First-principles calculation, thermodynamics, and semiconductor statistics

第一原理計算と熱力学、半導体統計

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First-principles calculation and Density functional theory (DFT)

第一原理計算と密度汎関数理論

Analytical mechanics: Hamilton equation

Hamiltonian $H(q,p,t) = \sum_r p_r \dot{q}_r - L(q,p,t)$

in Cartesian coord. $H(r,p,t) = \sum_r \frac{1}{2m_i} {p_i}^2 + V(r,p)$

Hamilton's eq of motion $\frac{\partial q_r}{\partial t} = \frac{\partial H}{\partial p_r}, \frac{\partial p_r}{\partial t} = -\frac{\partial H}{\partial q_r}$

Poisson bracket (classical commutation relation) $\{A,B\} = \sum_i \left(\frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i} - \frac{\partial B}{\partial p_i}\frac{\partial A}{\partial q_i} \right)$

Equation of motion $\dot{A} = \{H,A\} + \frac{\partial A}{\partial t}$ A, B: Physical quantities

If A is independent of time $\dot{A} = \{H,A\}$

Quantization: Heisenberg's uncertainty principle

Derived from quantum commutation relation for conjugate physical qunatities:

$$qp_q - p_q q = [q, p_q] i\hbar$$

Example:

$\hat{x} = x, \quad \hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$

$\hat{x} = i\hbar \frac{\partial}{\partial p_x}, \hat{p}_x = p_x$

Both the upper and the bottom combinations satisfy the quantum commutation relation

$$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$$

$$\Delta x \cdot \Delta p_x \sim h$$

Schrödinger equation

Classical Hamiltonian (phys quantities are **C (classical) numbers**)

$$H(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{p}_2,\mathbf{p}_1,\cdots,t)=\sum_r \frac{1}{2m_i}|\mathbf{p_i}|^2+V(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{p}_2,\mathbf{p}_1,\cdots)$$

Regard the physical quantities in H as **Q (quantum) numbers** and apply **the quantum commutation relations**

Commut. rel. $\hat{x}_i\hat{p}_{x,i}-\hat{p}_{x,i}\hat{x}_i=i\hbar$ ⇨ $\hat{x}_i=x_i,\ \hat{p}_{x,i}=\frac{\hbar}{i}\frac{\partial}{\partial x_i}$

$H\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)=E\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)$ **Schrödinger equation**

$$\left\{-\frac{1}{2}\sum_l \nabla_l{}^2+V(\mathbf{r}_1,\mathbf{r}_2,\cdots)\right\}\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)=E\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)$$

***E* is the eigenvalue of the H operator: Total energy**

Ψ: $|\Psi|^2$ corresponds to the electron density distribution

- Many number simultaneous partial differential equation (6 x number of electrons)
- Very difficult to solve analytically

One-electron equation

Schrödinger eq $H\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)=E\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)$ **Wave func** $\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots)$ **Total energy** E

Separation of variables

$$\Psi(\mathbf{r})=\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

$$H(\mathbf{r})=\sum h_i(\mathbf{r}_i)$$

$$h_i(\mathbf{r}_i)=-\frac{1}{2}\nabla_i^2-\sum_m\frac{Z_m}{r_{im}}+\sum_m\int\frac{\phi_m^*(\mathbf{r}_m)\phi_m(\mathbf{r}_m)}{r_{im}}d\mathbf{r}_m$$

$$h_i\phi(\mathbf{r}_i)=\varepsilon\phi(\mathbf{r}_i)$$ **One-electron Schrödinger eq**

- ε_i: Eigenvalues of one-e equation
- ϕ_i: Eigenvectors of one-e equation

What are their physical meaning?

Atomic unit (a.u.): Dimensionless equations

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2-\frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r}\right]\psi(\mathbf{r})=E\psi(\mathbf{r}) \qquad r'=ar \qquad E'=bE$$

$$\left[-\frac{\hbar^2}{2m_e a^2}\nabla'^2-\frac{e^2}{4\pi\varepsilon_0 a}\frac{Z}{r'}\right]\psi(a\mathbf{r}')=bE'\psi(a\mathbf{r}')$$

$$\left[-\frac{1}{2}\nabla^2-\frac{Z}{r}\right]\psi(\mathbf{r})=E\psi(\mathbf{r})$$

Atomic unit: a.u.

$$a=\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}=5.2918\times10^{-11}\,\mathrm{m}$$

Unit of length: boh

Radius of H 1*s* orbital

$$b=\frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2}=13.6\,\mathrm{eV}$$

Unit of energy #1: Rydberg

Energy level of H 1*s* orbital

$$\left[-\nabla^2-2\frac{Z}{r}\right]\psi(\mathbf{r})=E\psi(\mathbf{r})$$

$$b=\frac{m_e e^4}{(4\pi\varepsilon_0)^2\hbar^2}=27.2\,\mathrm{eV}$$

Unit of energy #2: Hartree

Definition of first-principles calculations

Broad definition:

Provide answers with required accuracy based on fundamental physics equation without empirical parameters

for Quantum calculations:

Provide high-accuracy total energy based on quantum physics equations only from atomic species and coordinates

What are known from total energy?

FP calculation: Provide high accuracy total energy *E*

=> In principle, all properties can be calculated

- **Stable structure:** Find lattice parameters & atom coordinates with minimum *E*
- **Electronic structure (band structure):** $e_i(\boldsymbol{k}) = E(n_{\boldsymbol{k},i}) - E(n_{\boldsymbol{k},i} - 1)$
- **Elastic tensors**

$U = U_0 + \frac{1}{2}\sum_{i,j,k,l} C_{ijkl} e_{ij} e_{kl}$ Calculate $U(e_{ij})$ from e_{ij}

$\sigma_{ij} = \sum_{k,l} C_{ijkl} e_{kl}$ Calculate stress σ_{ij} from e_{ij}

- **Dielectric tensors**

$U = U_0 + \frac{1}{2}\sum_{i,j} \varepsilon_{ij} E_i E_j$ Calculate $U(E_i)$ from E_i

$D_i = \varepsilon_0 + P_i = \sum_j \varepsilon_{ij} E_j$ Polarization P_i are calculated from **Berry phase**

Choice of energy function *U*:

0 K, constant *V*: Internal energy *E* (total energy given by DFT)

0 K, constant *P*: Enthalpy $H = U + PV$

>0 K, constant *V*: Helmholz energy

$F = U + F_{\text{electron}} + F_{\text{phonon}}$

from electron DOS from phonon DOS

Band theory from LCAO
(Linear Combination of Atomic Orbitals)

原子基底関数からのバンド理論

Linear combination and variational principle: Roothaan-Hall equation

Ritz's variational principle:

Expectation value of Hamiltonian $\langle E \rangle$ for any wave function ψ is equal to or larger than E_0, that of the ground state

$$\langle E \rangle = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle \geq E_0$$

ψ is approximated by **linear combination of basis functions u_n**

$$\psi = \sum_{n=0} C_n u_n$$

Based on the variational principle, C_n are obtained by minimizing $\langle E \rangle$

$$< E >= \frac{\sum_m \sum_n C_m^* C_n \langle u_m | H | u_n \rangle}{\sum_n C_n^* C_n \langle u_m | u_n \rangle}$$

$$\sum_m C_m \langle u_n | H | u_m \rangle - E \sum_m C_m \langle u_n | u_m \rangle = 0$$

Many quantum equations will lead to eigenvalue problems

Roothaan-Hall equation

$$\sum_m C_m \langle u_n | H | u_m \rangle - E \sum_m C_m \langle u_n \mid u_m \rangle = 0$$

$$\mathbf{HC} = E\mathbf{SC}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{ss} & & H_{2n} - ES_{2n} \\ \vdots & & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

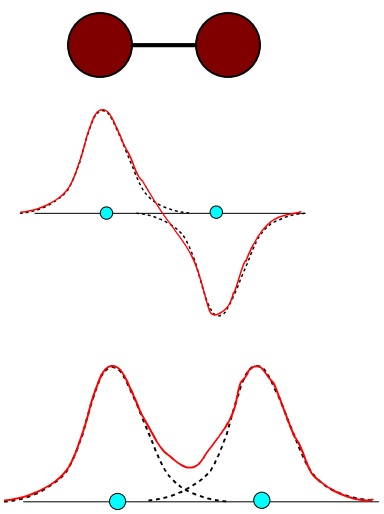
Fock matrix
Transfer matrix $H_{nm} = \langle u_n | H | u_m \rangle$

Overlap integral $S_{nm} = \langle u_n \mid u_m \rangle$

H_2 molecule

Ignore overlap integrals $S_{nm} = \delta_{nm}$

H_2



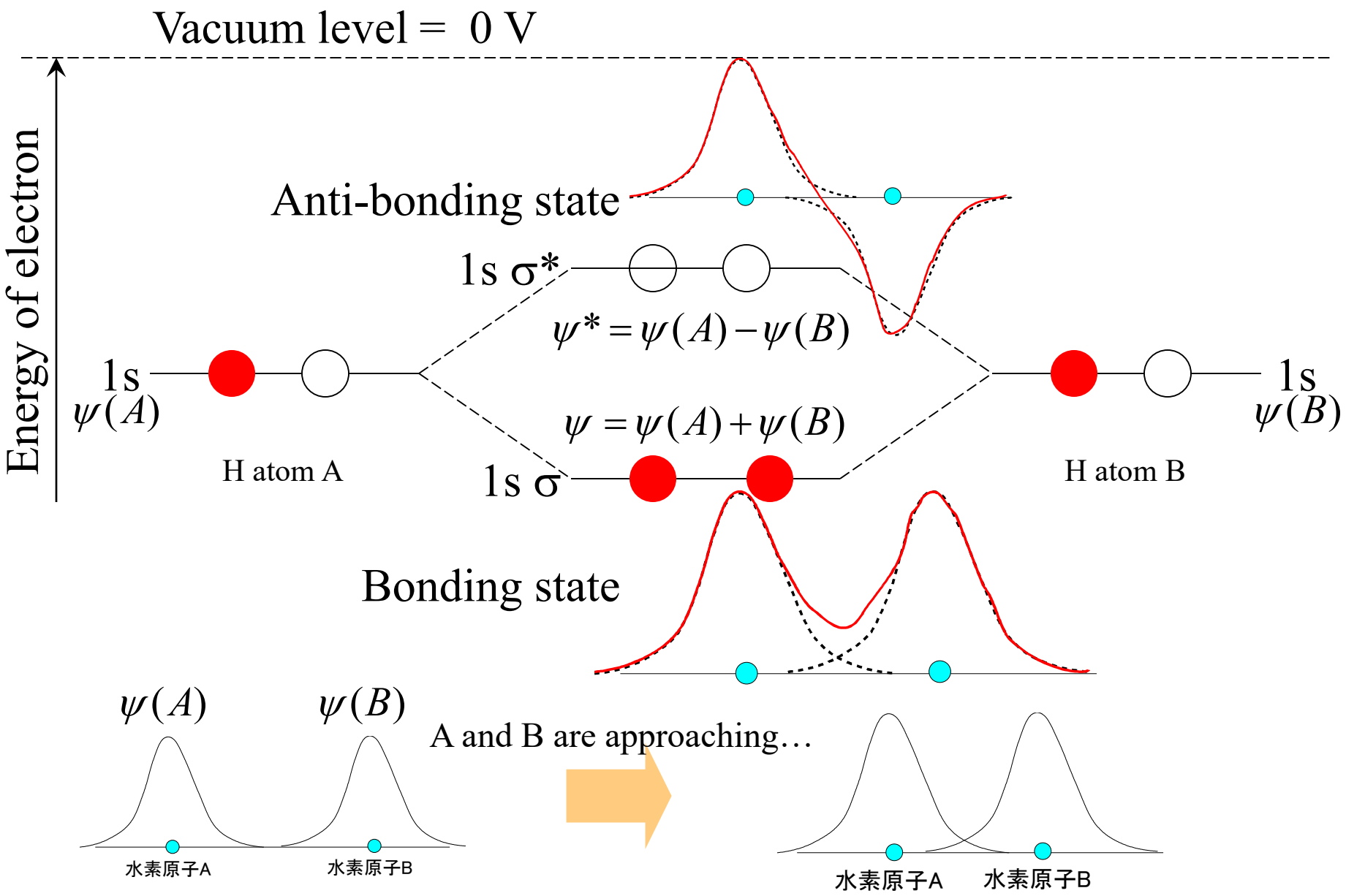
$$H_{1s1s} = \varepsilon_{1s}$$

$$\begin{vmatrix} \varepsilon_{1s} - \varepsilon & h_{12} \\ h_{12} & \varepsilon_{1s} - \varepsilon \end{vmatrix} = 0$$

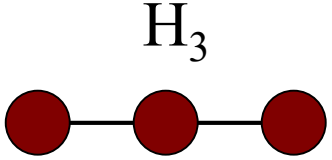
$$\varepsilon = \varepsilon_{1s} \pm h_{12}$$

$$\phi_{\pm} = \frac{1}{\sqrt{2}}(\varphi_1 \pm \varphi_2)$$

Electronic structure of H_2 molecule



H_3 molecules

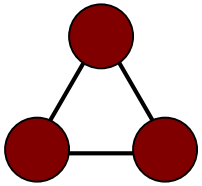


Linear

$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & 0 \\ h_{12} & \varepsilon_{1s} & h_{12} \\ 0 & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

$$\varepsilon_{\pm} = \varepsilon_{1s} \pm \sqrt{2} h_{12}\,,\ \varepsilon_{non-bonding} = \varepsilon_{1s}$$

$$\phi_{\pm} = \frac{1}{\sqrt{2}}\left(\varphi_{+} \pm \varphi_2\right),\ \varphi_{-} = \frac{1}{2}\left(\varphi_1 + \sqrt{2}\varphi_2 + \varphi_3\right)$$



Ring

$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} \\ h_{12} & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

$$c_i^{(l)} = \exp\left(i k_l x_j\right)$$

$$k_l = \frac{2\pi}{Na} l$$

l are integers from 0 to 2

a is interatomic distance

$$E\left(k_l\right) = \varepsilon_{1s} + 2h_{12}\cos\left(k_l a\right)$$

Solution for ring H_3 molecule

$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} \\ h_{12} & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

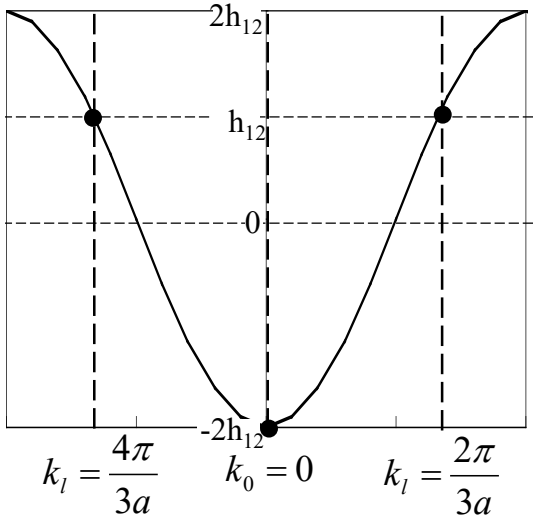
$$k_l = \frac{2\pi}{Na} l \qquad N=3,\ l=0,\ 1,\ 2,\ \cdot\ \cdot\ \cdot,\ N\text{-}1$$

$$\phi_{kl} = \sum_j \varphi_j \exp\left(ik_l x_j\right) \qquad E(k_l) = \varepsilon_{1s} + 2h_{12}\cos(k_l a)$$

$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} \\ h_{12} & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} 1 \\ \exp(ik_l a) \\ \exp(i2k_l a) \end{pmatrix} = \begin{pmatrix} \varepsilon_{1s} + h_{12}(\exp(ik_l a) + \exp(i2k_l a)) \\ \varepsilon_{1s}\exp(ik_l a) + h_{12}(1 + \exp(i2k_l a)) \\ \varepsilon_{1s}\exp(i2k_l a) + h_{12}(1 + \exp(ik_l a)) \end{pmatrix} = \left[\varepsilon_{1s} + h_{12}(\exp(ik_l a) + \exp(i2k_l a))\right] \begin{pmatrix} 1 \\ \exp(ik_l a) \\ \exp(i2k_l a) \end{pmatrix}$$

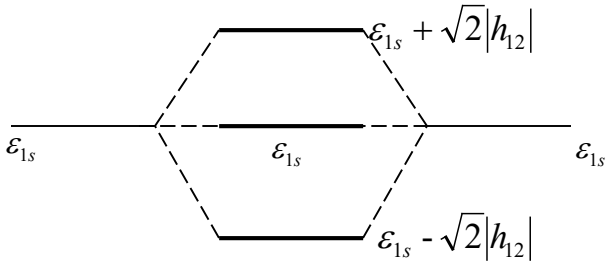
Energy levels of ring H_3

$$\varepsilon_{1s} - 2\,|\,h_{12}\,| \qquad \varepsilon_{1s} + |h_{12}| \qquad \varepsilon_{1s} + |h_{12}|$$



Energy levels of linear H_3

$$\varepsilon_{1s} - \sqrt{2}|h_{12}| \qquad \varepsilon_{1s} \qquad \varepsilon_{1s} + \sqrt{2}|h_{12}|$$



If same wave functions align periodically…

The result of the ring H_3 can be extended to ring H_N molecules

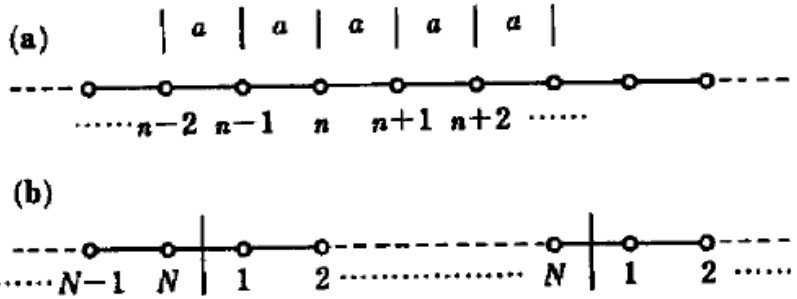
$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & 0 & 0 & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} & 0 & 0 \\ 0 & h_{12} & \varepsilon_{1s} & \ddots & \vdots \\ 0 & 0 & \ddots & \ddots & h_{12} \\ h_{12} & 0 & \cdots & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix}$$

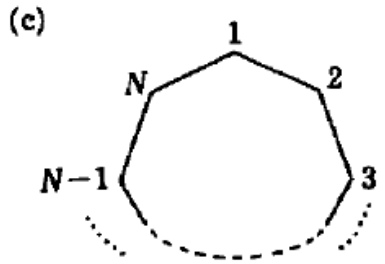
$$k_l = \frac{2\pi}{Na} l \qquad c_i^{(l)} = \exp\left(ik_l x_j\right)$$

$$\phi_{kl} = \sum_j \varphi_j \exp\left(ik_l x_j\right)$$

$$E\left(k_l\right) = \varepsilon_{1s} + 2h_{12}\cos\left(k_l a\right)$$

Solution of ring H_N molecule



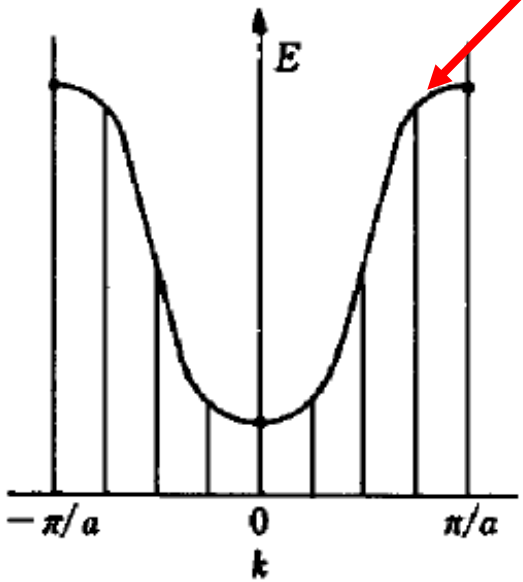


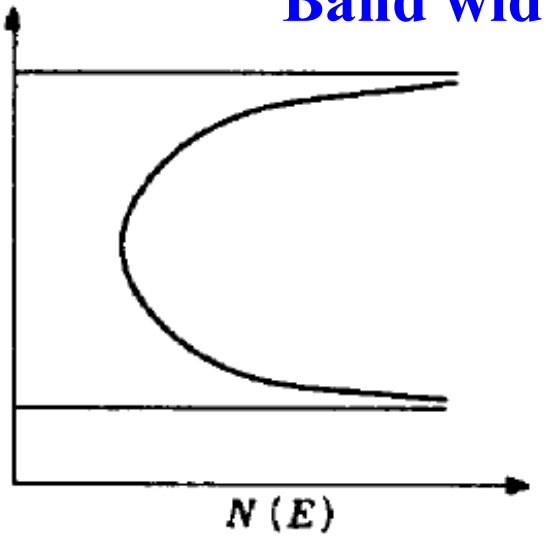
$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & 0 & 0 & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} & 0 & 0 \\ 0 & h_{12} & \varepsilon_{1s} & \ddots & \vdots \\ 0 & 0 & \ddots & \ddots & h_{12} \\ h_{12} & 0 & \cdots & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix}$$

$$\phi_{kl} = \sum_j \varphi_j \exp\left(ik_l x_j\right) \qquad k_l = \frac{2\pi}{Na} l$$

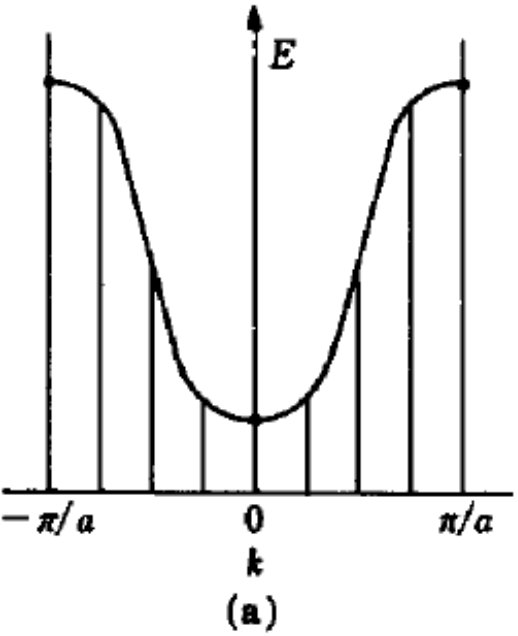
$$E(k_l) = \varepsilon_{1s} + 2h_{12}\cos(k_l a)$$

Band width: $4|h_{12}|$



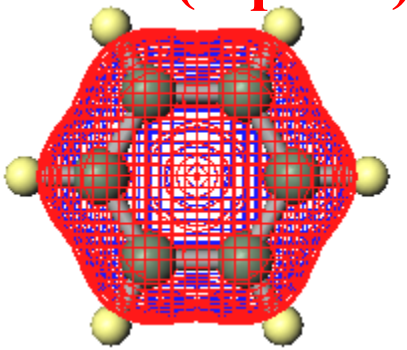


Wave function of benzene (C_6H_6) and Bloch's theorem



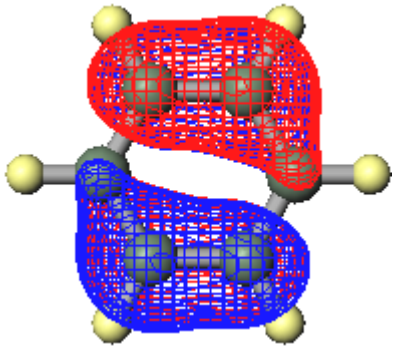
#11 A_{2u} –13.381 eV

***k* = 0 (Γ point)**



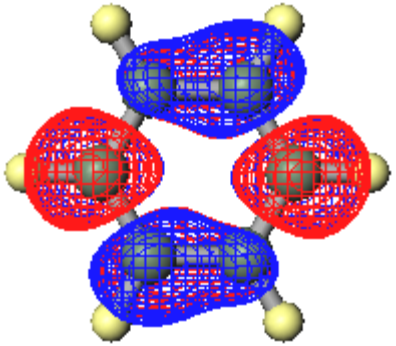
#14,15 E_{1g} –9.653 eV

***k* = 1/(3d)**



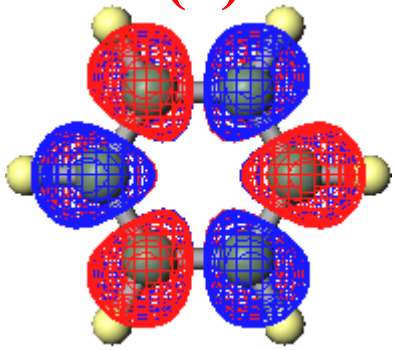
#16,17 E_{2u} 0.555 eV

***k* = 1/(2d)**



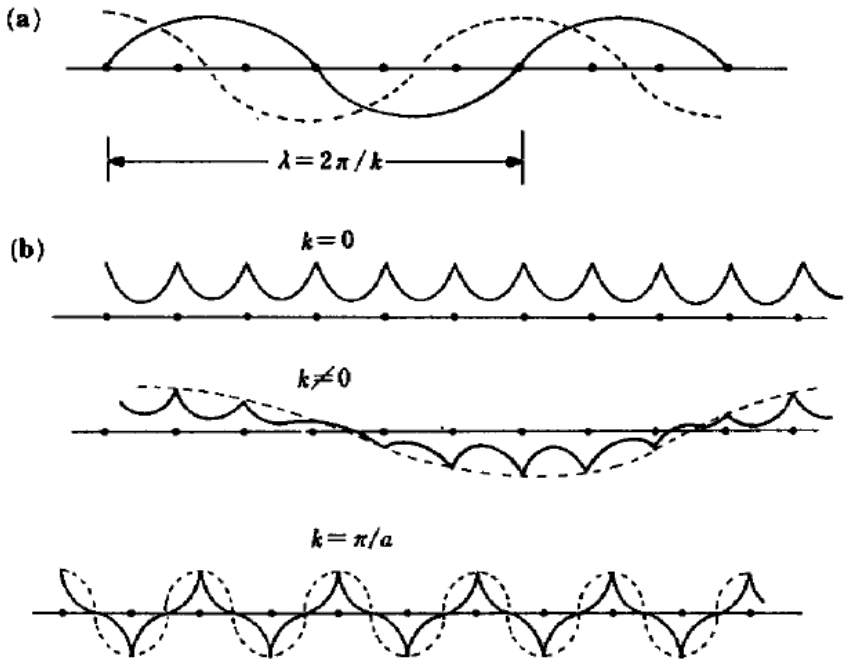
#18 B_{1g} 2.978 eV

***k* = 1/(d)**



Bloch's theorem

$$\begin{pmatrix} \varepsilon_{1s} & h_{12} & 0 & 0 & h_{12} \\ h_{12} & \varepsilon_{1s} & h_{12} & 0 & 0 \\ 0 & h_{12} & \varepsilon_{1s} & \ddots & \vdots \\ 0 & 0 & \ddots & \ddots & h_{12} \\ h_{12} & 0 & \cdots & h_{12} & \varepsilon_{1s} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix}$$



$$k_l = \frac{2\pi}{Na} l,\ c_i{}^{(l)} = \exp(ik_l x_j)$$

$$\varphi_{kl} = \sum_j c_i{}^{(l)} \phi_j = \sum_j \phi_j \exp(ik_l x_j)$$: **Bloch's theorem**

Periodic func Phase factor from Bloch's ***k***

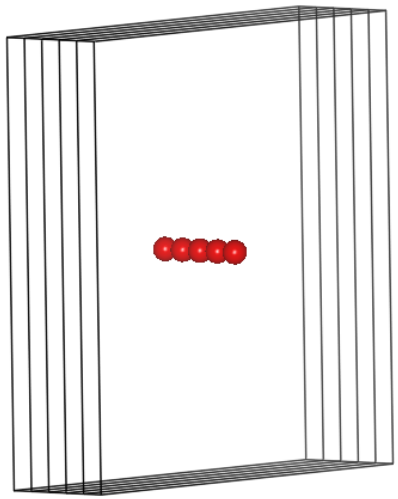
$$E(k_l) = \varepsilon_{1s} + 2h_{12}\cos(k_l a)$$

Bloch’s wave number, k

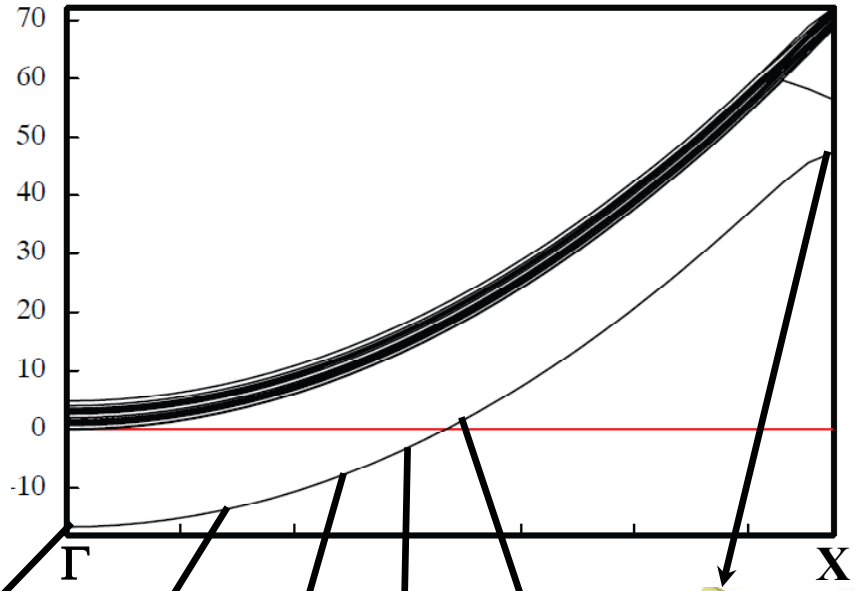
Blochの波数ベクトル *k*

1D H crystal: *k* and crystal orbitals

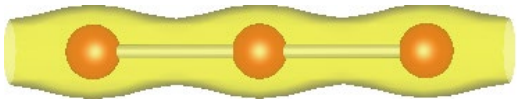
a=0.74, b=c=14.8 Å



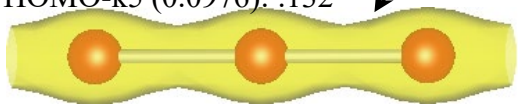
1/2a=0.676 Å^{-1}



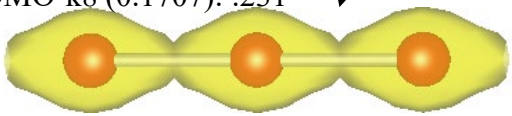
HOMO-k1 (0,0,0): 0



HOMO-k5 (0.0976): .132

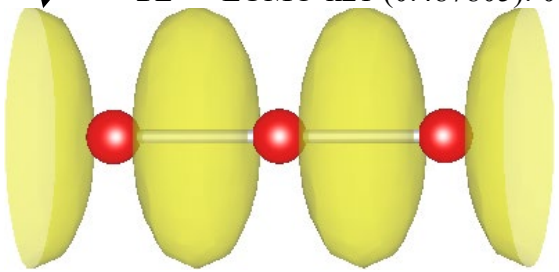


HOMO-k8 (0.1707): .231

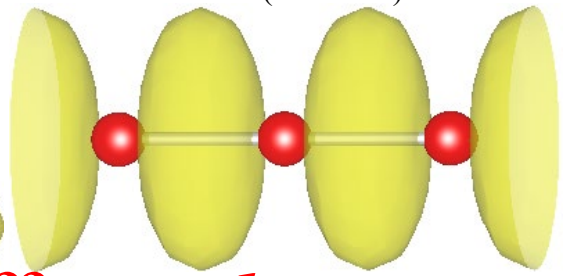


HOMO-k10 (0.21951): .297

LUMO-k21 (0.487805): 0.66



LUMO-k15 (0.341463): .46

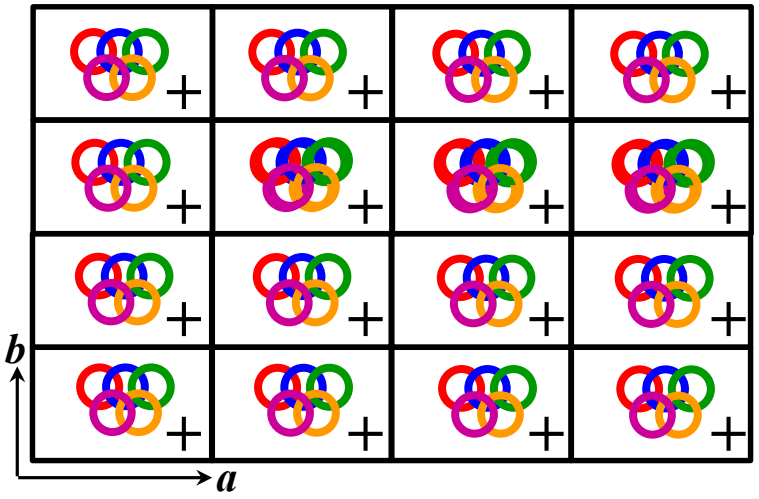


Different electron densities for different ***k***

Illustrative explanation of Bloch's k

Γ: k = (0, 0, 0)

$\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = 1$: Phases are the same for all unit cells

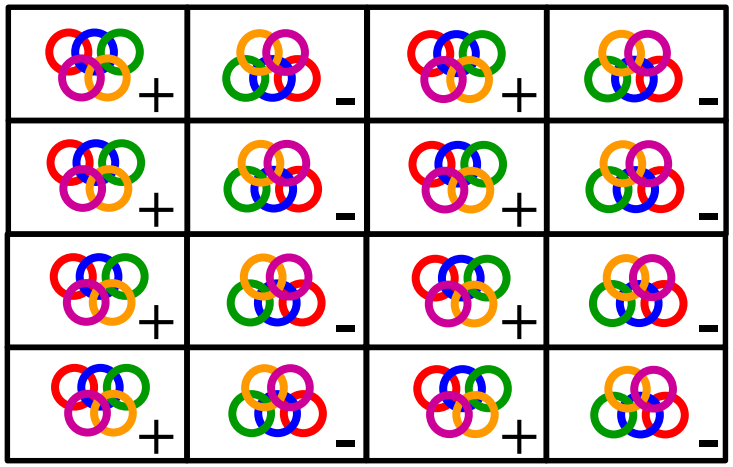


X: k = (π /a, 0, 0) [wave number unit]

(π, 0, 0) [phase unit]

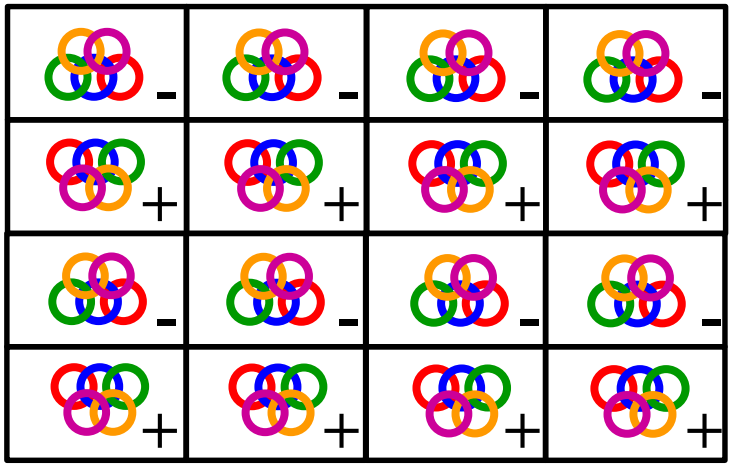
(1/2, 0, 0) [Recip. Lattice param unit, 2π/a]

$\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = \exp[i\pi(n_x)]$: Sign flip for odd n_x



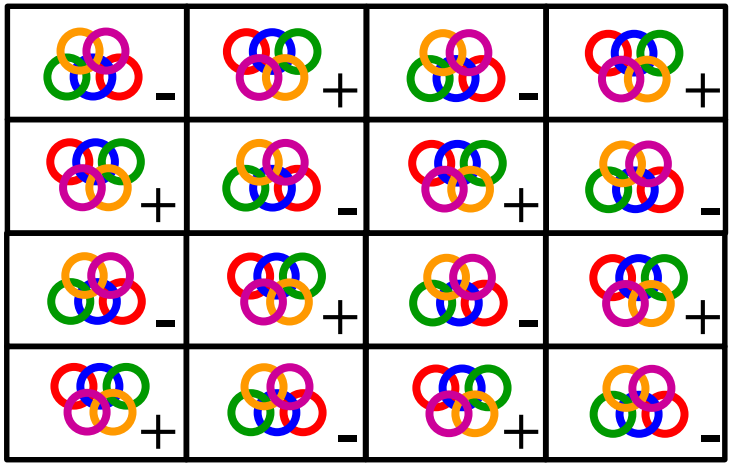
Y: k = (0, 1/2, 0)

$\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = \exp[i\pi(n_x)]$: Sign flip for odd n_y



M: k = (1/2, 1/2, 0)

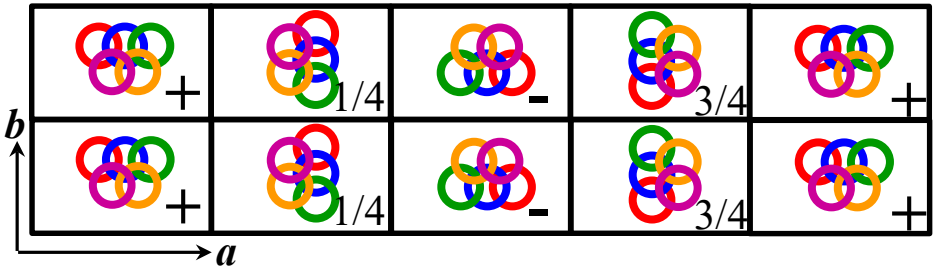
$\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = \exp[i\pi(n_x+n_y)]$: Sign flip for odd n_x+n_y



Illustrative explanation of Bloch's *k*

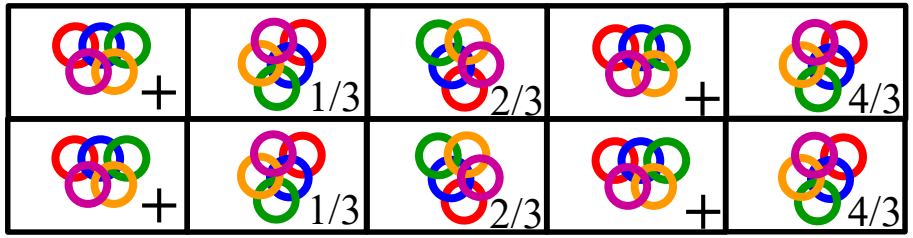
Δ_x : k = (1/4, 0, 0) [in (2π/a, 2π/b, 2π/c)]

exp(ik·r) = exp[iπ(n_x/2)]: Phase returns to zero for every 4 units along the ***a*** axis

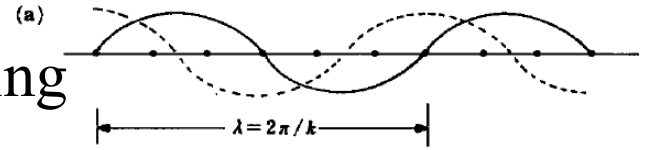


Δ_x : k = (1/3, 0, 0)

exp(ik·r) = exp[iπ(n_x/3)]: Phase returns to zero for every 3 units along the ***a*** axis

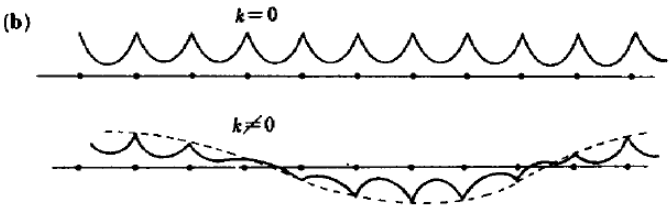


Γ point (k = 0): Bonding

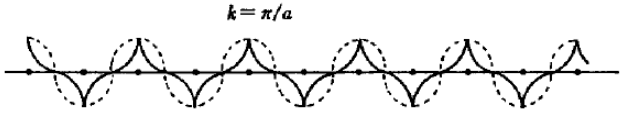


Arbitrary $k \neq 0$:

Many unit cells ($2\pi/ka$) are incorporated



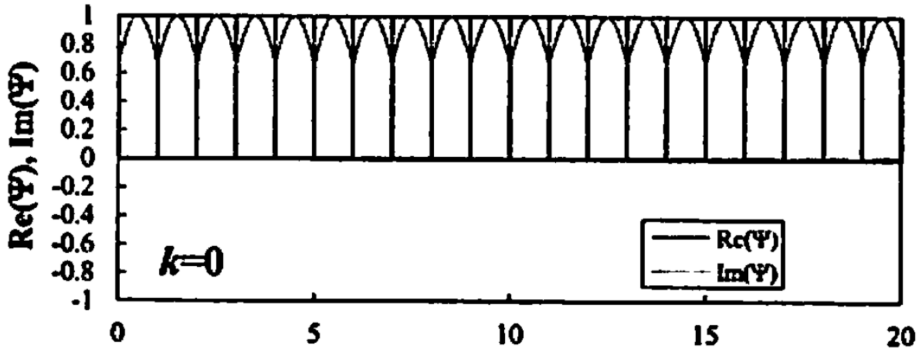
BZ bondary: Anti-bonding



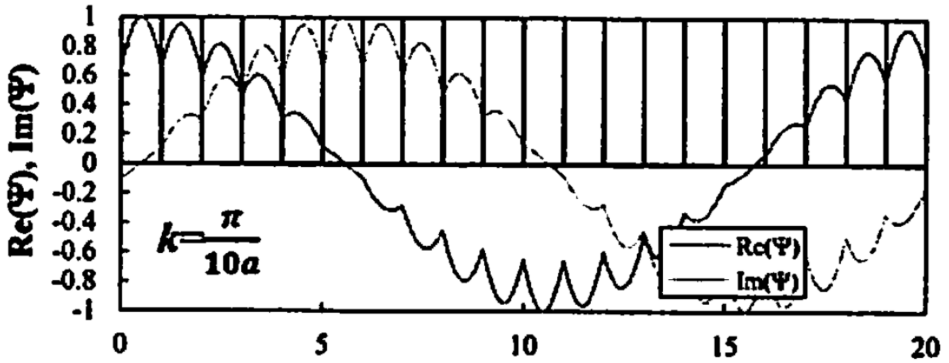
Effect of Bloch's *k*: Kronig-Penney model

杉山、結晶工学スクールテキスト p. 110

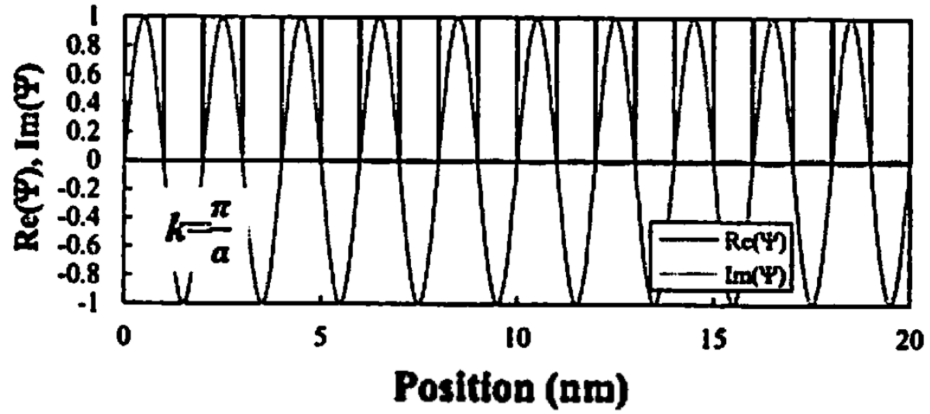
Γ point ($k = 0$): Bonding



Arbitrary $k \neq 0$:



BZ boundary: Anti-bonding

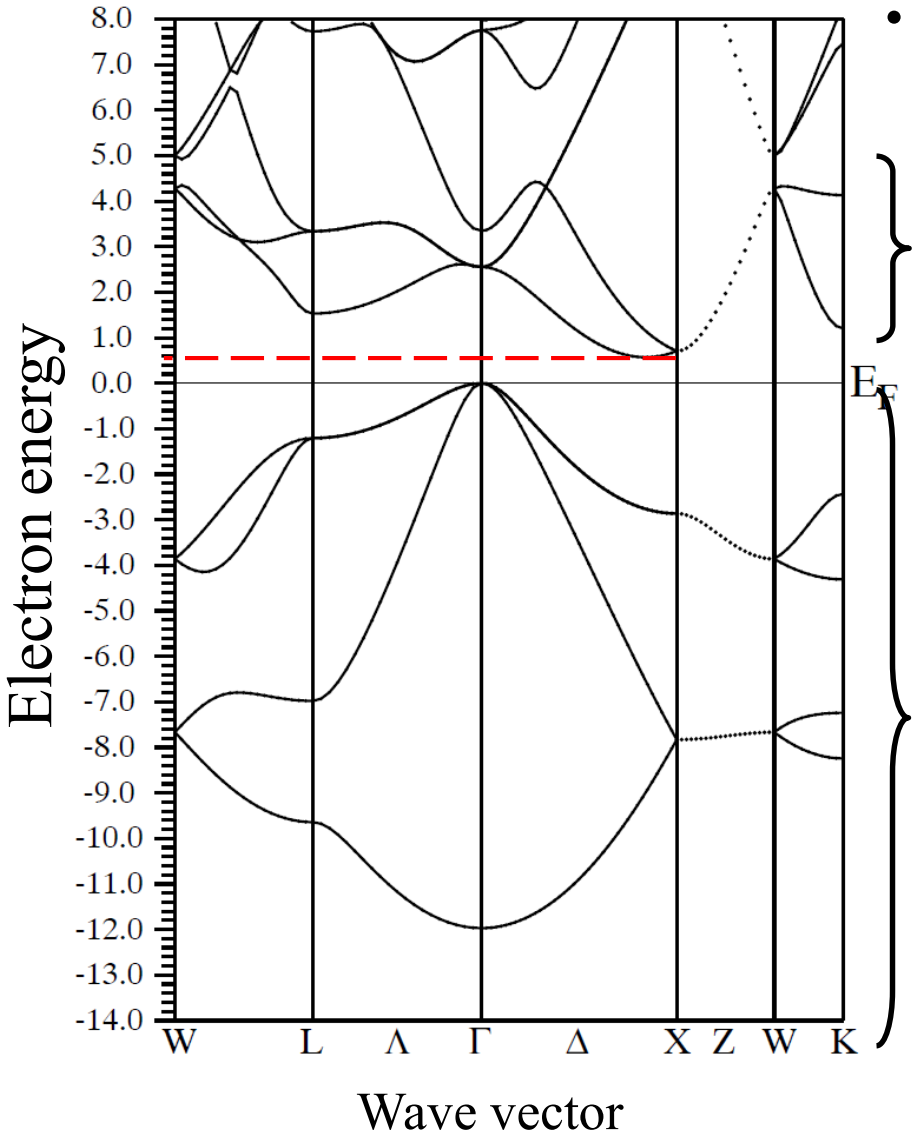


How to understand band structure

バンド構造の読み方

How to read band structure

Si (WIEN2k, PBE96)



- **Vertical axis indicate the energy of e^-**
  That is, electron is more stable for deeper energy
- If not explained explicitly
  The energy origin is the Fermi energy
- **e^- can take energy levels on the curves**

Unoccupied states (Conduction band)
Virtual states,
but empirically confirmed to reflect the actual CB

Occupied states
Valence band
Real states

How to read band structure

1. Horizontal axis indicates
   Bloch's **wave vector *k***
   k can roughly be regarded as
   the propagation direction of *e*⁻ momentum

What is wave number *k* …

Newton mech: $E = \frac{m}{2}v^2 + V = \frac{P^2}{2m} + V$

$\mathbf{P} \rightarrow \hbar\boldsymbol{k}$

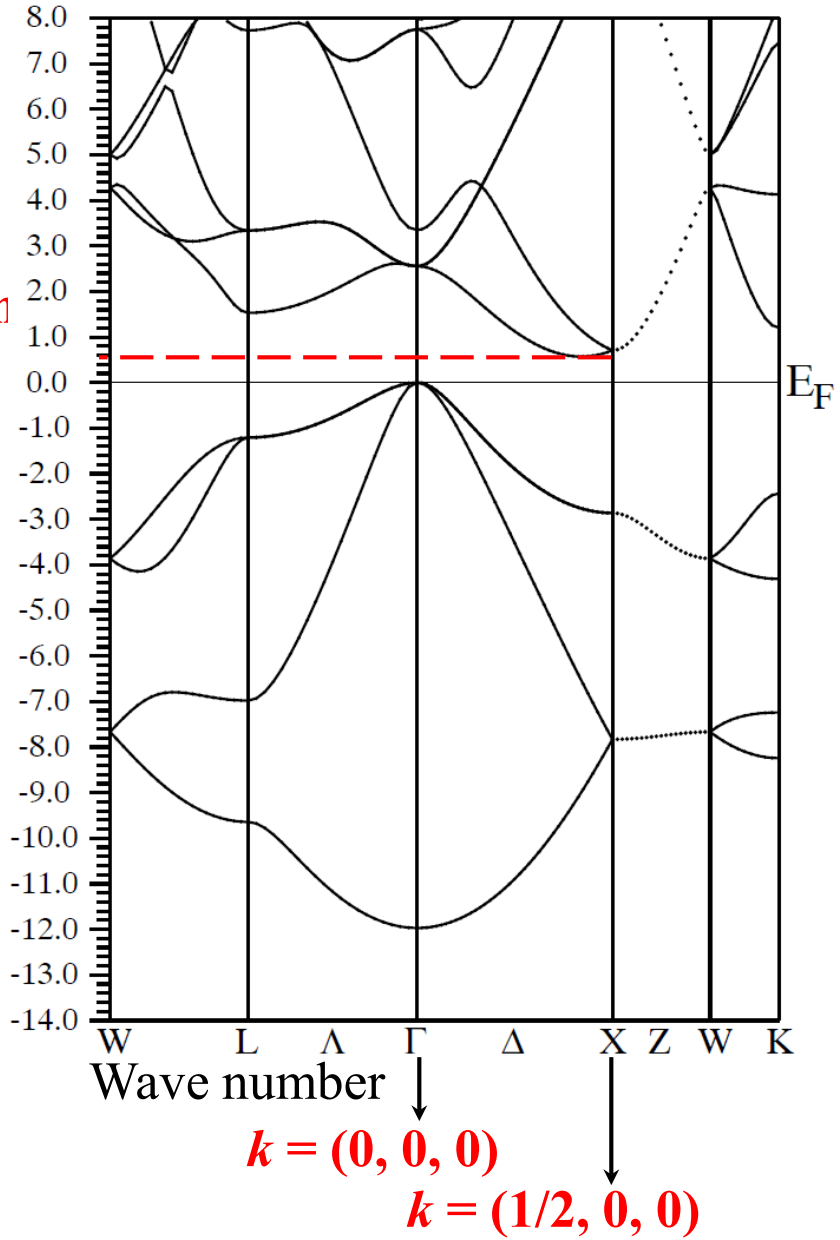
Quant mech: $E = \frac{\hbar^2}{2}k^2 + V$

バンド理論 (Blochの定理)

$$\phi_{kl} = \sum_j \exp\left(i\mathbf{k}\cdot\mathbf{r}_j\right)\cdot u_j(\mathbf{r}-\mathbf{r}_j)$$

k: Bloch's wave number
ħk: Crystal momentum

Note*: The direction of velocity is *–k* for negative *m

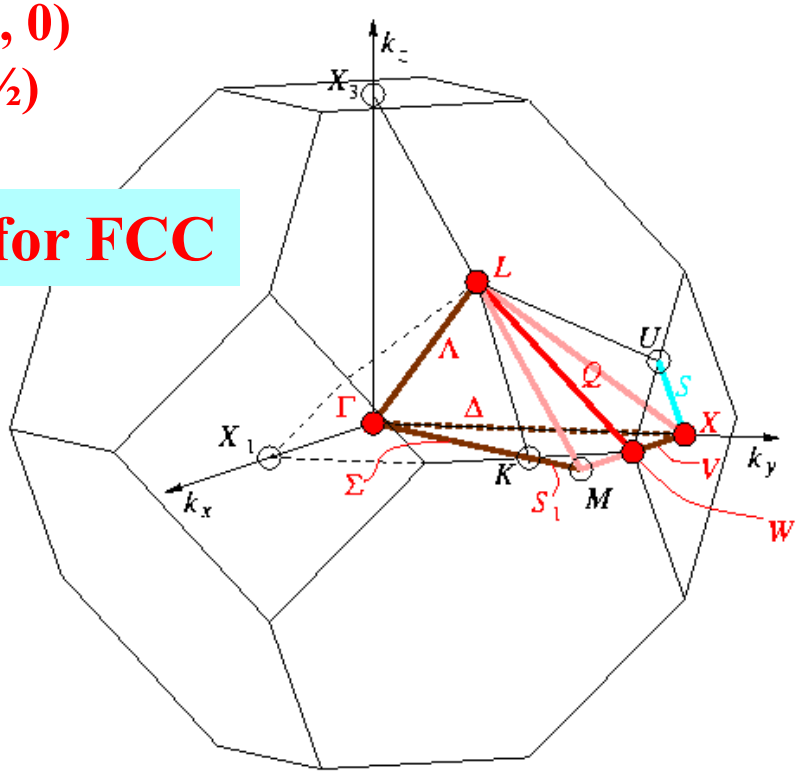


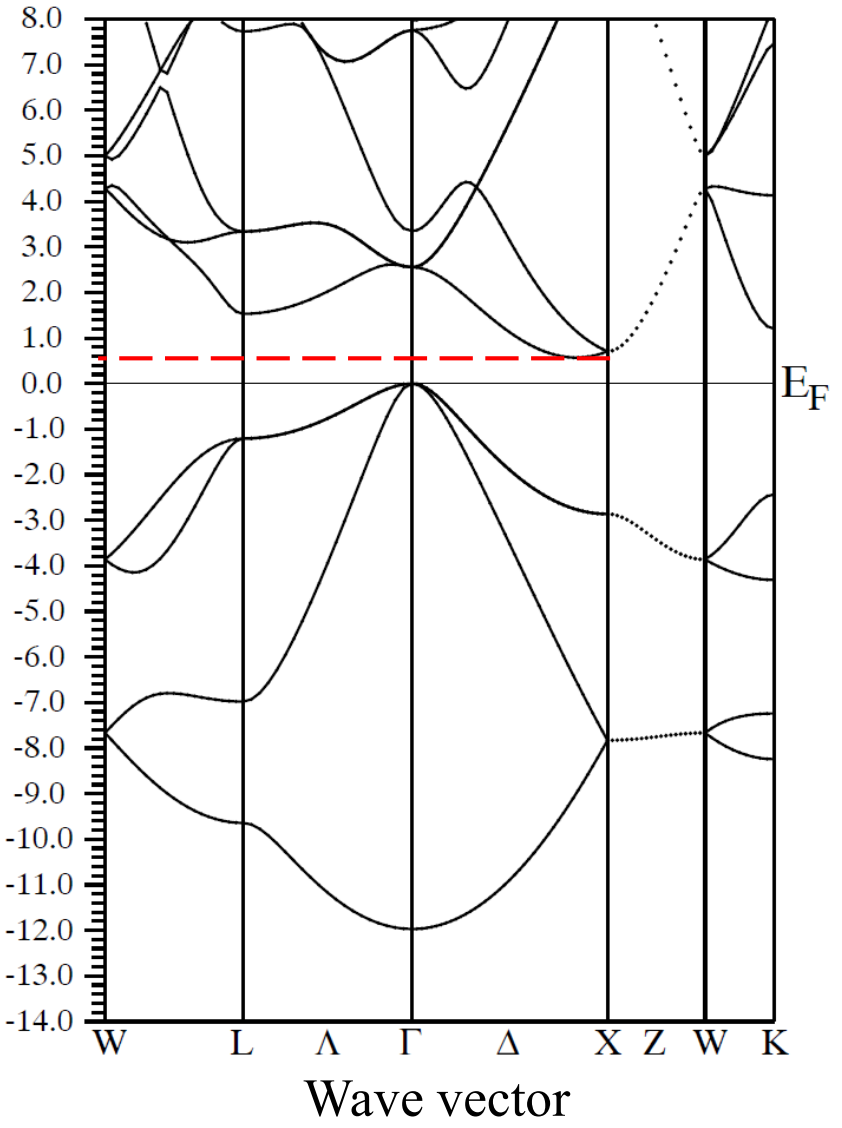
How to read band structure

Only high-symmetry ***k*** points are drawn
W, L, Γ, X, K etc indicate
the **high-symmetry *k* points and lines**
Check e.g. by databases

for simple lattice
Γ: *k* = (0, 0, 0) (unit may be in e.g. 1/*a*)
X: (1/2, 0, 0)
Z: (0, 0, ½)

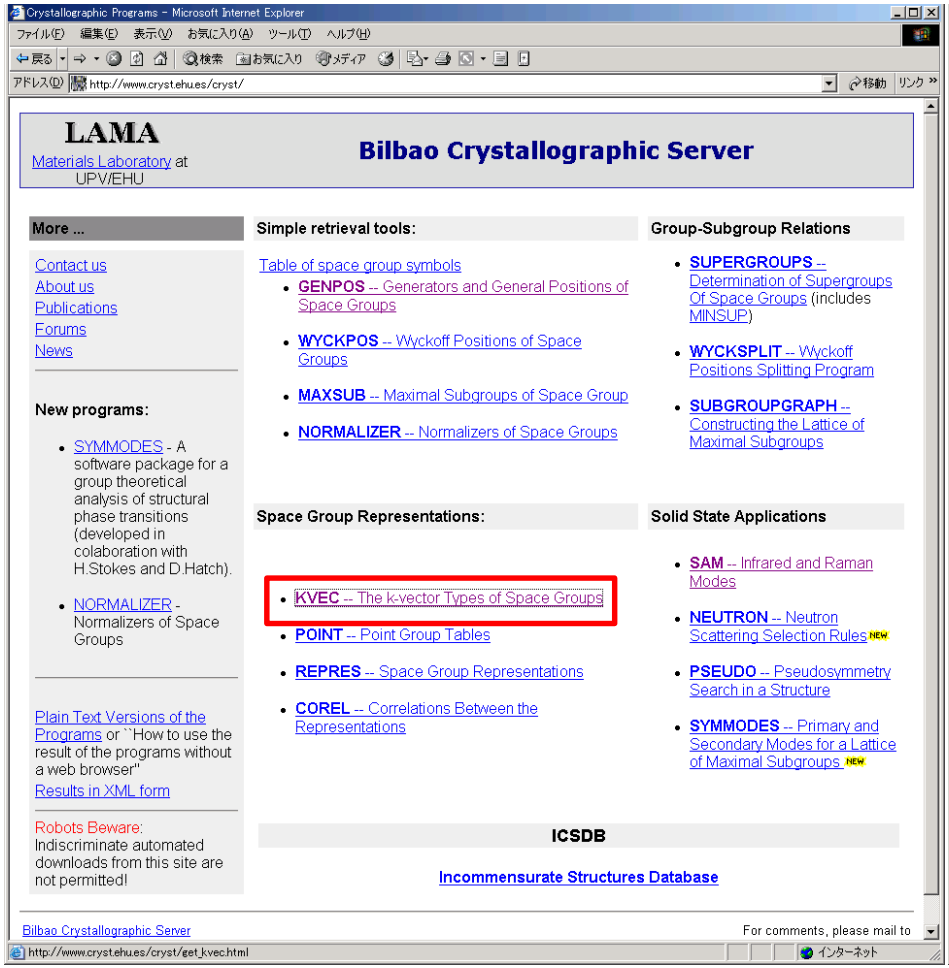
1st BZ for FCC

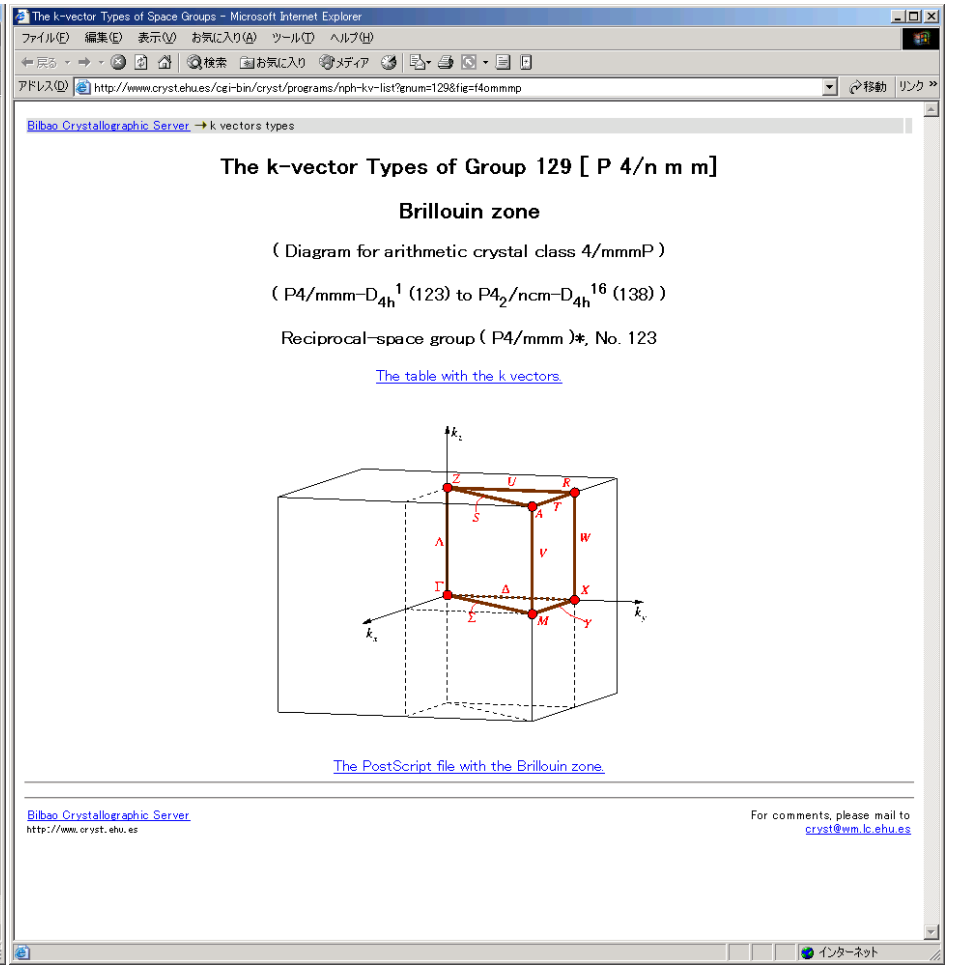




How to know the definitions of the symbols – Crystallographic database –

http://www.cryst.ehu.es/cryst/

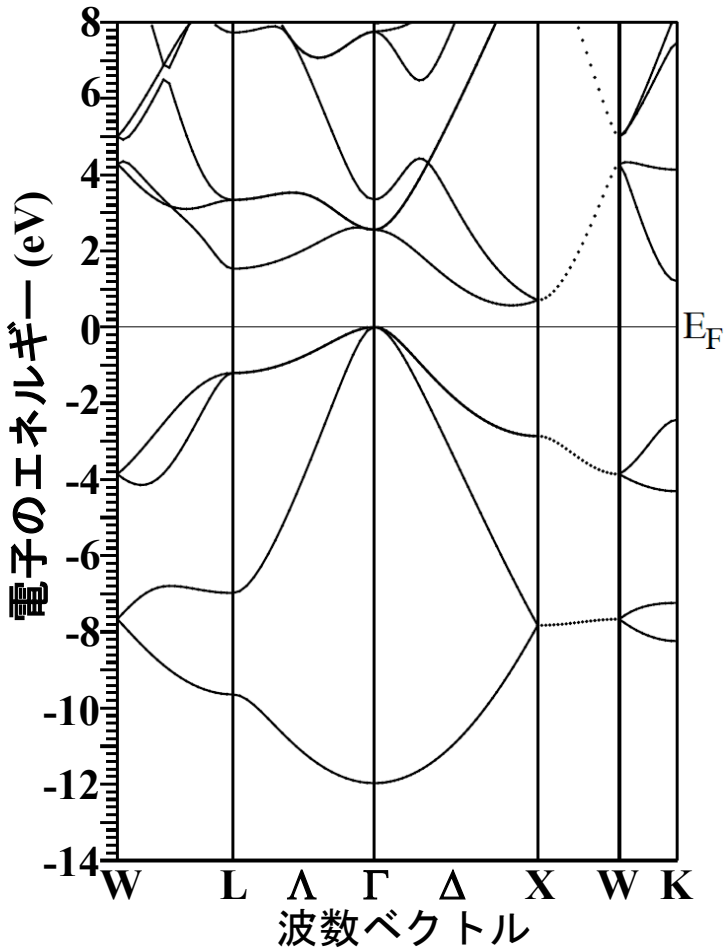


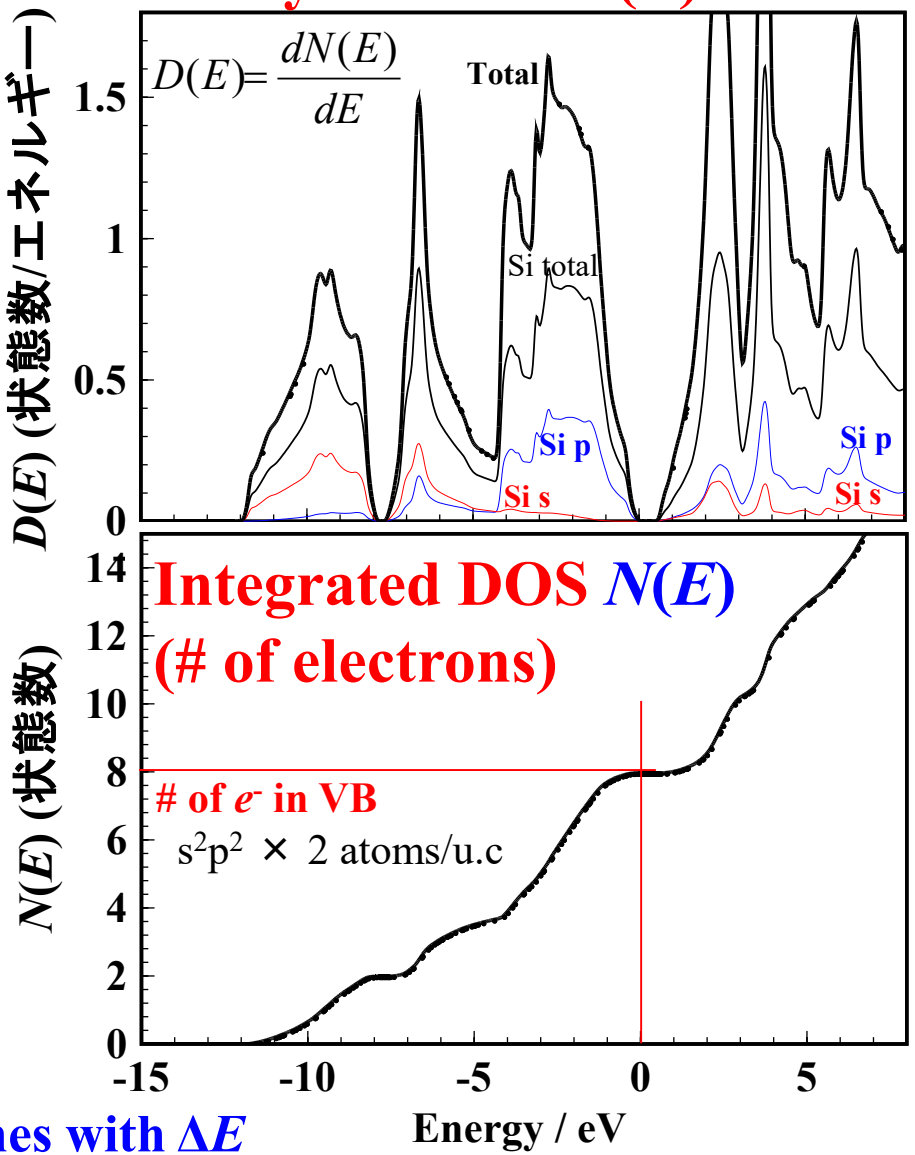


How to understand density of states (DOS)

状態密度の読み方
Density Of States: DOS

Density of states: DOS





Density of state function $D(E)$:

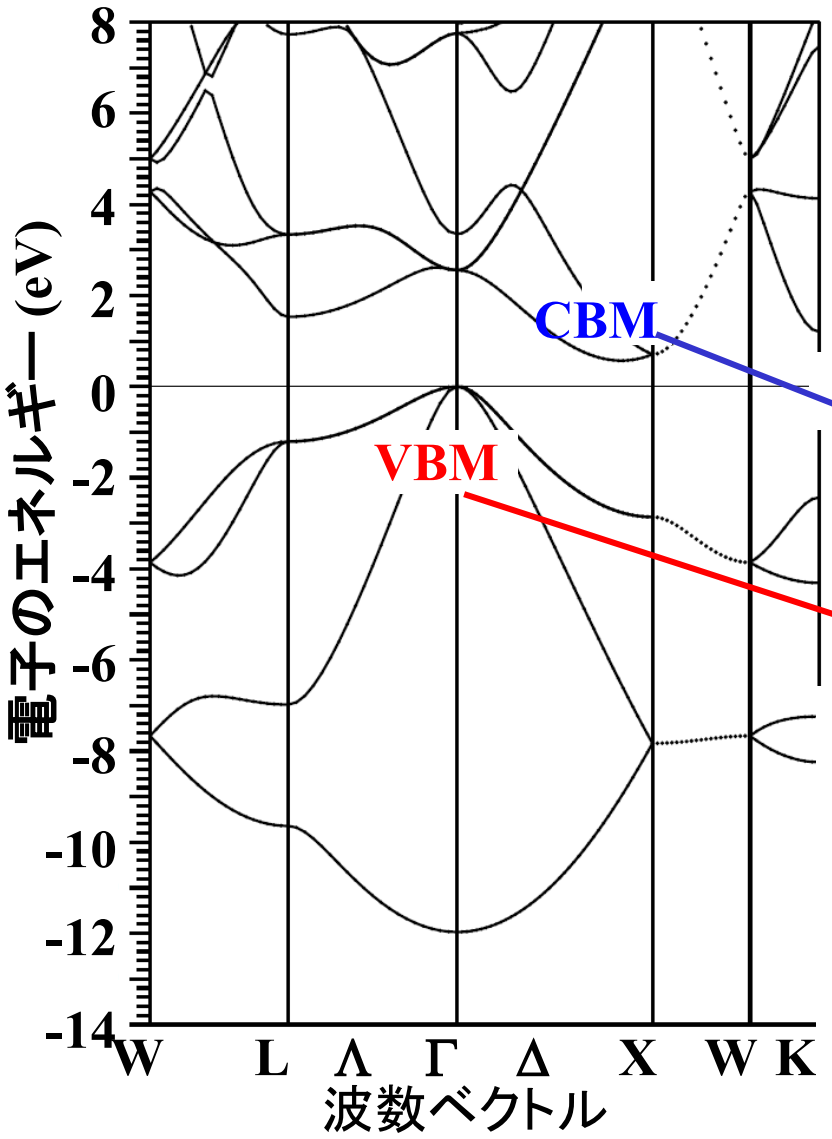
# of states between E – $E + dE$

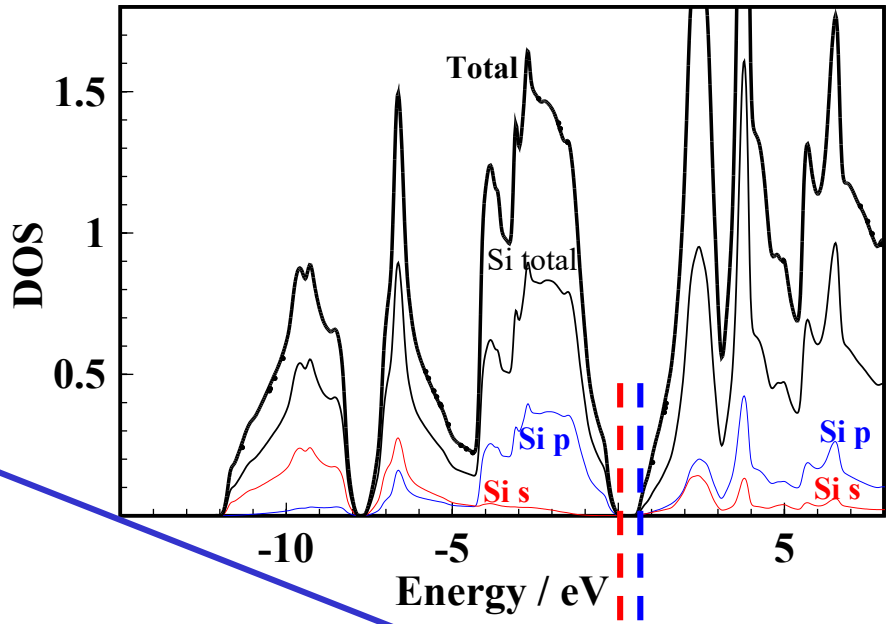
$$dN(E) = D(E)dE$$

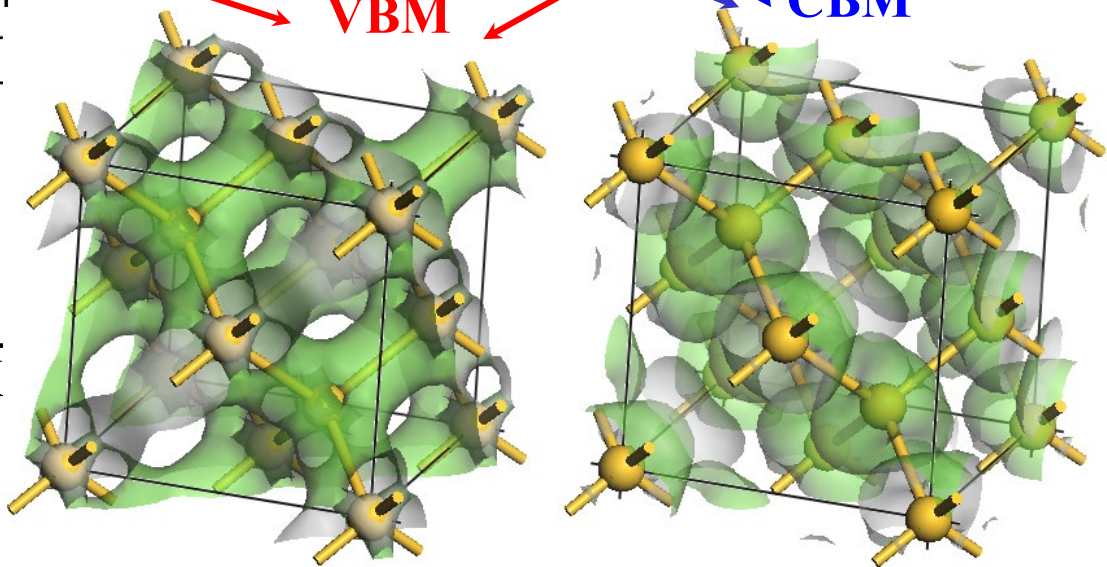
Calculation: Separate E to fine meshes with ΔE

and sum up the states in 1st B.Z. from E to $E + \Delta E$

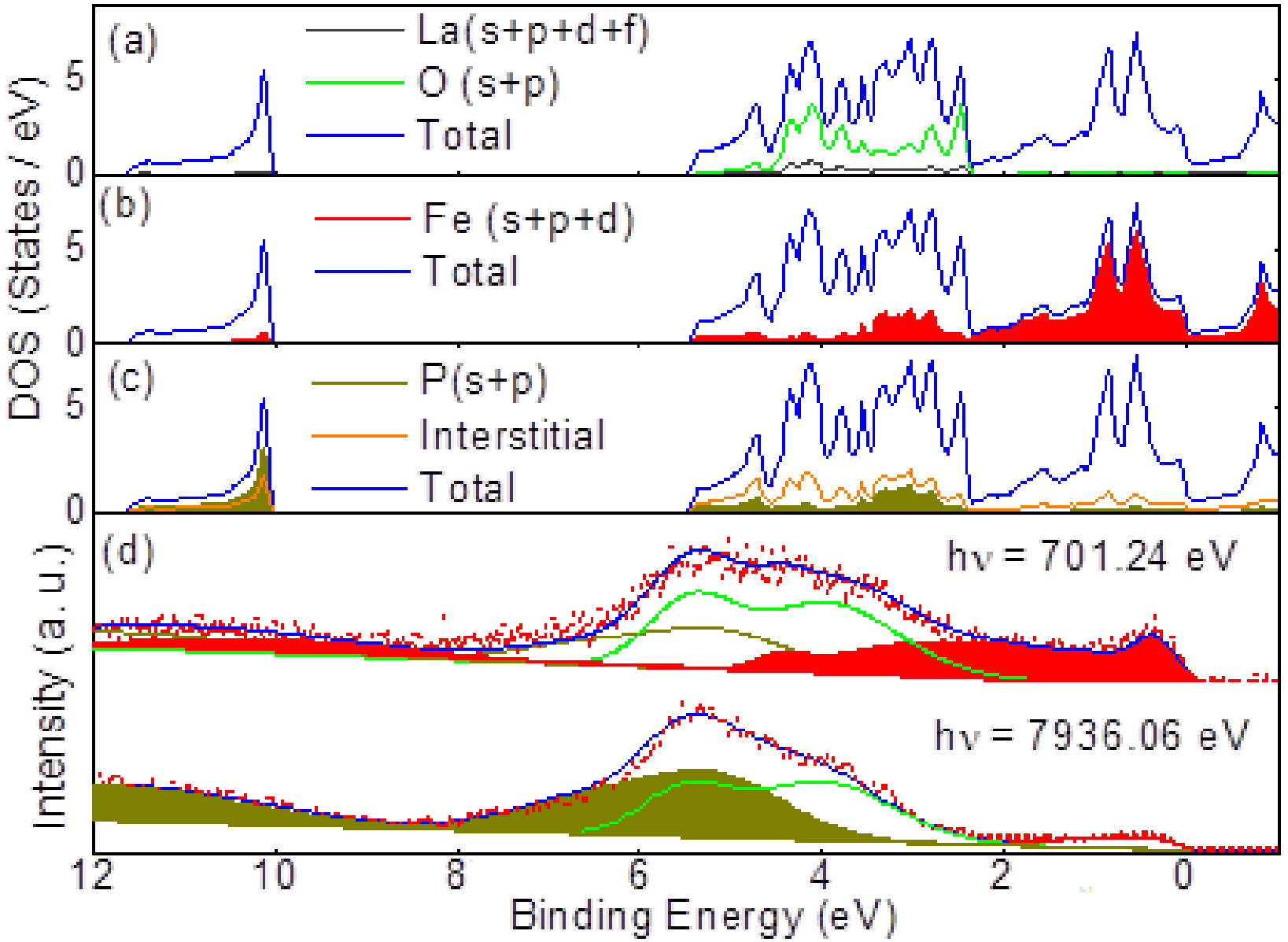
Visualization of bonding states







ex.: PDOS of LaFeOP



Semiconductor statistics

半導体統計

Procedure to calculate physical properties from distribution function

1. Total number of particles => Determine μ

$$N = \sum_i f(E_i) = \int f(\mathbf{r},\mathbf{p})\mathbf{drdp} = \int D(E) f(E) dE$$

2. Calculate average total energy

$$E = \sum_i E_i f(E_i) = \int E(\mathbf{r},\mathbf{p}) \cdot f(\mathbf{r},\mathbf{p})\mathbf{drdp} = \int E D(E) f(E) dE$$

3a. Calculate physical property *P* as statistical average

$$P = \sum_i P_i f(E_i) = \int P(\mathbf{r},\mathbf{p}) \cdot f(\mathbf{r},\mathbf{p})\mathbf{drdp} = \int P(E) D(E) f(E) dE$$

3b. Calculate physical properties from partition function (state sum) *Z*

Average energy $\dfrac{d}{d(1/k_BT)} \ln Z = -\sum \dfrac{E_i \exp\left(-\frac{E_i}{k_BT}\right)}{Z} = -\langle E \rangle$

# of particales $\langle N \rangle$ $\dfrac{d}{dE_i} \ln Z = -\dfrac{1}{k_BT} \sum \exp(-E_i/k_BT) \,/Z = -\dfrac{1}{k_BT} \langle N \rangle$

Polarization $\langle \mu \rangle$ $\dfrac{d}{dB} \ln Z = \dfrac{1}{k_BT} \sum \mu_i \exp(+\mu_i B/k_BT) \,/Z = \dfrac{1}{k_BT} \langle \mu \rangle$

3c. Calculate physical properties from free energy

Helmholtz energy $F = -Nk_BT \ln Z$

Volume modulus B_V $F = F_0 + (1/2) B_V (V/V_0)^2$ ⟹ $B_V = d^2F / d(V/V_0)^2$

Distribution function and μ

Maxwell's velocity distribution:

$$f(\boldsymbol{v})d\boldsymbol{r}d\boldsymbol{v} = \rho\left(\frac{m}{2\pi k_B T}\right)^{\mathbf{3/2}} \exp\left(-\frac{mv^2}{2k_B T}\right) d\boldsymbol{r}d\boldsymbol{v}$$

Maxwell-Boltzmann distribution:

$$f(E) = \boldsymbol{Z^{-1}}\exp\left(-\frac{E}{k_B T}\right) = \exp(-[E - \boldsymbol{\mu}]/k_B T)$$

(grand) canonical distribution: Same expression as MB

Fermi-Dirac distribution: Half-integer spin (e.g., electron)

$$f(E) = \frac{1}{\exp[(E-\mu)/k_B T] + 1}$$

Bose-Einstein distribution: Integer spin (e.g., ^{4}He)

$$f(E) = \frac{1}{\exp[(E-\mu)/k_B T] - 1}$$

Planck distribution: Integer spin, the number of particles not preserved (photon, phonon)

$$f(E) = \frac{1}{\exp[E/k_B T] - 1}$$

μ: chemical potential (identical to Fermi energy for electron)

Determined by the total number of the particle

$$N = \sum_i f(E_i) = \int D(E) f(E) dE$$

How to use partition function (State sum) Z

Partition function (State sum)

$$Z = \sum_i \exp\left(-e_i / k_B T\right)$$

$$d(\ln Z) = -\frac{\sum_i e_i \exp\left(-e_i / k_B T\right)}{\sum_i \exp\left(-e_i / k_B T\right)} d\left(\frac{1}{k_B T}\right) = -\frac{E}{N} d\left(\frac{1}{k_B T}\right)$$

Helmholtz energy $\boldsymbol{F = -N k_B T \ln Z}$

Average energy $\boldsymbol{\langle E \rangle = -N \frac{d \ln Z}{d(1/k_B T)}}$

Average particle number $\langle N \rangle$

$$\boldsymbol{\frac{d \ln Z}{d e_i} = -\frac{1}{k_B T} \sum_i \exp(-e_i / k_B T) / Z = -\frac{1}{k_B T} \langle N \rangle}$$

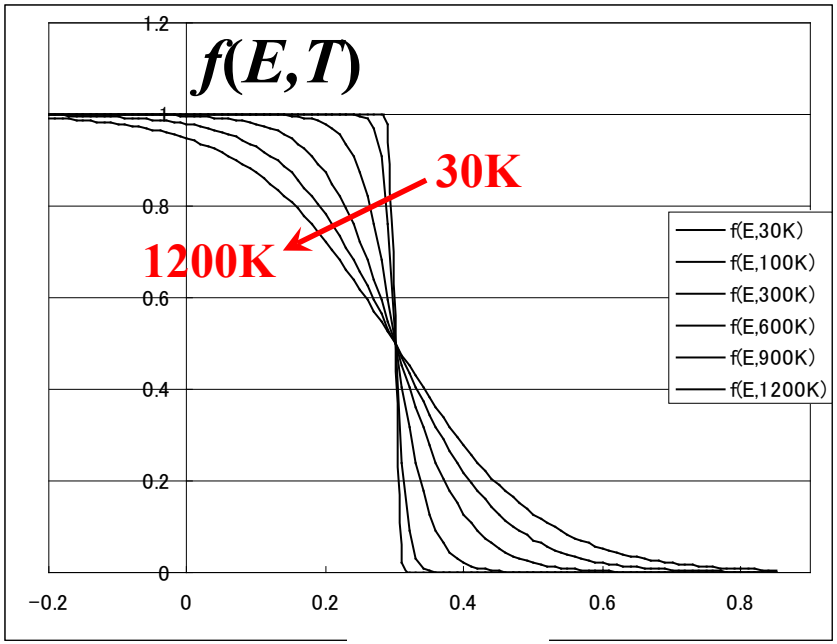
Grand partition function $Z_G = \sum_{\{ni\},i} \lambda^{n_i} \exp\left(-\beta E_{N,i}\right)$

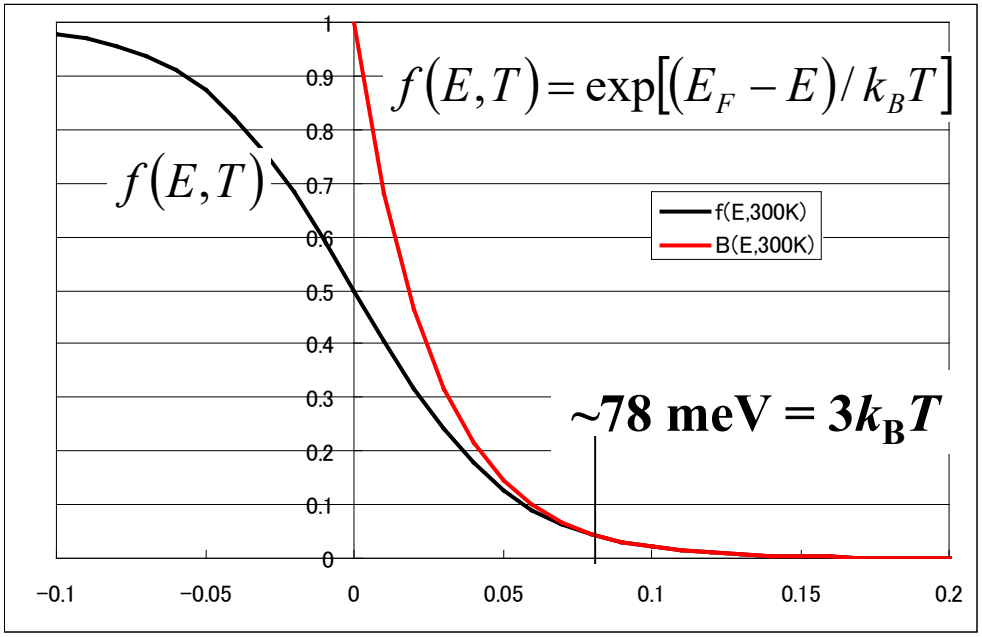
$$\lambda = e^{\beta \mu}$$

Grand potential

$$\Omega = -NkBT \ln Z_G$$

FD distribution function at finite T





$f(E,T) \Rightarrow 1 \quad (E - E_F << k_B T)$

$f(E,T) = 1/2 \quad (E = E_F)$

$f(E,T) = \exp[(E_F - E)/k_B T] \Rightarrow 0 \quad (E - E_F >> k_B T)$

Approaches to Boltzmann distribution at large $(E - E_F)/k_B T$

"Non-degenerated electron gas"

⇔ "Degenerated electron gas"

Free electron approximation: DOS and E_F

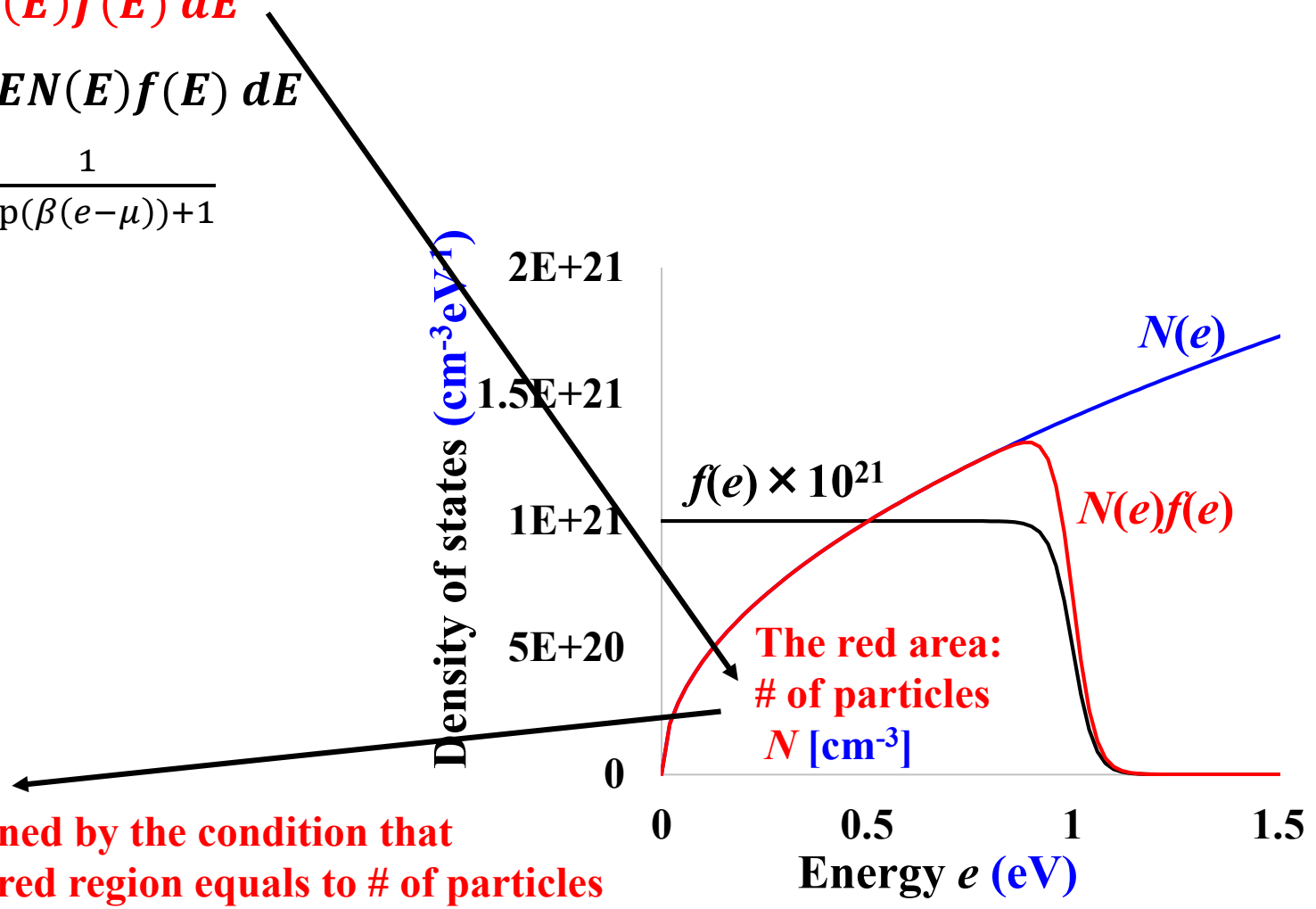
DOS function of free electron approximation

$$D(E) = (2S+1)V\frac{2\pi(2m)^{3/2}}{h^3}\sqrt{E}$$

$$N = \int_0^\infty D(E)f(E)\,dE$$

$$\langle E\rangle = \int_0^\infty EN(E)f(E)\,dE$$

$$f(E) = \frac{1}{\exp(\beta(e-\mu))+1}$$



E_F is determined by the condition that he are of the red region equals to # of particles

E_F in metal: python program

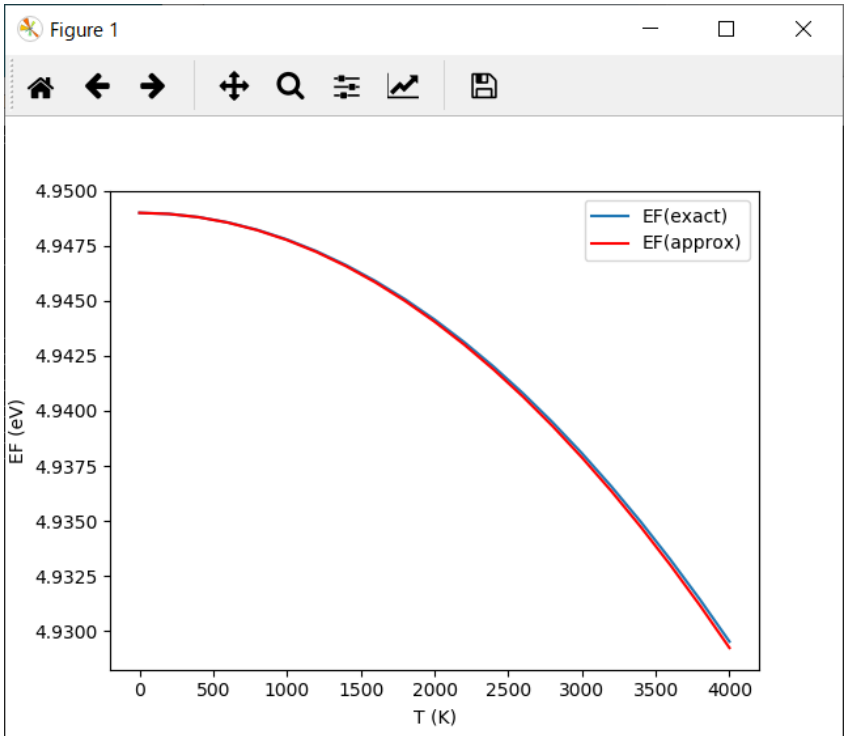
http://conf.msl.titech.ac.jp/Lecture/StatisticsC/index.html
http://conf.msl.titech.ac.jp/Lecture/StatisticsC/ef-t-metal.html
http://conf.msl.titech.ac.jp/Lecture/StatisticsC/ef-t-metal.html

How: Integrate $N(e)f(e, E_F)$ at finite T in the range を $E = 0 - \infty$ (actually up to $E_F + \alpha k_B T$) and find $E_F(T)$ that satisfy the integration equals to the electron number.
Employ $E_F(0)$ as the initial parameter, the Newton method may find the refined result with a good stability.

Compare with the approximation $E_F(T) = EF(0) - \frac{\pi^2}{6}(k_B T)^2 N'(E_F(0))/N(E_F(0))$

program: ef-t-metal.py
run: python ef-t-metal.py

T (K)	E_F (Newton, eV)	E_F (approx, eV)
0	4.948988	4.948988
600	4.948554	4.948544
1200	4.947248	4.947211
1800	4.945069	4.944990
2400	4.942013	4.941880
3000	4.938075	4.937882
3600	4.933247	4.932994
4000	4.929529	4.929243



Free electron & non-degenerate approximation

$$D_C(E) = (2S+1)\frac{2\pi(2m)^{\frac{3}{2}}}{h^3}\sqrt{E-E_C} = \frac{\sqrt{2}}{\pi^2}\frac{{m_e}^{*2/3}}{\hbar^3}\sqrt{E-E_C}$$

$$f(E) = \frac{1}{\exp[(E-E_F)/k_BT]+1} \sim e^{\beta(E-E_F)} \qquad \beta = 1/(k_BT)$$

$$n_e = \int_{E_C}^{\infty} D_C(E)f(E)\,dE \sim \frac{\sqrt{2}}{\pi^2}\frac{{m_e}^{*2/3}}{\hbar^3} e^{-\beta(E_C-E_F)} \int_0^{\infty} \sqrt{e}\exp(-\beta e)de$$

$$e = E - E_C$$

$$\sqrt{e} = x, e = x^2 \; de = 2xdx$$

$$\int_0^{\infty} \sqrt{e}\exp(-\beta e)de = \int_0^{\infty} 2x^2\exp(-\beta x^2)dx$$

$$\int_0^{\infty} x^2\exp(-x^2)dx = \frac{1}{4}\sqrt{\pi}$$

$$n_e \sim \frac{\sqrt{2}}{\pi^2}\frac{{m_e}^{*\frac{3}{2}}}{\hbar^3} e^{-\beta(E_C-E_F)} \int_0^{\infty} 2x^2\exp(-\beta x^2)dx = \frac{1}{2\pi^{3/2}}\frac{1}{\beta^{3/2}}\frac{{m_e}^{*\frac{3}{2}}}{\hbar^3} e^{-\beta(E_C-E_F)}$$

$$n_e \sim N_C \exp(-\beta(E_C - E_F))$$

$$N_C = 2\left(\frac{2\pi {m_e}^* k_B T}{h^2}\right)^{3/2}$$ Conduction band effective density of states

$$n_h \sim N_V \exp(-\beta(E_F - E_V))$$

$$N_V = 2\left(\frac{2\pi {m_h}^* k_B T}{h^2}\right)^{3/2}$$ Valence band effective density of states

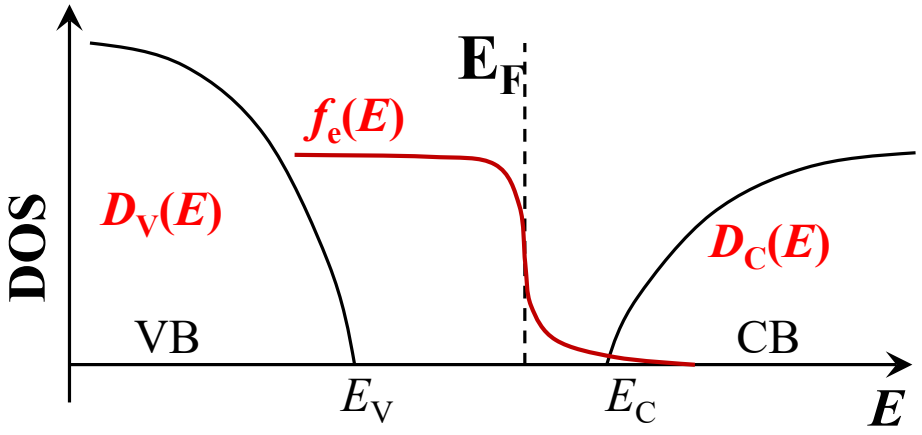
Semiconductor: Densities of free e^- and h^+

$$n_e = \int_{E_C}^{\infty} f_e(E) D_e(E) dE$$

$$f_e(E) = \frac{1}{exp(\beta(E-E_F))+1}$$

$$D_e(E) = D_{C0}\sqrt{E - E_C} \quad (9.41)$$

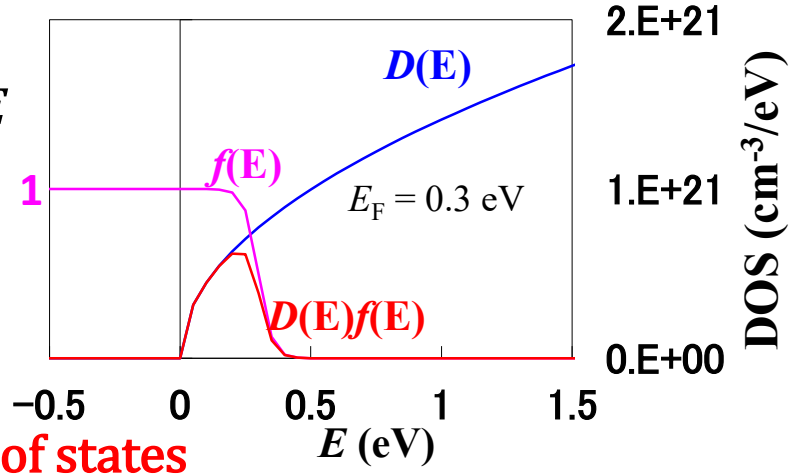
$$D_{C0} = \frac{\sqrt{2}}{\pi^2}\frac{{m_e}^{*3/2}}{\hbar^3}$$



Non-degenerated semi. $\beta(E - E_F) >> 1$ では

$$n_e \sim \int_{E_C}^{\infty} \frac{\sqrt{2}}{\pi^2}\frac{{m_e}^{*3/2}}{\hbar^3}\sqrt{E - E_C}\exp(-\beta(E - E_F))dE$$

$$= \frac{\sqrt{2}}{\pi^2}\frac{{m_e}^{*3/2}}{\hbar^3} e^{-\beta(E_C - E_F)} \int_0^{\infty} \sqrt{e}\exp(-\beta e)de$$



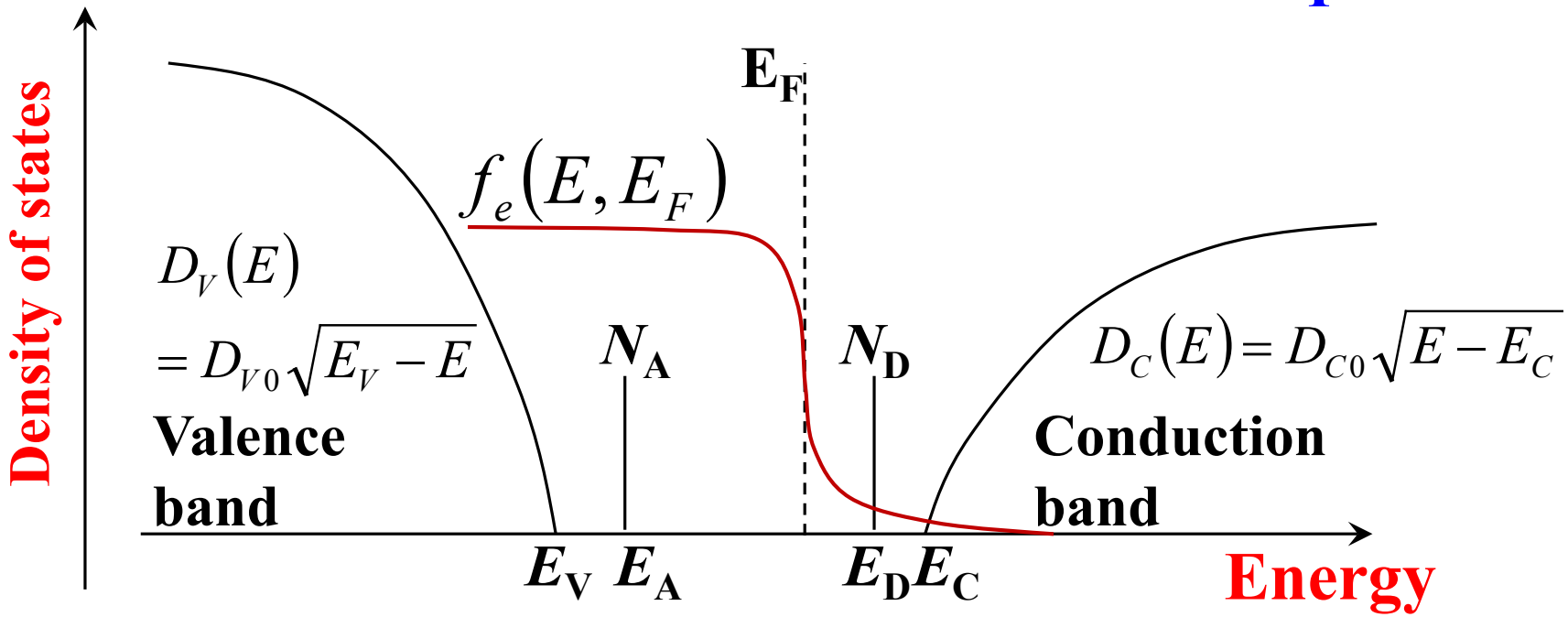
$$n_e = N_C \exp(-\beta(E_C - E_F))$$

$$N_C = 2\left(\frac{2\pi {m_e}^* k_B T}{h^2}\right)^{3/2}$$ CB effective density of states

$$n_h = N_V \exp(-\beta(E_F - E_V))$$

$$N_V = 2\left(\frac{2\pi {m_h}^* k_B T}{h^2}\right)^{3/2}$$ VB effective density of states

How to calculate Fermi level E_F



$$E_g = E_C - E_V$$

Charge neutrality condition

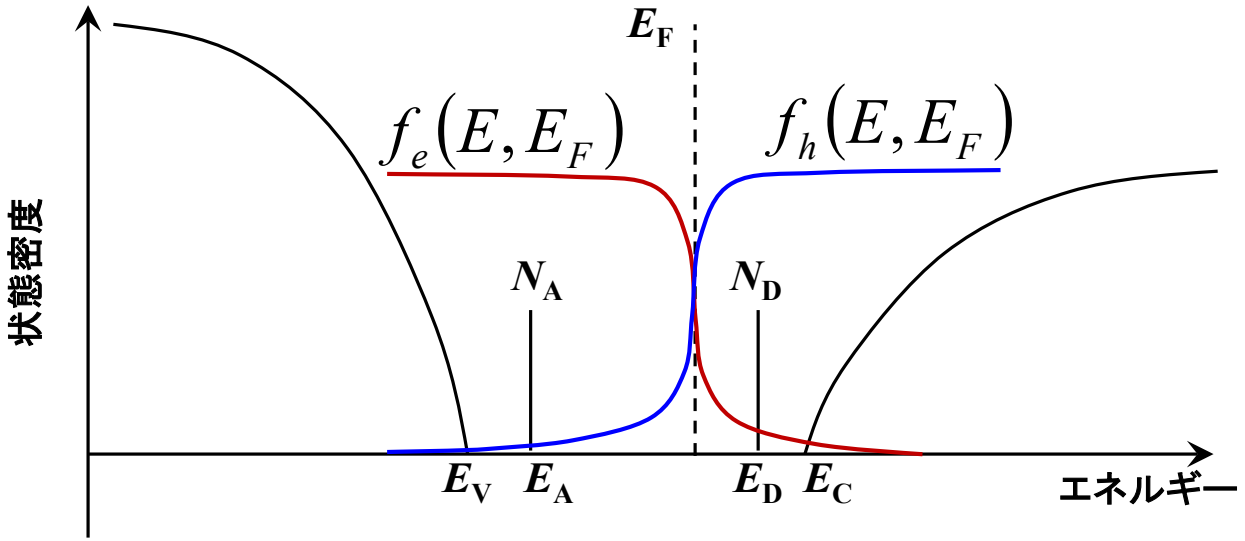
$$N_A^- + N_e = N_D^+ + N_h \quad \Rightarrow \quad E_F$$

$$N_e = \int_{E_C}^{\infty} D_C(E) f_e(E, E_F) dE$$

$$N_D^+ = N_D\left[1 - f_e(E_D, E_F)\right]$$

Semiconductor: DOS, n_e, n_h, etc

Total density of states: $D(E) = D_e(E) + D_h(E) + D_D(E) + D_A(E)$



VB region:

$D_h(E) = D_{V0}\sqrt{E_V - E}$

$D_A(E) = N_A\delta(E - E_A)$

$f_h(E, E_F) = \frac{1}{\exp(\beta(E_F - E))+1}$

Free hole

$n_h = \int_{-\infty}^{E_V} f_h(E, E_F) D_h(E) dE$

Non-dengerated approximation

$n_h \sim N_V \exp(-\beta(E_F - E_V))$

Ionized acceptor density

$N_A^- = N_D(1 - f_h(E_A, E_F))$

CB region:

$D_e(E) = D_{C0}\sqrt{E - E_C}$

$D_D(E) = N_D\delta(E - E_D)$

$f_e(E, E_F) = \frac{1}{\exp(\beta(E - E_F))+1}$

Free electron

$n_e = \int_{E_C}^{\infty} f_e(E) D_e(E) dE$

Non-degenerated approximation

$n_e \sim N_C \exp(-\beta(E_C - E_F))$

Ionized donor density

$N_D^+ = N_D(1 - f_e(E_D, E_F))$

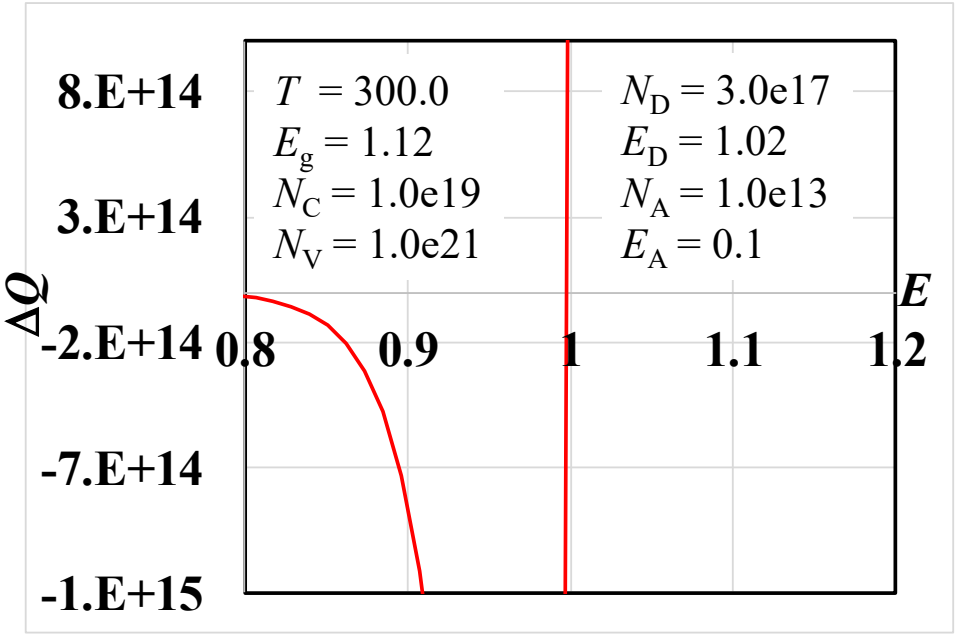
How to calculate E_F: Illustrative solution

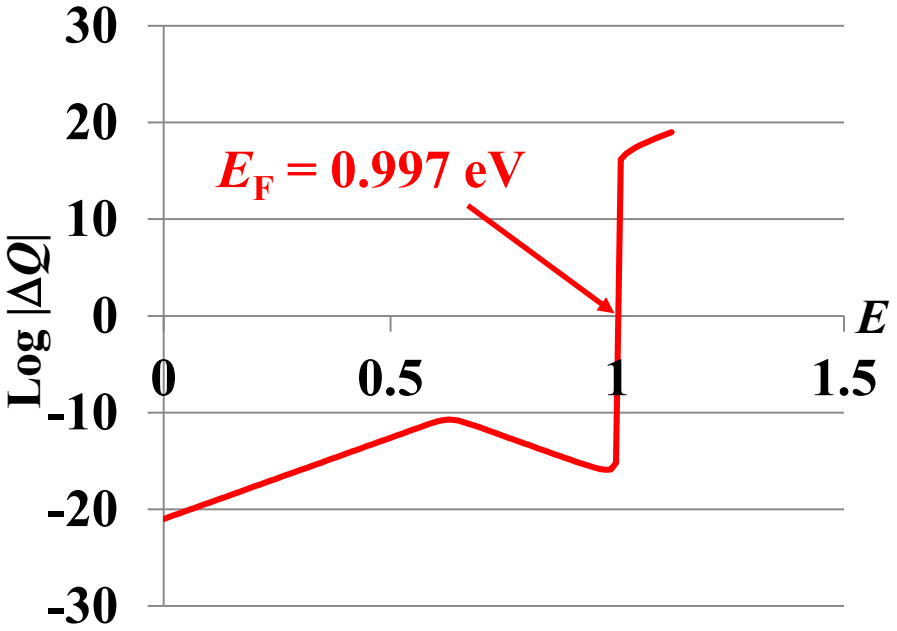
$$N_e = \int_{E_C}^{\infty} D_C(E) f_e(E, E_F) dE \qquad N_h = \int_{E_C}^{\infty} D_V(E) f_h(E, E_F) dE$$

$$N_D^+ = N_D\left[1 - f_e(E_D, E_F)\right] \qquad N_A^- = N_A\left[1 - f_h(E_A, E_F)\right]$$

$$f_h(E, E_F) = 1 - f_e(E, E_F)$$

Plot $\Delta Q = (N_A^- + N_e) - (N_D^+ + N_h)$ w.r.t. E_F and find $\Delta Q = 0$





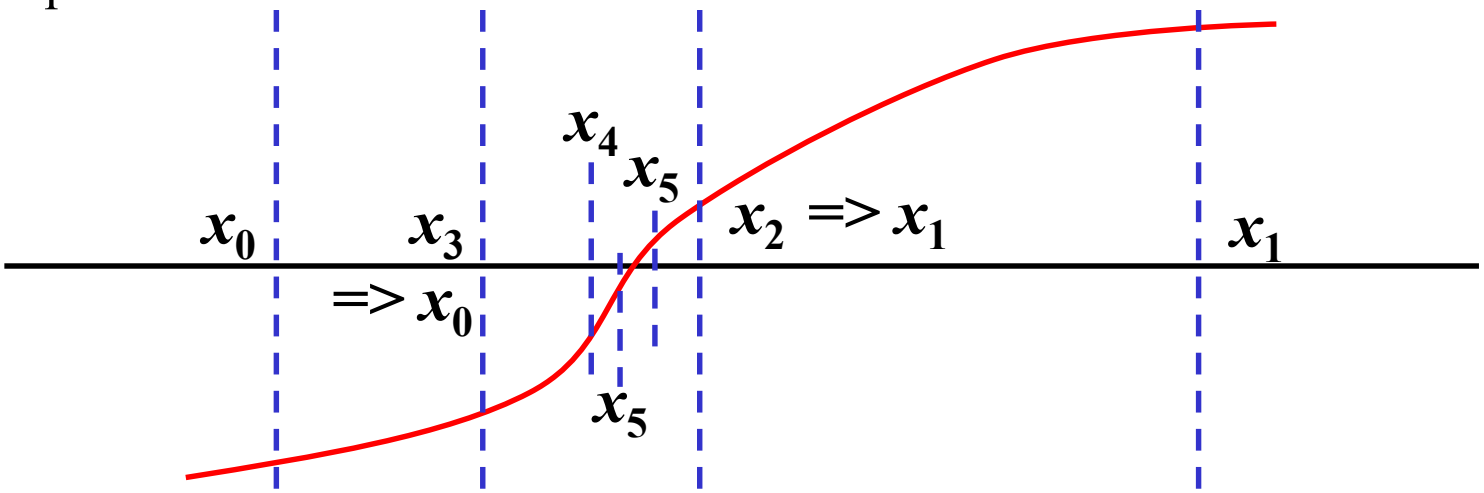
Bisection method (二分法): Monotonic func (単調関数)

Solution of $f(x) = 0$ for monotonic function $f(x)$

1. **Start from a range $[x_0, x_1]$ where $f(x_0) < 0$ & $f(x_1) > 0$**
   (or $f(x_0) > 0$ & $f(x_1) < 0$)
   * **Solution exist in this range for a monotonic function**
2. **Solve the equation by the following iterative procedure**

Case $f(x_0) < 0$ and $f(x_1) > 0$: Judge by $f(x_0) \cdot f(x_1) < 0$

1. $x_2 = (x_0 + x_1) / 2.0$
2. If $f(x_2) > 0$ ($f(x_0) \cdot f(x_2) < 0$), x_1 is replaced with x_2
   If $f(x_2) < 0$ ($f(x_1) \cdot f(x_2) < 0$), x_0 is replaced with x_2
3. Solution x_2 is obtained when $|x_1 - x_0|$, $|f(x_1) - f(x_0)|$ becomes less than EPS.
4. Repeat 1 – 3



Fermi level in semi.: python program

Program: EF-T-semiconductor.py

http://conf.msl.titech.ac.jp/Lecture/StatisticsC/EF-T-semiconductor.html

Usage: python EF-T-semiconductor.py EA NA ED ND Ec Nv Nc

Run: python EF-T-semiconductor.py 0.05 1.0e15 0.95 1.0e16 1.0 1.2e19 2.1e18

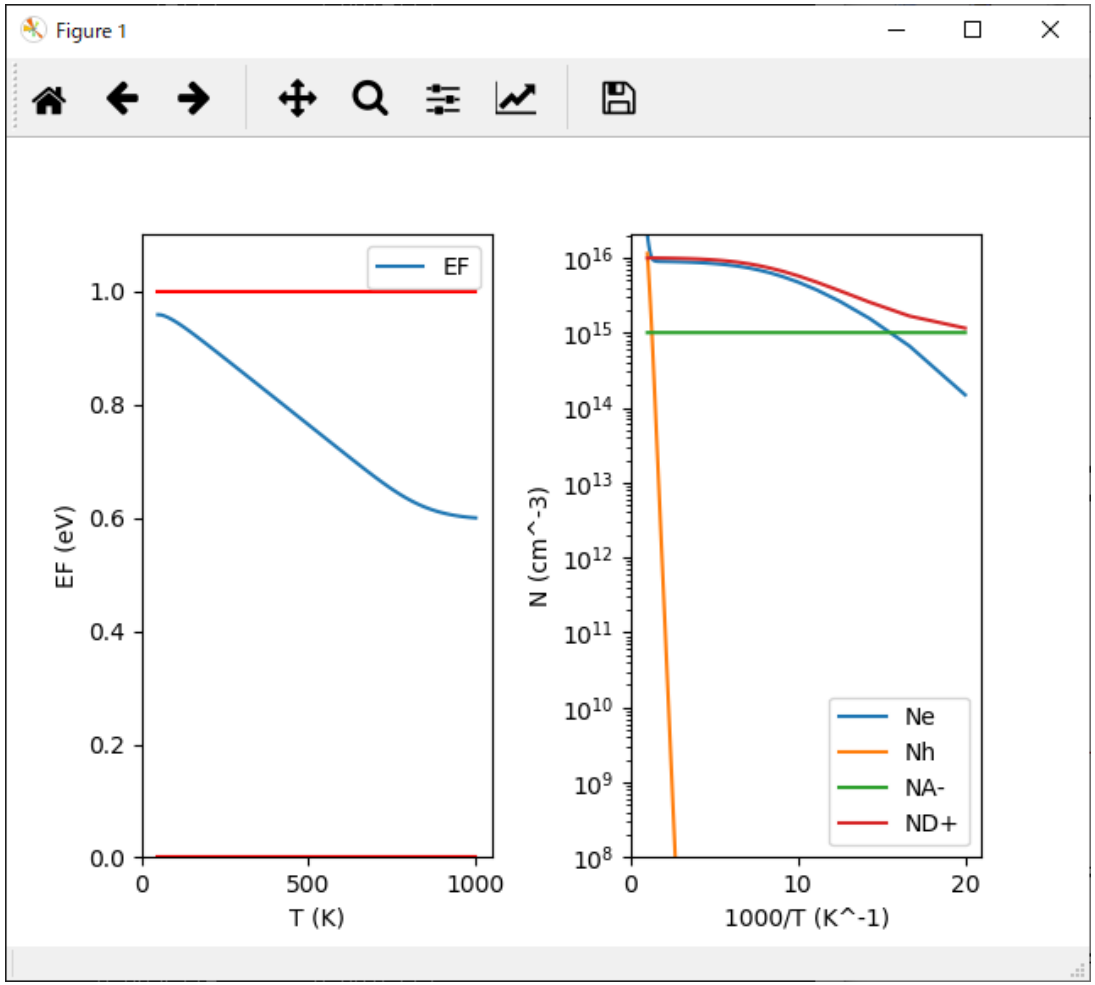
$E_c = 0$, $E_c = 1.0$ eV (= band gap)

$E_A = 0.05$ eV, $N_A = 10^{15}$ cm^{-3},

$E_D = 0.95$ eV, $N_D = 10^{16}$ cm^{-3}

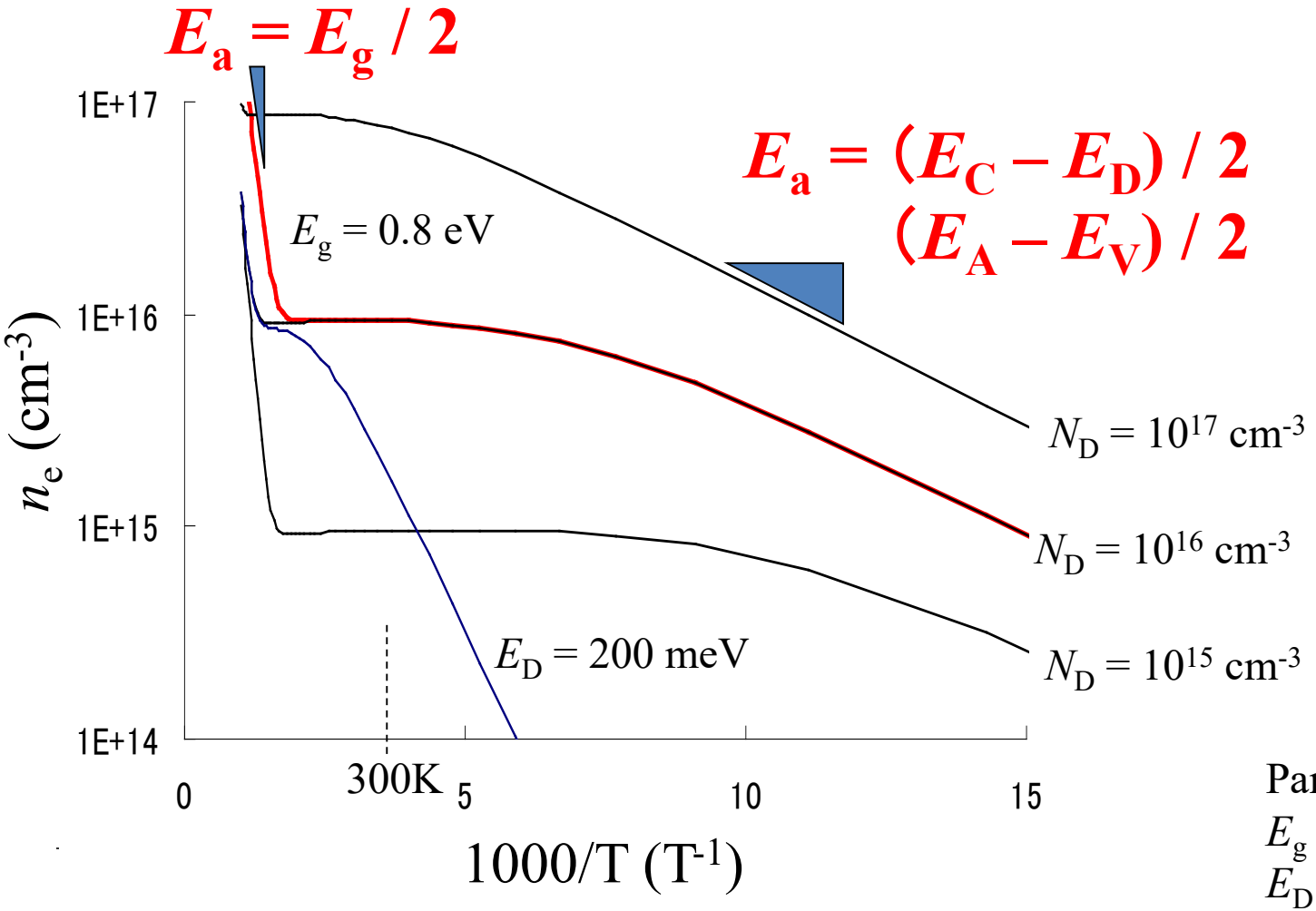
$N_c = 1.2 \times 10^{19}$ cm^{-3}

$N_v = 2.1 \times 10^{18}$ cm^{-3}



T dependence of carrier density and donor level

Intrinsic region – Depletion region – Impurity region



Parameters used:
E_g = 1.12 eV
E_D = 45 meV
N_D = 10^{16} cm^{-3}

Similar calculations are possible using $D(E)$ calculated by DFT

$$N_e = \int_{E_C}^{\infty} D_C(E) f_e(E, E_F) dE \qquad N_h = \int_{E_C}^{\infty} D_V(E) f_h(E, E_F) dE$$

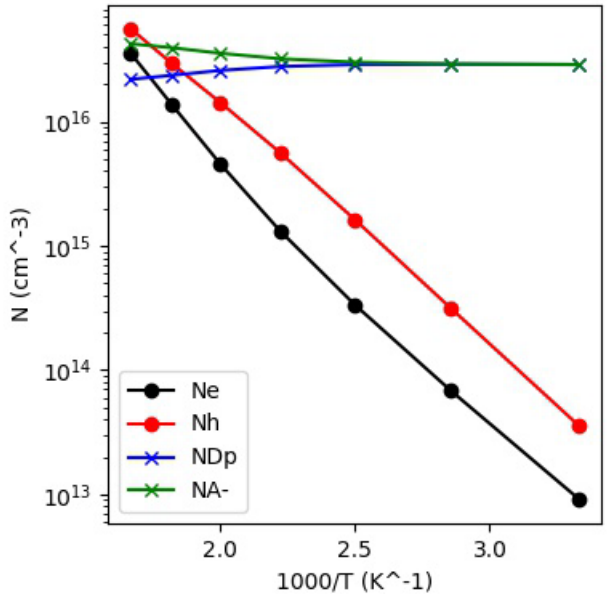
$$N_D^{+} = N_D\left[1 - f_e(E_D, E_F)\right] \qquad N_A^{-} = N_A\left[1 - f_h(E_A, E_F)\right]$$

$$\Delta Q = (N_A^{-} + N_e) - (N_D^{+} + N_h) = 0$$

EF-T-DOS.py, TotalDOS-SnSe.dat

http://conf.msl.titech.ac.jp/Lecture/inside/EF-T-DOS/EF-T-DOS.html

run python EF-T-DOS.py T

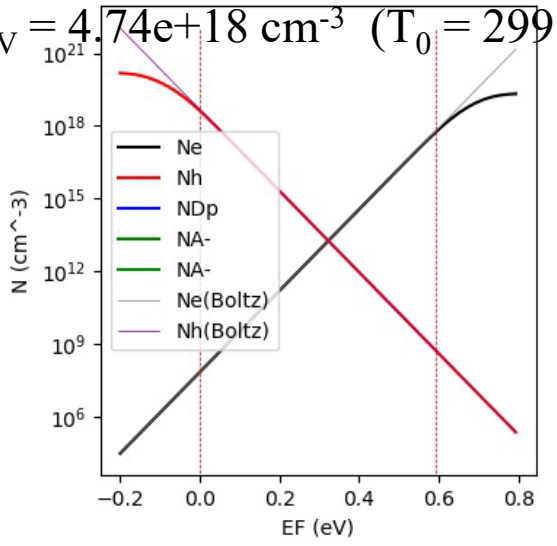


run python EF-T-DOS.py EF

Effective DOSs at the mid gap 0.2963 eV:

N_C = 6.26e+17 cm^{-3} (T_0 = 299.86 K)

N_V = 4.74e+18 cm^{-3} (T_0 = 299.86 K)



Hall effect

Assumption: All carriers with the charge *q* move with the same velocity *v*

$$\mathbf{F} = q\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right)$$

$$j_x = \frac{nq^2\tau}{m^*} E_x$$

$$E_{Hall} = \frac{H}{c} v_x = \frac{qH\tau}{m^* c} E$$

$$R_H = \frac{E_{Hall}}{j_x B} = \frac{1}{nq}$$

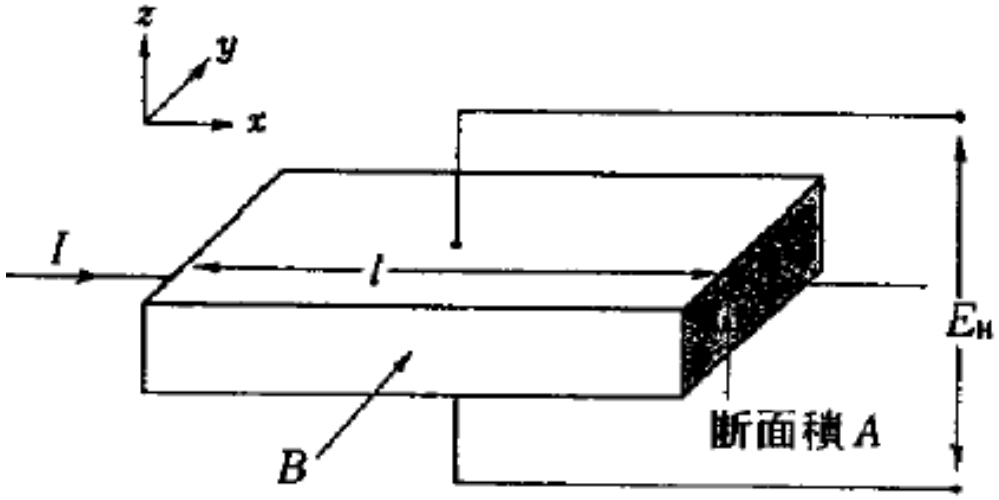


図 3·24 Hall 効果の実験

Carrier polarity, carrier density n_{Hall}, mobility μ_{Hall}

- **Valid for distributed *v*?**
- **Anisotorpy?**
- **Mixed conduction?**

Hall coefficient for multi-band / mixed conduction systems

Multi-band / Multi-layered

$$R_H = \gamma \sum \frac{\mathrm{sgn}_i \, n_i \mu_i^{\,2}}{q\left(\sum n_i \mu_i\right)^2} \qquad \sigma = q \sum n_i \mu_i$$

Electron – hole mixing conduction

$$R_H = \gamma \sum \frac{p\mu_p^{\,2} - n\mu_n^{\,2}}{q\left(n\mu_n + p\mu_p\right)^2} \qquad \sigma = q \sum n_i \mu_i$$

Electronic conductivity and mobility

Carrier dnesity

$$n_e = \int_{E_C}^{\infty} D_C(E) f_e(E) dE = \sum_{occupied\ states\ in\ CB} n_i$$

Conductivity and mobility

$$\sigma_x = e n_e \boxed{\frac{e}{m_e^*} \langle \tau^1 \rangle} \longrightarrow \mu_{drift}$$

$$\langle \tau^k \rangle = -\frac{2}{3} \int_{E_C}^{\infty} (E - E_m) \tau(E)^k D_C(E) \frac{\partial f_e(E)}{\partial E} dE \Big/ n_e$$

$$\tau(E,T) = \tau_0 T^p (E - E_m)^{r-1/2}$$

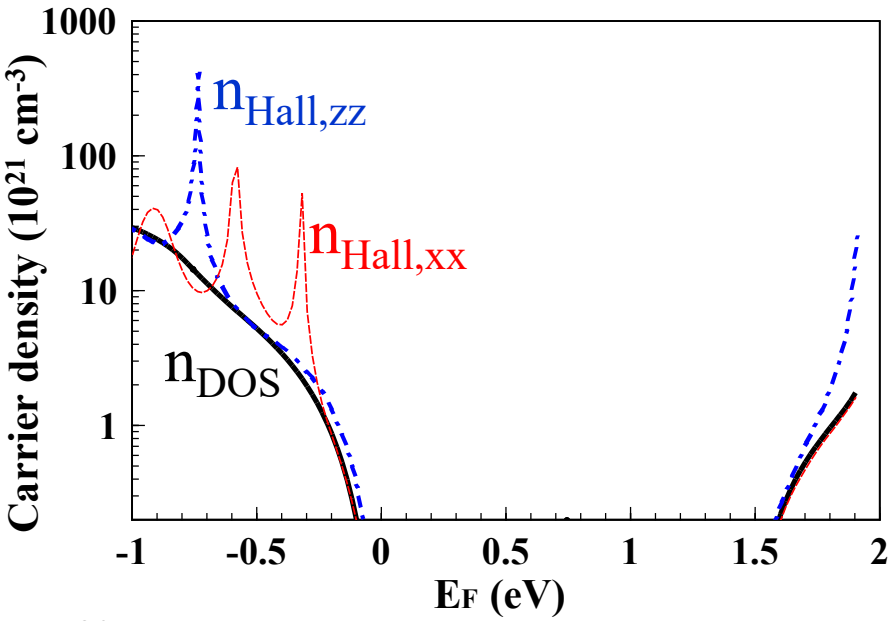
E.g., $\tau(E)$ = constant is approximated

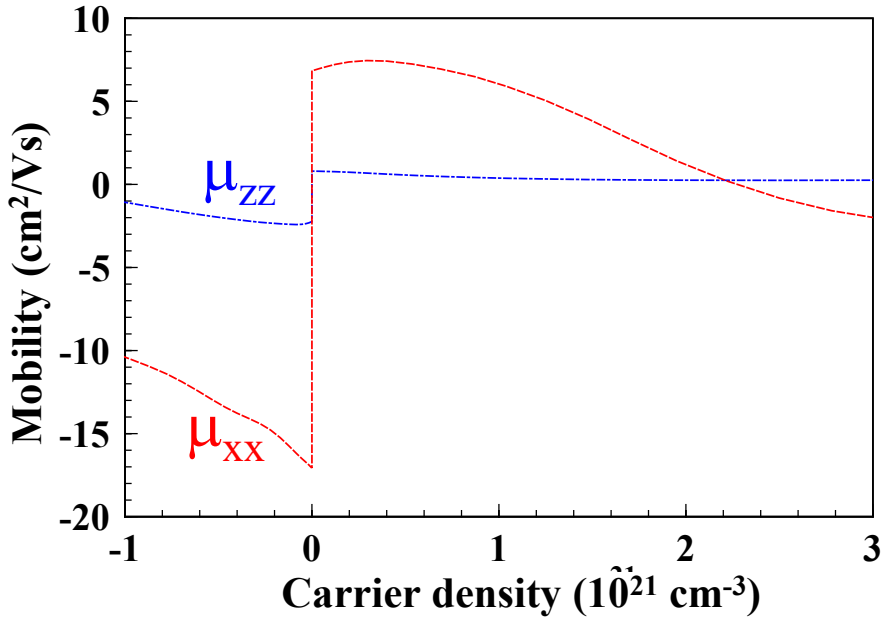
Seebeck coefficient

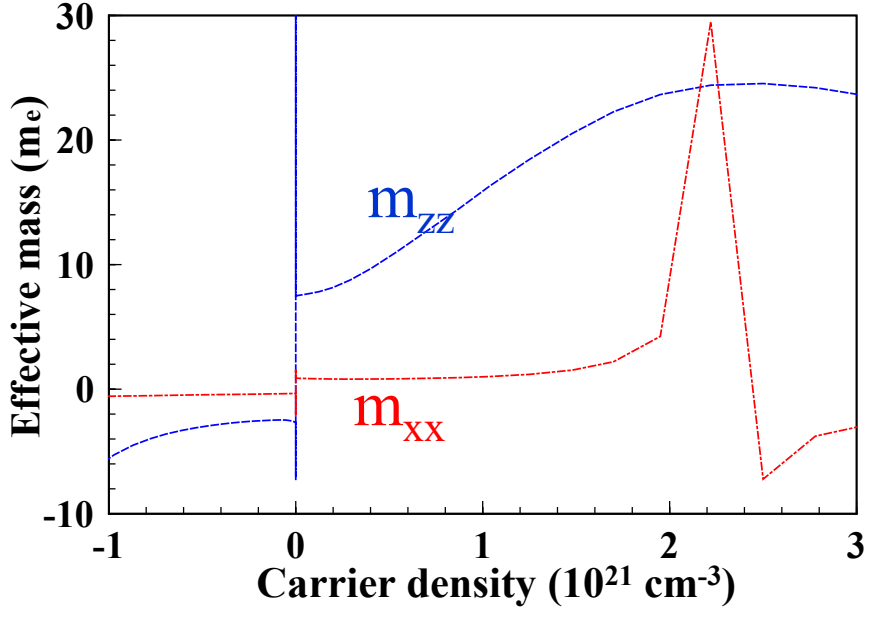
$$S = -\frac{k}{e}\frac{\int\left(-\frac{\partial f}{\partial E}\right)D(E)v^2\tau\left[\frac{E-E_F}{kT}\right]dE}{\int\left(-\frac{\partial f}{\partial E}\right)D(E)v^2\tau dE} + \frac{1}{e}\frac{\partial E_F}{\partial T}$$

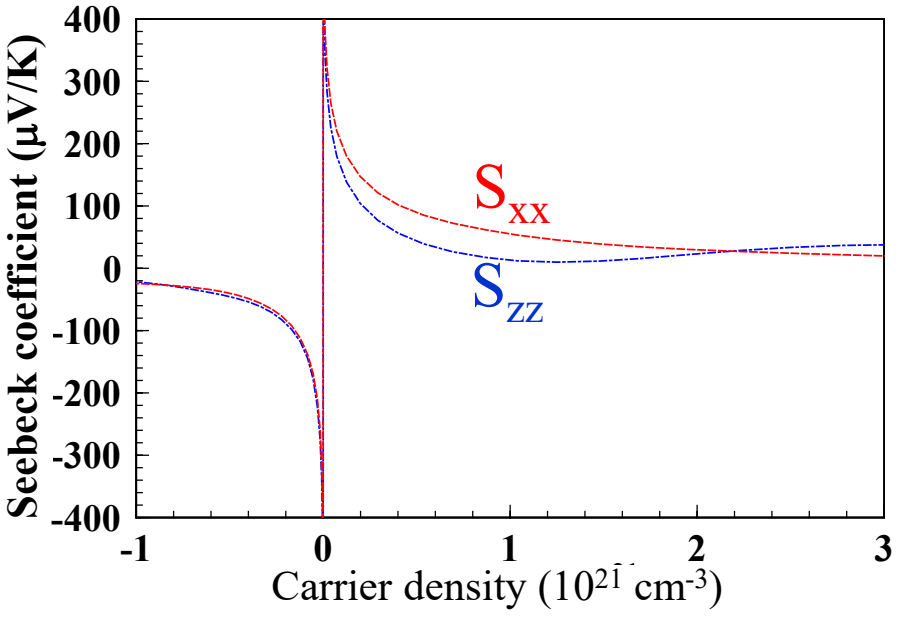
Calculation by DFT: BoltzTraP

LaCuOSe

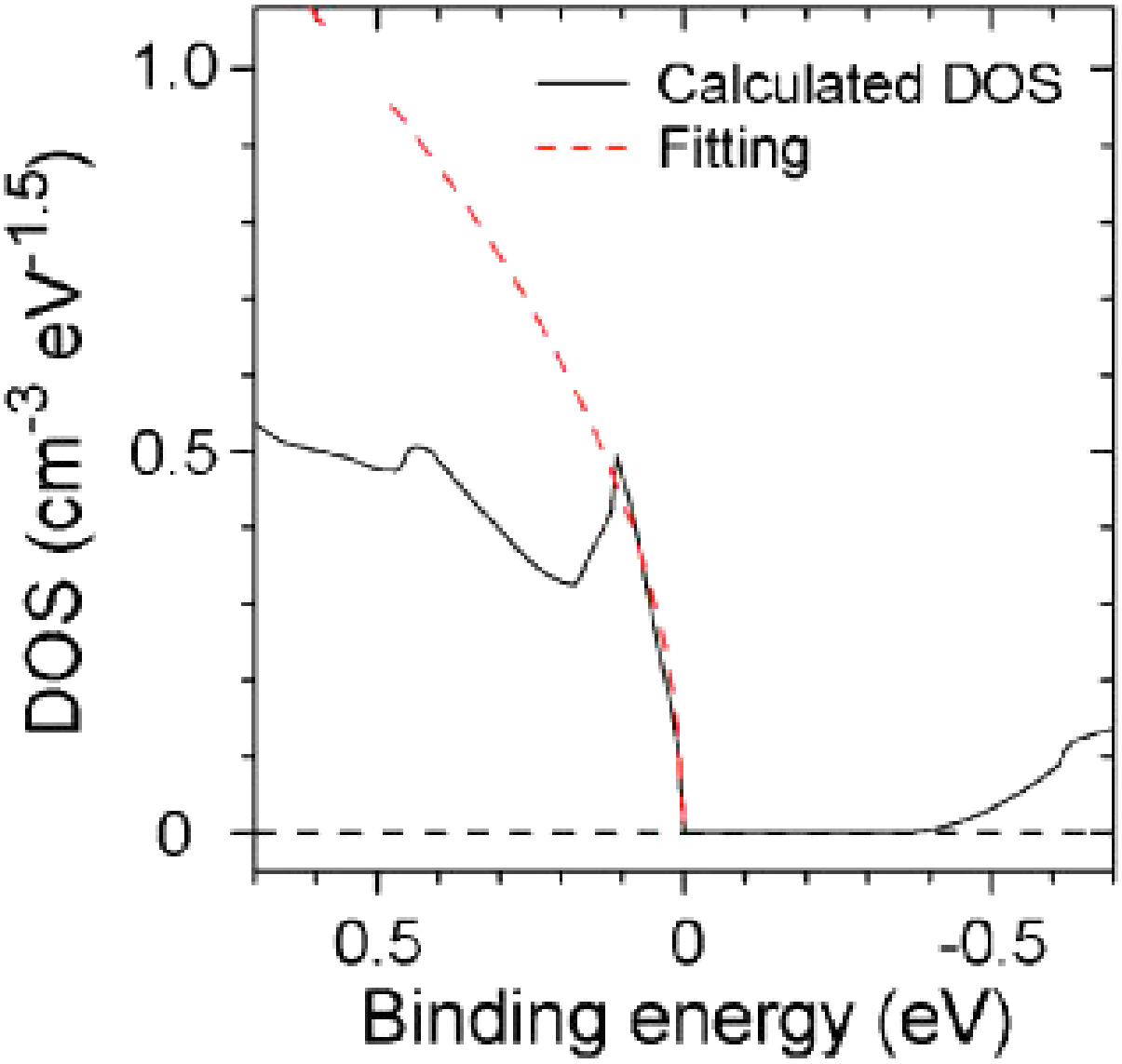




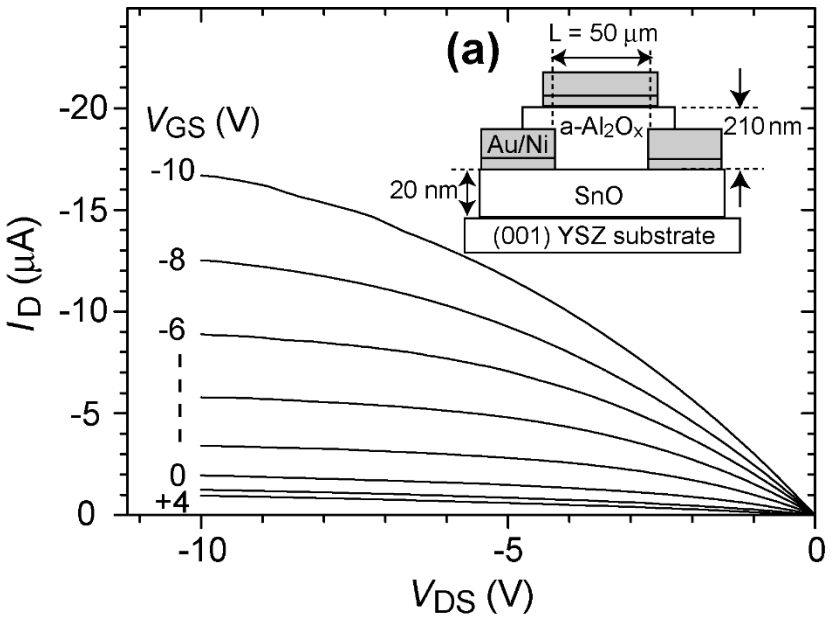


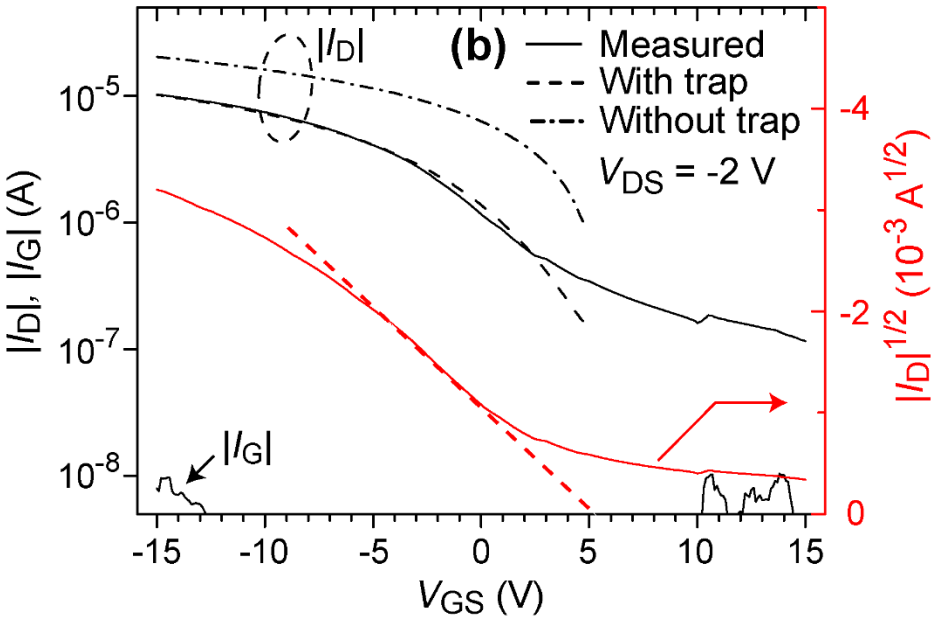


Effective DOS mass in SnO, m_{DOS}^*

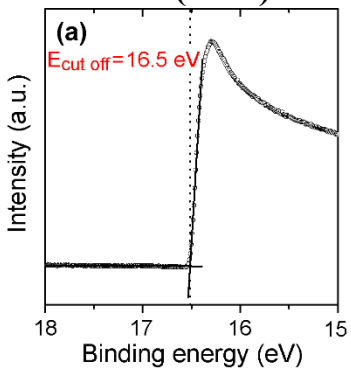


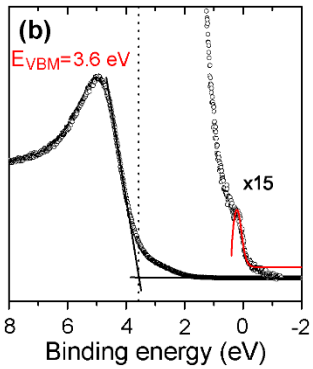
Application to device simulation: SnO TFT

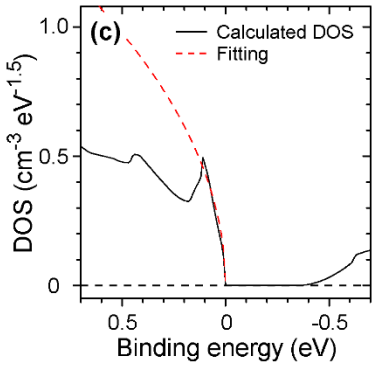


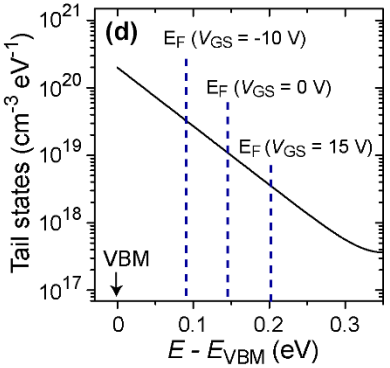


Parameters	Values
Band gap of SnO	0.7 eV
Ionisation potential of SnO	5.8 eV
VB DOS effective mass in SnO	2.05 m_e
Hole mobility in SnO at RT	2.4 $cm^2V^{-1}s^{-1}$
Hole density in SnO at RT	2.5×10^{17} cm^{-3}
Activation energy of hole density in SnO	45 meV
Gate insulator (a-Al_2O_x) thickness	210 nm
Relative permittivity of a-Al_2O_x	10
Relative permittivity of YSZ	27
Relative permittivity of SnO	15
Channel dimension (L/W)	50/300 mm





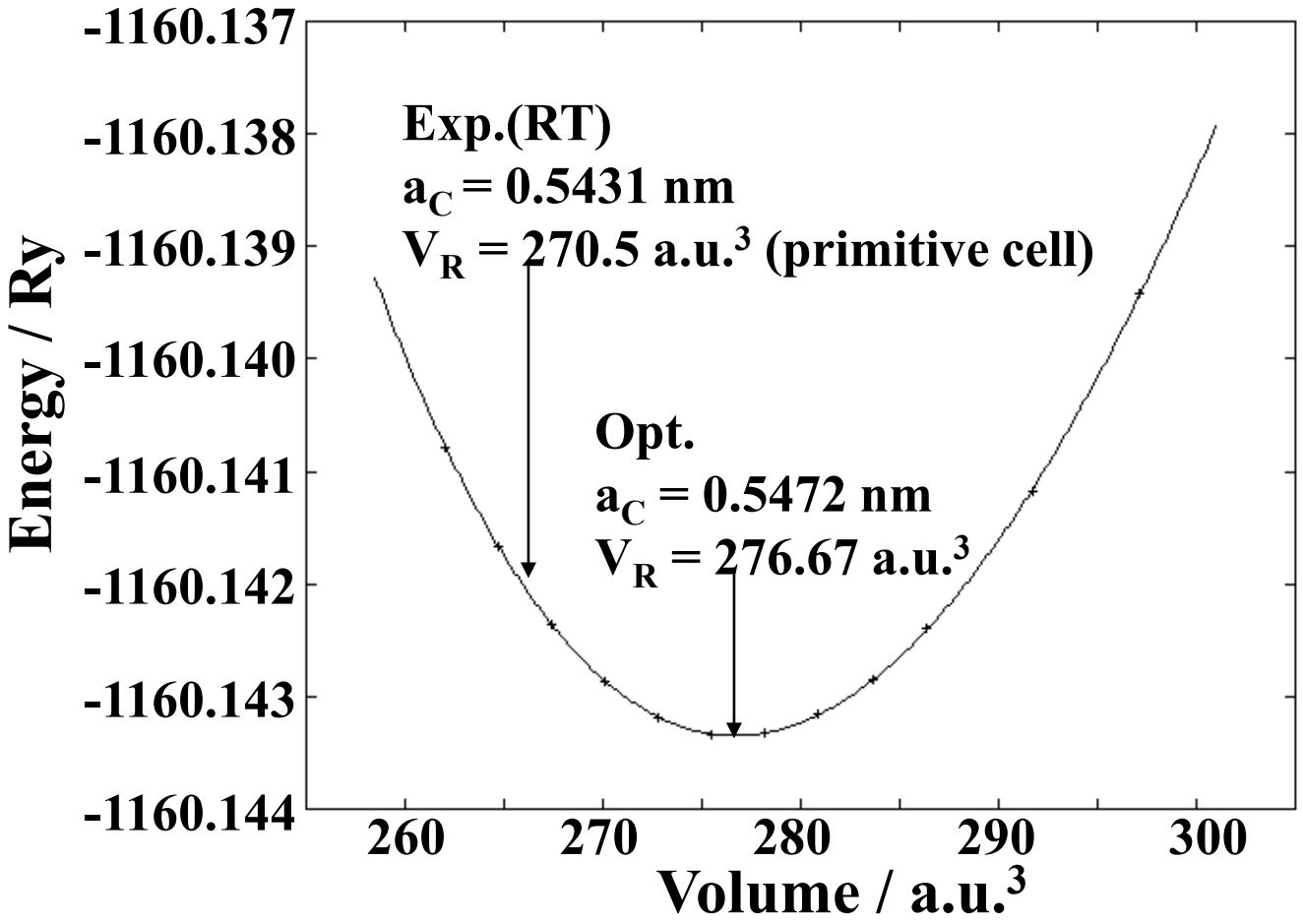




Stable structure at ground state (at 0 K)

絶対零度における安定構造

Structure relaxation and volume modulus: Si

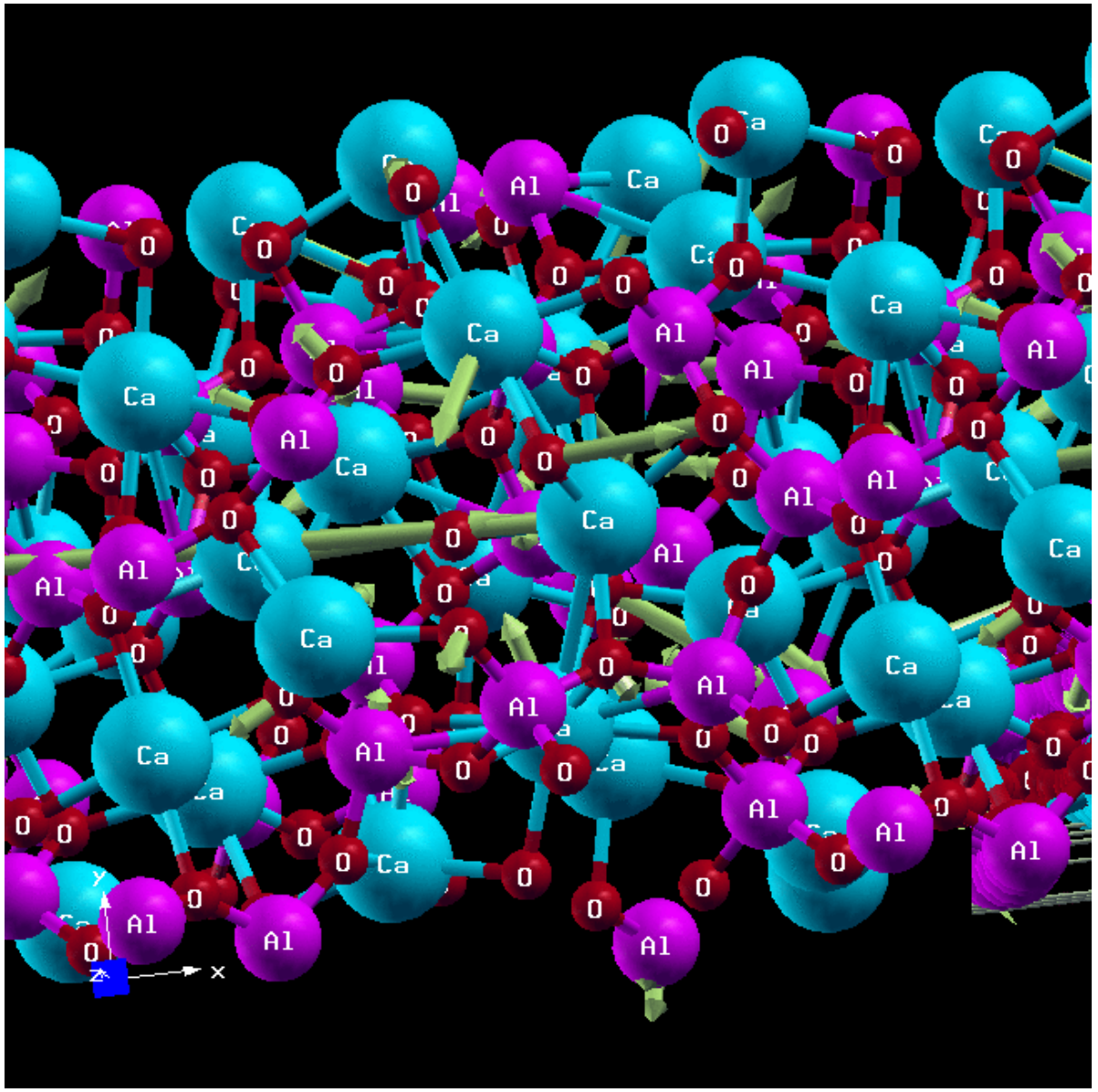


$$E = E_{\min} + 1/2 B_0 \left(V / V_0\right)^2$$

B_0 (GPa) = 87.57 GPa (exp: 97.88 GPa)

General structure relaxation: C12A7

VASP, PBE



General structure relaxation

PBE-calculated values are in () compared with exper. values at RT.

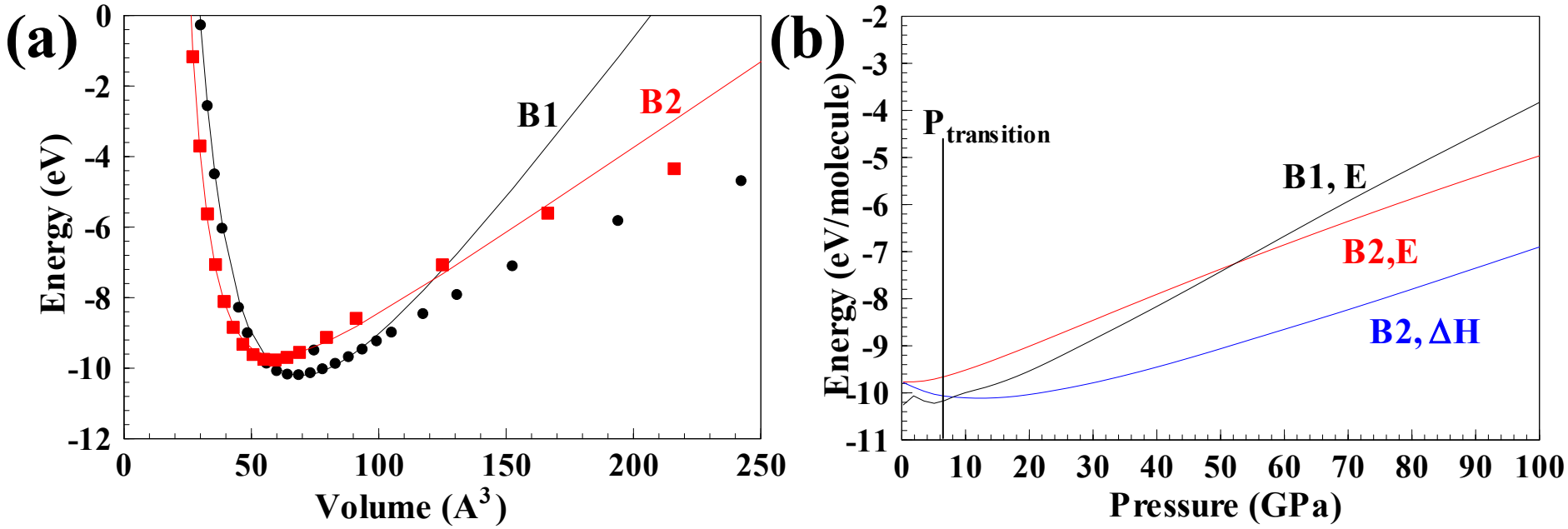
The errors are within 1-2 %

Al (FCC)	a = 4.04975 (4.0462)
Ca (FCC)	a = 5.5884 (5.51942)
Mg (HCP)	a = 3.2094 (3.1869) c = 5.2103 (5.19778)
Na (BCC)	a = 4.235 (4.20437)
Si	a = 5.41985 (5.46631)
GaAs	a = 5.65359 (5.7605)
GaN (wurzite)	a = 3.186 (3.24541) c = 5.176 (5.28965) z(N) = 0.375 (0.375783)
NaCl	a = 5.62 (5.65062)
MgO	a = 4.2109 (4.23617)
CaO	a = 4.8112 (4.83784)
ZnO	a = 3.2427 (3.25452) c = 5.1948 (5.21411) z(O) = 0.3826 (0.3816)
In_2O_3	a = 10.117 (10.0316)
SnO_2	a = 4.738 (4.71537) c = 3.1865 (3.18356)
TiO_2	a = 4.6061 (4.5941) c = 2.9586 (2.9589)
$SrCu_2O_2$	a = 5.458 (5.48) c = 9.837 (9.825)
$CuAlO_2$	a = 5.9169 (5.896) α = 27.915 (28.1)
β-Ga_2O_3	a = 12.23 (12.026) b = 3.04 (2.9927) c = 5.8 (5.7185) β = 103.7 (103.86)
$InGaO_3(ZnO)_1$	a = 3.299 (3.29491) b = 5.714 (5.70415) c = 26.101 (25.4037)
$12CaO \cdot 7Al_2O_3$ (C12A7)	a = 11.989 (12.0284, 11.997, 11.9884) α = 90 (α=89.9895, β=89.9334, γ=89.9619)

Pressure-induced phase transition in BaS: ΔH (0 K approximation)

Stable at atmospheric *P*: NaCl type structure (B1)
Stable at high *P* : CsCl type structure (B2)

$$\Delta G = \Delta(U + PV - TS)$$
$$\Rightarrow \sim \Delta H = \Delta E_{scf} + P\Delta V$$



Phase transition at finite T: VASP + Phonopy

$$F(V,T) = E_0(V) + F_{phonon}(V,T) + F_{electron}(V,T)$$

$$F_{phonon} = \frac{1}{2}\sum \hbar\omega_q + k_B T \sum ln\left(1 - e^{-\hbar\omega_q/k_B T}\right)$$

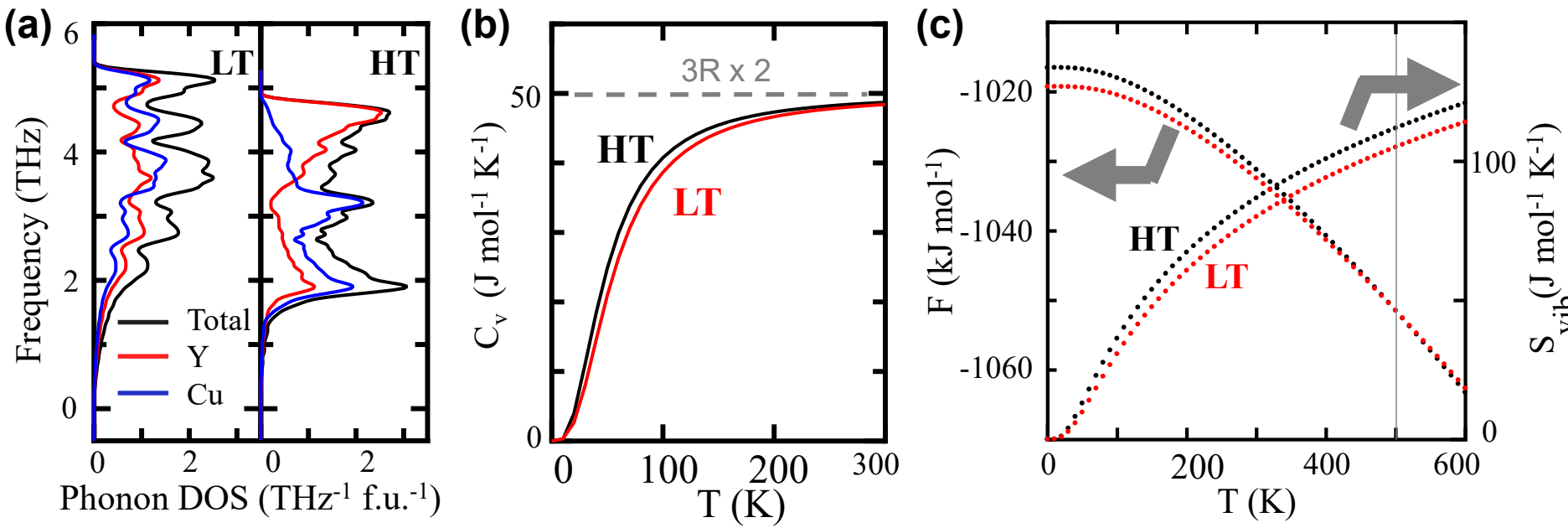
$$F_{electron} = E_{electron} - TS_{electron}$$

$$E_{electron} = \int_{-\infty}^{\infty} n(e)f(e)de - \int_{-\infty}^{E_F(0K)} n(e)de$$

$$S_{electron} = -k_B \int_{-\infty}^{\infty} n(e)[f(e)\ln f(e) + (1 - f(e)\ln(1 - f(e))]de$$

HT and LT phases of YCu

Mizoguchi et al., Inorg. Chem. ***58****, 11819 (2019)*



Reaction heat, Phase stability

反応熱、相安定性

Three laws of thermodynamics

- The zero law: If $T_A = T_B$ and $T_C = T_A$ then $T_C = T_B$

- The first law (Energy conservation)
  General system: $\Delta U = Q + W$
  Isolated system: $\Delta U = 0$
- The second law (law of entropy increase)
  The total entropy of universe increases: $\Delta S > 0$
- The third law(the origin of entropy)
  Entropy of a system approaches zero as T approaches 0 K.

How reaction proceeds

Three laws of thermodynamics

The first law : Energy conservation
The second law: Entropy increases
The third law : The origin of entropy

For non-isolated system:

		Free energy
Isolated system	$-\Delta S \leq 0$	**Entropy**
Const *T*, const *V*	$\Delta F \leq 0$	**Helmholtz energy**
Const *T*, const *P*	$\Delta G \leq 0$	**Gibbs energy**

- *Ex.*: *P*, *T*, and the number of particles are constant
  - Reaction proceeds so that the Gibbs energy of system will find minimum
  - $\Delta G = 0$ at equilibrium

Three conditions for equilibrium

When two systems A and B are in equilibrium, the following three conditions should be satisfied

- Thermal equib. : Temperature $T_A = T_B$
- Mechanical equib.: Pressure $P_A = P_B$
- Chemical equib. : Chemical potentials of constituent elements and e^-

$$\mu_{A,e} = \mu_{B,e}$$

Free energies

▪ Isolated (0 K, 0 atm)	Internal energy	U
▪ const P (0 K)	Enthalpy	$H = U + PV$
▪ const T, const V (0 atm)	Helmholtz energy	$F = U - TS$
▪ const T, const P	Gibbs energy	$G = U + PV - TS$

DFT: Born-Oppenheimer approx. (Separate motions of electrons and nuclei)

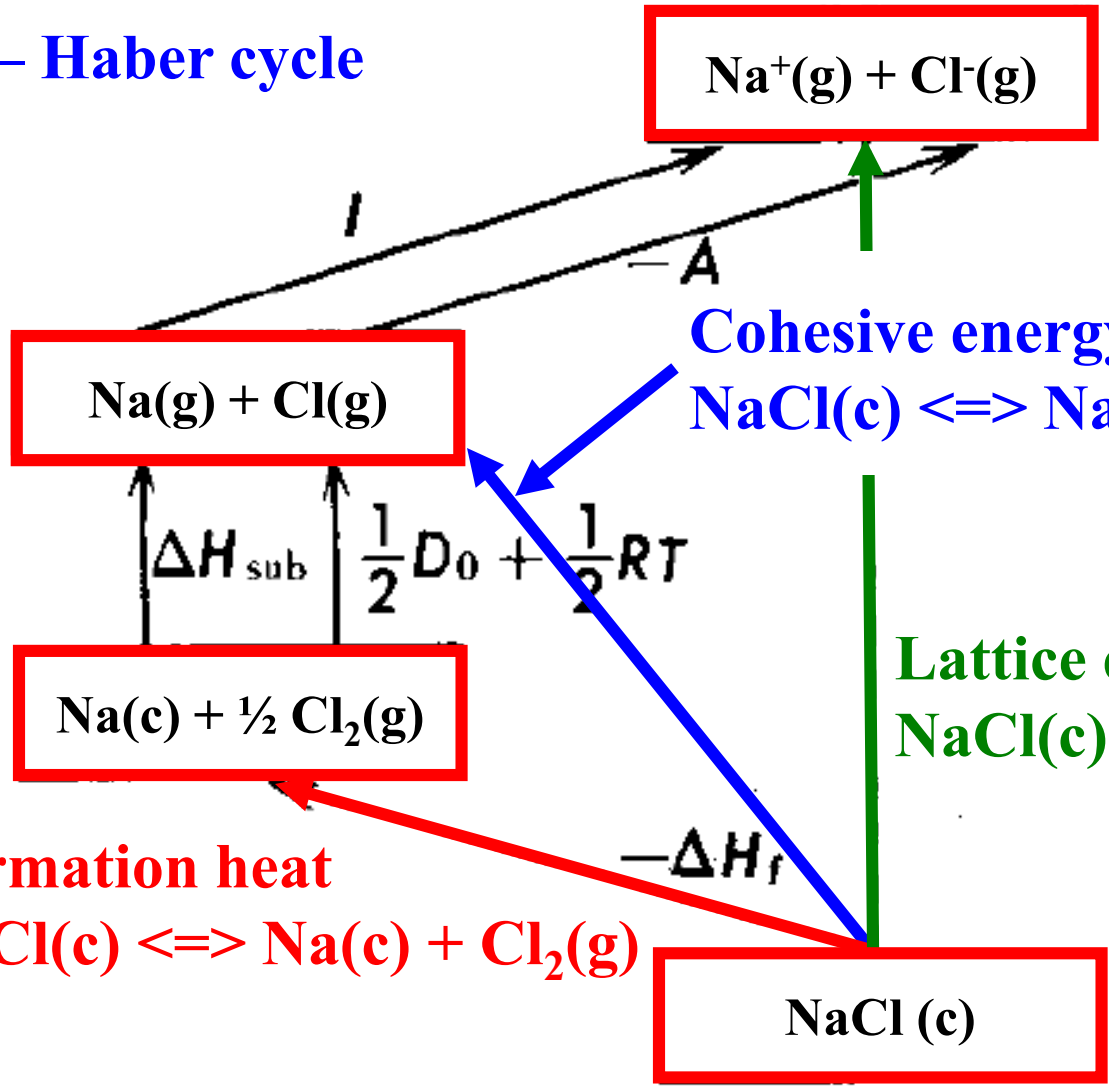
Electrons system : $U_{electron}$, V, P

Rigid band approx.: Excitation $\Delta U_{electron}(T)$, Configuration entropy $\Delta S_{elelctron}(T)$

Nuclei system : Phonon U_{phonon}, entropy S_{phonon} (or F_{phonon})

From total energy

Born – Haber cycle



Cohesive energy
NaCl(c) <=> Na(g) + Cl(g)

Lattice energy
NaCl(c) <=> $Na^+(g) + Cl^-(g)$

Formation heat
NaCl(c) <=> Na(c) + $Cl_2(g)$

Reaction heat, formation energy etc:
Write down reaction equation, and calculate the total energies of the components in the equation

A + B => C + D

0 K, 0 atm : $\Delta E = (E(\mathrm{C}) + E(\mathrm{D})) - (E(\mathrm{A}) + E(\mathrm{B}))$

0 K, finite *P* : $\Delta H = (H(\mathrm{C}) + H(\mathrm{D})) - (H(\mathrm{A}) + H(\mathrm{B}))$

$$H(\mathrm{a}) = E(\mathrm{a}) + PV(\mathrm{a})$$

finite *T*, finite *P* : $\Delta G = (G(\mathrm{C}) + G(\mathrm{D})) - (G(\mathrm{A}) + G(\mathrm{B}))$

$$G(\mathrm{a}) = E(\mathrm{a}) + PV(\mathrm{a}) - TS(\mathrm{a})$$

Ex.: Sublimation heat of Na

Na (crystal) => Na (atom)

※ E_{tot} of Na(crystal) : E = -2.6203 eV/cell

※ E_{tot} of Na(atom) : E = -0.0007 eV/atom

※ Na(crystal) => Na(atom) : ΔE = 1.3094 eV = 126 kJ/mol

※ add PV = RT = 2.49 kJ/mol (300 K) to obtain ΔH:

ΔH = 128 kJ/mol

※ Literature value: 108 kJ/mol

Formation / cohesive energies of NaCl

NaCl (crystal) => Na (crystal) + ½ Cl_2 (molecule gas)

※ E_{tot} of NaCl(crystal) : E = -27.2610 eV/cell (4NaCl)

※ E_{tot} of Na(crystal) : E = -2.6203 eV/cell (2Na)

※ E_{tot} of Cl_2(molecule) : E = -3.5504 eV/cell (2Cl)

※ Formation energy: NaCl(crystal) => Na(crystal) + 1/2 Cl_2(molecule)
-3.7301 eV/Na = 359.9 kJ/mol

※ Add ½ PV = ½ RT = 1.2 kJ/mol (300 K) to obtain ΔH
ΔH = 361 kJ/mol 文献値 411 kJ/mol

NaCl (crystal) => Na (atom gas) + Cl (atom gas)

※ E_{tot} of Na(atom) : E = -0.0007 eV/atom

※ E_{tot} of Cl(atom) : E = -0.0183 eV/atom

※ Cohesive energy: NaCl(crystal) => Na(crystal) + Cl(atom):
6.7962 eV/NaCl = 655.7 kJ/mol Literature 641 kJ/mol

※ Add 2PV = 2RT = 5.0 kJ/mol (300 K) to obtaine ΔH
ΔH = 660.7 kJ/mol 文献値 641 kJ/mol

Cohesive energy of Si

Si (Crystal) => Si (atom gas)

※ E_{tot} of Si(crystal) : E = -43.3748 eV / 8Si
= 523 kJ/mol

※ E_{tot} of Si(atom) -0.862 eV

※ Add $PV = RT$ = 2.49 kJ/mol (300 K) to obtain ΔH :
ΔH = 434 kJ/mol Literature 446 kJ/mol

Bonding energy is obtained by dividing ΔH with the number of bonds, 2

Si-Si bond energy: E = 217 kJ/mol Literature 224 kJ/mol

Chemical potential

Definition: Chemical potential of element:

$$\mu_a = \left(\frac{\partial G}{\partial N_a}\right)_{T,p,(other\ and\ N_a)}$$

Equilibrium between phases A and B: $\boldsymbol{\mu_{a,A} = \mu_{a,B}}$

Other relations

$$dS = \frac{P}{T}dV + \frac{dU}{T} - \frac{1}{T}\sum_{j=1}^{n}\mu_j dN_j$$

$$dF = -SdT - PdV + \sum_{j=1}^{n}\mu_j dN_j$$

$$dG = -SdT + VdP + \sum_{j=1}^{n}\mu_j dN_j$$

$$\boldsymbol{G(T,p,N_a) = \sum_a N_a \mu_a}$$

0 K: $\boldsymbol{H_A(T,p,N_a) = \sum_A (E_A + PV_A) = \sum_a N_a \mu_a}$

Chemical stability: $SrTiN_2$

1. **Search possible phases: Sr, Ti, N_2, SrN, Sr_2N, SrN_2, SrN_6, TiN, Ti_2N, etc**
2. **Thermodynamical conditions:** $G(T, p, N_a) = \sum_a N_a \mu_a$

   例: $\Delta\mu_{Sr} + \Delta\mu_{Ti} + 2\Delta\mu_N = \Delta H_{SrTiN_2}$ **(calculated by DFT)**

   $\mu_e = \mu_e{}^0 + \Delta\mu_e$: **$\mu$ of e ($\mu_e{}^0$ is μ of elemental e)**

   μ_a depend on experimental condition: Calculation result would be a function of μ_a
3. **Phase stability condition**

   $\Delta\mu_{Sr} + \Delta\mu_{Ti} + 2\Delta\mu_N = \Delta H_{SrTiN_2}$ **= -5.87eV< 0**

2. **Elementary phases are not segregated**

   $\Delta\mu_{Sr} < 0$ ①, $\Delta\mu_{Ti} < 0$ ②, $\Delta\mu_N < 0$ ③

3. **Other impurity phases are not segregated**

   $2\Delta\mu_{Ti} + \Delta\mu_N < \Delta H_{Ti_2N}$ ④

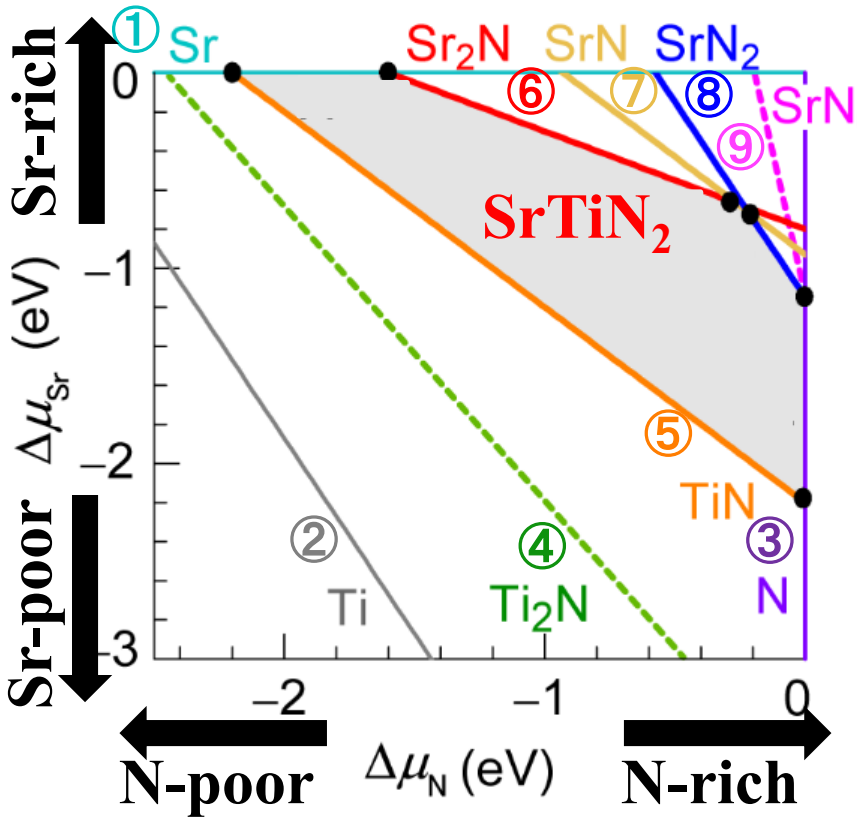
   $\Delta\mu_{Ti} + \Delta\mu_N < \Delta H_{TiN}$ ⑤

   $2\Delta\mu_{Sr} + \Delta\mu_N < \Delta H_{Sr_2N}$ ⑥

   $\Delta\mu_{Sr} + \Delta\mu_N < \Delta H_{SrN}$ ⑦

   $\Delta\mu_{Sr} + 2\Delta\mu_N < \Delta H_{SrN_2}$ ⑧

   $\Delta\mu_{Sr} + 6\Delta\mu_N < \Delta H_{SrN_6}$ ⑨



Eq. conditions at phase boundaries: $SrTiN_2$

1. **Equilibrium condition: Chemical potentials are equal among the phases under equilibrium for each species**

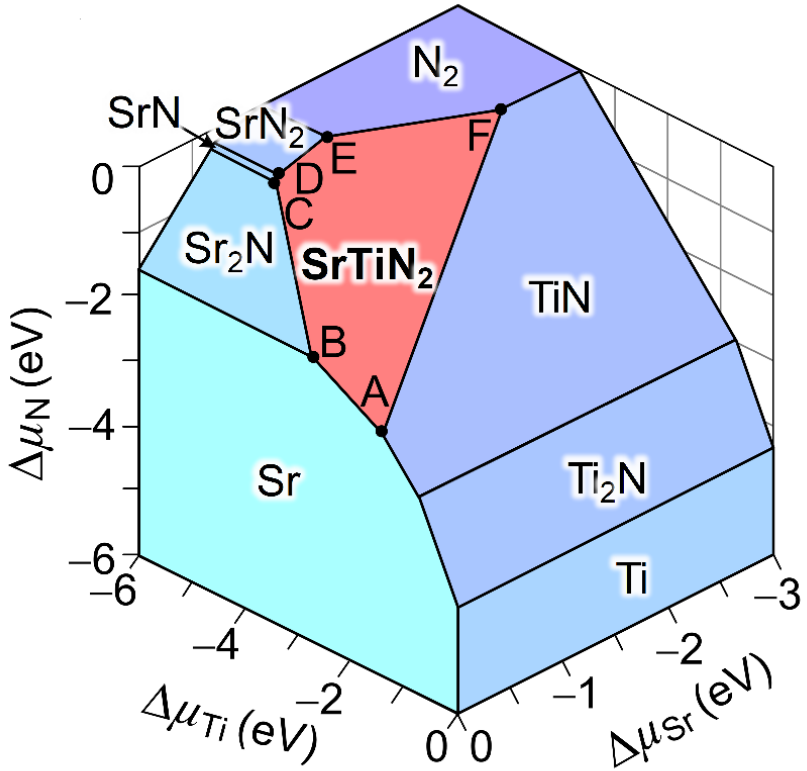
A point: $SrTiN_2$ is equilibrium with elemental Sr and TiN

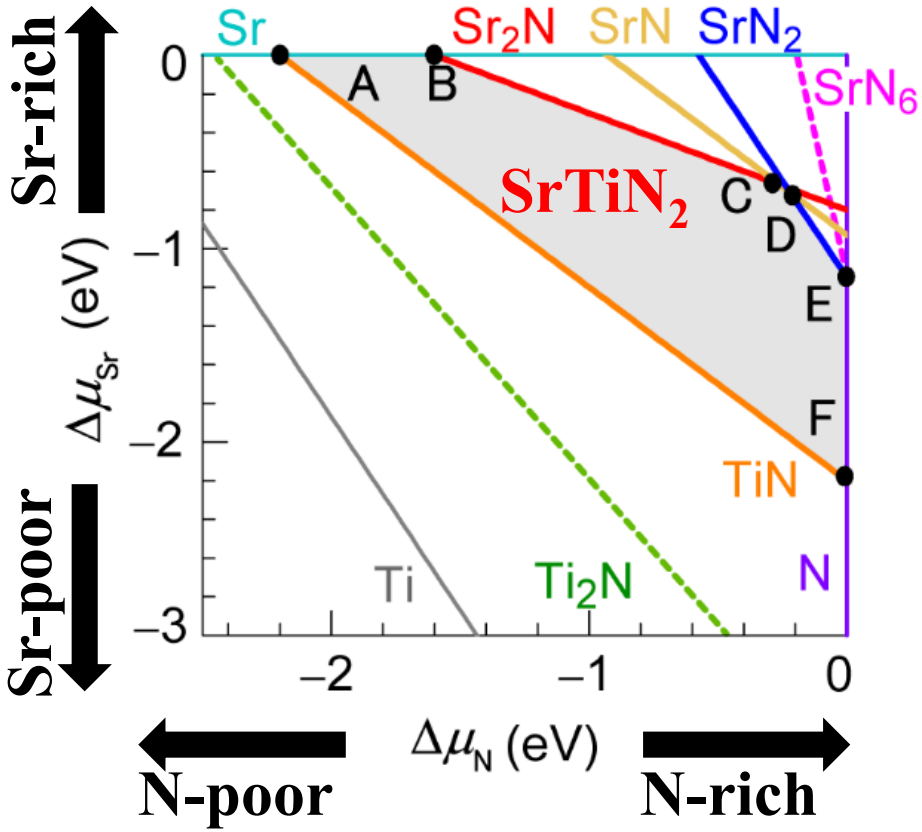
μ_{Sr} **is equal to that of elemental Sr** => $\Delta\mu_{Sr} = 0$

μ_{Ti} **and** μ_N **are equal to** μ **of TiN** => $\Delta\mu_{Ti} + \Delta\mu_N = \Delta H_{TiN}$ **(calculated by DFT)**

Condition for $SrTiN_2$ => $\Delta\mu_{Sr} + \Delta\mu_{Ti} + 2\Delta\mu_N = \Delta H_{SrTiN_2}$ **(calculated by DFT)**

=> $\Delta\mu_{Sr}, \Delta\mu_{Ti}$ **and** $\Delta\mu_N$ **are all determined**





cf. drawn by Chesta
https://www.aqua.mtl.kyoto-u.ac.jp/wordpress/chesta.html

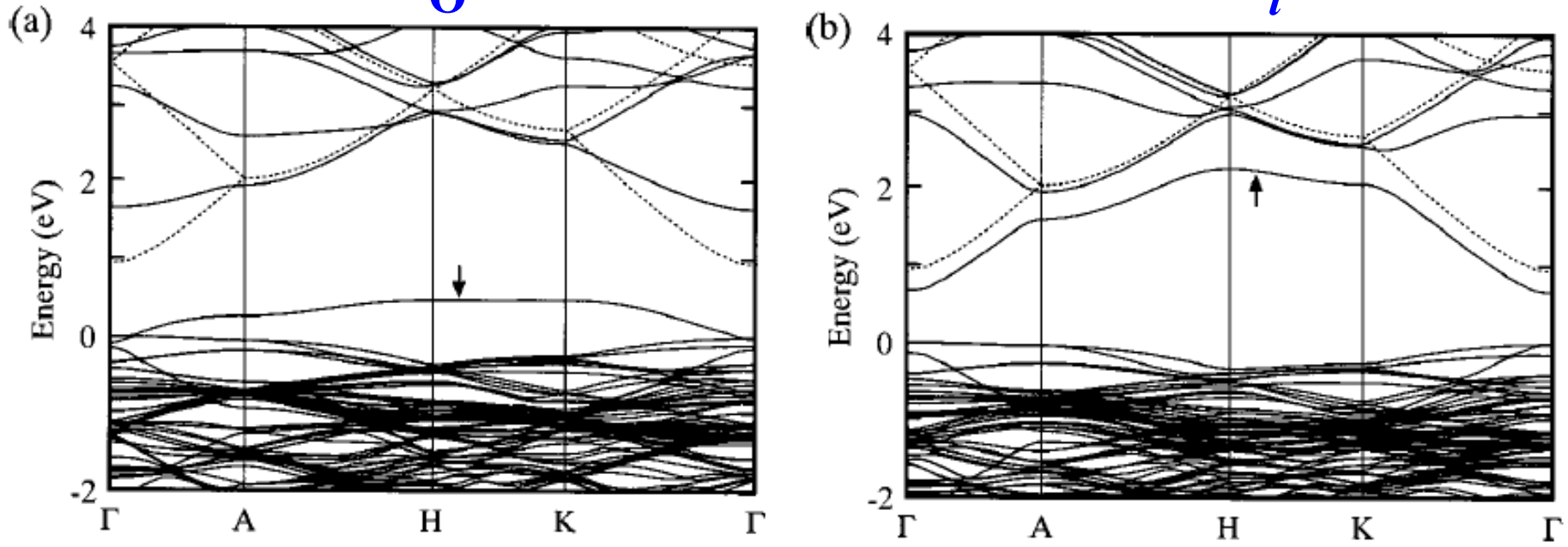
Defect formation enthalpies

欠陥の生成エネルギー

Problem of defect calculation (One-particle levels in defective ZnO)

One defect in a 128-atom supercell model

V_O Zn_i

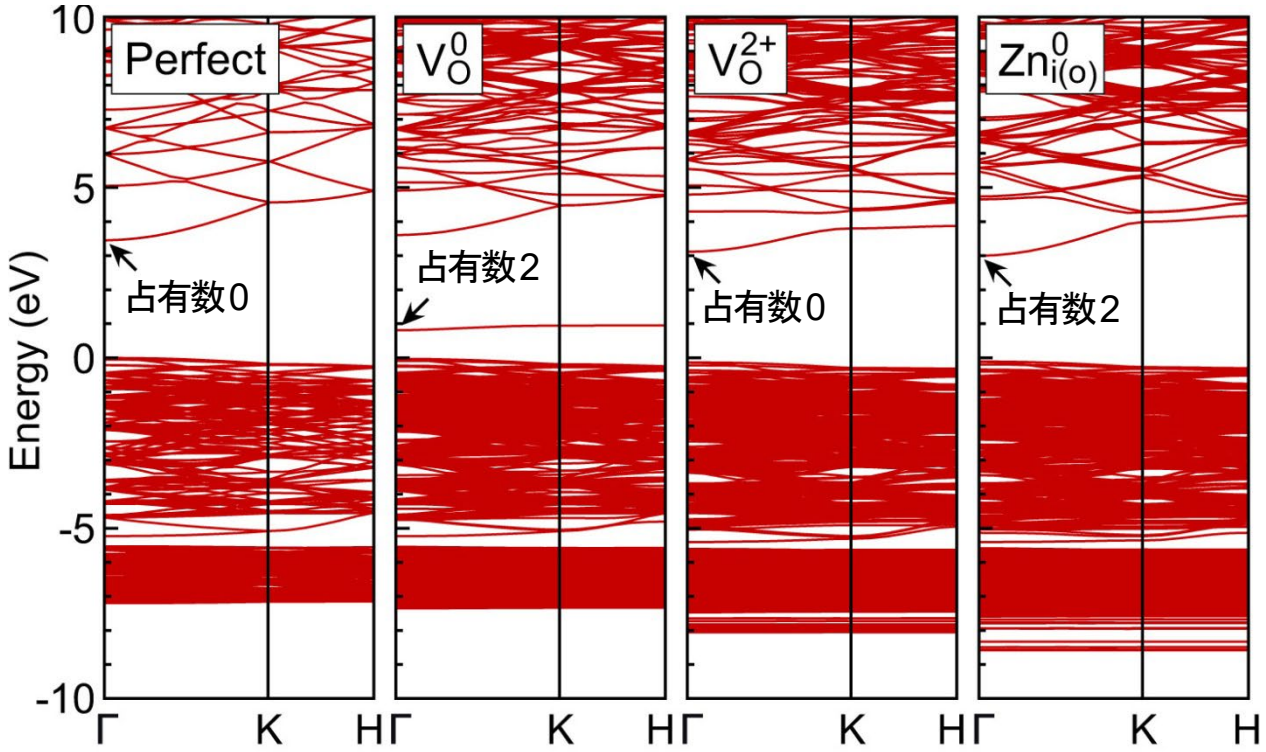


Small dispersion for defect band: Localized defect
Parallel to the dispersion of ideal crystal: Delocalized by strong hybridization with host

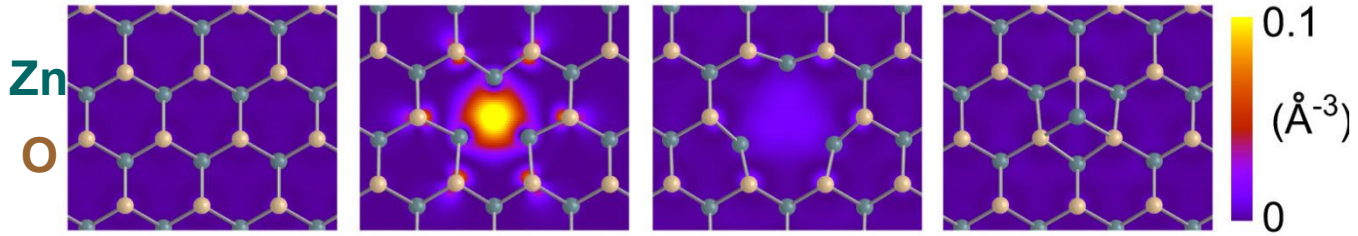
Oba et al., J. Appl. Phys.. 90, 824 (2001)

Problem of defect calculation (One-particle levels in defective ZnO)

Band structures of perfect crystal and defective crystals



e^- density map ($|\phi(\mathbf{r})|^2$)



F. Oba *et al.*, *Phys. Rev. B*, **77**, 245202 (2008).

Problem of defect calculation

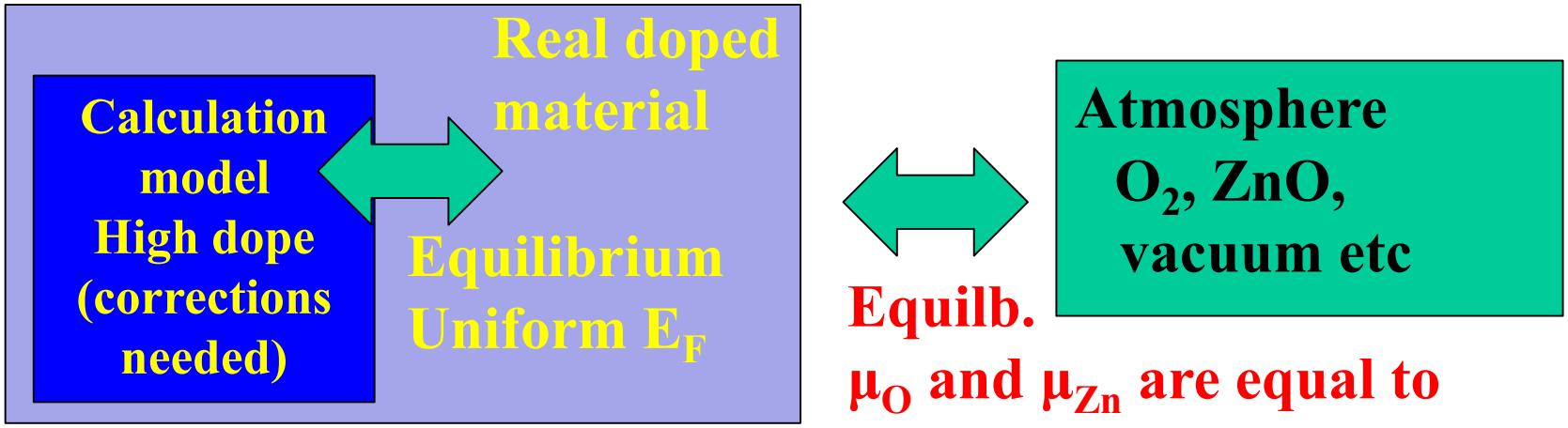
Typical carrier densities in TCO

$< 10^{21}$ cm^{-3} (< 1/100, **E_F up to E_C + 1.0 eV**)

Typical carrier densities in semiconductors

$10^{15} - 10^{18}$ cm^{-3} (1/10^8 ~ 1/10^5, **$E_F = E_C - 0.5$ to $E_C - 0.2$ eV**)

[Note] Defect calculation is at the 'dilution limit'



μ_O and μ_{Zn} are equal to those in atmosphere

$$E^f{}_{D,q}(E_F, \mu)$$
$$= E_{D,q} - E_0 - n_{Zn}\mu_{Zn} - n_O\mu_O$$
$$+ q\left(E_F - E_{VBM}{}^0\right)$$

Eq. condition with ZnO: $\mu_{Zn} + \mu_O < \mu_{ZnO}$

Zn-rich cond. : $\mu_{Zn} = \mu_{Zn(bulk)}$

O-rich cond. : $\mu_O = \mu_{O2}$

Intermediate cond.: $\mu_O < \mu_{O2}$, $\mu_{Zn} < \mu_{Zn(bulk)}$

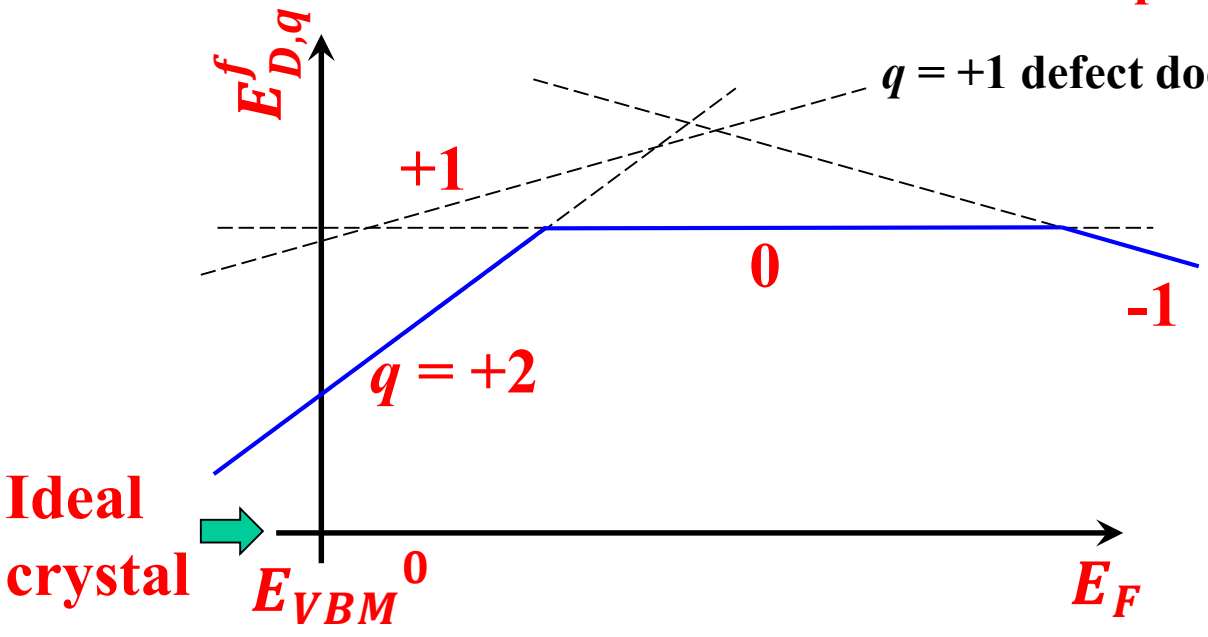
How to read $E^f{}_{D,q}(E_F)$ diagram

$$E^f{}_{D,q}(E_F,\mu) = E_{\mathrm{D,q}} - E_0 - n_{\mathrm{Zn}}\mu_{\mathrm{Zn}} - n_{\mathrm{O}}\mu_{\mathrm{O}} + q\left(E_F - E_{VBM}{}^0\right)$$

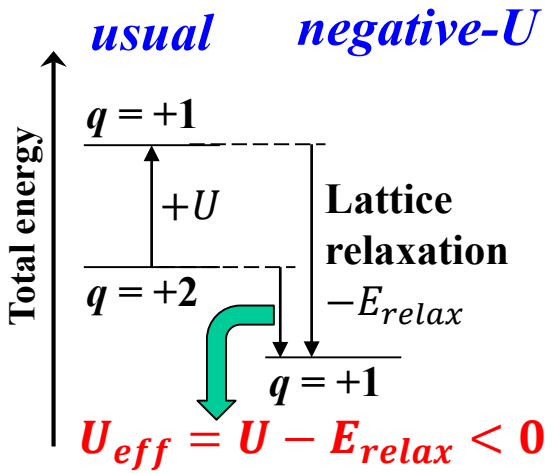
***q*: Charge of defect with respect to the charge of the ideal crystal site**
e.g., H^- at O^{2-} site: $q = +1$, $H_O{}^+$

Define $E_{VBM}{}^0 = 0$

$$E^f{}_{D,q}(E_F,\mu) = E^f{}_{D,q}(0,\mu) + qE_F \qquad \text{slope } \frac{\partial E^f_{D,q}}{\partial E_F} = q$$



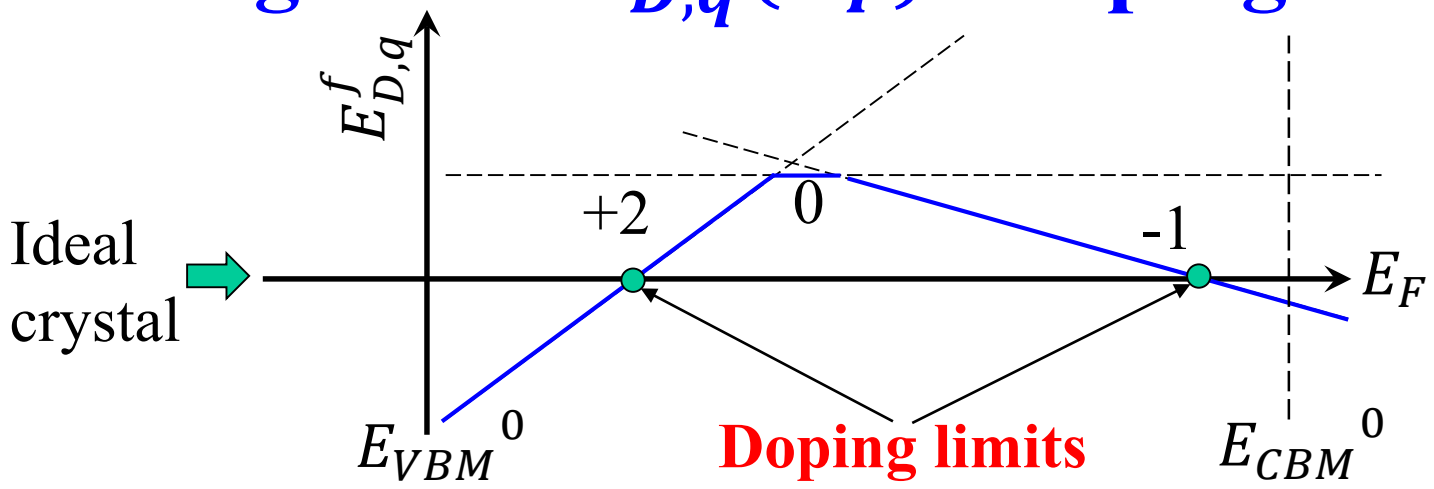
***q* = +1 defect does not appear: Negative-U**



from canonical distribution (Boltzmann / Gibbs distribution)

$$[\text{ideal}]:[D^{+2}]:[D^{+1}]:[D^0]:[D^{-1}] = 1: N_{site}^{D,+2} e^{-\frac{E^f_{D,+2}(E_F)}{k_B T}} : N_{site}^{D,+1} e^{-\frac{E^f_{D,+1}(E_F)}{k_B T}} : N_{site}^{D,0} e^{-\frac{E^f_{D,0}(E_F)}{k_B T}} : N_{site}^{D,-1} e^{-\frac{E^f_{D,-1}(E_F)}{k_B T}}$$

Negative $E^f{}_{D,q}(E_F)$: Doping limit



For negative $E^f{}_{D,q}$, $[D^q] \gg$ [ideal] (the total crystal sites),

Indicating E_F is pinned between $E_F{}'s$ of $E^f{}_{D,q}(E_F) \sim 0$

$[D^q]$ can be calculated as follows,
but not consistent with the assumption of 'dilution limit'

Grand partition function: $Z(E_F) = \sum_{site,D,q} e^{-\beta G_{D,q}(E_F)} = \sum_{D,q} N_{site} e^{-\beta G_{D,q}(E_F)}$

Probability of D_q: $P_{D,q} = N_{site} e^{-\beta G_{D,q}(E_F)} / Z$

$\langle N_{D,q} \rangle = N_{site} P_{D,q} / Z$

For $e^{-\beta G_{D,q}(E_F)} \ll 0$, $Z(E_F) \sim N_{site}$, $\langle N_{D,q} \rangle \sim N_{site} e^{-\beta G_{D,q}(E_F)}$

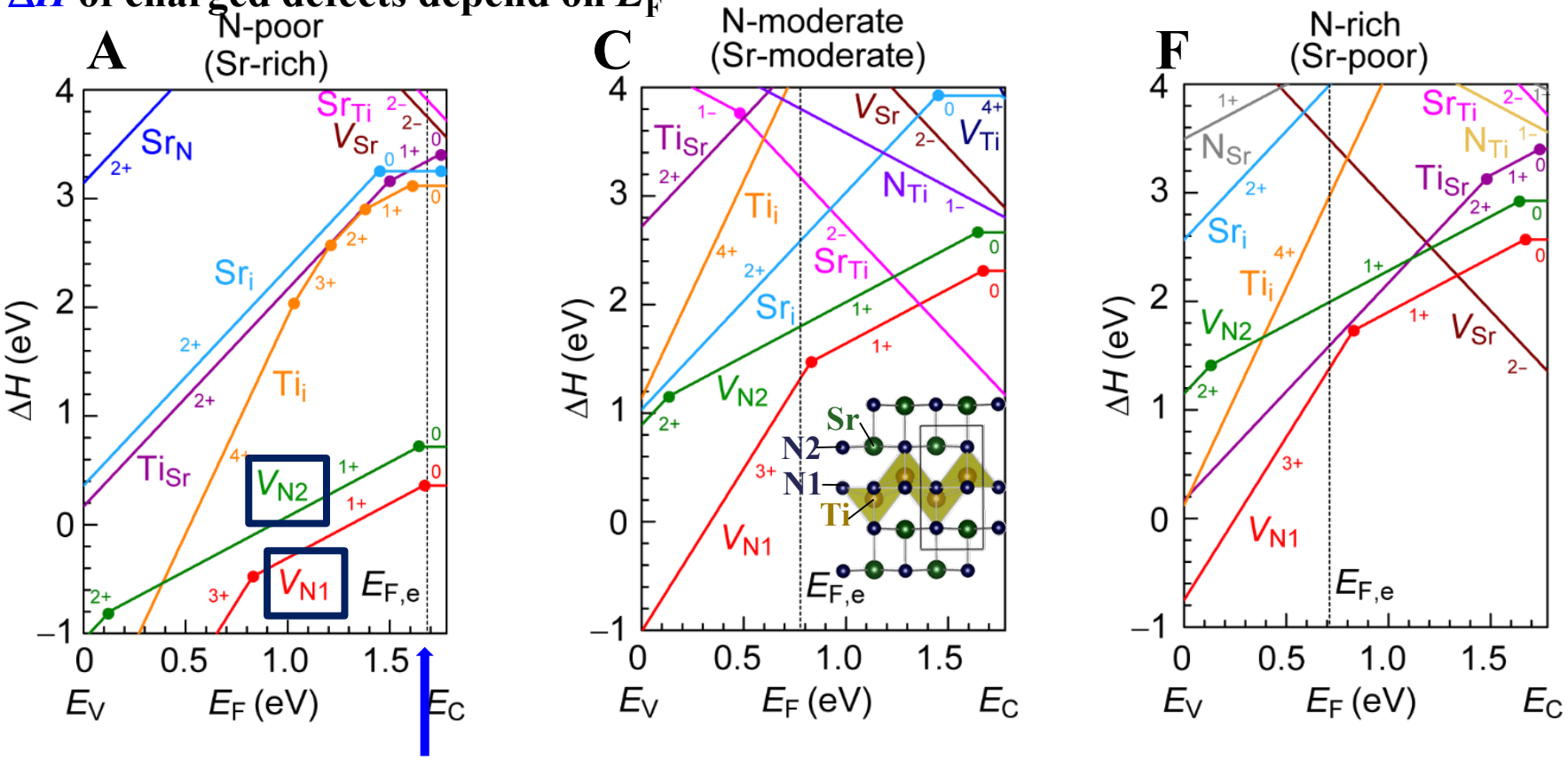
ΔH of defects at representative phase boundaries

ΔH is a function of μ of constituent elements and electron

μ of e^-: Fermi level, E_F

ΔH of charged defects depend on E_F

Graph depends on E_F



Equilibrium E_F ($E_{F,eq}$): Determined by charge neutrality condition

Sum of defect charges + free h^+ charge + free e^- charge = 0

$E_{F,eq}$ closer to E_C => native n-type conductor、equib. carrier dens: 1.1×10^{18} cm^{-3}

X. He et al., J. Phys. Chem. C **123** (2019) 19307

Donor level, acceptor level: SnS (:H)

Defect charges are relative to those of the ideal crystal sites:

If replace O^{2-} with F^{-} => F_O^{-}

Neutral O vacancy: V_O^{o}: An O^{2-} is missed and $2e^{-}$ are trapped

=> If no e^{-} is trapped, it should be $V_O^{\cdot\cdot}$ (V_O^{2+})

Donor : A state that can emit an e^{-} from the neutral state

Ionized donor has a positive charge

Acceptor : A state that can capture an e^{-} from the neutral state

Ionized acceptor has a negative charge

Donor level (charge transfer level):

Crossing point of positive-slope ΔH

Slope +1 => 0, +2 => +1:

Single donor

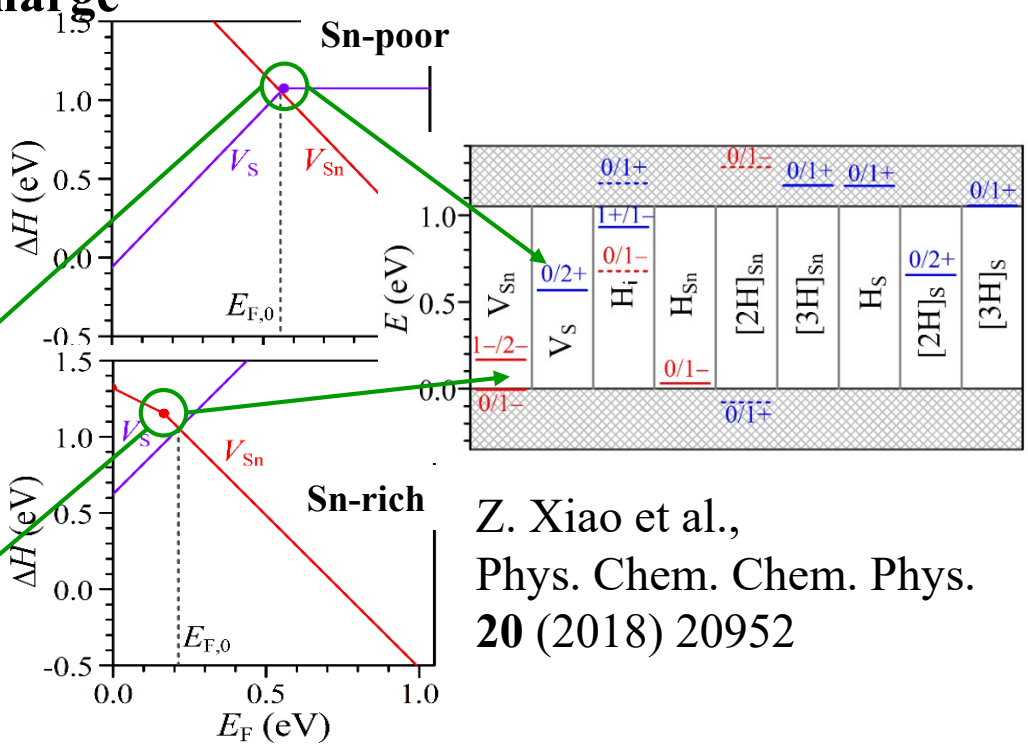
Slope +2 => 0: Double donor

Acceptor level:

Crossing point of negative-slope ΔH

Slope 0 => -1, -1 => -2:

Single acceptor



Z. Xiao et al., Phys. Chem. Chem. Phys. **20** (2018) 20952