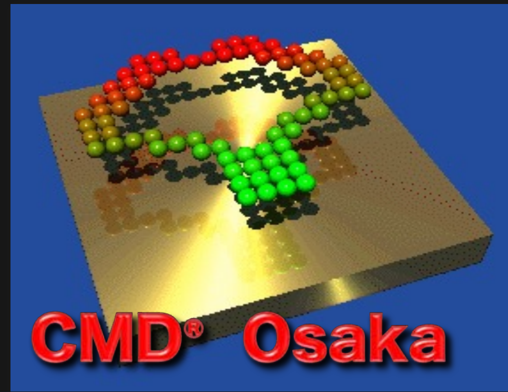
省エネルギー・創エネルギーデザイン

スピノダル・ナノテクノロジーの太陽電池・熱電材料・触媒への応用



東京大学大学院工学系研究科・CSRN
吉田　博

大阪大学での学生生活

Takinoue-cho, Hokkaido, 1970.

“釣りをしない人は、人生の半分が無意味なものになる”（釣魚大全, Izaak Walton）
⇒　“釣りをすれば、人生は二倍楽しくなる”

“神の肩越しに見よ”
⇒　“神に独創的なデザイン情報を伝授する”

基礎工物性物理工学科（中村傳研究室），1974

1987年3月

2011年5月

Harry Suhl

Harry Suhl, who made seminal contributions to condensed-matter physics and was among the founding faculty at the University of California, San Diego, died on 3 March 2020 after an enviably long, happy, and productive life. He was also well known and much beloved as a quick wit, a gourmet, a sharp dresser, and an all-around bon vivant.

Harry was born in Leipzig, Germany, on 18 October 1922. In 1938, during a threatening period for German Jews such as Harry and his family, his father, Bernard, wrote to a tenuous British business contact requesting that they be sponsored for immigration as refugees. In May 1939 the Suhls emigrated from Leipzig to London, where Harry finished his secondary schooling.

A year later Harry and Bernard were taken to a series of internment camps, which the British government had established for aliens with potential Axis sympathies. At Huyton, near Liverpool, a community developed among the Jewish intelligentsia, who were permitted access to books and records and who sponsored public lectures on subjects such as the new "quantum theory." It was in that setting where Harry's interest in physics was first kindled. Following a string of happy accidents, he found himself released from internment and studying at the University of Wales. After earning his BSc in 1943, he worked on radar for the British Navy until he began his PhD studies in ionospheric physics at Oxford University in 1946.

By late 1948 Harry had his PhD and a job at Bell Labs. It was a remarkable period at the R&D company, especially for solid-state physics. The technical staff at the Murray Hill, New Jersey, campus was brimming with current and future luminaries, such as John Bardeen, Charles Kittel, Bernd Matthias, Philip Anderson, George Feher, and Theodore Geballe. Also, far less of a distinction was made between experimentalists and theorists at that time than now.

TO NOTIFY THE COMMUNITY about a colleague's death, visit https://contact.physicstoday.org and send us a remembrance to post.
Select submissions and, space permitting, a list of recent postings will appear in print.

Suhl's earliest work at Bell Labs was on charge-carrier dynamics in semiconductors in magnetic fields. In 1953 Suhl and Larry Walker comprehensively analyzed wave propagation in waveguides that are filled with gyromagnetic and gyroelectric media, relevant to various microwave devices. In 1955–56 Suhl provided the definitive explanation of nonlinear effects in ferromagnetic resonance, now known as the Suhl instability. That work led to his getting a patent for a ferromagnetic parametric amplifier in 1956 and inspired wide use of parametric amplification in general. In 1957 Suhl and Tuto Nakamura independently uncovered a major source of broadening of NMR lines in magnetically ordered media, now known as the Suhl–Nakamura interaction.

Suhl's interests then turned to superconductivity, where he extended the Bardeen-Cooper-Schrieffer theory to two-band systems, and to quantum many-body problems. In 1961, shortly after arriving at the just-opened University of California, La Jolla—later renamed UC San Diego—he made major contributions to the theory of many-body effects on impurity states in metals. Suhl showed how the recently discovered Kondo singularity was replaced by a Fermi surface resonance, a feature now known as the Abrikosov–Suhl resonance, in dilute magnetic alloys. Throughout the remainder of his career, Suhl continued to work on various aspects of magnetism, but he also branched out into such areas as surface physics, catalysis and reaction kinetics, nonlinear dynamics, and biological physics.

Suhl served on the editorial board for *Physical Review* in 1963–72 and for *Solid State Communications* in 1961–90; was coeditor with George Rado of the highly influential five-volume series *Magnetism: A Treatise on Modern Theory and Materials* (Academic Press, 1963–73); and authored the 2007 monograph *Relaxation Processes in Micromagnetics* (Oxford University Press). He also twice served as chair of the UC San Diego physics department, and he was director of its Institute for Pure and Applied Physical Sciences from 1980 to 1991.

Among his friends and colleagues, Harry was regarded with deep affection for his wit and conviviality. When once asked what he did to keep fit, Harry

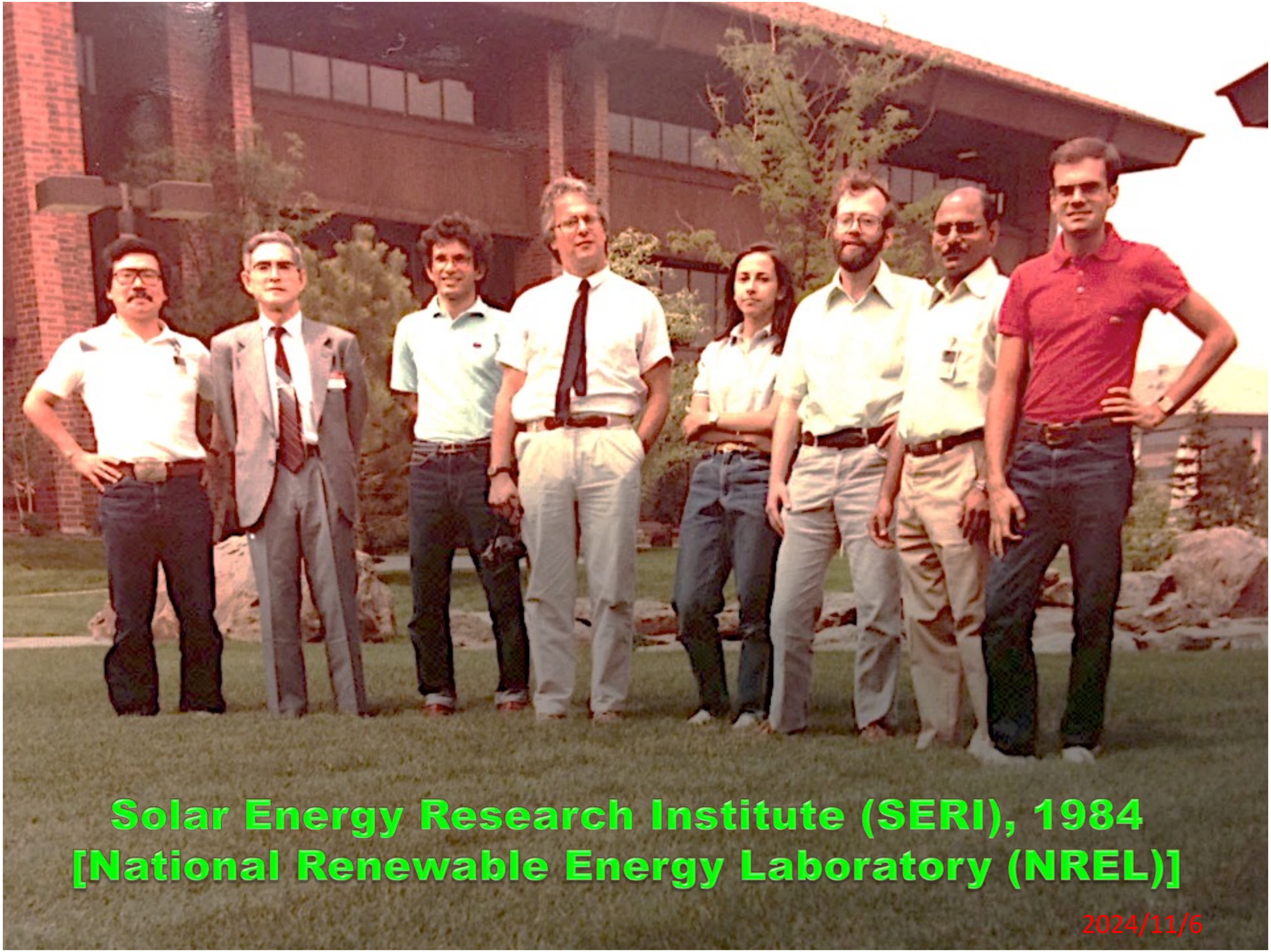
replied, "Oh, I really don't subscribe to strenuous exercise. However, I do get up every morning and wind my watch by an open window." At a wonderfully inspiring and generous speech at his own 70th birthday conference, Harry offered the following "unwelcome advice to the younger people": "Above all, don't get wiser as you get older. If you do, you will become too inhibited to try the impossible, and one can achieve the limits of the possible only by occasionally venturing beyond them. The famous proverb should really be transposed: Angels rush in where fools fear to tread."

Daniel Arovas
M. Brian Maple
University of California, San Diego
La Jolla
Pradeep Kumar
University of Florida
Gainesville PT

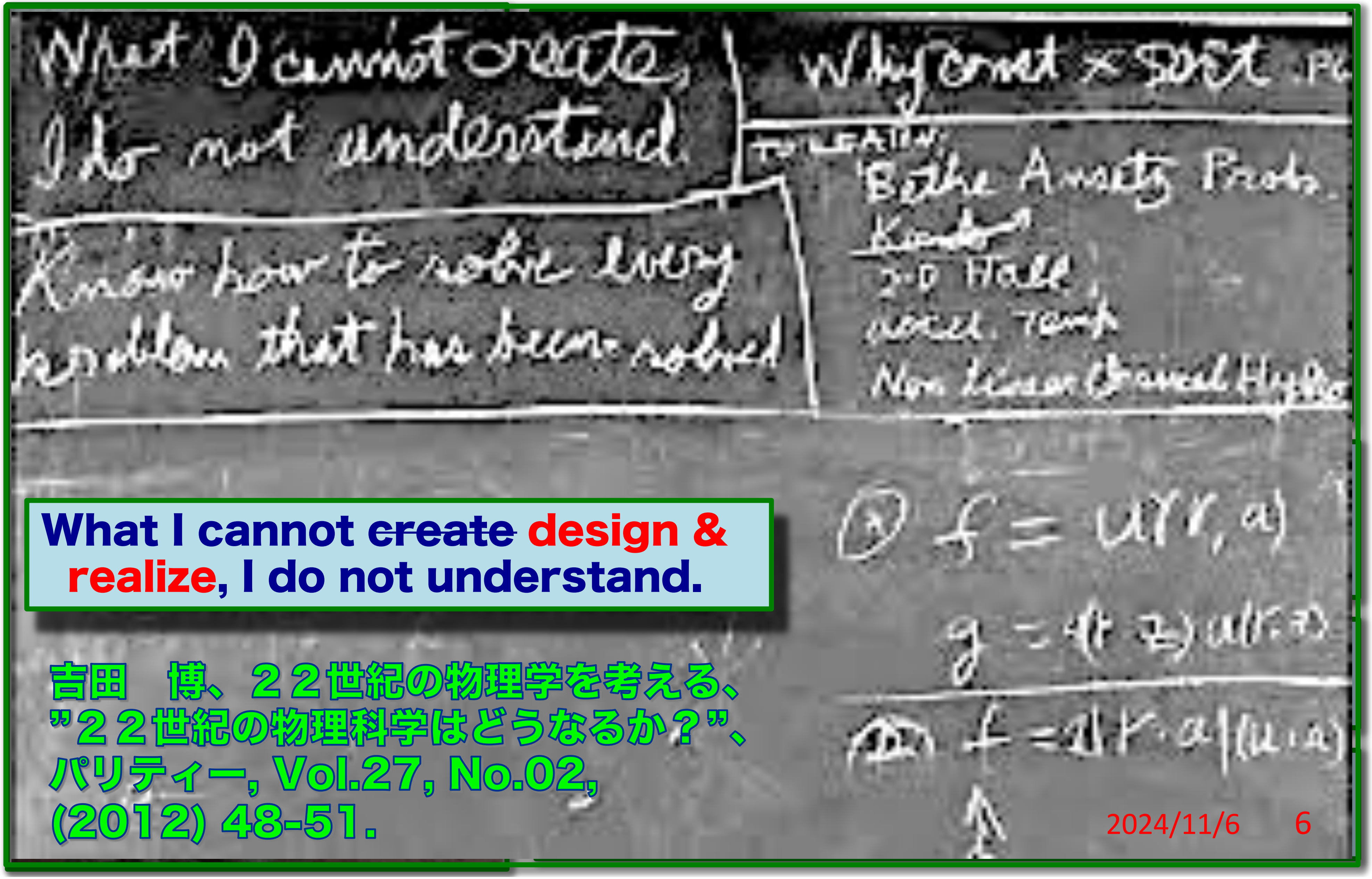
RECENTLY POSTED NOTICES AT www.physicstoday.org/obituaries

Guido Münch
9 June 1921 – 29 April 2020
Otto Sankey
11 January 1951 – 21 March 2020
Alexander Patashinski
8 August 1936 – 22 February 2020
Jorge Ramiro Antillón Matta
13 April 1931 – 6 February 2020

理学研究科（金森順次郎研究室）, 1979


Solar Energy Research Institute (SERI), 1984
[National Renewable Energy Laboratory (NREL)]
2024/11/6

What I cannot create, I do not understand. 1988 R. Feynman

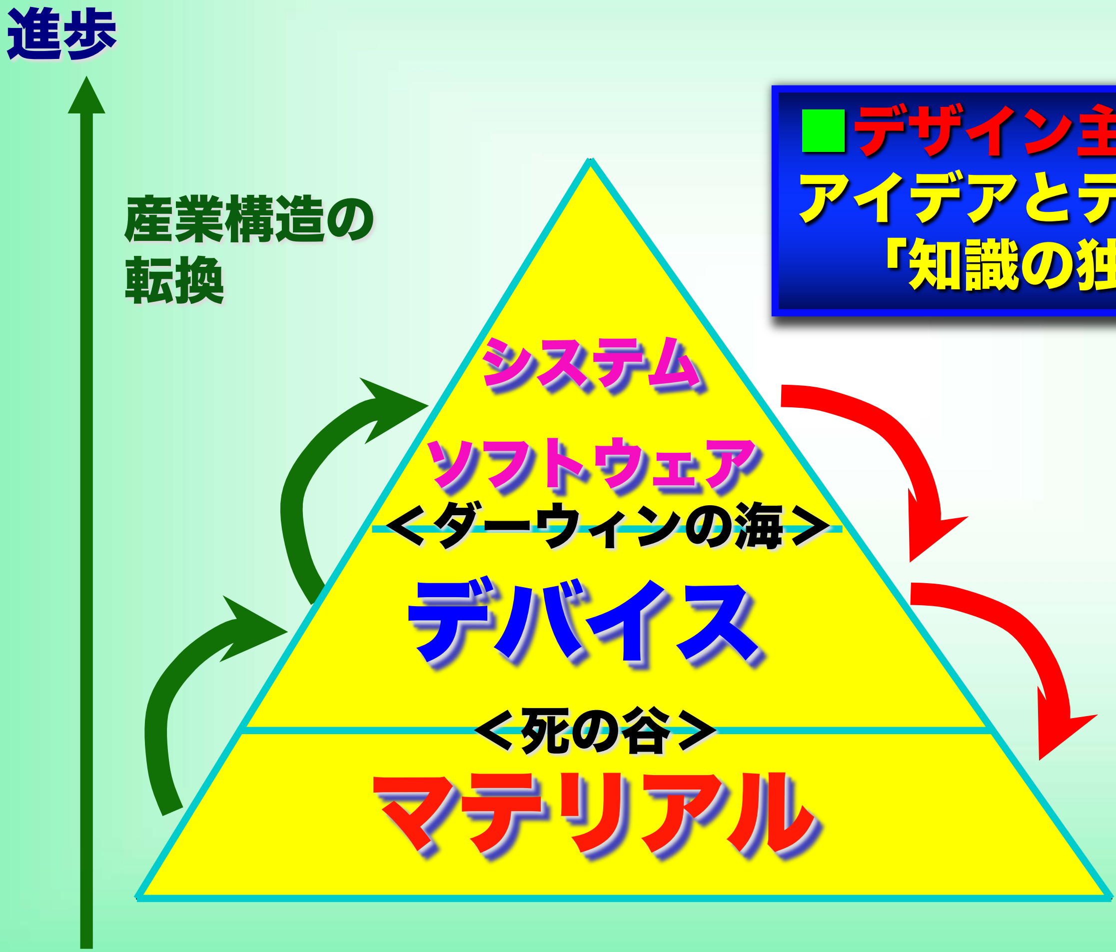


What I cannot ~~create~~ design & realize, I do not understand.

吉田　博、２２世紀の物理学を考える、
”２２世紀の物理科学はどうなるか？”、
パリティー, Vol.27, No.02,
(2012) 48-51.

■産業構造の転換：工業化社会から知識社会へ

産業構造の階層性



■デザイン主導による階層間の接続
アイデアとデザインによるものづくり
「知識の独創性」＝「利益率」

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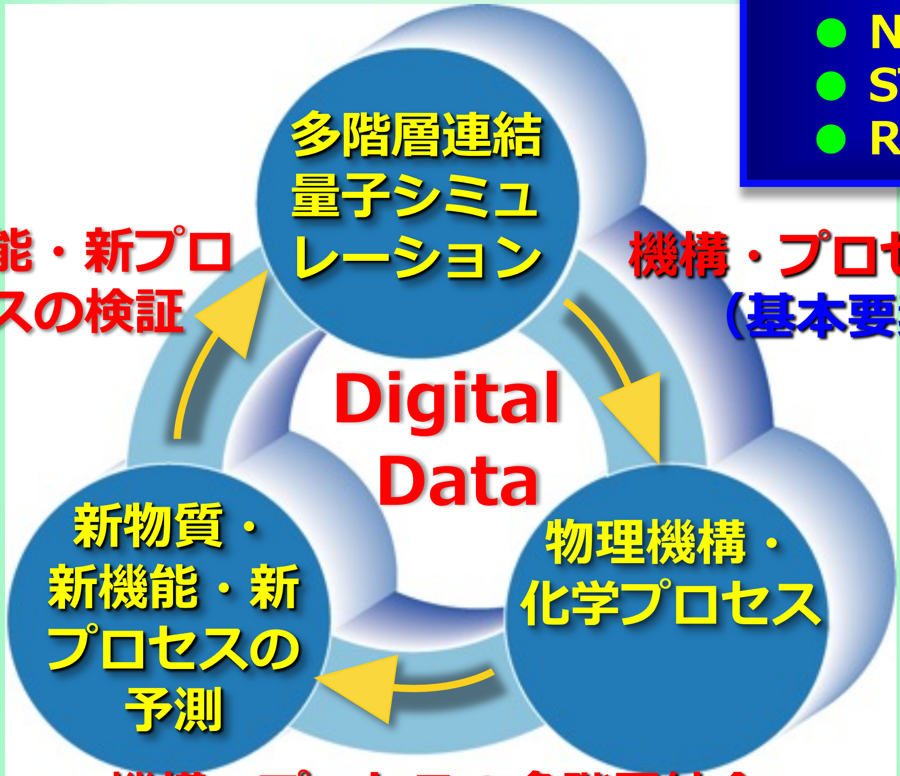
計算機ナノマテリアルデザイン CMD®

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）

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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

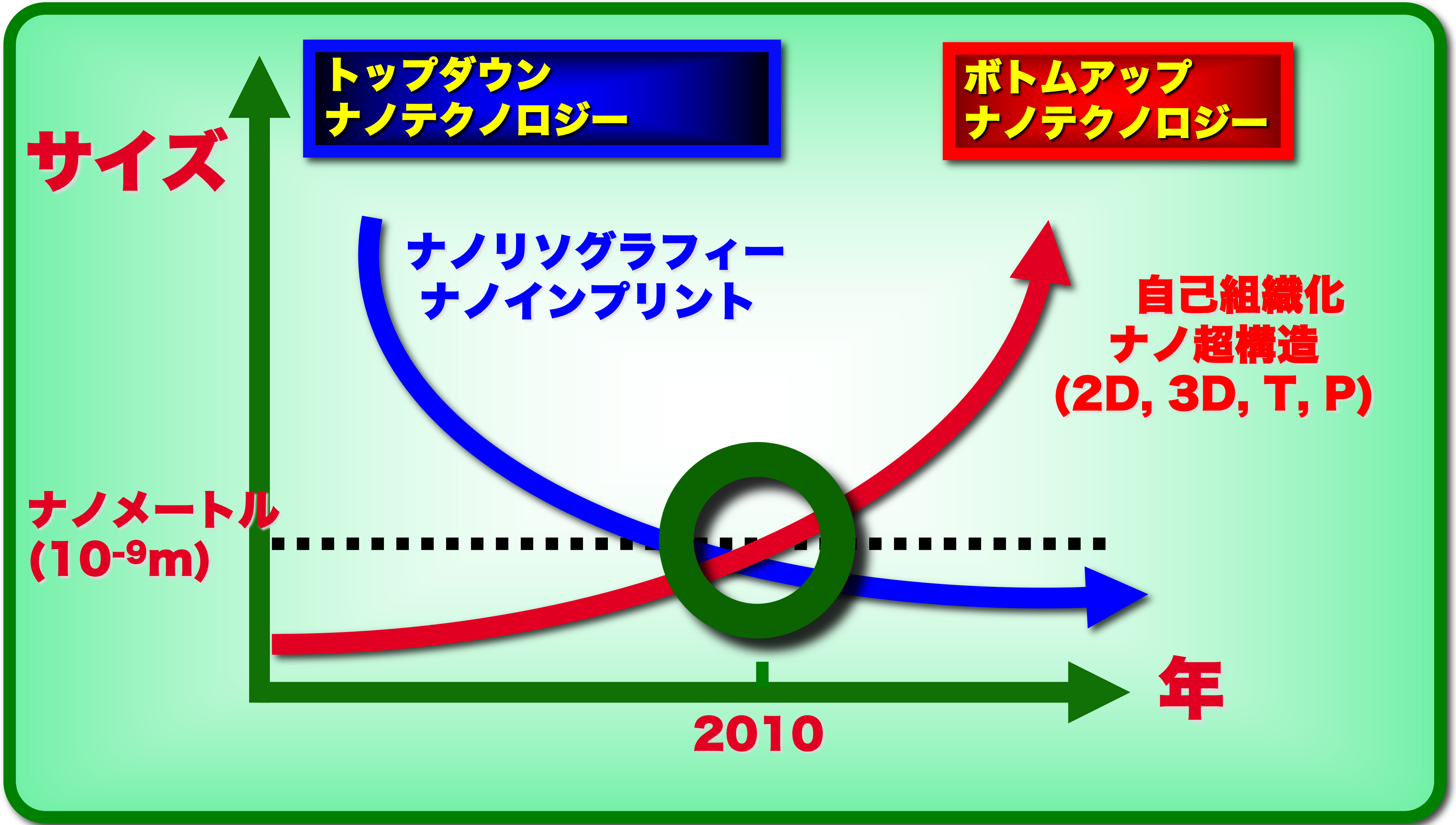
1-st Computational Materials Design Workshop
CMD®（2002年から年二回、5日間/回）

Computational Materials Design (CMD®) Workshop

■ナノテクノロジー

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

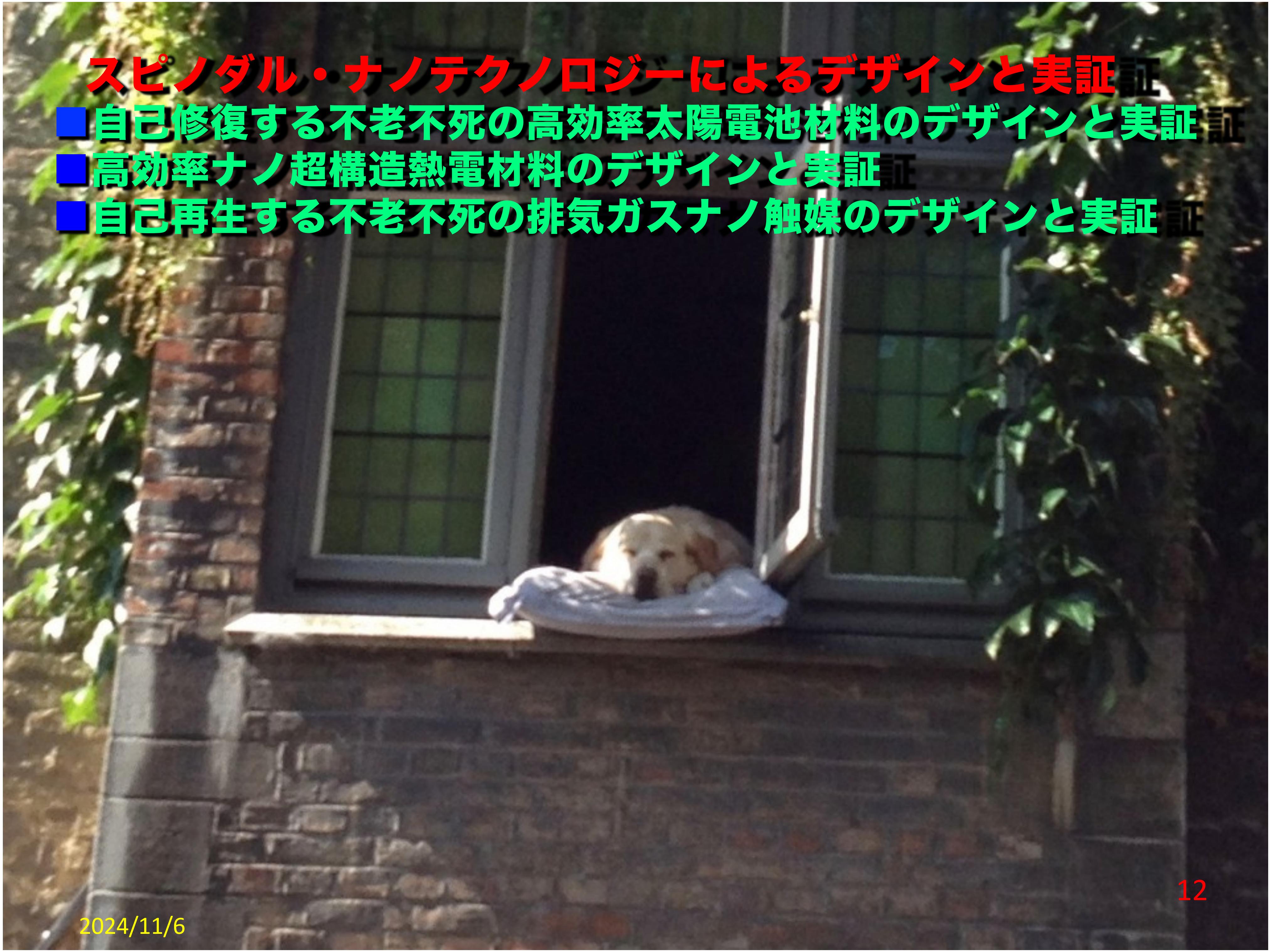
"Father of nanotechnology", APS, 12/29/1959 at CALTECH



吉田博©

スピノダル・ナノテクノロジーによるデザインと実証

- 自己修復する不老不死の高効率太陽電池材料のデザインと実証
- 高効率ナノ超構造熱電材料のデザインと実証
- 自己再生する不老不死の排気ガスナノ触媒のデザインと実証



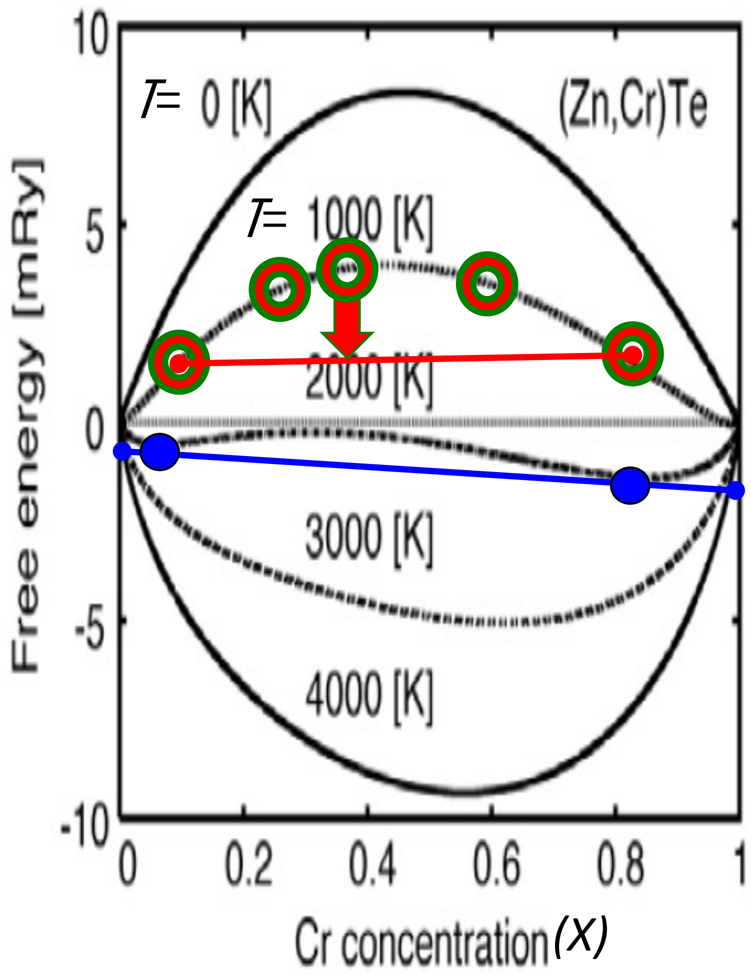
Part 【1】
スピノダル・ナノテクノロジー
■自己組織化ナノ超構造

2024/11/6

スピノダル・ナノ分解

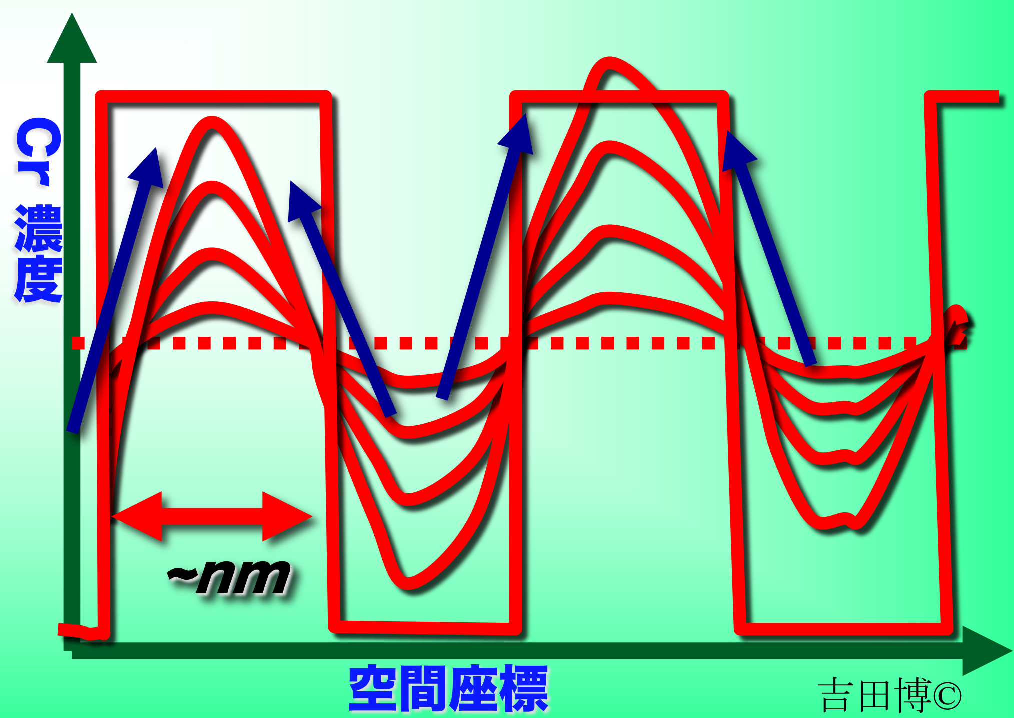
Sato, Katayama-Yoshida, Dederichs, JJAP, 44 (2005) L948.

$F = E - TS$



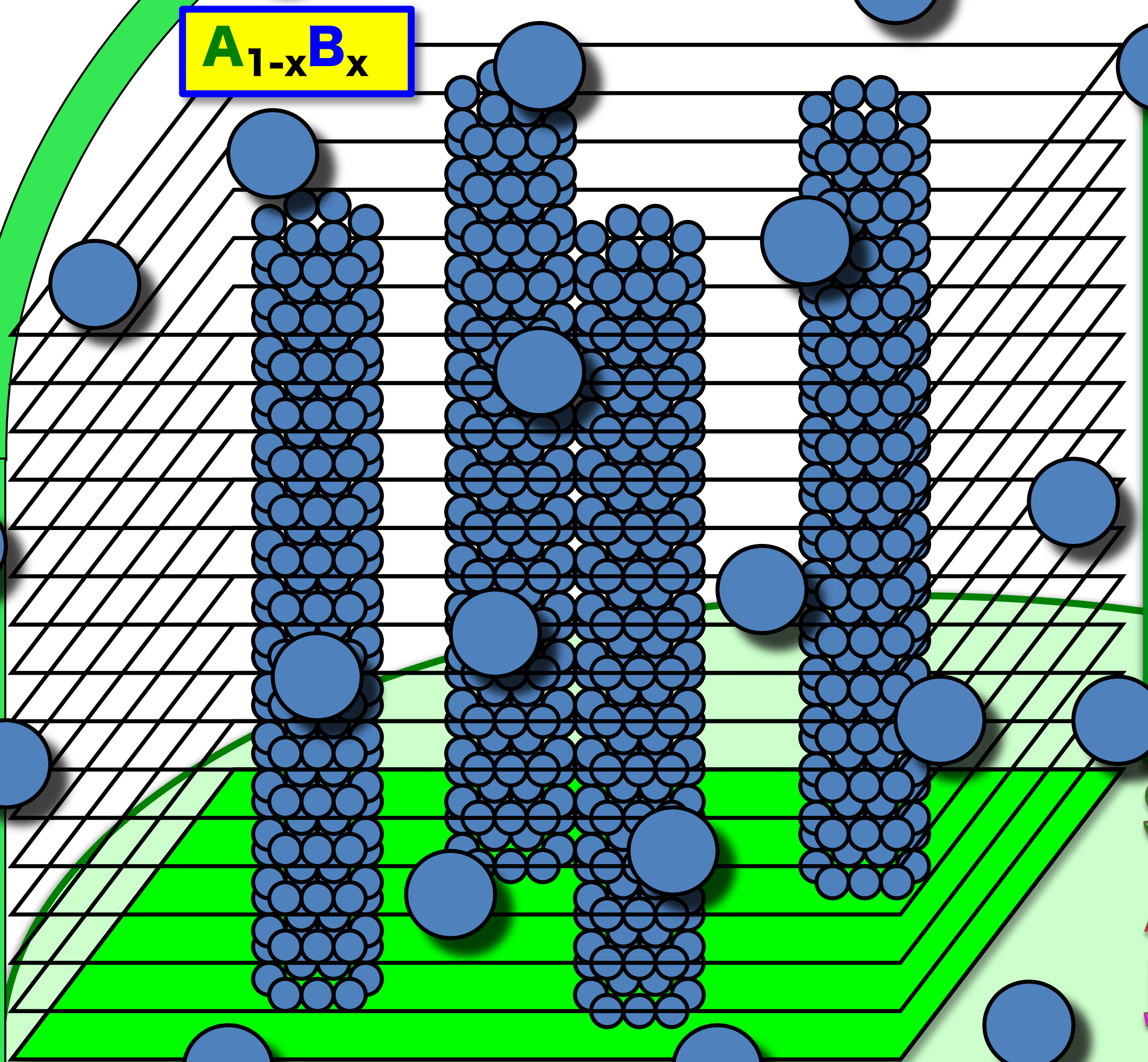
☑ $(\partial^2 F / \partial x^2) < 0$

☑ Up-Hill Diffusion



２次元スピノダル・ナノ分解結晶成長シミュレーション

- ■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.



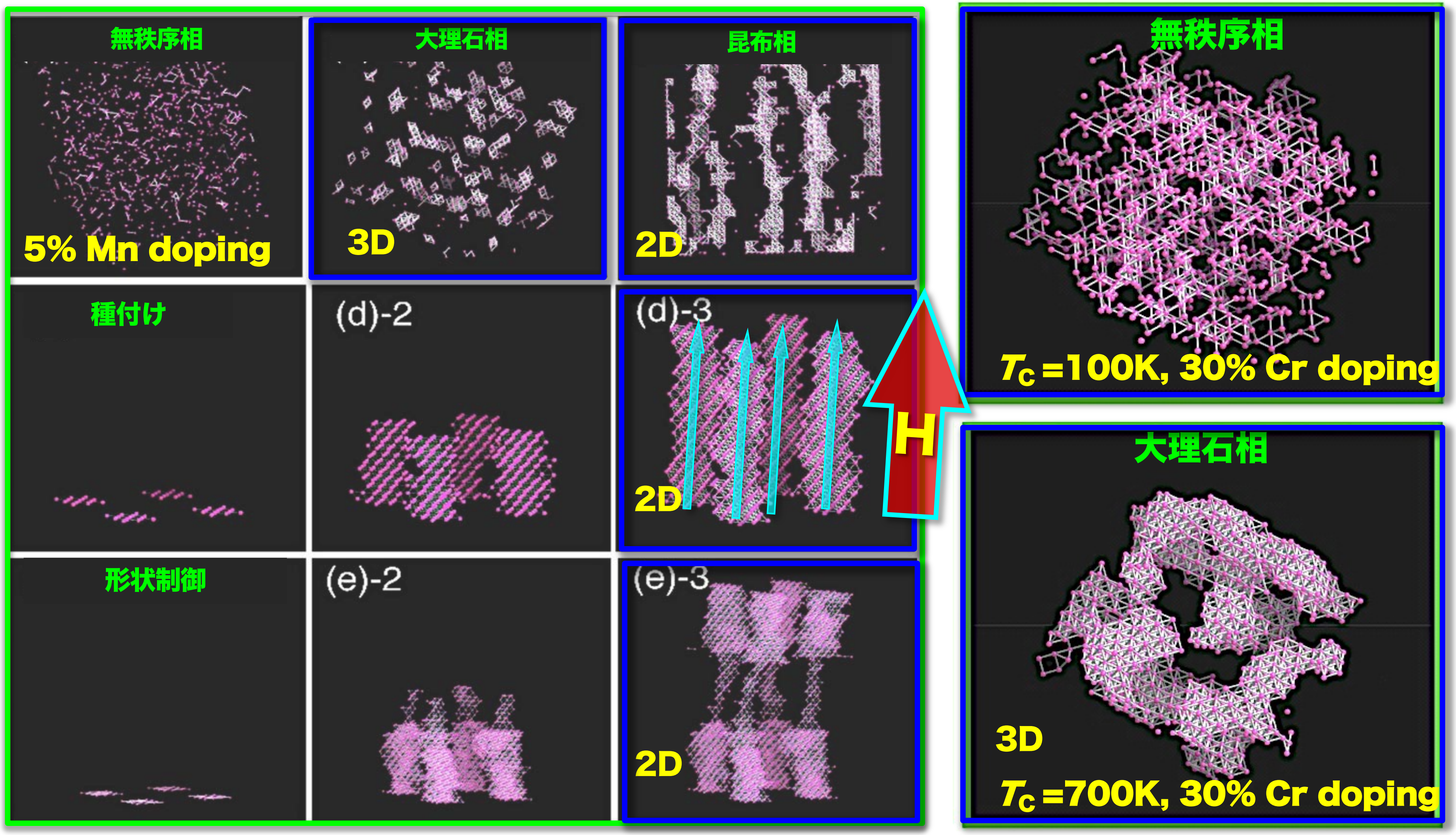
Self-organized

Konbu-Phase

昆布相（海帯相）

スピノダル・ナノ分解: $(Ga_{1-x}TM_x)$ N

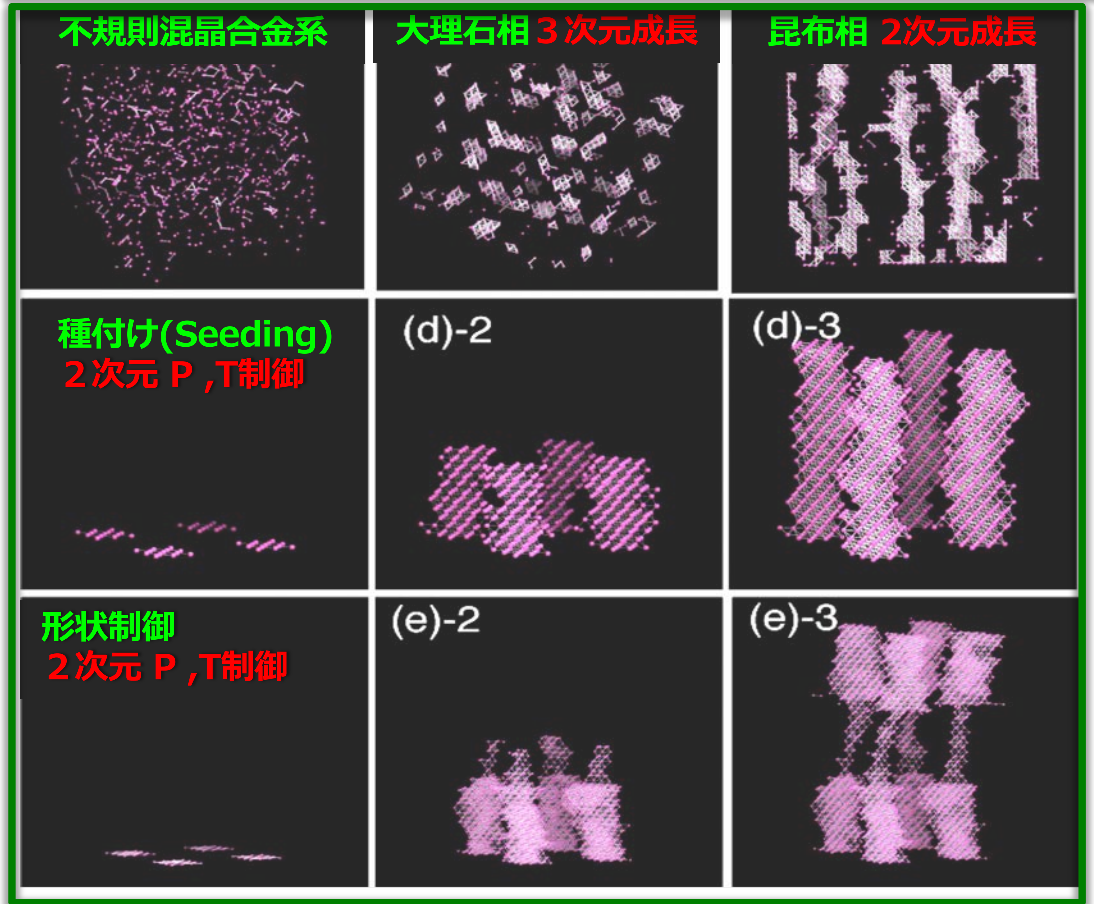
- K. Sato et al., JJAP, 44 (2005) L948.
- T. Fukushima, et al., JJAP, 45 (2006) L416.

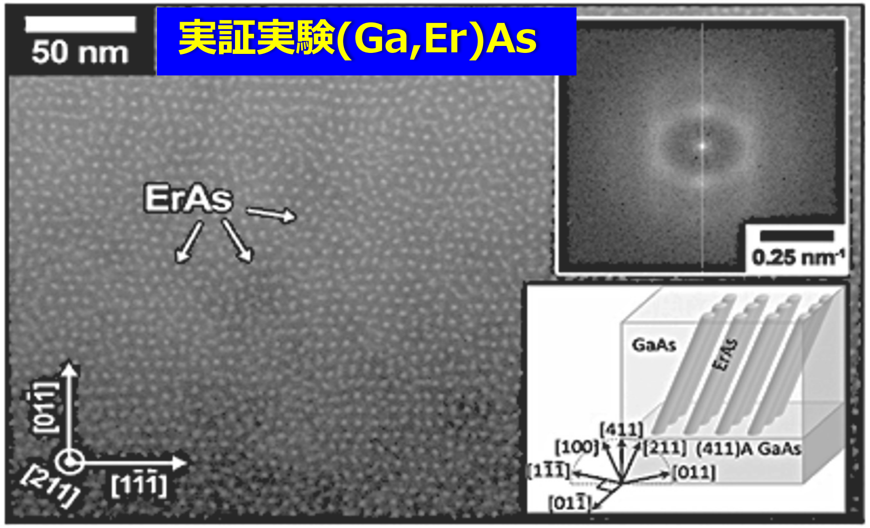


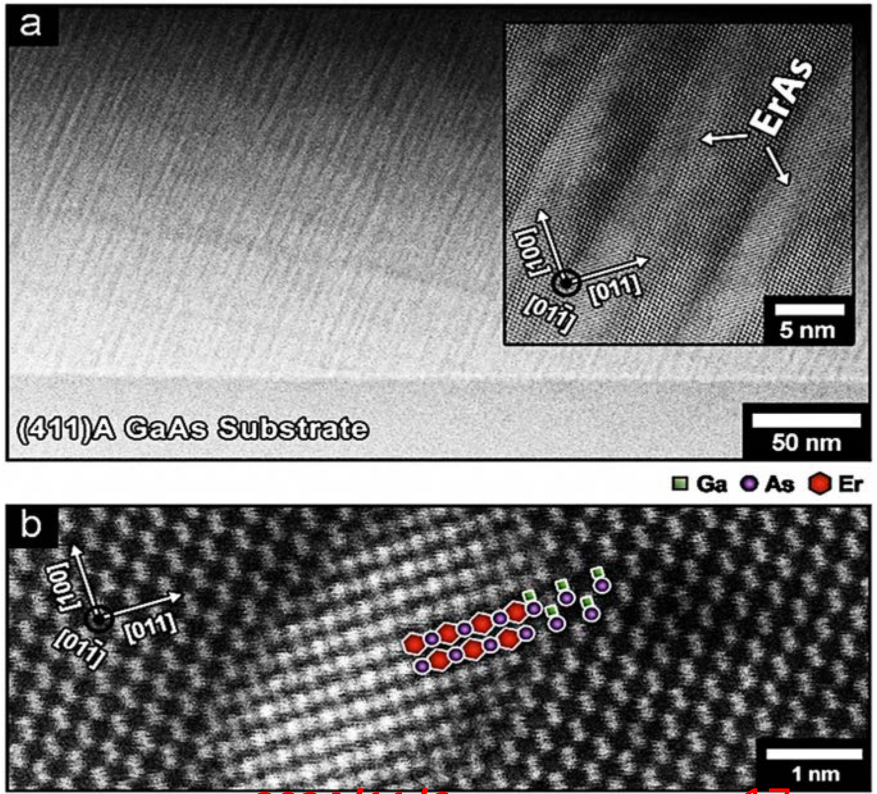
- K. Sato, L. Bergqvist et al., Rev. Mod. Phys. 82, (2010) 1633.
- H. Katayama-Yoshida et al., phys. stat. soli. (a), 204 (2007) 15.

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.

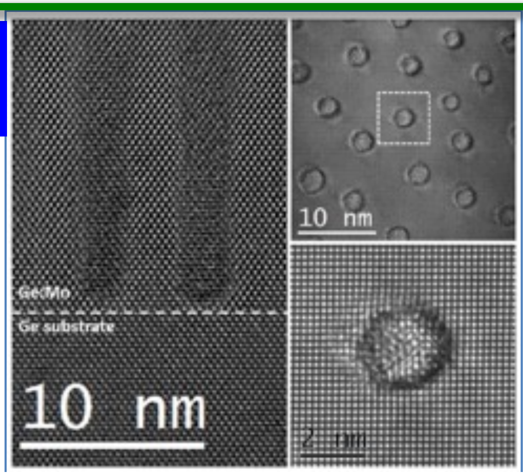


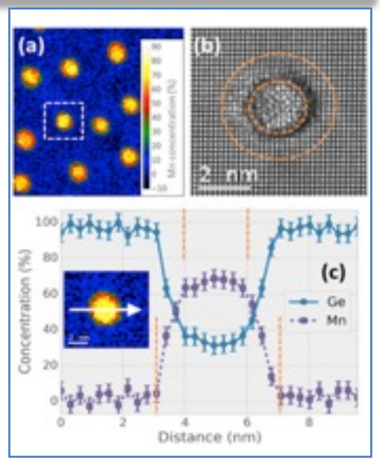




実証実験
GeMn

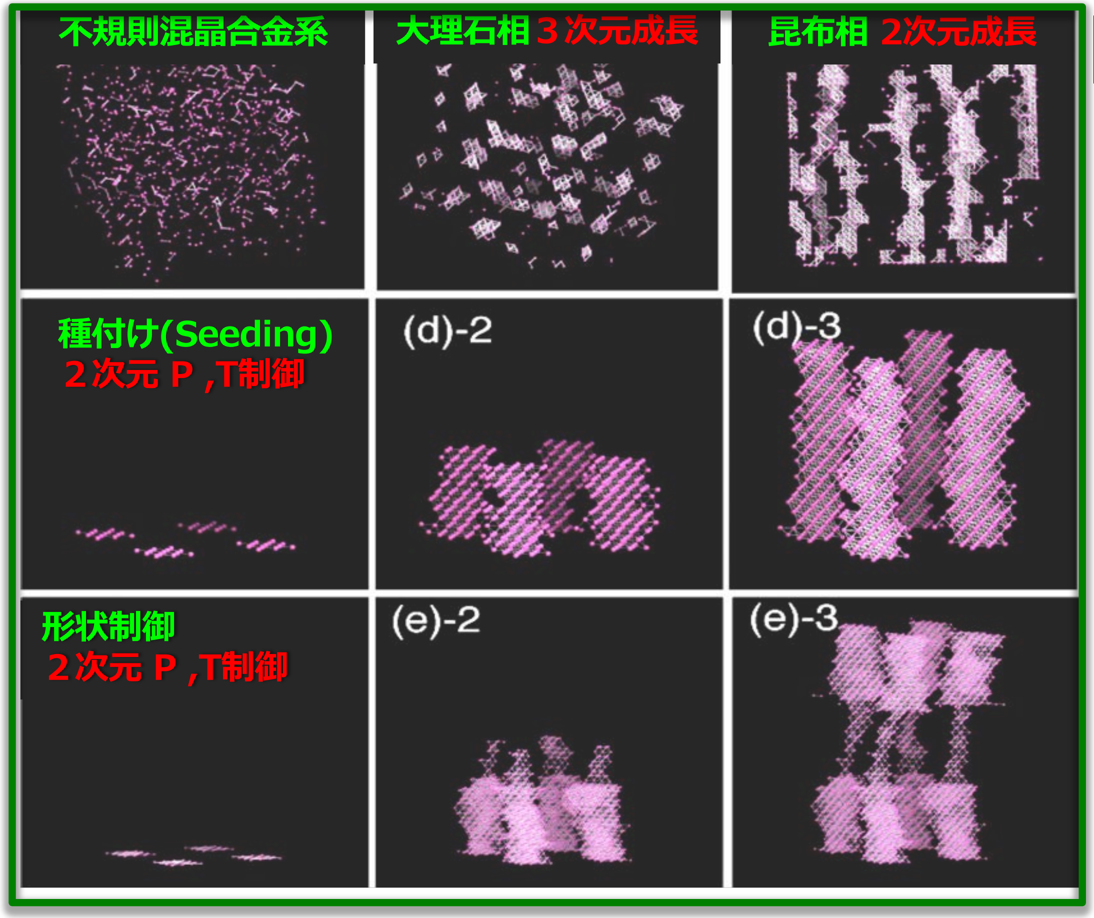
M.Jamet
Grenoble
JAP
(2014).

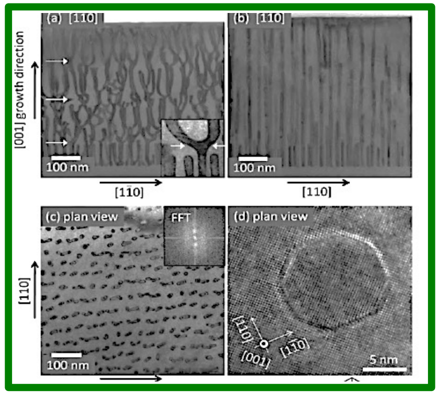


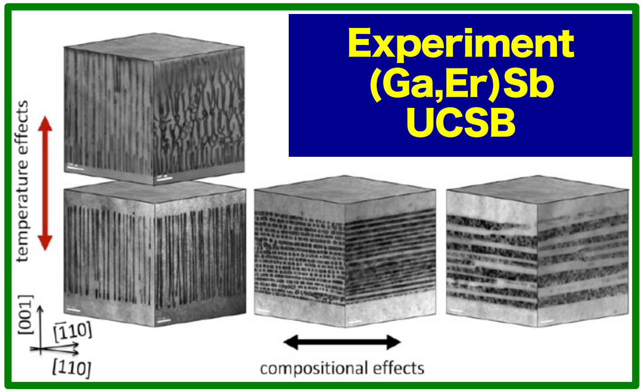


スピノダル・ナノ分解による自己組織化ナノ超構造：大理石相と昆布相

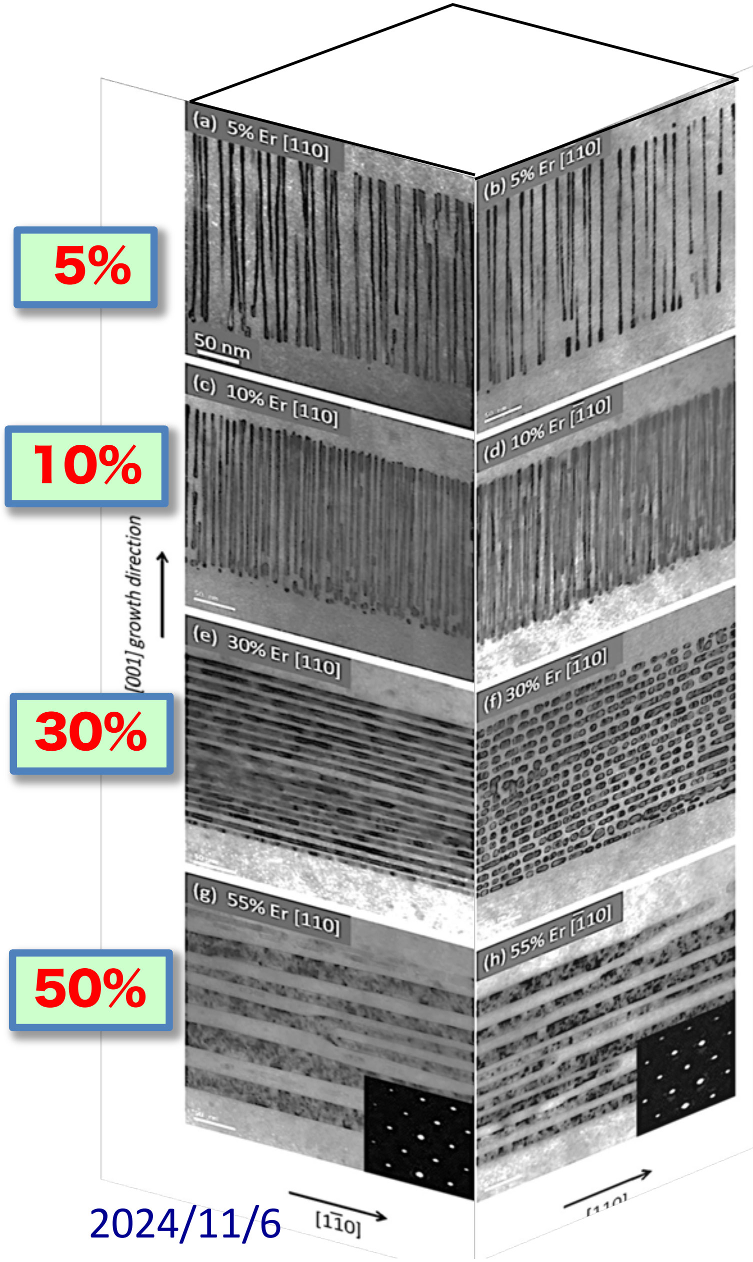
Sato et al., JJAP, 44 (2005) L948.　　Fukushima et al., JJAP, 45 (2006) L416.



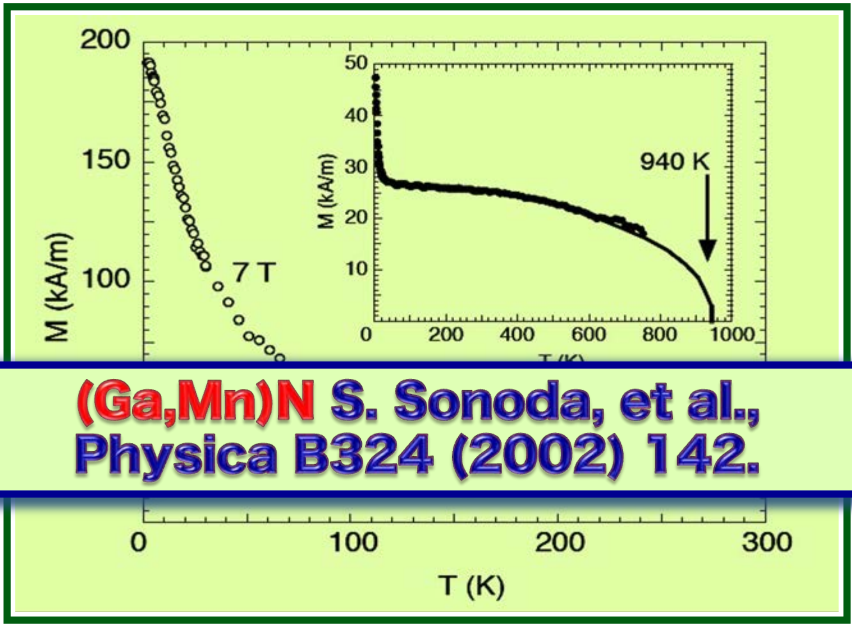




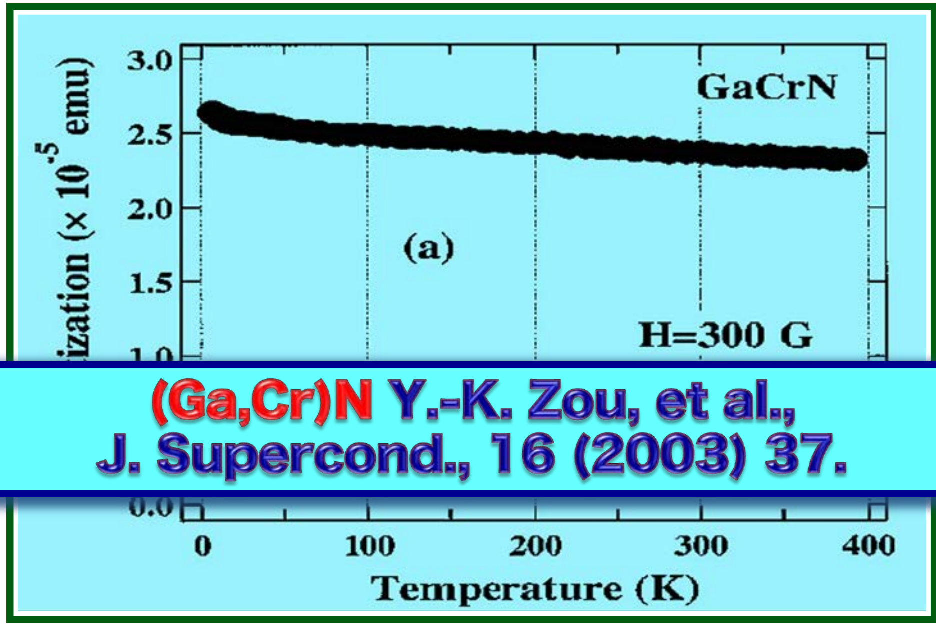
Christopher Palmstrom (UCSB), 2015



■昆布相・大理石相における高いブロッキング温度：T_B

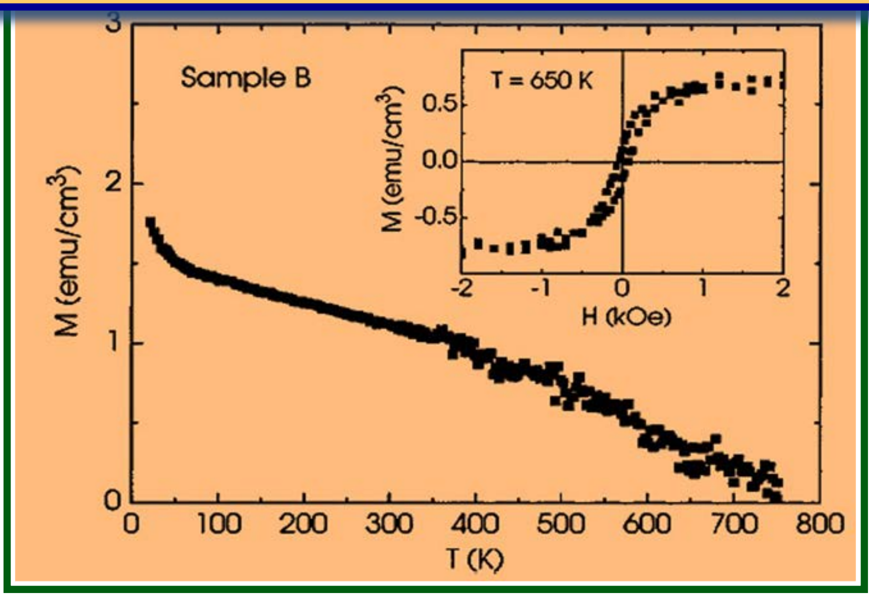


(Ga,Mn)N S. Sonoda, et al., Physica B324 (2002) 142.



(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)

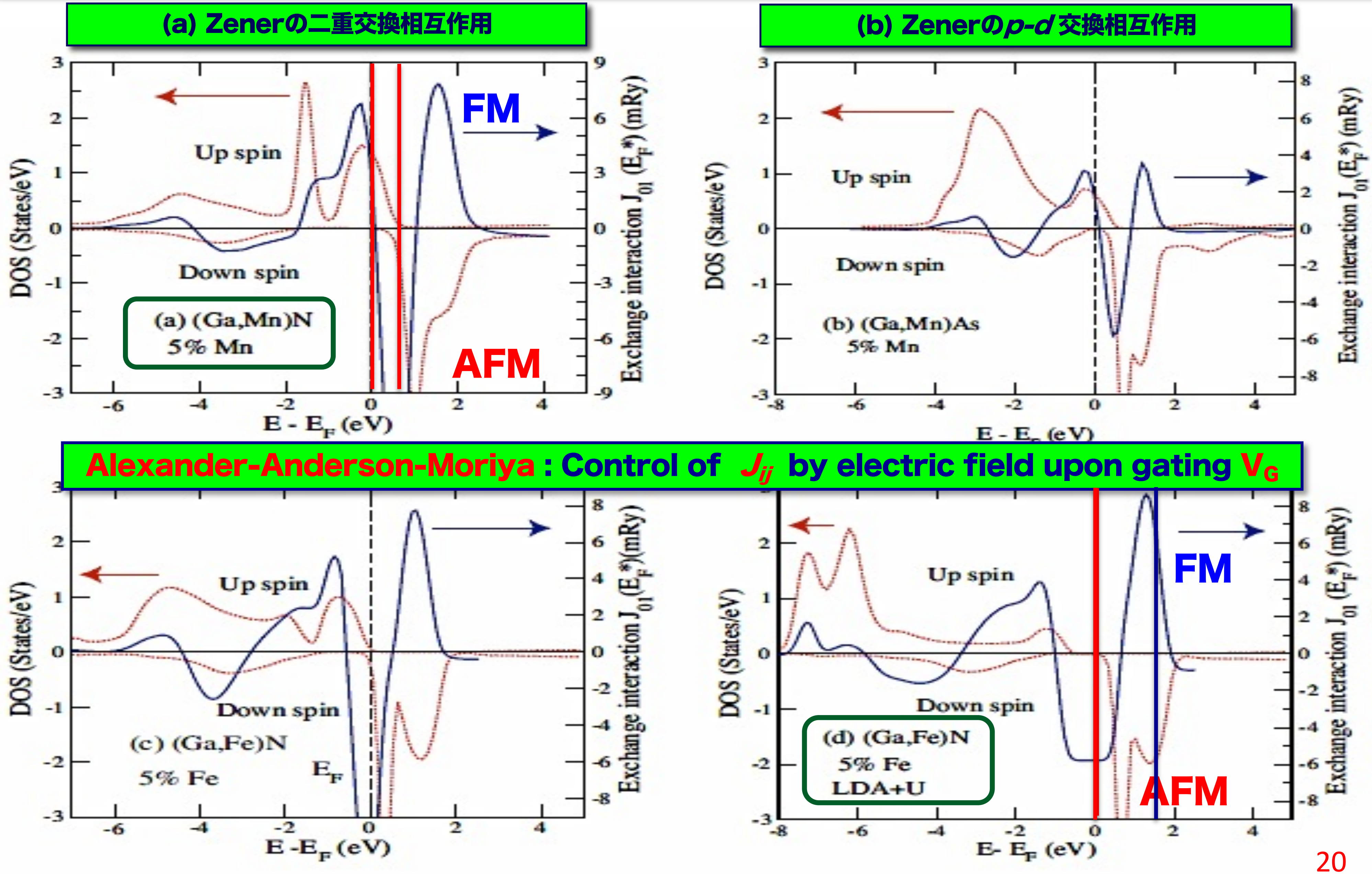
基本特許(EU, USA, Japan)

H.Katayama-Yoshida, K. Sato

- ■EP-1219731B1,
- ■USP-0112278A1,
- ■EP-1367151A1
- ■JP2001-059195, 0593030

交換相互作用の一般則と電場制御： $\mathcal{H} = -\sum_{i \neq j} J_{ij}(E_F)\, \mathbf{S}_i \cdot \mathbf{S}_j$

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



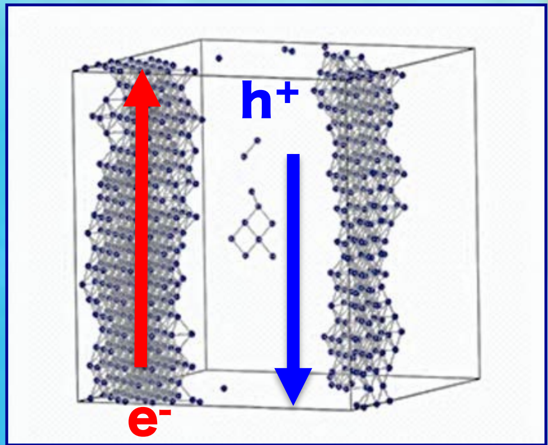
Part 【2】

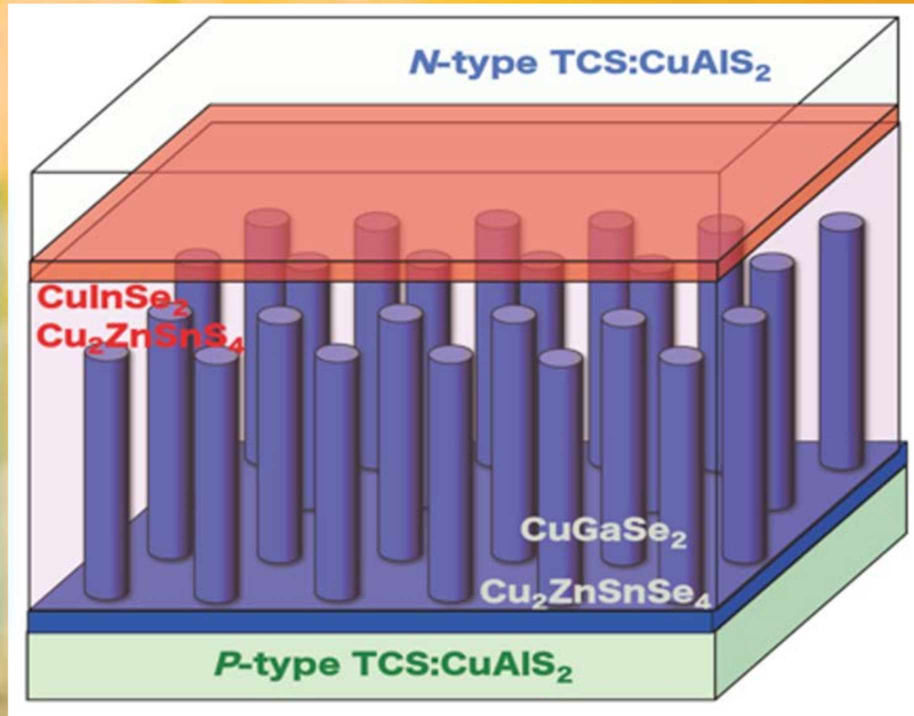
■超高効率エネルギー変換スピノダル・ナノテクノロジー

＜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）



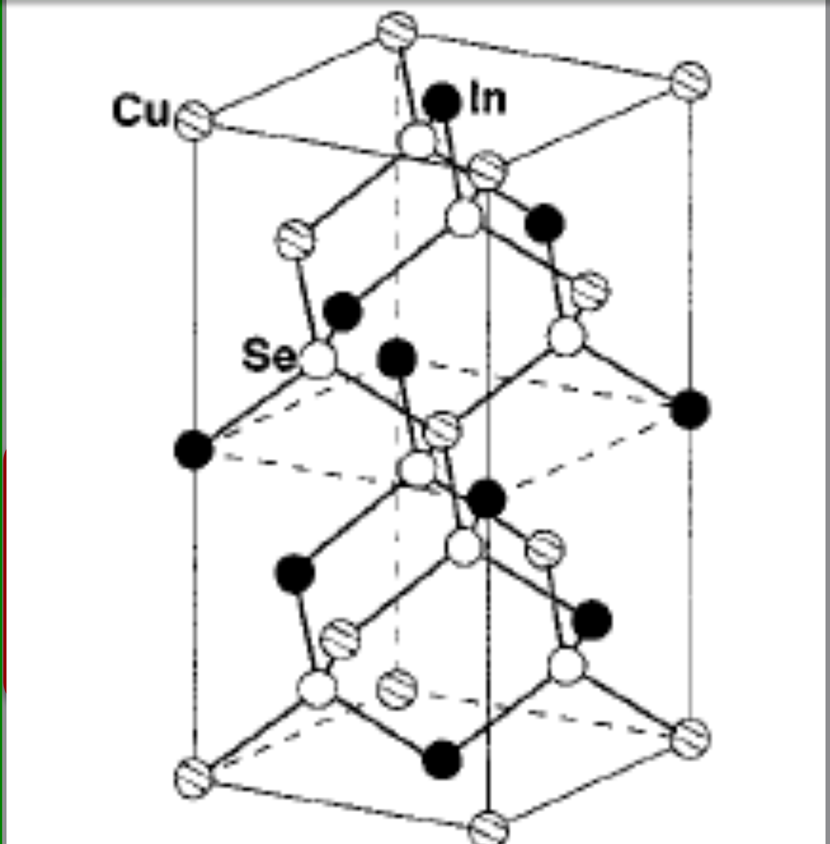


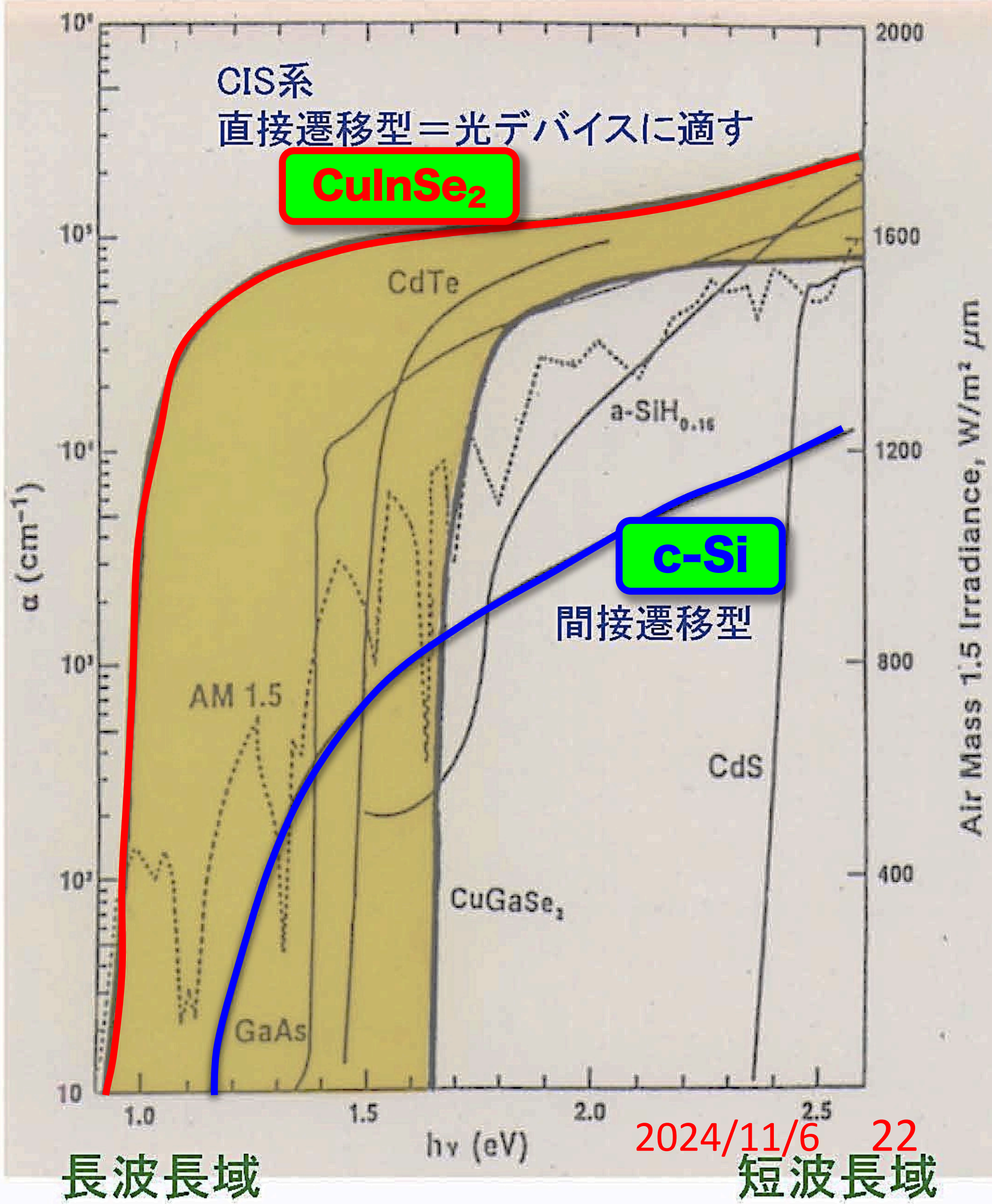
ダイヤモンド・ミューテーション： $CuInSe_2$

Diamond Mutation

- Zn_2Se_2 ⇒ $CuInSe_2$
  ($2Zn^{2+}$ ⇒ Cu^{+} + In^{3+})

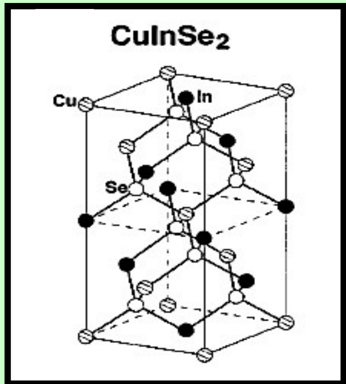
- $Cu_2In_2Se_4$ ⇒ $Cu_2ZnSnSe_4$
  ($2In^{3+}$ ⇒ Zn^{2+} + Sn^{4+})





自己修復機構(Co-doping)：反結合状態が電子で占有
カルコパイライト, 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：$Cu_2ZnSnSe_4$



E

CBM

$[2V_{Cu}+In_{Cu}]$

$[V_{Cu}+ Zn_{Cu}]$

Band-gap
(~*1eV*)

VBM

反結合状態

xy, yz, zx

非結合状態

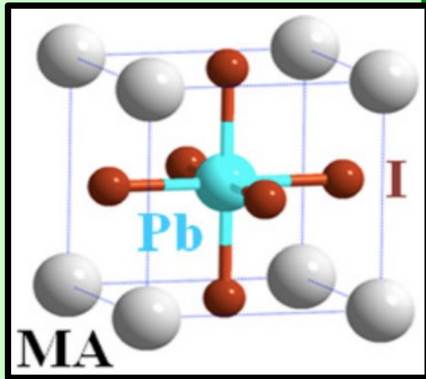
$x^2-y^2, 3z^2-r^2$

xy, yz,zx

結合状態

Se_p

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



CBM

$[V_{MA}+Pb_{MA}]$

$[V_{Cs} + Sn_{Cs}]$

Band-gap
(~*1.5eV*)

VBM

反結合状態

I_p

Sn_s Pb_s

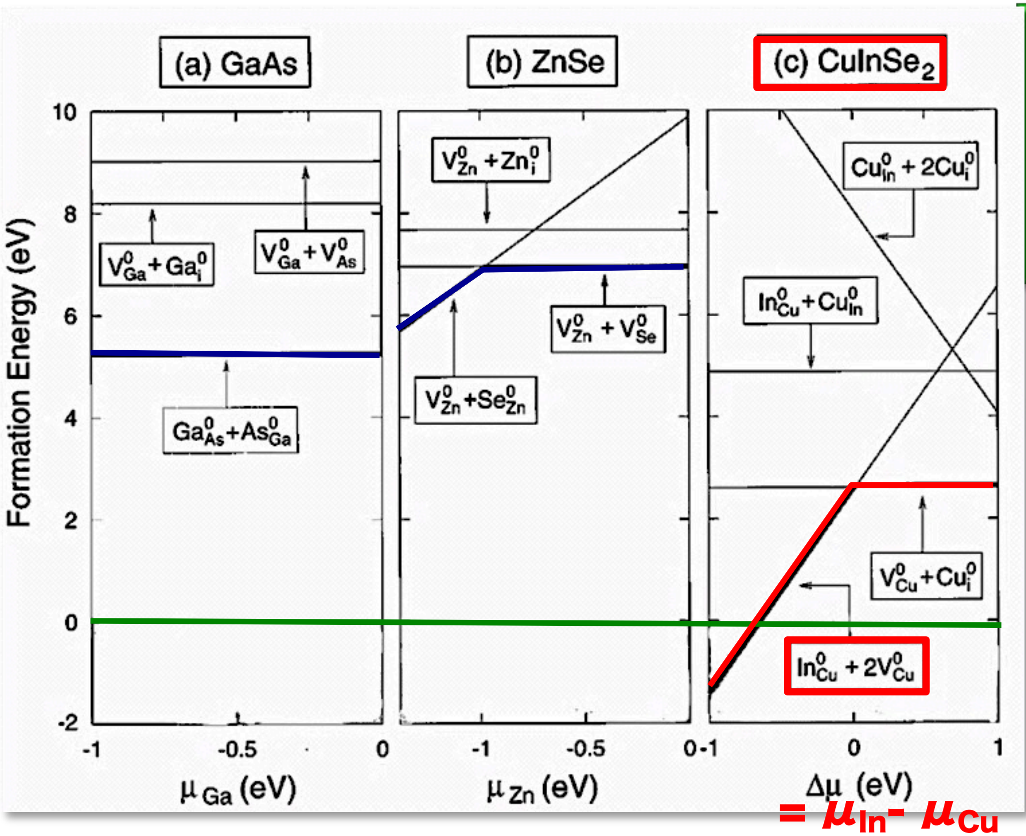
結合状態

■Yamamoto, Katayama-Yoshida, JJAP, 38 (1999) L166.
■Zhang, Wei, Zunger, Katayama-Yoshida, Phys. Rev. B57 (1998) 9642.

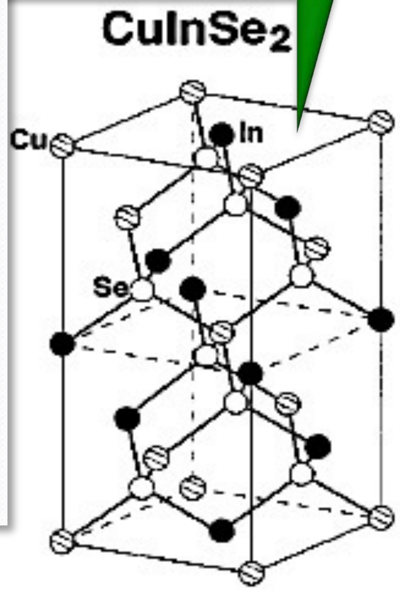
■$CuInSe_2$の自己修復機構[$2V_{Cu}$ + In_{Cu}]デザイン：結晶成長条件（Cu-poor & In-rich）

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.
■Yamamoto, Katayama-Yoshida, J. Crystal Growth, 214 (2000) 552.
■Yamamoto, Katayama-Yoshida, JJAP, 38 (1999) L166.
■Yamamoto, Katayama-Yoshida, PHYSICA B, 302 (2001) 115.

自己修復機構：$CuInSe_2$ [一般則]

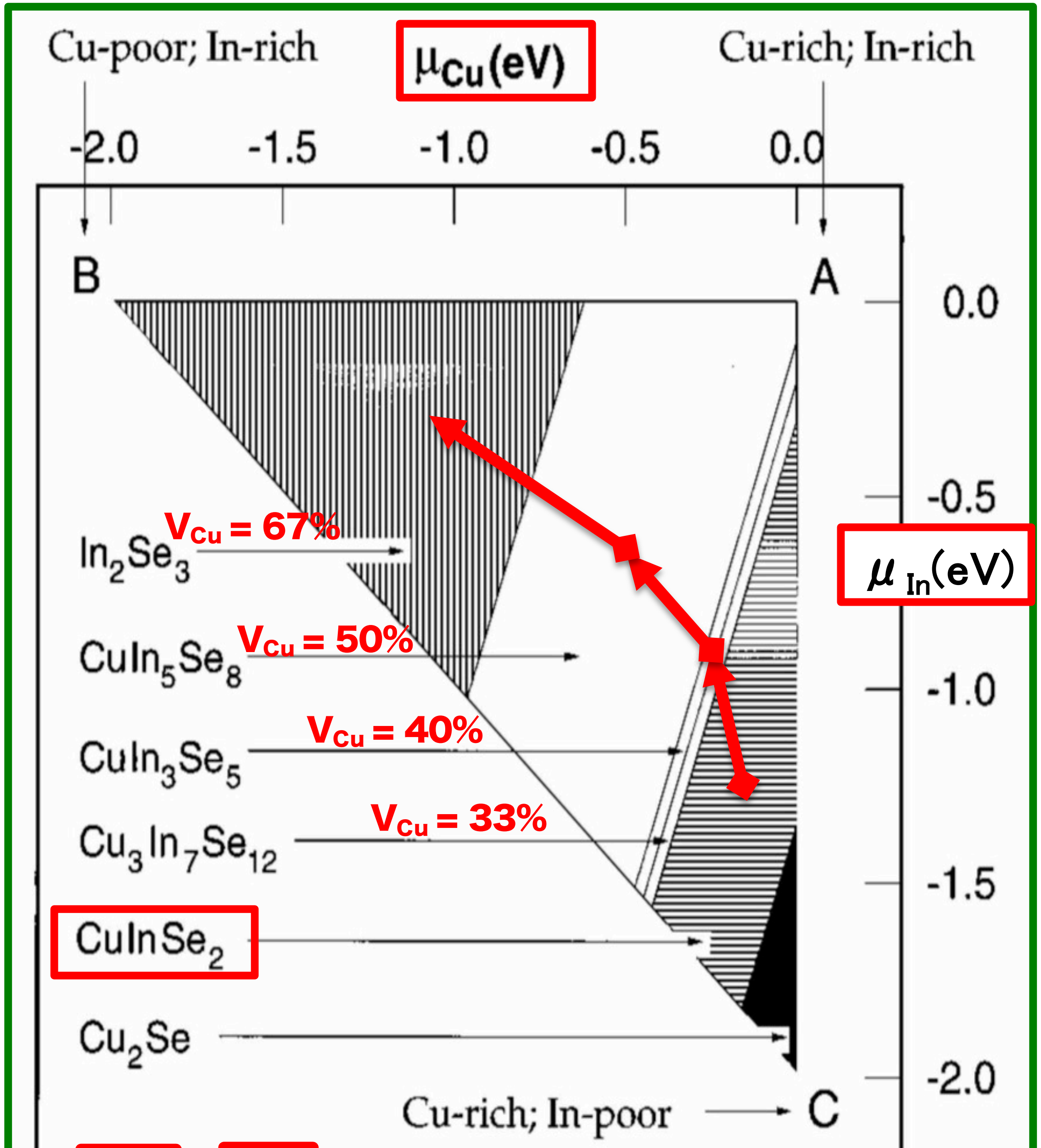
$$n \times [CuInSe_2] + m \times [2V_{Cu}^{-} + In_{Cu}^{2+}] = Cu_{n-3}In_{n+1}Se_{2n} \ (m = 1)$$

(n = 3)	$Cu_3In_3Se_6$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =		In_2Se_3
(n = 4)	$Cu_4In_4Se_8$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =		$CuIn_5Se_8$
(n = 5)	$Cu_5In_5Se_{10}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =		$CuIn_3Se_5$
(n = 6)	$Cu_6In_6Se_{12}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =		$Cu_3In_7Se_{12}$
(n = 7)	$Cu_7In_7Se_{14}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_4In_8Se_{14}$ ⇒	$Cu_2In_4Se_7$
(n = 8)	$Cu_8In_8Se_{16}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =		$Cu_5In_9Se_{16}$
(n = 9)	$Cu_9In_9Se_{18}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_6In_{10}Se_{18}$ ⇒	$Cu_3In_5Se_9$
(n = 10)	$Cu_{10}In_{10}Se_{20}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =		$Cu_7In_{11}Se_{20}$
(n = 11)	$Cu_{11}In_{11}Se_{22}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_8In_{12}Se_{22}$ ⇒	$Cu_4In_6Se_{11}$
(n = 12)	$Cu_{12}In_{12}Se_{24}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =		$Cu_9In_{13}Se_{24}$
(n = 13)	$Cu_{13}In_{13}Se_{26}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_{10}In_{14}Se_{26}$ ⇒	$Cu_5In_7Se_{13}$
(n = 14)	$Cu_{14}In_{14}Se_{28}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	⇒	$Cu_{11}In_{15}Se_{28}$
(n = 15)	$Cu_{15}In_{15}Se_{30}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_{12}In_{16}Se_{28}$ ⇒	$Cu_3In_4Se_7$
(n = 16)	$Cu_{16}In_{16}Se_{32}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	⇒	$Cu_{13}In_{17}Se_{32}$
(n = 17)	$Cu_{17}In_{17}Se_{34}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_{14}In_{18}Se_{34}$ ⇒	$Cu_7In_9Se_{17}$
(n = 18)	$Cu_{18}In_{18}Se_{36}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	⇒	$Cu_{15}In_{19}Se_{36}$
(n = 19)	$Cu_{19}In_{19}Se_{38}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	⇒	$Cu_{16}In_{20}Se_{38}$
(n = 20)	$Cu_{20}In_{20}Se_{40}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	⇒	$Cu_{17}In_{21}Se_{40}$
(n = 21)	$Cu_{21}In_{21}Se_{42}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_{18}In_{22}Se_{42}$ ⇒	$Cu_9In_{11}Se_{21}$
(n = 22)	$Cu_{22}In_{22}Se_{44}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	⇒	$Cu_{19}In_{23}Se_{44}$
(n = 23)	$Cu_{23}In_{23}Se_{46}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_{20}In_{24}Se_{46}$ ⇒	$Cu_{10}In_{12}Se_{23}$
(n = 24)	$Cu_{24}In_{24}Se_{48}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	⇒	$Cu_{21}In_{25}Se_{48}$
(n = 25)	$Cu_{25}In_{25}Se_{50}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_{22}In_{26}Se_{50}$ ⇒	$Cu_{11}In_{13}Se_{25}$
(n = 26)	$Cu_{26}In_{26}Se_{52}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	⇒	$Cu_{23}In_{27}Se_{52}$
(n = 27)	$Cu_{27}In_{27}Se_{54}$ +	$(2V_{Cu}^- + In_{Cu}^{2+})$ =	$Cu_{24}In_{28}Se_{54}$ ⇒	$Cu_{12}In_{14}Se_{27}$

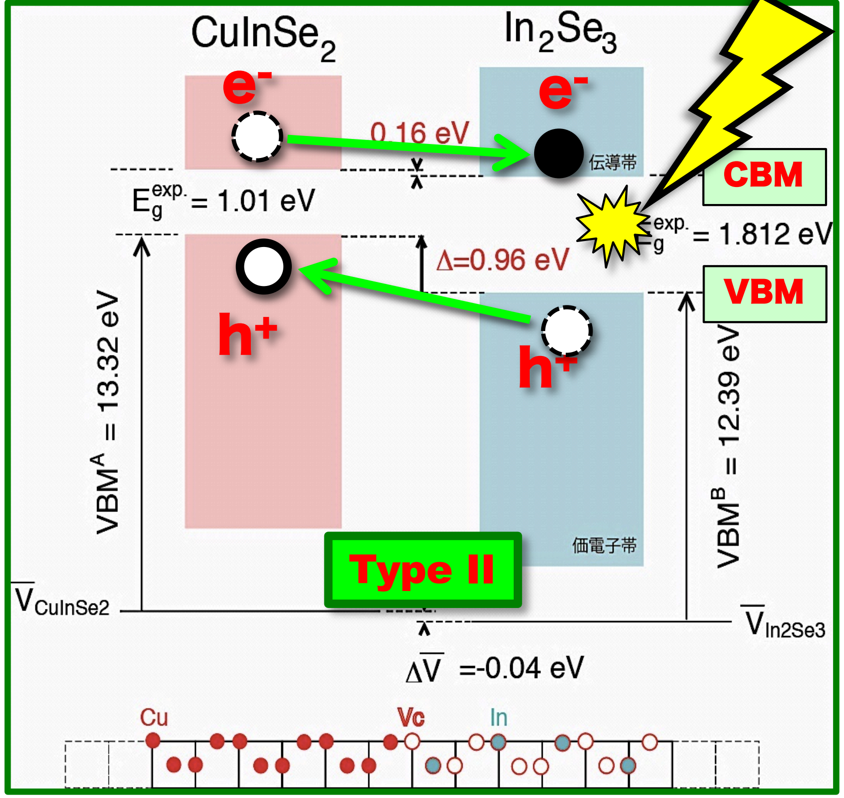
....

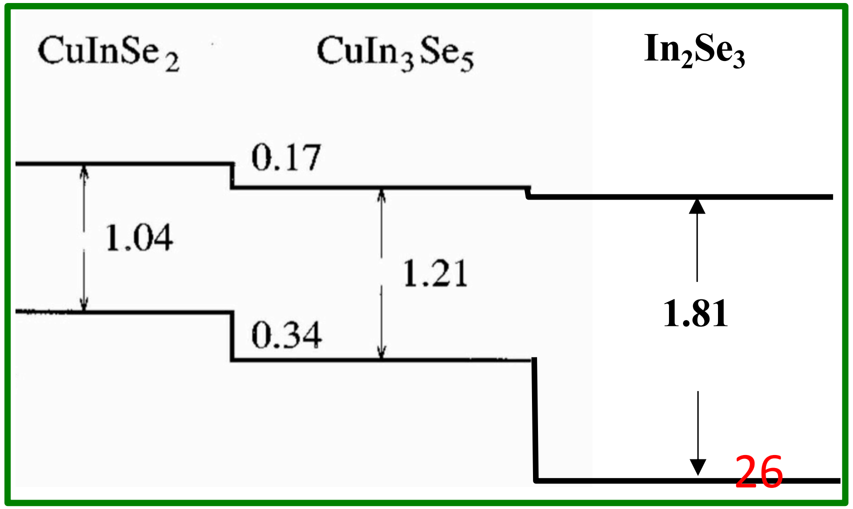
赤字：実験的で実証 2015.

■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

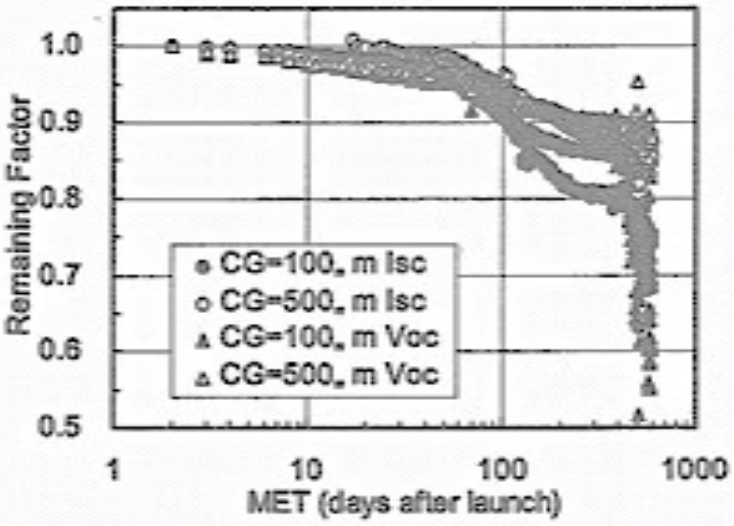


$\mu_{Cu} + \mu_{In} + 2\mu_{Se} = \mu_{CuInSe_2}$

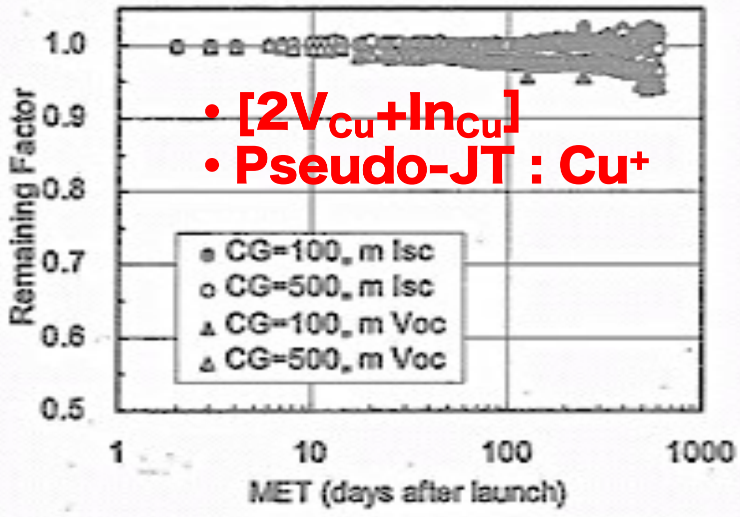




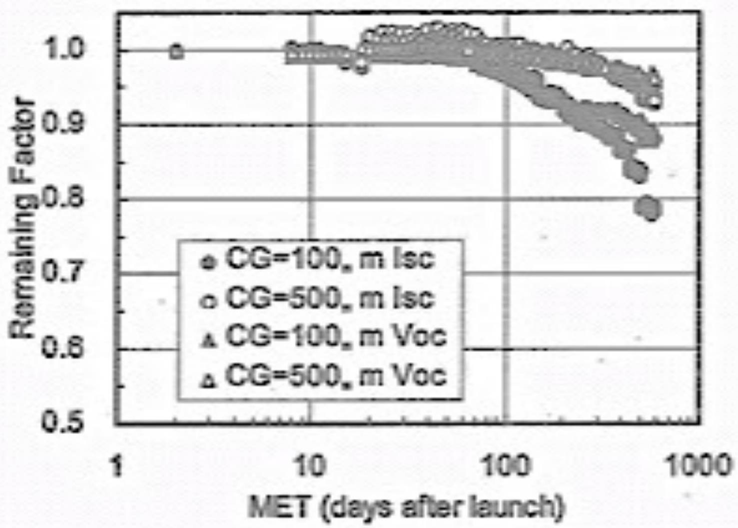
バン・アレン帯宇宙線放射損傷下での自己修復機構の実証実験
JAXA・「つばさ」： $Cu(In,Ga)Se_2$



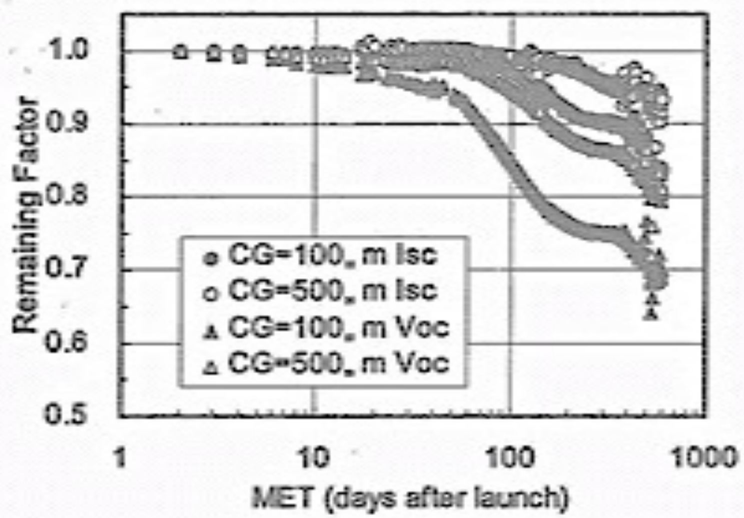
(b) バルク多結晶 Si 太陽電池



(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(10 Ωcm)

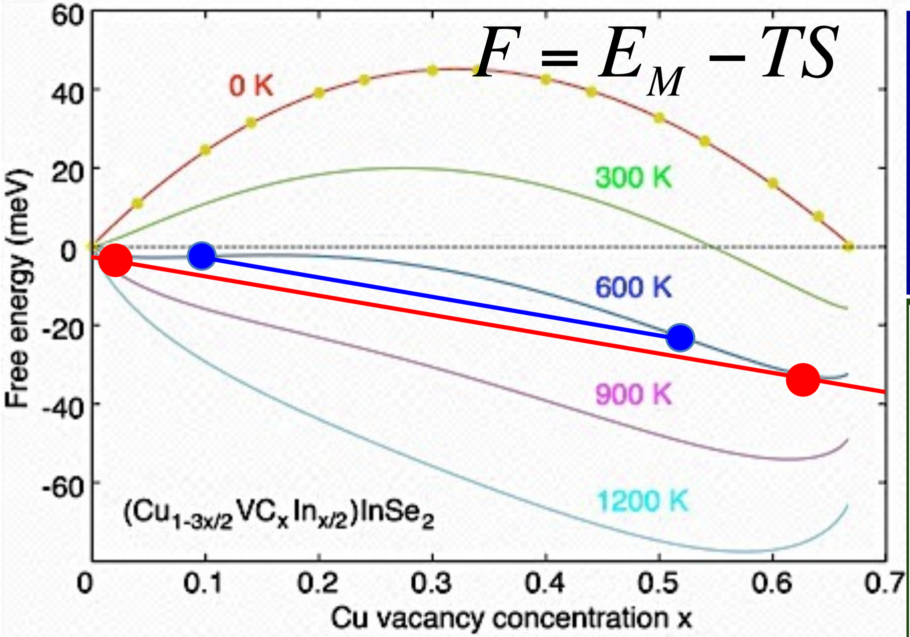
M. Imaizumi et al (JAXA)., 2002.

My Parent's Country House（岡山吉備中央町・下加茂）

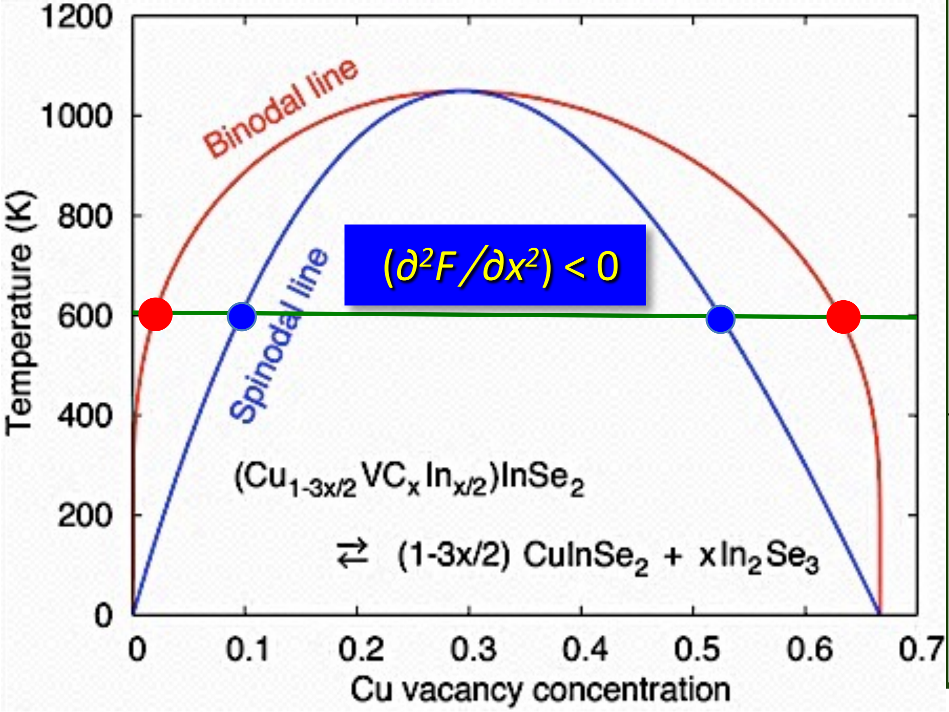
Buy :　7 Yen/kW・h
Sell : 42 Yen/kW・h

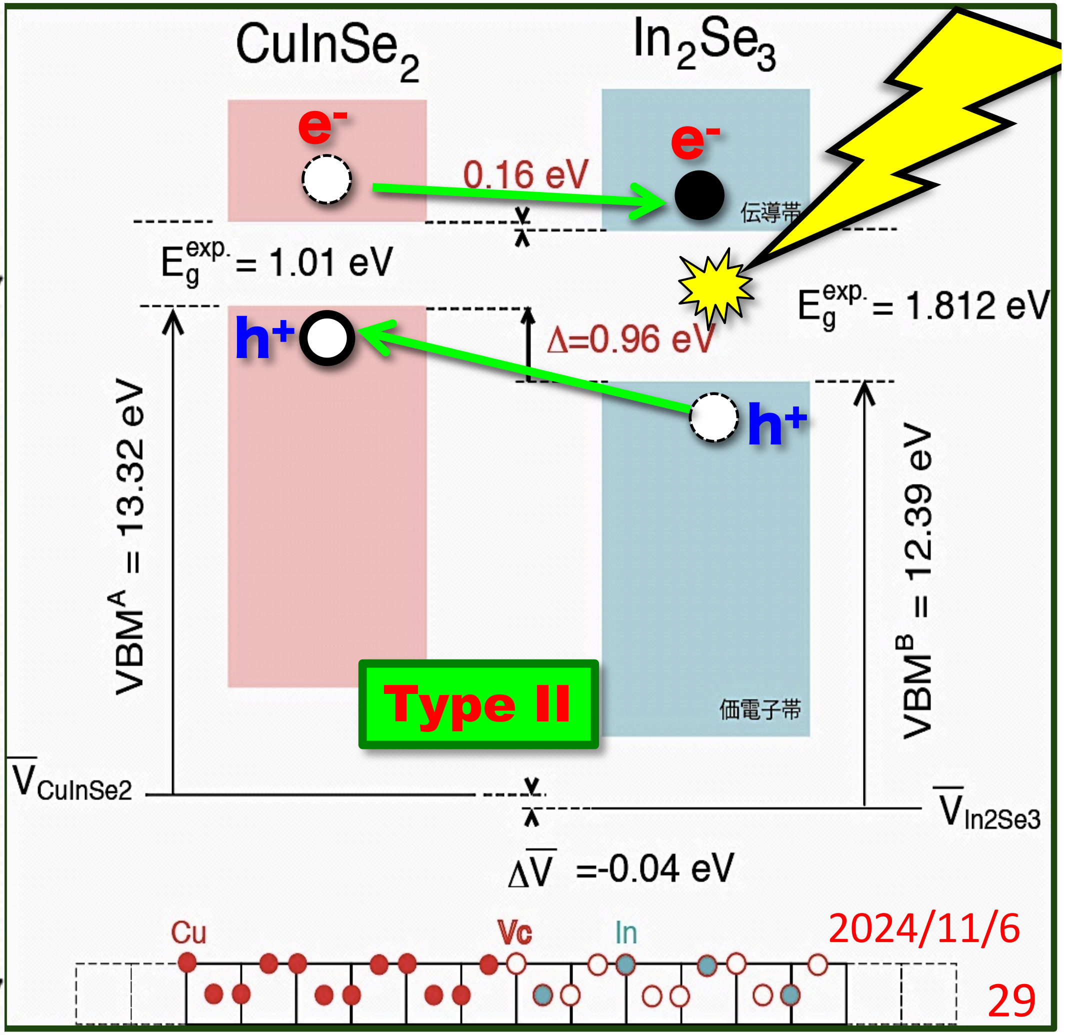
順位	都道府県名	降水量1mm未満の日数(日)
1	岡 山	276.8
2	山 梨	273.8
3	兵 庫	271.6
4	広 島	270.5
5	和歌山	269.0
6	埼 玉	268.8
7	香 川	267.8
8	大 分	267.6
9	徳 島	267.5
10	大 阪	266.8
	全国平均	247.8

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



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





2024/11/6

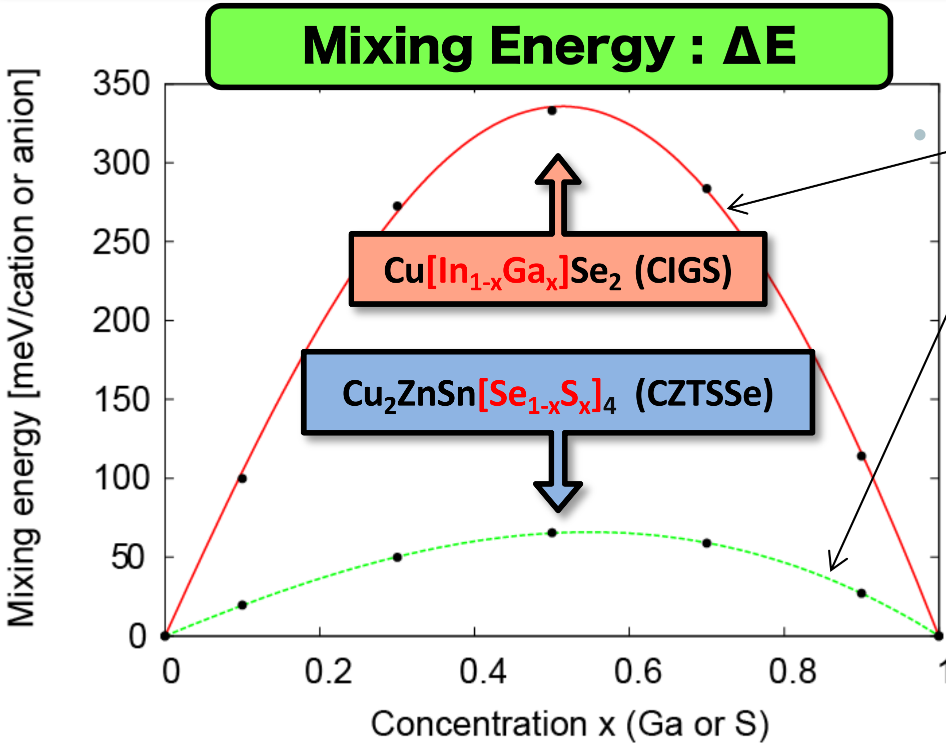
スピノダル・ナノ分解: Tani et al.,(2010)
$Cu(In,Ga)S_2$ & $Cu_2ZnSn(S,Se)_4$

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



Positive and Convex upward ΔE

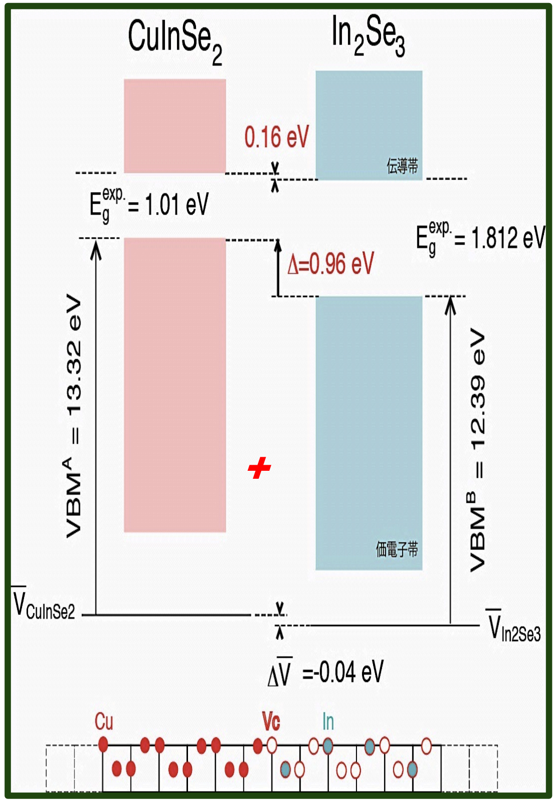
⇩

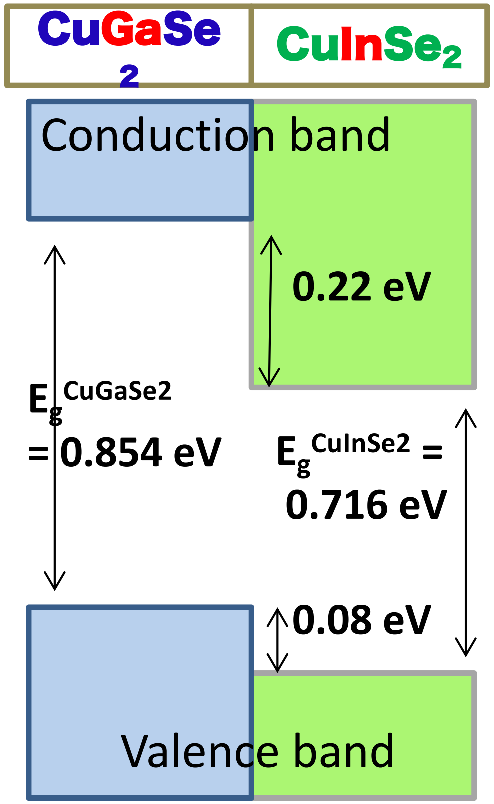
Spinodal Nano-decomposition.

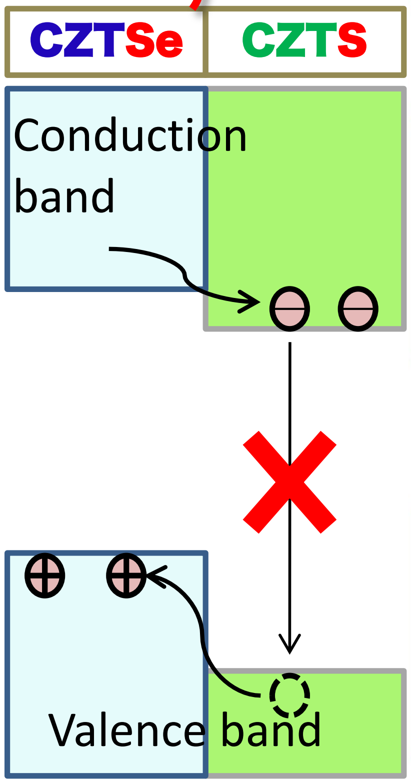
- $CuIn_{1-x}Ga_xSe_2$ → $(1-x)\,CuInSe_2 + x\,CuGaSe_2$
- $Cu_2ZnSn(S_{1-x}Se_x)_4$ → $(1-x)\,Cu_2ZnSnS_4 + x\,Cu_2ZnSnSe_4$

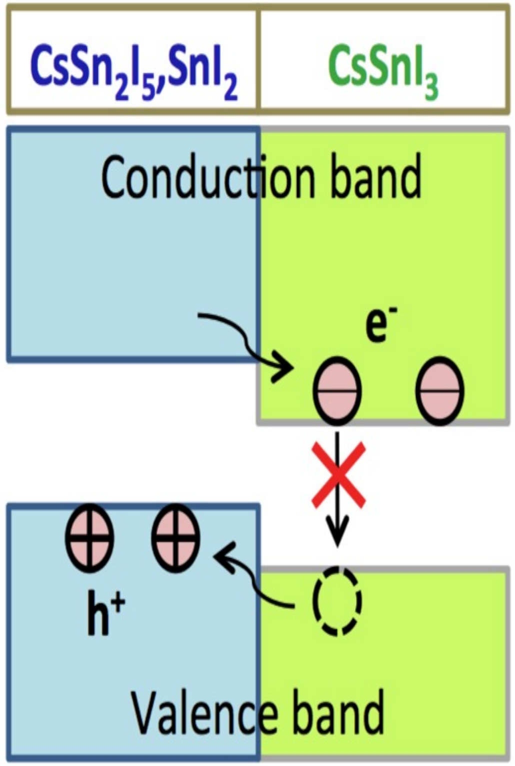
自己組織化ナノ超構造によるType II バンド構造：キャリアーの超高速分離と長寿命化

Chalcopyrite: (Cu,V_{Cu})	Chalcopyrite: (Ga,In)	Kesterite: (Zn,V_{Cu}),(S,Se)	Perovskite: (Cs,V_{Cs}), (Pb,V_{MA})







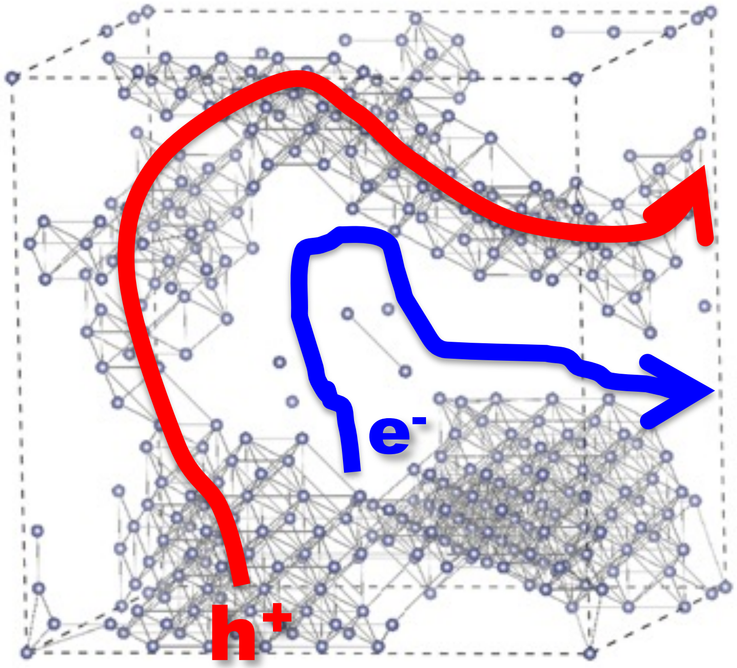


■非平衡状態の結晶成長: ➡ スピノダル・ナノ分解（ e^- と h^+ の高速分離）

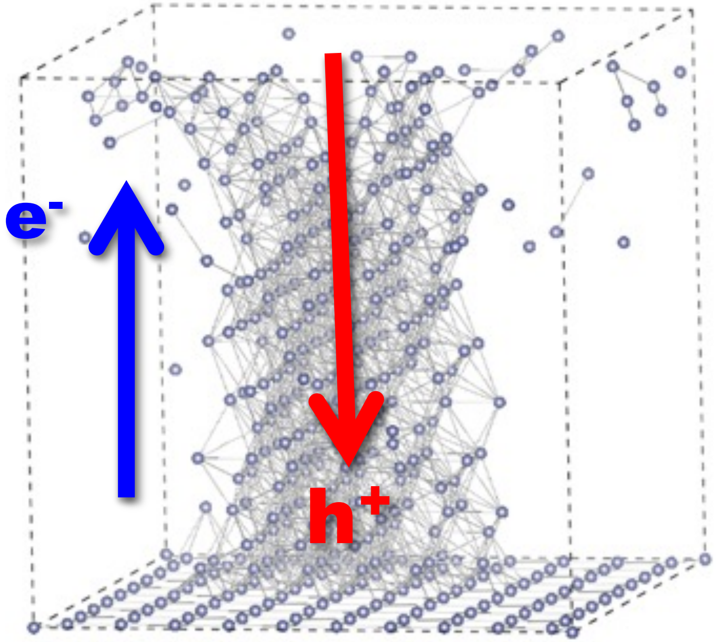
■熱平衡状態: ➡ 核形成を伴う相分離（バイノーダル分解）

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

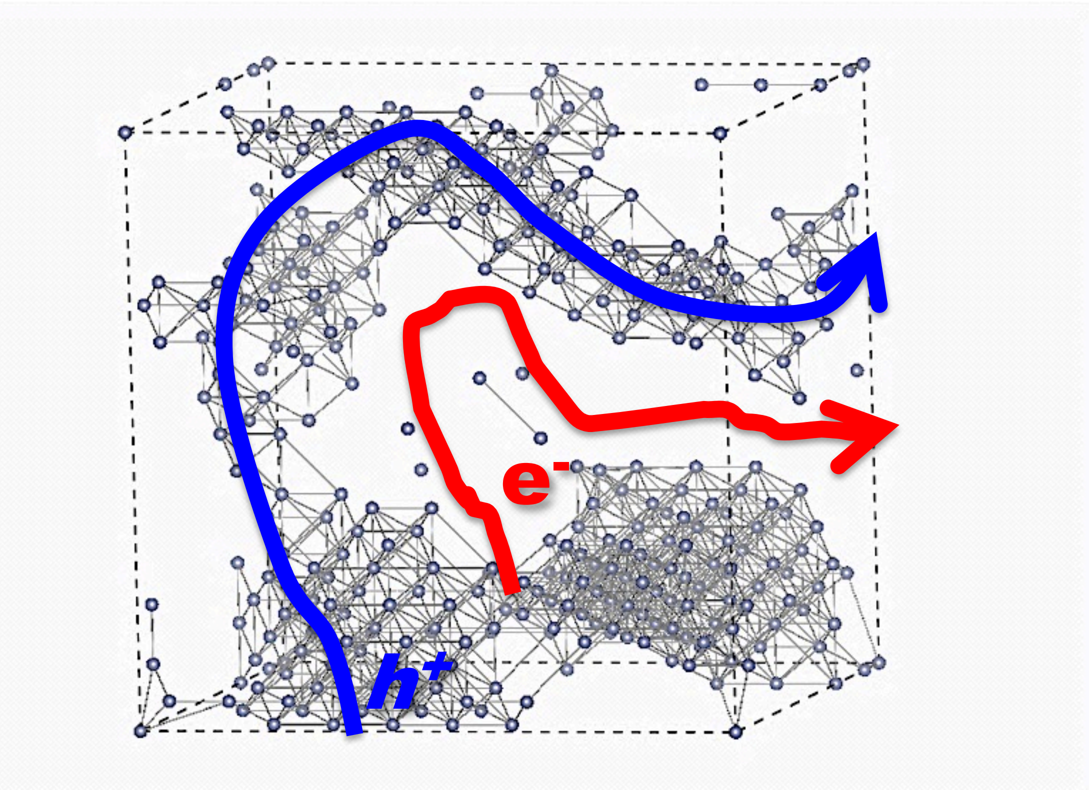
2024/11/6

- 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).

スピノダルナノ分解 (大理石相)
Cu(In$_{1-X}$Ga$_X$)Se$_2$： X_{Ga} = 0.3

■ *Tani, Sato, Katayama-Yoshida, (2010).* ■ *Y. Yan, M.M. Al-Jassim., (2012).*

Multi-scale Simulation of 3D Spinodal Nano-Decomposition
Cu(In$_{1-X}$Ga$_X$)Se$_2$： X=0.15



3D Crystal Growth
Dairiseki-Phase

Z-contrast STEM (EDX) Image

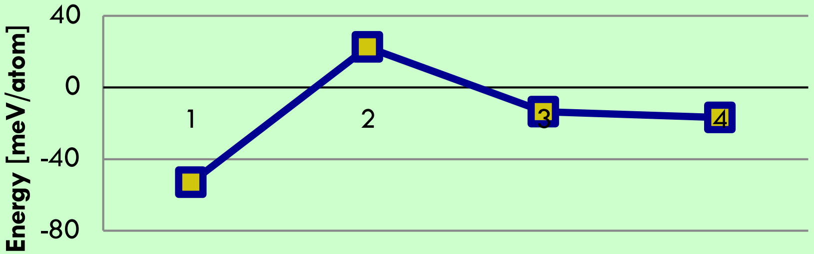
吉田博©

自己修復[V_{Cu}+Zn_{Cu}]とスピノダル・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:

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



イジング・モデル

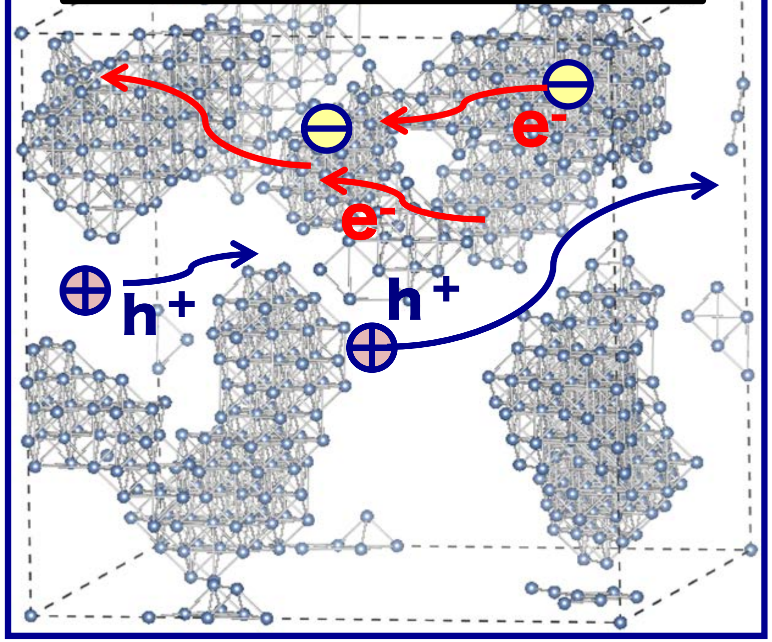
$$H = -\frac{1}{2} \Sigma_{i \neq j} v_{ij} \sigma_i \sigma_j$$

v_{ij} : pair interaction

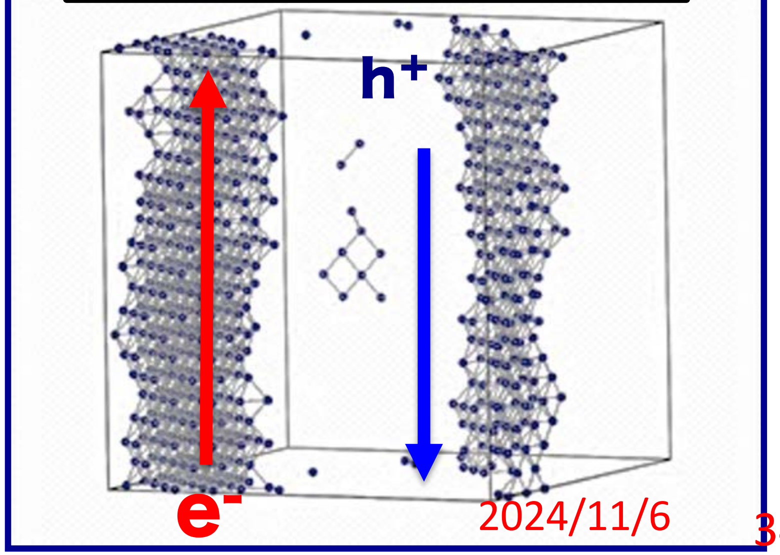
σ_i : occupation number

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

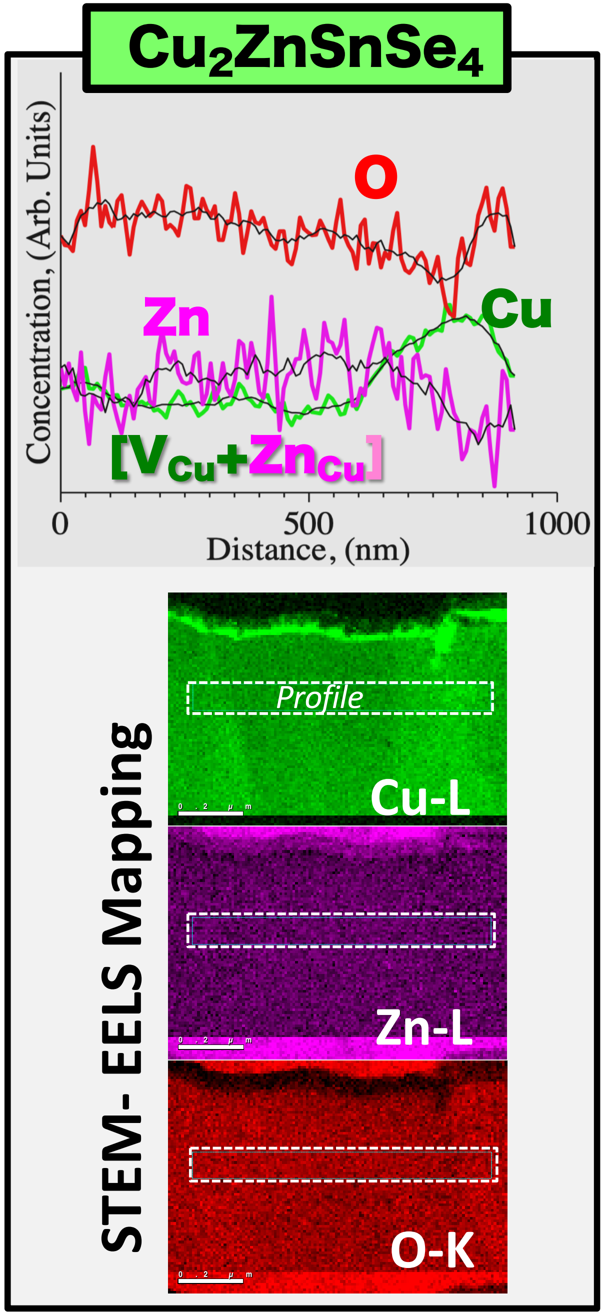
3次元結晶成長（大理石相）

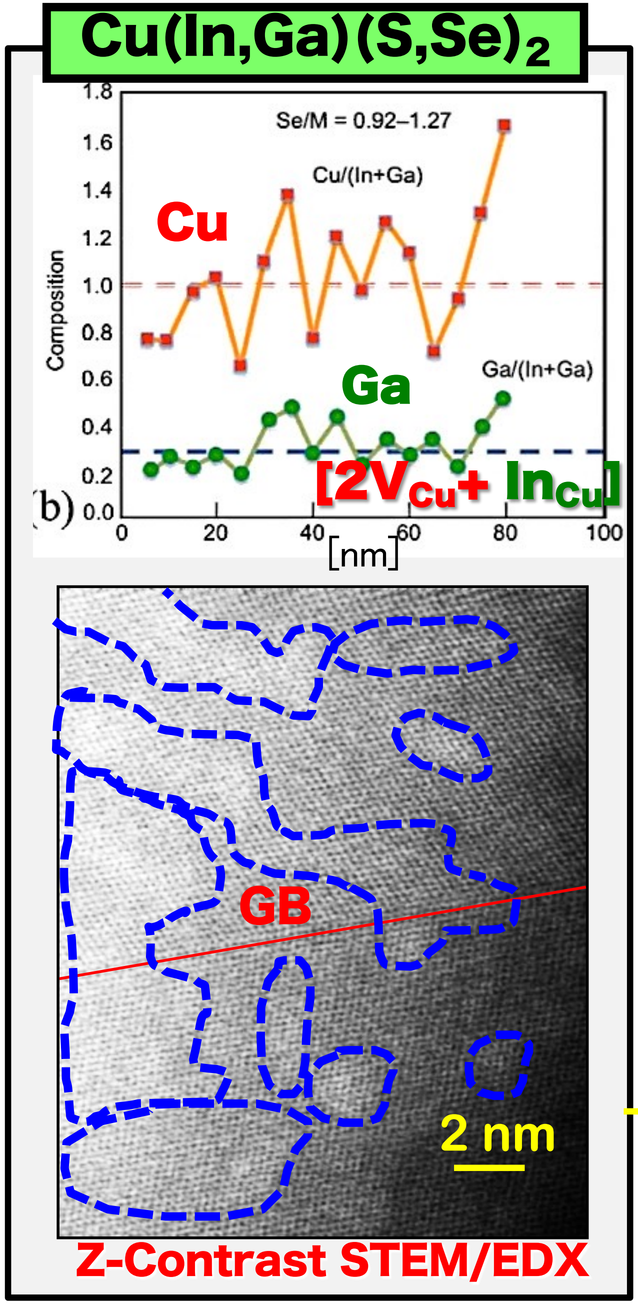


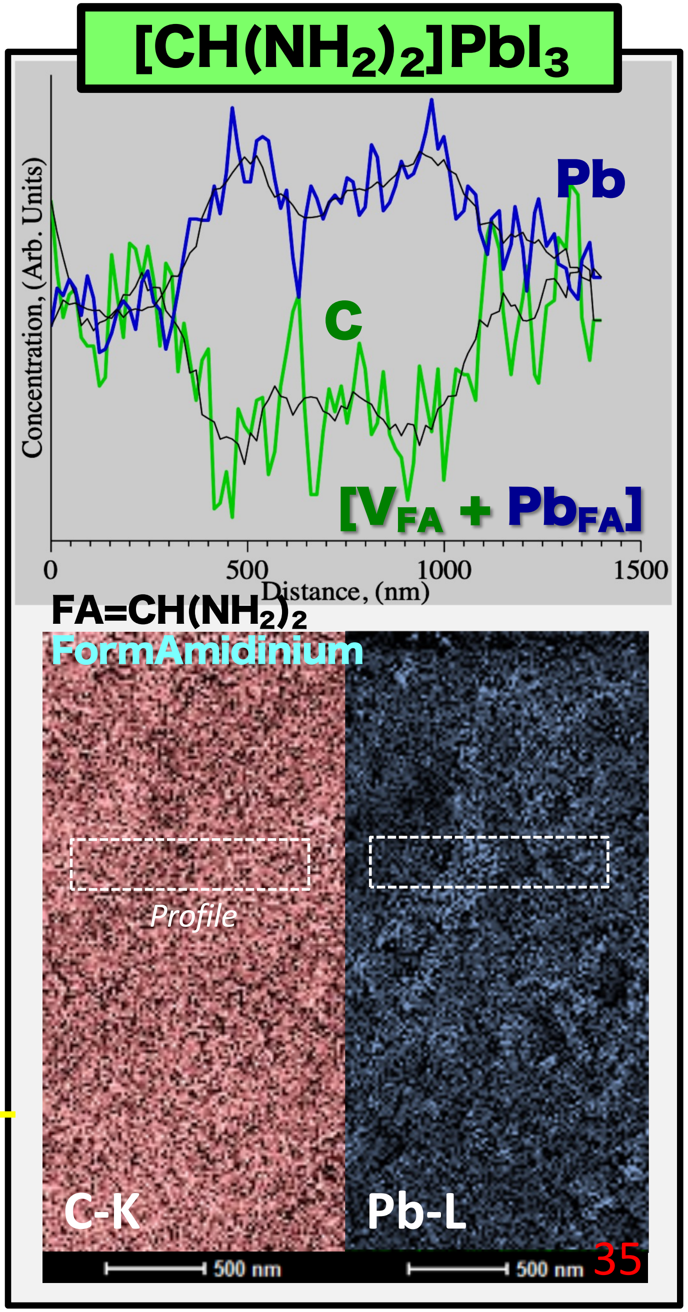
２次元結晶成長（昆布相）



自己修復とスピノダル・ナノ分解の実証実験
STEM/EELS, STEM/EDX : CZTSSe, CIGSSe, (FA)PbI$_3$



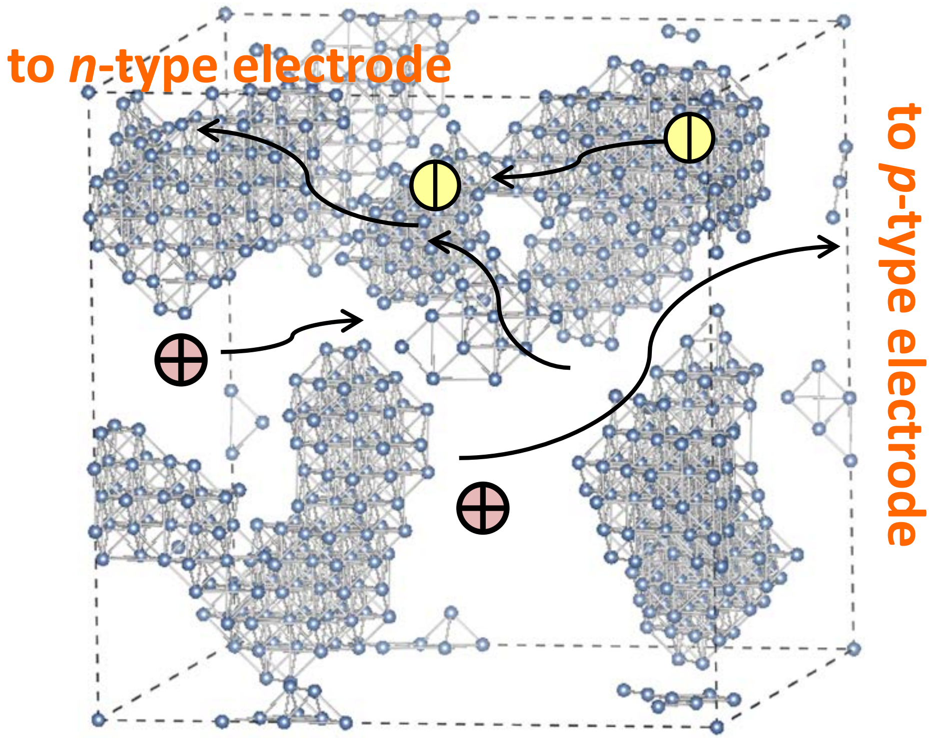




3D スピノダルナノ分解： $Cu_2ZnSn(Se,S)_4$

- **3D Monte Carlo simulation of Spinodal Nano-Decomposition in $Cu_2ZnSn(Se,S)_4$**

$Cu_2ZnSn(Se_{1-x}S_x)_4$ X_S =0.15



Calculation details

- Concentration x = 0.15
- Temperature = 300 K
- 250 MCS / atom
- $H = -\frac{1}{2} \Sigma_{i \neq j} v_{ij} \sigma_i \sigma_j$

  v_{ij} : pair interaction

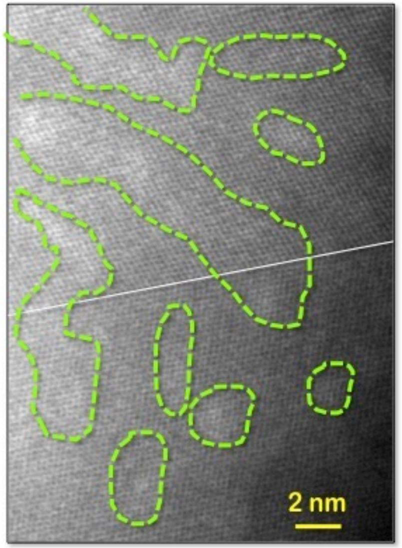
  σ_i : occupation number

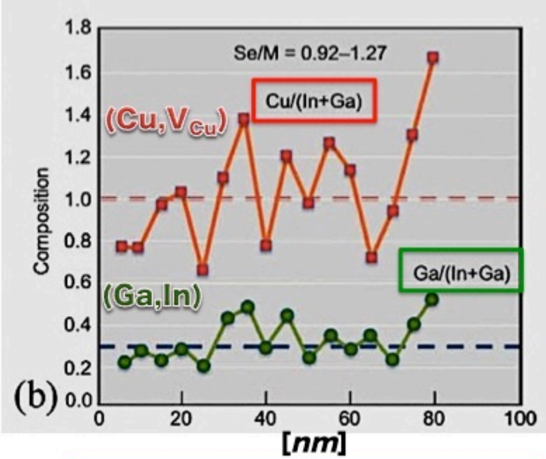
$$V_{ij} = V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB}$$

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

エネルギー変換効率20%以上の$Cu(In_{1-x}Ga_x)Se_2$
X = 0.3 ：自己修復とスピノーダル・ナノ分解 (大理石相)

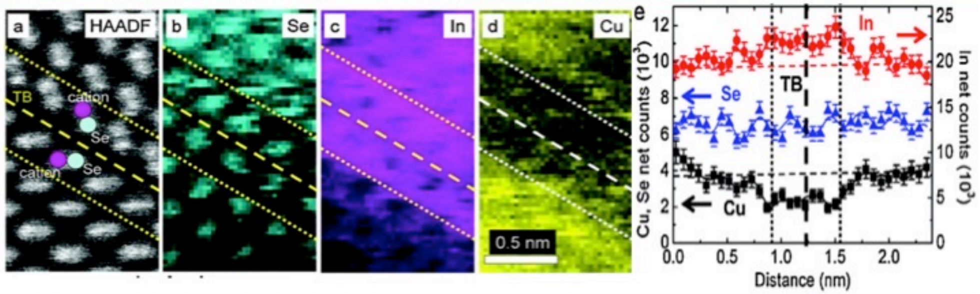
■ *Y. Yan, M.M. Al-Jassim & R. Noufi, NREL.*



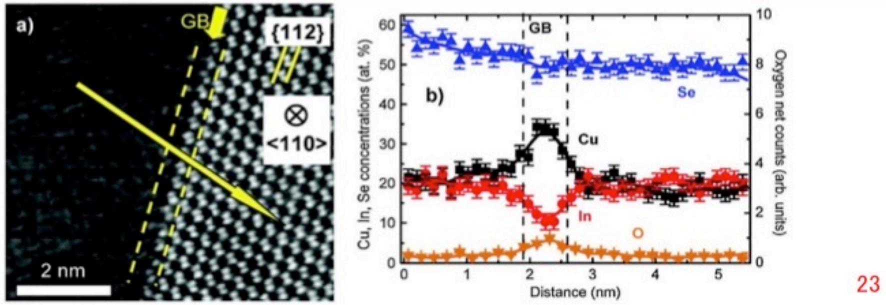


Z-contrast STEM (EDX) Image :
自己修復機構： [$2V_{Cu}$ + In_{Cu}]

$Cu(In,Ga)(Se,S)_2$: STEM/EELS/EDS *D. Abou-Ras et al.*



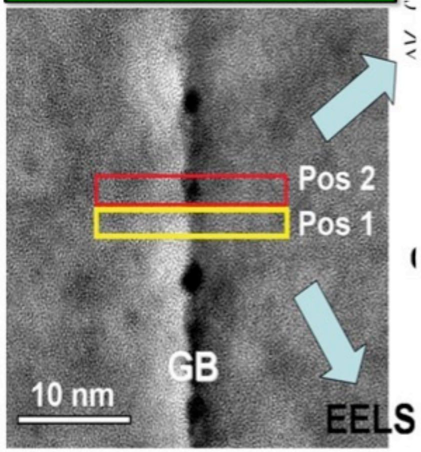
■Spinodal Nano-decomposition : (Cu,V_{Cu}) , (Se, O), (In, Ga)
■Self-Regeneration : [$2V_{Cu}$ + In_{Cu}]Anti-correlation： Cu/In & Se/O.

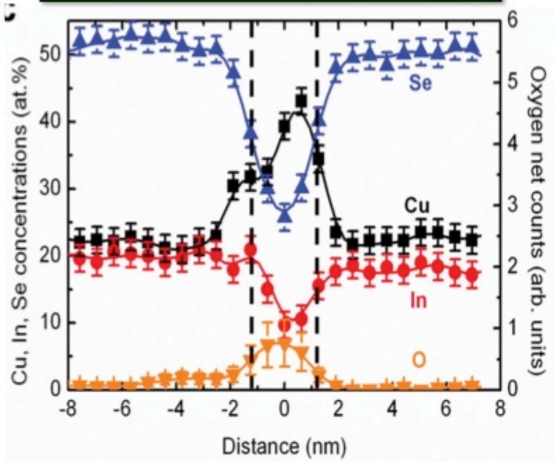


Cu(In,Ga)(Se,O)$_2$: 結晶粒界周辺

STEM/EELS image

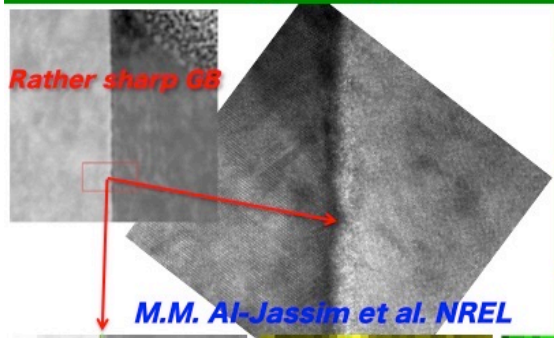
D. Abou-Ras et al.



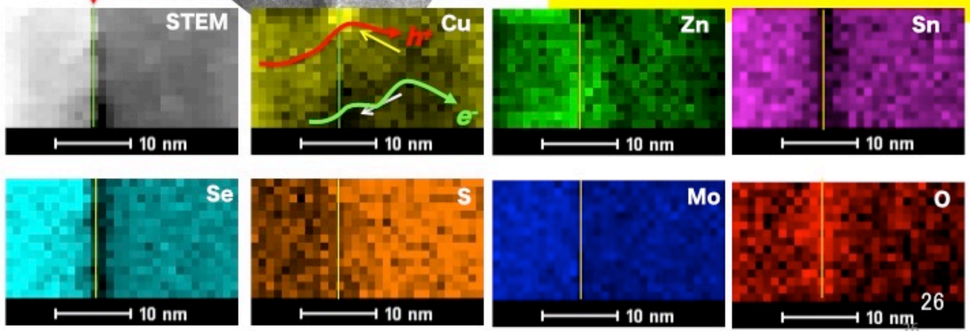


■スピノーダル・ナノ分解： (Cu,V_{Cu}) , (Se, O), (In, Ga)
■自己修復機構： [$2V_{Cu}$ + In_{Cu}]
・反相関： Cu/In & Se/O.

STEM-EDSによる$Cu_2ZnSn(S,Se)_4$ 結晶粒界周辺の自己修復[V_{Cu}+Zn_{Cu}]とスピノーダル・ナノ分解[SND]



- ✓ 結晶粒界ではCu濃度は一様ではなく、Cu原子空孔の多い領域は自己修復機構[V_{Cu}+Zn_{Cu}]によりZn濃度が高い.
- ✓ Se濃度が高いところではS濃度が低く、一方、S濃度が高いところではSe濃度が低い.[SND]
- ✓ 結晶粒界ではSeとSnの濃度は低く、イオン性の強いO濃度が高い.



Part 【3】自己組織化ナノ超構造による高効率熱電材料のデザインと実証

熱流

ゼーベック効果(Seebeck effect) →

← ペルチエ効果（Peltier effect）

Environmental-friendly

電気

◀ **Voyager 1**
(RTG: radioisotope thermoelectric generator)
(http://www.nasa.gov)

Seebeck watch ▶
(http://www.natureinterface.com)

▲
Wine cooler
(http://www.newair.com/products)

熱電材料マテリアルデザインのガイドライン

***ZT*：*B* 因子表現**

G. D. Mahan, Solid state physics 51, 81 (1997).

$$ZT = f\left(\underline{B}, \underline{\beta E_g}\right)$$

B factor　band-gap

~~$$ZT = \frac{S^2\sigma}{\kappa}T$$~~

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

$$\sigma = ne\mu$$

$$\kappa_e = ne\mu LT$$

Band degeneracy
(ex.) Multi-valley

Effective mass
(ex.) Flat-band

$$B = \frac{Tk_B^2}{e\kappa_L} N_j \mu_j \left(\frac{m_j^* k_B T}{2\pi\hbar^2}\right)^{3/2}$$

Lattice thermal conductivity
(ex.) Phonon scattering

Carrier mobility
(ex.) Low electronegativity

物質	高効率の起源
Bi_2Te_3	フラットバンドによる大きな m^*
PbTe	多重バレーによる大きな N
Zn_4Sb_3	アモルファスZnによる小さい κ_L
$CeFe_3CoSb_{12}$	ラットリングによる小さい κ_L
$Bi_2Sr_2Co_2O_y$	ミスフィットした構造によるフォノン散乱による小さい κ_L
$(GeTe)_x(AgSbTe_2)_{1-x}$	小さい κ_L ？？？
$CuGaTe_2$	小さい κ_L ？？？

N, m^*, κ, μ,を
調整し、高 ZT をデザイン

カルコパイライト・$CuGaTe_2$ 高効率熱電材料

COMMUNICATION

ADVANCED MATERIALS
www.advmat.de
MaterialsViews
www.MaterialsViews.com

Chalcopyrite $CuGaTe_2$: A High-Efficiency Bulk Thermoelectric Material

Theerayuth Plirdpring, Ken Kurosaki,* Atsuko Kosuga, Tristan Day, Samad Firdosy, Vilupanur Ravi, G. Jeffrey Snyder, Adul Harnwunggmoung, Tohru Sugahara, Yuji Ohishi, Hiroaki Muta, and Shinsuke Yamanaka

T. Plirdpring, K. Kurosaki, A. Kosuga, T. Day, S. Firdosy, V. Ravi, G. J. Snyder, A. Harnwunggmoung, T. Sugahara, Y. Ohishi, H. Muta, and S. Yamanaka, Adv. Mater. 24(27), 3622–3626 (2012).

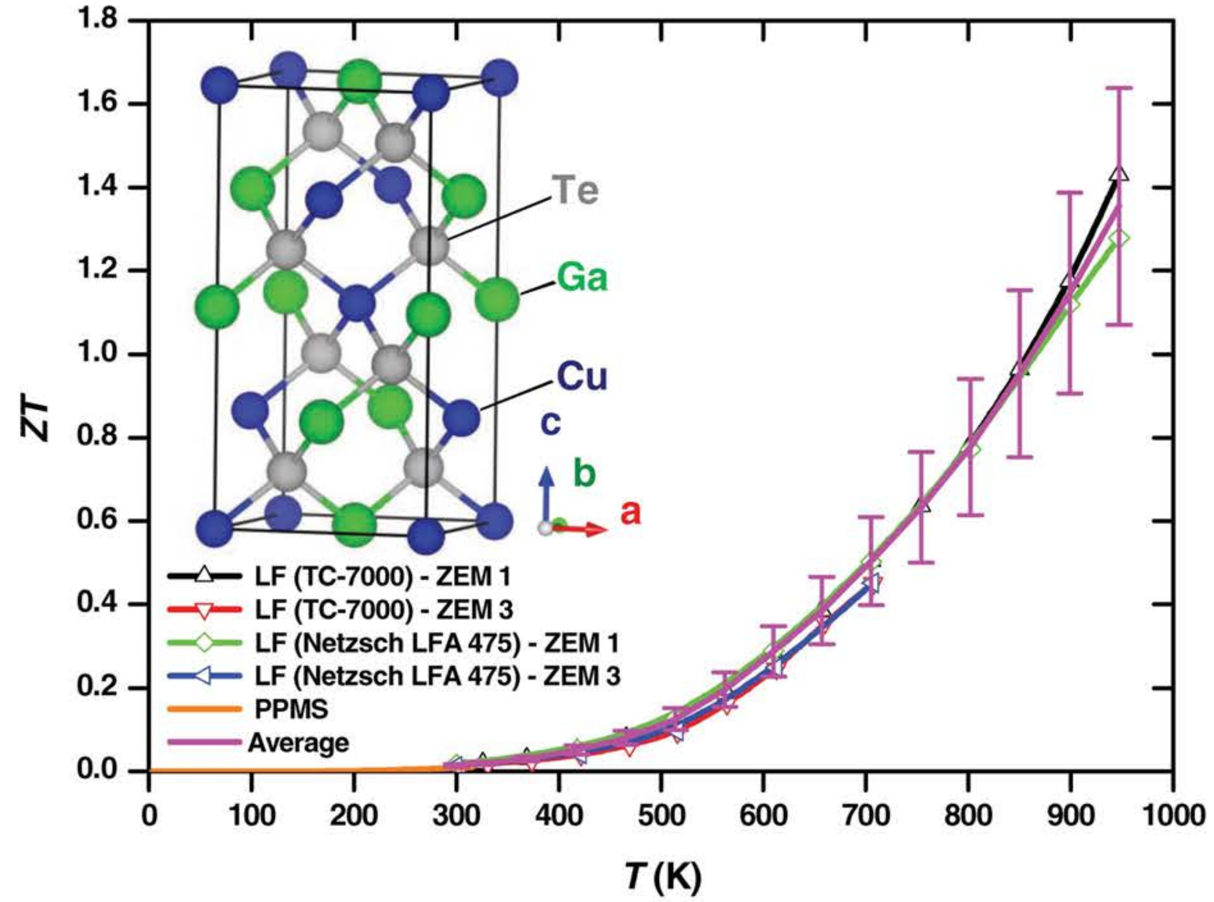


Figure 1. Temperature dependence of the dimensionless figure of merit *ZT* of polycrystalline bulk samples of $CuGaTe_2$. The inset illustrates the crystal structure of $CuGaTe_2$. Considering the uncertainty in the measurements of electrical resistivity, Seebeck coefficient, and thermal diffusivity, the error bars are a maximum of 21% for *ZT*.

カルコパイライト・ $CuGaTe_2$ 高効率熱電材料

Journal of Applied Physics ARTICLE scitation.org/journal/jap

Structure and thermoelectric transport analysis of defect-containing $CuGaTe_2$ prepared by room-temperature high-pressure treatment

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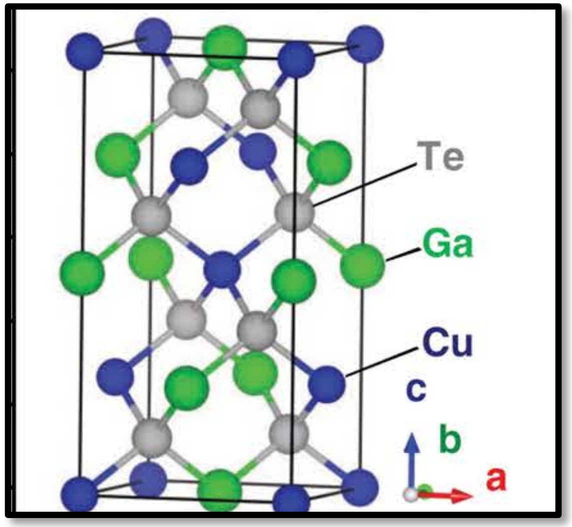
Diamond Mutation
Zn_2Te_2 ⇒ $CuGaTe_2$
($2Zn^{2+}$ ⇒ $Cu^+ + Ga^{3+}$)



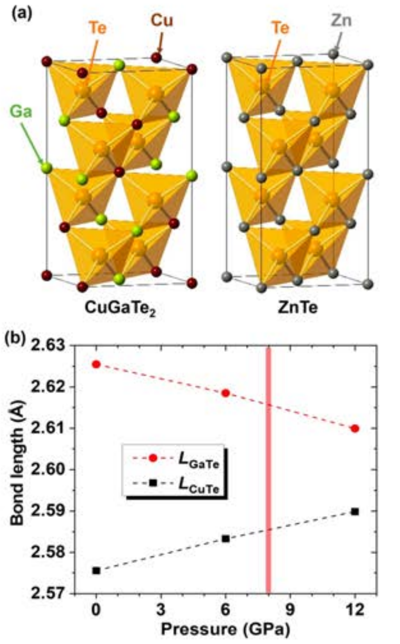


FIG. 3. (a) Crystal structure of chalcopyrite $CuGaTe_2$ and zinc-blende ZnTe. (b) Dependence of bond length between Cu and Te sites (L_{CuTe}) and Ga and Te sites (L_{GaTe}) on pressure intensity of the RTHP treatment. The data at 0 GPa reflect $CuGaTe_2$ before the RTHP treatment. The red line represents the pressure at which $CuGaTe_2$ exhibits pressure-induced structural modification.

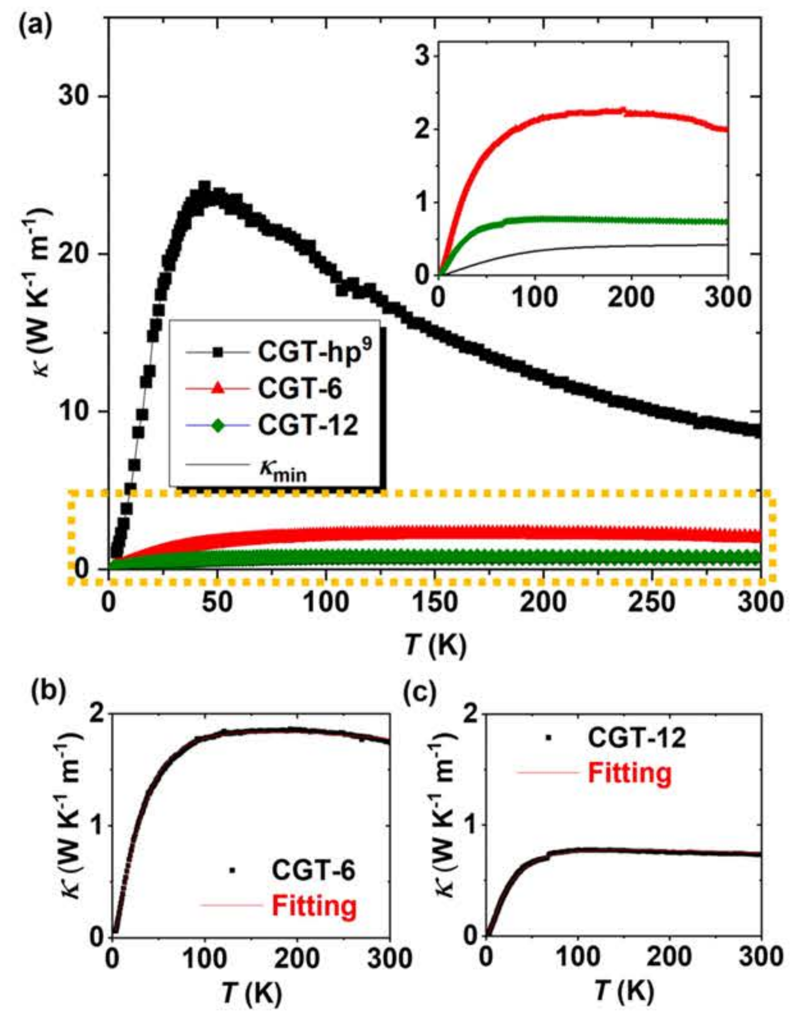
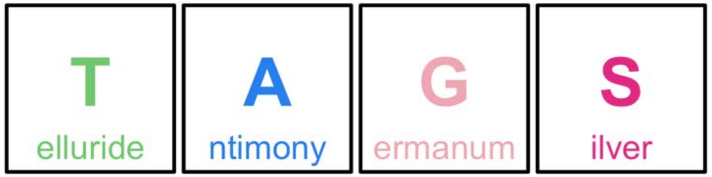


FIG. 1. (a) Temperature dependence of κ of CGT-6, CGT-12, and CGT-hp[9] together with the theoretical minimum thermal conductivity κ_{min}. The upper-right inset presents an expanded view of the rectangular area enclosed by the orange dotted lined in (a). Comparisons between the experimental and fitting data for κ_{lat} for (b) CGT-6 and (c) CGT-12.

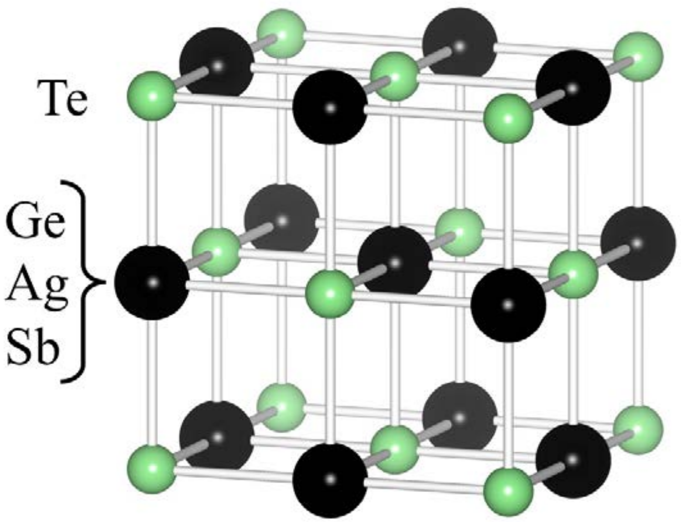
$(GeTe)_x(AgSbTe_2)_{1-x}$

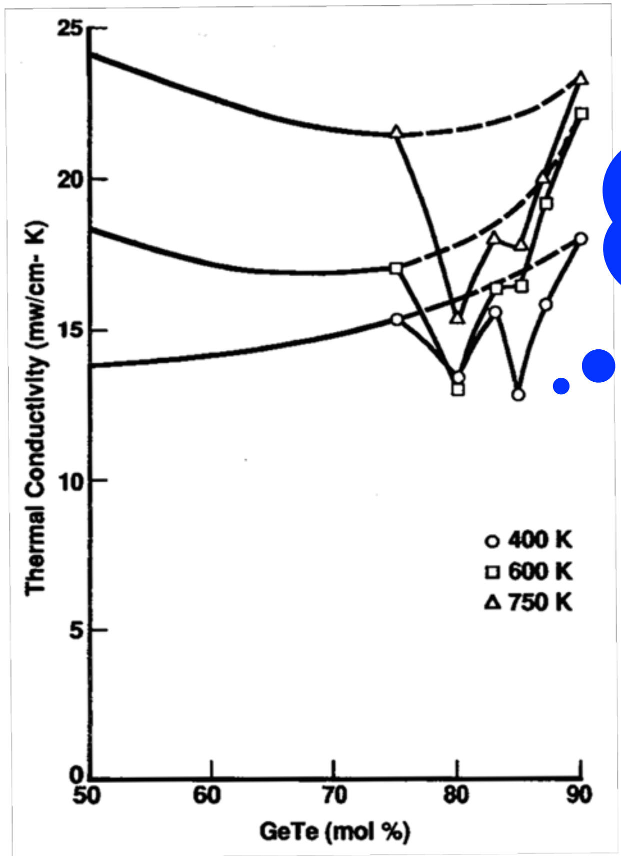
[1] A. J. Thompson, *et al.*, J. Electron. Mat. 38, 1407 (2009).
[2] E. Skrabek, *et al.*, March 1976. U.S. Patent No. 3945855.

擬2元合金： $(GeTe)_x(AgSbTe_2)_{1-x}$:
- 良い熱電特性 ZT~1.5[1]
- 異常な κ ：GeTe 80%[2]
- 結晶構造からミステリーを解明する？



NaCl構造





スピノダル・ナノ分解

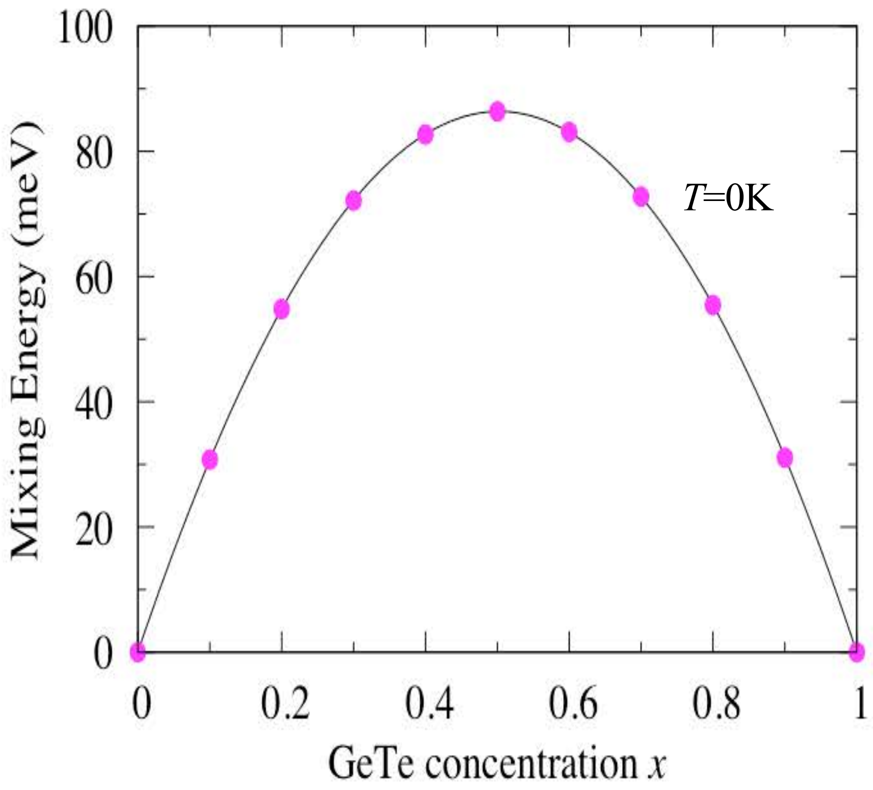
第一原理計算:

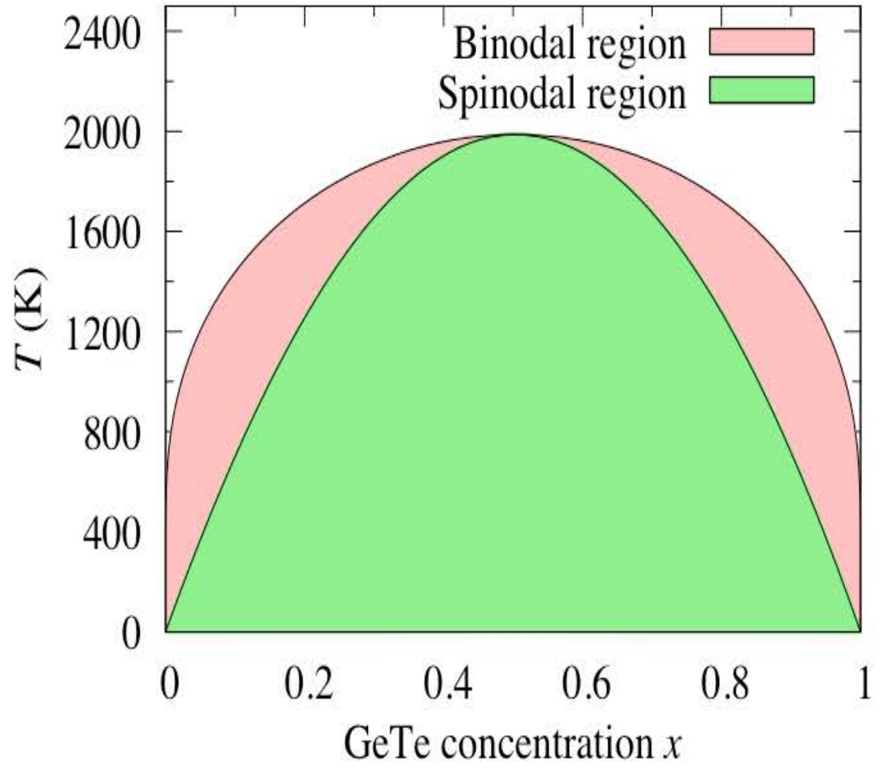
H. Shinya, *et al.*, Jpn. J. Appl. Phys. 53, 111201 (2014).

- **混合エネルギー:**

$$\Delta E(x) = E((\mathrm{GeTe})_x(\mathrm{AgSbTe_2})_{1-x}) - [xE(\mathrm{GeTe}) + (1-x)E(\mathrm{AgSbTe_2})]$$

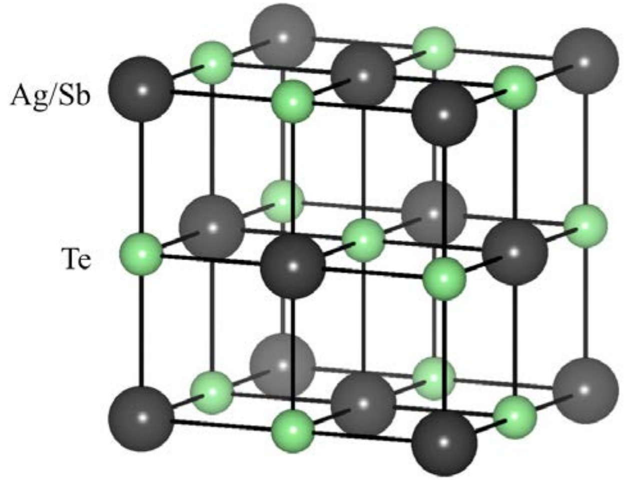
- **自由エネルギー:** $\Delta F(x) = \Delta E(x) - T\Delta S$
- **スピノダル線:** $\partial^2 F/\partial x^2 = 0$
- **バイノーダル線: 共通接線**





AgSbTe$_2$

[1] J.D. Sugar, *et al.*, J. Alloy. Compd. **478**, 75 (2009).
[2] J. Ma, *et al.*, Nature Nanotechnology **8**, 445 (2013).

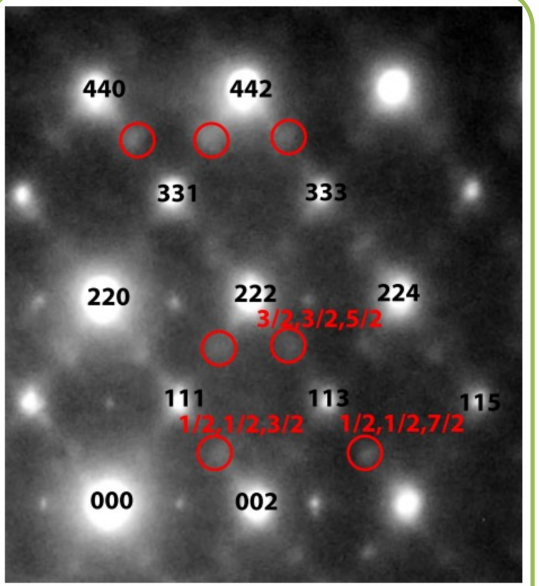


結晶構造:

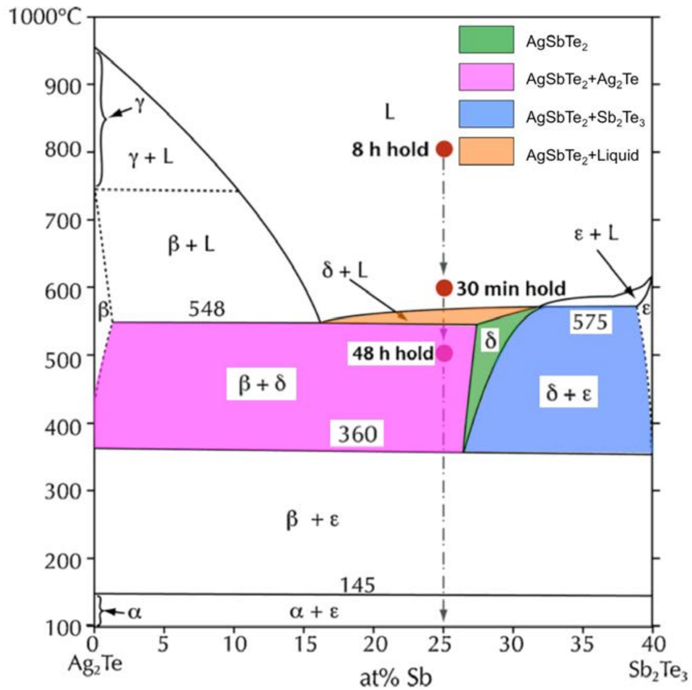
- **NaCl型**
- **カチオンの配置が不明**
  - **複雑な相図**
  - **製造過程で構造が変化？**

Random distribution ?[1]

or



Arrange systematically ?[2]

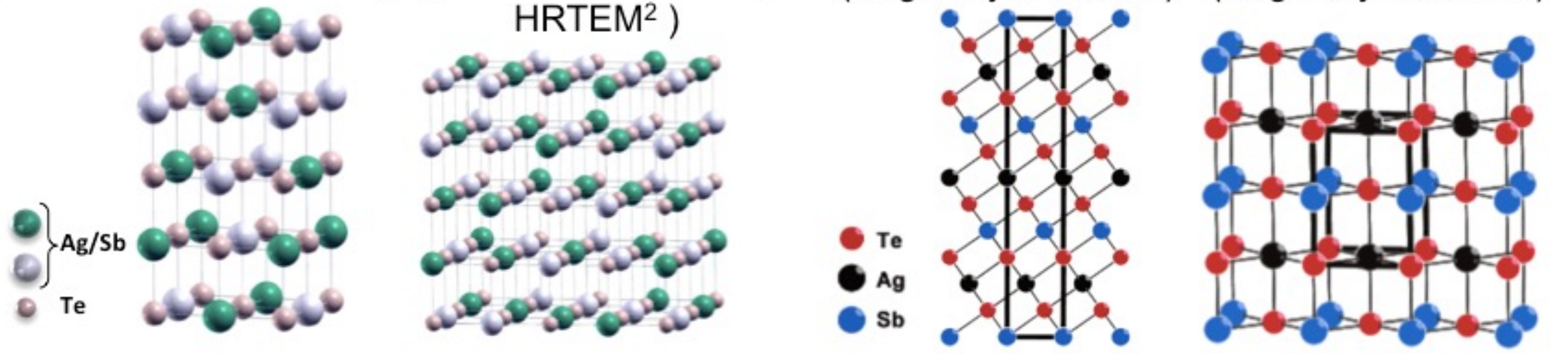


TAGSにおける異常なκの可能性？

[1] K. Hoang, *et al.*, Phys. Rev. Lett., 99, 156403 (2007).
[2] J. Ma, *et al.*, Nature Nanotechnology 8, 445 (2013).
[3] E. Quarez *et al.*, J. Am. Chem. Soc. 127, 9177 (2005).

① 多重相の出現:

$I4_1/amd$ (bct) (Monte Carlo simulation[1]) | $Fd\bar{3}m$ (fcc) (*ab initio* calculation[1], HRTEM[2]) | $R\bar{3}m$ (rhombohedral) (single crystal XRD[3]) | $P4/mmm$ (tetragonal) (single crystal XRD[3])

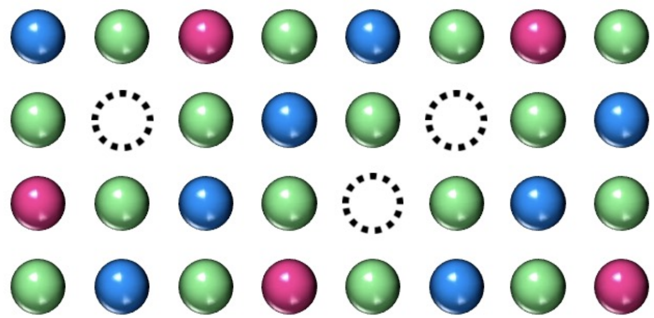


② 原子空孔秩序相:

Non-stoichiometric compounds

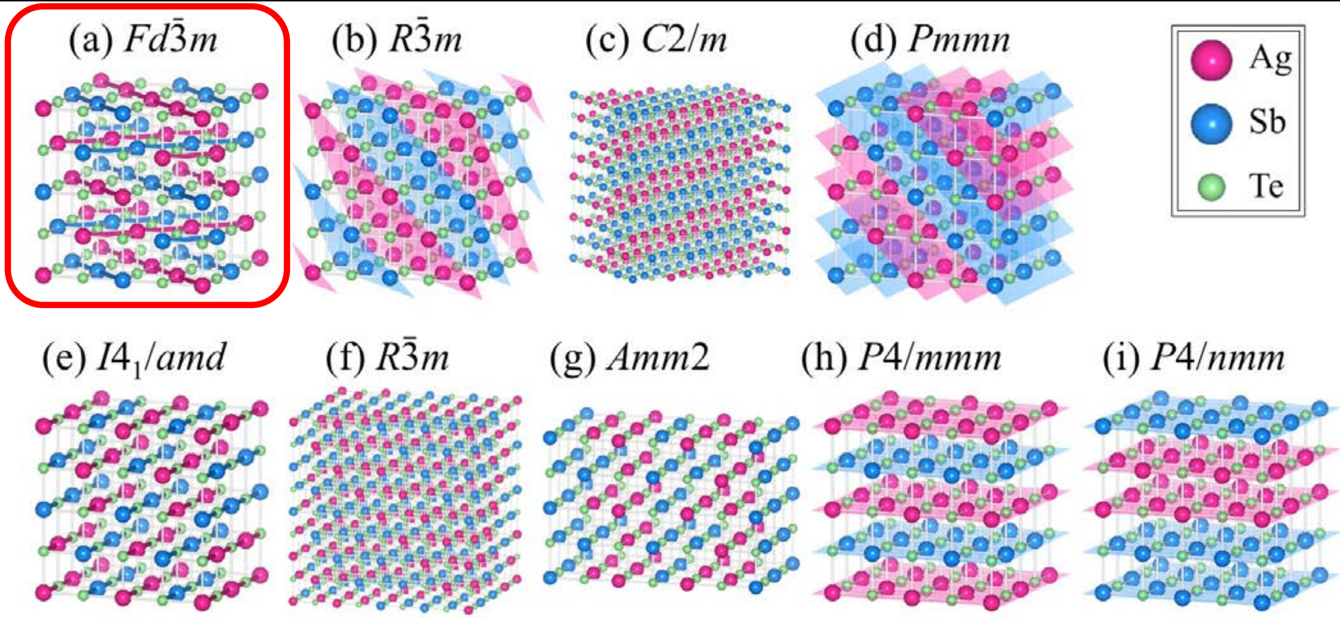
Sb_2Te_3, $Ag_2Sb_4Te_7$, $Ag_7Sb_{11}Te_{20}$, $Ag_4Sb_6Te_{11}$, $Ag_5Sb_7Te_{13}$, $Ag_{15}Sb_{19}Te_{36}$, $Ag_{10}Sb_{12}Te_{23}$, ...

[1] James P. Mchugh, *et al.*, U. S. Patent 3,073,883 (1963).
[2] J. Ma, *et al.*, Nature Nanotechnology 8, 445 (2013).
[3] T. L. Anderson, *et al.*, Acta Crystallogr. Sec. B 30, 1307 (1974).



$AgSbTe_2$の安定構造

H. Shinya, *et al.*, Jpn. J. Appl. Phys. 53, 111201 (2014).



Stable

Unstable

Label	Space group		H_f(meV)	Previous works
(a)	227	$Fd\bar{3}m$	-190.863	First principles calculation[1] HRTEM[2]
(b)	166	$R\bar{3}m$	-189.588	Single crystal XRD[3]
(c)	12	$C2/m$	-158.139	-
(d)	59	$Pmmn$	-157.887	-
(e)	141	$I4_1/amd$	-136.233	Monte Carlo Simulation[1]
(f)	166	$R\bar{3}m$	-124.632	-
(g)	38	$Amm2$	-97.676	-
(h)	123	$P4/mmm$	-84.651	Single crystal XRD[3]
(i)	129	$P4/nmm$	-83.602	-

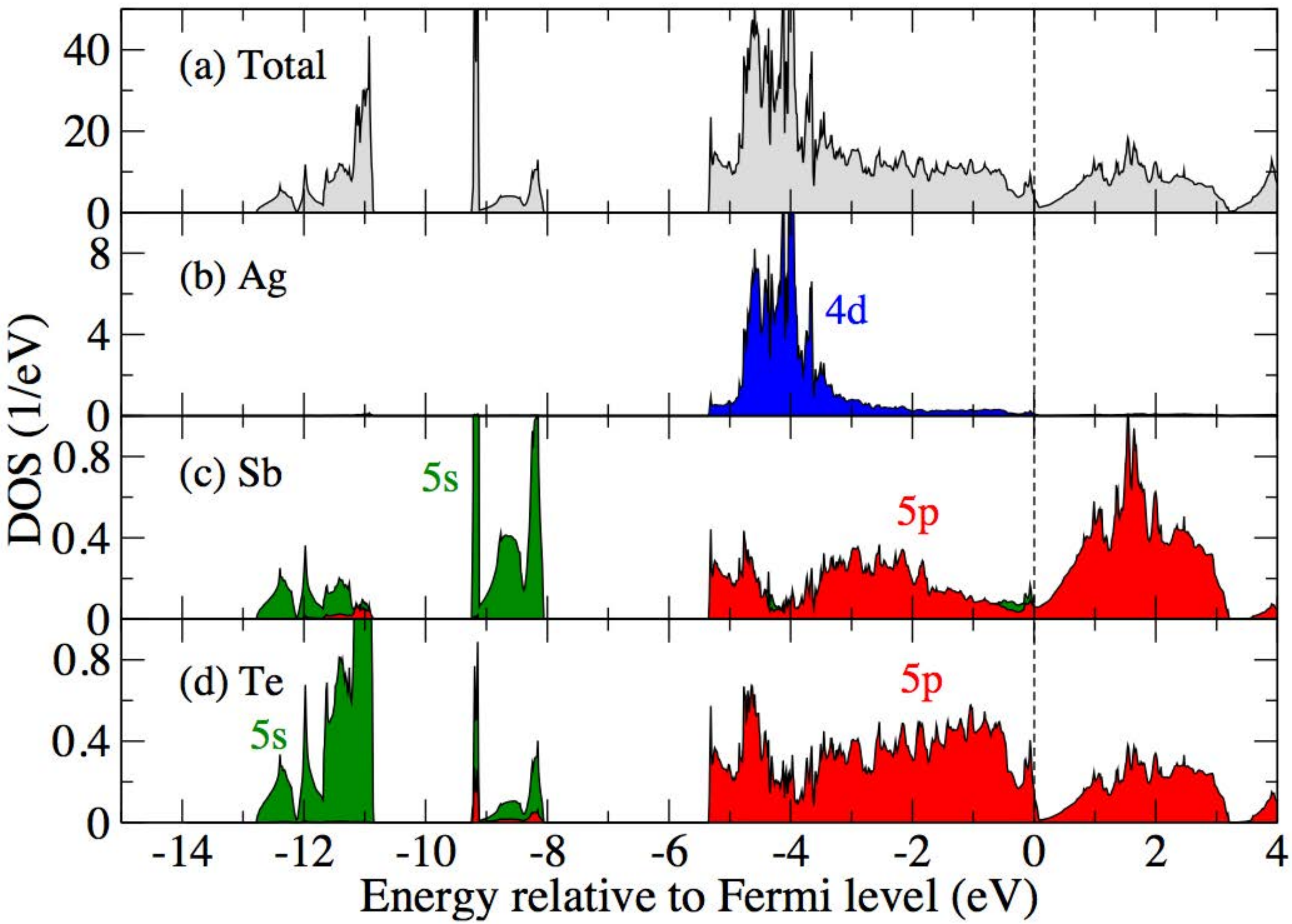
安定性の起源…？

[1] K. Hoang, *et al.*, Phys. Rev. Lett., 99, 156403 (2007).
[2] J. Ma, *et al.*, Nature Nanotechnology 8, 445 (2013).
[3] E. Quarez *et al.*, J. Am. Chem. Soc. 127, 9177 (2005).

価電子帯のトップが反結合状態→金属イオンの原子空孔

状態密度: H. Shinya, *et al.*, Jpn. J. Appl. Phys. 53, 111201 (2014).

・**価電子帯トップ: Te-5*p* 状態** ⇒ Ag-4d、Sb-5sと混成

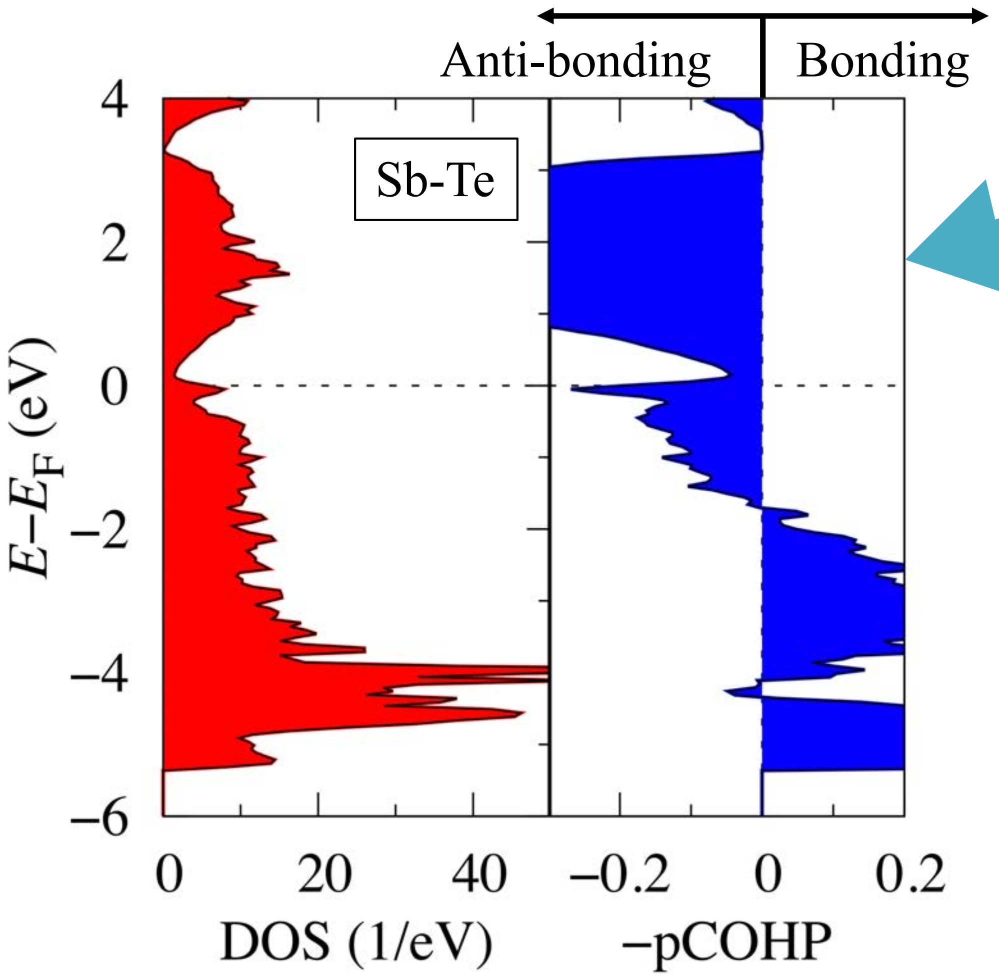


価電子帯のトップが反結合状態→金属イオンの原子空孔

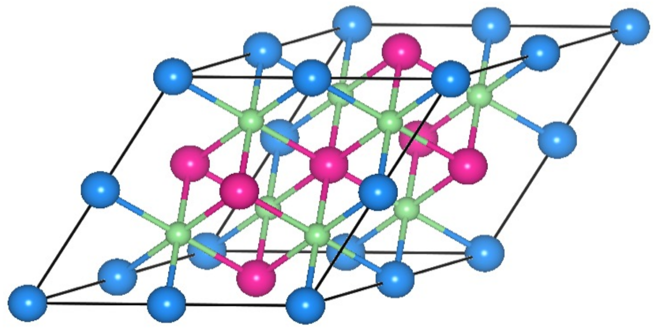
H. Shinya, *et al.*, Jpn. J. Appl. Phys. 53, 111201 (2014).

Crystal Orbital Hamilton Population (COHP) between Sb-5*s* and Te-5*p*:

- **Strong coupling between Sb-5*s* and Te-5*p* (Ag-4*d* and Te-5*p*)**
  → push up Te-5*p* states



Total energy
॥
Atomic energy
+
Local bonding energy



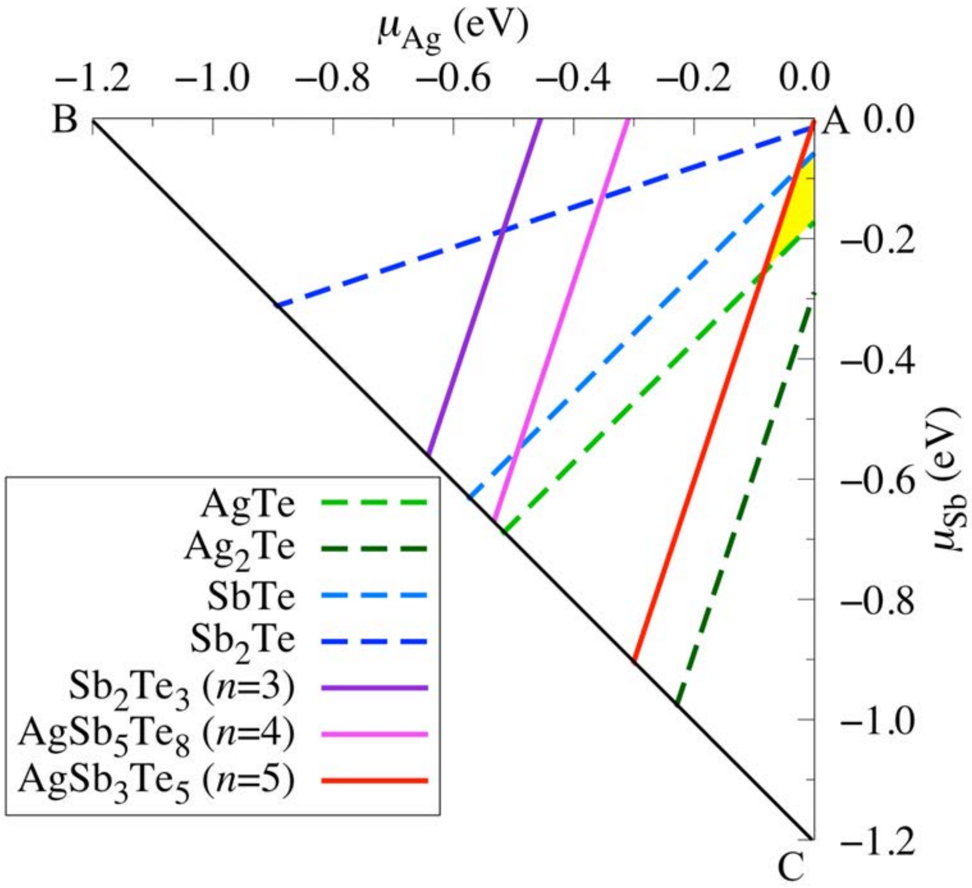
(a) $Fd\bar{3}m$

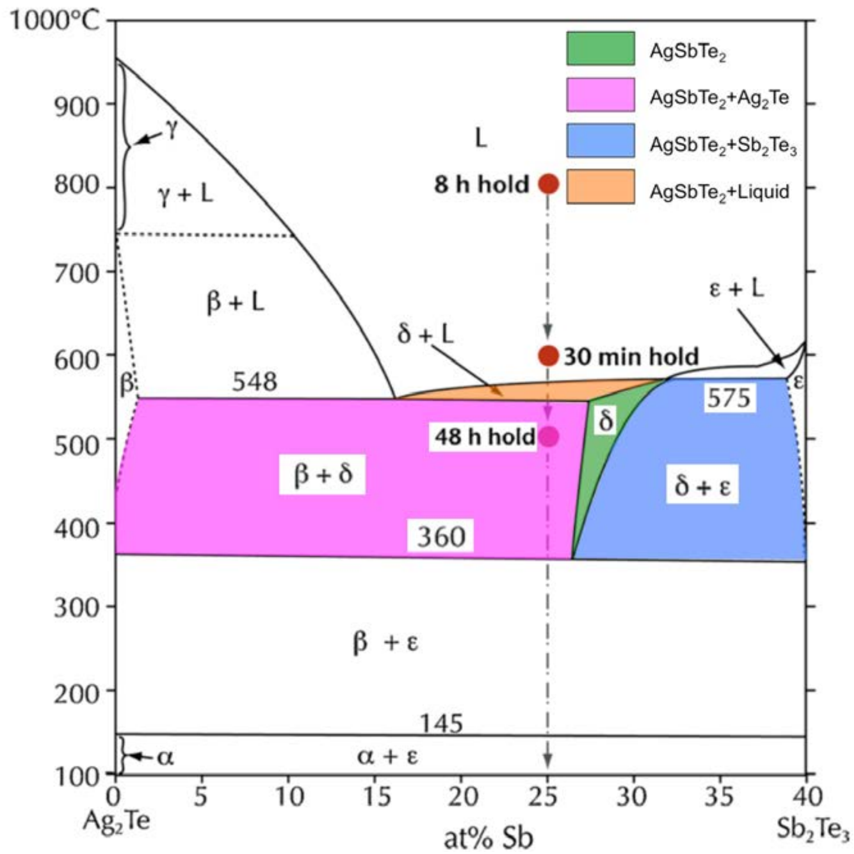
Crystal growth condition

Thermal equilibrium condition:

- **$AgSbTe_2$ is stable in the yellow area**
  - **Consistent with experimental phase diagram**
  - **Important for making single phase $AgSbTe_2$ to control μ**

J.D. Sugar, *et al.*, J. Alloy. Compd. 478, 75 (2009).





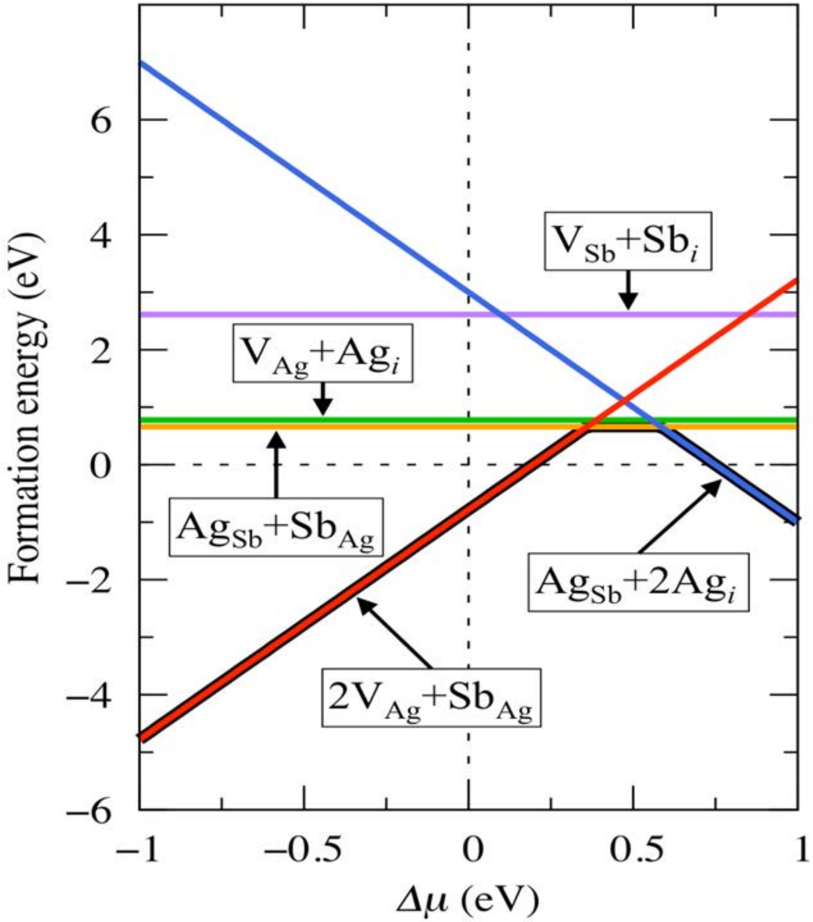
熱平衡条件下での結晶成長

H. Shinya, *et al.*, Jpn. J. Appl. Phys. 53, 111201 (2014).

- 欠陥対［2 V_{Ag}+Sb_{Ag}］の形成エネルギー： 128 atoms supercell

$$\Delta E_F = E(\mathrm{Ag_{29}Sb_{33}Te_{64}}) - E(\mathrm{Ag_{32}Sb_{32}Te_{64}}) + \underbrace{3\mu_{\mathrm{Ag}} - \mu_{\mathrm{Sb}}}_{\Delta\mu}$$

$$n(\mathrm{AgSbTe_2}) + m(2V_{\mathrm{Ag}} + \mathrm{Sb_{Ag}}) = \mathrm{Ag}_{n-3m}\mathrm{Sb}_{n+m}\mathrm{Te}_{2n}$$



Ag低分圧，Sb高分圧
ミューテーション相

n	Composition	n	Composition
3	Sb_2Te_3	11	$Ag_4Sb_6Te_{11}$
4	$AgSb_5Te_8$	12	$Ag_9Sb_{13}Te_{24}$
5	$AgSb_3Te_5$	13	$Ag_5Sb_7Te_{13}$
6	$Ag_3Sb_7Te_{12}$	14	$Ag_{11}Sb_{15}Te_{28}$
7	$Ag_2Sb_4Te_7$	15	$Ag_6Sb_8Te_{15}$
8	$Ag_5Sb_9Te_{16}$	16	$Ag_{13}Sb_{17}Te_{32}$
9	$Ag_3Sb_5Te_9$	17	$Ag_7Sb_9Te_{17}$
10	$Ag_7Sb_{11}Te_{20}$	18	$Ag_{15}Sb_{19}Te_{36}$

(Red box): Observed experimentally (n = 3, 7, 10, 11, 13, 18)

原子空孔秩序化合物相

Mother Nature's Co-doping:

反結合状態(VBM)が
電子で占有されていて不安定。

$$2V_{Ag}^{-} + Sb_{Ag}^{2+}$$

$$n(AgSbTe_2) + m(2V_{Ag} + Sb_{Ag}) = Ag_{n-3m}Sb_{n+m}Te_{2n}$$

n	Composition	n	Composition	n	Composition
3	**Sb_2Te_3**	**11**	**$Ag_4Sb_6Te_{11}$**	19	$Ag_8Sb_{10}Te_{19}$
4	$AgSb_5Te_8$	12	$Ag_9Sb_{13}Te_{24}$	20	$Ag_{17}Sb_{21}Te_{40}$
5	$AgSb_3Te_5$	**13**	**$Ag_5Sb_7Te_{13}$**	21	$Ag_9Sb_{11}Te_{21}$
6	$Ag_3Sb_7Te_{12}$	14	$Ag_{11}Sb_{15}Te_{28}$	22	$Ag_{19}Sb_{23}Te_{44}$
7	**$Ag_2Sb_4Te_7$**	15	$Ag_6Sb_8Te_{15}$	**23**	**$Ag_{10}Sb_{12}Te_{23}$**
8	$Ag_5Sb_9Te_{16}$	16	$Ag_{13}Sb_{17}Te_{32}$	24	$Ag_{21}Sb_{25}Te_{48}$
9	$Ag_3Sb_5Te_9$	17	$Ag_7Sb_9Te_{17}$		•
10	**$Ag_7Sb_{11}Te_{20}$**	**18**	**$Ag_{15}Sb_{19}Te_{36}$**		• •

In the case of m=1

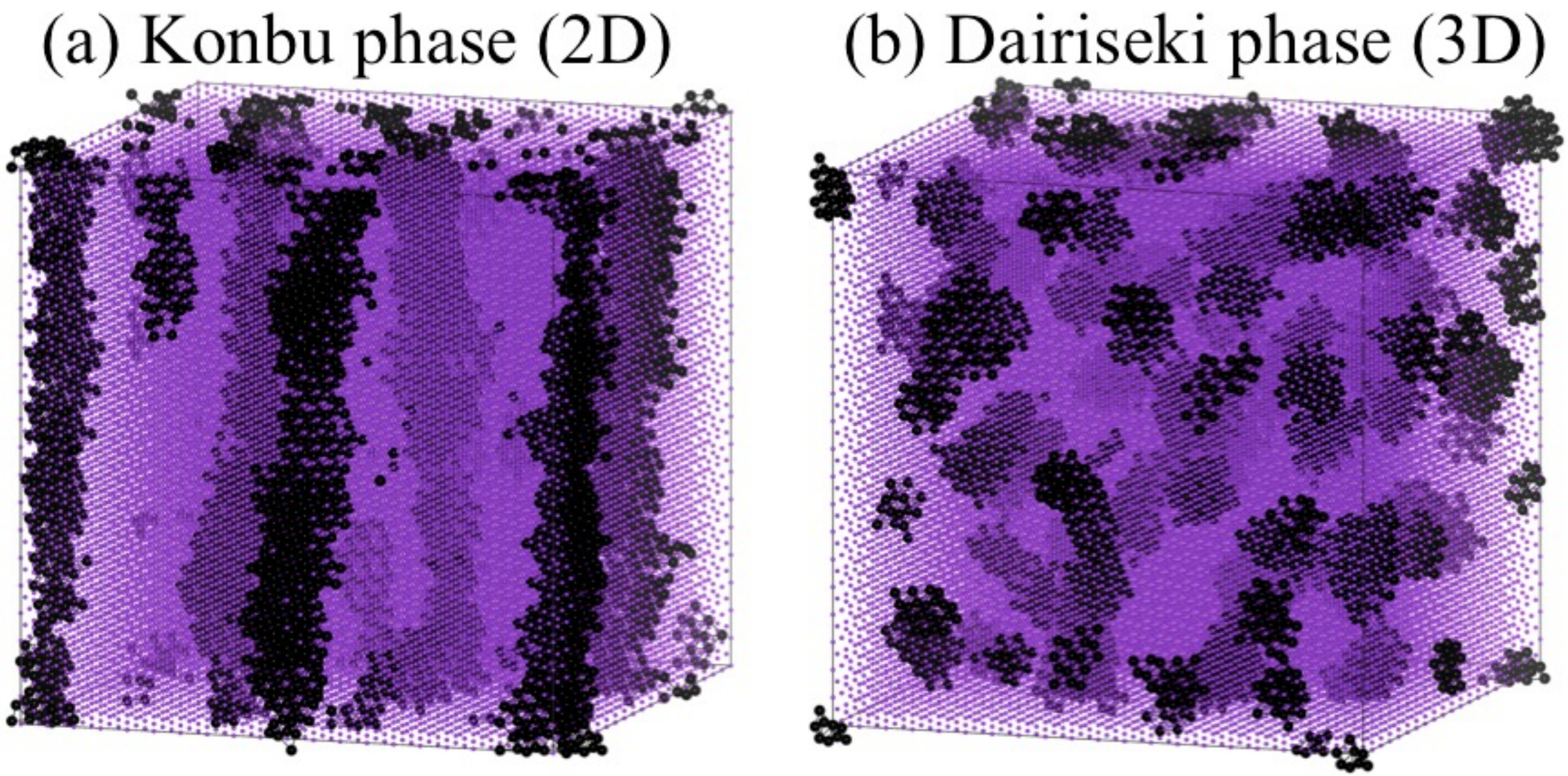
: Observed experimentally

[1] James P. Mchugh, *et al.*, U. S. Patent 3,073,883 (1963).
[2] J. Ma, *et al.*, Nature Nanotechnology 8, 445 (2013).
[3] T. L. Anderson, *et al.*, Acta Crystallogr. Sec. B 30, 1307 (1974).

スピノダル・ナノ分解

H. Shinya, *et al.*, Jpn. J. Appl. Phys. 53, 111201 (2014).

原子空孔秩序化合物相と母体化合物とのスピノダル・ナノ分解:



Discussion

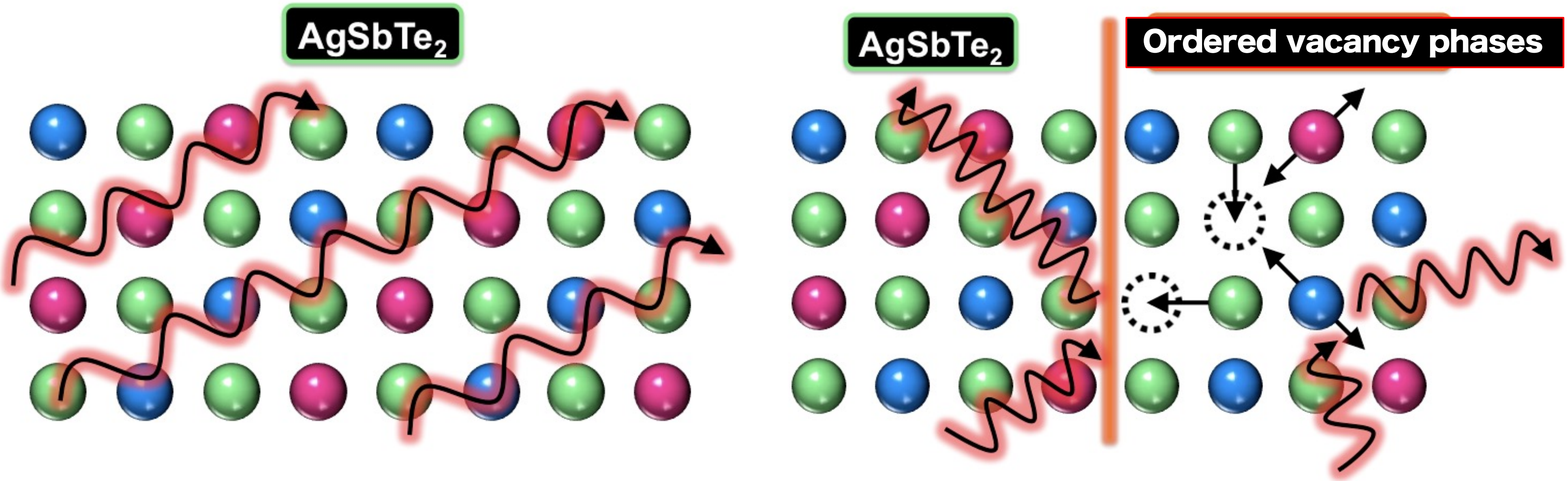
原子空孔秩序化合物相と母体化合物とのスピノダル・ナノ分解:

- **原子空孔秩序化合物相：Sb_2Te_3, $AgSb_5Te_8$, $AgSb_3Te_5$, ...**
- **フォノン散乱： 結晶粒界 と原子空孔秩序化合物相**

= high Vacancy concentration

In **Ag-rich** condition, κ_L is large

In **Ag-poor** condition, κ_L is small



Part 【4】自己再生する不老不死の排気ガスナノ触媒のデザインと実証

■自己再生する不老不死の自動車排気ガス三方触媒

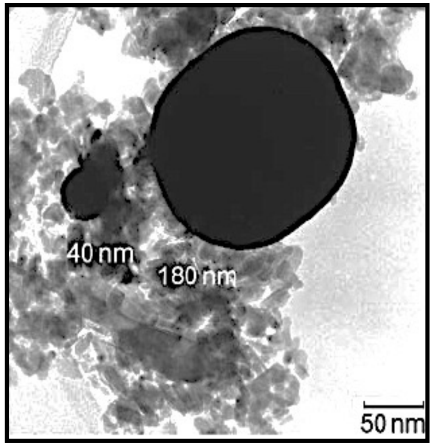
■自動車排気ガスの清浄化

- $CO + O_2 \rightarrow CO_2$ ……………… (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

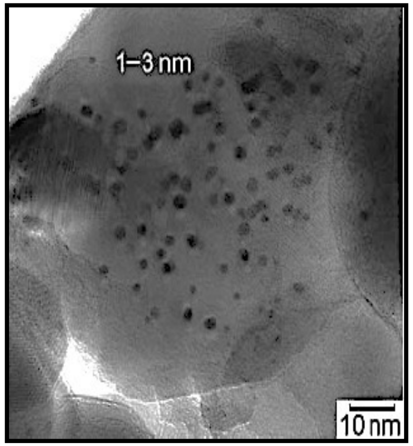
Pt : 南アフリカ 74%, ロシア 14%
Pd : 南アフリカ 25%, ロシア 70%
Rh : 南アフリカ 67%, ロシア 17%

■焼結による触媒機能劣化の問題



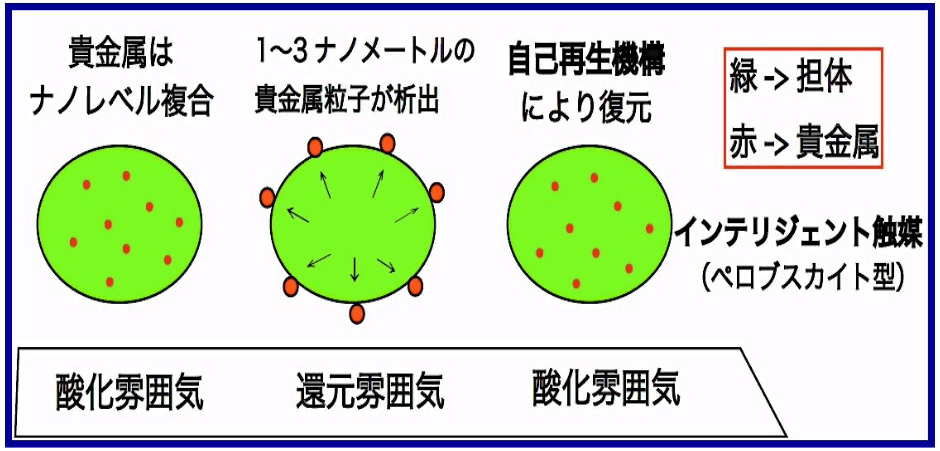
Al_2O_3 担持では焼結のため、触媒機能が消失

焼結の抑制



$CaTi_{0.95}Pt_{0.05}O_3$

自己再生機構:
インテリジェント触媒

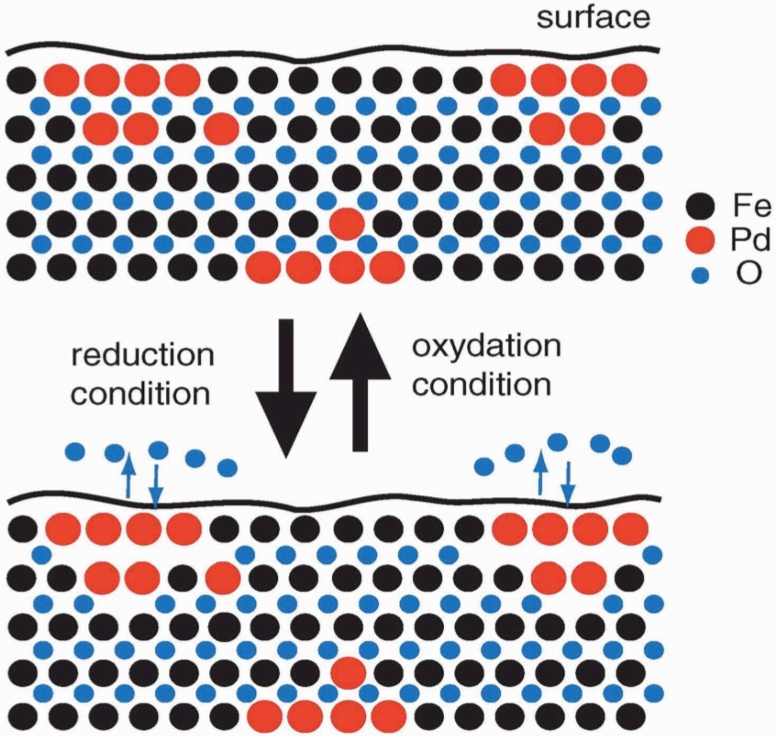


■Y. Nishihara et al., Nature, 418 (2002) 164.
■H. Tanaka et al., Angew. Chem. Int. Ed. 45 (2006) 5998 .

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

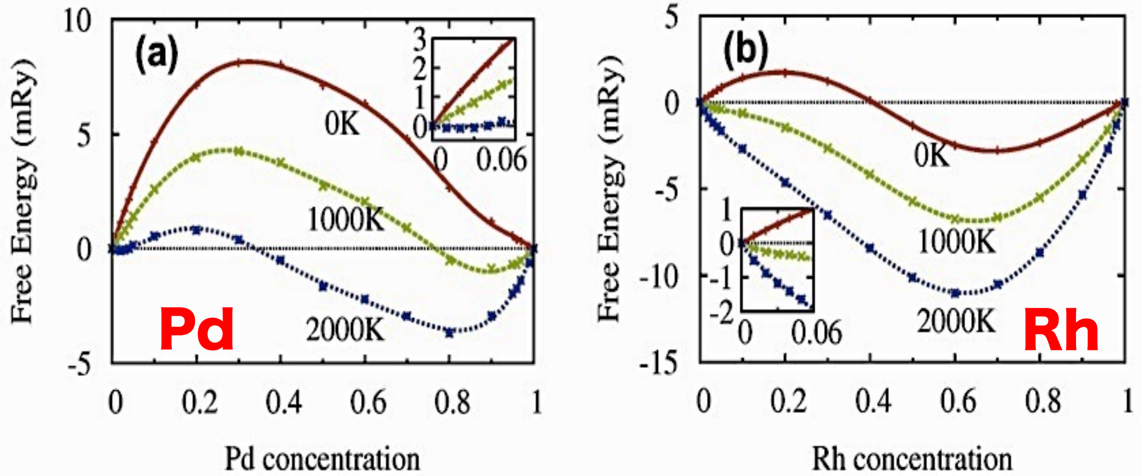
La(Fe, Pd)O_3



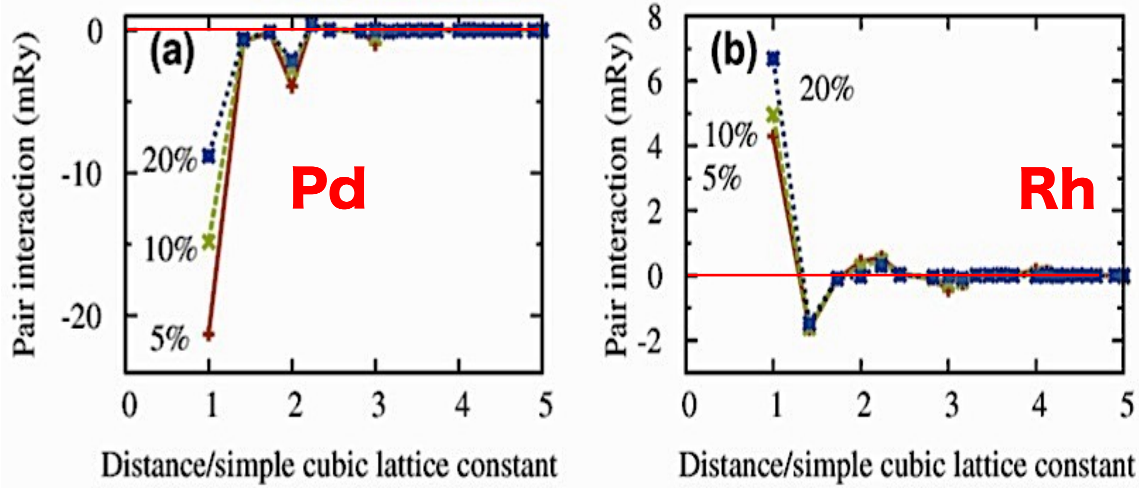
$$V_{ij} = V_{ij}^{Pd\text{-}Pd} + V_{ij}^{Fe\text{-}Fe} - 2\,V_{ij}^{Pd\text{-}Fe}$$

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

■Free Energy of La(Fe,M)O_3



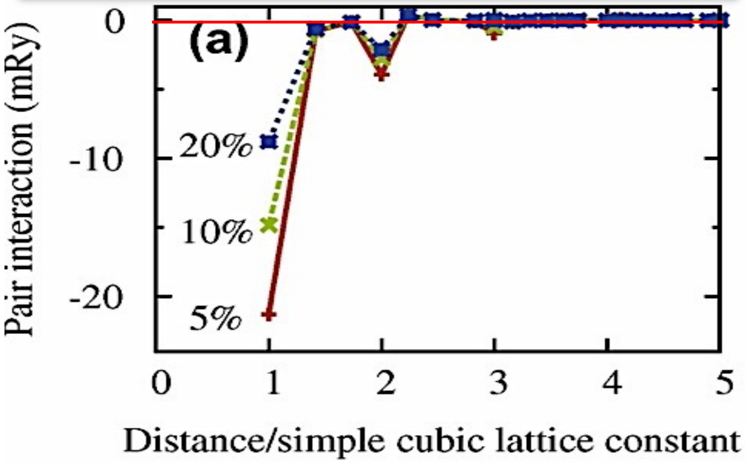
■Chemical Pair Interactions

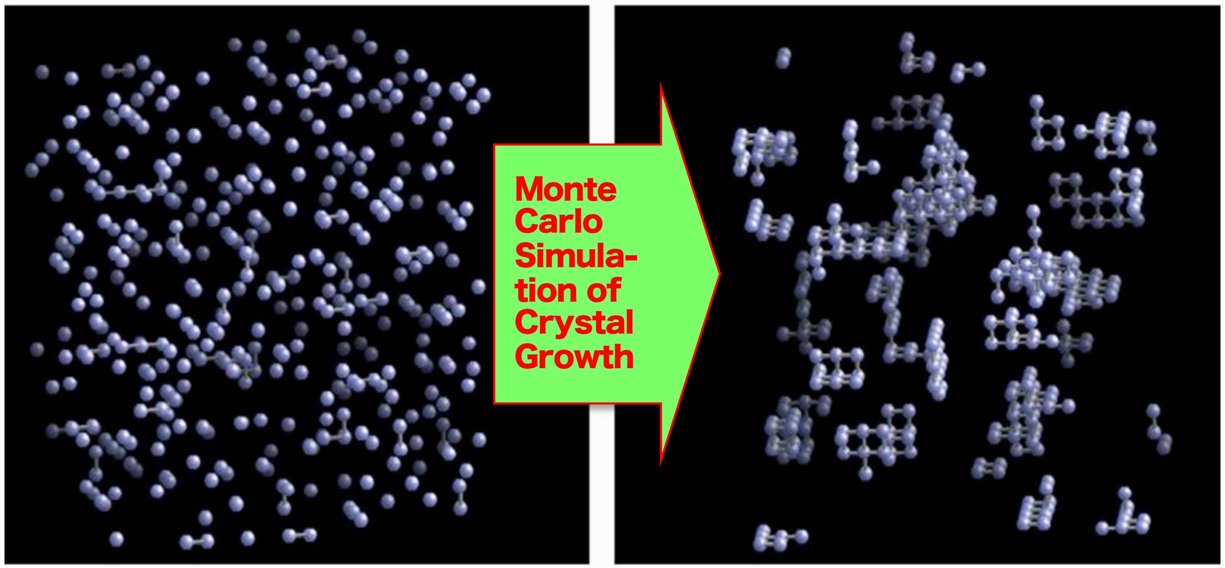


■ H. Kizaki et al., Applied Physics Express, 1 (2008) 104001.
■ H. Kizaki et al., Chemical Physics Letters, 579 (2013) 85.

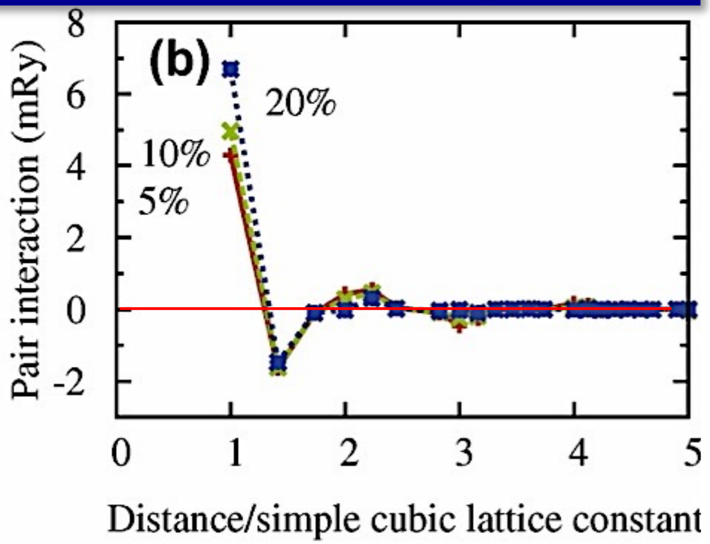
H. Kizaki and H. Katayama-Yoshida, Chemical Physics Letters, 579 (2013) 85.

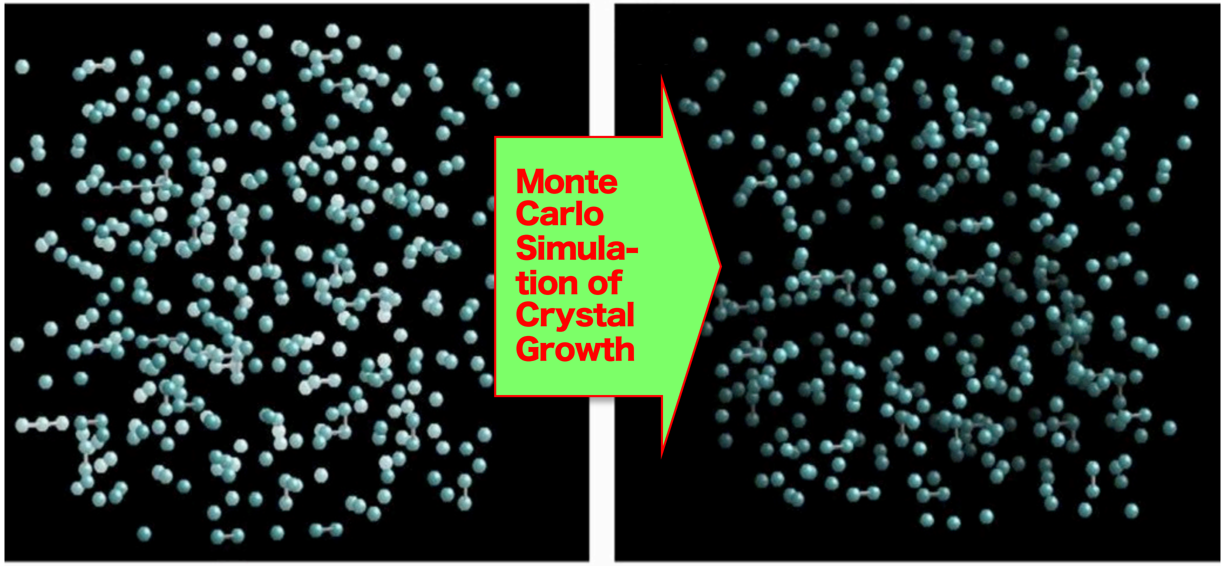
La(Fe,Pd)O_3





La(Fe,Rh)O_3



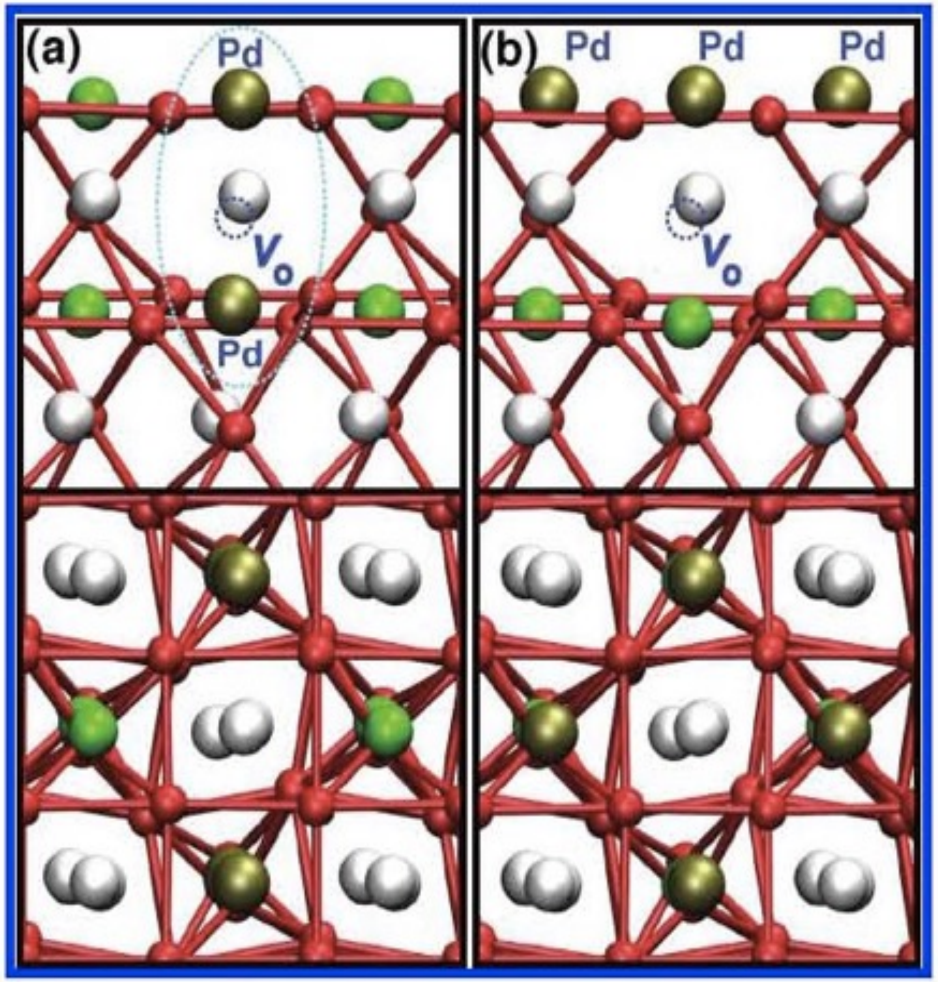


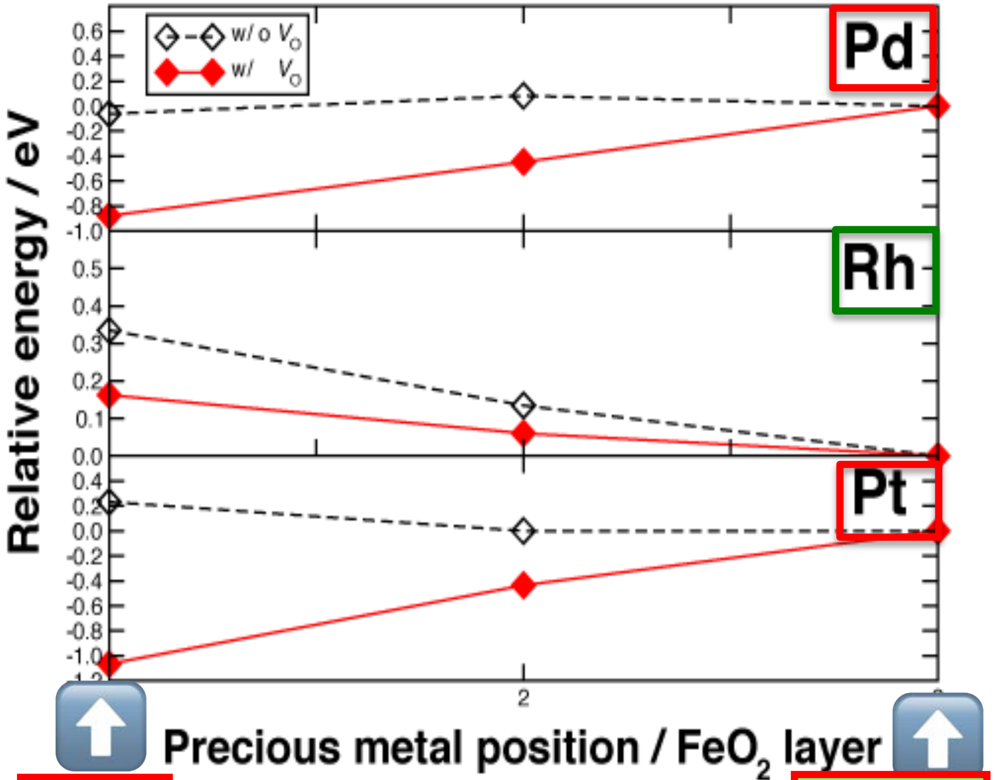
JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
133 (2011) 18506.
COMMUNICATION

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[∥]



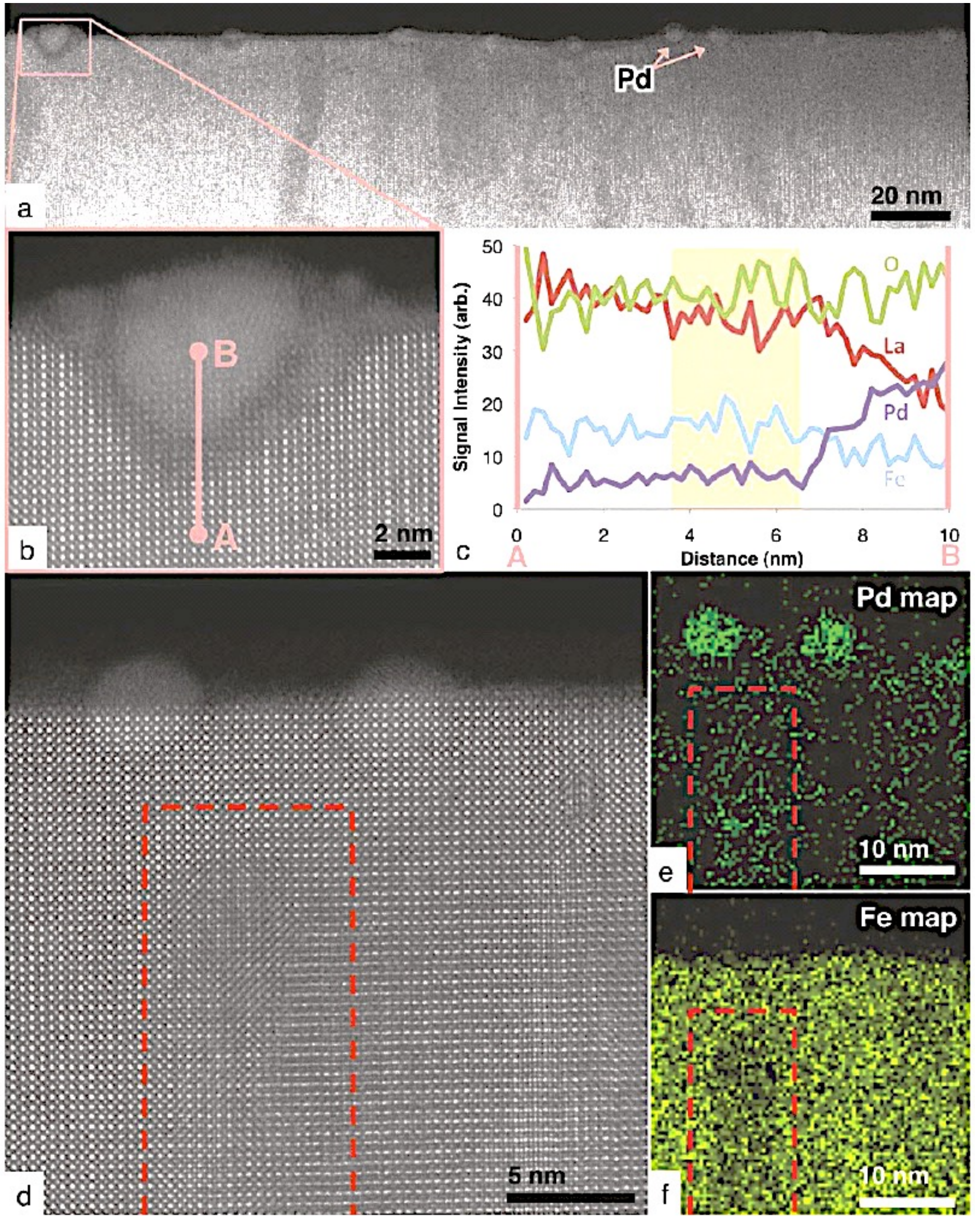


表面

バルク

■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



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

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(Pd-rich, Fe-poor)

■昆布相
(Pd-rich, Fe-poor)