Analytic Description of Zinc-Blende Nanocrystals as Function of Size, Shape and Surface Orientation to Interpret Solid State Spectroscopy Data

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For details and respective number series, see
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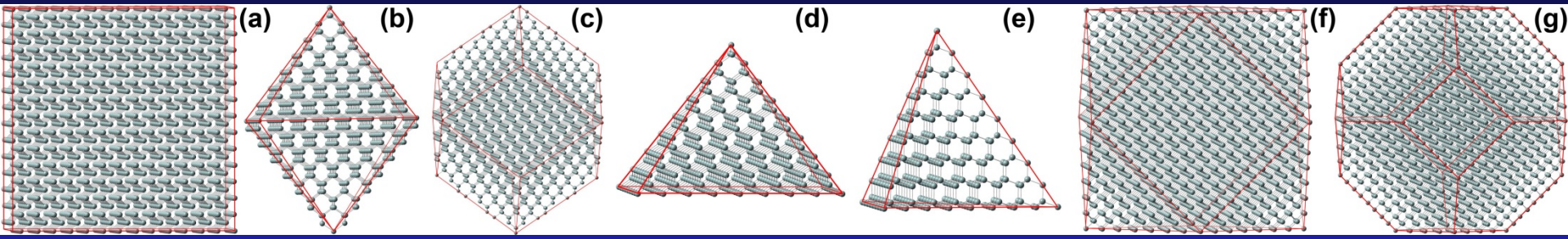
1. Types of zb-NCs investigated, Surface Energies & Densities, Size Derivation

We focus on Si-based NCs; results are valid for zb- and diamond lattice NCs



zb-NCs described: **(a)** {001}-faceted cube, **(b)** {111}-faceted octahedra, **(c)** {110}-faceted dodecahedra, **(d)** {111} pyramids with {001} base, **(e)** {111}-faceted tetrahedra, **(f)** {001}- [dominant]/{111}-faceted quatrodecahedra, **(g)** {111}- [dominant]/{001}-faceted quatrodecahedra

TABLE I. Bond densities and free energies per square for low index Si facets. Bond density values taken from[25], experimental surface energy values taken from[26].

facet orientation	surface bond density [cm^{-2}]	surface free energy [Jm^{-2}]
{001}	1.36×10^{15}	1.36
{110}	0.96×10^{15}	1.43
{111}	0.78×10^{15}	1.23

- {111} facets have lowest surface energy, {001} facets have 2nd lowest surface energy up to {433} facets[25,26] → {111}, {001} and {110} facets most relevant for NC surface orientations

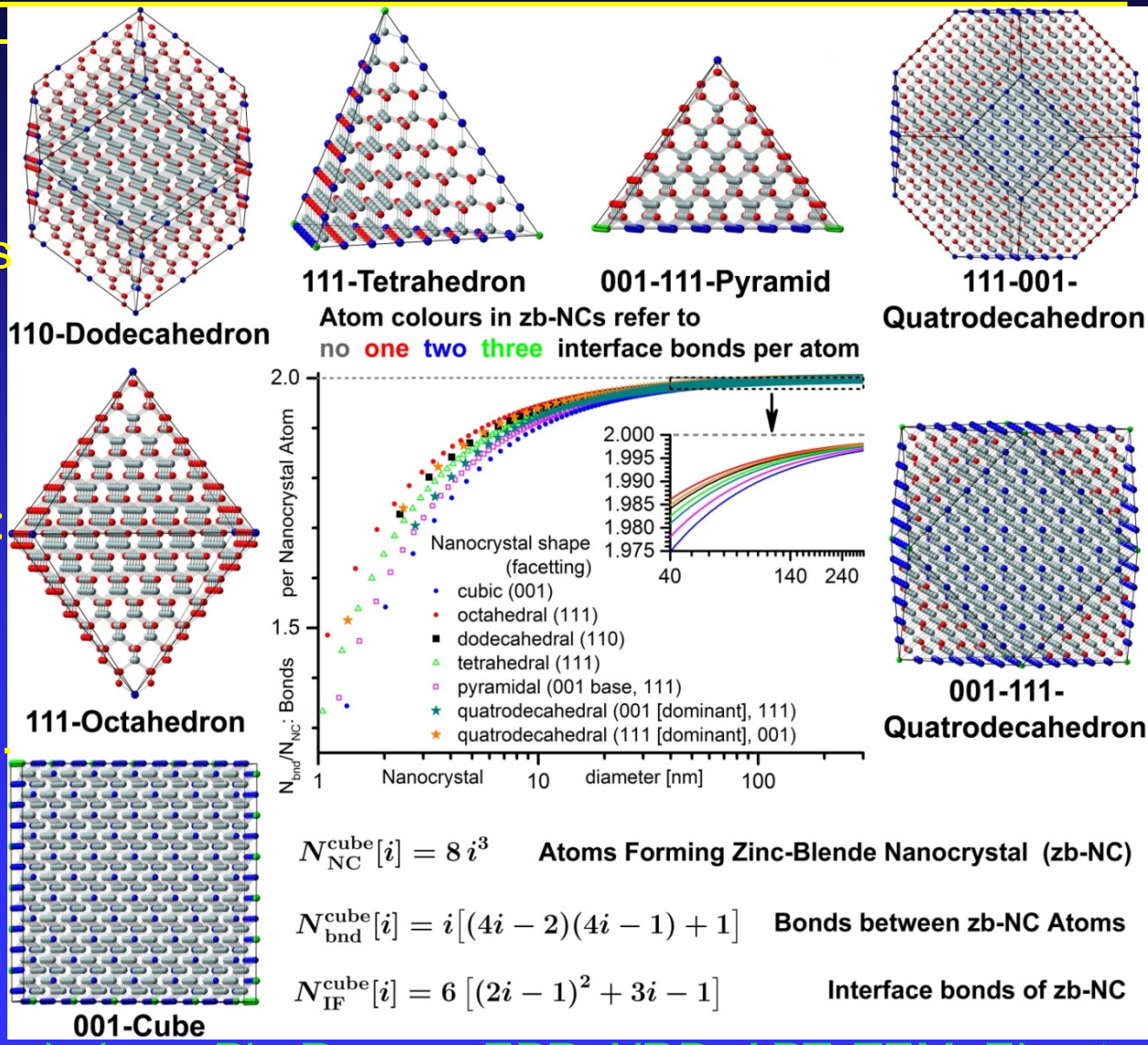
- NC size from atomic volume, assuming spheres to compare different NC shapes

$$d_{\mathrm{NC}}[i] = \sqrt[3]{\frac{6}{\pi} N_{\mathrm{NC}}[i] \times V_{\mathrm{atom}}}$$

[25] J. Electrochem. Soc. **140**, 1080 (1993)
[26] PRL **70**, 1643 (1993)

2. Key Variables Derived for zb-NCs: Significance and Usage

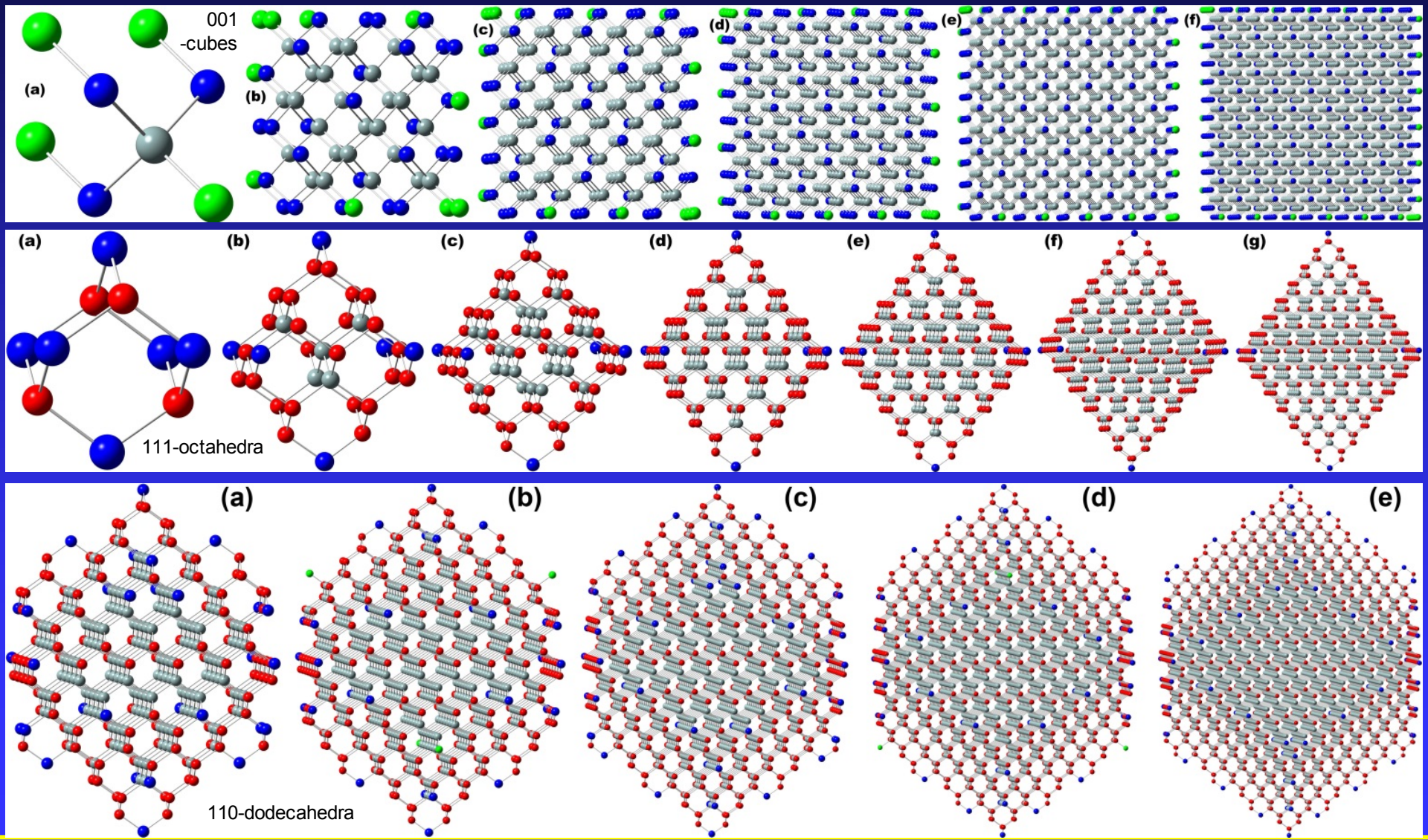
- Three numer series calculated over run index i:
  - # $N_{NC}[i]$ – number of atoms forming zb-NC
  - # $N_{bnd}[i]$ – number of bonds between zb-NC atoms
  - # $N_{IF}[i]$ – number of bonds from zb-NC to its environment = interface bonds
- further very useful results:
  - # $N_{bnd}[i] / N_{NC}[i]$ – NC response to external stress like impurity doping
  - # $N_{IF}[i] / N_{bnd}[i]$ – internal vs. external stress balance, e.g. NC shape as $f(d_{NC})$
  - # $N_{IF}[i] / N_{NC}[i]$ – interface charge transfer, impact on electronic structure of NC



For *any* NC spectroscopy technique: PL, Raman, EPR, XRD, APT, TEM, EL, etc.

3. Graphical Description of zb-NCs: Symmetry Arguments

No IF bond 1 IF bond 2 IF bonds 3 IF bonds



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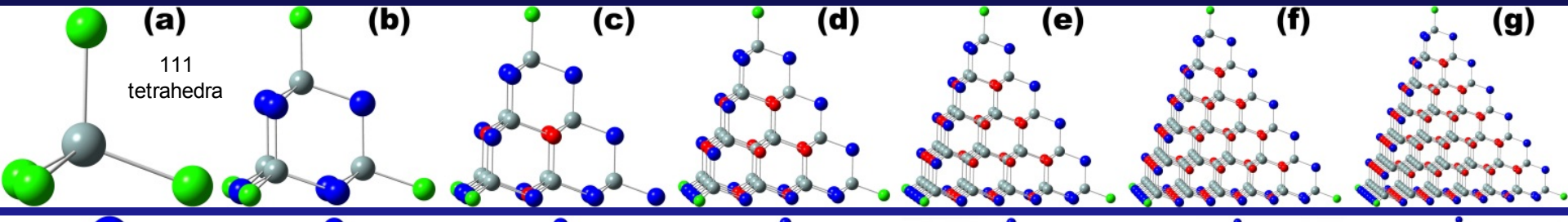
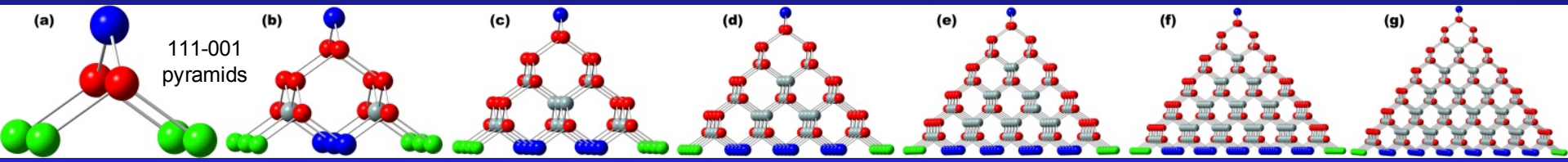
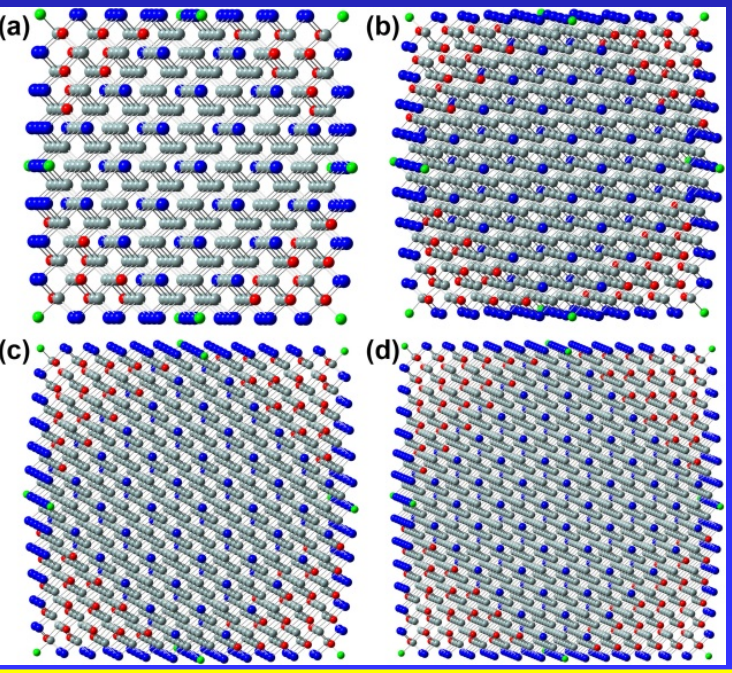
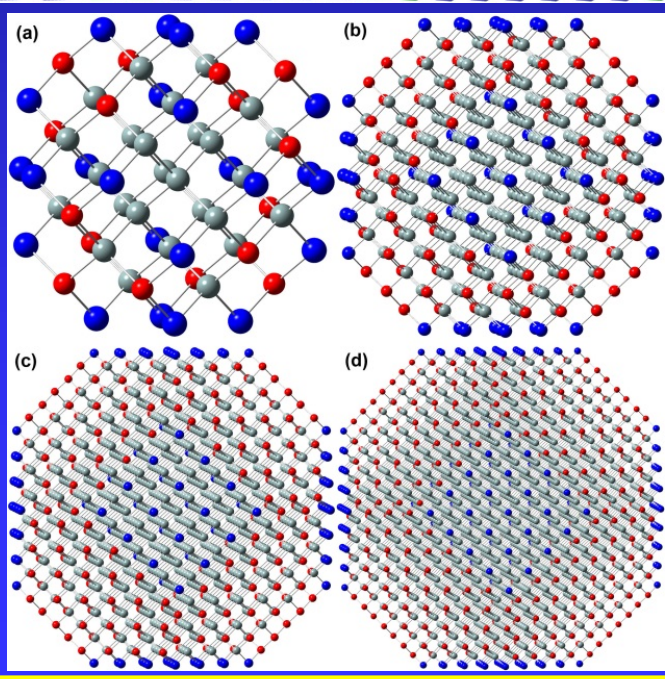






111-001-quatrodecahedra

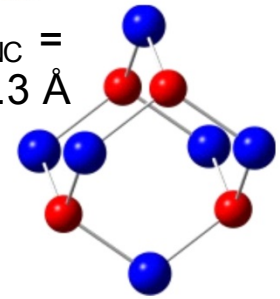


001-111-quatrodecahedra

4. Simple Example: Derivation of Number Series for {111} Octahedral zb-NCs

Si_{10}, i = 1

d_{NC} = 7.3 Å



Σ atoms: 1, 2, 4, 4, 2, 1 → = 3+4+3 = **10**

Σ NC bonds: 2, 4, 4, 2 → = 6+6 = **12**

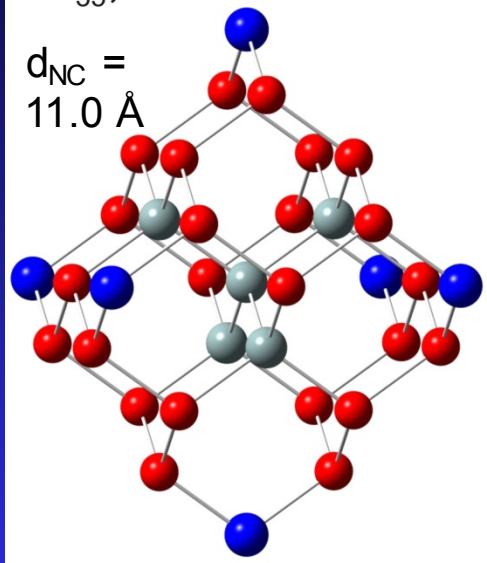
Σ **IF bonds** = 6x2_{001} + 8x1_{111}

= 12 + 4x(1x1) + 4x(0x1)

= 12 + 4 = **16**

Si_{35}, i = 2

d_{NC} = 11.0 Å



Σ atoms: 1, 2, 4, 6, 9, 6, 4, 2, 1 → = 13+9+13 = **35**

Σ NC bonds: 2, 4, 8, 12, 12, 8, 4, 2 → = 26+26 = **52**

Σ **IF bonds**

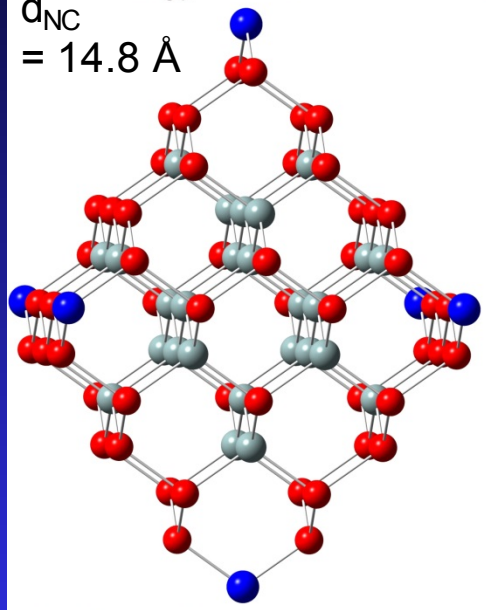
= 6x2_{001} + 8x1_{111}

= 12 + 24 = **36**

4. Simple Example: Derivation of Number Series for {111} Octahedral zb-NCs

Si_{84}, i = 3

d_{NC} = 14.8 Å



Σ atoms	Σ NC bonds
1	2
2	4
4	8
6	12
9	18
12	24
16	24
12	18
9	12
6	8
4	4
2	2
1	
= 34+16+34	= 68+68
= 84	**= 138**

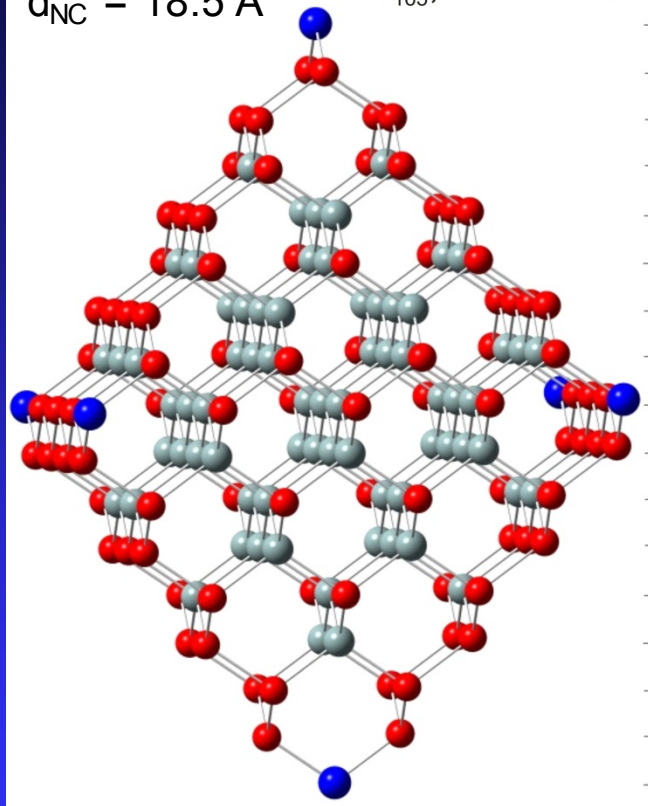
Σ IF bonds

= $6x2_{001}$ + $8x\triangle 1_{111}$

= 12 + 52 **= 64**

d_{NC} = 18.5 Å

Si_{165}, i = 4



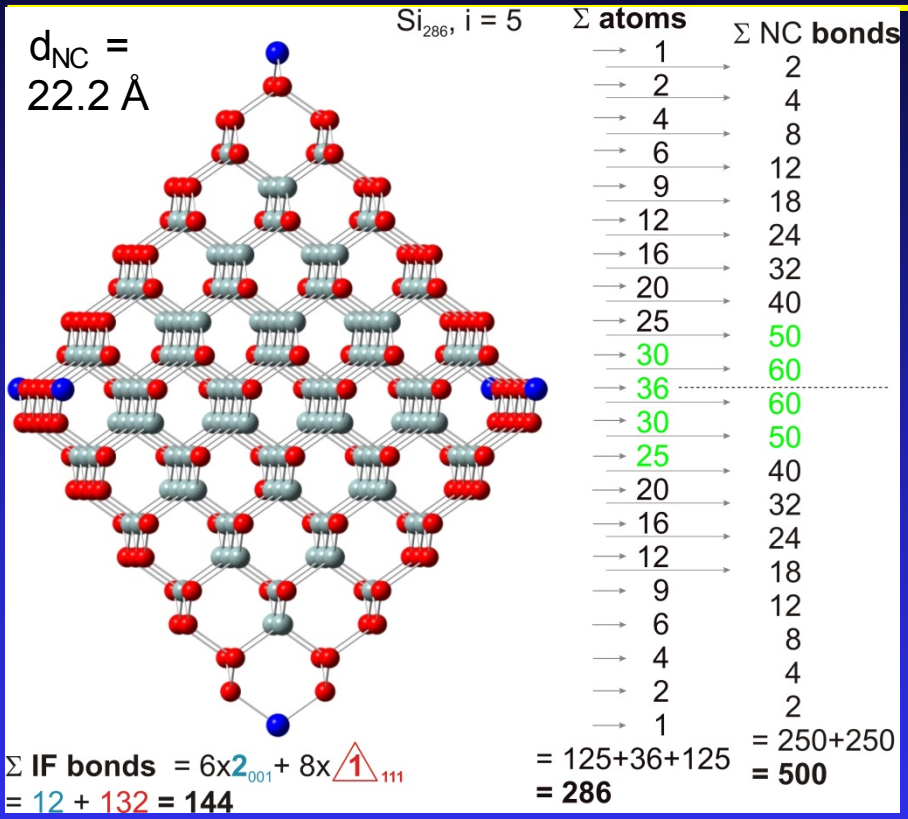
Σ atoms	Σ NC bonds
1	2
2	4
4	8
6	12
9	18
12	24
16	32
20	40
25	40
20	32
16	24
12	18
9	12
6	8
4	4
2	2
1	
= 70+25+70	= 140+140
= 165	**= 280**

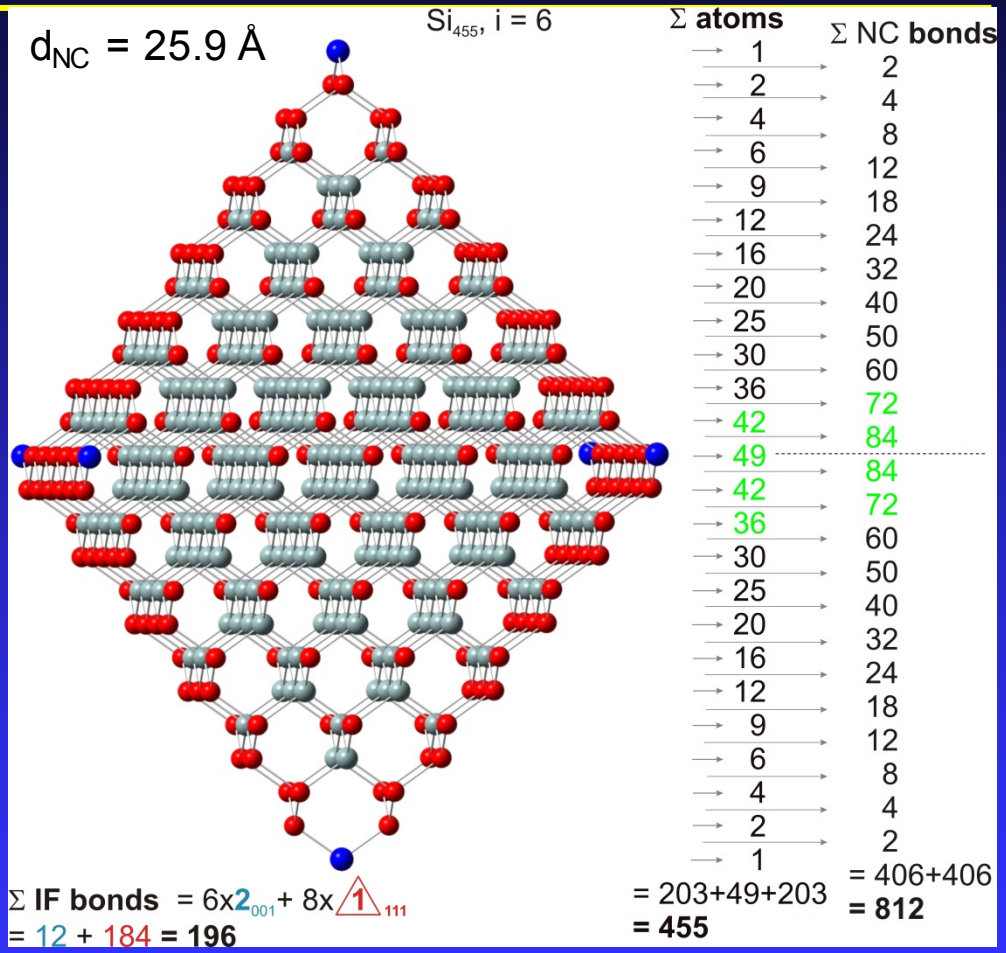
Σ IF bonds

= $6x2_{001}$ + $8x\triangle 1_{111}$

= 12 + 88 **= 100**

4. Simple Example: Derivation of Number Series for {111} Octahedral zb-NCs





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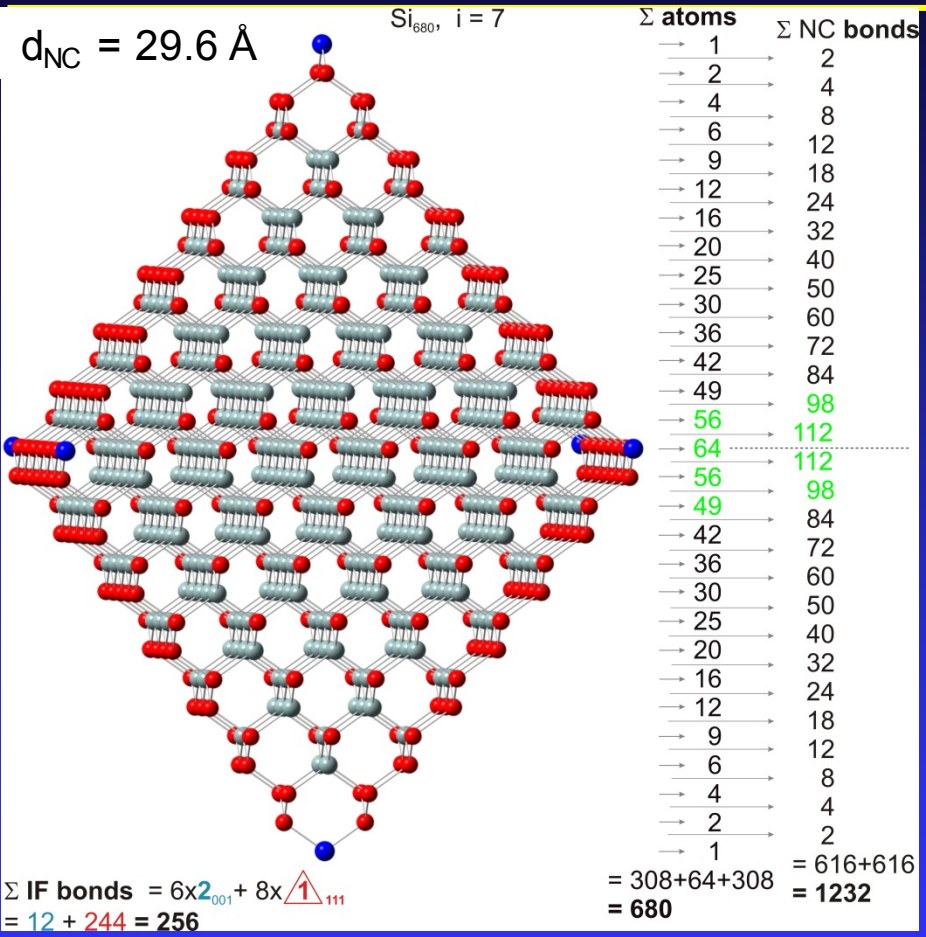
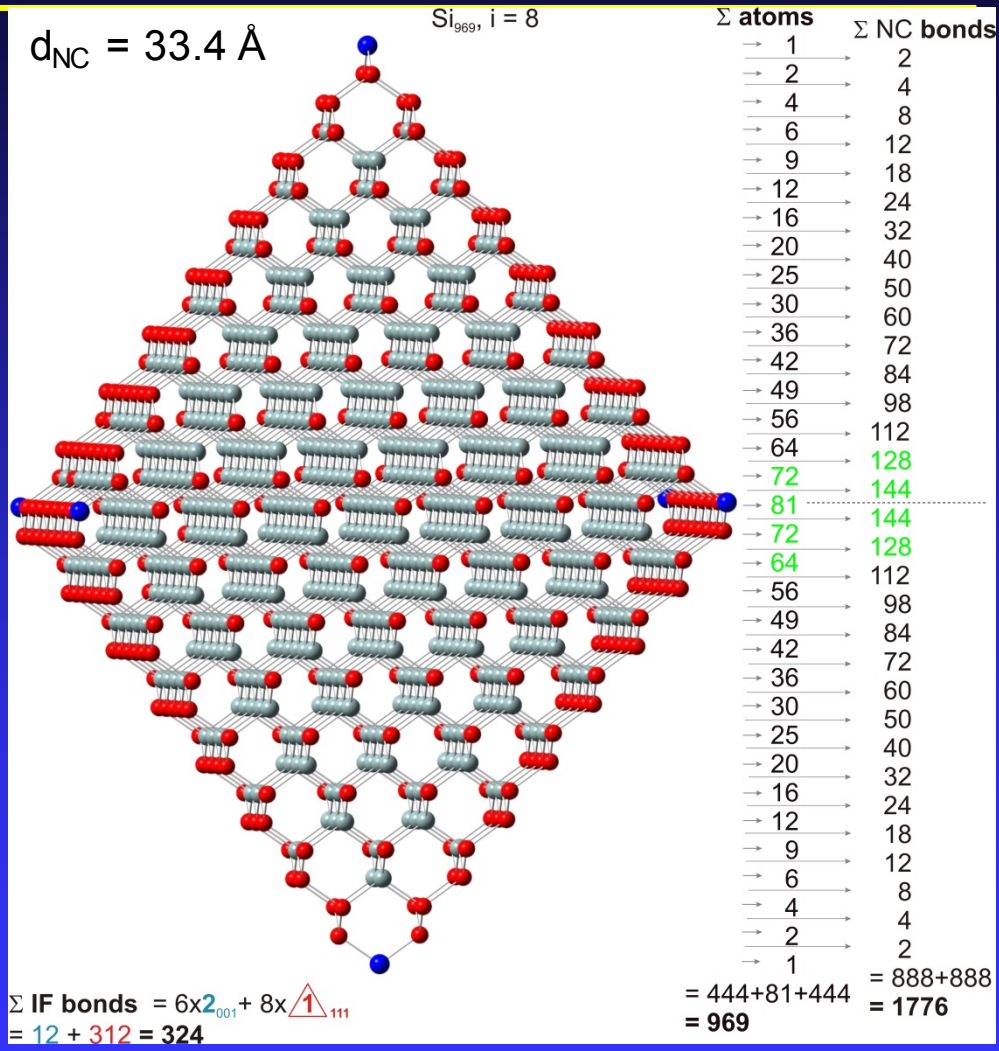




4. Simple Example: Deriving the Number of NC Atoms for {111} Octahedral zb-NCs

i	$N_{\mathrm{NC}}^{\mathrm{octa}}[i]$	$\frac{d\,N_{\mathrm{NC}}^{\mathrm{octa}}[i]}{d\,i}$	
	offset		
0	1		
		9	$\rightsquigarrow = (1+2\times 1)^2$
1	10		
		25	$\rightsquigarrow = (1+2\times 2)^2$
2	35		
		49	$\rightsquigarrow = (1+2\times 3)^2$
3	84		
		81	$\rightsquigarrow = (1+2\times 4)^2$
4	165		
		121	$\rightsquigarrow = (1+2\times 5)^2$
5	286		
		169	$\rightsquigarrow = (1+2\times 6)^2$
6	455		
		225	$\rightsquigarrow = (1+2\times 7)^2$
7	680		
		289	$\rightsquigarrow = (1+2\times 8)^2$
8	969		
		...	...
...	...		
		$\rightsquigarrow = (1+2i)^2$	$\rightsquigarrow = (1+2i)^2$

Silane (SiX_4): not a crystal but still zero element [i = 0] of number series (offset)

→ differential quotient …

$$N_{\mathrm{NC}}^{\mathrm{octa}}[i] - N_{\mathrm{NC}}^{\mathrm{octa}}[i-1] = (2i+1)^2$$

rearranging to recursive number series …

$$N_{\mathrm{NC}}^{\mathrm{octa}}[i] = N_{\mathrm{NC}}^{\mathrm{octa}}[i-1] + (2i+1)^2 + \overbrace{N_{\mathrm{NC}}^{\mathrm{octa}}[i=0]}^{\text{offset}:=1}$$

unravel it …

$$N_{\mathrm{NC}}^{\mathrm{octa}}[i] = (2i+1)^2 + (2[i-1]+1)^2 + (2[i-2]+1)^2 + \cdots + (2[1]+1)^2 + \underbrace{1}_{\text{offset}}$$

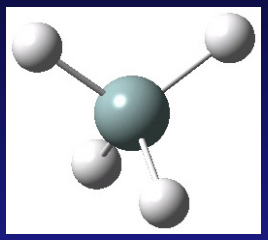
and convert into sum formula:

$$N_{\mathrm{NC}}^{\mathrm{octa}}[i] = \overbrace{1}^{\text{offset}} + \sum_{k=1}^{i}\left[(2k+1)^2\right] = 1 + 4\sum_{k=1}^{i}k^2 + 4\sum_{k=1}^{i}k + \sum_{k=1}^{i}1$$

$$= 4\left[\frac{i(i+1)(2i+1)}{6} + \frac{i(i+1)}{2}\right] + (i+1) = (i+1)\left[\frac{2i(2i+1)}{3} + 2i + 1\right]$$

4. Simple Example: Deriving the Number of Bonds Between NC Atoms for {111} Octahedral zb-NCs

i	$N_{\mathrm{bnd}}^{\mathrm{octa}}[i]$	$\frac{d\,N_{\mathrm{bnd}}^{\mathrm{octa}}[i]}{d\,i}$	$\frac{1}{i} \times \frac{d\,N_{\mathrm{bnd}}^{\mathrm{octa}}[i]}{d\,i}$	
0	0			
1	12	12	$12/1 = 12$	$\rightsquigarrow = 8 \times 1 + 4$
2	52	40	$40/2 = 20$	$\rightsquigarrow = 8 \times 2 + 4$
3	136	84	$84/3 = 28$	$\rightsquigarrow = 8 \times 3 + 4$
4	280	144	$144/4 = 36$	$\rightsquigarrow = 8 \times 4 + 4$
5	500	220	$220/5 = 44$	$\rightsquigarrow = 8 \times 5 + 4$
6	812	312	$312/6 = 52$	$\rightsquigarrow = 8 \times 6 + 4$
7	1232	420	$420/7 = 60$	$\rightsquigarrow = 8 \times 7 + 4$
8	1776	544	$544/8 = 68$	$\rightsquigarrow = 8 \times 8 + 4$
...	...	...	...	...
		$\rightsquigarrow = i(8i+4)$		$\rightsquigarrow = 8i + 4$



No offset for i = 0 due to Silane (SiX_4) as the zero element of the number series – no intra-crystalline bonds

→ differential quotient …

$$N_{\mathrm{bnd}}^{\mathrm{octa}}[i] - N_{\mathrm{bnd}}^{\mathrm{octa}}[i-1] = i(8i+4)$$

recursive number series …

↓ convert to sum formula … ←

$$N_{\mathrm{bnd}}^{\mathrm{octa}}[i] = N_{\mathrm{bnd}}^{\mathrm{octa}}[i-1] + i(8i+4)$$

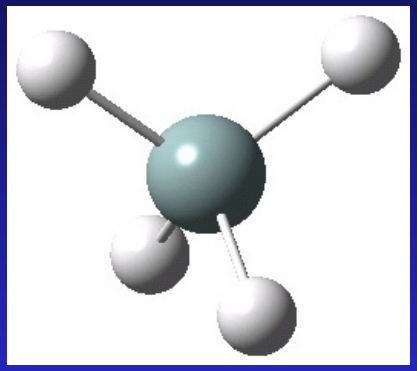
$$N_{\mathrm{bnd}}^{\mathrm{octa}}[i] = \sum_{k=1}^{i} [k(8k+4)] = 4 \sum_{k=1}^{i} [k(2k+1)] = 4\left(2\sum_{k=1}^{i} k^2 + \sum_{k=1}^{i} k\right)$$

$$= 4\left(2\,\frac{i(i+1)(2i+1)}{6} + \frac{i(i+1)}{2}\right) = \frac{4}{3}i(i+1)(2i+1) + 2i(i+1)$$

4. Simple Example: Deriving the Number of Interface Bonds for {111} Octahedral zb-NCs

i	$N_{\mathrm{IF}}^{\mathrm{octa}}[i]$	
0	4	$\rightsquigarrow = 4\,(0+1)^2$
1	16	$\rightsquigarrow = 4\,(1+1)^2$
2	36	$\rightsquigarrow = 4\,(2+1)^2$
3	64	$\rightsquigarrow = 4\,(3+1)^2$
4	100	$\rightsquigarrow = 4\,(4+1)^2$
5	144	$\rightsquigarrow = 4\,(5+1)^2$
6	196	$\rightsquigarrow = 4\,(6+1)^2$
7	256	$\rightsquigarrow = 4\,(7+1)^2$
8	324	$\rightsquigarrow = 4\,(8+1)^2$
...	...	...
	$\rightsquigarrow = 4(i+1)^2$	$\rightsquigarrow = 4(i+1)^2$

Silane (SiX_4): not a crystal but still zero element [i = 0] of the number series, having four IF bonds

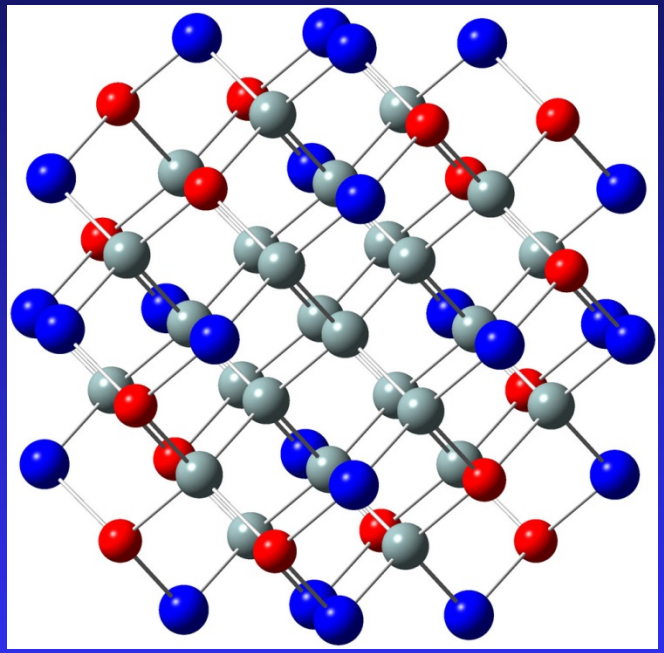


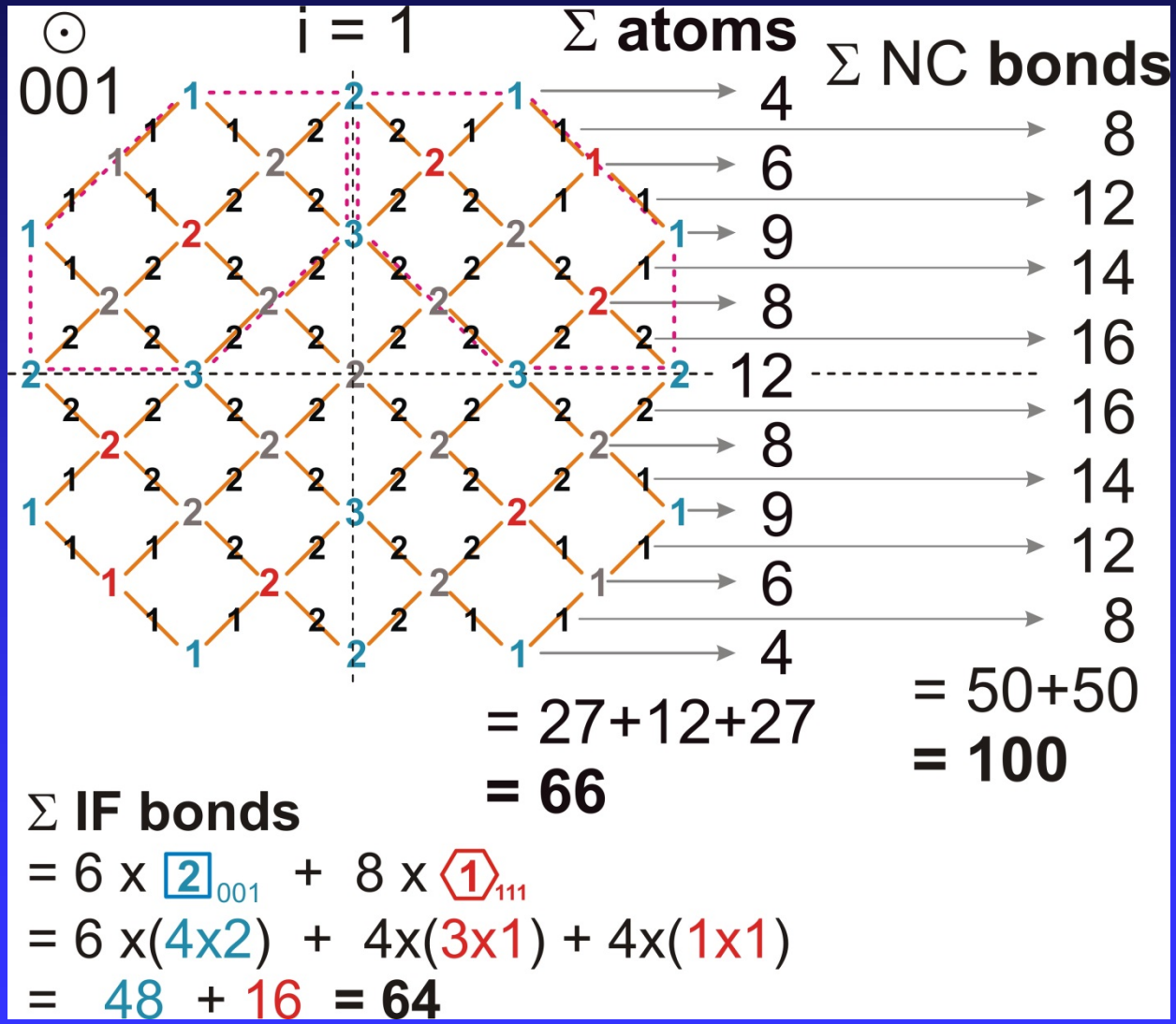
Number series for IF bonds can be derived directly:

$$N_{\mathrm{IF}}^{\mathrm{octa}}[i] = 4(i+1)^2$$

$$d_{\mathrm{NC}}[i] = \sqrt[3]{\frac{6}{\pi} N_{\mathrm{NC}}[i] \times V_{\mathrm{atom}}}$$

4.1 More Complex Example: A Glimpse on {111} (dominant)-{001} Faceted Quatrodecahedral zb-NCs





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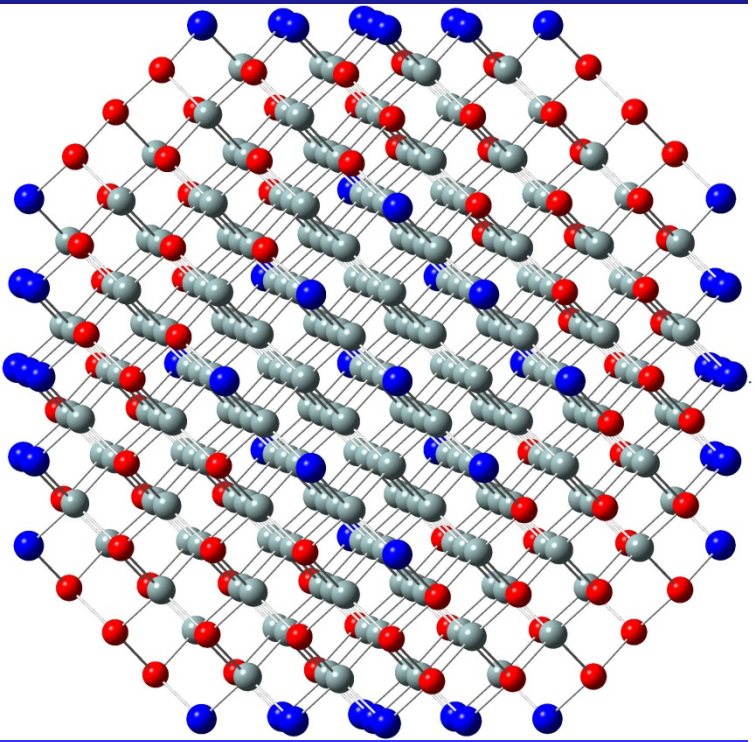

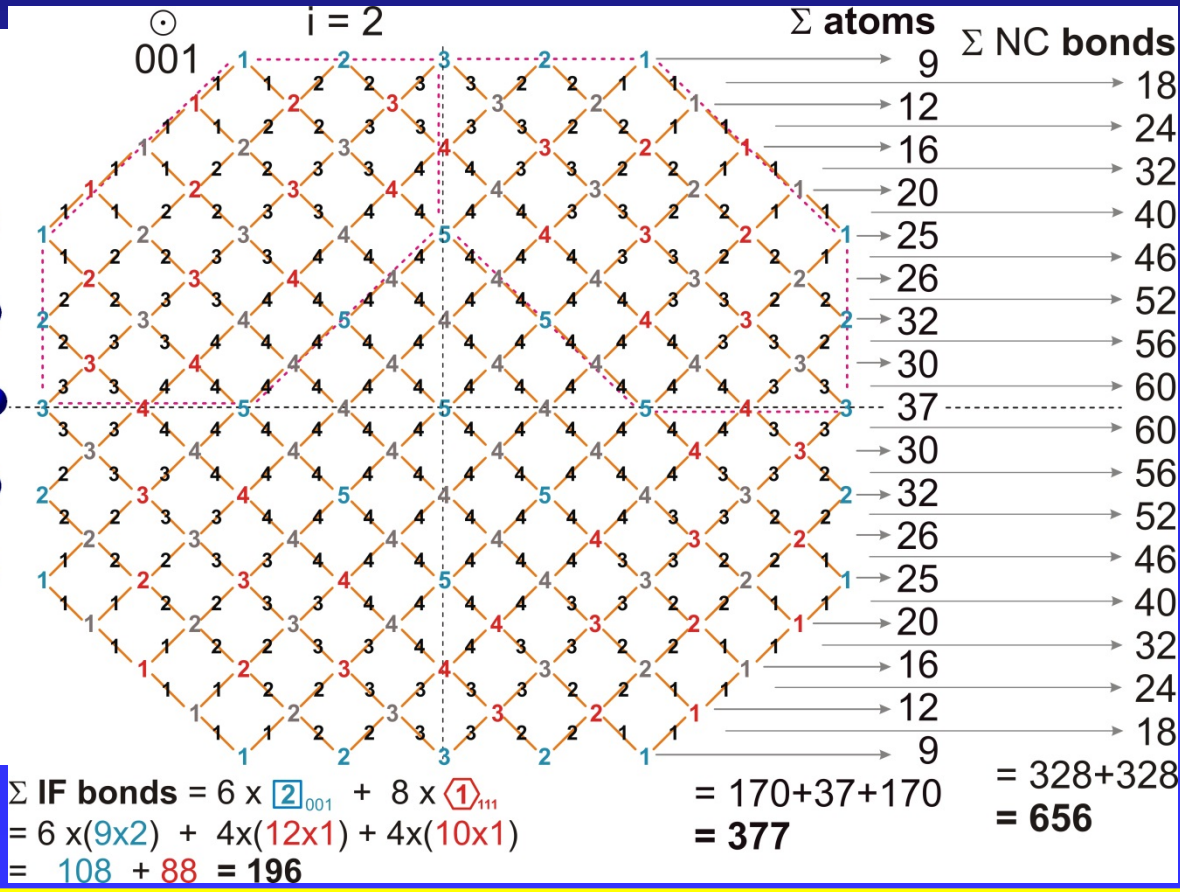

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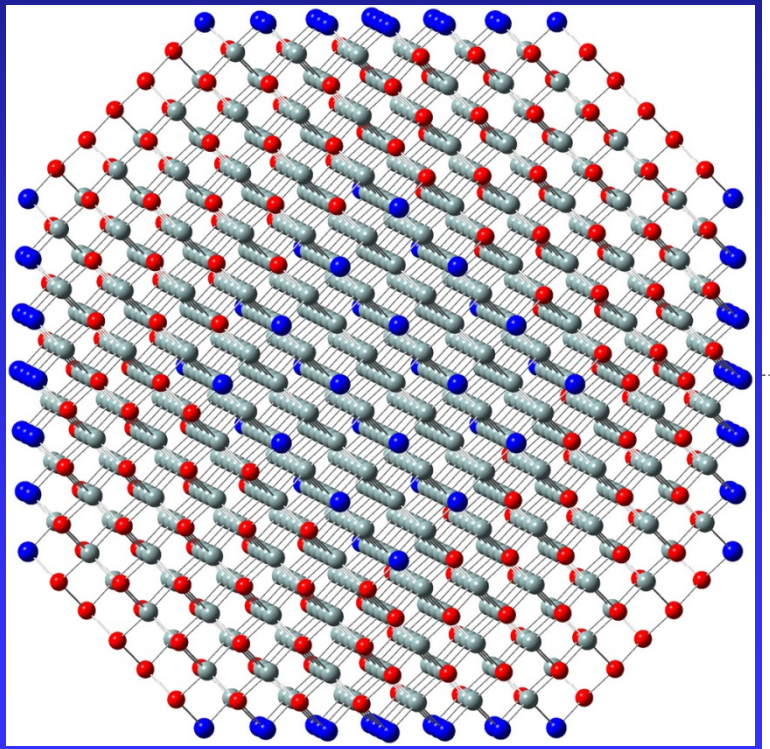

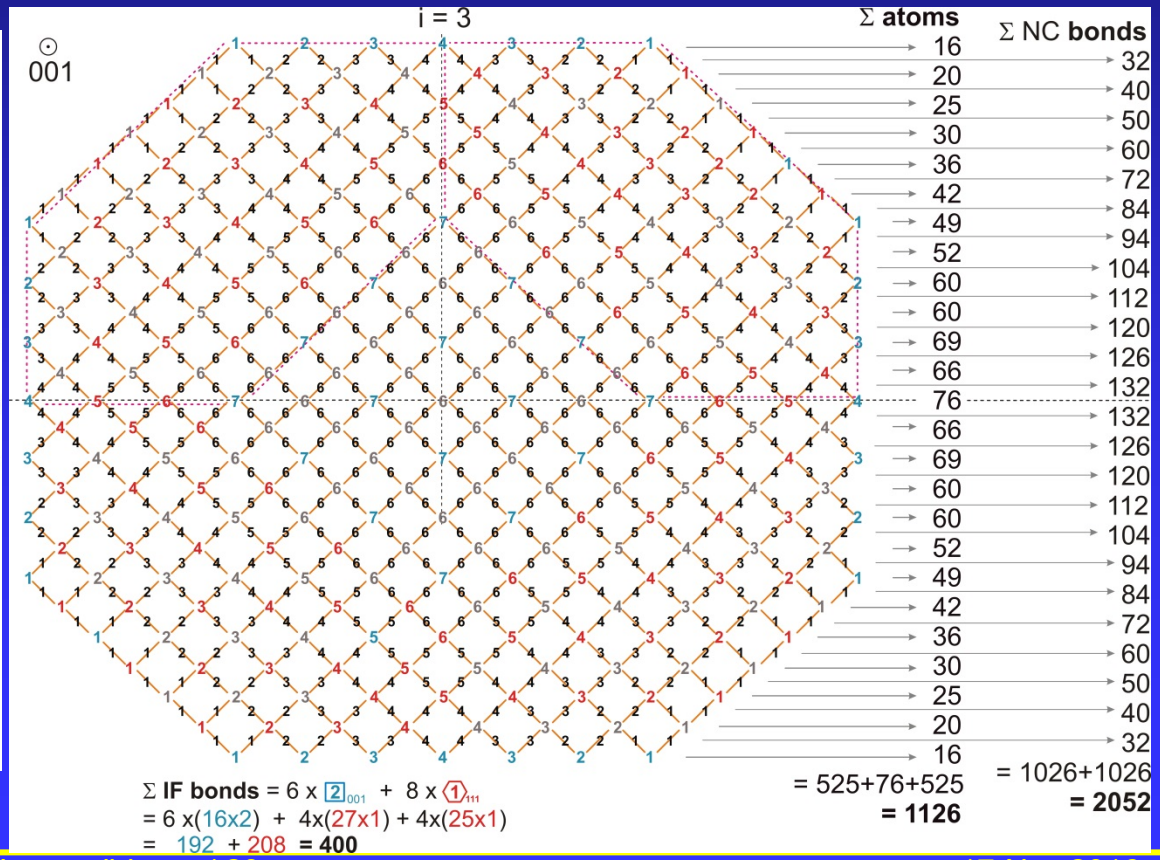

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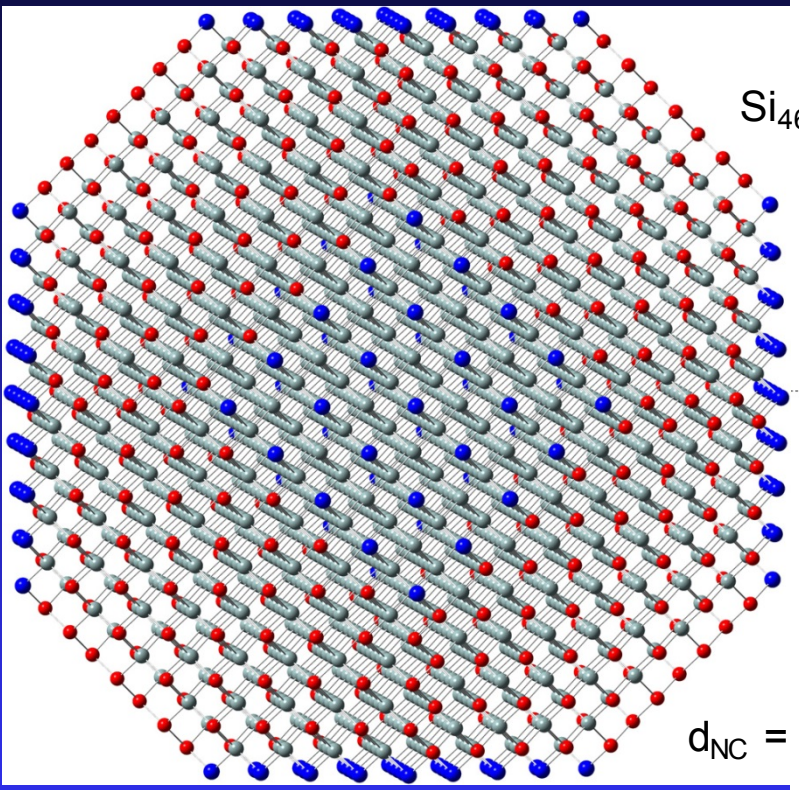
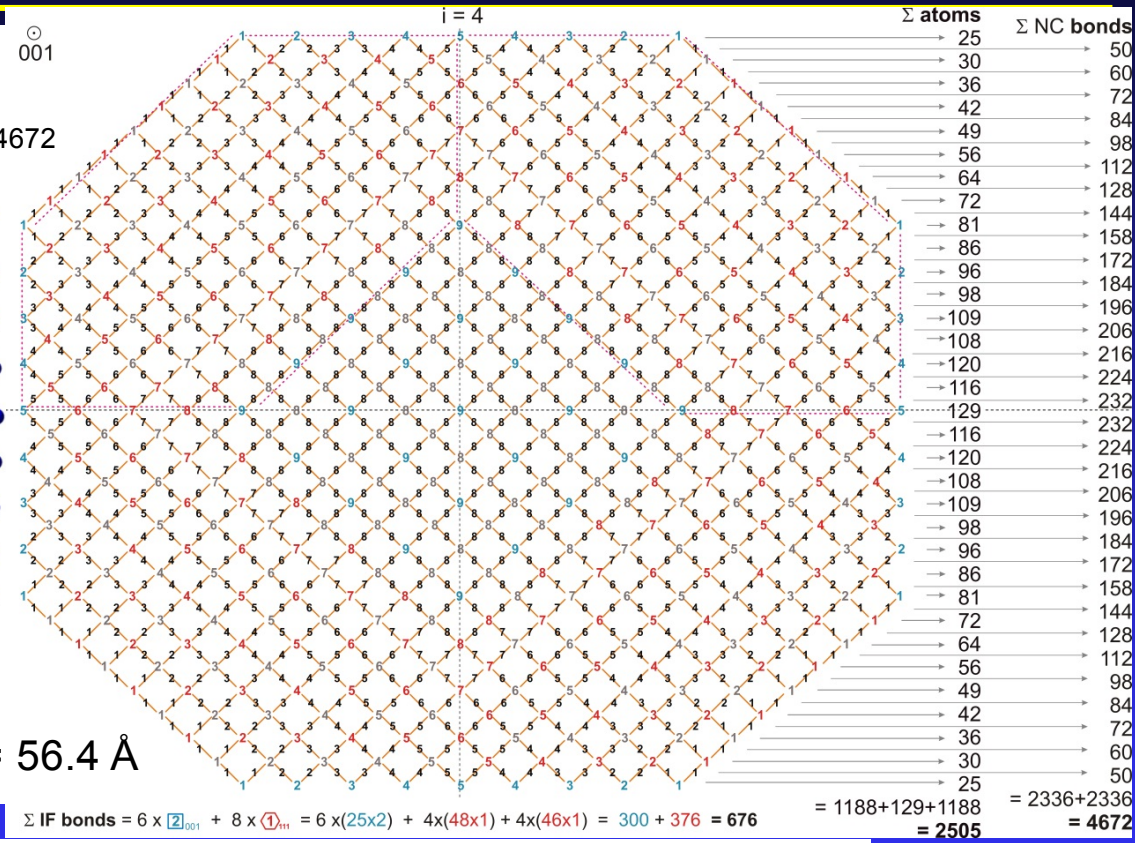




$$\mathbf{N_{NC}^{q.111}[i] = 9i(2i+1)^2 + (2i+1) - i(4i+5)(i+1)\,,\ \forall i \geq 1}$$

$$\mathbf{N_{bnd}^{q.111}[i] = 2i(3i+1)(12i+5) - [4i(i+1)(2i+1) + 6i(i+1)]\,,\ \forall i \geq 1}$$

$$\mathbf{N_{IF}^{q.111}[i] = (6i+2)^2\,,\ \forall i \geq 1} \rightarrow$$

$$N_{IF,\langle 001\rangle}^{q.111}[i] = 12(i+1)^2\,,\ \forall i \geq 1$$

$$N_{IF,\langle 111\rangle}^{q.111}[i] = 8(3i^2-1)\,,\ \forall i \geq 1$$

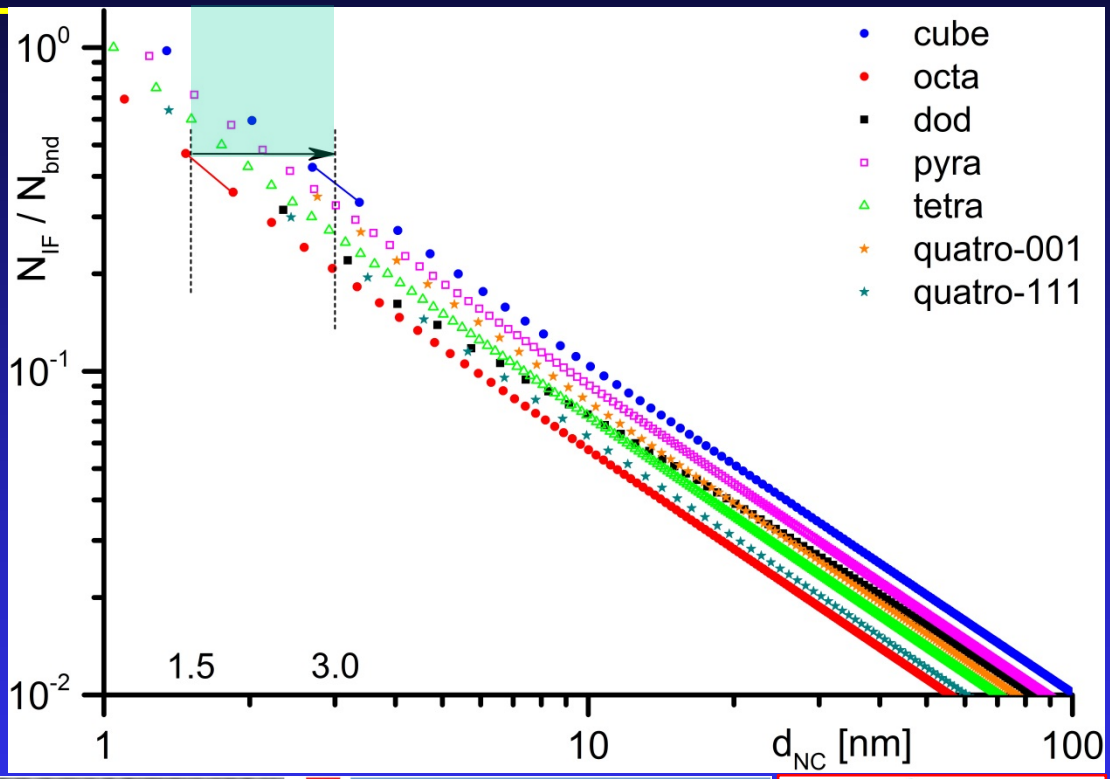
Important for EPR

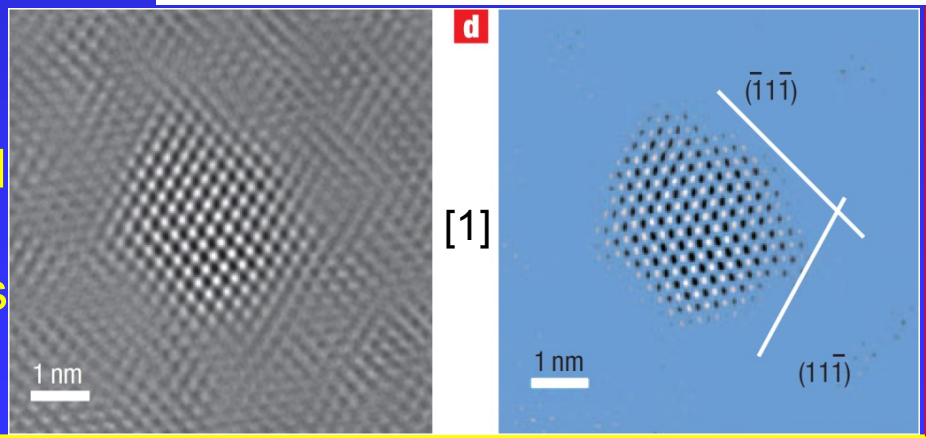
5.1 Applications – the Ratio N_{IF}/N_{bnd}: Stress balance Between zb-NC and Embedding Matrix

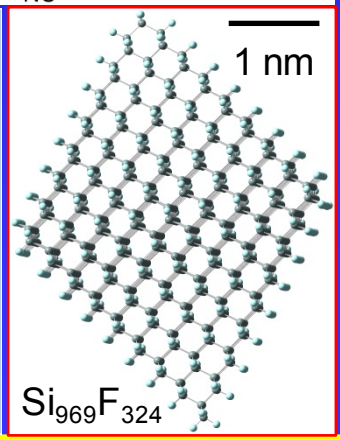
- significant influence of stress on balance zb-NC vs. embedding: matrix dominates NC growth and hence NC shape as function of NC size
- octahedral Si NCs is dominant shape for $d_{NC} \leq$ ca. 3 nm[1]
- porous Si etching & self-limiting oxidation provided smallest Si NCs = 1.5 ± 0.2 nm[2]

→ no Si NC formation for $N_{IF}/N_{bnd} \geq 0.41 \pm 0.06$;

- value specific to NC- and matrix-material, e.g. smallest Si NC size should be bigger in Si_3N_4 due to its higher Young's modulus



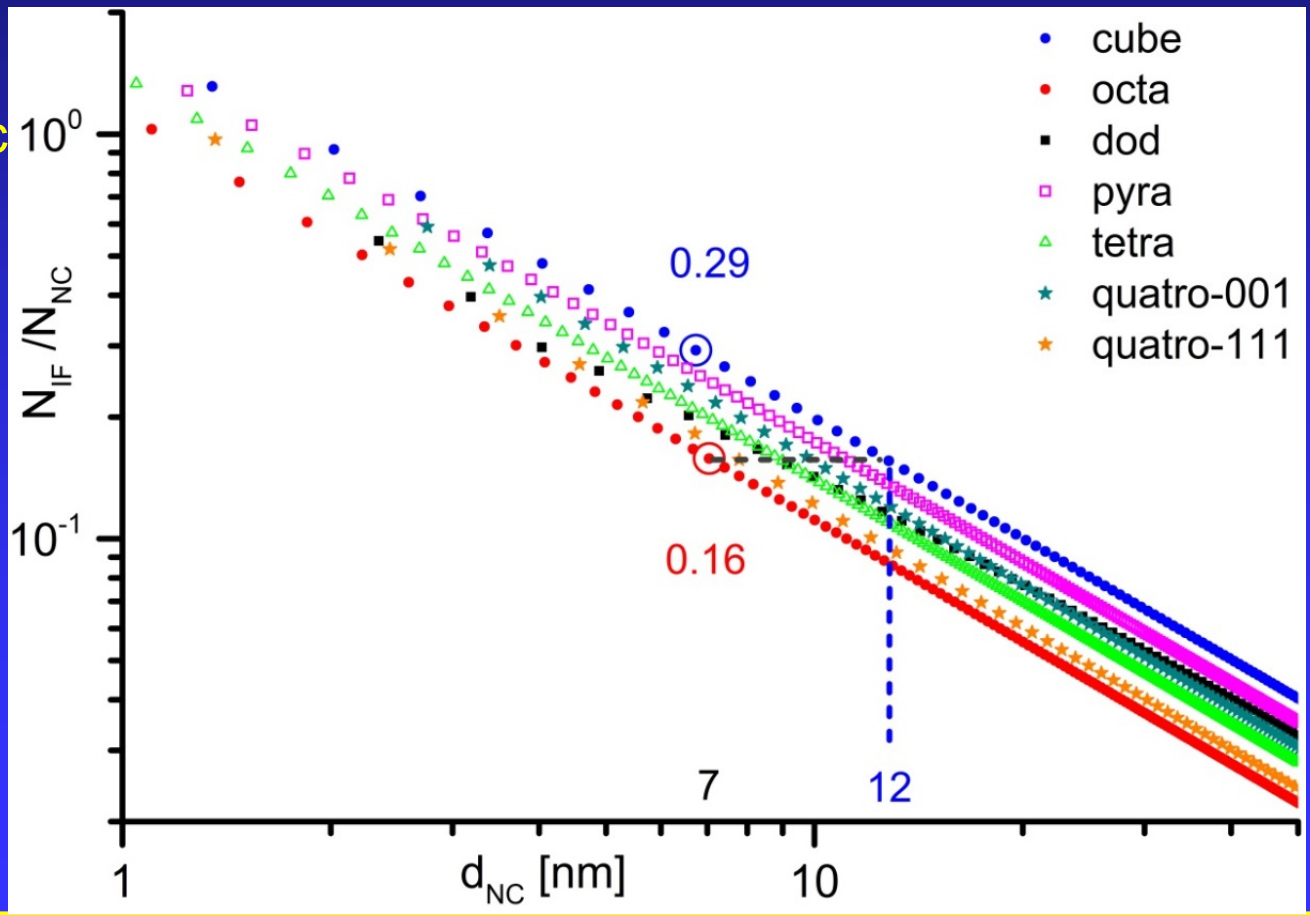




[1] Nature Nanotech **3**, 174 (2008)
[2] PRL **72**, 2648 (1994)

5.2 Applications – the Ratio N_{IF}/N_{NC}: Interface Dipoles, Interface Charge Transfer (ICT)

- N_{IF}/N_{NC} depends on
  # surface density of IF bonds, hence interface faceting – {001}, {110}, {111}
  # ratio of surface atoms to all atoms which form zb-NC
- N_{IF}/N_{NC} much higher for elongated structures; fins (fin-FETs) vs. {001} cube
- N_{IF}/N_{NC} decisive for NC electronic structure modification by dielectric
- graph shows N_{IF}/N_{NC}, ICT dominates electronic structure of Si NCs for $d_{NC} \geq 7$ nm[1]; going to a {001}-cube extends the NC size to 12 nm, further increase in structure length can be obtained by cubicle (fin-FET, 14 nm technology)

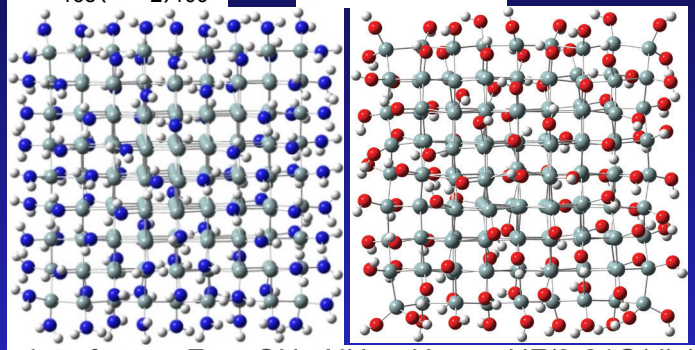


[1] Appl. Mater. Interfaces **1**, 1400359 (2014); DOI: 10.1002/admi.201400359

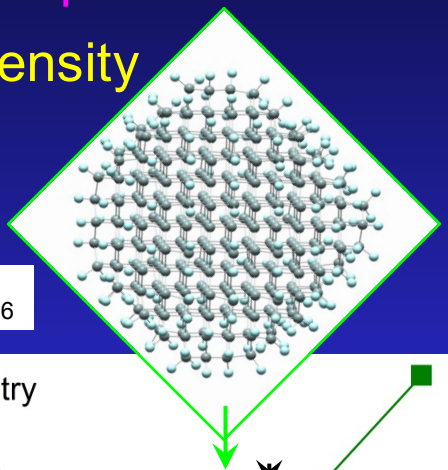
5.2 Applications – the Ratio N_{IF}/N_{NC}: Interface Dipoles, Interface Charge Transfer (ICT)

- Density Functional Theory for for $Si_x(NH_2)_y$ vs. $Si_x(OH)_y$[1,2]: HOMO ↗ 1.5eV, LUMO ↗ 2.1eV, E_{gap} ↗ 0.6 eV (also in experimental data[3])

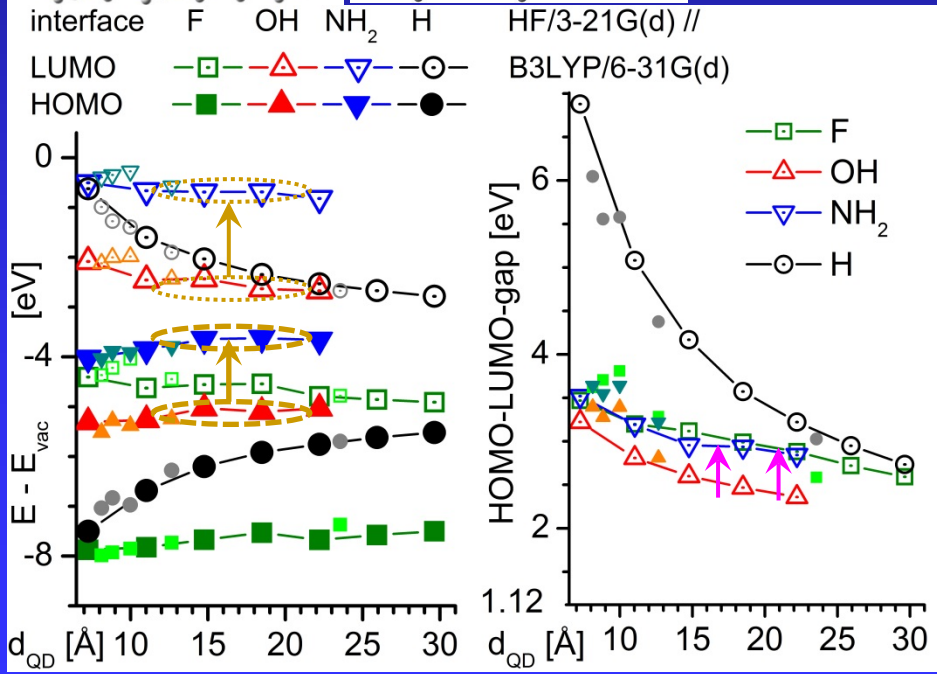
$Si_{165}(NH_2)_{100}$ $Si_{165}(OH)_{100}$

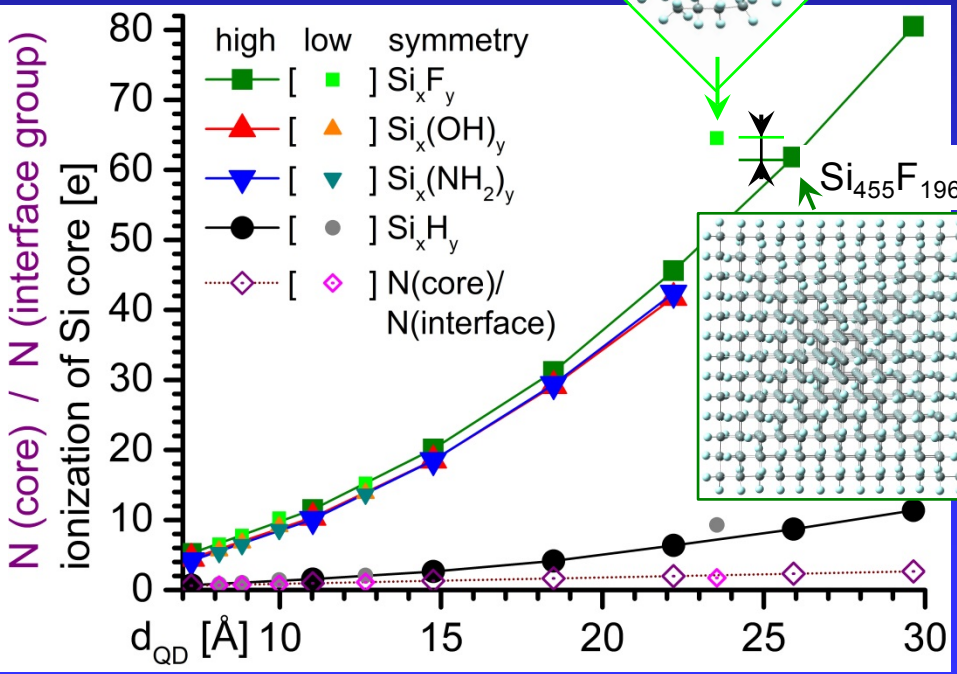


- ICT is ∝ IF area × IF bond density
  → ∝ d_{NC}^2 for *same* NC type;
  higher N_{IF}/N_{NC} ratio
  → higher ICT



$Si_{341}F_{196}$





[1] PRB **78**, 035339 (2008) [2] Adv Mater Interfaces **1**, 1400359 (2014) [3] JAP **113**, 033528 (2013)

5.2 Applications – the Ratio N_{IF}/N_{NC}: Interface Dipoles, Interface Charge Transfer (ICT)[1]

- Highest occupied (HO-) electronic DOS (top valence) of Si QWs by UV-Photoelectron Spectroscopy (UPS)
- HO-DOS relative to E_V(bulk Si):

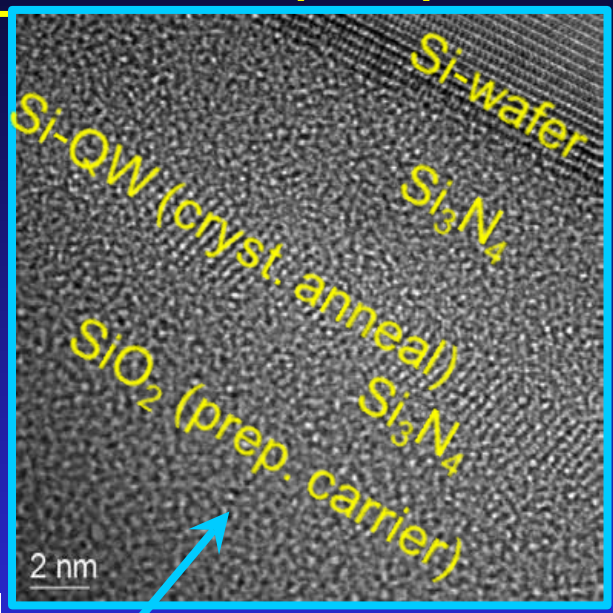
20 Å QW in SiO_2 0.87 eV below

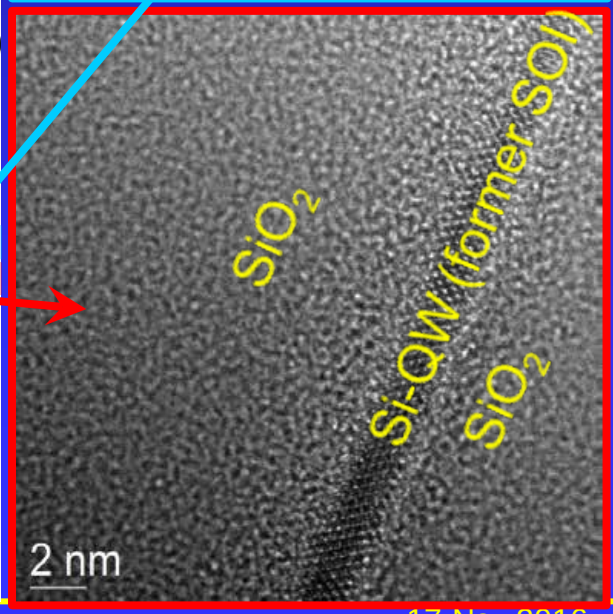
20 Å QW in Si_3N_4 0.02 eV *above* à type II band offset

à HO-DOS offset = 0.9 eV for SiO_2 vs. Si_3N_4

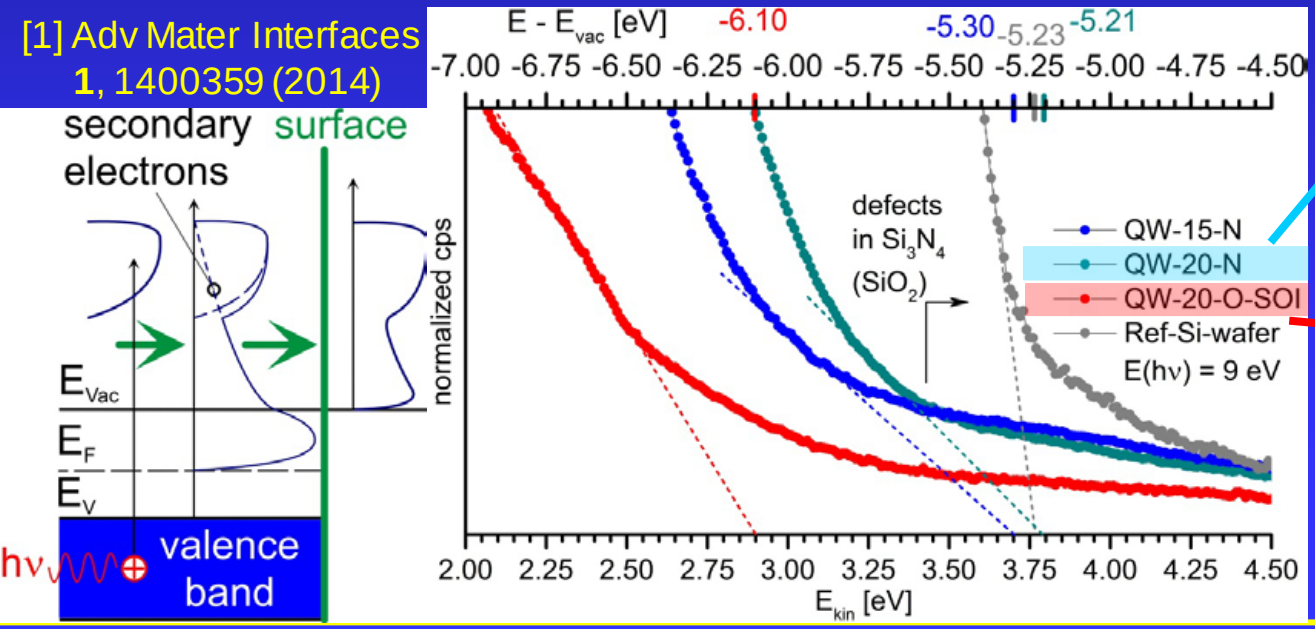
- PL: E_{gap}(Si-NC in SiO_2) < E_{gap}(Si-NC in Si_3N_4)

à lowest unoccupied (LU-) QW-DOS offset > 0.9 eV



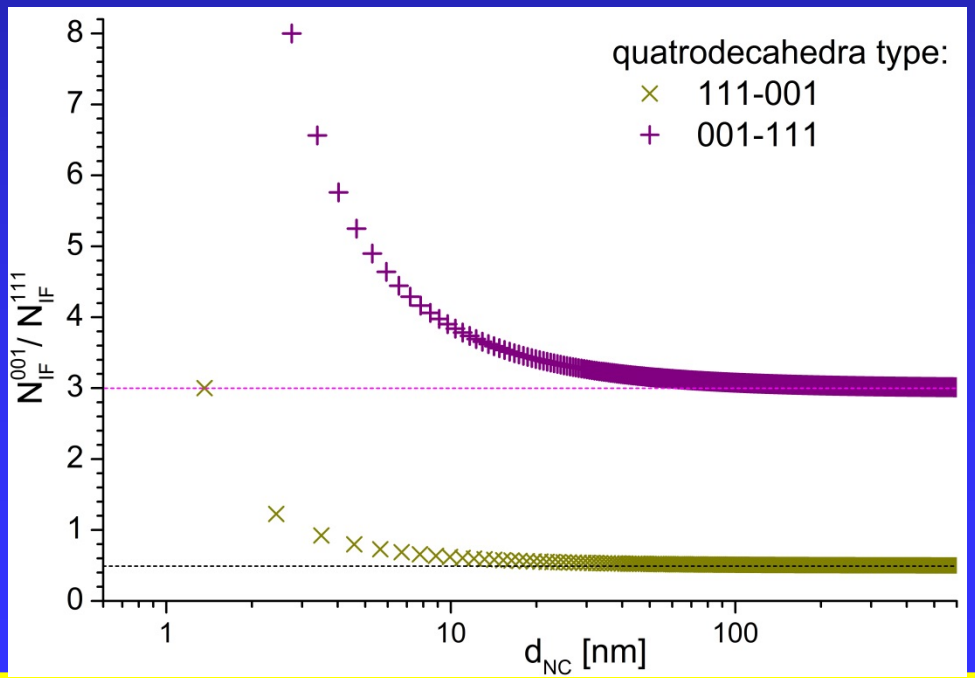


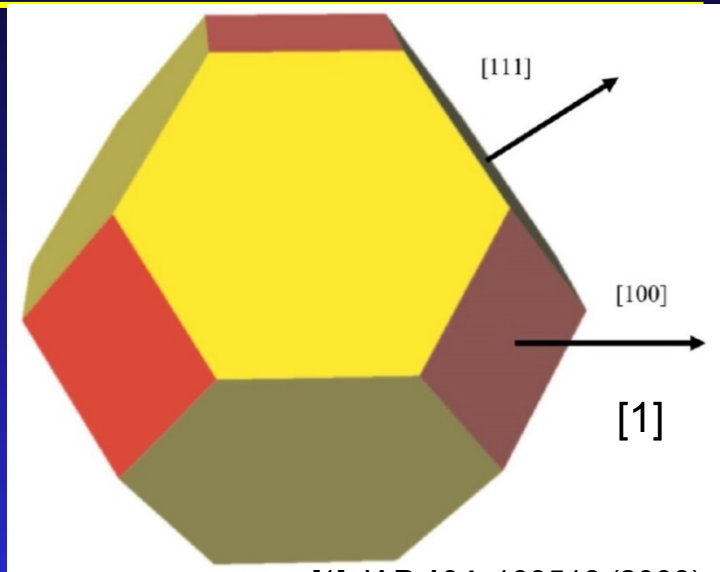
[1] Adv Mater Interfaces **1**, 1400359 (2014)



5.3 Applications – the Ratio $N_{IF}^{001}/N_{IF}^{111}$: Detecting Quatrodecahedral NC Shape/Size by EPR

- Si NCs in SiO_2, Electron Paramagnetic Resonance (EPR) Spectroscopy[1]: Interface-specific DB signals $P_{b(0)}$ (111 IF) and P_{b1} (001 IF) → Si NC morphology by $P_{b(0)}$ / P_{b1}
- split N_{IF} of 001-111 & 111-001 quatrodecahedra into partitions of 111 and 001 interfaces → N_{IF}^{001}, N_{IF}^{111}; calculate N_{IF}^{001} /N_{IF}^{111} per type of quatrodecahedra to identify NC morphology or size (depending on which is known)

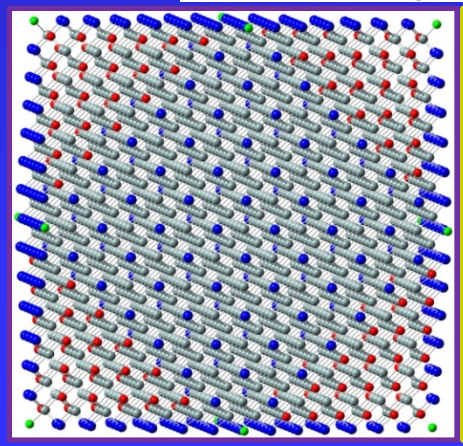




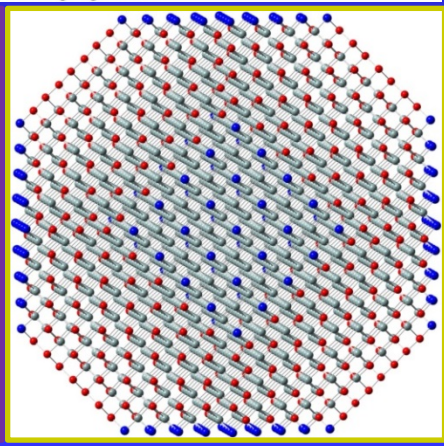
[1]

[1] JAP **104**, 103518 (2008)

FIG. 7. (Color online) Idealized average morphology [[100] truncated (111) octahedron] of embedded NC-Si particles in phase-separated SiO/SiO_2 entities as inferred from the occurring $P_{b(0)}$ and P_{b1} (Si/SiO_2) interface defects, based on microscopic defect properties.



001-111 Quatrodecahedron



111-001 Quatrodecahedron

5.4 Applications – the Ratio N_{bnd}/N_{NC}: Response to External Stress – Self-Purification

- $N_{bnd}[i] / N_{NC}[i] = 2$ for $i \rightarrow \infty$: each atom has four 1-nn atoms, each bond shared between two atoms; 4/2 = 2
- $N_{bnd}[i] / N_{NC}[i] \searrow$ with $d_{NC}[i] \searrow$, less bonds/atom for stress compensation: self-purification, introduction of DBs, stacking faults, GBs

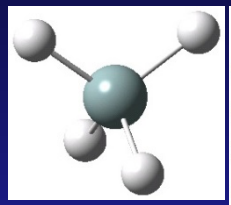
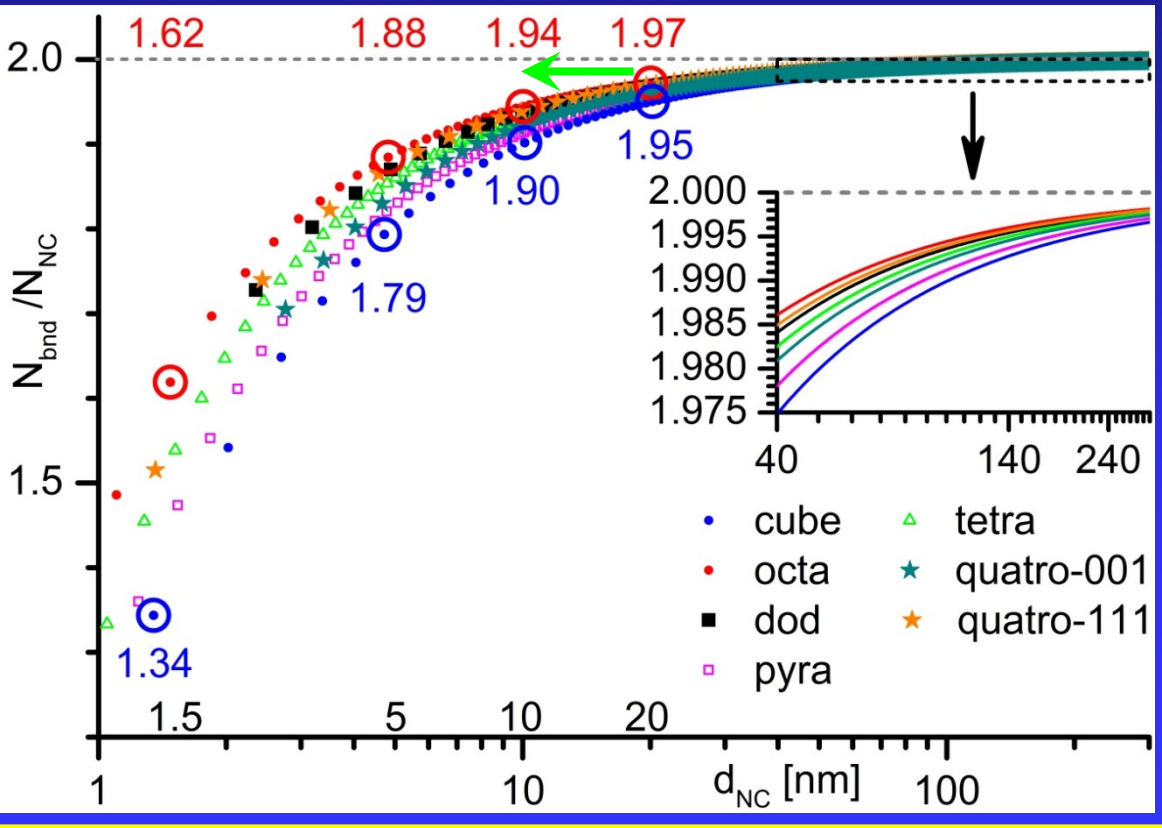
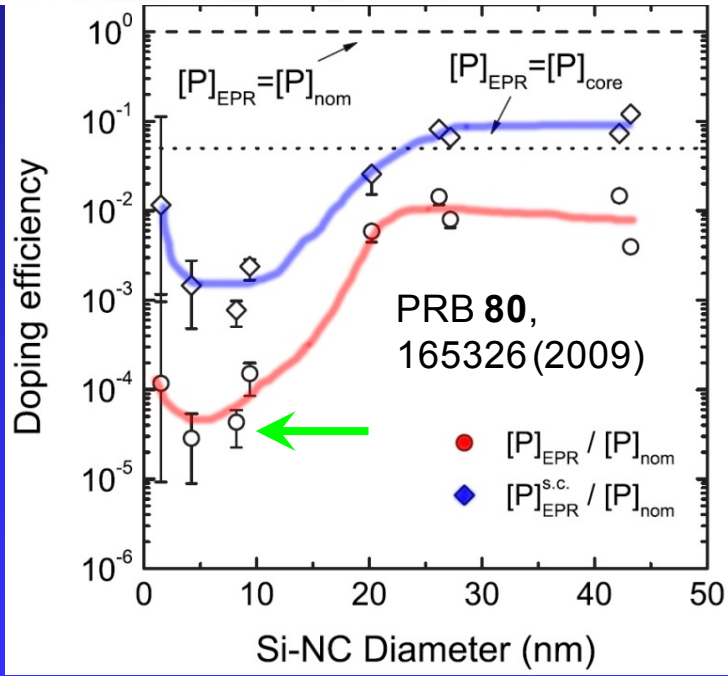


FIG. 7. P-doping efficiency as determined from the spin density of the $g = 1.998$ peak at $T = 20$ K as a function of the Si-NC diameter. The circles show the measured $[P]_{EPR}$ normalized to $[P]_{nom}$ and the diamonds show the same data after correcting for charge compensation of donors by Si-dbs ($[P]^{s.c.}_{EPR}$), assuming the model described in the text. The dashed and dotted lines show the cases $[P]_{EPR}=[P]_{nom}$ and $[P]_{EPR}=[P]_{core}$, respectively.

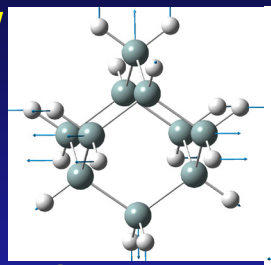




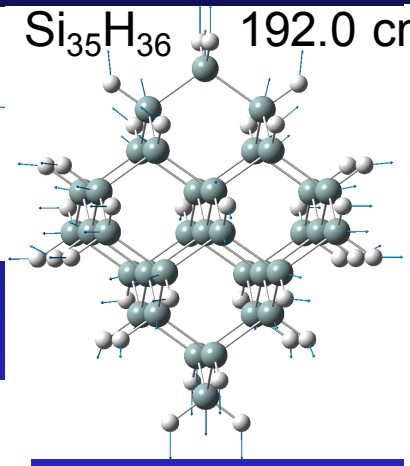
- $Si\text{-}NC/SiO_2$ system: self-purification for $N_{bnd}[i] / N_{NC}[i] = 1.96 \pm 0.01 \ldots 1.92 \pm 0.02$

5.4 Applications – the Ratio N_{bnd}/N_{NC}: Size and Response to Embedding, Raman (Breathing)

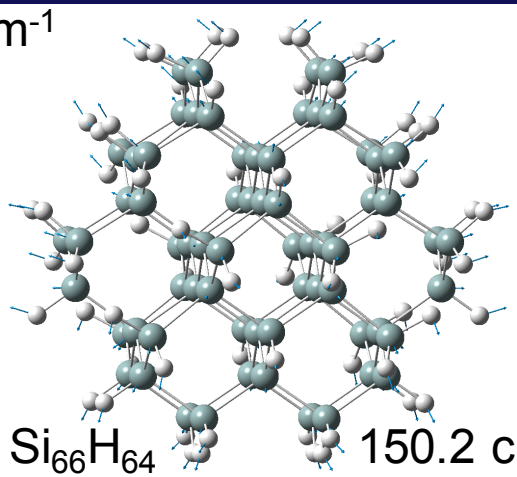
- DFT: B3LYP/6-31G(d), struct. opt. and force constant (FC) / spec-trum



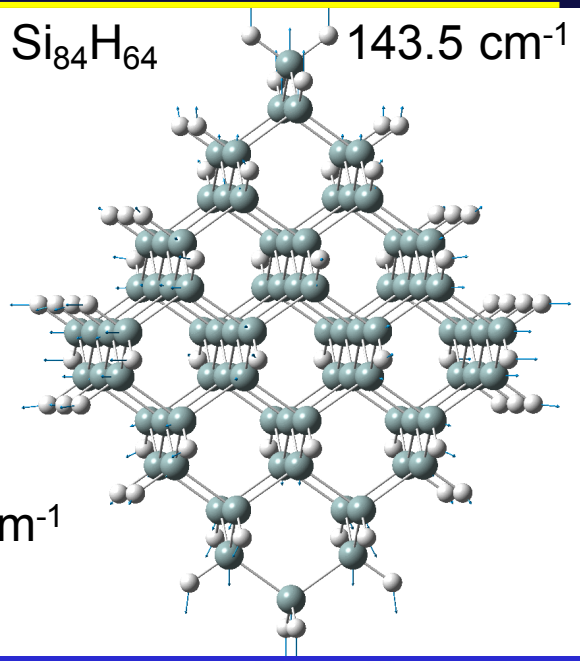
$Si_{10}H_{16}$ 304.1 cm^{-1}



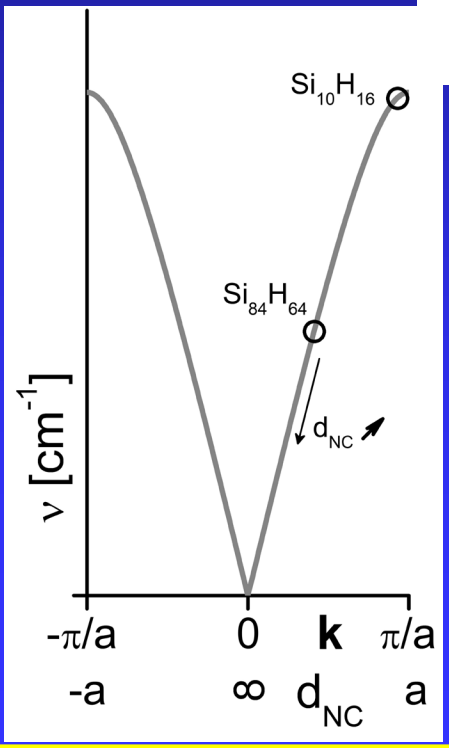
$Si_{35}H_{36}$ 192.0 cm^{-1}



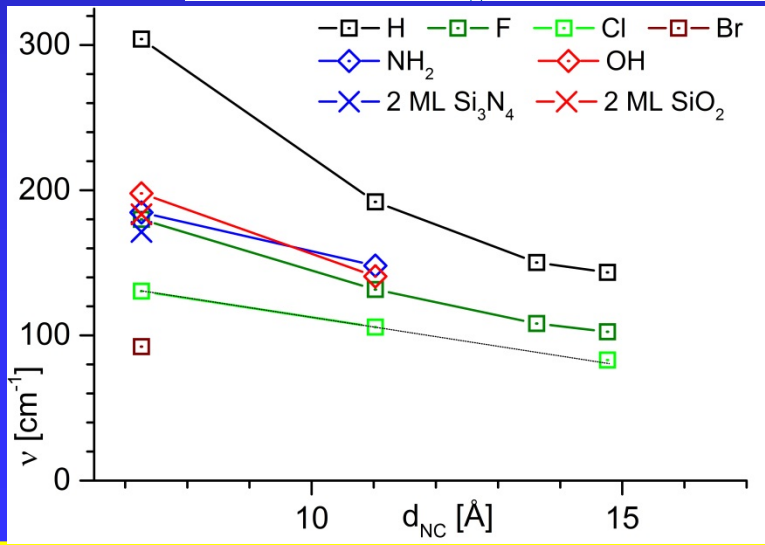
$Si_{66}H_{64}$ 150.2 cm^{-1}



$Si_{84}H_{64}$ 143.5 cm^{-1}

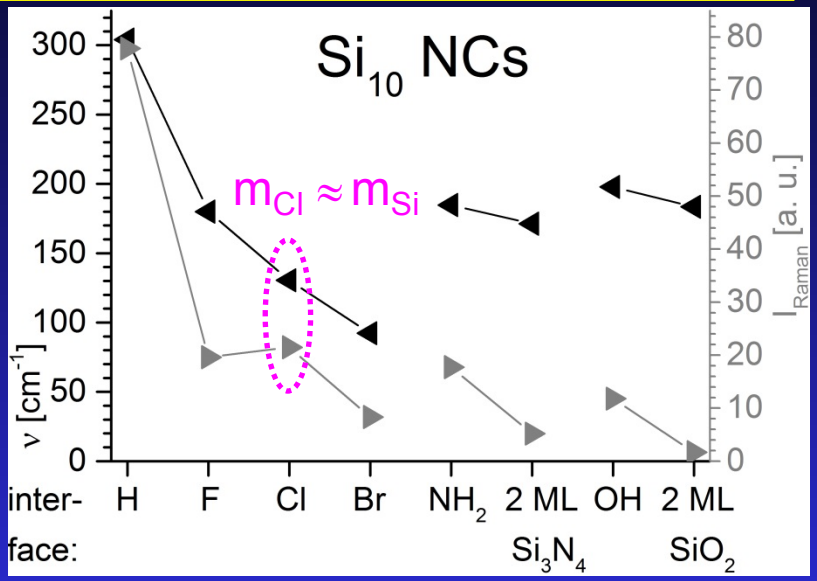


- NC breathing mode is longitudinal-acoustic (LA) with $\nu_{LA} \rightarrow 0$ for $d_{NC} \rightarrow \infty$ ($k \rightarrow 0$ for $d_{NC} \rightarrow \infty$)
- breath modes well known from organic molecules (e.g. C_{60}); should be observable in colloidal solutions with small NCs

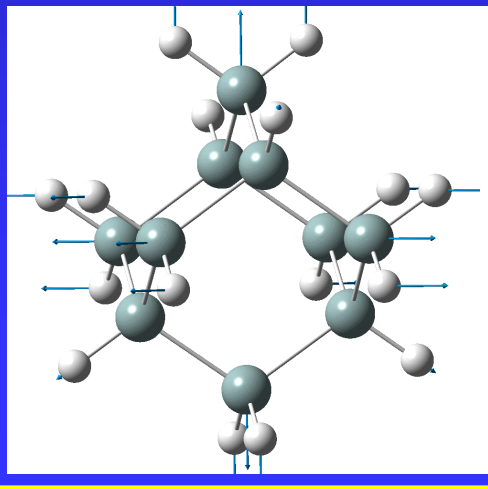


5.4 Applications – the Ratio N_{bnd}/N_{NC}: Size and Response to Embedding, Raman (Breathing)

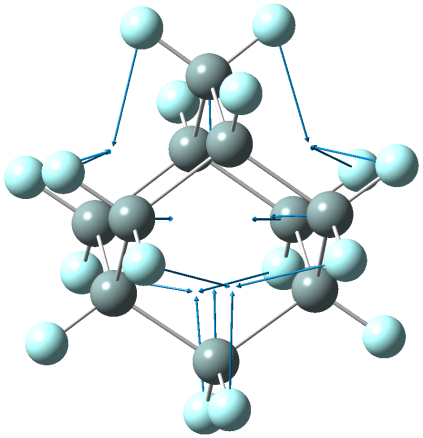
- breath ν_{LA} has low electromagnetic (EM) dipole moment → approximate by force constant (FC) model: $N_{NC}[i]$, $N_{bnd}[i]$
- IF atoms shift breath ν_{LA} with: their mass m_{IF} ↗ → ν ↘, I_{Raman} ↘ and with FC(Si–X) bigger or smaller FC(Si–Si) → ν ↗ or ↘
- shift of breath ν_{LA} by embedding rather small
- ν_{LA} intensity ↗ by Cl termination: resonance



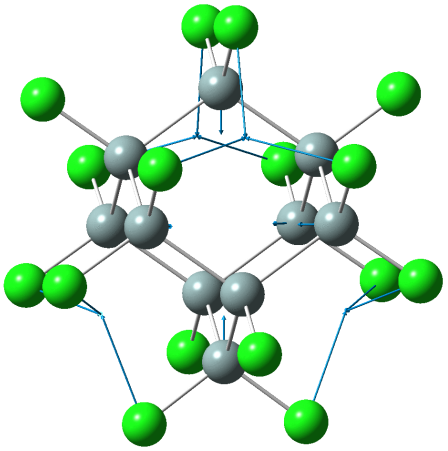
$Si_{10}H_{16}$ 304.1 cm^{-1}



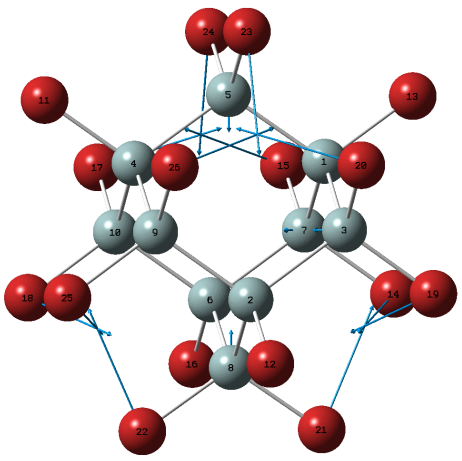
$Si_{10}F_{16}$ 179.9 cm^{-1}



$Si_{10}Cl_{16}$ 130.5 cm^{-1}

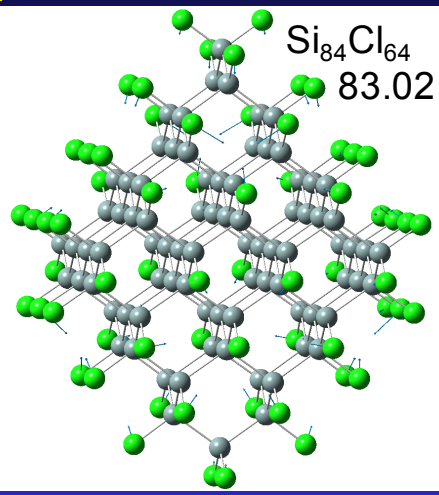


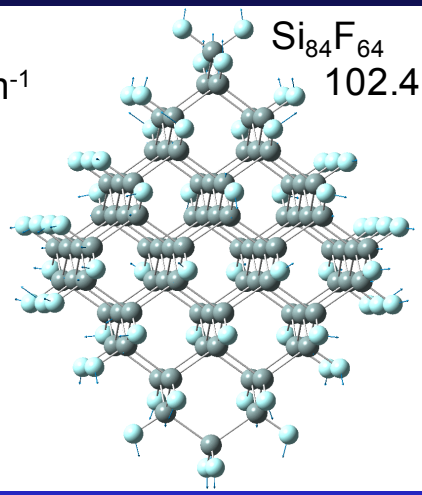
$Si_{10}Br_{16}$ 92.3 cm^{-1}

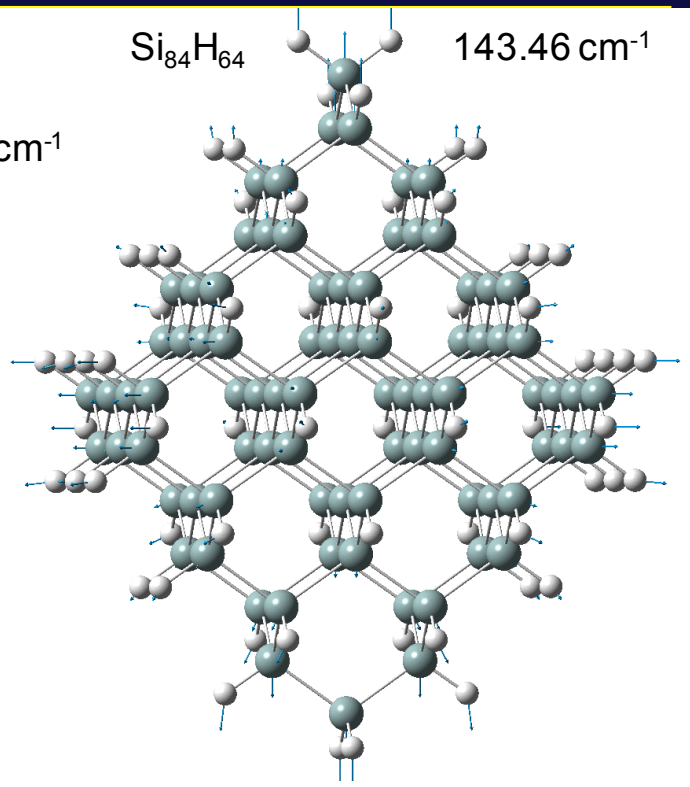


5.4 Applications – the Ratio N_{bnd}/N_{NC}: Size and Response to Embedding, Raman (Breathing)

- breath ν_{LA} is *in-phase vibration of all Si atoms*
  → mostly depends on $\frac{N_{bnd}[i]}{N_{NC}[i]}$
  → use $\nu_{LA}(1,X)$ in fit to include interface termination and matrix strain





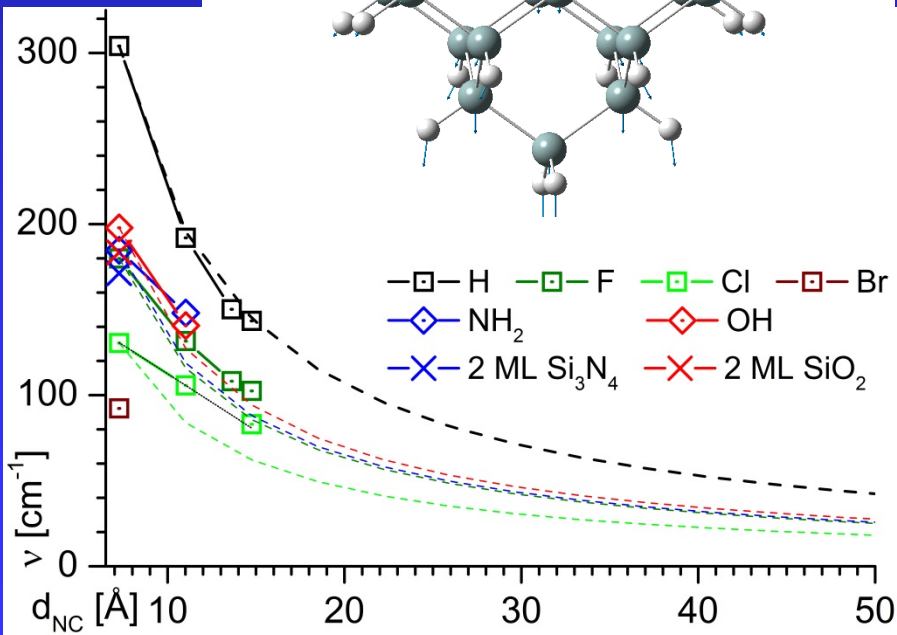


$$\nu_{\mathrm{Si}}^{\mathrm{breath,\,LA}}(i,\,\mathrm{X}) = \frac{\lim\limits_{i\to\infty}\frac{N_{\mathrm{bnd}}(i)}{N_{\mathrm{NC}}(i)} - \frac{N_{\mathrm{bnd}}(i)}{N_{\mathrm{NC}}(i)}}{\lim\limits_{i\to\infty}\frac{N_{\mathrm{bnd}}(i)}{N_{\mathrm{NC}}(i)} - \frac{N_{\mathrm{bnd}}(1)}{N_{\mathrm{NC}}(1)}}\,\nu_{\mathrm{Si}}(1,\,\mathrm{X})$$

- good ν_{LA} fit for Si_xH_y, fair for X = OH, F; not so good yet for X = NH_2, Cl; requires refined input/model

$$\nu_{\mathrm{Si}}^{\mathrm{breath,\,LA}}(i,\,\mathrm{X}) = \frac{2 - \frac{N_{\mathrm{bnd}}(i)}{N_{\mathrm{NC}}(i)}}{0.8}\,\nu_{\mathrm{Si}}(1,\,\mathrm{X})$$

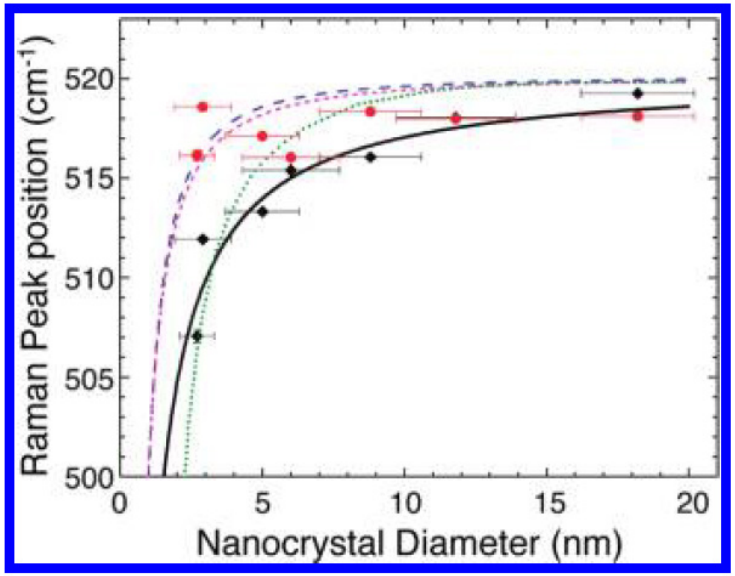
$$d_{\mathrm{NC}}[i] = \sqrt[3]{\frac{6}{\pi}N_{\mathrm{NC}}[i]} \times V_{\mathrm{atom}}$$



5.4 Applications – the Ratio N_{bnd}/N_{NC}: Size and Response to Embedding, Raman (Si Bulk Mode)

- no analytical description of fundamental LO/TO Si $\nu^{LO/TO}$ mode (521 cm^{-1}) as $f(d_{NC})$ which fit experimental data, just least square fits[1]
  → no causality, hence no interpretation and assignment of results

- analytical fits with NC-specific parameters (N_{NC}, N_{bnd}, N_X) allow for real data interpretation



[1]

More theoretical work is needed to provide a quantitatively accurate model of the size dependence of the Raman spectra of Si nanocrystals. However, a convenient scaling relationship between the Raman peak position and nanocrystal size might be used[28,29,31]

$$\omega(D) = \omega_0 - A\left(\frac{a}{D}\right)^{\gamma} \quad (2)$$

$\omega(D)$ is the diameter-dependent peak Raman frequency, ω_0 is the bulk Raman peak position of bulk crystalline Si (521 cm^{-1} for crystalline Si), a is the lattice constant (0.543 nm for Si), and D is the particle diameter. A and γ are fitting parameters

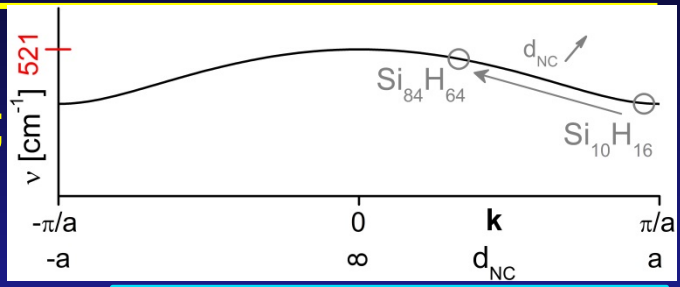
Figure 3. Raman peak position as a function of the nanocrystal diameter for freestanding ligand-passivated (black diamonds) and oxide-embedded (red circles) nanocrystals. The black line is a least-squares analysis fit of eq 2 to the Raman peak positions of the ligand-passivated freestanding nanocrystals; the blue and magenta curves are the predicted Raman peak positions versus size from the RWL and BP models, respectively. The green dotted curve shows recent model predictions by Faraci et al.[17] The error bars represent the particle size polydispersity determined from SAXS.

[1] J. Phys. Chem. Lett. **3**, 1089 (2012)

5.4 Applications – the Ratio N_{bnd}/N_{NC}: Size and Response to Embedding, Raman (Si Bulk Mode)

embedded NCs, fundamental optical mode (LO/TO)

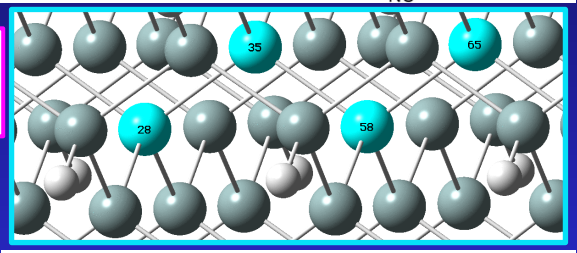
- $\nu^{LO/TO} \rightarrow 521\ cm^{-1}$ *from below* for $d_{NC} \rightarrow \infty$ ($k \rightarrow 0$);
  influence of ligand/matrix (N_X/N_{bnd}) ↘ with d_{NC} ↗,
  influence of NC interior (N_{bnd}/N_{NC}) ↗ with d_{NC} ↗



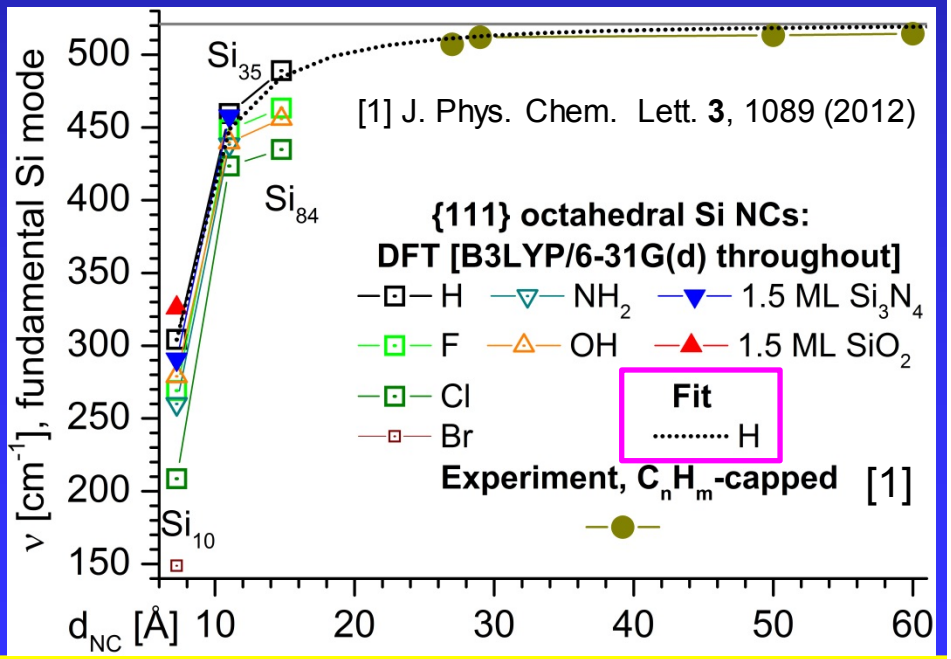
$$\nu_{Si}^{LO/TO}(i, X) = \nu_{Si}^{LO/TO}(1, X) + \left(\nu_{Si}^{LO/TO}(i \rightarrow \infty) - \nu_{Si}^{LO/TO}(1, X)\right)\left(1 - \frac{1}{\mathcal{A}(1)}\mathcal{A}(i)\right)$$

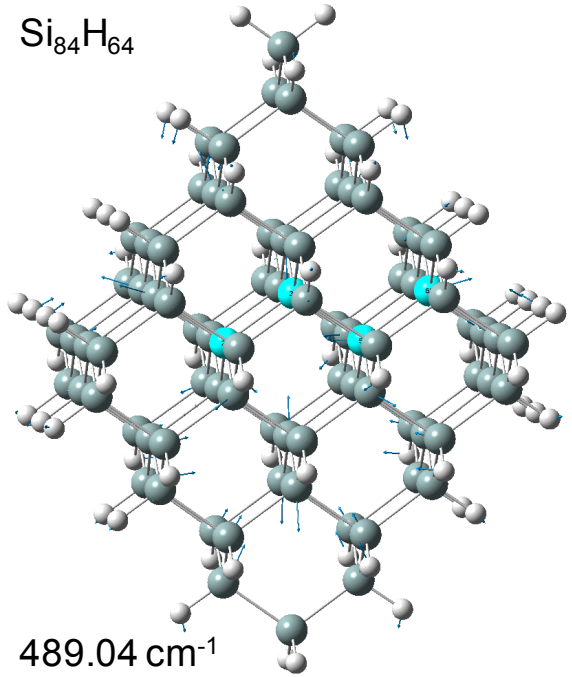
$$\mathcal{A}(i) = \frac{N_X(i)}{N_{bnd}(i)}\left(2 - \frac{N_{bnd}(i)}{N_{NC}(i)}\right)$$

$$d_{NC}[i] = \sqrt[3]{\frac{6}{\pi}N_{NC}[i] \times V_{atom}}$$



→ $\nu^{LO/TO}(1,X)$ includes kinetics of interface termination and matrix strain





6. Conclusions

- seven high symmetry zb-NCs with minimum surface energy (max. occurrence): 001 cubes, 111 octahedra, 001 dodecahedra, 111 tetrahedra, 111 pyramids with 001 base, 111-001 quatrodecahedra, 001-111 quatrodecahedra
- Analytical description of NC atoms ($N_{NC}[i]$), number of bonds between these ($N_{bnd}[i]$) and NC interface bonds ($N_{IF}[i]$) by explicit number series as $f(d_{NC}[i])$, surface faceting and shape; useable for *any* solid state spectroscopy technique
- $N_{IF}[i] / N_{bnd}[i]$ as $f(d_{NC}[i])$: stress balance zb-NC $\leftrightarrow$ embedding matrix; crystallization limit and polymorphism (segregation anneal, gas phase formation, …)
- ratio $N_{IF}[i] / N_{NC}[i]$ as $f(d_{NC}[i])$: interface dipoles, interface charge transfer which dominates (influences) electronic properties of Si (III-V) NCs
- ratio $N_{IF}^{001}[i] / N_{IF}^{111}[i]$ as $f(d_{NC}[i])$: key tool to detect shape of quatrodecahedral NCs (and other zb-NC shapes, see above) using Electron Paramagnetic Resonance (EPR) Spectroscopy
- $N_{bnd}[i] / N_{NC}[i]$ as $f(d_{NC}[i])$: gauge for stress response of zb-NC by DBs, stacking faults, self-purification; working on analytic Raman-fits (maintaining causality)

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