The 3rd International ABINIT Developer Workshop 2007
(Liège, Belgium (Jan/30/2007))

Business through Innovation

Virtual Crystal Approximation for Heterovalent Ions

(MM, Uheda, Kijima, ICTMC-15(Kyoto), Physica Status Solidi(a) 203, 2705 (2006))

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Contents:

1. Background:

CaAlSiN$_3$:Eu^{2+} (efficient red phosphor for **white-LED**)

→ Al/Si occupies the same crys. site with occ.=0.5 each

calculations with Al/Si-ordered models & VCA

2. Methodology

DFT-GGA, Virtual Crystal Approximation (VCA)

3. Results & Conclusion

CASN: Geometry optimization, bandstructure/DOS => OK!

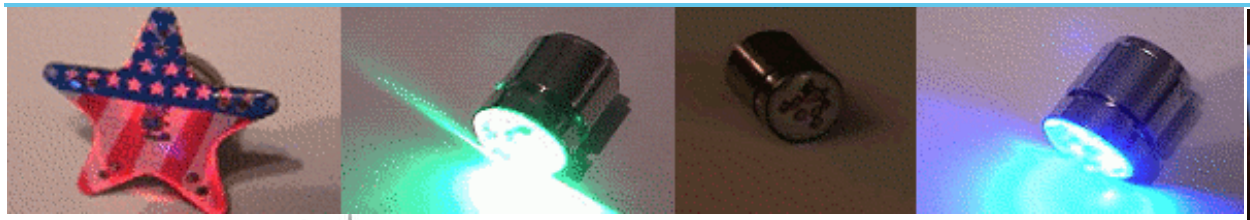
4. Further Tests

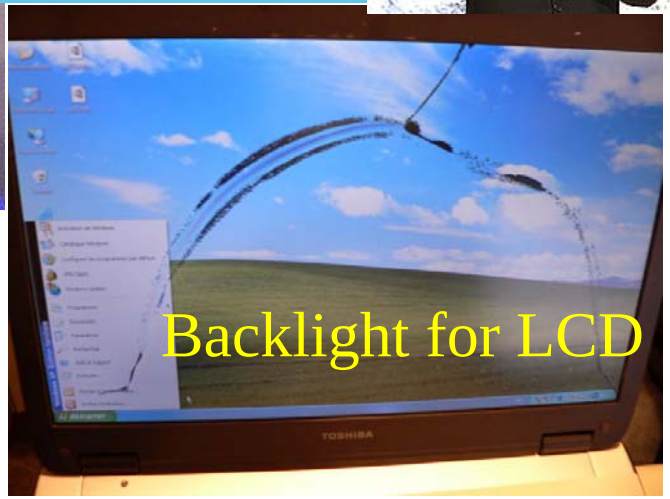
How about other such ionic crystals ?

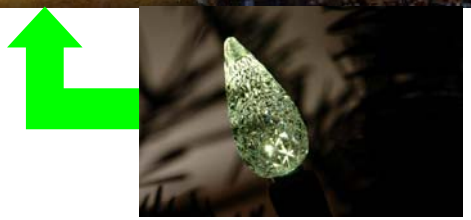
(e.g. gehlenite, celcian, Al-doped Si_2N_2O, …)

LED for next generation illumination

(http://en.wikipedia.org/wiki/LED etc.) **“Convenient Truth”**







white LEDs : LED chip and phosphors

Present type:

Blue-LED + yellow phosphor

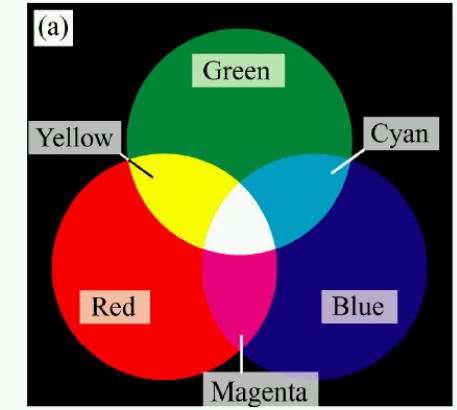
Next generation:

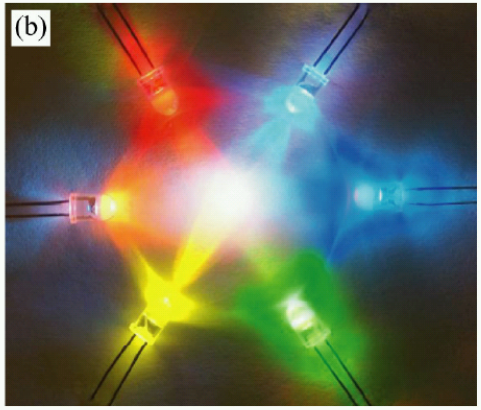
High color rendering types

Blue-LED + yellow&red

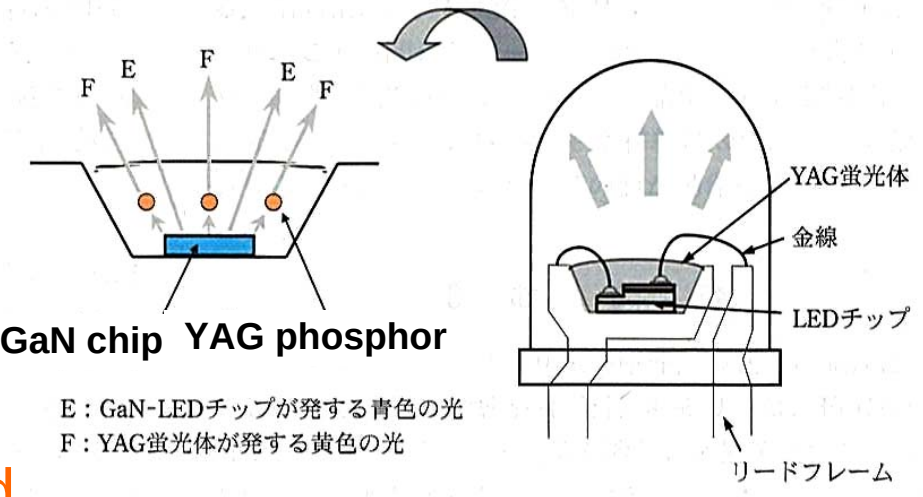
Near UV-LED + blue&green&red

Blue-LED + green&red

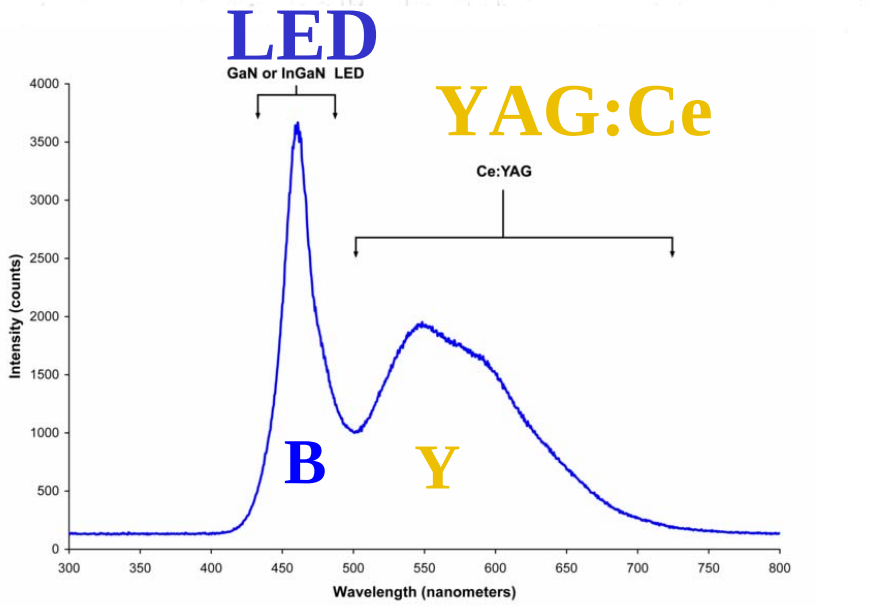




from "**www.lightemittingdiodes.org**"



YAG：Yttrium Aluminum Garnet $(Y_a,Gd_{1-a})_3(Al_b,Ga_{1-b})_5O_{12}:Ce^{3+}$



Example of color rendition

B+G+R = natural White **B+Y = pseudo-White (lacking R)**

- Clear differences in the color rendition can be seen in this August Renoir painting (left-hand side: high CRI; right-hand side: low CRI)

www.LIGHTEMITTINGDIODES.org © E. F. Schubert 138

Capsule Endoscope

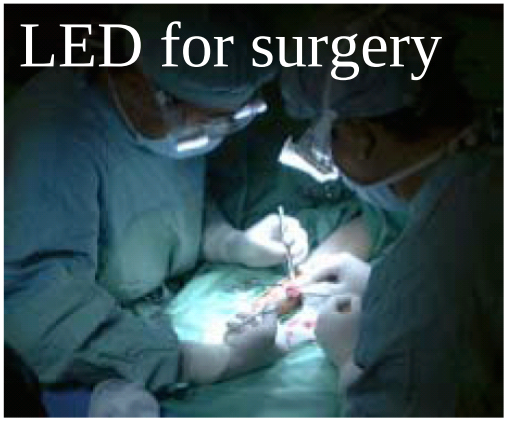


図 8. 3. 3 世界初の LED を用いた外科手術

Distinguish between artery and vein !!

Red phopshors for white LED :

$M_2Si_5N_8:Eu^{2+}$, $MAlSiN_3:Eu^{2+}$, …

(*M*=alkaline earth elements)

Green and red phosphors for white-LEDs presented by Mitsubishi Chemical Corp.

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"The accomplishment of white LEDs with high color rendering, Ra≥93%"

"High luminance and stability"

"Patent free"

Ra: General color rendering index

1. Background

Al/Si-disorder v.s. Pauling 2nd crystal rule

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Efficient host (phosphor/pigment)

$CaAlSiN_3$ (#36 ($Cmc2_1$))

Al^{3+}/Si^{4+}: 4-coord.→ $Z^{3.5+}$

Ca^{2+} : 5-coord.

$N^{[2]}$: 2-coord., $N^{[3]}$: 3-coord.

Pauling 2nd Crystal Rule (PSCR):

$$V_{anion} \fallingdotseq -\Sigma V_{cation}/C_{cation}$$

$N^{[2]}$: -(3.5/4×2+2/5×3)= -2.95

$N^{[3]}$: -(3.5/4×3+2/5)= -3.025

Approximately satisfies the PSCR!

(N.B.) Si_2N_2O (#36 ($Cmc2_1$))

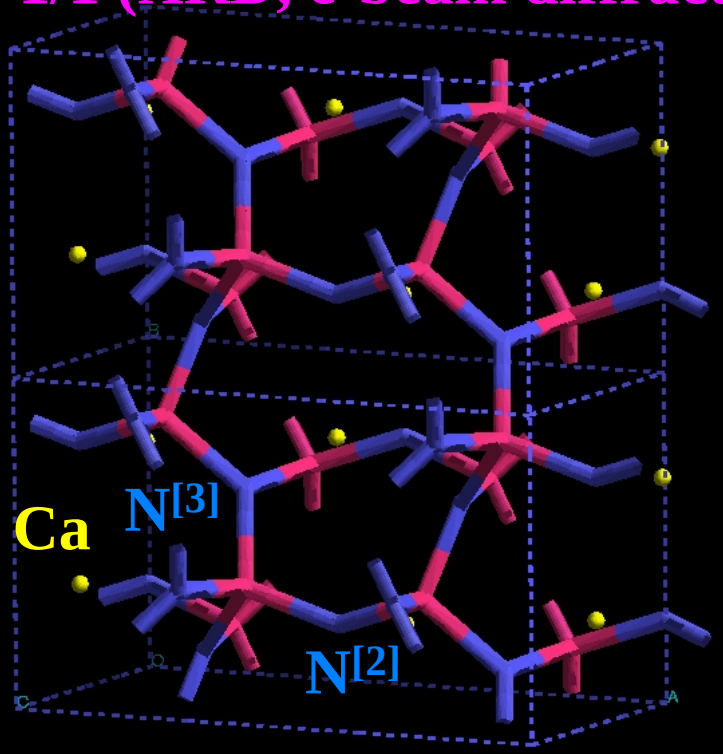
no Ca, Si only, $N^{[2]}$ →O

Si:4-coord, N:3-coord, O:2-coord.

O: -(4/4)×2= -2

N: -(4/4)×3= -3

Al/Si=1/1 (XRD, e-beam diffraction)



Eu^{2+}@ Ca → red luminescence

White LED（Hg-free）using InGaN

(K. Uheda et al., Electrochem. Solid State Lett. 9, H22(2006) etc)

1. Background

Why not Al/Si-ordered models ?

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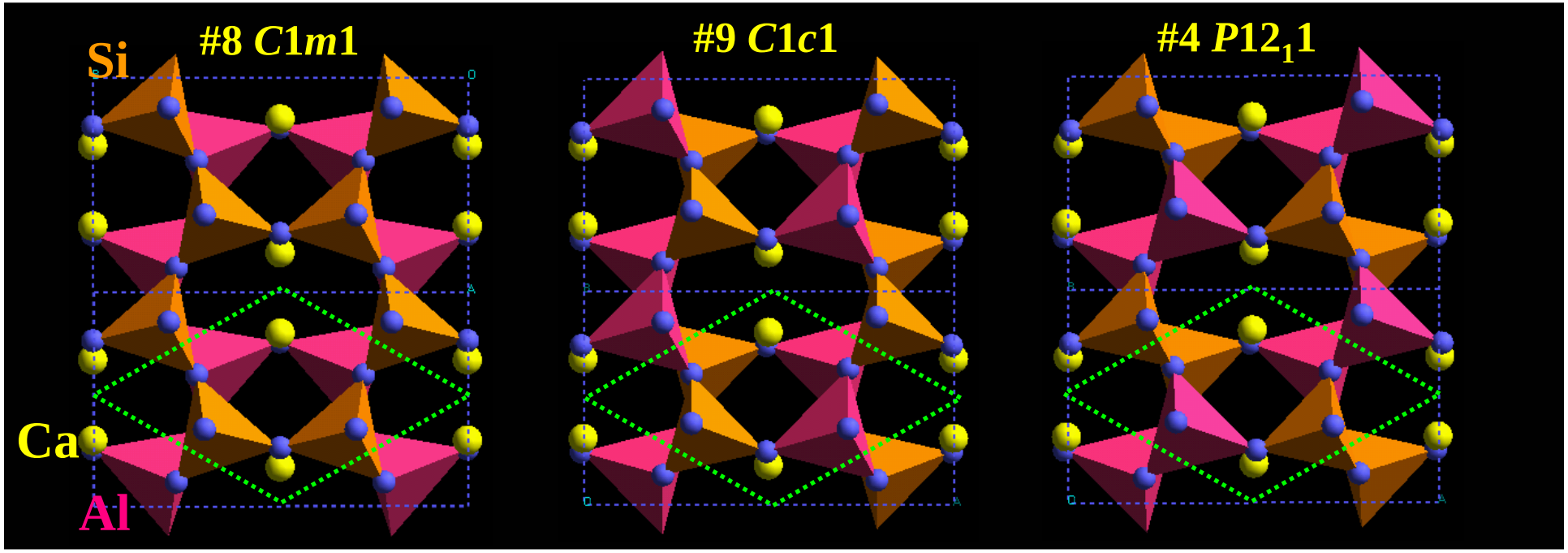
Q1 : Assume Al/Si-order ? →**symmetry lower than #36, *monoclinic***
The monoclinic models remain close to orthorhombic(#36) ?
Energetics among the Al/Si-ordered models explain Al/Si-disorder ?



Q2 : Virtual Crystal Approximation(VCA) can treat the Al/Si-mixed case?
VCA results (with $Z^{3.5+}$) ←→ results of the Al/Si-ordered models ?

NB: *rare* heterovalent VCA:Vanderbilt: $(BiScO_3)_{1-x}(PbTiO_3)_x$: PRB67, 224107(2003)

2. Methodology

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Density Functional Theory – Generalized Gradient Approximation :
Perdew-Burke-Ernzerhof (PBE)-type functional :
Phys. Rev. Lett. 77, 3865 (1996), ibid 80, 891 (1998)

First-Principles Band Calculation : ABINIT code (www.abinit.org)
Reference: X. Gonze et al., Comp. Mater. Sci. 25, 478 (2002)

Troullier-Martins-type pseudopotentials, prepared with FHI98PP code
FHI98PP : www.fhi-berlin.mpg.de/th/fhi98md/fhi98PP
M. Fuchs and M. Scheffler, Comp. Phys. Comm. 119, 67 (1999)
VCA : mixing Al/Si ionic potential (1:1 ratio) → details in Next page
keywords : ntypalch, mixalch (NB: npsp,znucl,ntypat,algalch=1)

Energy cut-off: 100Ry (∵ Ca: shallow core electrons as valence)

BZ integral : Monkhorst-Pack grid, $\Delta k \leqq 0.05$ Å^{-1}

SCF sycle : Conjugate Gradient based on the minimum of the energy
X. Gonze, Phys. Rev. B54, 4383 (1996)

Convergence ≤ 0.6 kcal/mol should be expected for energetics (1eV=23.06kcal/mol)

Virtual Atom Pseudopotential (implemention in ABINIT, already available !)

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$$V_{\mathrm{VCA}}^{\mathrm{ps}}[x] = xV_{\mathrm{Al}}^{\mathrm{ps}} + (1-x)V_{\mathrm{Si}}^{\mathrm{ps}} \rightarrow Z_{\mathrm{Al/Si}} = 3x+4(1-x) \text{ for Ewald sum}$$

$$V^{\mathrm{ps}}(r,r') = V^{\mathrm{loc}}(r)\delta(r-r') + \sum_{l,m} \frac{\left|\Delta V_l^{\mathrm{ps}}\right|\phi_{lm}\rangle\langle\phi_{lm}\left|\Delta V_l^{\mathrm{ps}}\right|}{\langle\phi_{lm}\left|\Delta V_l^{\mathrm{ps}}\right|\phi_{lm}\rangle}$$

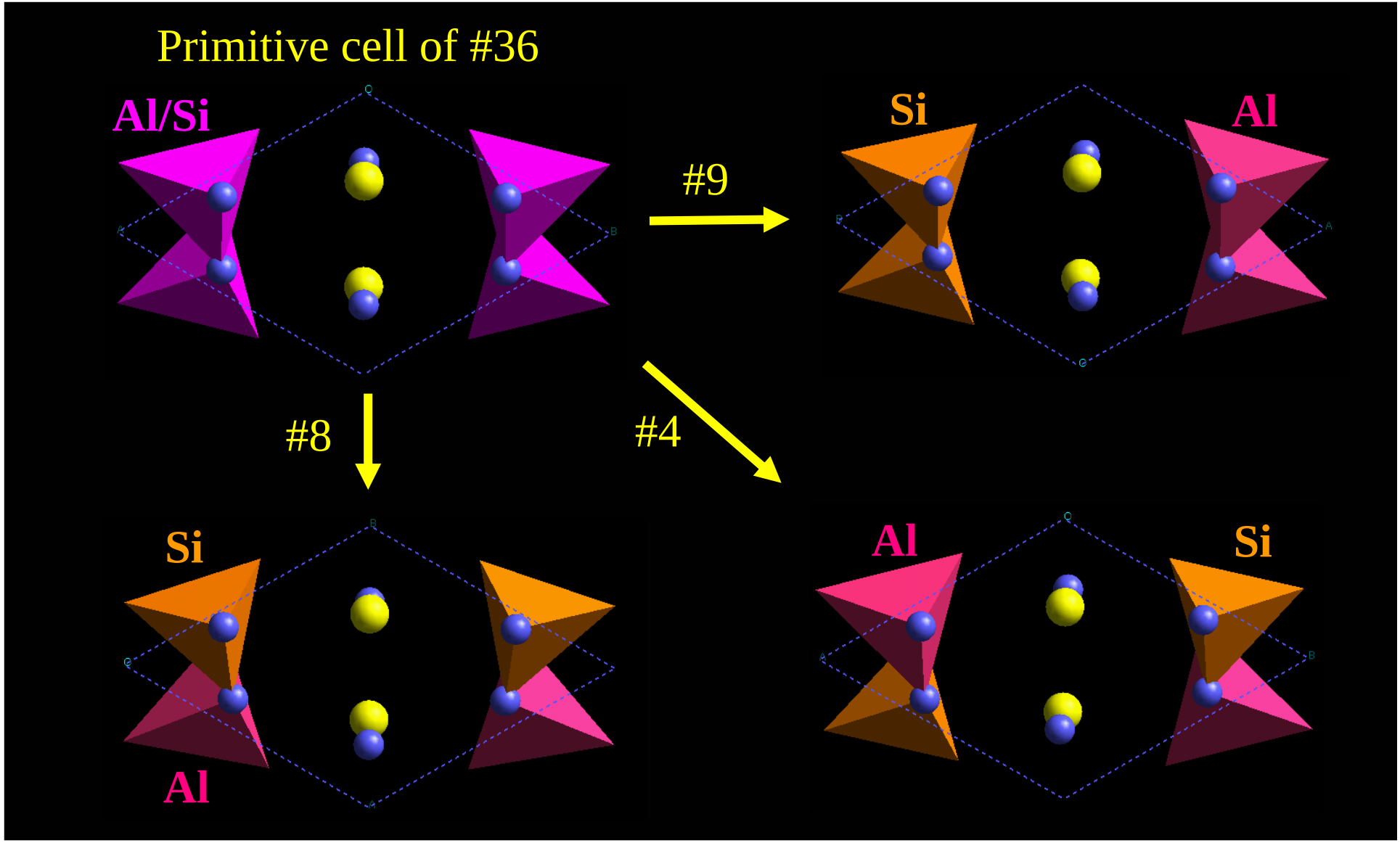
$$V_{\mathrm{VCA}}^{\mathrm{ps}}(r,r') = \left[xV_{\mathrm{Al}}^{\mathrm{loc}}(r) + (1-x)V_{\mathrm{Si}}^{\mathrm{loc}}(r)\right]\delta(r-r')$$

$$+ \sum_{l,m} \frac{\left|x\Delta V_{\mathrm{Al},l}^{\mathrm{ps}}\right|\phi_{lm}^{\mathrm{Al}}\rangle\langle\phi_{lm}^{\mathrm{Al}}\left|x\Delta V_{\mathrm{Al},l}^{\mathrm{ps}}\right|}{\langle\phi_{lm}^{\mathrm{Al}}\left|x\Delta V_{\mathrm{Al},l}^{\mathrm{ps}}\right|\phi_{lm}^{\mathrm{Al}}\rangle}$$

$$+ \sum_{l,m} \frac{\left|(1-x)\Delta V_{\mathrm{Si},l}^{\mathrm{ps}}\right|\phi_{lm}^{\mathrm{Si}}\rangle\langle\phi_{lm}^{\mathrm{Si}}\left|(1-x)\Delta V_{\mathrm{Si},l}^{\mathrm{ps}}\right|}{\langle\phi_{lm}^{\mathrm{Si}}\left|(1-x)\Delta V_{\mathrm{Si},l}^{\mathrm{ps}}\right|\phi_{lm}^{\mathrm{Si}}\rangle}$$

(Ref. Ph.Ghosez, D.Desquesnes, X.Gonze, K.M.Rabe, AIP Conf. Proc. 535, 102 (2000))

3. Results : models



3. Results：Geom. Opt. (calc. v.s. expt.)

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	#36	#8	#9	#4	expt1	expt2
a	9.8859	9.8717	9.9112	9.9114	9.8020	9.851
b	5.6645	5.6455	5.6887	5.6839	5.6506	5.654
c	5.0840	5.1219	5.0701	5.0726	5.0633	5.071
α	90.00	89.67	90.00	90.00	90.00	90.00
β	90.00	90.00	90.09	90.00	90.00	90.00
γ	90.00	90.00	90.00	89.82	90.00	90.00

→ Al/Si-ordered models approximately keep the orthorhombic cell

expt1: K. Uheda et al. (2006)、expt2: F. Ottinger, Ph.D Thesis (2004)

3. Results : Geom. Opt. (calc. v.s. expt.)

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	#36	#8	#9	#4	expt1	expt2
Ca-N	2.420(x 2) 2.479 2.525 2.612	2.509 2.516(x 2) 2.630 2.633 2.342(x 2) 2.351 2.467 2.754	2.406 2.432 2.492 2.521 2.603	2.407 2.424 2.481 2.524 2.599	2.405 (x 2) 2.490 2.539 2.586	2.430 (x 2) 2.503 2.520 2.609
typical Al-N 1.87	1.806 1.819 1.829 1.833	1.839 1.859 1.877 1.949	1.880 1.881 1.890 1.907	1.872 1.883 1.889 1.920	1.783 1.809 1.811 1.833	1.797 1.807 1.819 1.831
typical Si-N 1.74		1.726 1.777 1.786 1.792	1.737 1.742 1.783 1.787	1.742 1.745 1.773 1.788		

Why not Al/Si-ordered models ?

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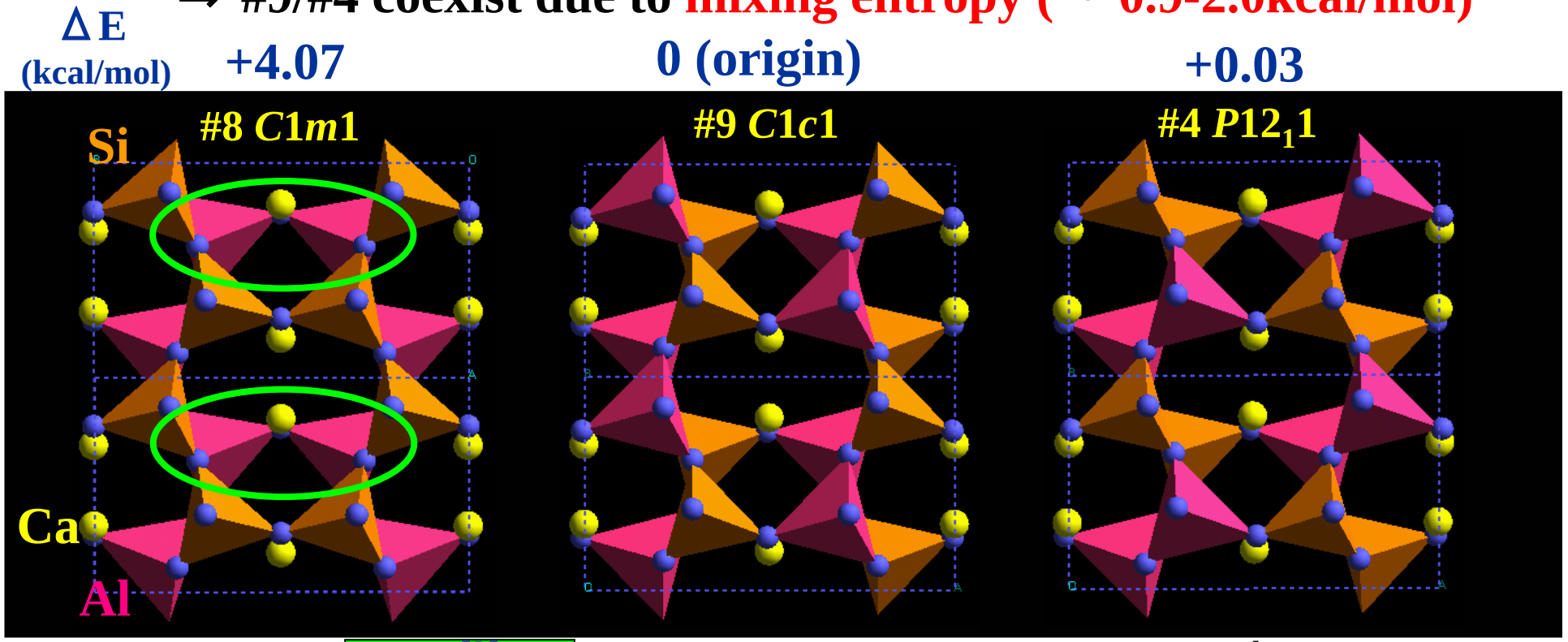
Q1 : Assume Al/Si-order ? →**symmetry lower than #36, *monoclinic***

The monoclinic models remain close to orthorhombic(#36) ?→ **YES**

Energetics among the Al/Si-ordered models explain Al/Si-disorder ?

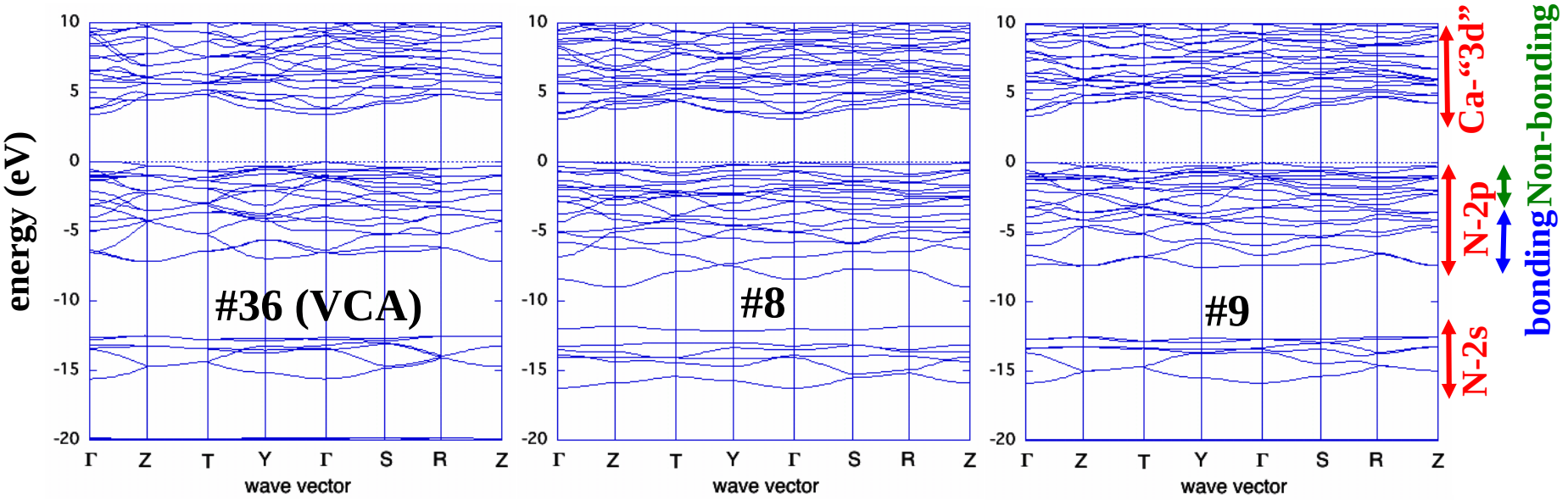
⇒ **#9/#4 coexist due to mixing entropy (～ 0.9-2.0kcal/mol)**



corner-sharing **Al-N[2]-Al** seems unstable (∵ Pauling's 2nd crystal rule)

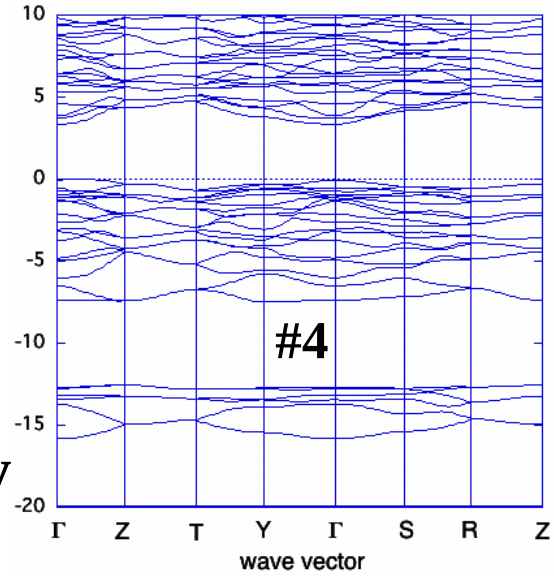
→ analogy to Loewenstein's rule (avoid corner-sharing **Al-O[2]-Al**) ?

3. Results : Electronic structure (Band)

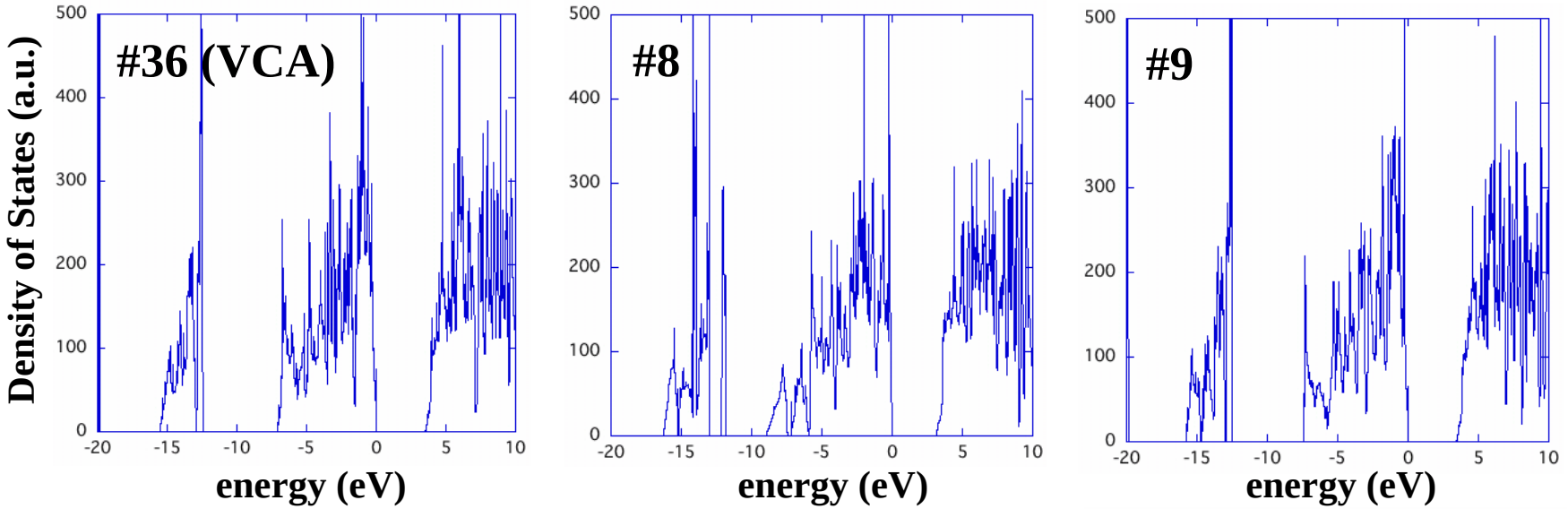


Based on the geometry optimized by VCA

- **Overall, topology appears very similar !**
  #9 v.s. #4 … almost the same !!
  (∵ ΔE_{tot} < 0.1kcal/mol)
- ***Indirect band gap***
- **Band splitting due to the lower symmetry due to "Al/Si order"**



3. Results : Electronic structure (DOS)



Based on the geometry optimized by VCA

#36 similar with #9/#4

#9 v.s. #4 … almost the same !!

(NB: DOS (#4/#8/#9) remains
almost the same even after the geom. opt.)

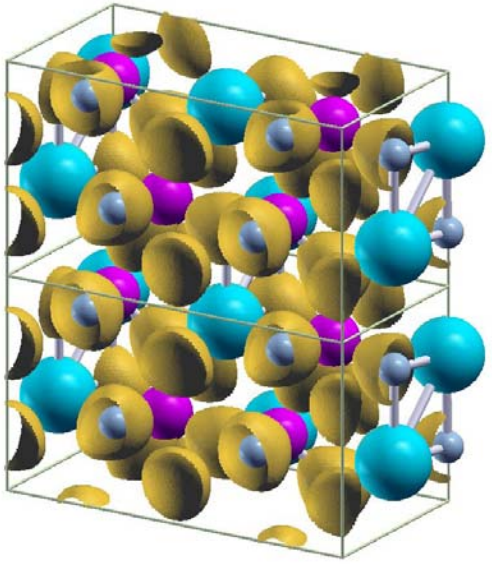
Why the heterovalent VCA worked ??

$$V_{\mathrm{VCA}}^{\mathrm{ps}}[x] = x V_{\mathrm{Al}}^{\mathrm{ps}} + (1-x) V_{\mathrm{Si}}^{\mathrm{ps}}$$ → $Z_{\mathrm{Al/Si}}$ = 3x+4(1-x) for Ewald sum

High ionicity

→ electron clouds around N ions

→ less sensitive about the pseudization of Al/Si site ?



→ How about pseudoatom with Z=(13+14)/2=13.5 ?
FHI98PP adopted for the PP with Z=13.5

(NB: Shiraishi-method for "H"-termination of GaAs surface models
H(Z=0.75) for As-surface, H(Z=1.25) for Ga-surface)

3. Results：Geom. Opt. (calc. v.s. expt.)

(#36: with () … Z=13.5)

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	#36 (Z=13.5)	#8	#9	#4	expt1	expt2
a	**9.8859 (9.8757)**	9.8717	9.9112	9.9114	9.8020	9.851
b	**5.6645 (5.6642)**	5.6455	5.6887	5.6839	5.6506	5.654
c	**5.0840 (5.0805)**	5.1219	5.0701	5.0726	5.0633	5.071
α	90.00	89.67	90.00	90.00	90.00	90.00
β	90.00	90.00	90.09	90.00	90.00	90.00
γ	90.00	90.00	90.00	89.82	90.00	90.00
ΔE (kcal/mol)		**+4.07**	**0 (origin)**	**+0.03**		**⇒ #9/#4 coexist**

expt1: K. Uheda et al. (submitted)、expt2: F. Ottinger, Ph.D Thesis (2004)

3. Results : Geom. Opt. (calc. v.s. expt.)

(#36: with () … Z=13.5)

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	#36	#8	#9	#4	expt1	expt2
Ca-N	**2.420(x 2)** **2.479** **2.525** **2.612** **(2.420(x2))** **(2.476)** **(2.525)** **(2.609)**	2.509 2.516(x 2) 2.630 2.633 2.342(x 2) 2.351 2.467 2.754	2.406 2.432 2.492 2.521 2.603	2.407 2.424 2.481 2.524 2.599	2.405 (x 2) 2.490 2.539 2.586	2.430 (x 2) 2.503 2.520 2.609
Al-N	**1.806** **1.819** **1.829** **1.833**	1.839 1.859 1.877 1.949	1.880 1.881 1.890 1.907	1.872 1.883 1.889 1.920	1.783 1.809 1.811 1.833	1.797 1.807 1.819 1.831
Si-N	**(1.805)** **(1.817)** **(1.827)** **(1.832)**	1.726 1.777 1.786 1.792	1.737 1.742 1.783 1.787	1.742 1.745 1.773 1.788		

NB: Results : Electronic structure (Band)

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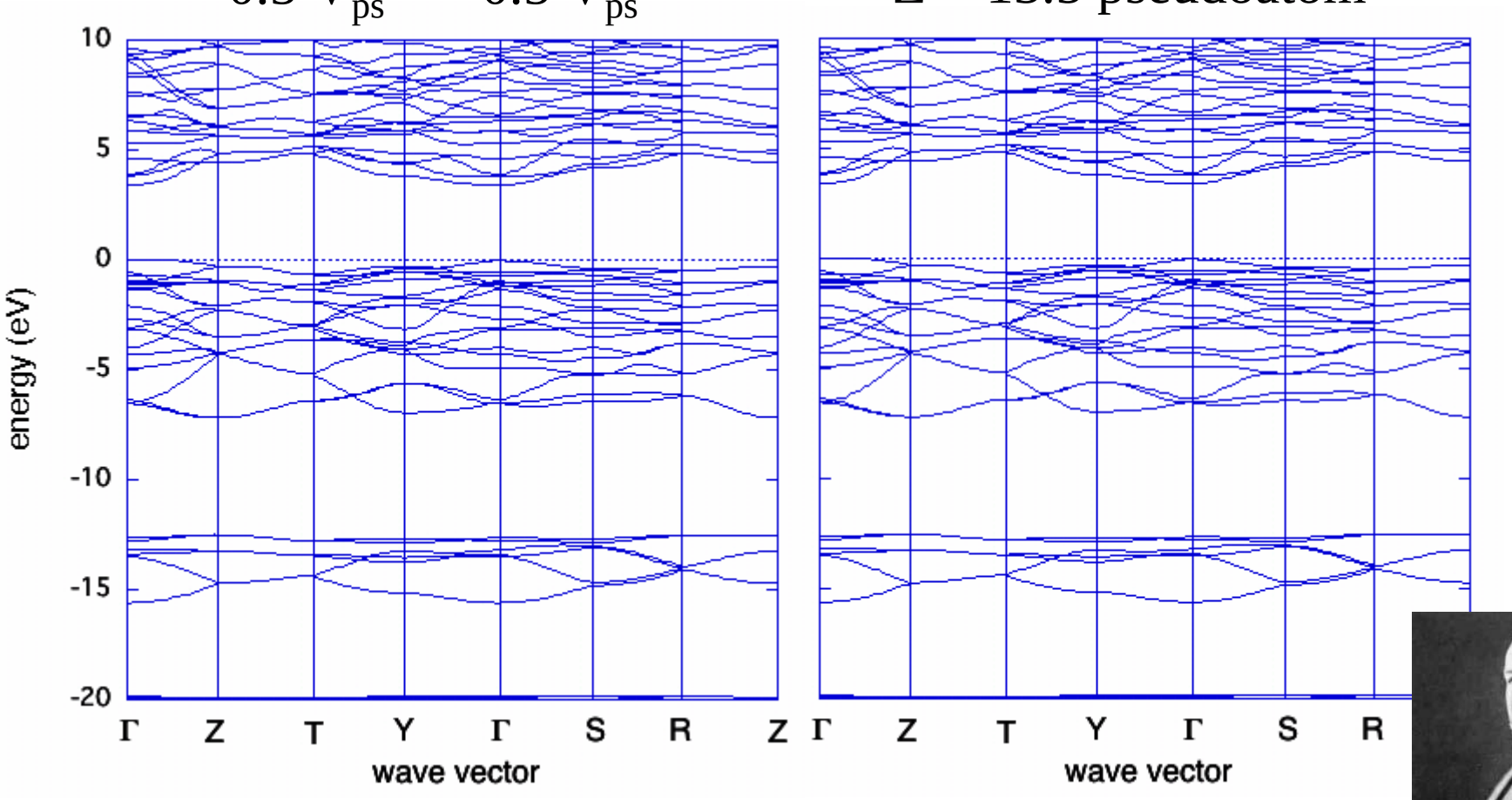
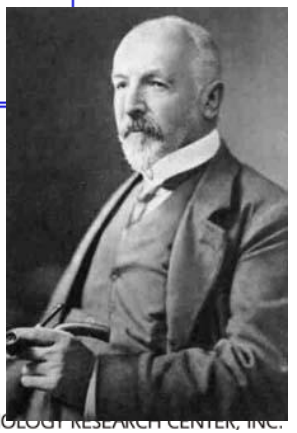
$0.5\ V_{ps}^{Al} + 0.5\ V_{ps}^{Si}$ Z = 13.5 pseudoatom

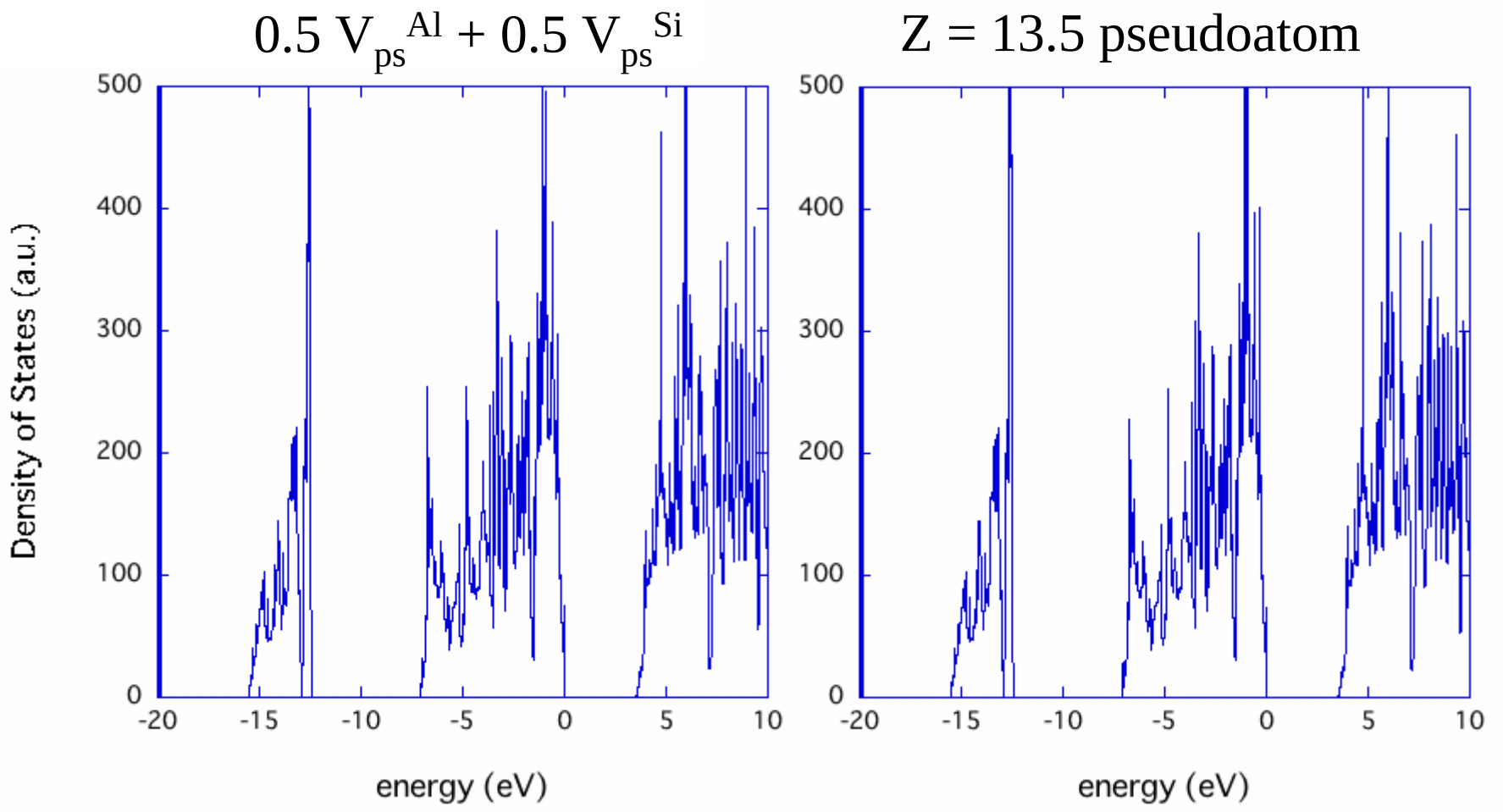




"Je le vois, mais je ne le crois pas !"

(Georg Cantor)

NB. Results : Electronic structure (DOS)



4. Conclusion

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☺ Experimental crystal structures **approximately reproduced** by aliovalent VCA & Al/Si-ordered models

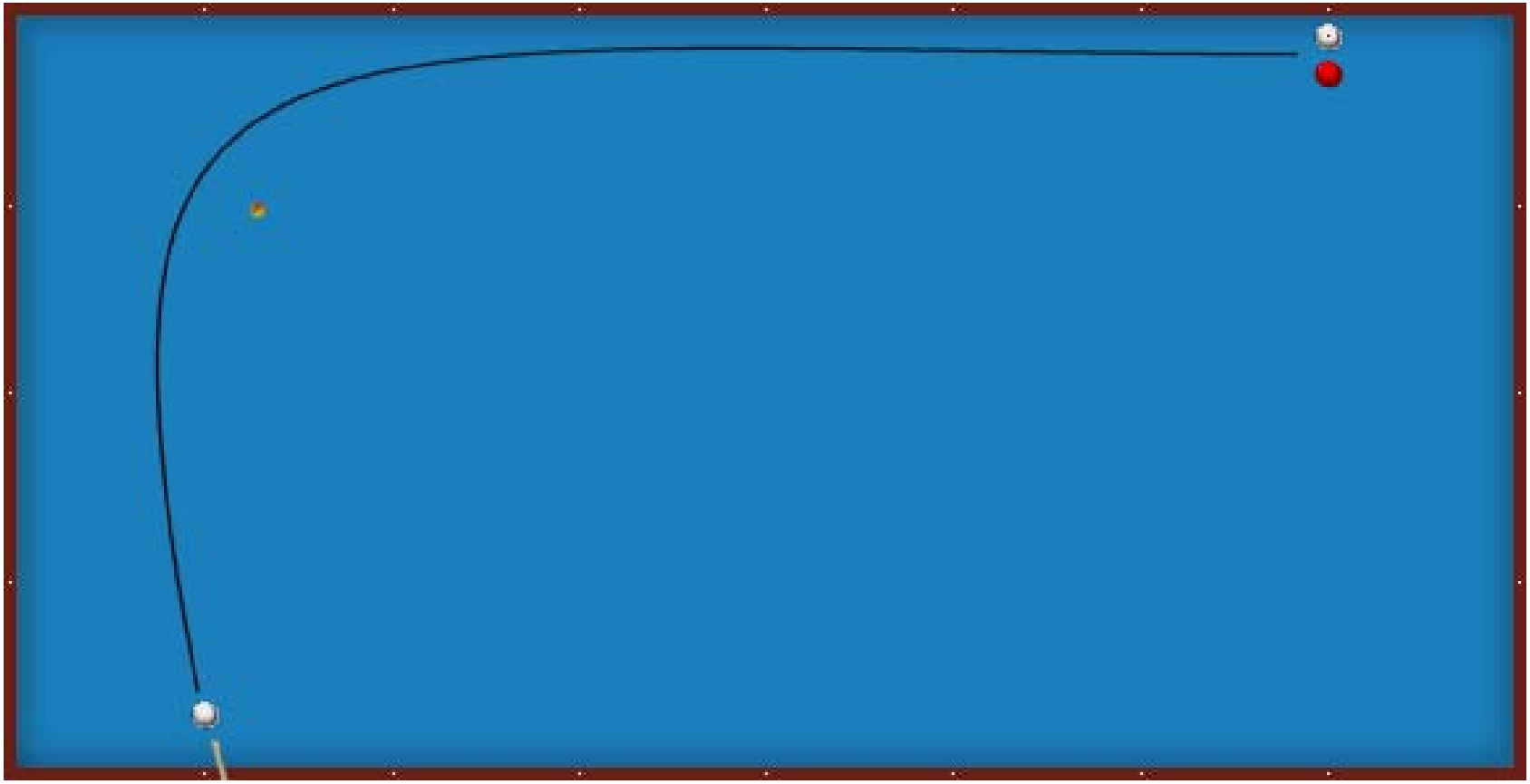
☺ Al/Si-ordered model: #9/#4, similarity in atomic/electronic structure
ΔE < 0.1 kcal/mol → #9/#4 will coexist due to ***mixing entropy***
→ a mosaic structure of #9/#4 cells → XRD determination as # 36

☺ #8 less stable than #9/#4 by 4.1 kcal/mol
→ avoidance of Al-$N^{[2]}$-Al network ? (analogy of Loewenstein's rule)

☺ Similarity of electronic structure (Band/DOS) among #36/#4/#8/#9
→ reproduces the experimental structure, ***Indirect band gap***

☺ Why heterovalent VCA worked ? → chemical similarity of Al and Si
e.g. ionic size, electronegativity … but ***how to justify ?***
→ may encourage such heterovalent VCA to other ionic compounds ?
→ may be useful for solid-solution compounds such as **SiAlON** ?

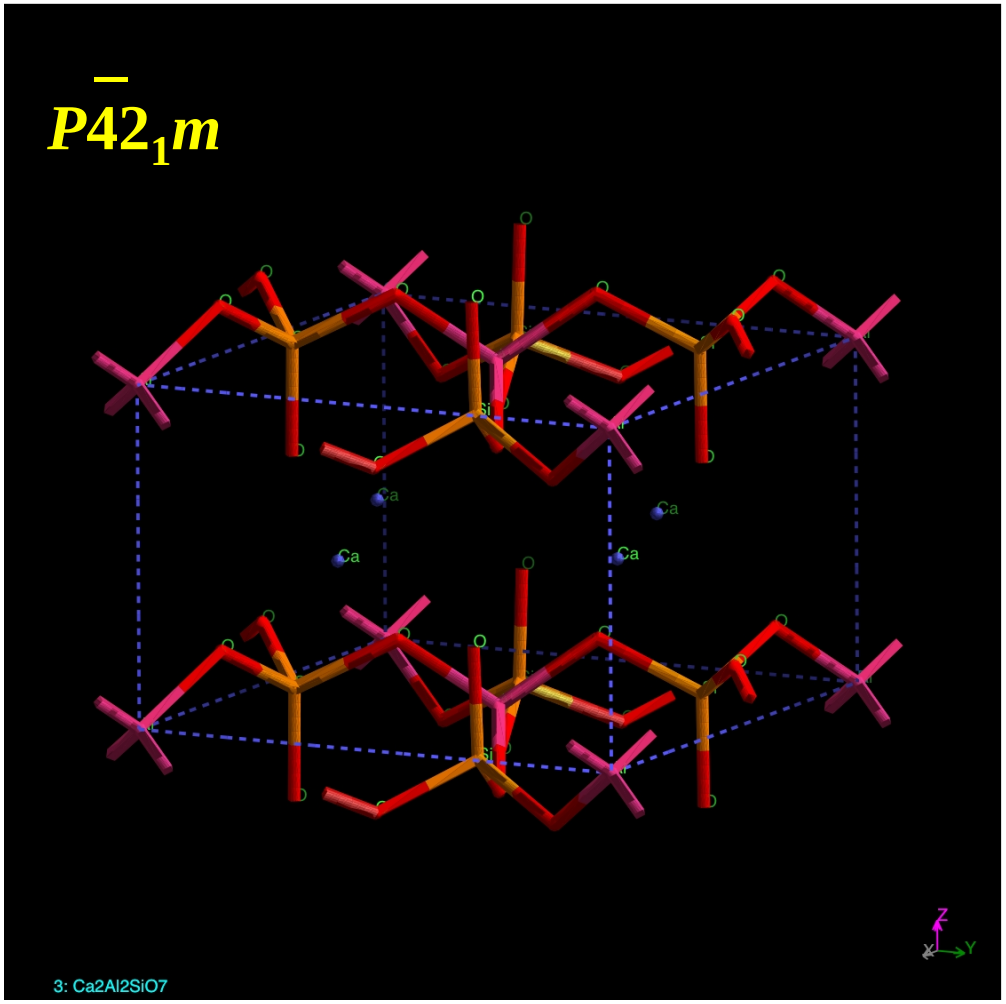
Well, our case is just a "fluke" ?!



How about other ionic crystals ?

How about other ionic crystals ? (#1:gehlenite)

$CaAl_2SiO_7$ → $CaAl(Al/Si)O_7$ with Al/Si disorder



	a(Å)	c(Å)
Expt	7.6850	5.0636
LDA	7.5918	4.9438
GGA	7.7491	5.0902
GGA	7.6407	5.0455

(Winker et al. CPL362, 266 (2002)
CASTEP code: Ultrasoft PP)

The VCA worked again !

How about other ionic crystals ? (#2:celsian)

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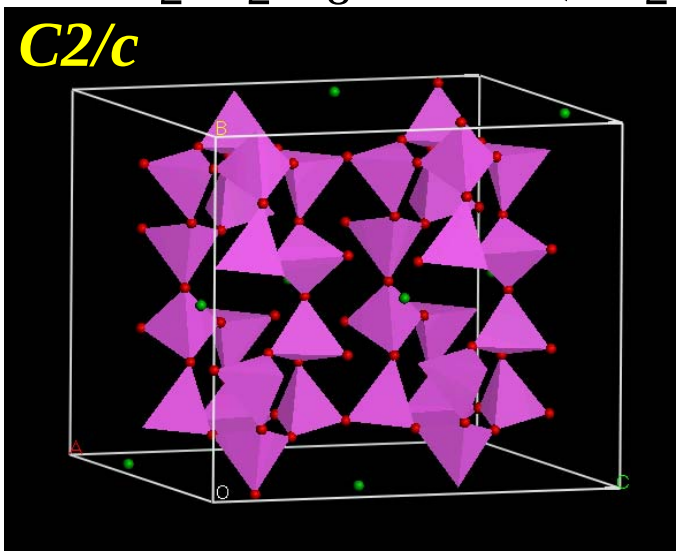
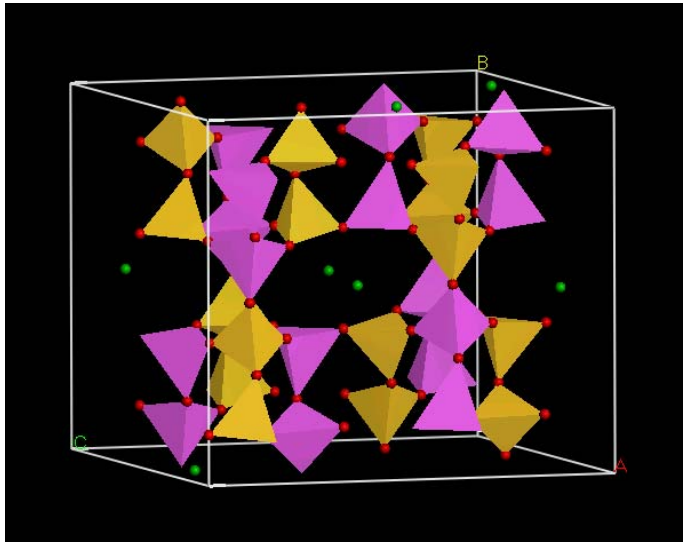
$BaAl_2Si_2O_8$ → $Ba(Al_2/Si_2)O_8$ with Al/Si disorder





	a	b	c	β
Expt	**8.622**	**13.078**	**14.411**	**115.09°**
GGA (VCA)	**8.7058**	**13.1977**	**14.5617**	**115.13°**

The VCA worked again and again !

(You still say, “This is a fluke” ?!)

GGA 8.7607 13.2110 14.6108 115.10°
(an ordered model (keeping C2/c))

How about other ionic crystals ? (#3: sinoite)

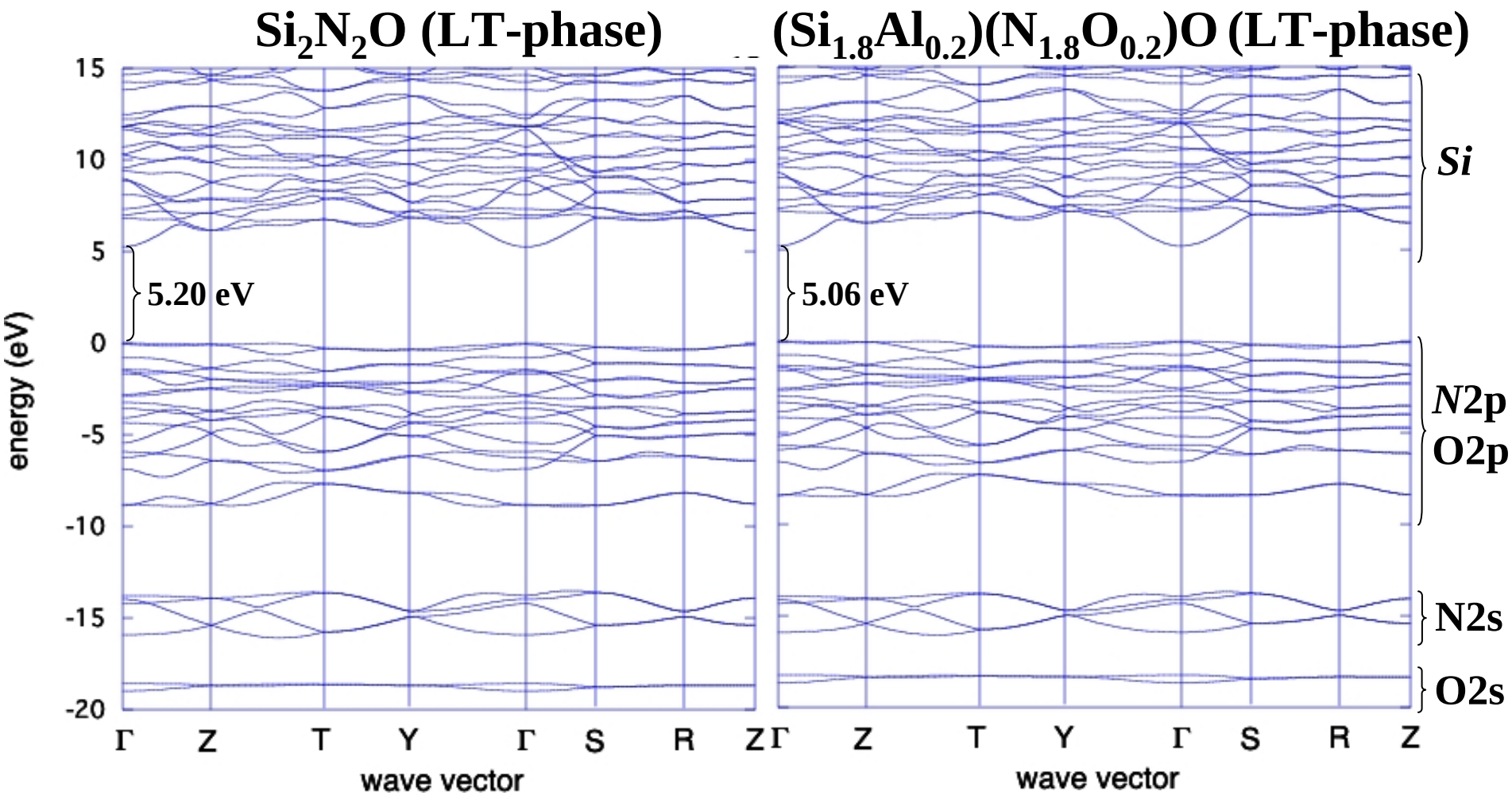
	Si_2N_2O(HT)		Si_2N_2O(LT)	$Si_{1.8}Al_{0.2}N_{1.8}O_{1.2}$(LT)	
	calc.	expt.[1]	calc.	calc.	expt.[2]
a	8.9641	8.866	8.8953	8.9518	8.8488
b	5.5415	5.486	5.4099	5.4105	5.3752
c	4.8893	4.845	4.8674	4.8727	4.8355

- HT($Cmc2_1$) is more stable than LT(*Bba*2) by 1.5 kcal/mol
  → Expt.[2] : LT phase transforms to HT phase at T > ～1350℃
- Substitution of (Si,N) with (Al,O) → larger Vo. (known in HT(O'-sialon))[3]

Refractive indices
may also be discussed

Ref.1: S.R.Srinivasa and L. Cartz, J. Appl. Cryst. 10, 167 (1977)
Ref.2: M.E. Bowden et al. J.Am.Ceram.Soc.81, 2188 (1998)
Ref.3: O.Lindqvist et al., Acta Cryst. B47, 672 (1991)

How about other ionic crystals ? (#3: sinoite)



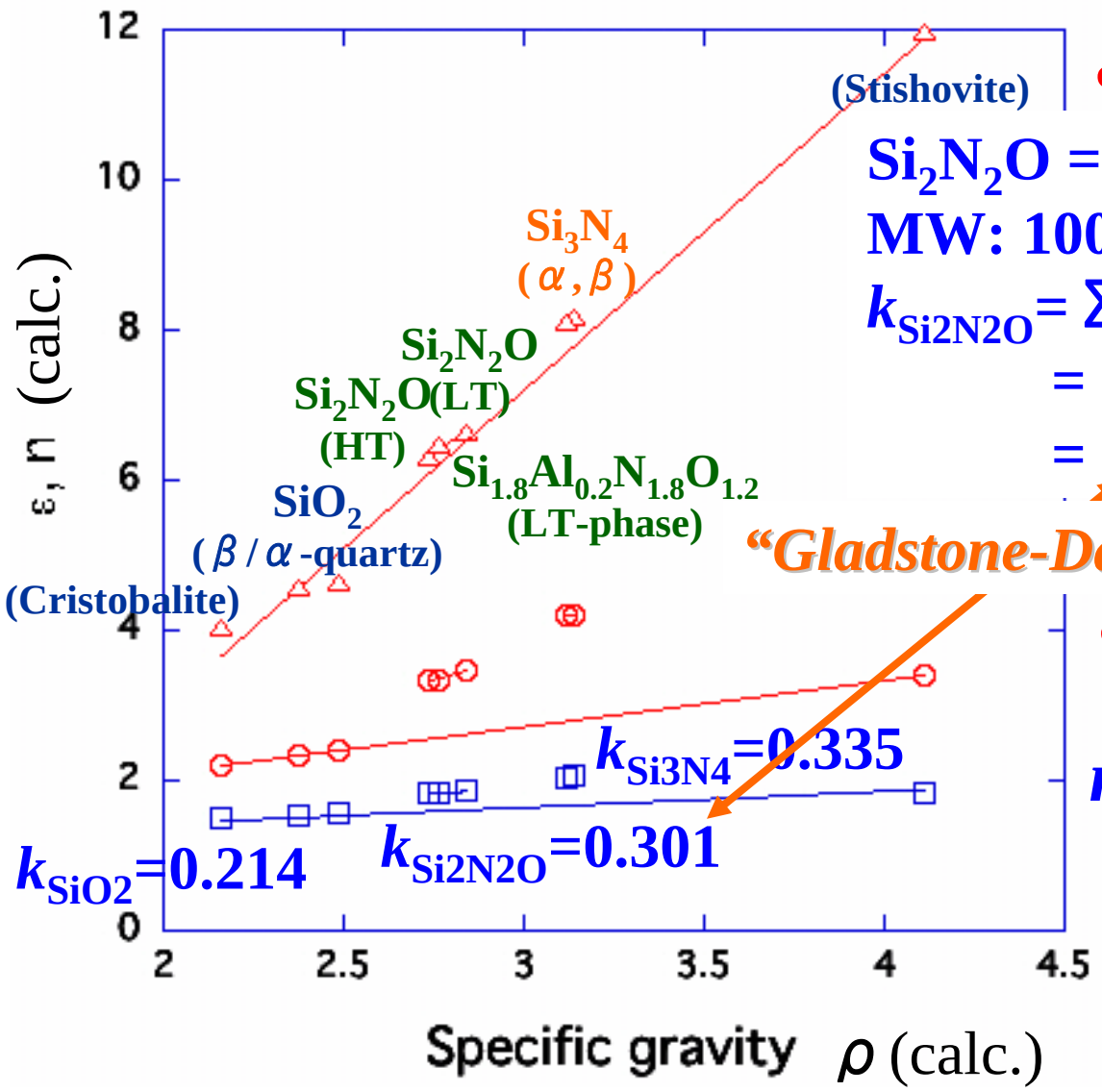
Mixed PPs (Al-SI, N-O) seemingly works … ε (optic) can be computed ("Gladstone-Dale" comfirmed)

We are gathering experience now …

Thank you for your attention !

Specific gravity v.s. Dielectric Properties (Gladstone-Dale Relationship)

Business through Innovation



ε^0

$Si_2N_2O = 0.5Si_3N_4 + 0.5SiO_2$

MW: $100 = 0.5 \cdot 140 + 0.5 \cdot 60$

$k_{Si2N2O} = \Sigma p_i k_i$

$= 0.7 \cdot k_{Si3N4} + 0.3 \cdot k_{SiO2}$

$= 0.299$

"Gladstone-Dale" seems OK !

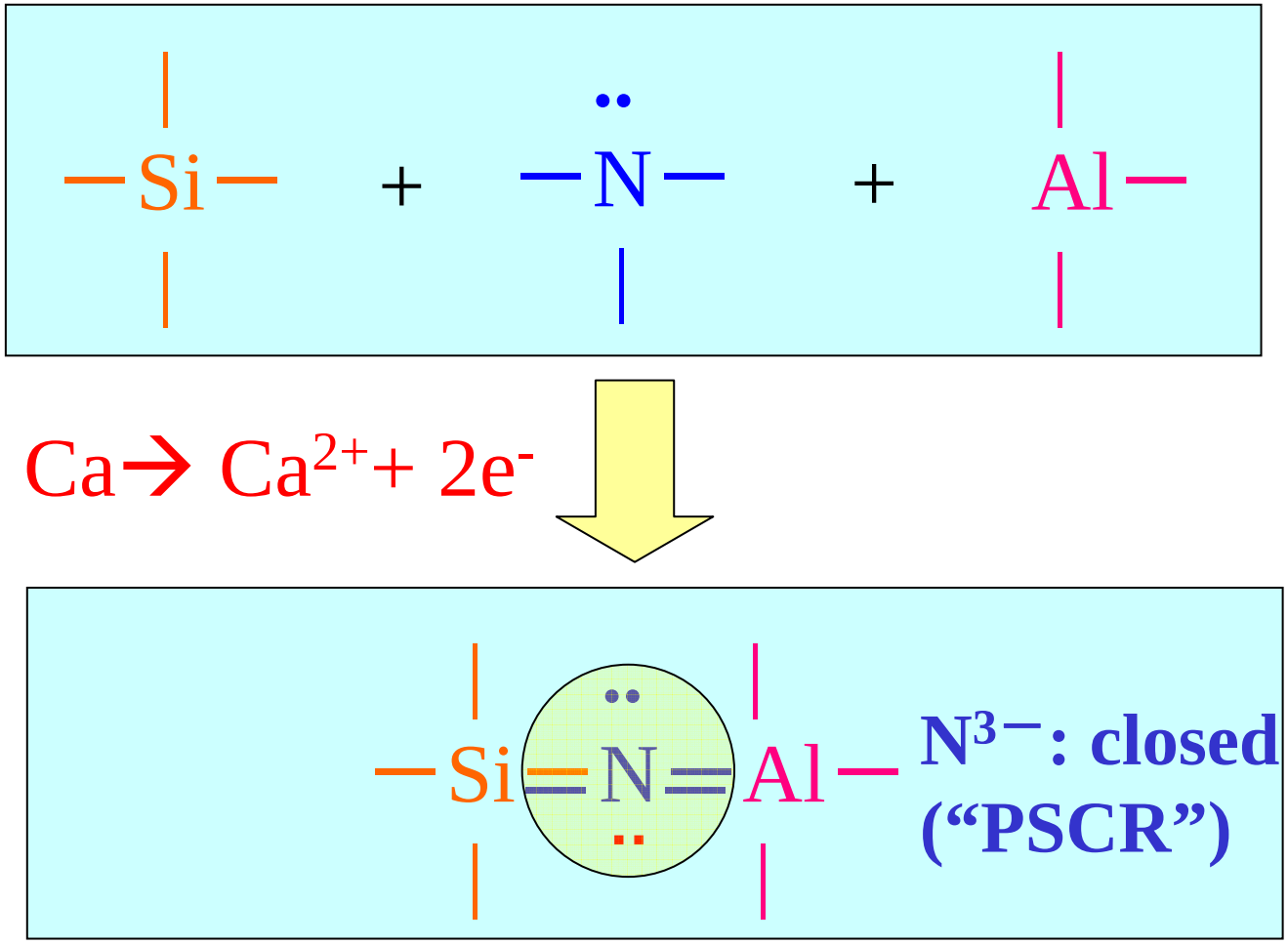
ε^∞

$n = \sqrt{\varepsilon^\infty}$

$n = 1 + k \cdot \rho$

where $k = \Sigma p_i k_i$ (Gladstone-Dale)

local charge around $N^{[2]}$ in $CaAlSi(N^{[3]})_2N^{[2]}$



NB: (#8) -Si-$N^{[2]}$-Si-/-Al-$N^{[2]}$-Al- linkage do not satisfy “PSCR”

→ less stability than #9/#4 by 4.1 kcal/mol