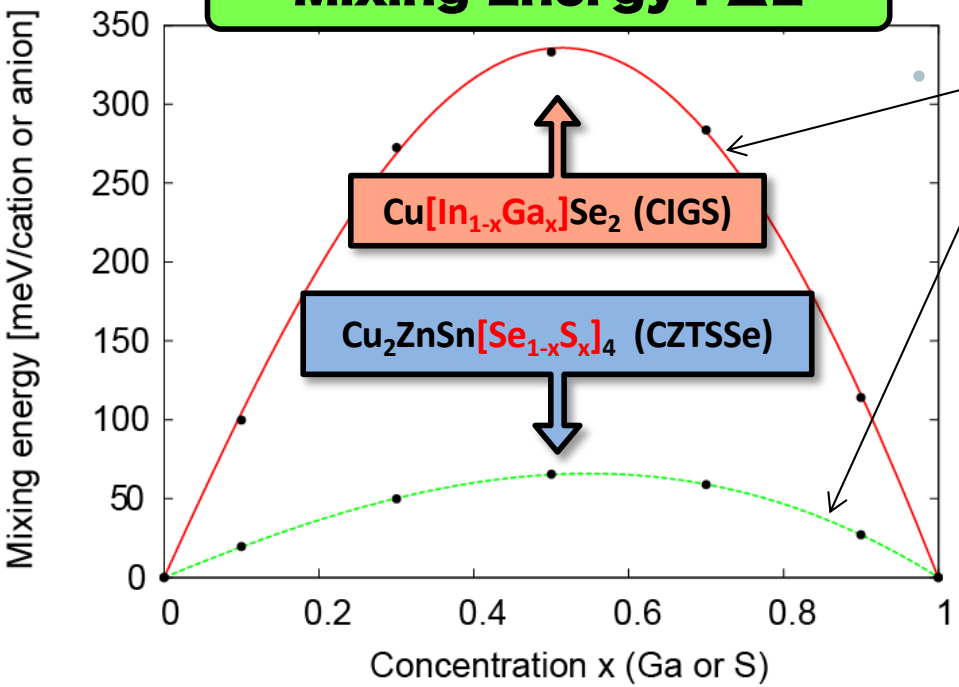
Mixing Energy : ΔE

ΔE [CIGS] = $E[Cu(In_{1-x}Ga_x)Se_2]$ − $(1-x)\,E[CuInSe_2] + x\,E[CuGaSe_2]$

ΔE [CZTSSe] = $E[Cu_2ZnSn(Se_{1-x}S_x)_4]$ − $(1-x)\,E[Cu_2ZnSnS_4] + x\,E[Cu_2ZnSnSe_4]$

Mixed States — Phase Separated States

Mixing Energy : ΔE



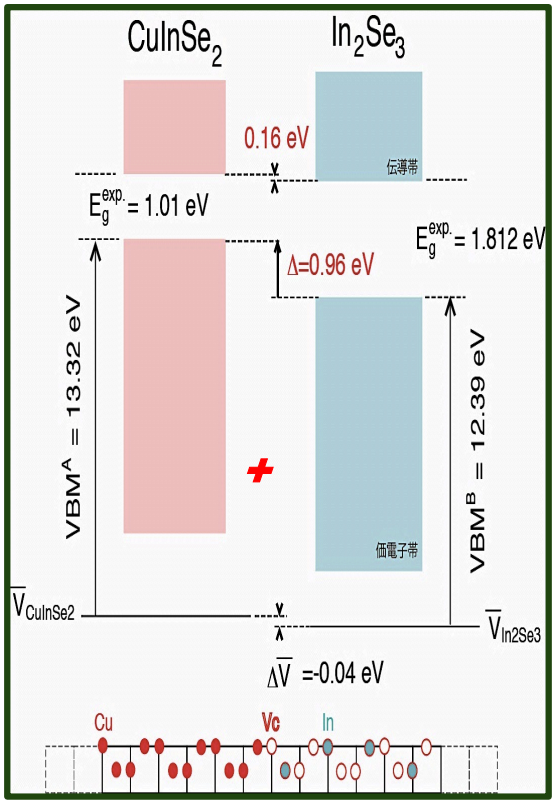
Positive and Convex upward ΔE

Spinodal Nano-decomposition.

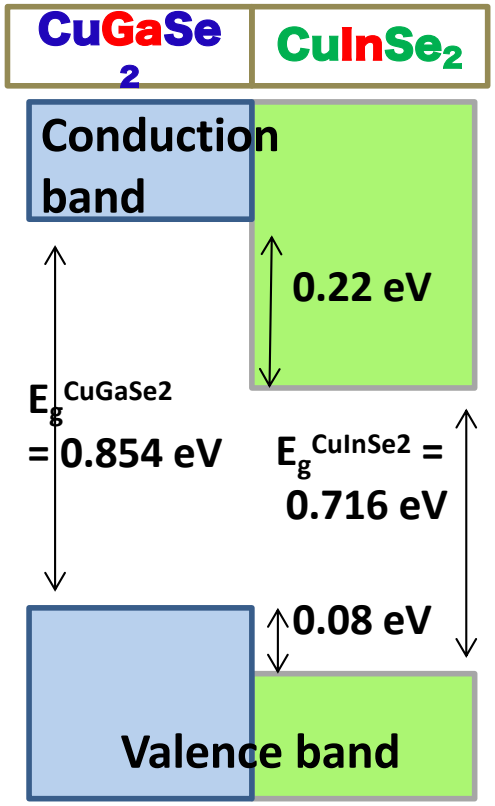
- $CuIn_{1-x}Ga_xSe_2 \rightarrow (1-x)\,CuInSe_2 + x\,CuGaSe_2$
- $Cu_2ZnSn(S_{1-x}Se_x)_4 \rightarrow (1-x)\,Cu_2ZnSnS_4 + x\,Cu_2ZnSnSe_4$

自己組織化ナノ超構造によるType II バンド構造：
キャリアーの超高速分離と長寿命化

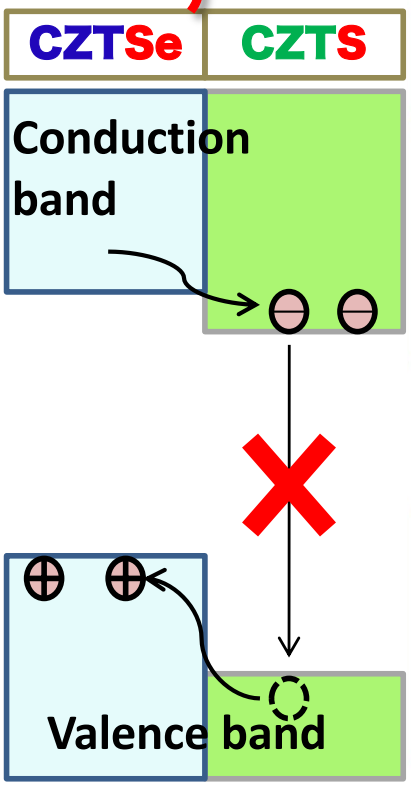
Chalcopyrite: (Cu,V_{Cu})



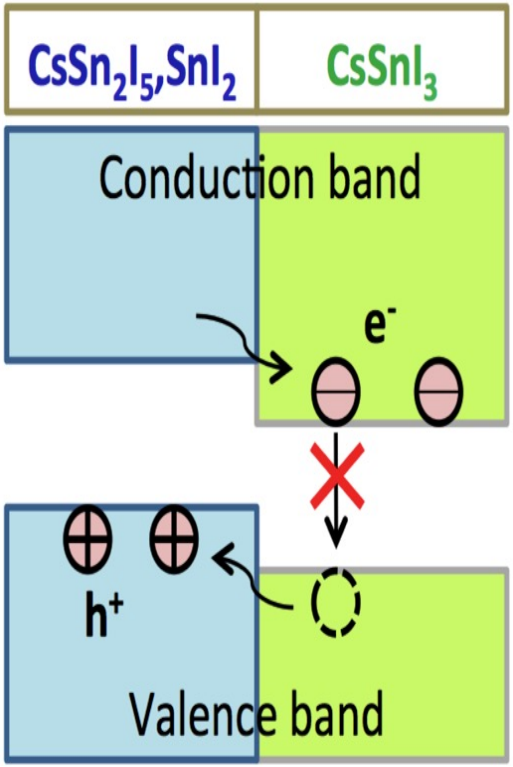
Chalcopyrite: (Ga,In)



Kesterite: (Zn,V_{Cu}),(S,Se)



Perovskite: (Cs,V_{Cs}), (Pb,V_{MA})



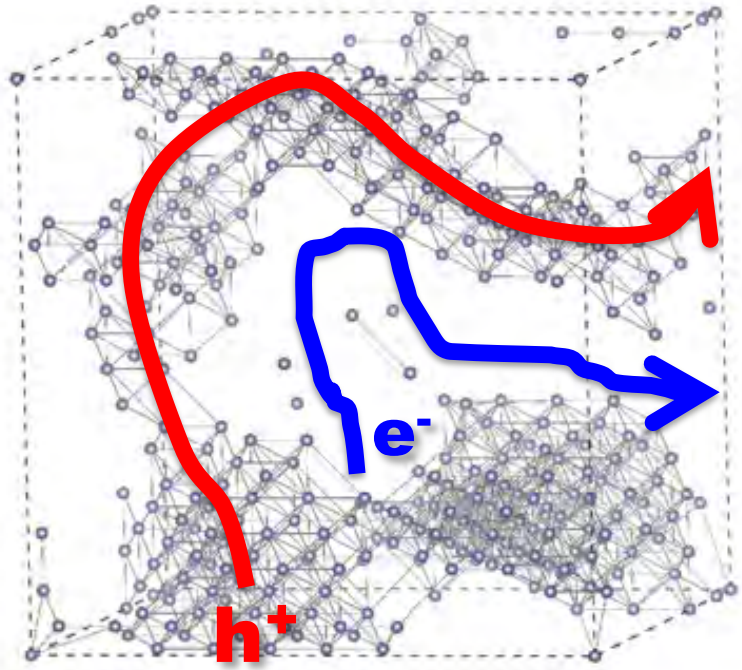
■非平衡状態の結晶成長: ➡ スピノーダル・ナノ分解（ e^- と h^+ の高速分離）

■熱平衡状態: ➡ 核形成を伴う相分離（バイノーダル分解）

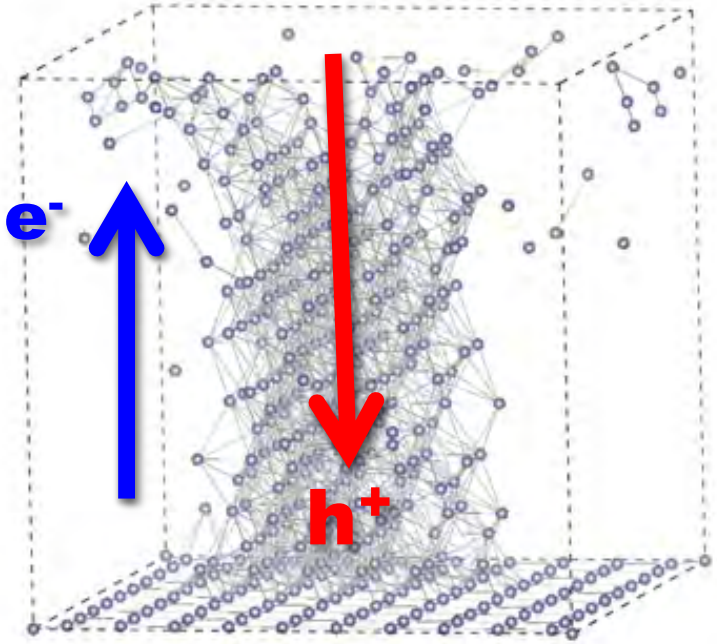
スピノーダル・ナノ分解：$Cu(In_{1-X}Ga_X)Se_2$　X_{Ga}=15%

Tani, Sato et al., APEX, (2012)

ナノスケール・サイズでのTypeⅡ半導体による e^- と h^+ の超高速分離



3次元結晶成長
大理石相



2次元結晶成長
昆布相

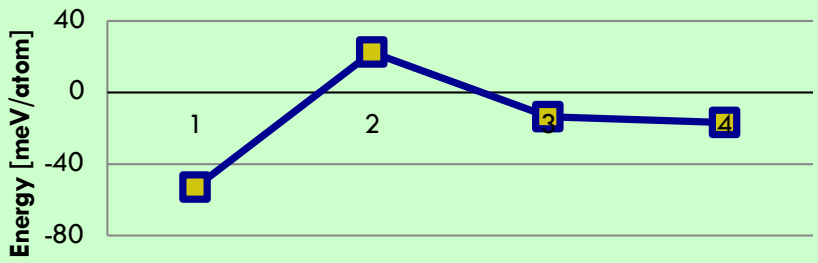
- *Sato, Katayama-Yoshida, Dederichs, JJAP, 44 (2005) L948.*
- *Fukushima, Sato, et al., JJAP, 44 (2005) L948.*
- *Sato, Bergqvist et al., Rev. Mod. Phys. 82 (2010) 1633.*
- *Dietl, Sato, Fukushima et al., Rev. of Mod. Phys. 87 (2015).*

自己修復[V_{Cu}+Zn_{Cu}]とスピノーダル・ナノ分解：$Cu_2ZnSn(Se,S)_4$

$Cu_2ZnSn(Se_{1-x}S_x)_4$　X_S =0.15

化学的対相互作用:

$$v_{ij} = v_{ij}^{S-S} + v_{ij}^{Se-Se} - 2v_{ij}^{S-Se}$$



イジング・モデル

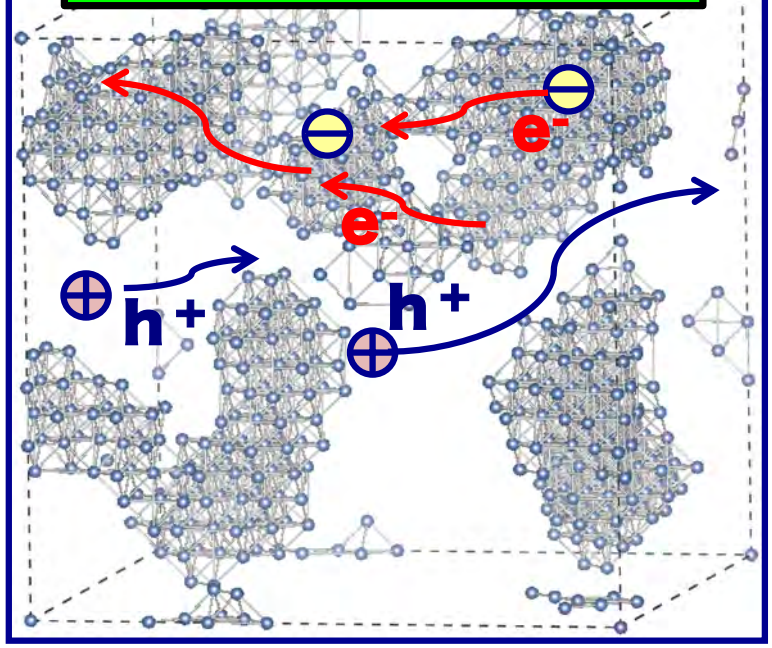
$$H = -\tfrac{1}{2} \Sigma_{i \neq j} v_{ij} \sigma_i \sigma_j$$

v_{ij} : pair interaction

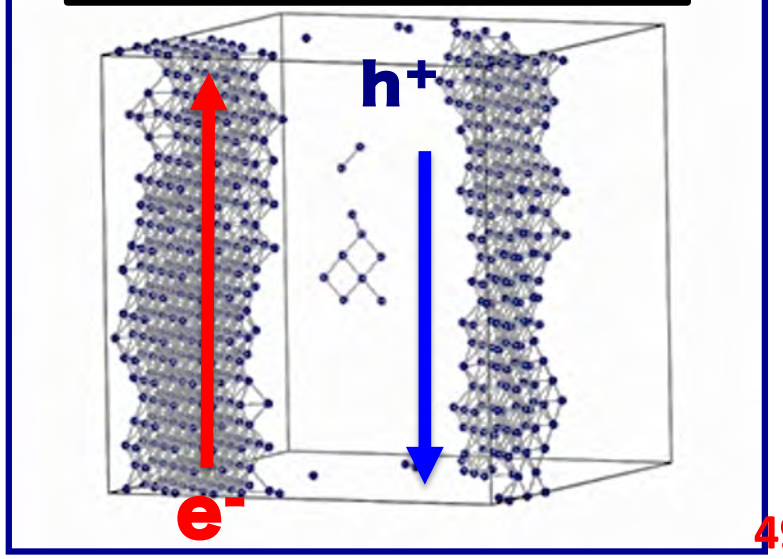
σ_i : occupation number

Y. Tani et al., J. Non-crystal. Solid. 2012.
Y. Tani et al., , JJAP, 51 (2012) 050202.

3次元結晶成長（大理石相）



２次元結晶成長（昆布相）



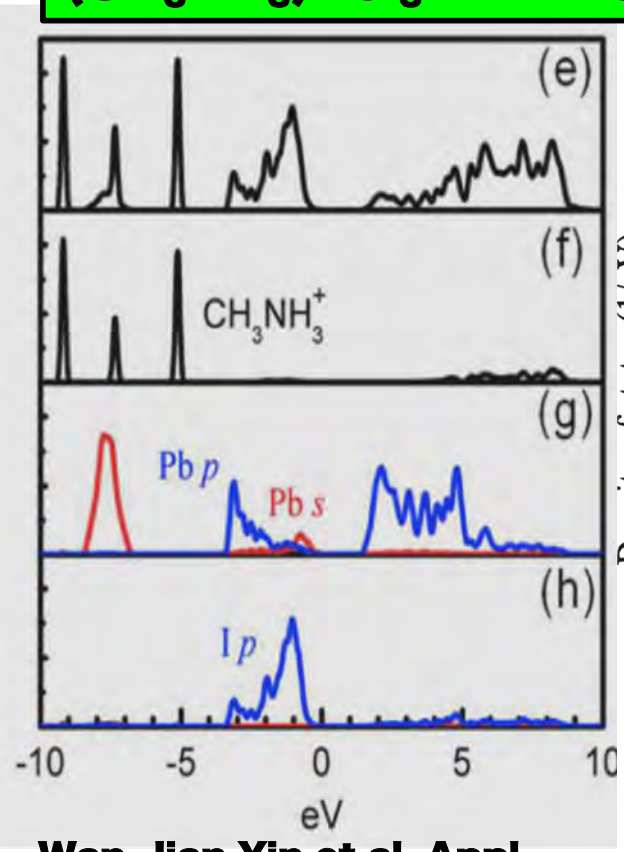
$CsSnI_3$, $(MA)PbI_3$の自己修復機構とスピノーダル・ナノ分解

T. Kishida, T. Fukushima, K. Sato, H. Katayama-Yoshida, 2015.

Perovskite : $(CH_3NH_3)^+Pb^{2+}(I,Cl)^-_3$ η=20.1% (～ 24%)

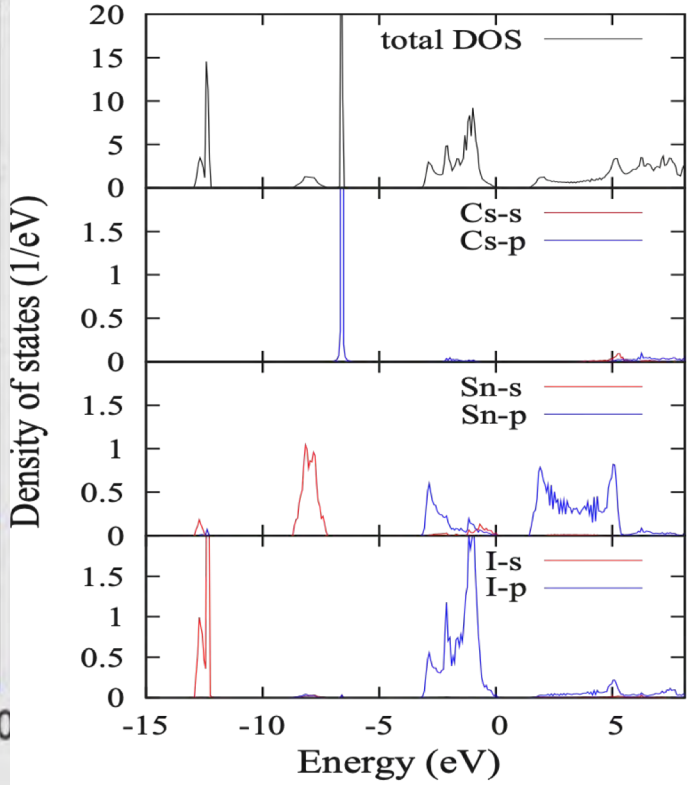
Pb^{2+} ➡ Sn^{2+}, $(CH_3NH_3)^+$ ➡ Cs^+

$(CH_3NH_3)PbI_3$ = MAPbI

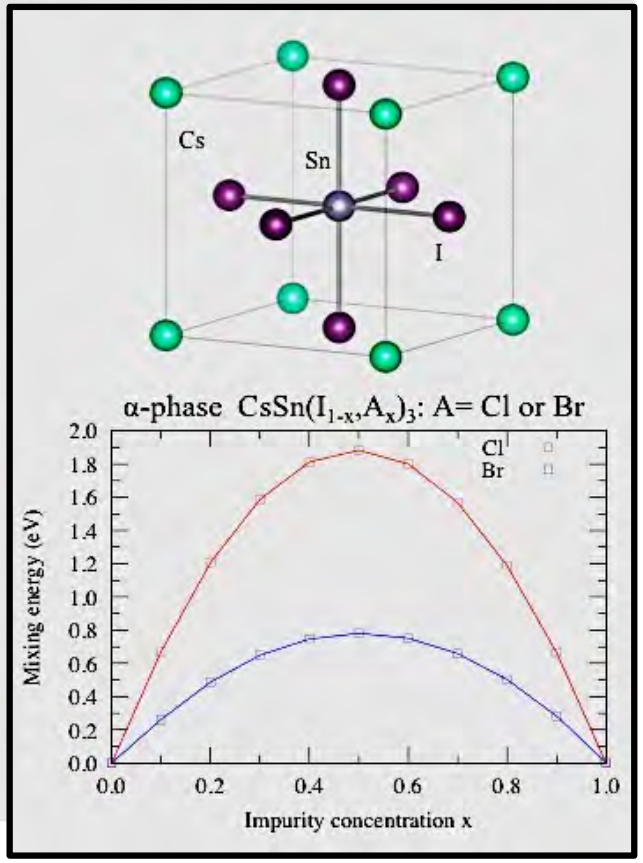


Wan-Jian Yin et al. Appl. Phys. Lett. 104, 063903 (2014).

$CsSnI_3$ = CTI



$CsSn(I,Cl)_3$, $CsSn(I,Br)_3$



電子に占有された反結合状態 I_p 価電子帯

➡ 自己修復機構（V_{Cs}+Sn_{Cs}, V_{MA}+Pb_{MA}）

Part 【3】自己再生する不老不死の排気ガス触媒

■自己再生する不老不死の自動車排気ガス三方触媒

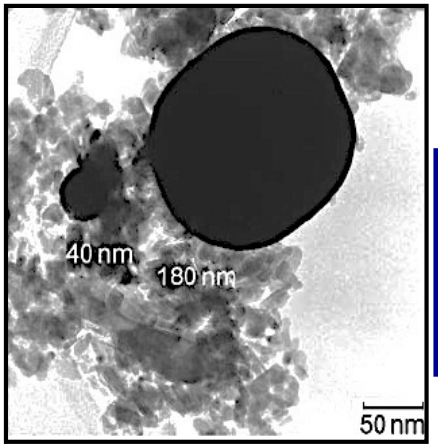
■自動車排気ガスの清浄化

- $CO + O_2 \rightarrow CO_2$ …… (酸化雰囲気)
- $NO_X + CO \rightarrow CO_2 + N_2$…… (還元雰囲気)
- $HC + O_2 \rightarrow CO_2 + H_2O$ …… (酸化雰囲気)

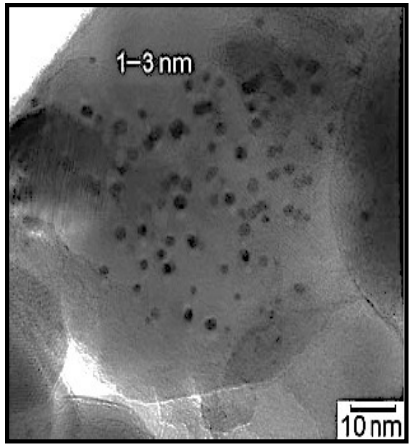
■Pt, Pd, Rh: 地域的に偏在

Pt : 南アフリカ 74%, ロシア 14%
Pd : 南アフリカ 25%, ロシア 70%
Rh : 南アフリカ 67%, ロシア 17%

■焼結による触媒機能劣化の問題



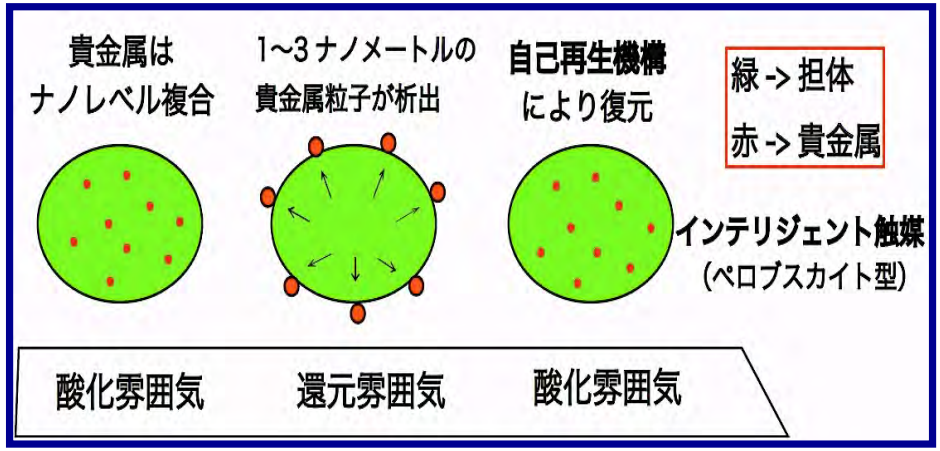
焼結の抑制



Al_2O_3 担持では焼結のため、触媒機能が消失

$CaTi_{0.95}Pt_{0.05}O_3$

自己再生機構: インテリジェント触媒

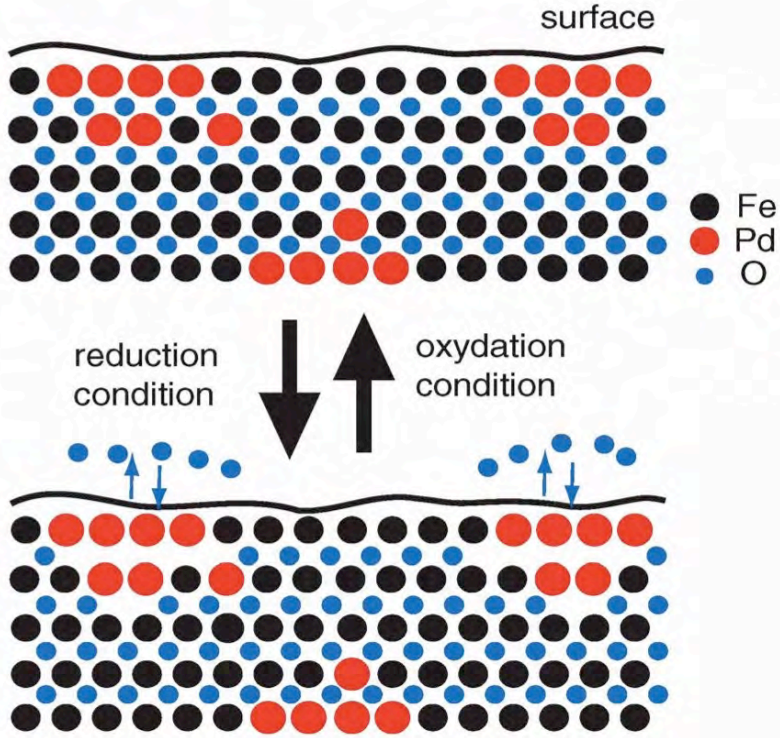


■*Y. Nishihara et al., Nature, 418 (2002) 164.*
■*H. Tanaka et al., Angew. Chem. Int. Ed. 45 (2006) 5998 .*

スピノーダル・ナノ分解による自己再生する不老不死の触媒

ペロブスカイト中の貴金属原子の固溶度は小→スピノーダル・ナノ分解

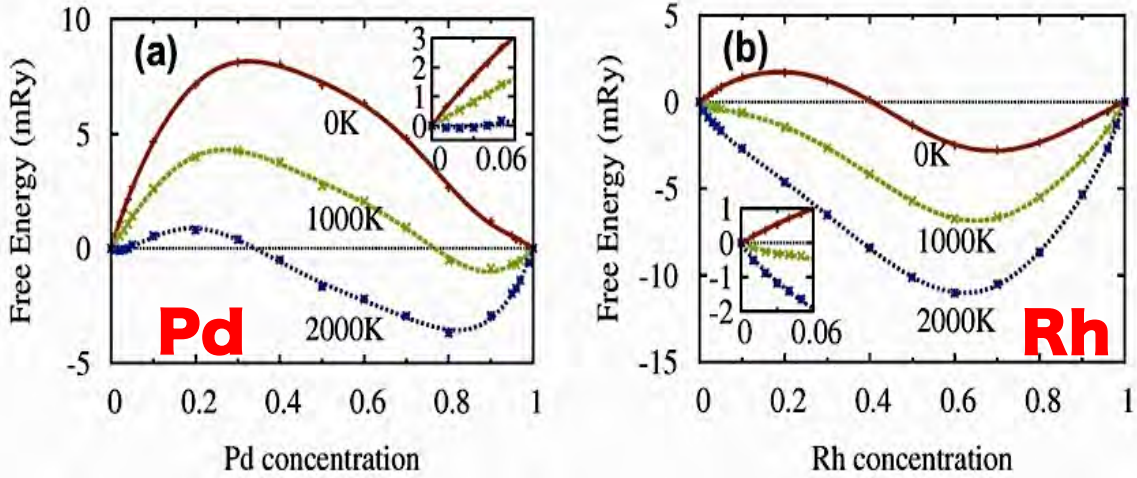
La(Fe, Pd)O_3



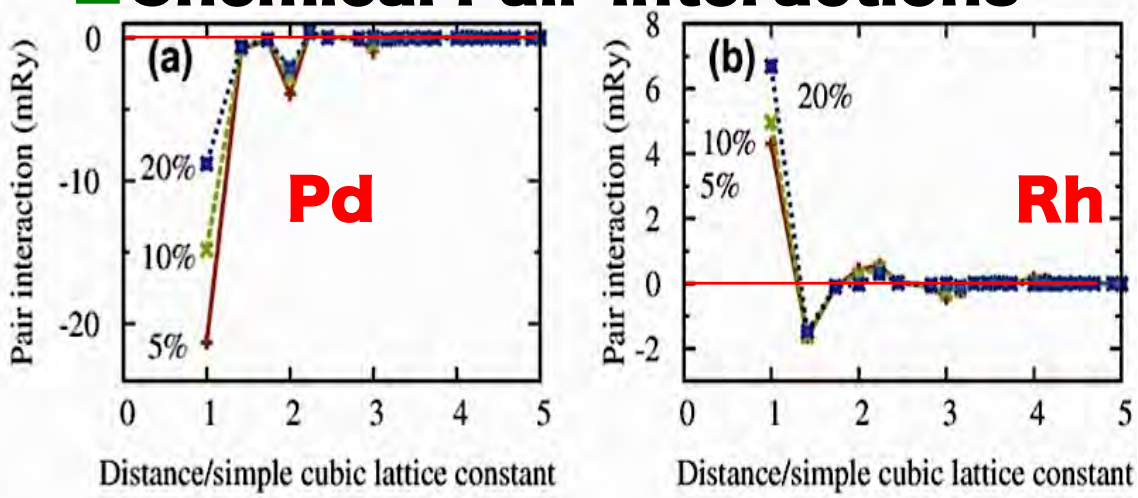
$$V_{ij} = V_{ij}^{Pd\text{-}Pd} + V_{ij}^{Fe\text{-}Fe} - 2\,V_{ij}^{Pd\text{-}Fe}$$

$$V_{ij} = V_{ij}^{Rh\text{-}Rh} + V_{ij}^{Fe\text{-}Fe} - 2\,V_{ij}^{Rh\text{-}Fe}$$

■Free Energy of La(Fe,M)O_3



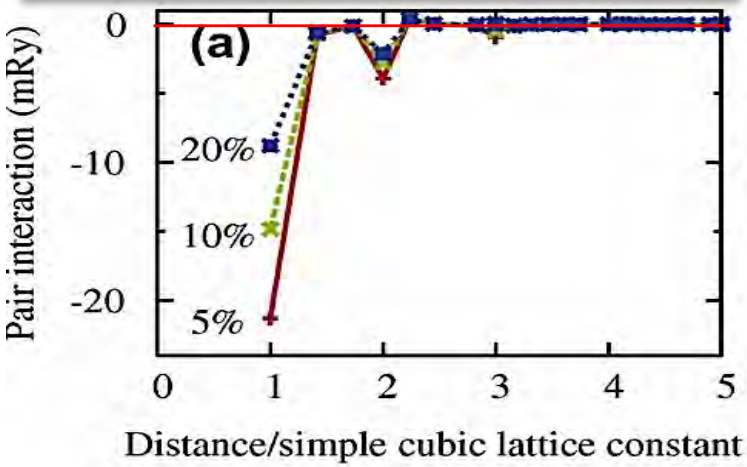
■Chemical Pair Interactions

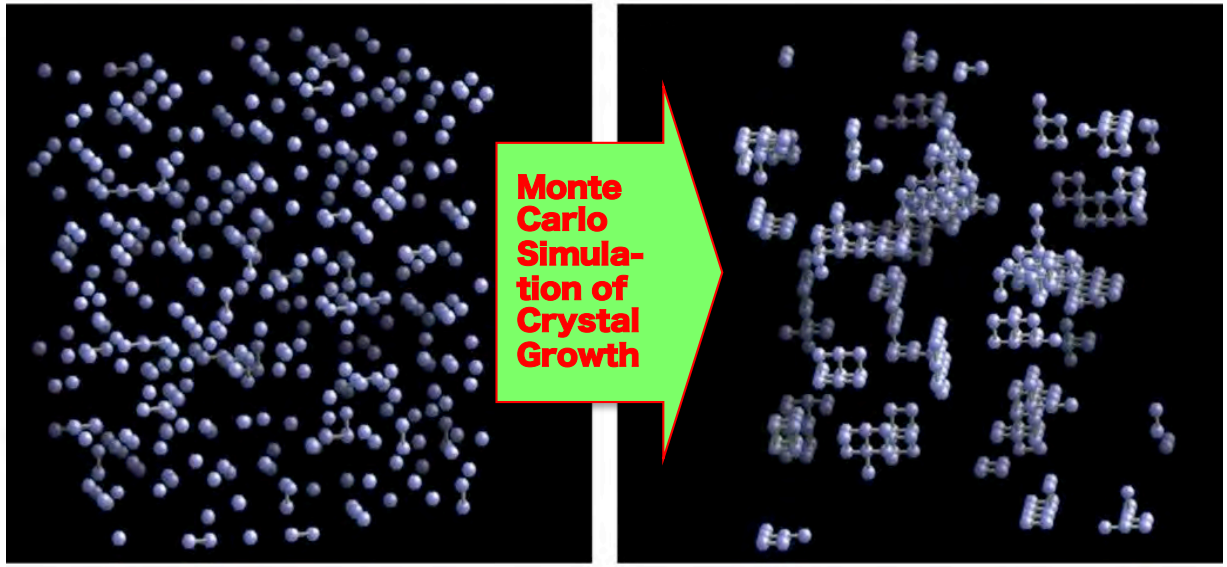


■ *H. Kizaki et al., Applied Physics Express, 1 (2008) 104001.*
■ *H. Kizaki et al., Chemical Physics Letters, 579 (2013) 85.*

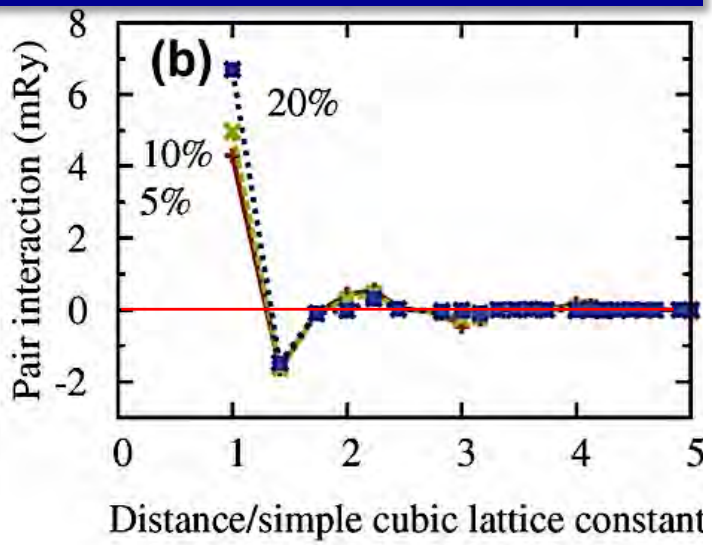
H. Kizaki and H. Katayama-Yoshida, Chemical Physics Letters, 579 (2013) 85.

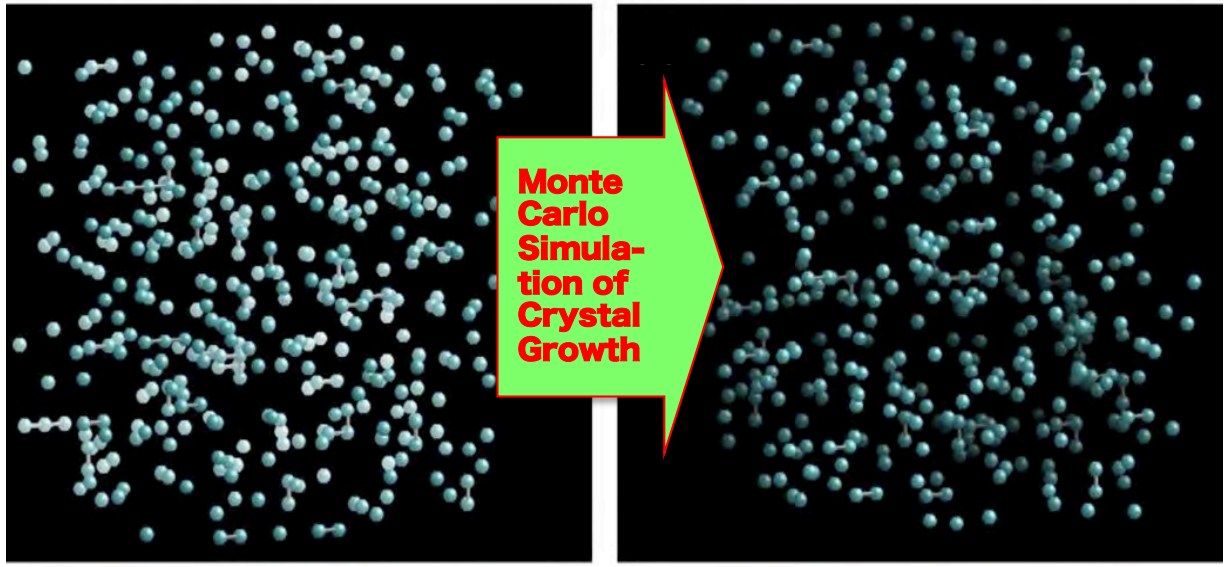
La(Fe,Pd)O_3





La(Fe,Rh)O_3





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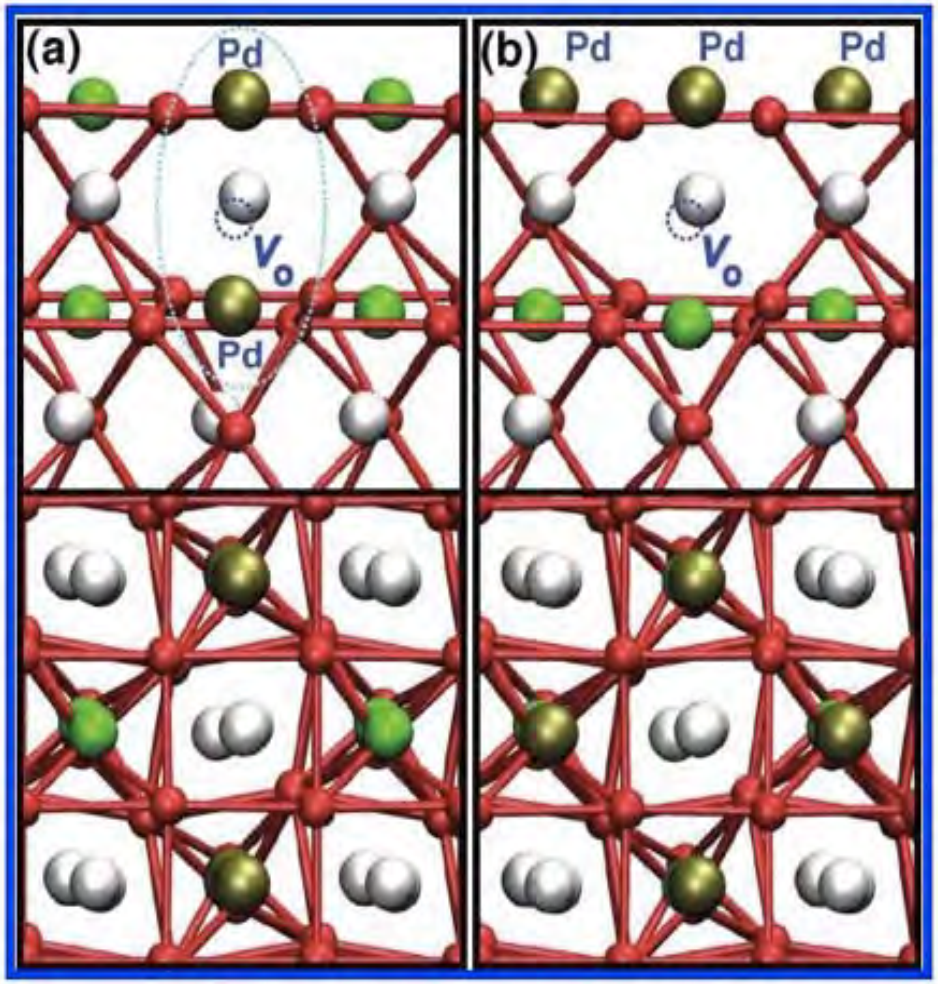
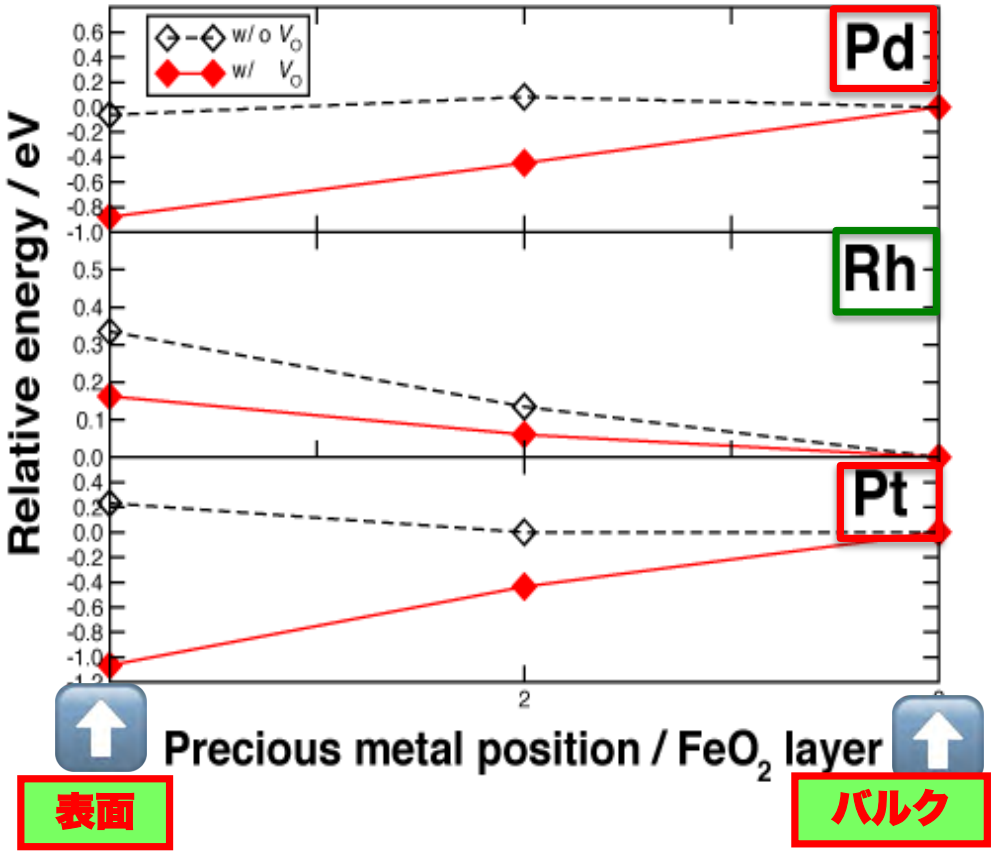
133 (2011) 18506.
COMMUNICATION

表面効果と酸素原子空孔 (V_O)の効果

A Density Functional Theory Study of Self-Regenerating Catalysts $LaFe_{1-x}M_xO_{3-y}$ (M = Pd, Rh, Pt)

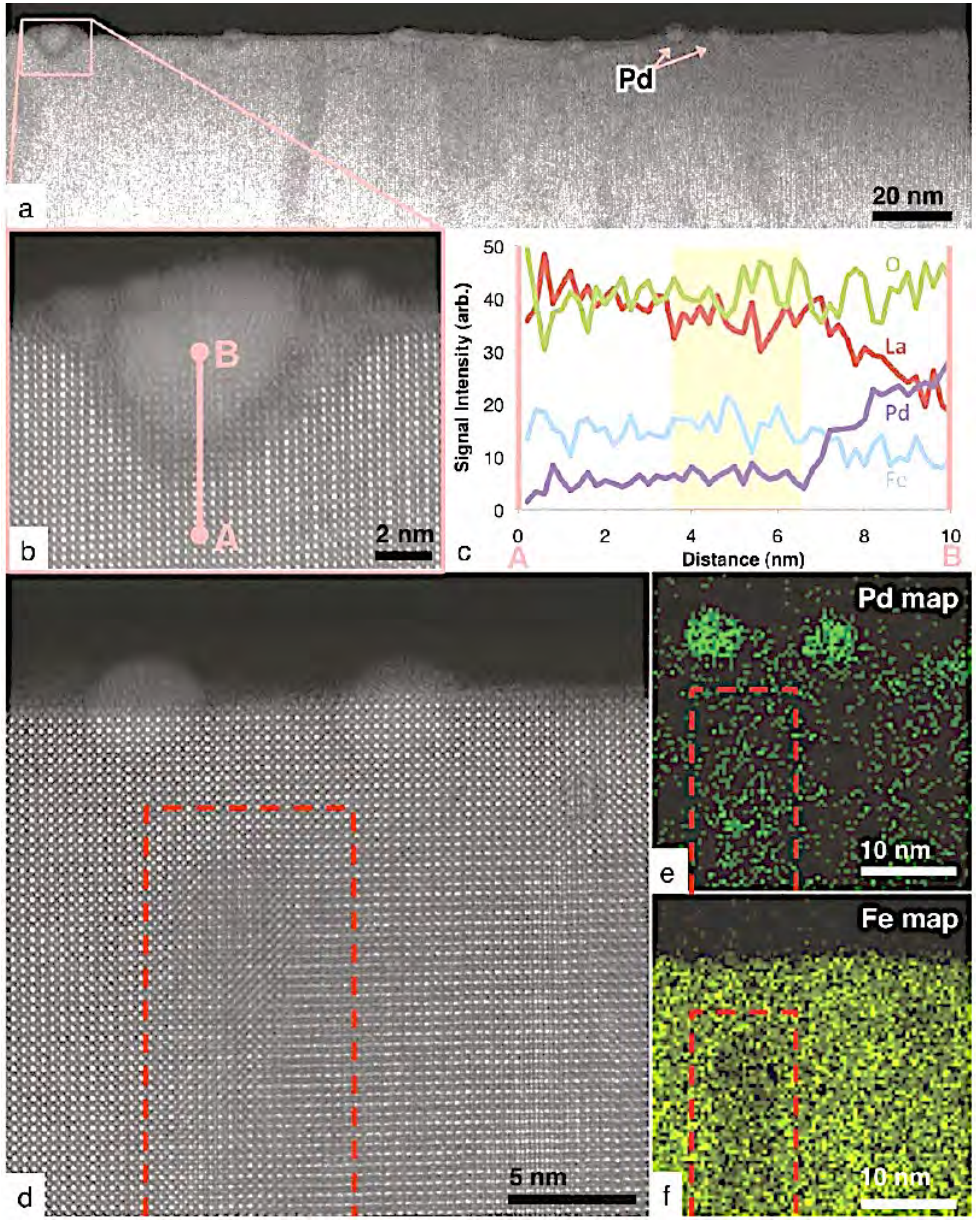
Ikutaro Hamada,*[,†] Akifumi Uozumi,[‡] Yoshitada Morikawa,[§] Akira Yanase,[⊥] and Hiroshi Katayama-Yoshida[∥]





■酸素原子空孔 (V_O) が表面での Pd と Pt のナノ粒子化を促進するが、Rhはしない。

■高分解能 STEM/EDX 実験：
昆布相, 大理石相



JACS 133 (2011) 1809
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pubs.a

Self-Regeneration of Pd–$LaFeO_3$ Catalysts: New Insight from Atomic-Resolution Electron Microscopy

Michael B. Katz,[†] George W. Graham,[†] Yingwen Duan,[†] Hong Liu,[†] Carolina Adamo,[‡] Darrell G. Schlom,[‡] and Xiaoqing Pan[*,†]

[†]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States
[‡]Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, United States

■大理石相
(Pd-rich, Fe-poor)

■昆布相
(Pd-rich, Fe-poor)