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OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly journals in all aspects of Science, Engineering, Management and Technology journals. OMICS Group has been instrumental in taking the knowledge on Science & technology to the doorsteps of ordinary men and women. Research Scholars, Students, Libraries, Educational Institutions, Research centers and the industry are main stakeholders that benefitted greatly from this knowledge dissemination. OMICS Group also organizes 300 International conferences annually across the globe, where knowledge transfer takes place through debates, round table discussions, poster presentations, workshops, symposia and exhibitions.

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OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Pharma scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bengaluru and Mumbai.

Ceramics-2016 (Aug. 17-18, Chicago, US) (OMIC Int'l Conf.)

New Comprehenisive 'Defect Crystal Chemistry' Approach to Defect-Fluorite (DF) Oxides; $M_{1-y}Ln_yO_{2-y/2}$

(M^{4+} =Zr, Hf, U, Th, Pu, Np, *etc*, Ln^{3+}= lanthanide)

- New model to coupled Non-Vegardianity & Non-Random Defect Structure-

Akio Nakamura (ASRC, JAEA)

Proposal of a comprehensive Defect Crystal Chemistry (DCC) model for highly-defective DF oxide solid solutions (ss)

with various electrochem., ceramic & nulcear *etc* appli's,

but their real physical / chemical face largely ellusive still now,

clarifying macroscopic lattice parameter (a_0(ss)) → microscopic mutually non-random detailed cation ↔ anion coordination structure behaviour →

New σ(ion)(max) & defect-thermodynamic description

(Key role of Mössbauer, NMR & EXAFS *etc* local-structure data)

Highly-Defective DF Oxides MO_2-$LnO_{1.5}$ = $M_{1-y}Ln_yO_{2-y/2}(\underline{Vo})_{y/2}$

- Structure, Property & Applications Issues -

Key Target Properties;
Long-term σ(ion), phase & structure stability, radiation tolerance, catalytic activity & bio-compatibility, mechan. strength *etc.*

for

Electrochemical, Nuclear & Ceramic Appls;
Solid electrolytes for O_2 sensors & for SOFC, Nucl. fuels / waste-form, TBC, Catalyst, Refrac. & Structure Ceramics, & Synthetic Teeth / Jewels

Various local (defect) & crystal-structure studies:

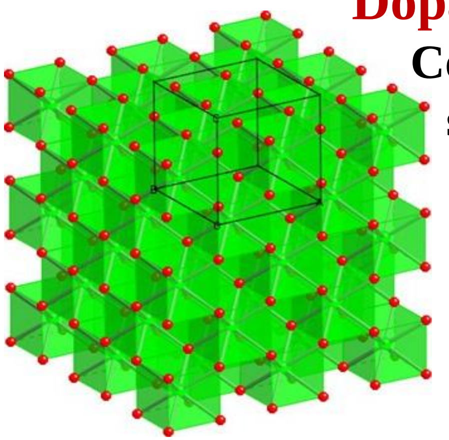
Diffraction (XRD, ND, ED) & Spectroscopic (NMR, XAFS, Moessbauer, Raman,) &Theoretic (defect-chem., statistical-thermodyn.(QC, CVM) & Comput.'l (Calphad, MD, MC, DFT ab-initio calculations) methods.

Yet, 'what is the real face DF oxides? ' remains largely ellusive !

DF Oxides: Solid Solution (ss) of F $M^{4+}O_2$ and C $Ln^{3+}O_{1.5}$

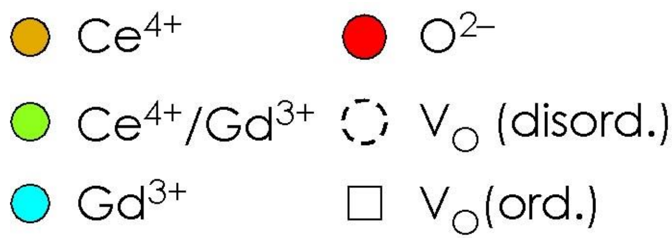
Dopant(Ln^{3+})-Vo & Vo-Vo *etc* interactions →

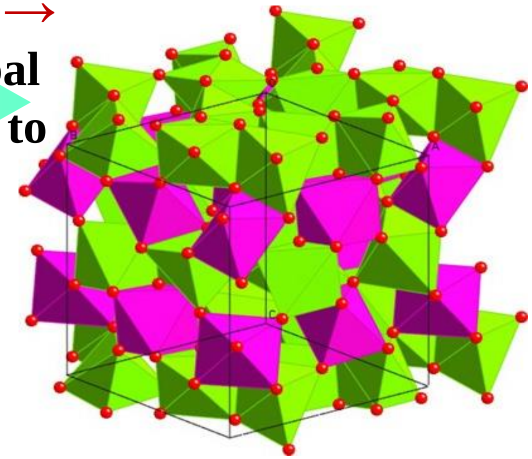
Complex non-random / distorted local / global structure formation beyond naive random to Ln^{3+}-Vo associative one presumably for simply F-C binary M^{4+}=Ce(Th)



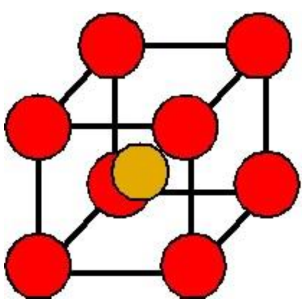
Ce(Th,U,Pu)O_2

(except M^{4+}=Zr & Hf)

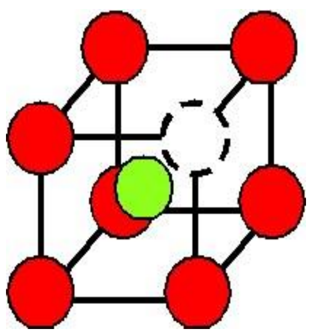




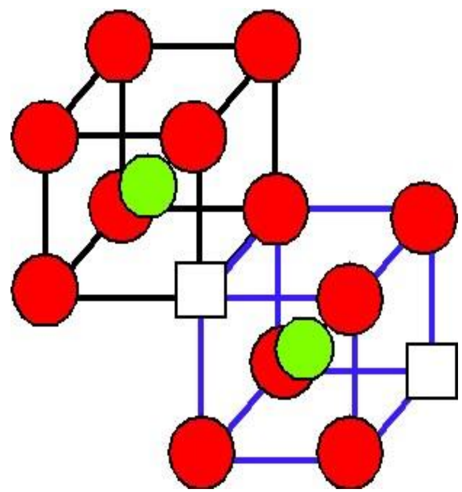
C-type $GdO_{1.5}$



(CN=8)

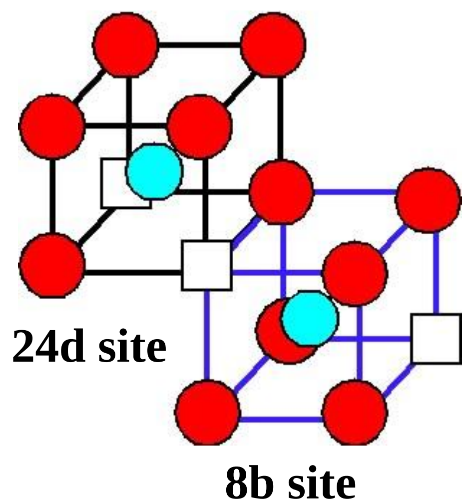


defect fluorite F-phase



C-phase

(CN=8-2y)



(CN=6)

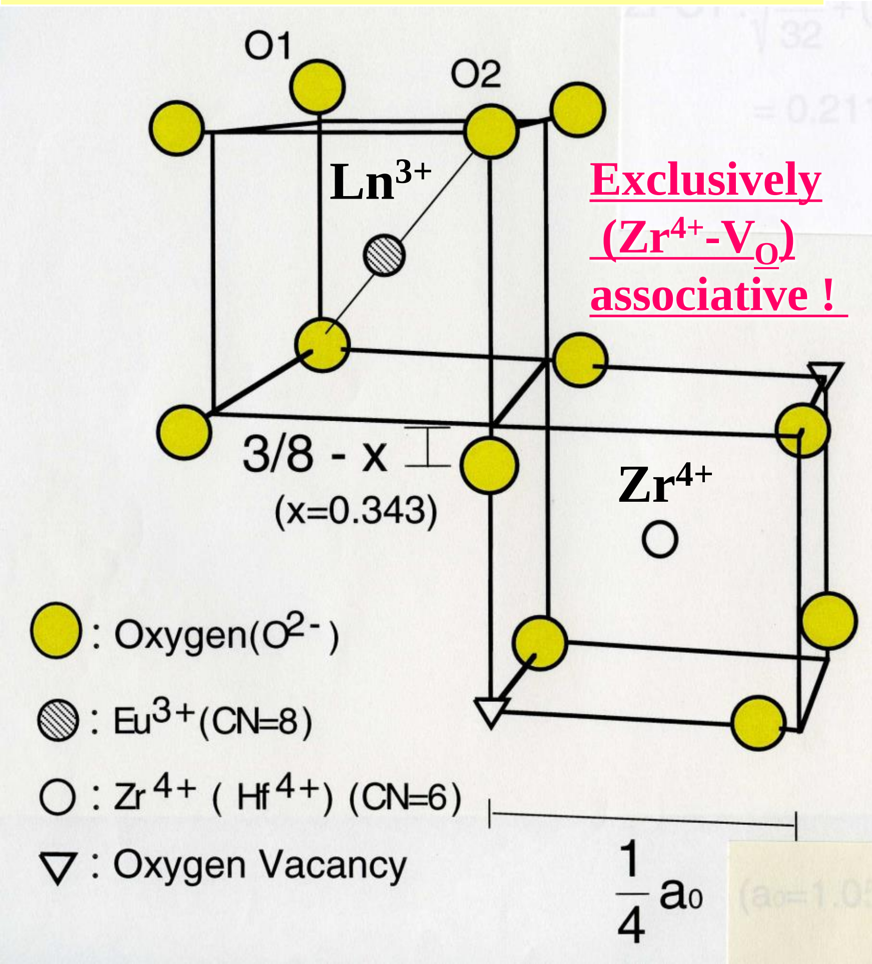
• Stabilized M^{+4} = Zr (Hf) : Intermediate pyrochlore (P) (& δ) ordering

Pure $Zr(Hf)^{4+}O_2$: *monocl*.CN=7
(r_cVIII)=0.084(83)nm <<0.097nm for Ce^{4+})

Pyrochlore(P): $Ln_2Zr_2O_7$ (at *y*=0.5):
$[Ln^{3+}{}_2\,(VIII)]_A\,[Zr^{4+}{}_2(VI)]_B O(1)_6 O(2)_1$
for larger Ln^{3+} (=La-Gd)

$LnO_{1.5}$ ↑ →

Stabilized Cubic $ZrO_2(HfO_2)$:
$(Zr(Hf))_{1-y}Ln_yO_{2-y/2}$
(~0.15-0.20 ≤ y ≤ ~0.80 (CN=8-2y)

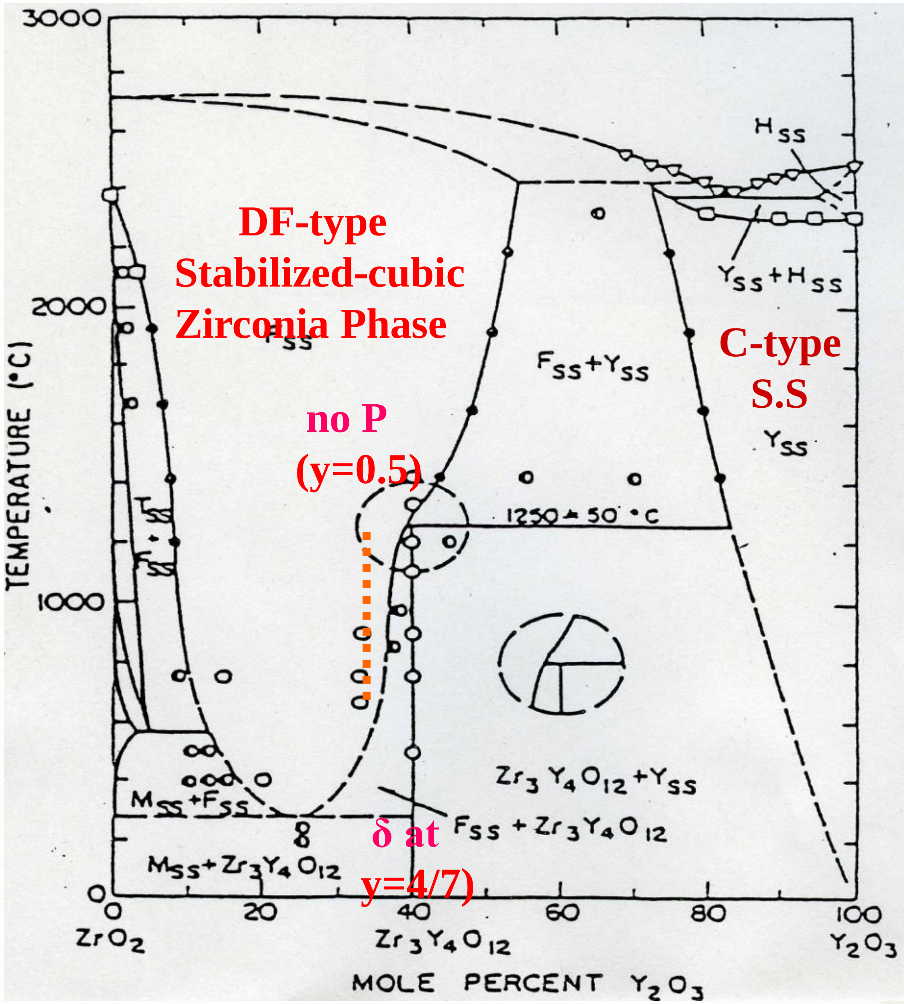


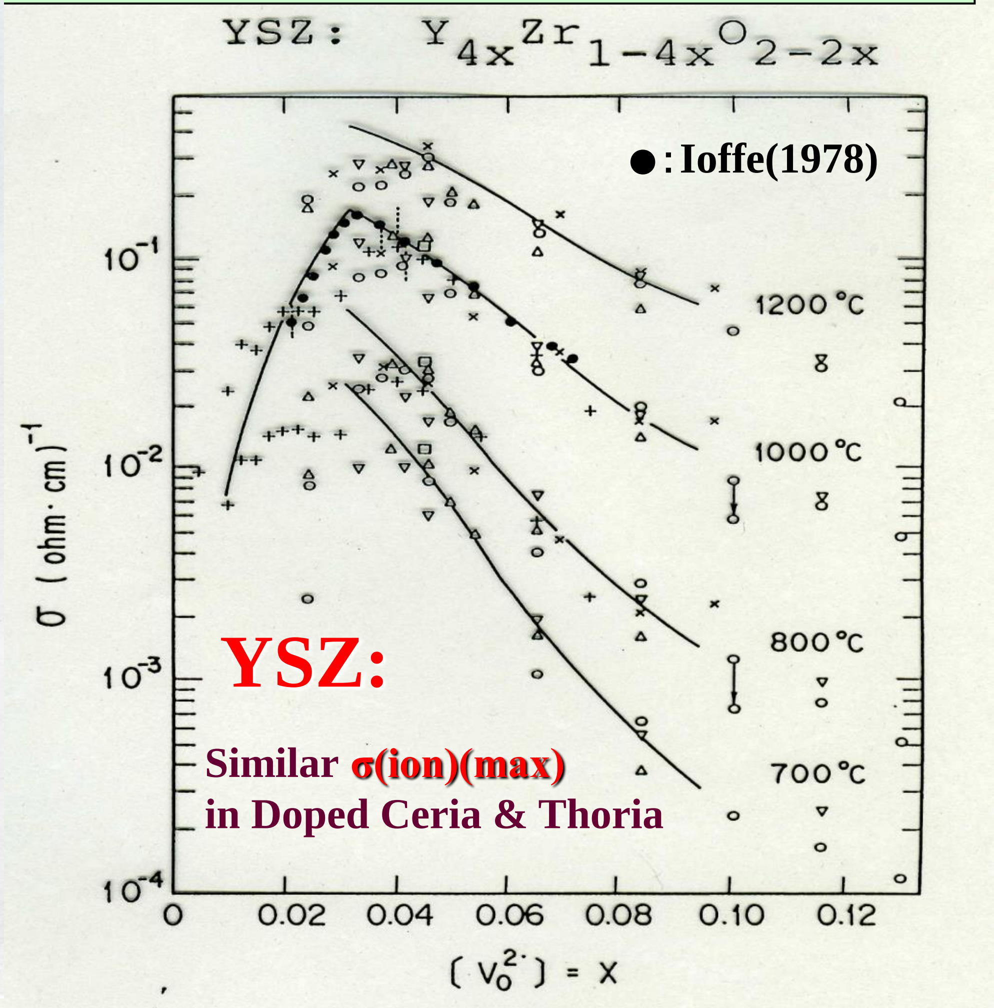
Not 'Disordered' DF-type but
'Ordered' (Defect)-Pyrochlore (P)-type
long-range ordered: for Δ*y*~±0.05
Short-range " : for y>0.45 & <0.55
(From EXAFS, Raman, Single-Crystal XRD, etc.)
to δ $Zr(Hf)_3Ln_4O_{12} = [Zr]_{VI}[Zr_2Ln_4]_{VII}O_{12}$
for smaller Ln^{3+} = Y, Dy, Er, Yb, Sc, etc.
After all, as a rough sketch;
Parent-F based M^{4+} =Ce & Th (An); (Ln^{3+}-V_O)
Stabilized M^{4+} =Zr(Hf) (SZ(SH)) ; (Zr^{4+}-V_O)
(key parametr; M^{4+}/Ln^{3+} ionic-radii (r_c) ratio)

YSZ ($Zr_{1-y}Y_yO_{2-y/2}V_{Oy/2}$): The Most Representative Solid Electrolyte:

(b) ZrO_2 - Y_2O_3 Phase diagram : Non-P forming YSZ (CSZ)

σ(ion)(max) at $y/2=0.03125$, despite random σ(ion)~{O^{2-}}{V_O}·u ~ $(2-y/2)y\cdot u$:
Vo-Vo repulsion, Ln-Vo association, P micro-domain model, microscopic heterogenuity, *etc.*

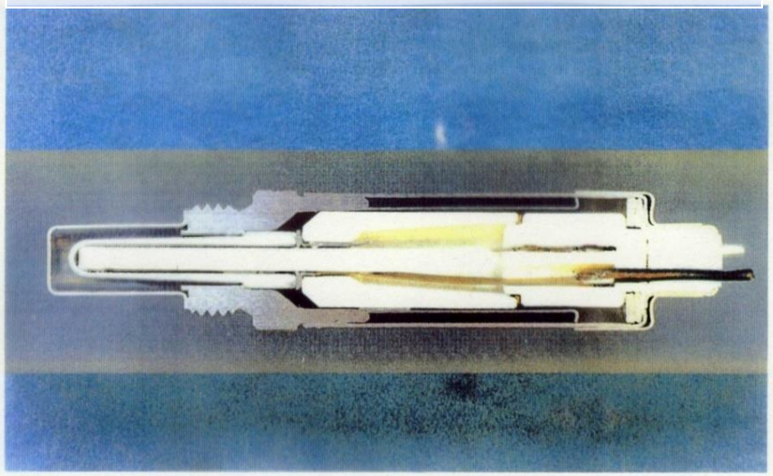


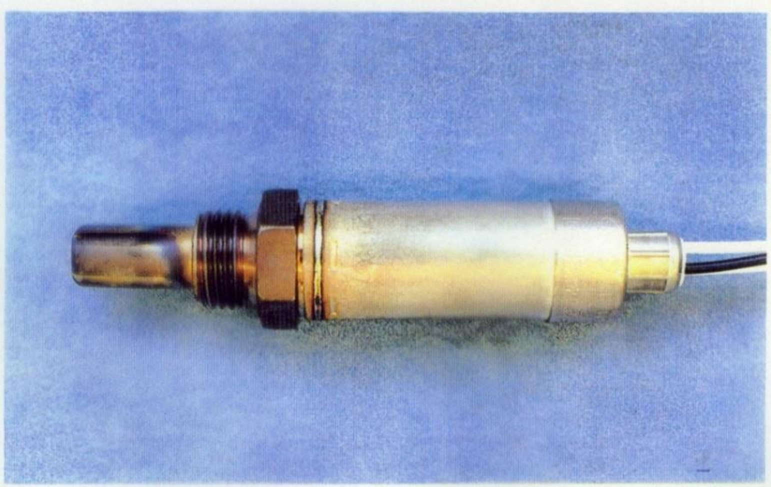


YSZ: Electrochem. Applications
(→ higher-σ(ion) Sc-SZ Ce-Ln (& perovskite oxides) for lower-temperature operation & applications)

O_2 Sensor & Monitor for Automobile & Steel-making

(NGK)





SOFC (Solid Oxide Fuel Cell): Ene-Farm（~ 1 KW）

(Eneos)

Water-boiler unit →

Electricity-generator unit ↓

Kitchen remo.con

Bath-room remo.con

New Defect-Crystal-Chemical Approach to Non-Vegardianity & Complex Defect Structure of Defect-Fluorite MO_2-$LnO_{1.5}$ Solid Solutions (M^{4+} = Ce, Th, (Zr, Hf); Ln^{3+} = lanthanide)

A Possible Unified *Generalized Vegard-Law* Model &Picture of Non-Vegardianity & Non-Random Defect Structure of F-C binary M^{4+} = Ce &Th as a New Direct Link to their Controversial Defect Structure

Part I : $\Delta a_0(ss)$ (=$a_0(ss)$-$a_0(VL)$) analysis → Non-Random Oxygen CN(Ln^{3+}, M^{4+})
(as coupled macroscopic→ microscopic distortional dilation) (SSI, 181 (2010)1543-64)

↓

Part II : Detailed Mutually Non-Random Cation & Anion Concentrations →
Ionic-Conductivity(σ(ion)) maximum behavior (SSI, 181 (2010)1631-53)

↓

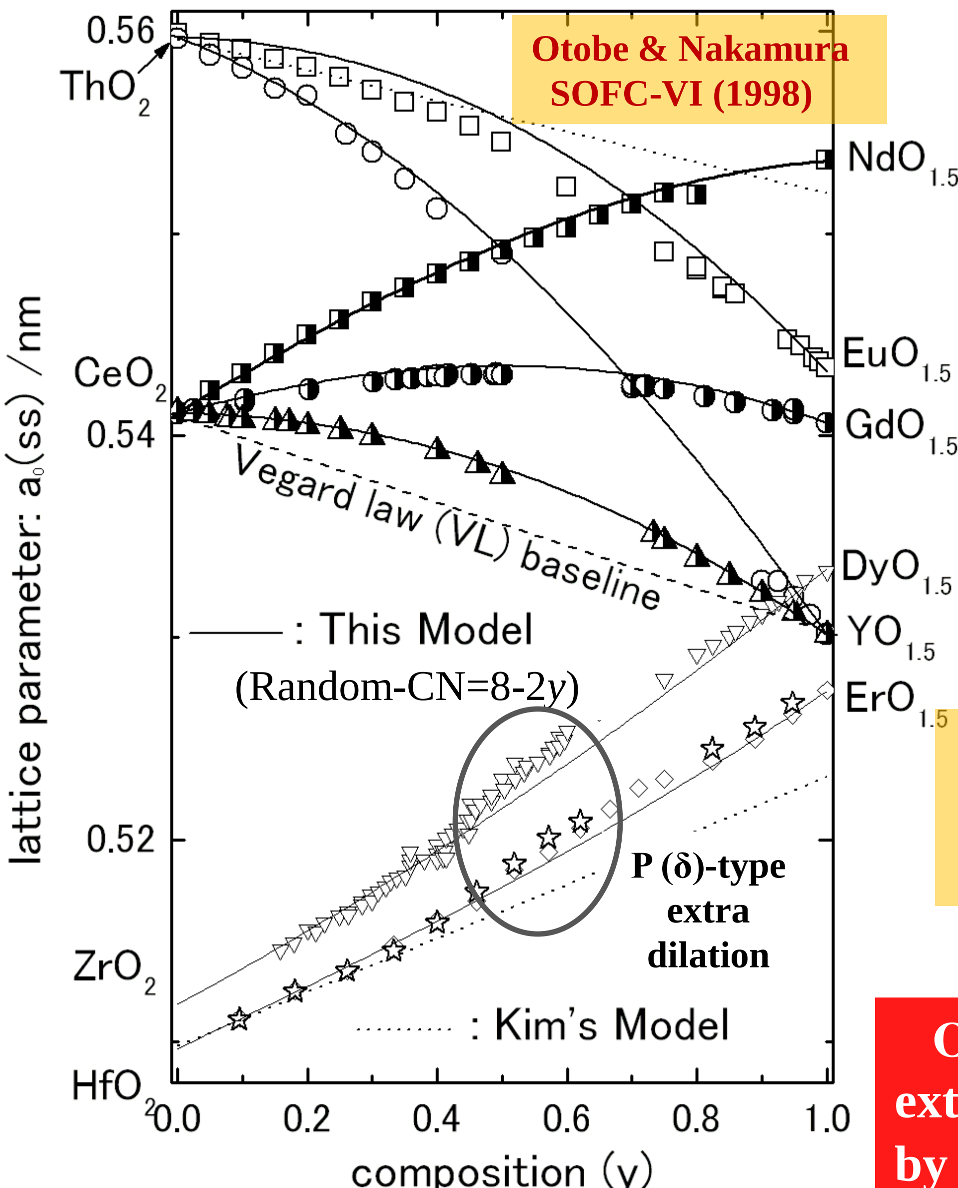
Part III : Defect-Thermodynamic Descrition of Highly-Defective DF Phase as a real local-structure based CALPHAD beyond the previous one. (ICCT2011)

↓

Part IV : $\Delta a_0(ss)$ model extension to stabilized pyrochlore-type M^{4+}=Zr & Hf

(Hyperfine Int. 217 (2013) 17-26.)

Part-I: Remarkably Non-Vegardian a_0(ss) Data of $M^{4+}_{1-y}Ln^{3+}_yO_{2-l/2}(V_{Oy/2})$: Apparent $\Delta a_0 >> 0$ for M^{4+} = Th & Ce, and $\Delta a_0 < 0$ for M^{4+} = Zr & Hf



Their Previous Modeling Attempt

Kim's Model (1989):

$$a_0(ss)-a_0(0) = y\cdot [a_h+b_h\cdot\{r_C(M^{4+}) - r_C(Ln^{3+})\}]$$

Ion-Packing (I-P) Model:

$$(\sqrt{3}/4)a_0(ss) = (1-y)\cdot r_C(M^{4+})+y\cdot r_C(Ln^{3+}) + r_a(O^{2-})+y\,\{r(V_O)-r_a(O^{2})\}/4$$

$(r_a(O^{2-})=0.138\text{nm}, r(V_O)=0.15\text{ nm, etc.})$

after all y-linear approximations with numerical adjustable. parameters

↓

A Generalized Vegard-Law(VL) a_0 Model in the random solid solutions (ss) level by fitting each Shannon $r_C(M^{4+}, Ln^{3+})$ data

↓

Our interest here is in 'whether we can extract the non-random CN (M^{4+}, Ln^{3+}) data by using Systematized Shannon data (Yes !)

The Generalized VL a_0(ss) Expression of $M_{(1-y)}Ln_yO_{2-y/2}$:

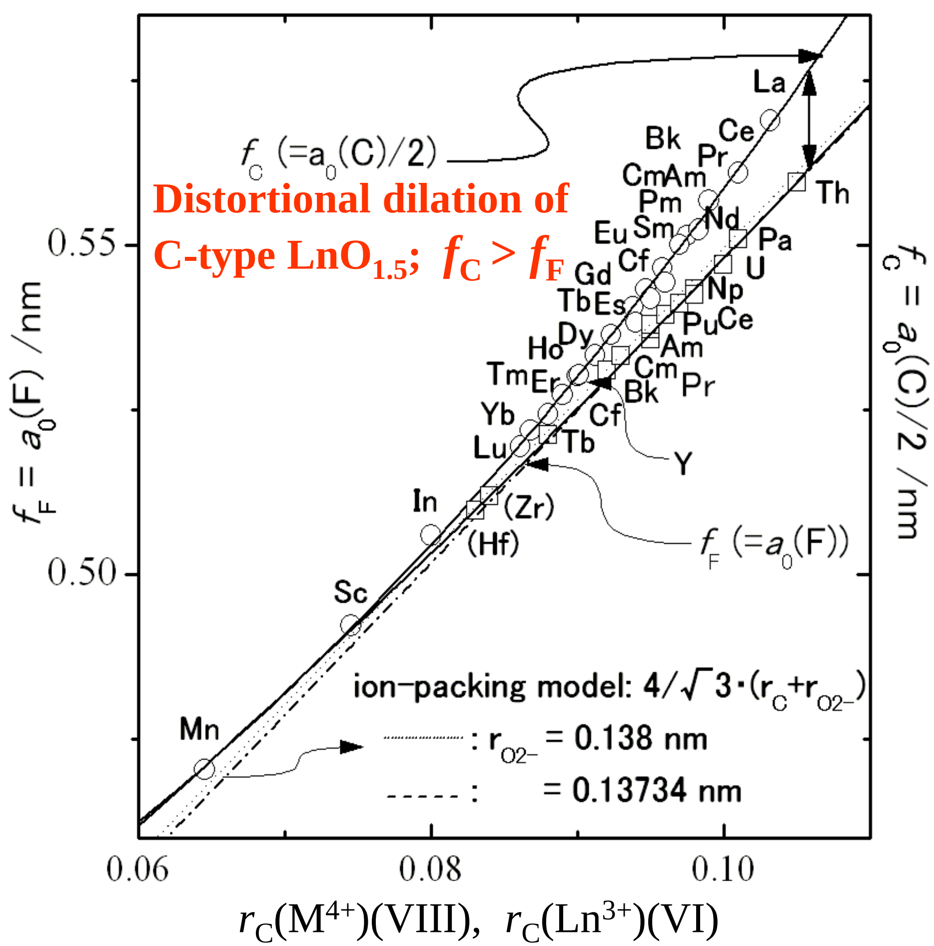
$$a_0(ss) = (1-y)\, f_F(r_C(ss)) + y\, f_C(r_C(ss))$$

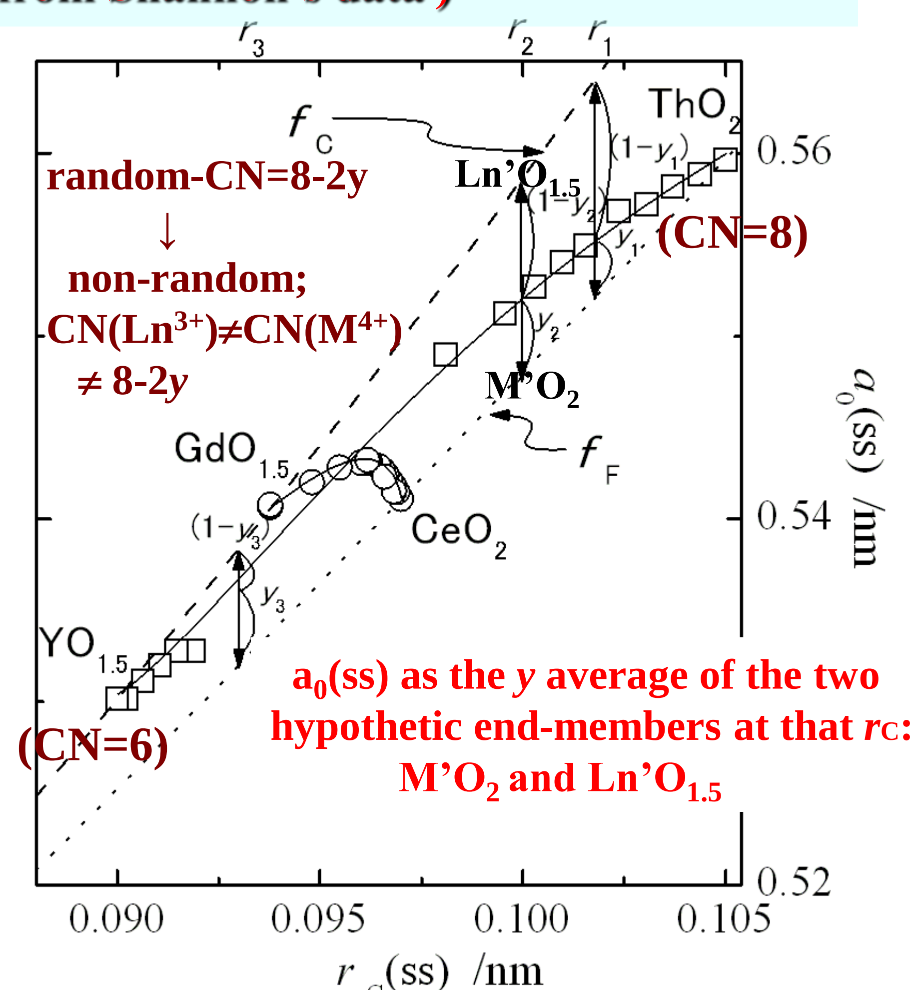
where $f_F(r_C(ss)) = 0.3571 + 1.5016\, r_C + 4.076\, r_C^2$

$f_C(r_C(ss)) = 0.40693 + 0.037411 r_C + 14.7973\, r_C^2$

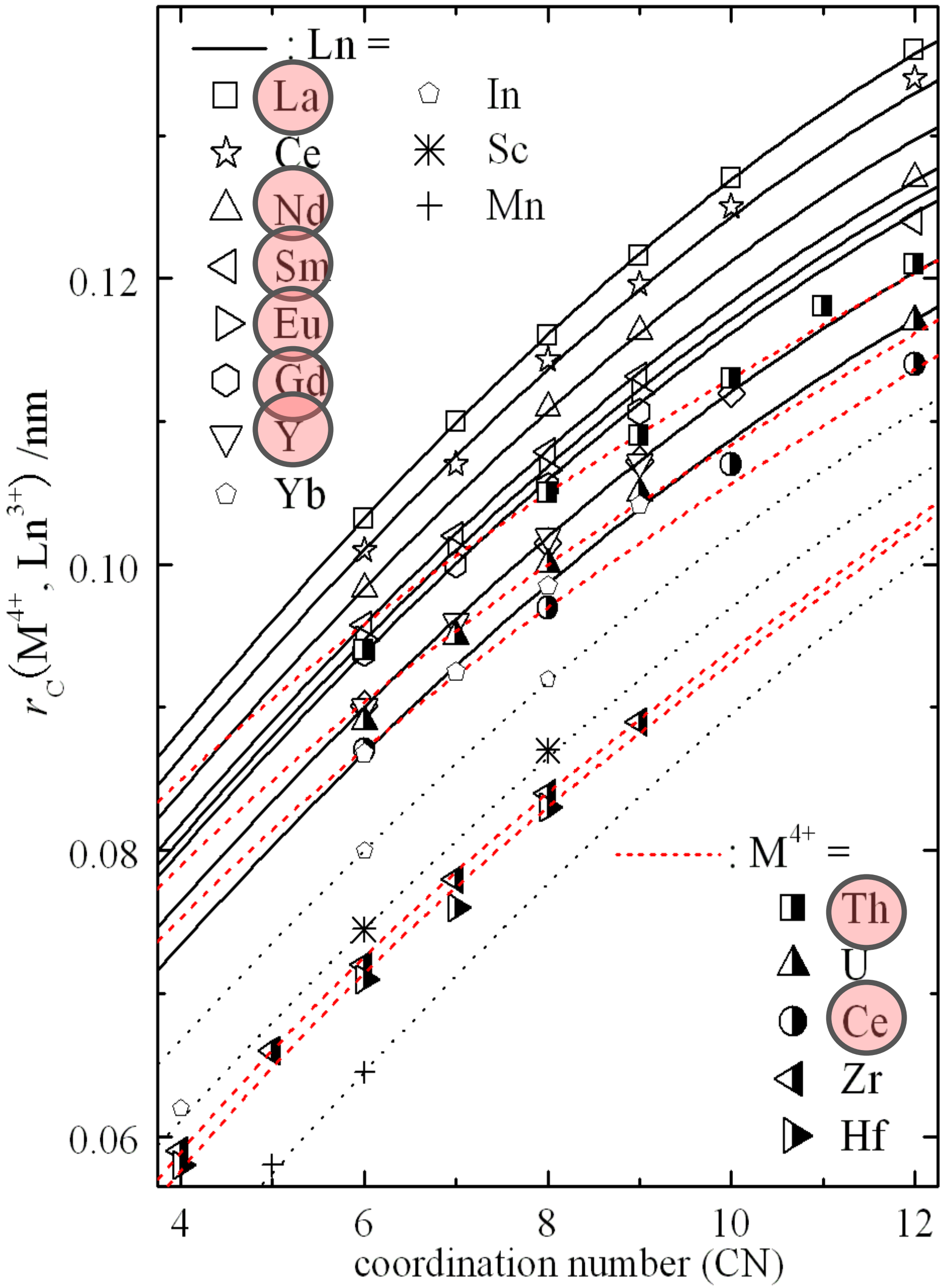
at $r_C(ss) = (1-y)\, r_C(M^{4+}) + y\, r_C(Ln^{3+})$,

($r_C(M^{4+}, Ln^{3+})$ from Shannon's data)





·Systematized Shannon's $r_C(M^{4+}, Ln^{3+})$ Expressions



To minimize the effect of random-error of Shannon's $r_C(M^{4+}, Ln^{3+})$ data

$$r_C(M^{4+}) = r_C(VIII) + \{4.46\cdot10^{-3}(CN-8) - 1.546\cdot10^{-4}(CN-8)^2 + 1.2\cdot10^{-5}(CN-8)^3\} / r_C(VIII)$$

$$: r_C(Ln^{3+}) =$$

$$r_C(VI)\{1 + \underline{F}\cdot 6.7\cdot10^{-2}(CN-6) - 2.3\cdot10^{-3}(CN-6)^2 - 2.0\cdot10^{-5}(CN-6)^3\}$$

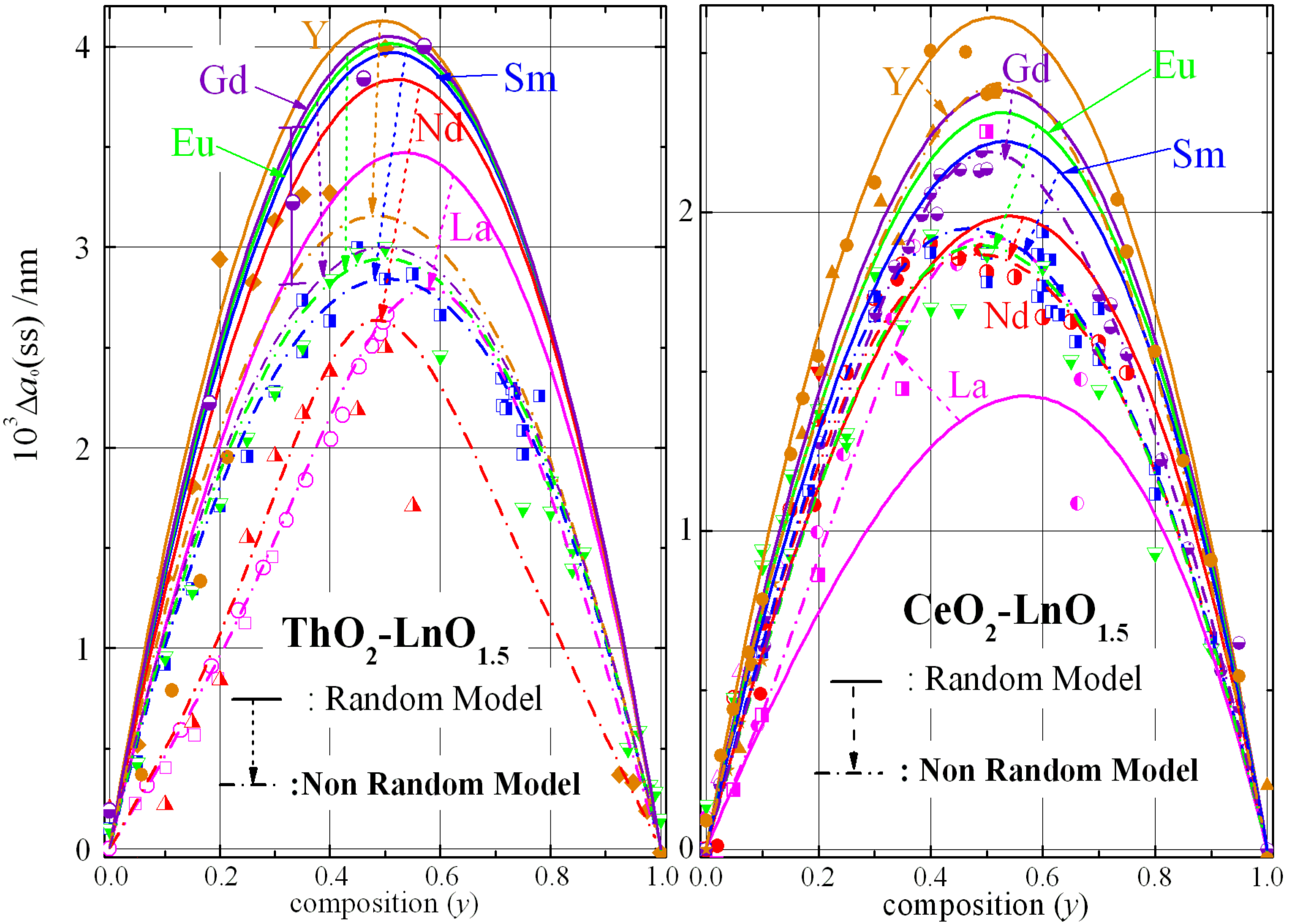
Where

$$\underline{F} = \exp[\{r_C(VI)(La^{3+})/r_C(VI)(Ln^{3+}) - 1\}^{1.5}]$$

Slope difference of $r_C(M^{4+})$ & $r_C(Ln^{3+})$= $\delta\alpha_{Ln\text{-}M}$: Essential for Random→Non-Random $\Delta r_c(ss) \rightarrow \Delta a_0(ss)$ Change:

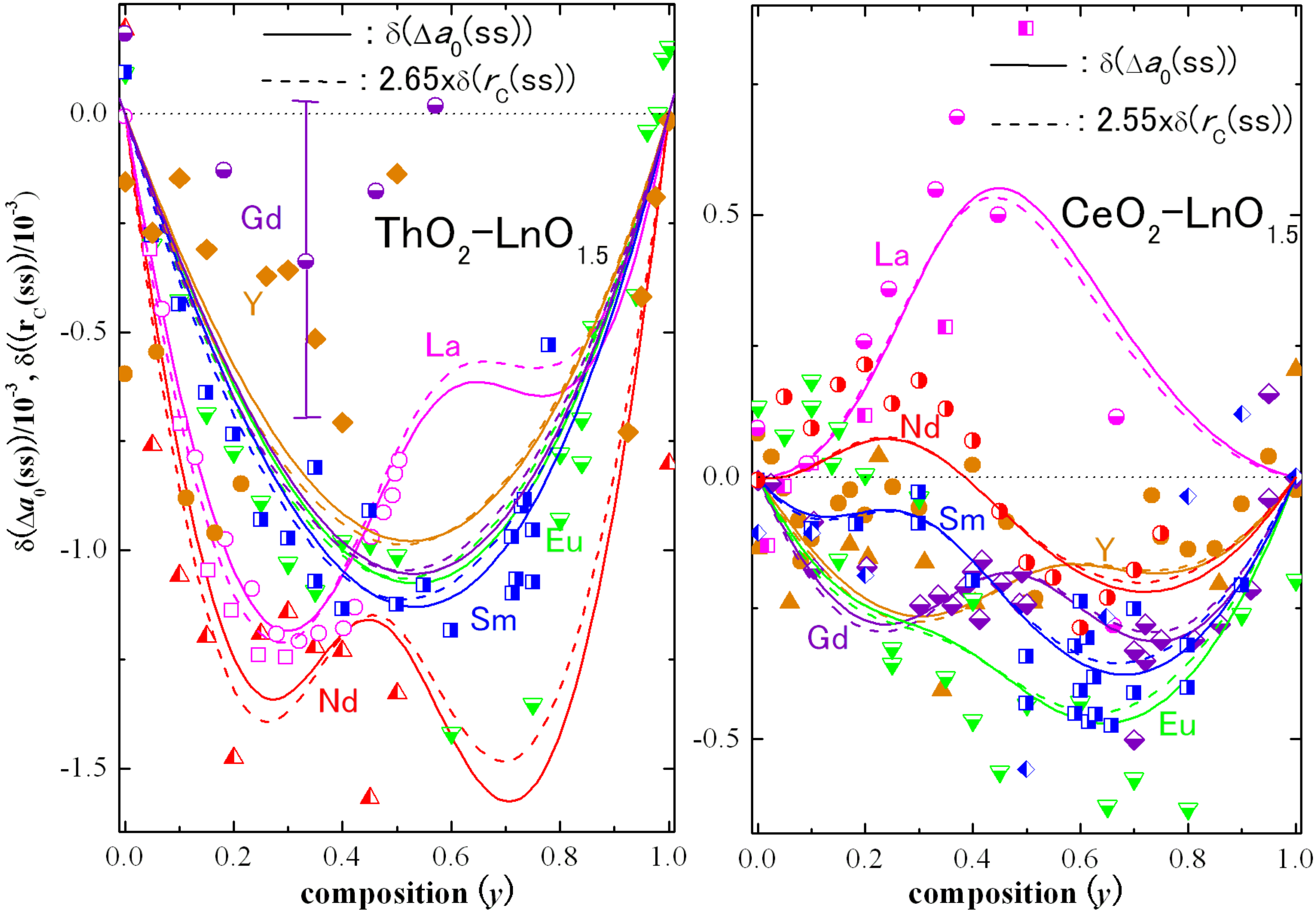
$$\delta\Delta a_0(ss) \propto \delta(\Delta r_C(ss))_{RM\rightarrow NRM} \propto y\cdot(\alpha_{Ln} - \alpha_M)\cdot\delta CN(Ln^{3+})$$

Random→Non-Random Model fitting to apparent Δa_0(ss)-data



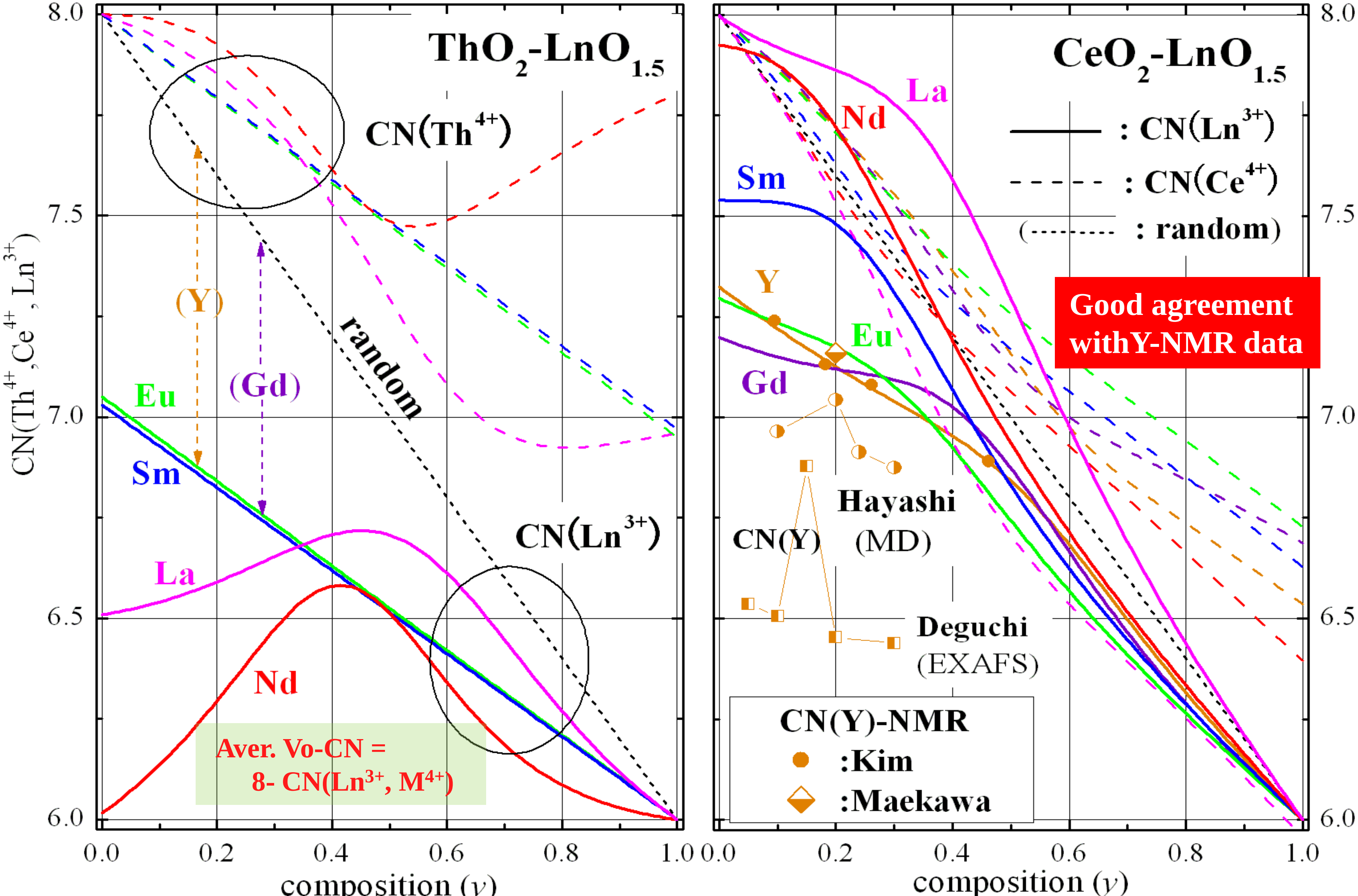
Genralized Non-Vegardianity $\delta\Delta a_0(ss)=\Delta a_0(ss)-\Delta a_0(random)$

Largely Negative ThO_2-$LnO_{1.5}$ vs. Negative to Positive CeO_2-$LnO_{1.5}$



Largely (Ln^{3+}-V_O)-type M^{4+}=Th vs. Weakly & variably Non-Randdom M^{4+}=Ce

Consistent both with σ(ion) data and a theor. prediction (Andersson et al PNAS 03(2006) 3518) that 'the most near-random Ce-Pm in between Ce-Sm & Ce-Nd is most conductive'.



Compatibility with Ion-Packing (I-P) Model

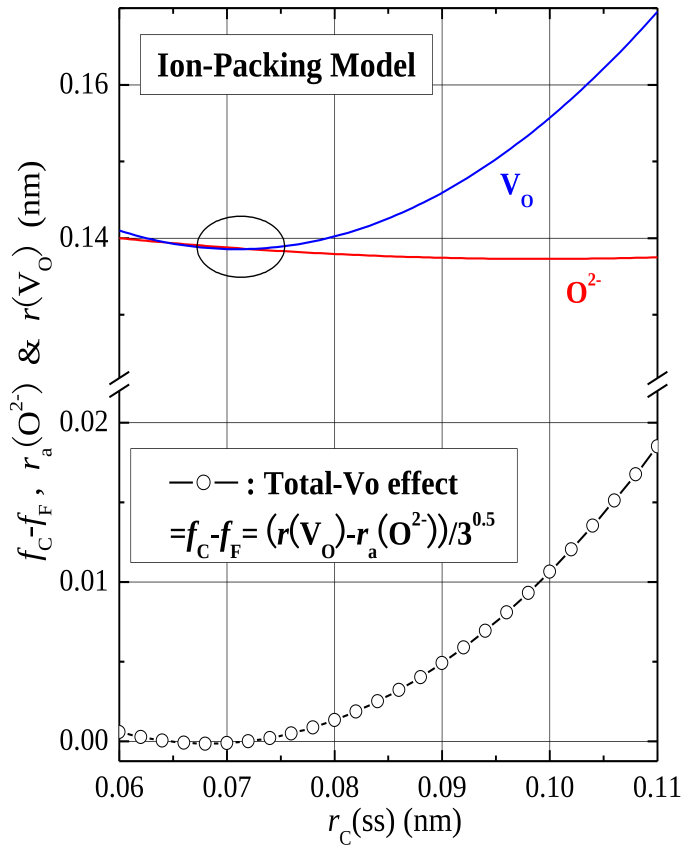
$a_0(ss) = (1-y)\, f_F(r_C) + y\, f_C(r_C)$
$= f_F(r_C) + y\, \{f_C(r_C) - f_F(r_C)\}$ →

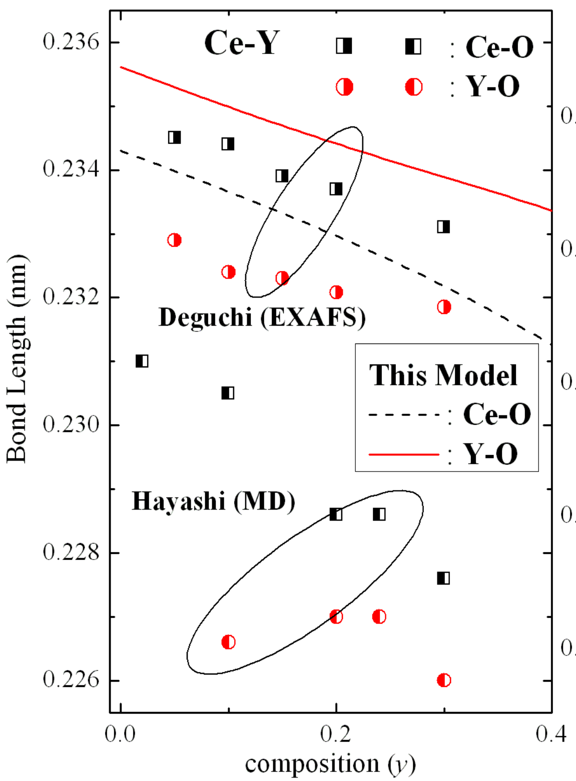
$a_0(ss)(\text{I-P}) = (4/\sqrt{3}) \times [r_C + r_a(O^{2-}) + (y/4)\{(r(V_O) - r_a(O^{2-})\}]$

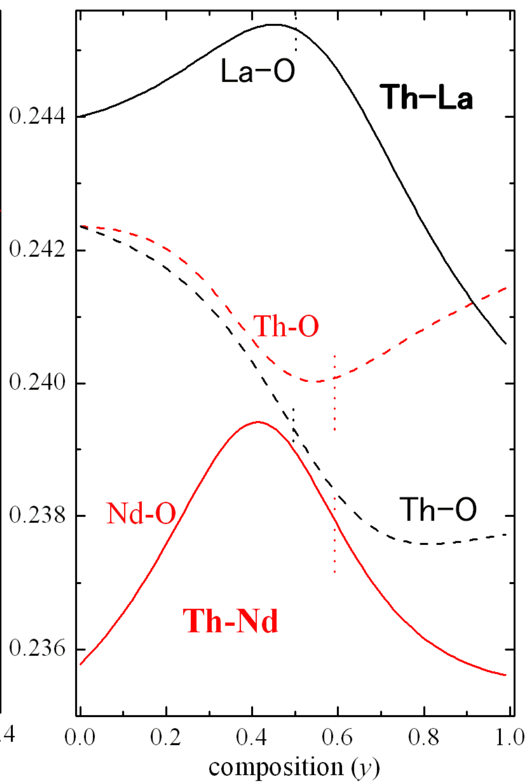
↙

$f_F(r_C) = (4/\sqrt{3})\{ r_C + r_a(O^{2-})\}$
$f_C(r_C) - f_F(r_C) = \{(r(V_O) - r_a(O^{2-})\}/4$

Bond Length (M^{4+}-O^{2-} & Ln^{3+}-O^{2-}) Derivation & Comparison





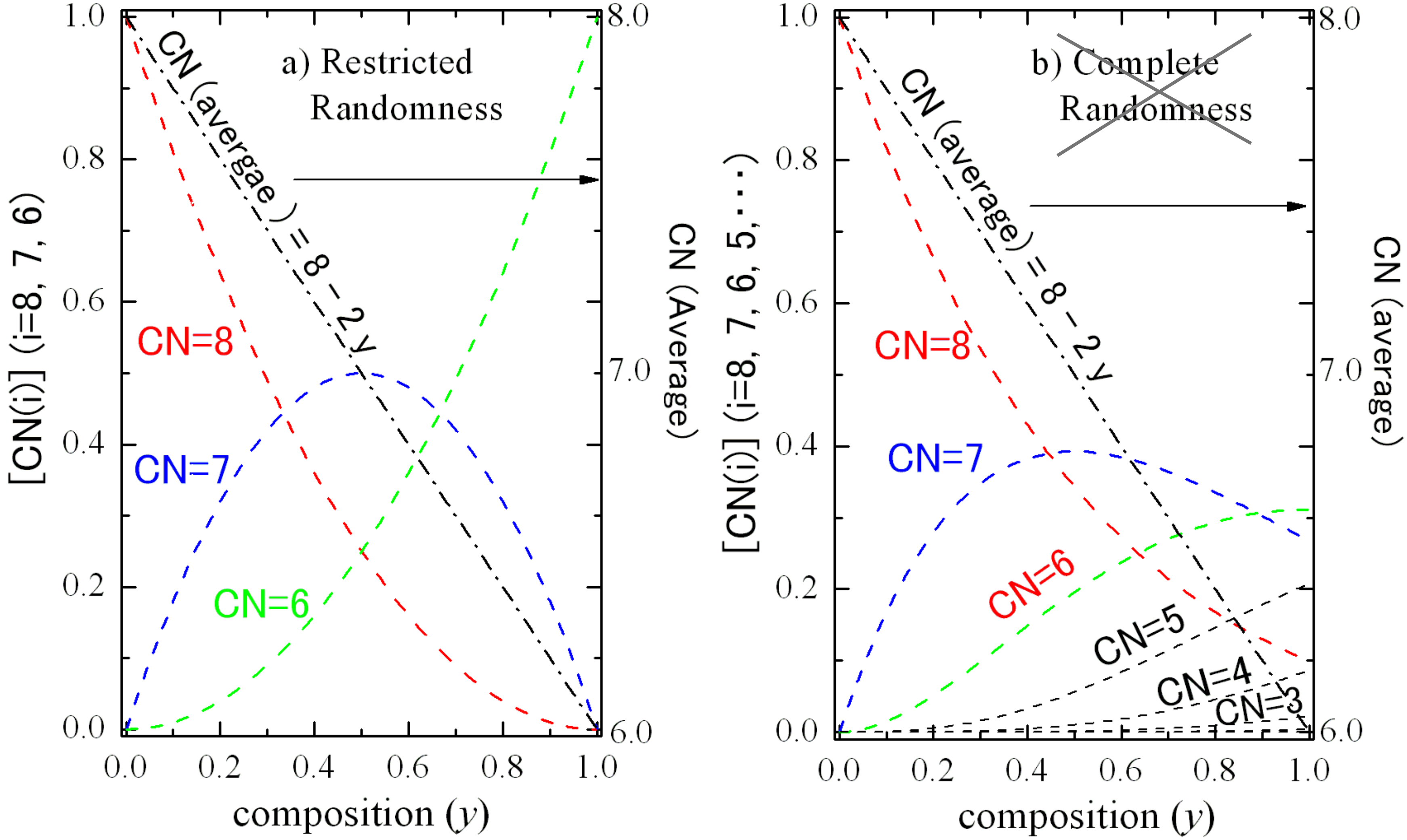


Part-II: Detailed Local-Structure & σ(ion) Analysis from CN data

<u>Restricted (Non-)Randomness</u> (left a) of DF oxides: Its two evidences;

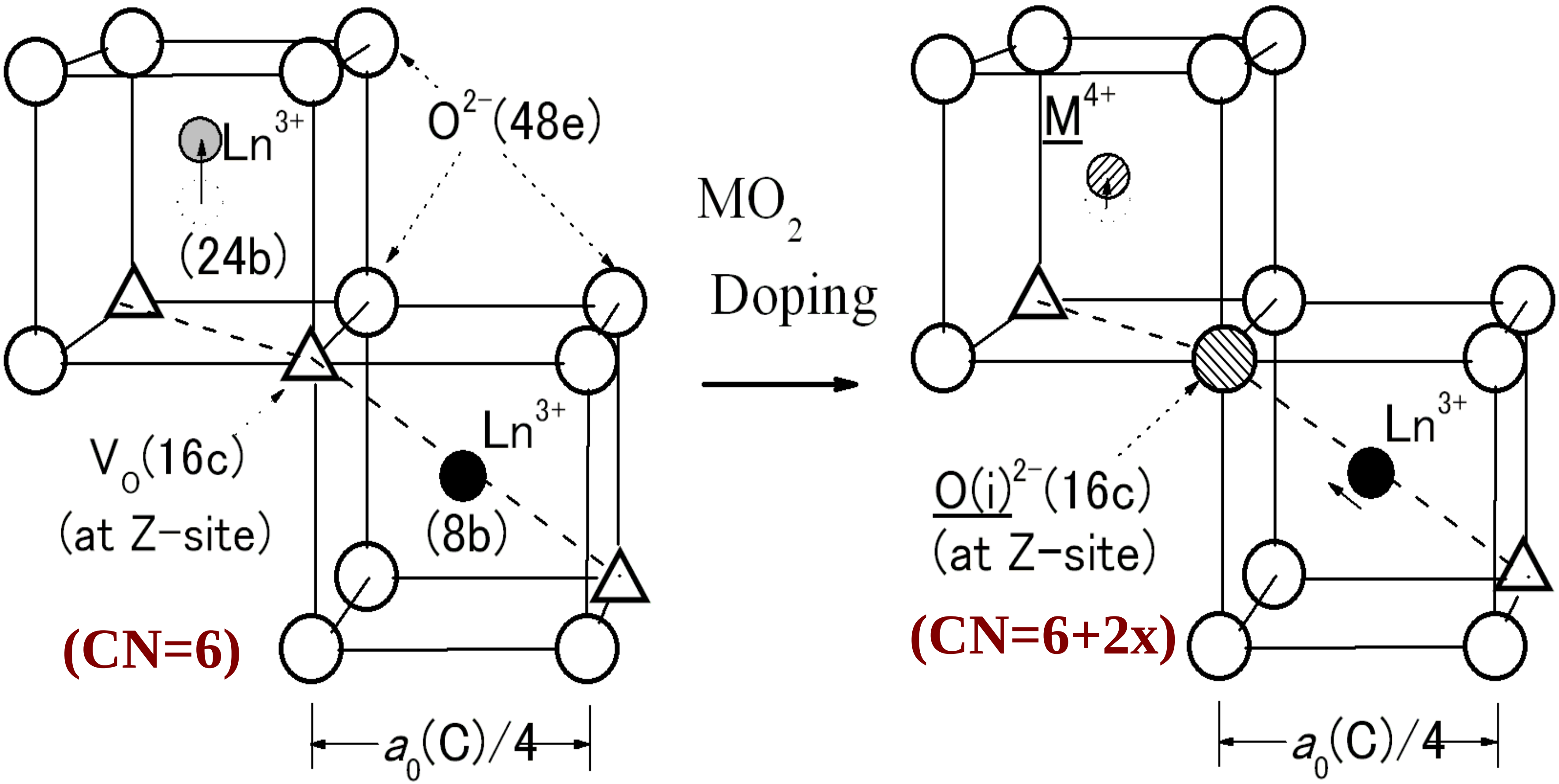
(1) The absence of Shannon's $r_C(M^{4+}, Ln^{3+})$ data for CN<6.

(2) MAS-NMR direct $^{89}Y^{3+}$(CN=8, 7, and 6) data in Ce-Y & Zr-Y



Ln-rich side C-type ordered SS with three CN=VI, VII & VIII sites:

(**Restricted randomness ~ exclusion of 1st NN V_O-V_O config. // a_0-direction**)

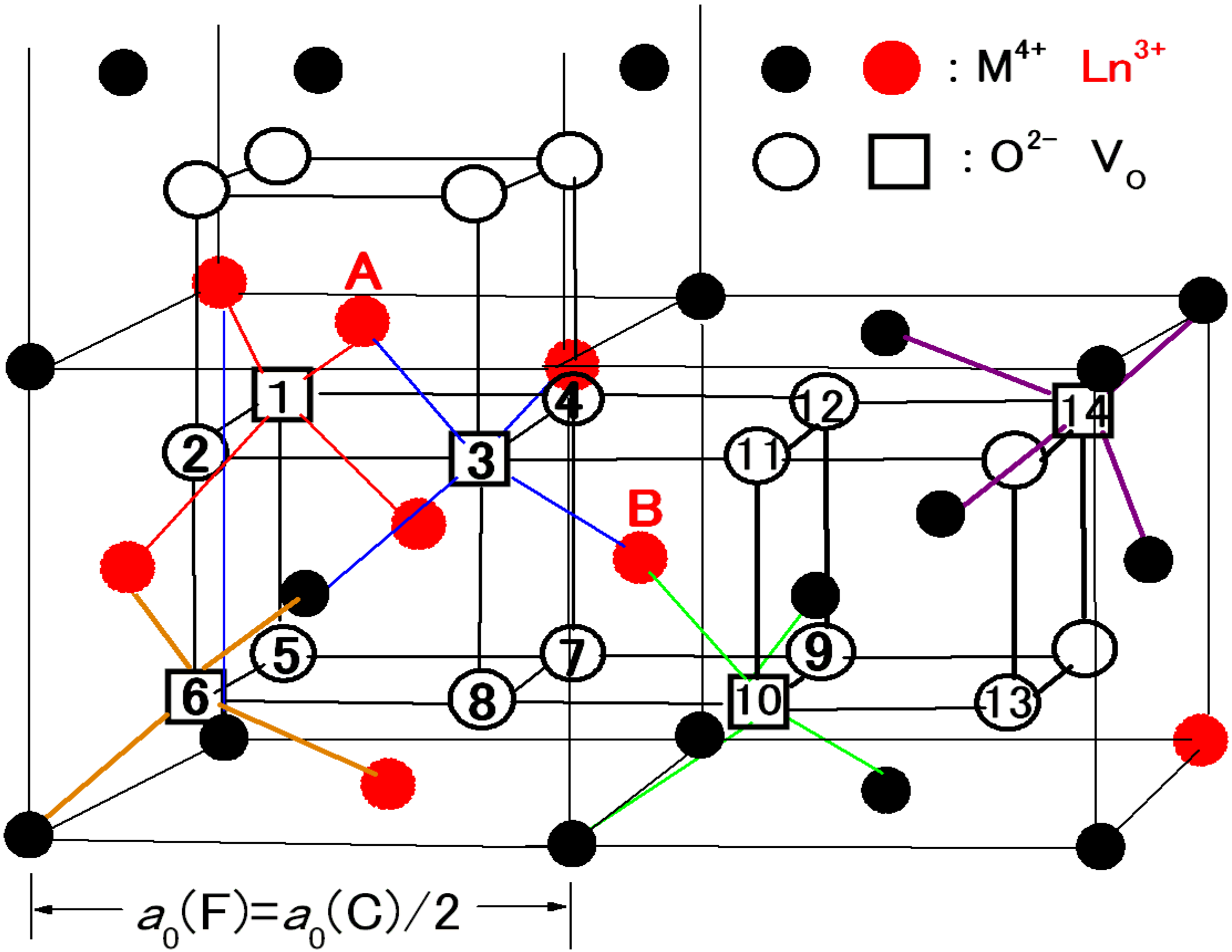


(a) C-type $LnO_{1.5}$

(b) Oxygen-excess C-type $Ln_{1-x}M_xO_{1.5+x/2}$

M-rich side disordered three site (CN=VI, VII & VIII) DF-type SS Model:

1st NN V_O-V_O exclusion occurs in a more disordered (randomized) fashion



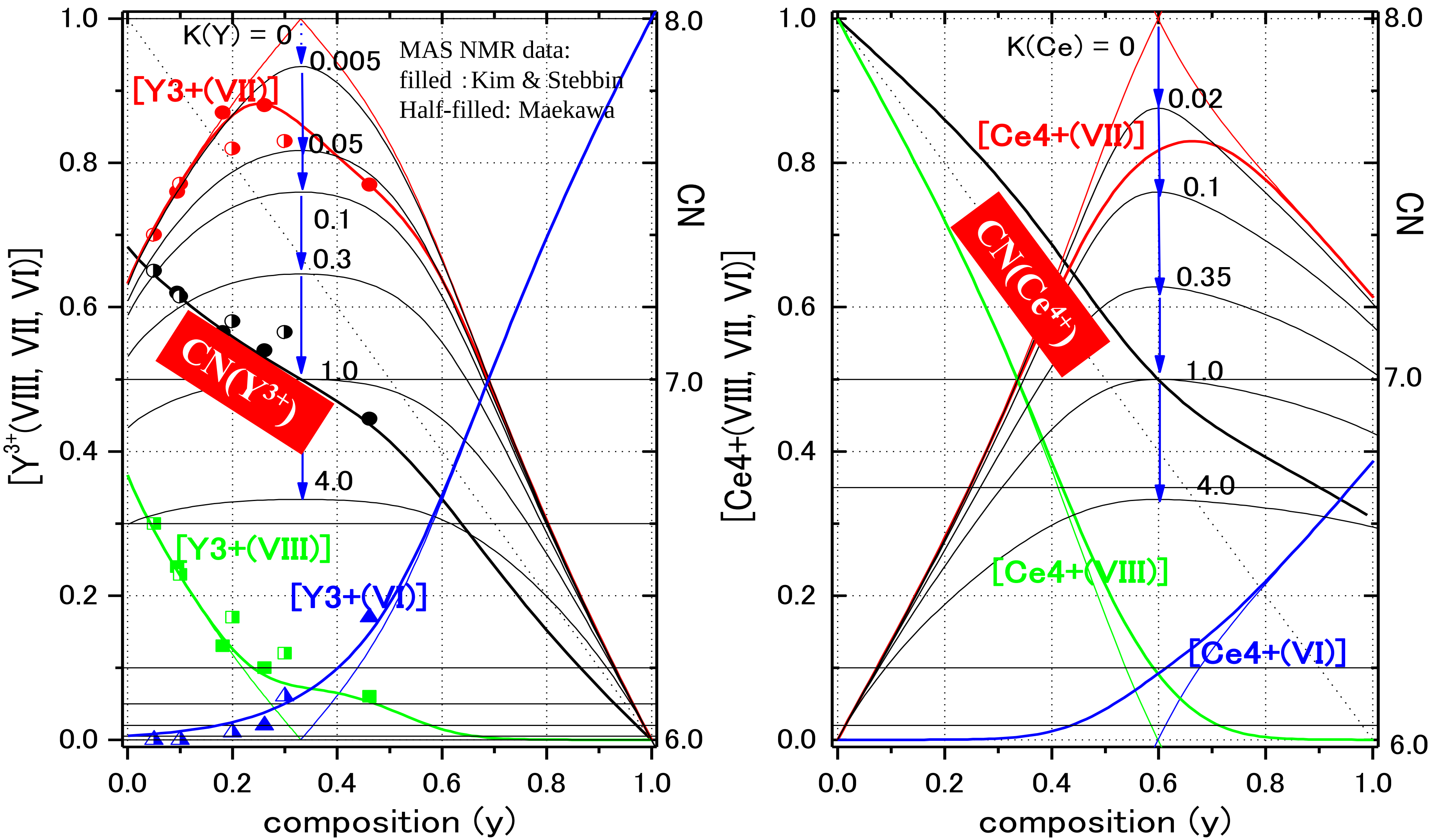
Non-Random Y^{3+} & Ce^{4+}(VI, VII, VIII) site-F profile in CeO_2-$YO_{1.5}$

▪ 2- to 3-site Approach to CN(Y^{3+}) → MAS-NMR [Y^{3+}(VIII,VII,VI)](left):

Site-F ([Y^{3+}(VIII)]+[Y^{3+}(VII)]+[Y^{3+}(VI)]=1) & CN (8[Y^{3+}(VIII)]+7[Y^{3+}(VII)]+6[Y^{3+}(VI)]=CN(Y^{3+})):

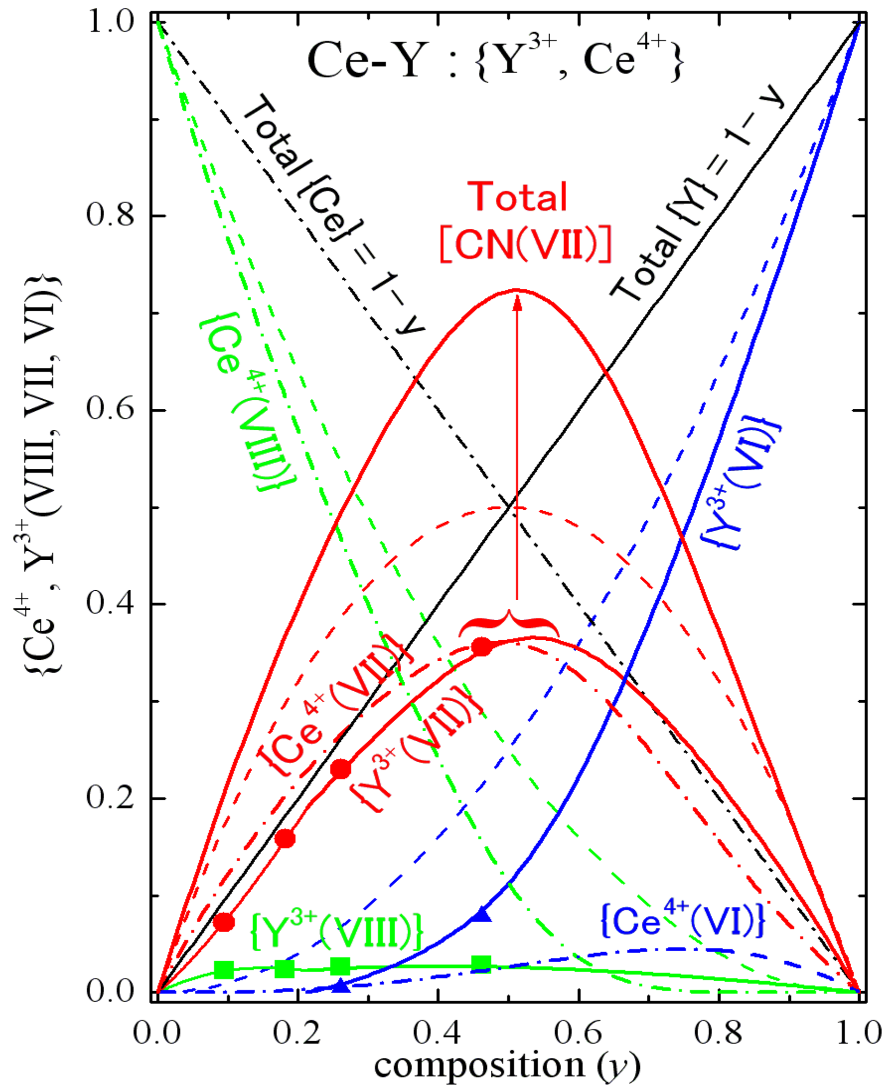
Limiting 2-site case: [Y^{3+}(8, 7)] for $0 \le y \le 0.33$ ($8 \ge CN(Y) \ge 7$) & [Y^{3+}(7, 6)] for $0.33 \le y \le 1$ ($7 \ge CN(Y) \ge 6$)

→ Actual 3-site case by $2Y^{3+}(VII) \rightarrow Y^{3+}(VI) + Y^{3+}(VIII)$ (with K(Y)≠const. but *y* dependent).

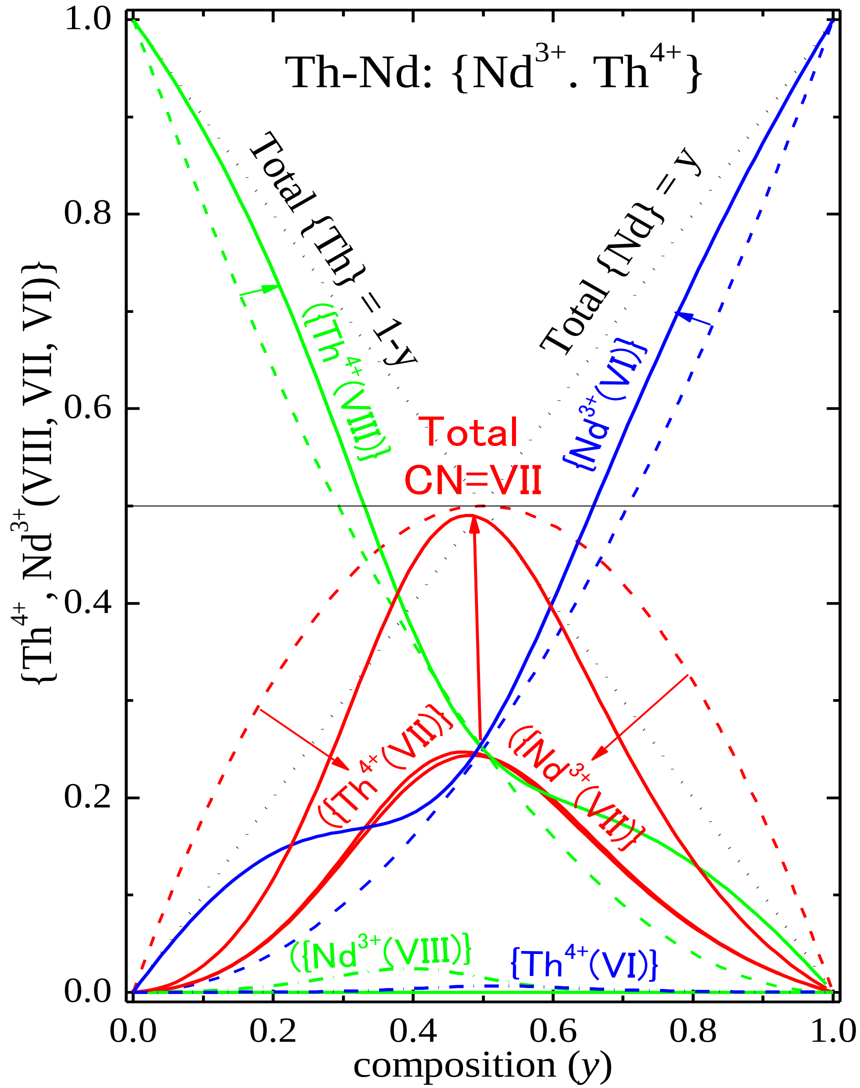


Non-Random Ln^{3+} & M^{4+}(VI, VII, VIII) Mol-Fraction profile in MO_2-$LnO_{1.5}$:
(Mol-Fraction: $\{Ln^{3+}(CN)\}=y[Ln^{3+}(CN)]$, $\{M^{4+}(CN)\}=(1-y)[M^{3+}(CN)]$)

Ce-Y; middle [CN=VII)] enchanced



Th-Nd; middle [CN=VII)] retarded

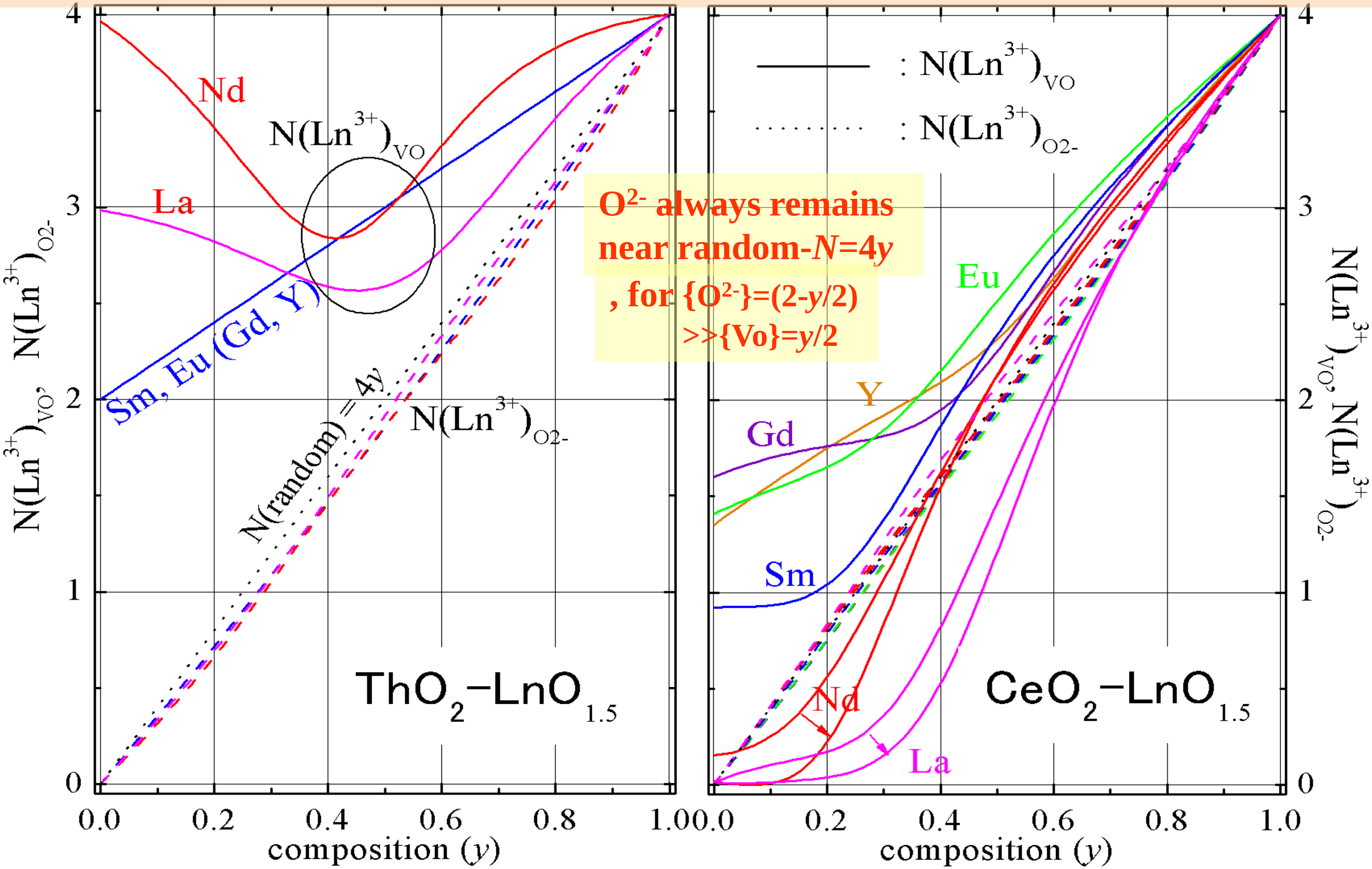


Converse average non-random dopant (Ln^{3+}) CN of anions (V_O, O^{2-}):

Cations & Anions; mutually 8- & 4-fold coordinated :

Aver. Ln^{3+} CN around V_O; $N(Ln^{3+})_{Vo}=2\{8-CN(Ln^{3+})\}$ ($N(Ln^{3+})_O{}^{2-}=2\,y\cdot CN(Ln^{3+})/(4-y)$)

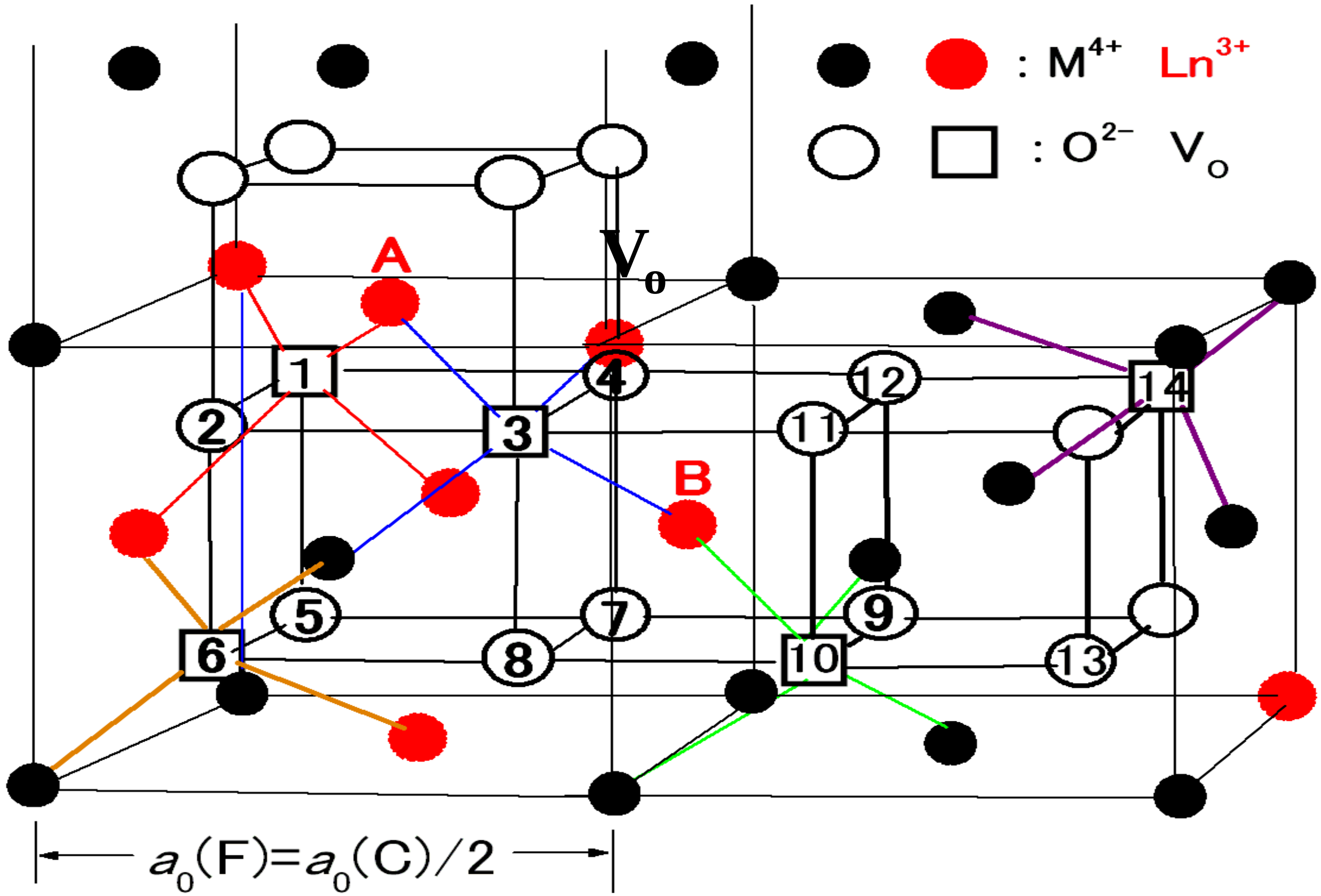
(C-type $LnO_{1.5}$ $N(Ln^{3+})_{Vo}$ = 4 corresponds to $\{8-CN(Ln^{3+})\}$=2).



O²⁻ always remains near random-*N*=4*y*, for {O²⁻}=(2-*y*/2) >>{Vo}=*y*/2

If the system is (Ln^{3+}-V_O) associative and hence Ln^{3+} has more V_Os than random (8-CN(Ln^{3+})) > 2*y*), V_O should also have more Ln^{3+}s than random,

∴ Aver. Ln^{3+} CN of V_O; $N(Ln^{3+})_{Vo}=2\{8-CN(Ln^{3+})\}$



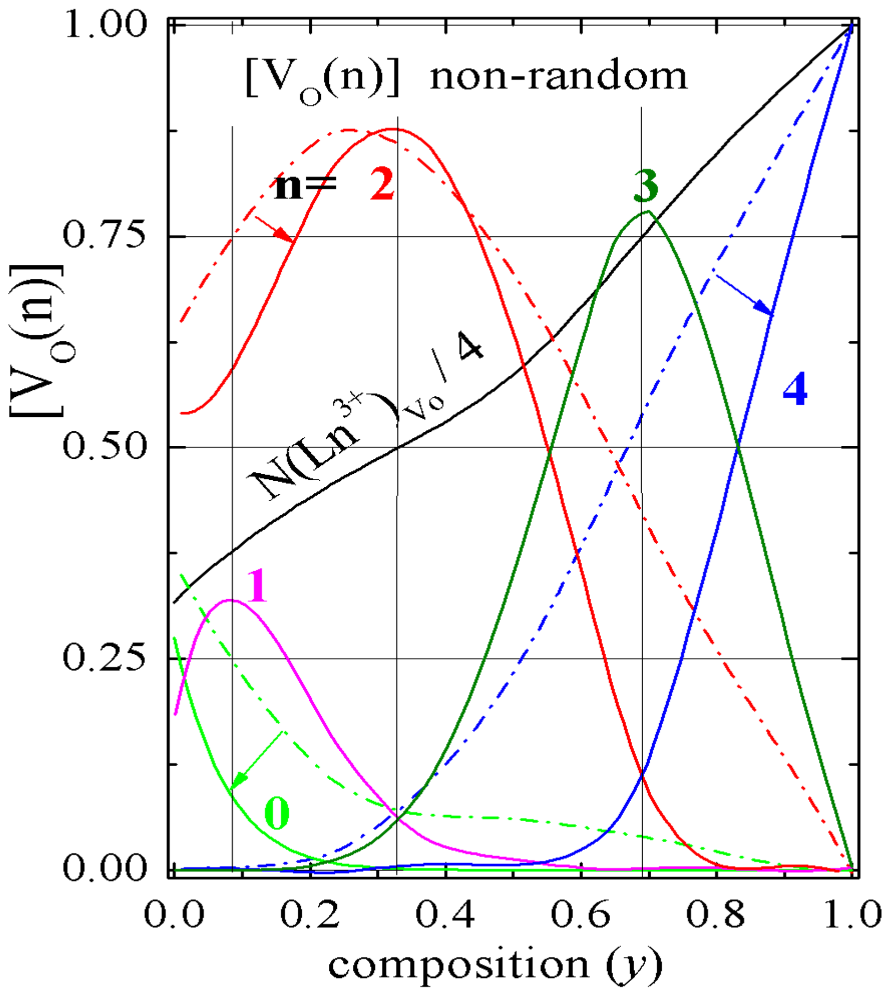
Anion (V_O(n=0-4)) & O^{2-}(n=0-4)) site-fraction Profile in Ce-Y:

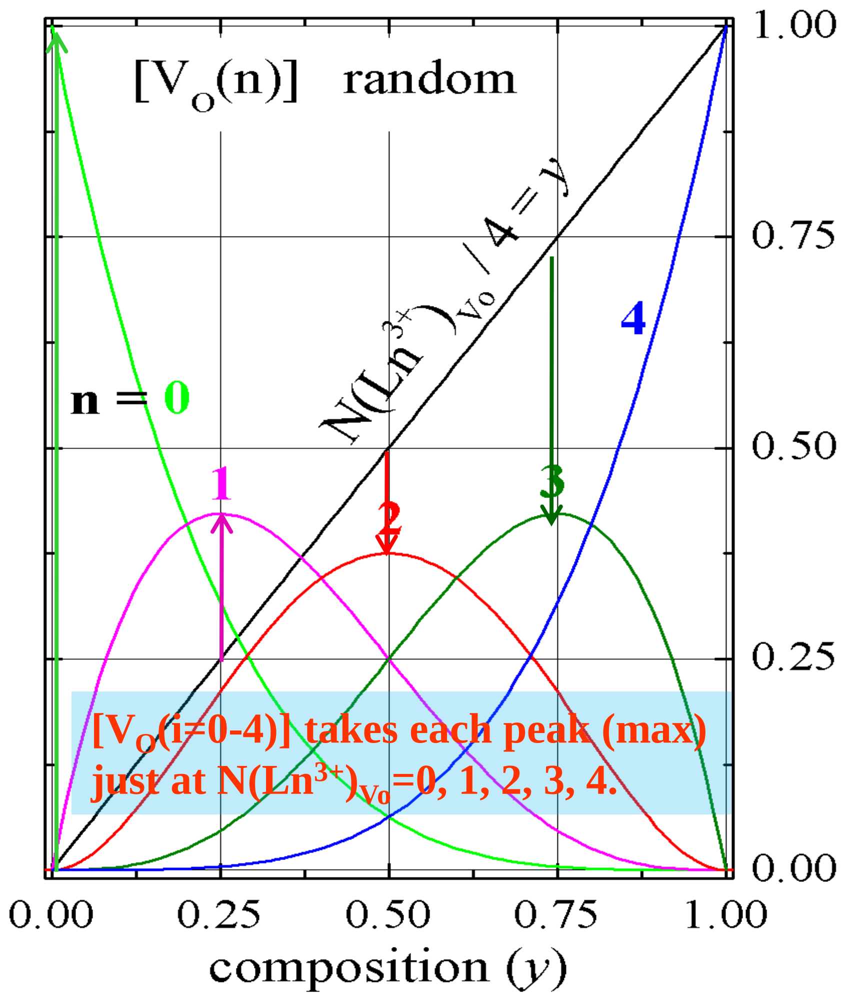
$[Y^{3+}(VIII)] \rightarrow [V_O(0)]$, $[Y^{3+}(VII)] \rightarrow [V_O(2)]$, $[Y^{3+}(VI)] \rightarrow [V_O(4)]$

Combination Reactions: $V_O(0)+V_O(2) \leftrightarrow 2V_O(1)$, $V_O(2)+V_O(4) \leftrightarrow 2\,V_O(3)$

V_O(n=0-4) (initial→Final)

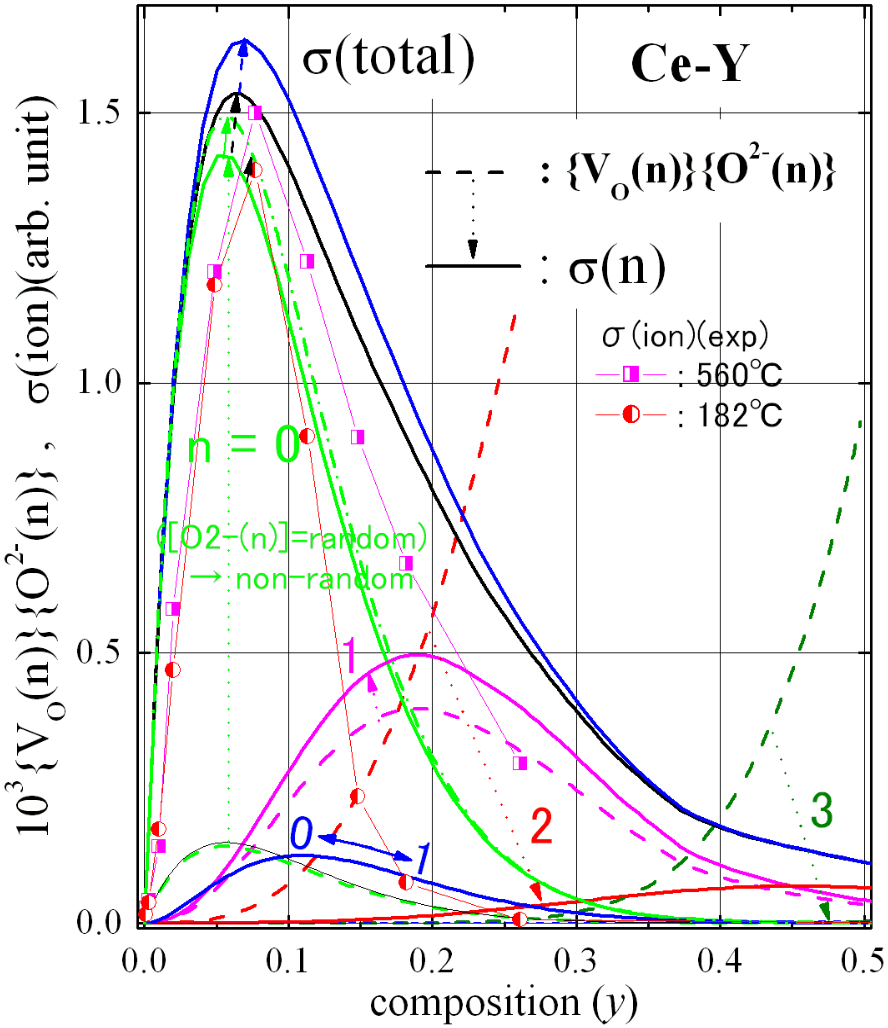
O^{2-}(n=0-4) (~random)



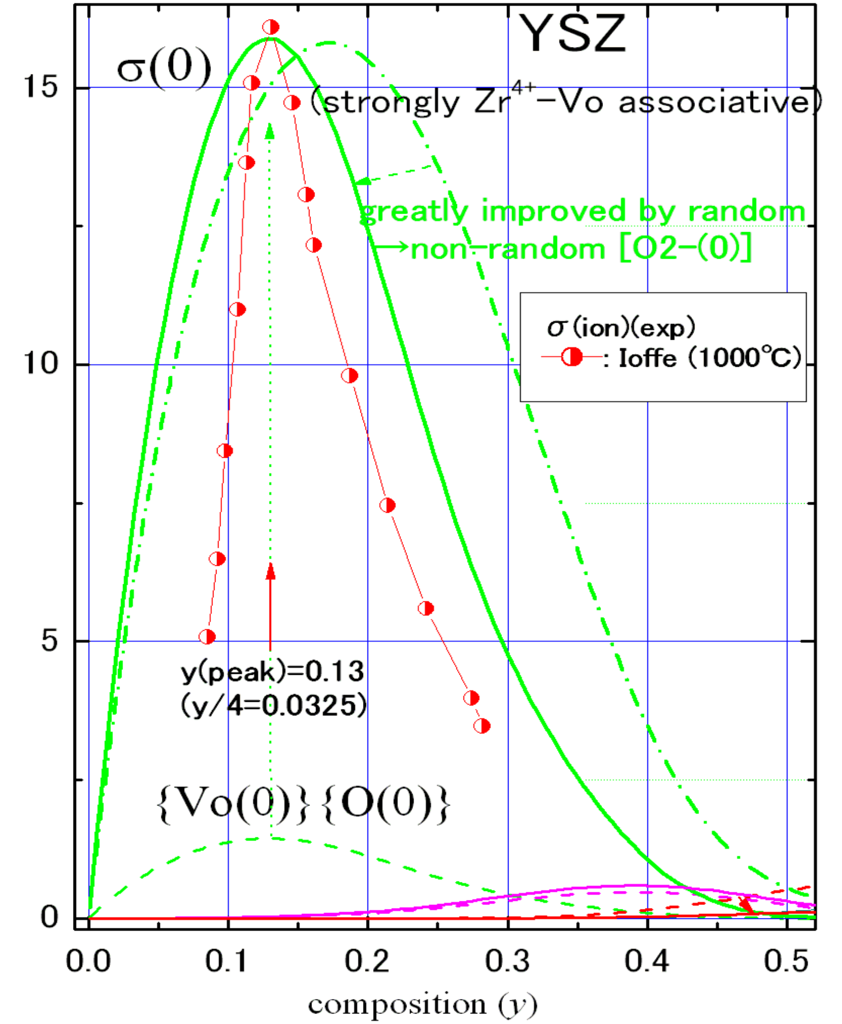


Ionic-conductivity: $\sigma(\text{ion}) \propto \sigma(i\text{-}j) \propto \Sigma\mu_m(i\text{-}j)\cdot\{V_O(i)\}\cdot\{O^{2-}(j)\}$
$= (y/4)\cdot(1-y/4)\ \Sigma\mu_m(i\text{-}j)\cdot[V_O(i)]\cdot[O^{2-}(j)]$ (only i, j=0, 1 effective)

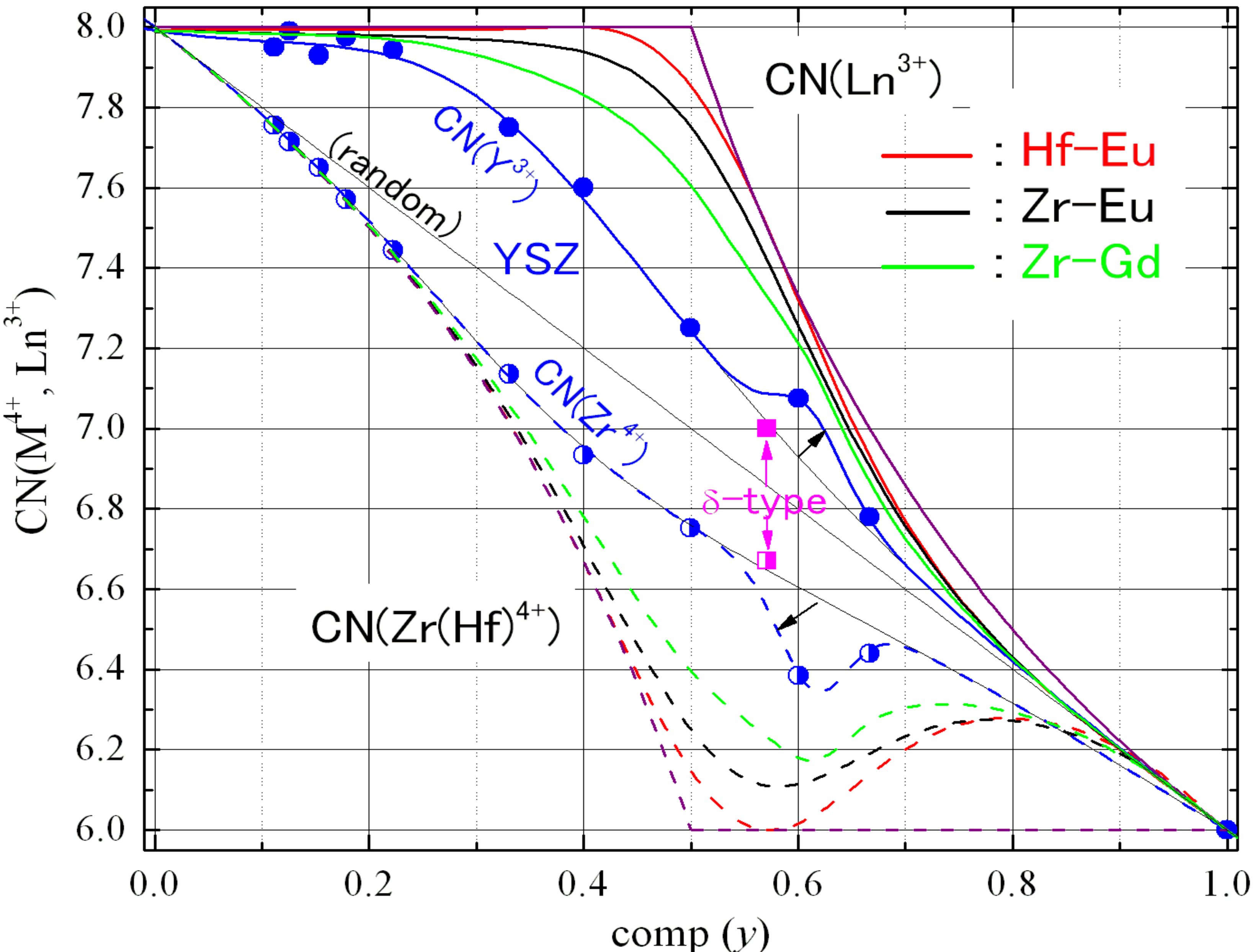
The Model reproduces well reported σ(ion)(exp) (Wang et al, SSI, 2(1981)95) .



σ(ion) analysis of YSZ based on ^{89}Y-NMR CN(Y, Zr) data



YSZ: ^{89}Y-NMR-based CN(Y^{3+}, Zr^{4+}) data



Part-III: Toward Quantitative Defect-Thermodynamic Description

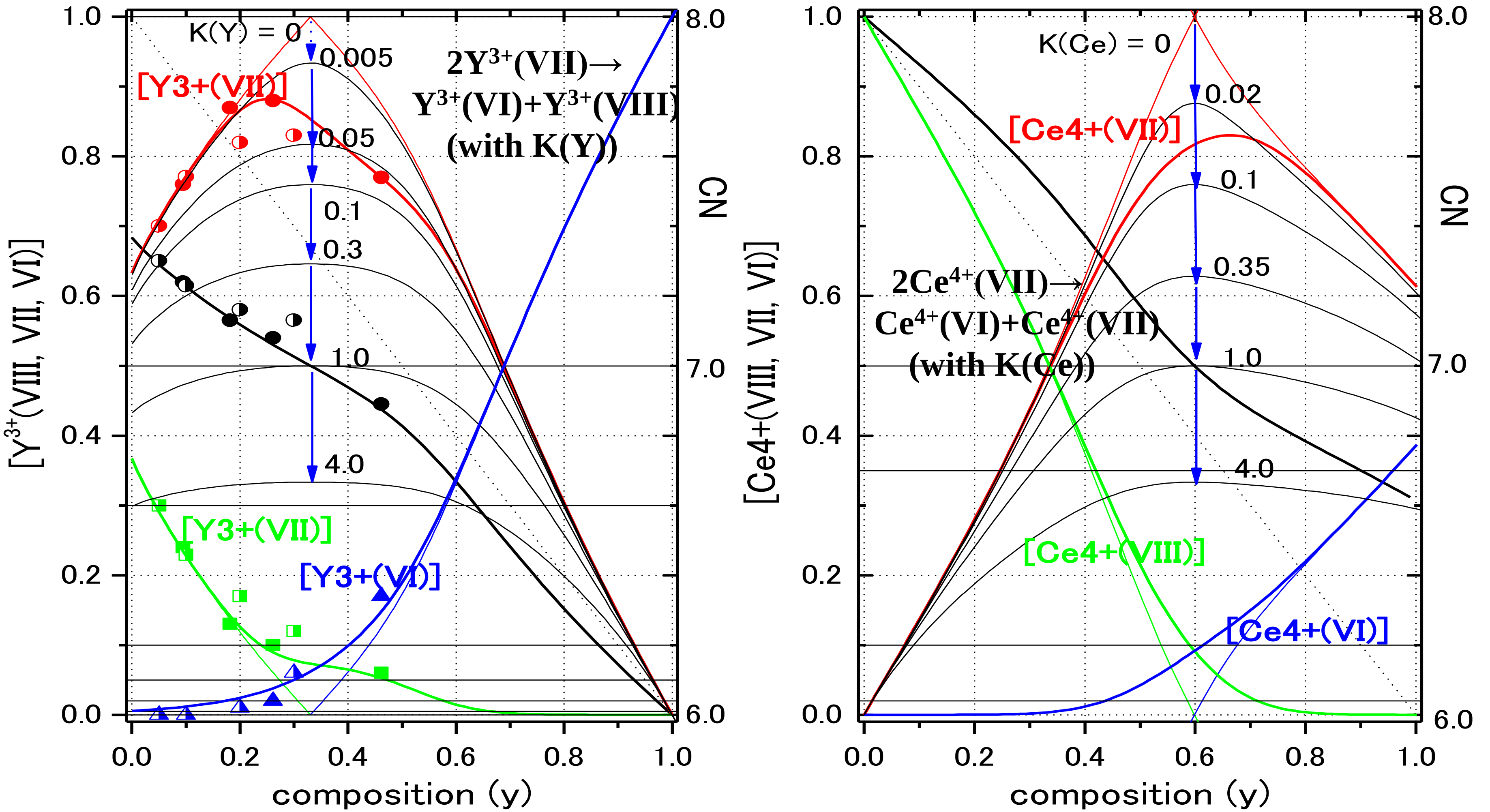
- **Cations site-fraction profile in CeO_2-$YO_{1.5}$ by Simple 2- to 3-site model in Part II:**

$$2Y^{3+}(VII) \rightarrow Y^{3+}(VIII) + Y^{3+}(VI) \quad \therefore \underline{[Y^{3+}(VII)] = (-1+\sqrt{1+(K(Y)-1)\cdot(CN(Y)-6)\cdot(8-CN(Y))}\,/(K(Y)-1)}$$

Site fraction condition : $[Y^{3+}(VIII)] + [Y^{3+}(VII)] + [Y^{3+}(VI)] = 1$

Average-CN condition: $8[Y^{3+}(VIII)]+7[Y^{3+}(VII)] + 6[Y^{3+}(VIII)]=CN(Y^{3+})$

→ **<u>K(Y, Ce) are not constant but *y* dependent</u>!**



QC-approach to three-site (CN=VIII, VII, VI) Model

(as a minumum theoretical framework)

- **Inter Y – Ce sub-site disproportionation reaction:**

$Y^{3+}(VII) + Ce^{4+}(VII) \rightarrow Y^{3+}(VI)+Ce^{4+}(VIII)$

$\Delta g(Ce\text{-}Y)=-RT\cdot \ln K(Ce\text{-}Y)= RT\cdot \ln (4[Y^{3+}(VI)]\cdot[Ce^{4+}(VIII)]/ Y^{3+}(VII)][Ce^{4+}(VII)])$

(or its complementary $Y^{3+}(VII) + Ce^{4+}(VII) \rightarrow Y^{3+}(VIII)+Ce^{4+}(VI)$)

In addition to Intra-Y & Ce-sub-site ones:

$2Y^{3+}(VII)\rightarrow Y^{3+}(VIII)+Y^{3+}(VI)$ & $2Ce^{4+}(VII)\rightarrow Ce^{4+}(VIII)+Ce^{4+}(VI)$

$\Delta g(Y)=-RT\cdot \ln K(Y)= RT\cdot \ln (4[Y^{3+}(VIII)]\cdot[Y^{3+}(VIII)]/[Y^{3+}(VII)]^2)$

$(\Delta g(Ce)=-RT\cdot \ln K(Ce)= RT\cdot \ln (4[Ce^{4+}(VIII)]\cdot[Ce^{4+}(VIII)]/[Ce^{4+}(VII)]^2\ )$

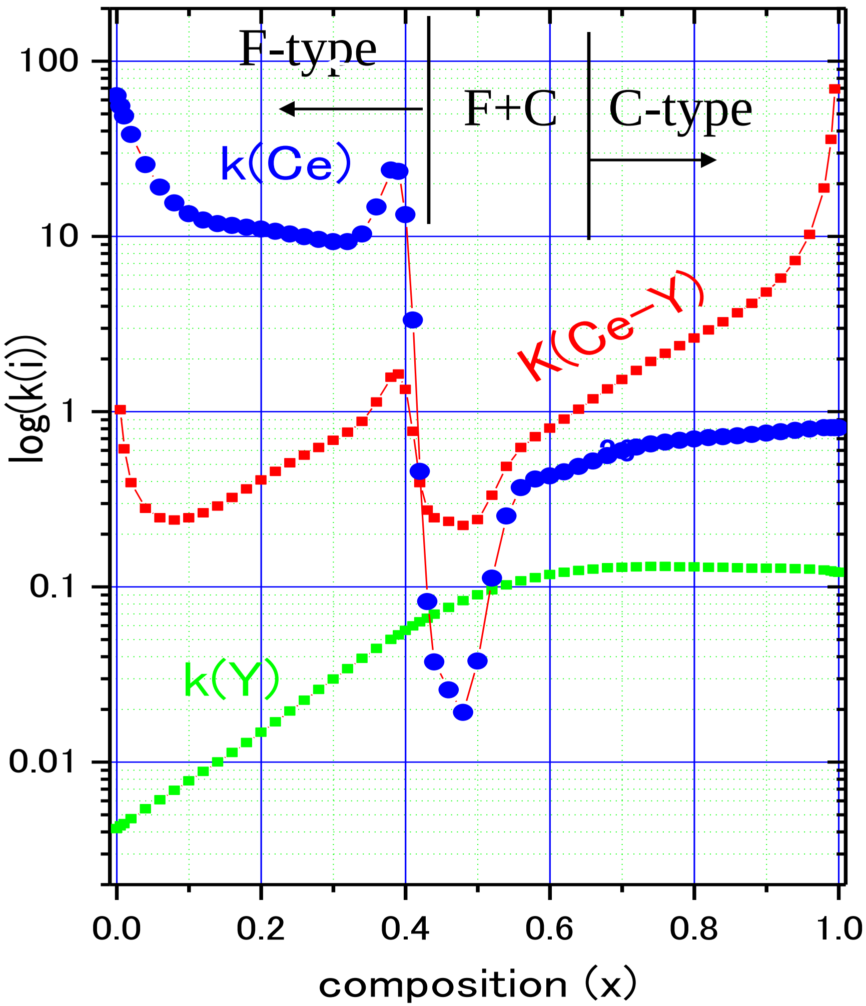
Δg(Y, Ce, Ce-Y)s with suitable y dependence are used to derive all the CN(Y^{3+}, Ce^{4+}), [Y^{3+} & Ce^{4+}(VIII,VII,VI)] & Enthalpy (h(mix)) curves, to construct a self- consistent defect-thermodynamic model of DF phase.

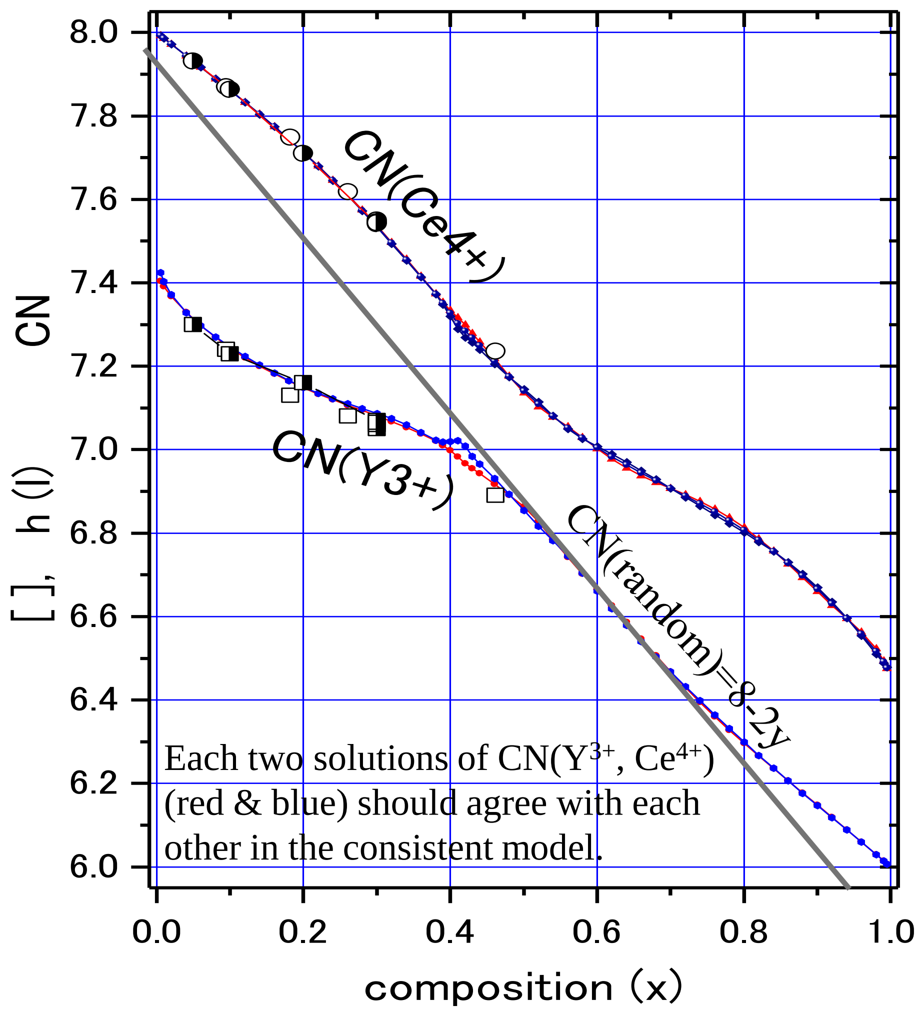
Results of CN(Y^{3+}, Ce^{4+}) Calculations in Ce-Y

Ce^{4+} site : A drastic change over the DF→C di-phasic region from a very disproport'ed (K(Ce)>>1) state to a weakly Ce^{4+}(VII)-enhanced (K(Ce)<1) state.

Y^{3+} site : Only a modest gradual change in the constantly more Y^{3+}(VII)-enhanced state (K(Y)<1) than the former.

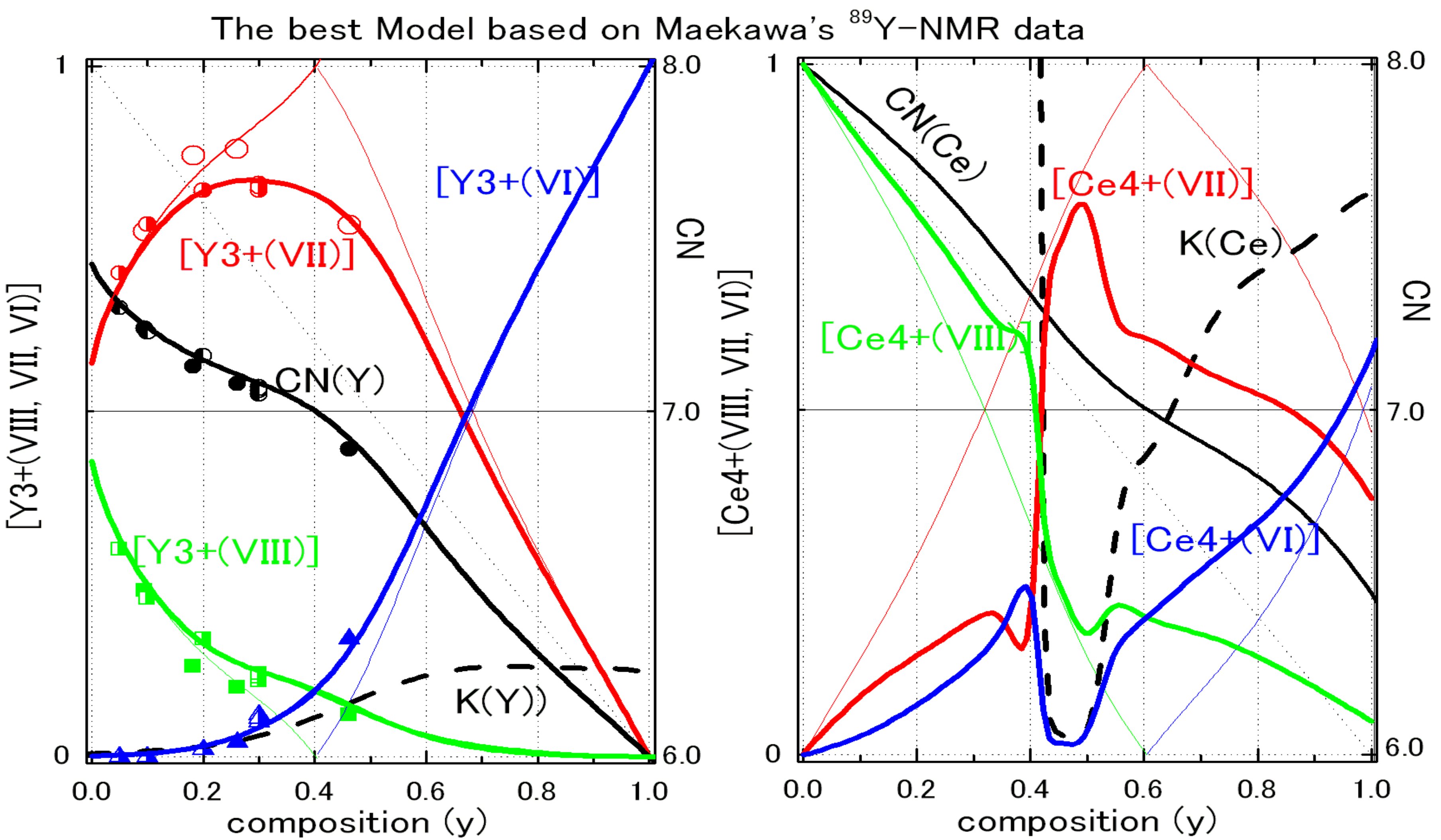
The best model based on Maekawa's 89Y-NMR data





Calculated Individual Y^{3+} and Ce^{4+} site-fraction data

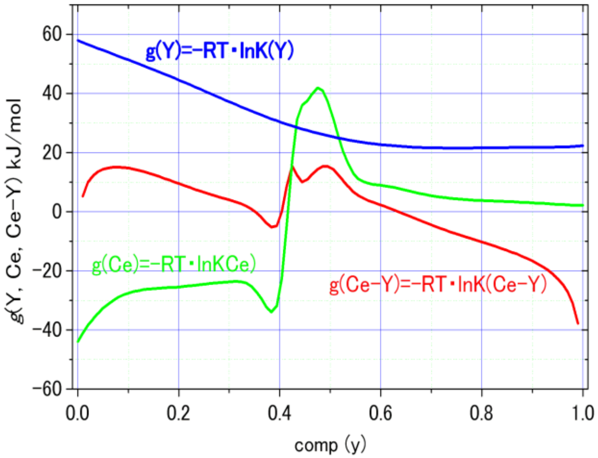
A very steep Ce^{4+} site-F change from a largely disproportionated to a Ce^{4+}(VII)-enhanced state is indeed found in the F+C di-phase area around *y*=0.4-0.55, corresponding to that of the above K(Ce).



h(*g*)(mix) calculation

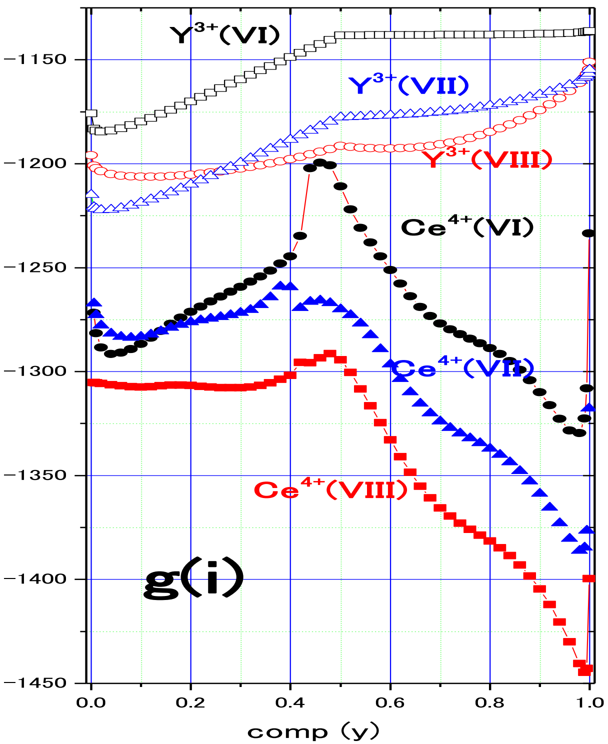
▪Imputs : *g*(Y^{3+}(VIII, VII, VI)) ⟶

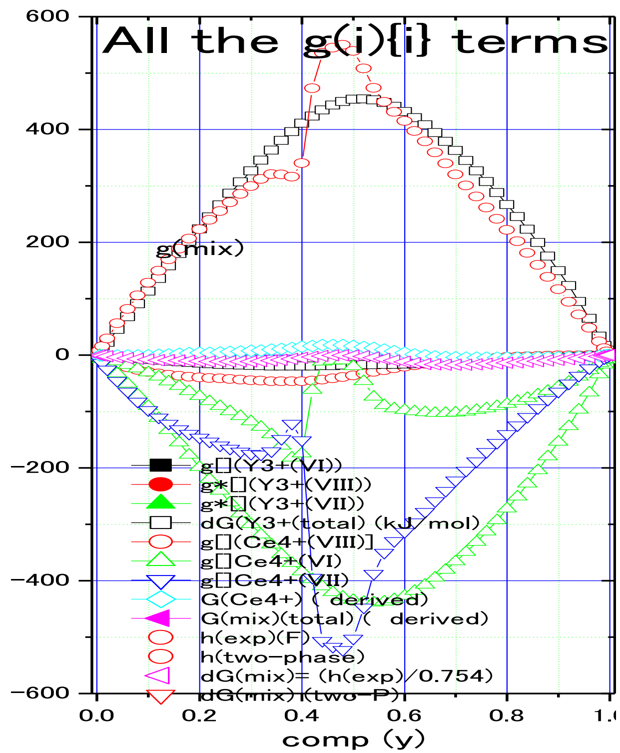
Outputs : *g*(Ce^{4+}(VIII, VII, VI)), *g*(i){i} & *h*(*g*)(mix)



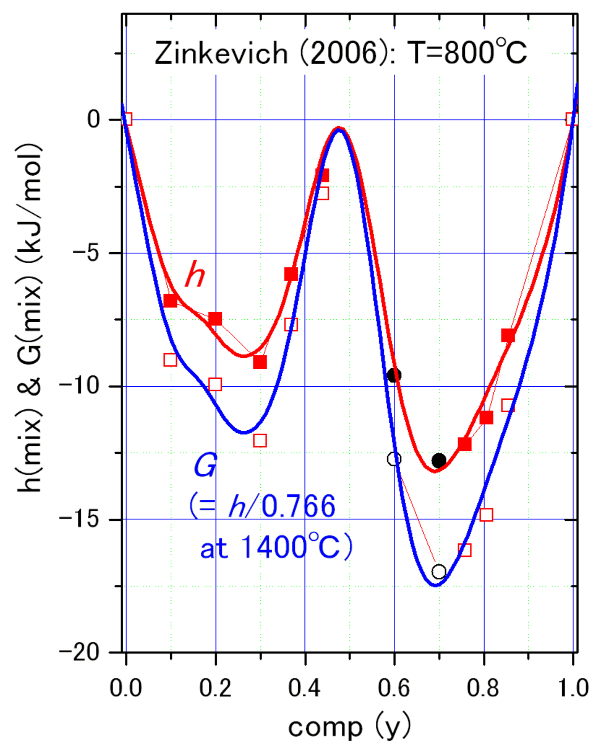
Problem & Prospects:

- **Frozen-in Non-Random Cation sublattice vs. measured lower-*T* *h*(mix) data (at 800℃) relationship**
- **y-dependent *g(h)*(i)s: partly reasonable, for, e.g., Ce^{4+}(VIII) would have different *g(h)* value from that at y=0.**
- **To derive the Full G(SS) exression including complex & restricted non-random Cation-Anion *S*(config) terms.**



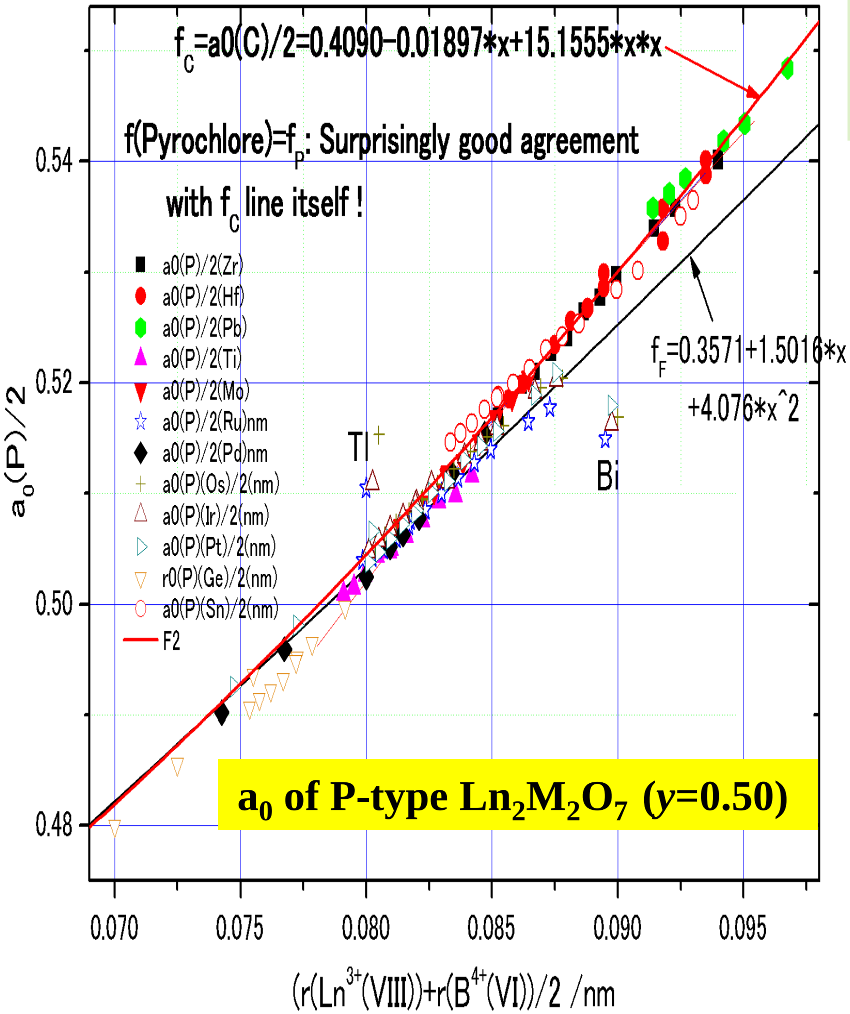


h(mix) (& *g*(mix)) data of Ce−Y



Part IV: Extention to F-P-C ternary a_0(ss) Model for Stabilized M^{4+}=Zr(Hf)) (SZ(SH)s) with inermediate a_0 hump

P (pyrochlore) (or δ)-type distortional dilation effect at y=0.5



a_0 of P-type $Ln_2M_2O_7$ (y=0.50)

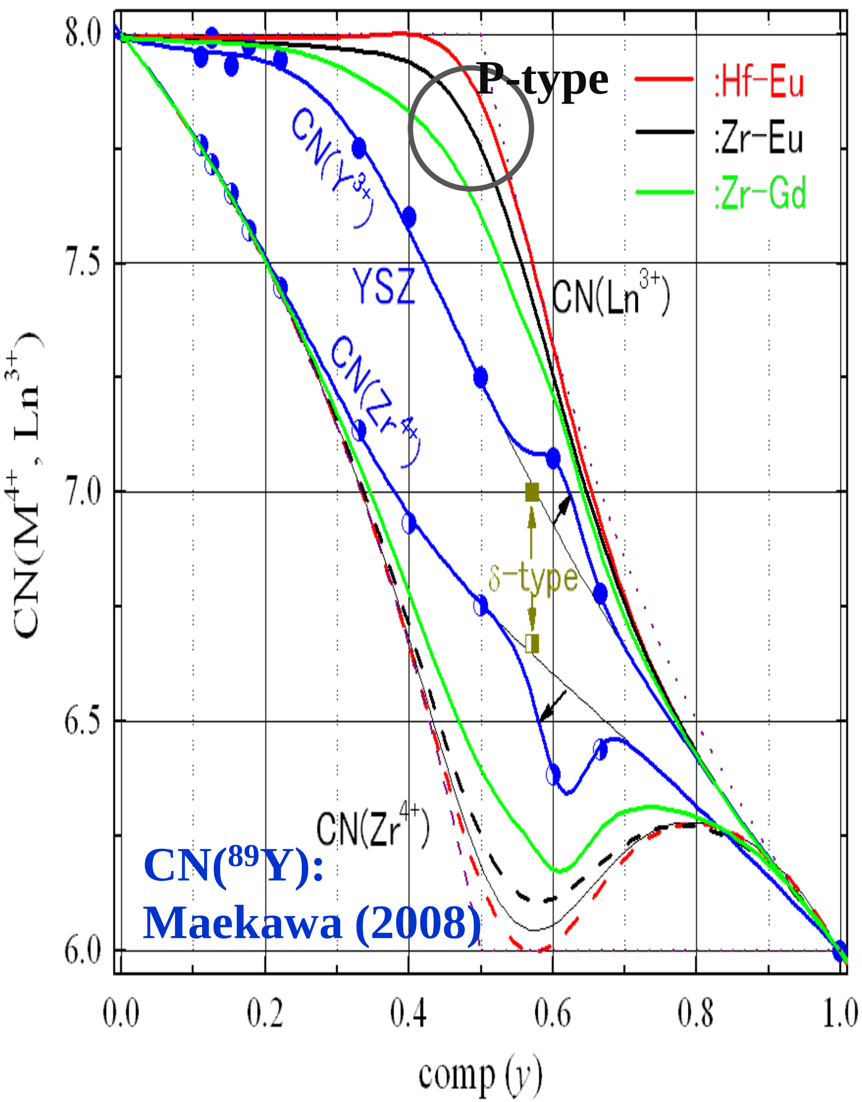
F-P-C Ternary Model (or F-P (for y<0.50) & P-C (y>0.50) quasi binary model)

- $a_0(ss)(F-P) = (1-2y) \cdot f_F + 2y \cdot f_P$
  (for $0 \le y \le 0.50$)
- $a_0(ss)(P\text{-}C) = (1-2y) \cdot f_F + 2y \cdot f_P$
  (for $0.5 \le y \le 1.00$)

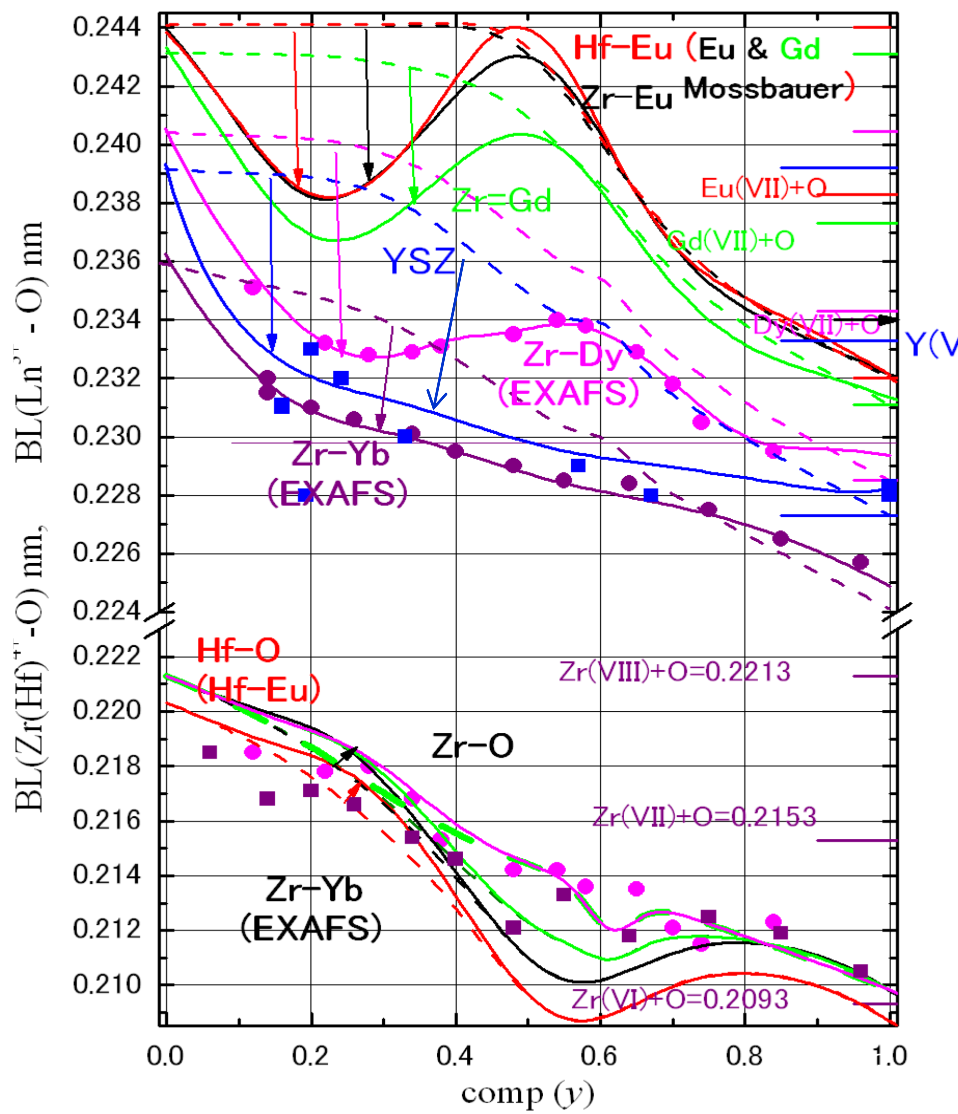
But, its combination with systematized Shannon's $rc(Ln^{3+}, M^{4+})$ expressions is not enpough to describe their a_0(ss) behaviour !

Stabilzied zirconia (Hafnia); NMR, Moessbauer, EXAF data

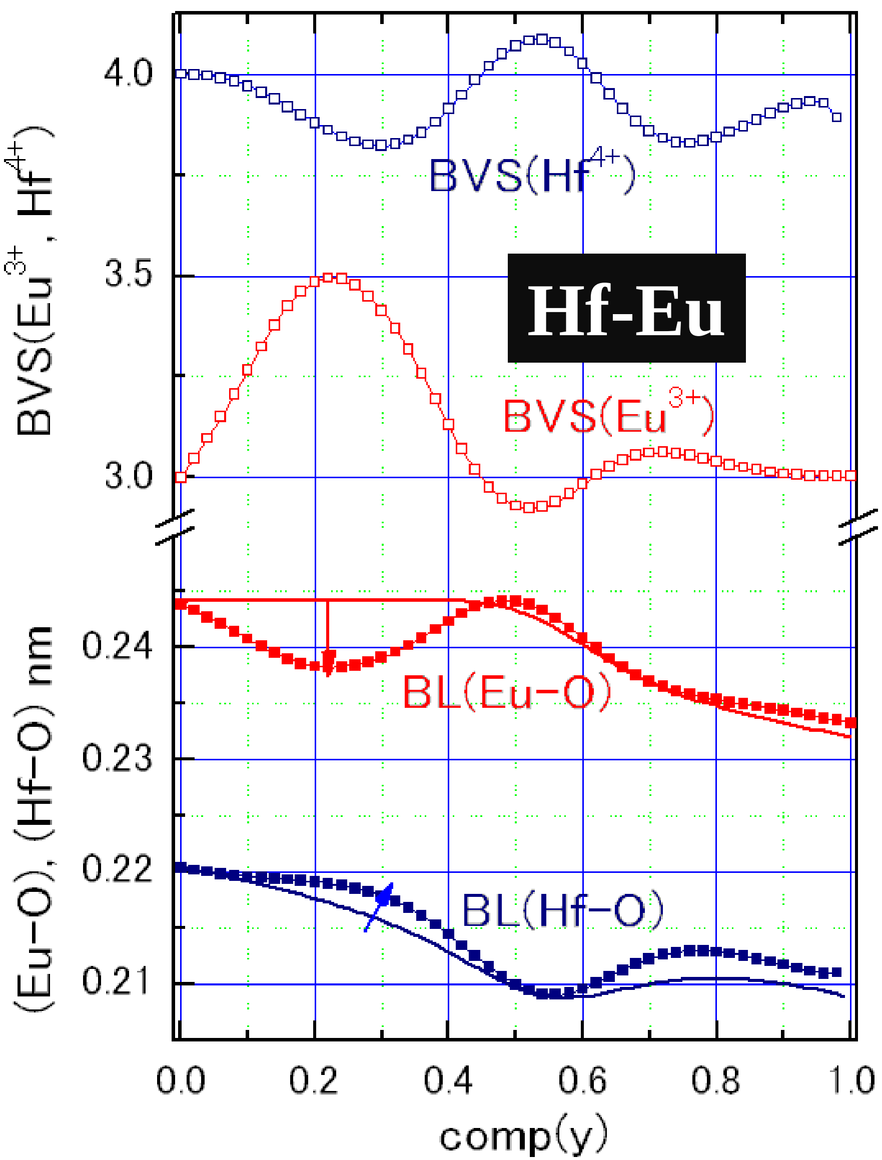
^{89}Y MAS-NMR based non-random CN(Ln, Zr(Hf))



Non-Shannonian (→) Ln(Zr)-O Bond-length (BL(Ln-O)) alteration inSZ(SH)



What does this Non-Shannonian large BL Alteration mean ?



Extended BVS rule

$$(1\text{-}y)\ BVS(M^{4+}) + y\ BVS(Ln^{3+}) = 2\cdot(2-y/2) = 4 - y$$

where

$$BVS(Hf^{4+}) = CN(M^{4+})s(i)$$

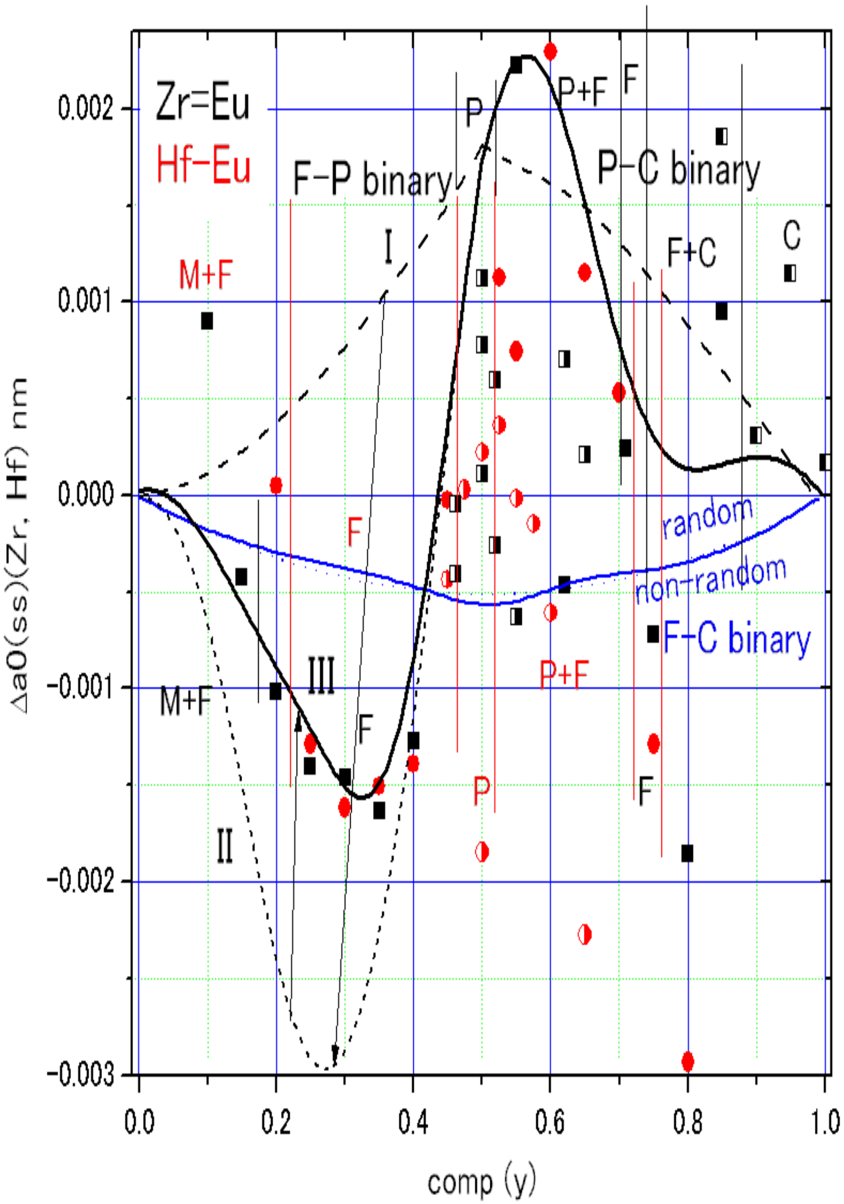
and

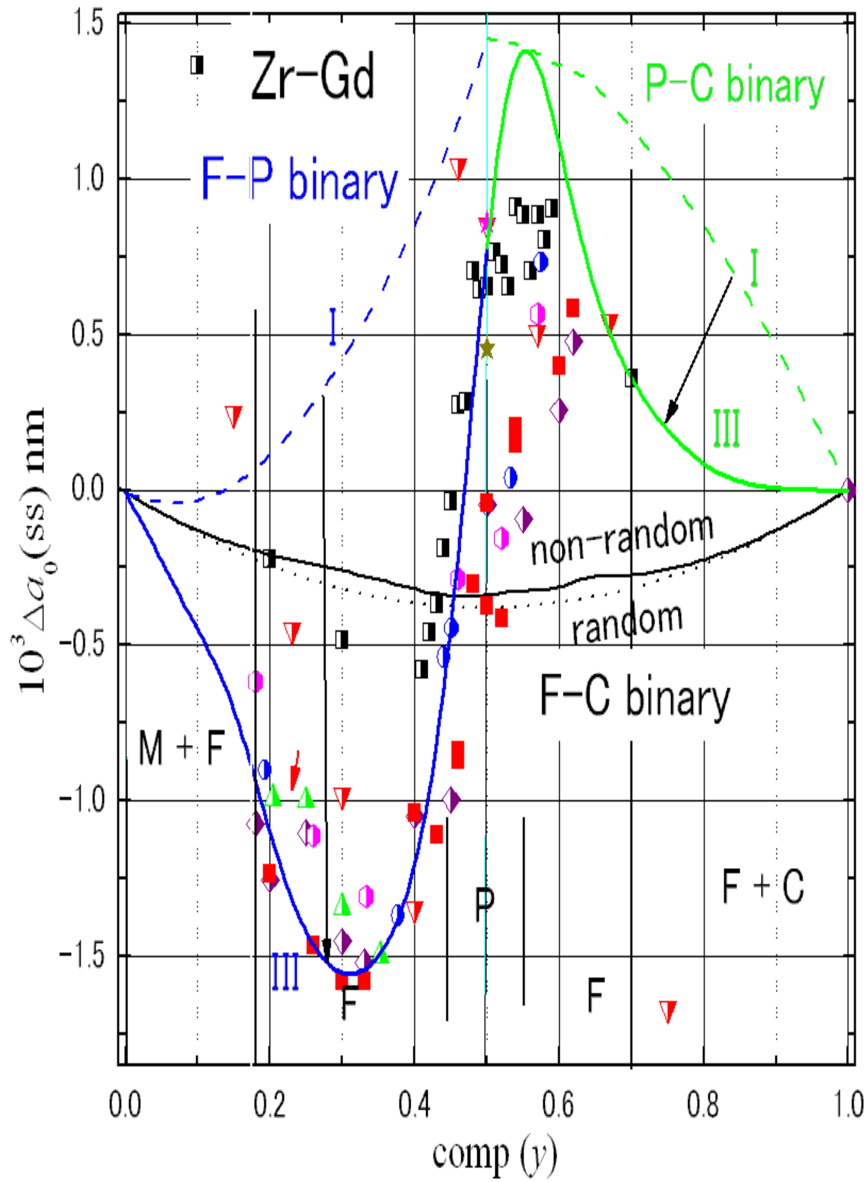
$$s(i) = \exp\{(R_0 - BL(M^{4+}\text{-}O))/0.037\}$$

(Brown)

BL(calc) ~ BL (a_0(ss) model)

Arrival at Quantitative a_0(ss) model (III) with conversely shunken BL(Ln^{3+}-O) & elongated BL(BL(Zr(Hf)$^{4+}$-O)





Summary

New Defect Crystal-Chemical Approach to Non-Vegardianity and Complex Defect Structure of Fluorite-based MO_2-$LnO_{1.5}$ Solid Solutions.

- **Part I:** **A possible unified picture of Δa_0(ss) & Non-Random Defect Structure as a coupled Distortional-Dilation phenomenon in the macroscopic a_0- & microscopic rc-level, respectively.**

- **Part II:** **The aver. non-random CN(Ln^{3+}, M^{4+}) data + restricted non-randomness → mutually non-random cation-anion coordination structure → a new consistent description of intriguing σ (ion)(max) at low-*y* range**

- **Part III:** **A new real local-structure based defect-thermodynamic model of DF phase**

- **Part IV :** **Δa_0(ss) model extension to stabilized pyrochlore-type M^{4+}=Zr & Hf**

The DCC Model is expected to be useful as a macroscopic approach to their comprehenisve a_0(ss), defect-structure & thermodynamic analysis in conjunction with other various exp. & theor. techniques.

Thank you for your kind attention.