4/30 +5/7 (홍용상)

시험풀이

Chap. 3

다음주 수업시간 변경

Steel

정연욱 숙제 +5

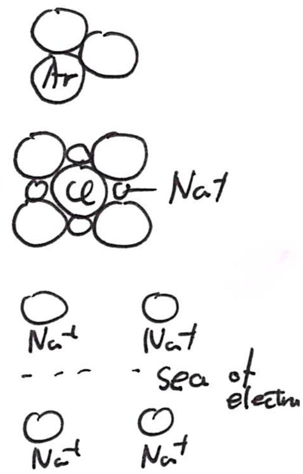
Steel 예제

Chap.3 Crystal Binding & Elastic Constants

· What holds a crystal together?

· Bond types. (Force)

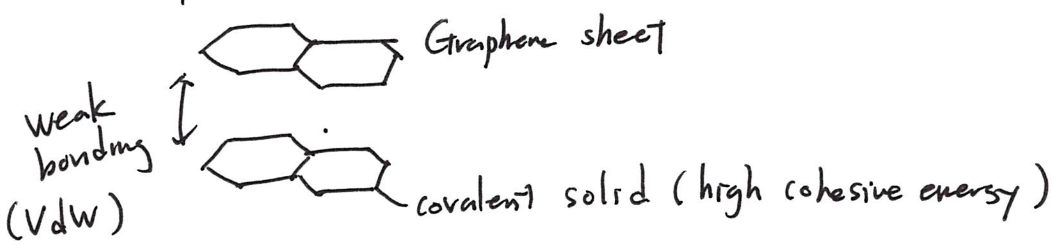
- van der Waals (crystalline argon, inert gas)
- Ionic (NaCl)
- metallic (sodium, Fe..)
- covalent (Diamond)



· Cohesive energy Ar --- Ar neutral. , inert gas, molecular solid..
(infinite)

lattice energy Na^+ --- Na^+
ion

· Graphite (흑연) - Strong bond of layer, · Weak bond btw layers.



Solids

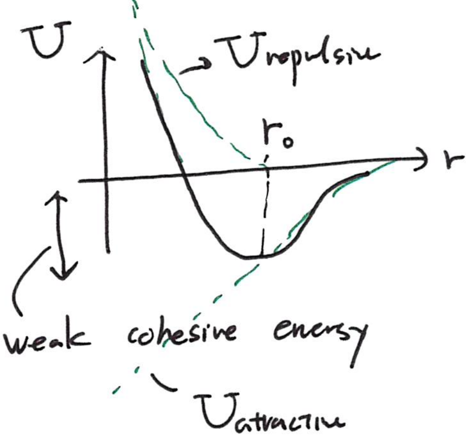
- electron density distribution in real-space

1. Molecular Solids.

LJ potential로 설명가능

: Weak cohesion
Ne, Ar, Xe
vdW (dipole-dipole interaction)

$$U = -\frac{\alpha}{r^6} + U_{repulsive} = \underbrace{\frac{B}{r^{12}}}_{\text{repulsive}} - \underbrace{\frac{A}{r^6}}_{\text{attractive}}$$

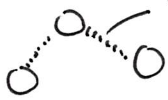


H과 = E과
설명가능 증명가능, 해석가능 e.g) Ca = 2+4
Ca = metal..

실제로 구분 모호

2. Covalent Solid

: Strong cohesion
C, Si, ~~Ge~~, ~~Sn~~



e^- 분포 → chemical bond 형성

3. Metallic Solid

: hcp, fcc, bcc
Na, ~~Cu~~, Fe, Hg

cohesive energy
C, Si, ~~Ge~~, ~~Sn~~
⩔
Na, ~~Cu~~, Fe, Hg
⩔
Ne, Ar, Xe.

4. Ionic Solid

: NaCl → Na^+Cl^- (very stable)
Molecular solid 와 비슷해짐.

. Coulomb interaction (attraction)

. or Electrostatic attraction

+1 vs −1
∧
+2 vs −2

coordination
=
nearest neighbor atom #

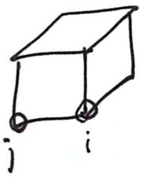
다른 모든 solid
⩔
covalent (diamond)

VdW-London Interaction

- Atoms induce dipole moments in each other, and the induced moments cause an attractive interaction btw the atoms.

- Molecular Solid, Inert gas..

- $u(r) = \frac{B}{r^{12}} - \frac{A}{r^6} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$; $A = 4\varepsilon\sigma^6$, $B = 4\varepsilon\sigma^{12}$



$$\sum_{i,j} u(r_{ij})$$

if) $i=1$ & $j=2$, $\sum_{i,j} u(r_{ij}) = \cancel{u(r_{11})}^{\,0} + \cancel{u(r_{22})}^{\,0}$ → no self interaction

$+\, u(r_{12}) + u(r_{21})$ → counted twice

$\downarrow$

$$\frac{1}{2}\sum_{i\neq j} u(r_{ij})$$

$\downarrow$ Many atoms

$$U_{TOTAL} = N \sum_{i\neq j} u(r_{ij}) \cdot \frac{1}{2}$$

N: # of sites in a crystal, # of cells..

$$\frac{U_{TOTAL}}{N} = \sum_{i\neq j} \frac{4}{2}\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right]$$

, $r_{ij} = R p_{ij}$ (R: distance to 1st nearest nbr.)

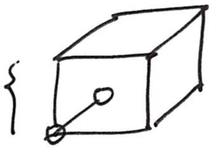
$$= 2\varepsilon\left(\frac{\sigma}{R}\right)^{12}\sum_{i\neq j}\frac{1}{p_{ij}^{12}} - 2\varepsilon\left(\frac{\sigma}{R}\right)^6\sum_{i\neq j}\frac{1}{p_{ij}^6}$$

$$= 2\varepsilon\left[A_{12}\left(\frac{\sigma}{R}\right)^{12} - A_6\left(\frac{\sigma}{R}\right)^6\right]$$

, $A_{12} = \sum_{i\neq j}\frac{1}{p_{ij}^{12}}$

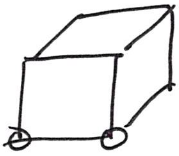
$A_6 = \sum_{i\neq j}\frac{1}{p_{ij}^6}$

- FCC case.

a 

$\frac{a}{2}\langle 110\rangle$, $\cancel{R}\ r = \frac{a}{\sqrt{2}}$, $P_{ij} = 1$, # of nbrs 12

$\quad \parallel R$



$a\langle 100\rangle$, $\cancel{R}\ r = a$, $P_{ij} = \sqrt{2}$, 6

$$r_{ij} = R P_{ij}$$

$$A_{12} = \sum_{i\neq j} \frac{1}{P_{ij}^{12}} = \left(\frac{1}{1}\right)^{12}\cdot 12 + \left(\frac{1}{\sqrt{2}}\right)^{12}\cdot 6 \cdots \approx 12.13$$

$$A_6 = \sum_{i\neq j} \frac{1}{P_{ij}^{6}} = \left(\frac{1}{1}\right)^{6}\cdot 12 + \left(\frac{1}{\sqrt{2}}\right)^{6}\cdot 6 \cdots \approx 12.8$$

- $$\frac{U_{total}}{N} = 2\varepsilon\left[A_{12}^{FCC}\left(\frac{\sigma}{R}\right)^{12} - A_6^{FCC}\left(\frac{\sigma}{R}\right)^{6}\right]$$

- Determin R^* at $\left(\frac{U_{total}}{N}\right)_{min}$.

$$\frac{\partial U_{total}(R)}{\partial R} = 0$$

$$= -12A_{12}\cdot\frac{\sigma^{12}}{R^{13}} + 6A_6\cdot\frac{\sigma^6}{R^7}$$

$$\therefore R^* = \left[\frac{2A_{12}}{A_6}\right]^{1/6}\cdot\sigma = \underline{1.09\sigma}$$

preferred distance of atoms for FCC inert gas.

- Experimental data

	Ne	Ar	Kr	Xe
R^*/σ	1.14	1.11	1.10	1.09
Ecohesive	−0.02	−0.08	−0.11	−0.17

이론값

atom이 가벼울수록 Kinetic energy가 전체 E에 미치는 영향이 커서 R^*이 커진다.

- Cohesive energy of Molecular Solids (Inert gas)

$$\frac{U_{TOT}(R^*)}{N} = -\frac{\varepsilon}{2}\frac{A_6^2}{A_{12}}$$ ← 숙제.

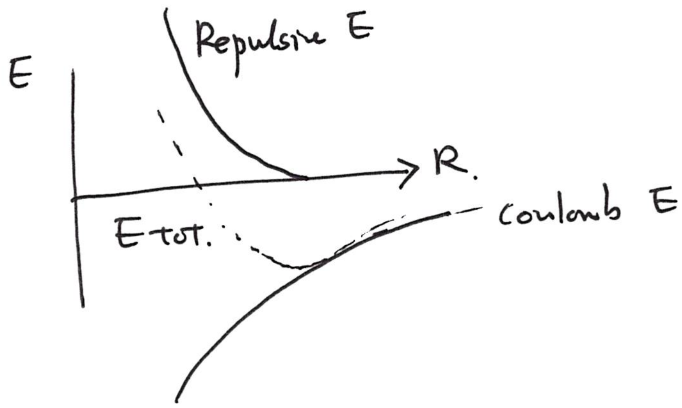
- Cohesive energy of Ionic Solid.

$$U(r_{ij}) = U_{rep}(r_{ij}) + U_{att}(r_{ij})$$

$$= \lambda e^{-r_{ij}/\rho} - \underbrace{\frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}}}_{\text{Coulomb interaction}}$$

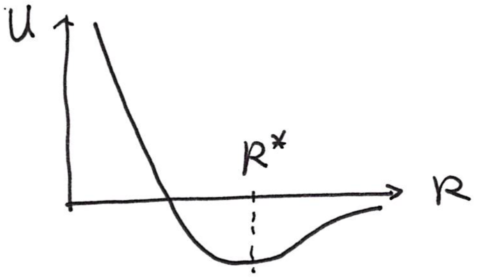
Electrostatic

$$= -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$



Elastic Constants

$U_{tot}(R)$

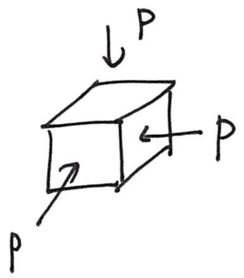


cohesive energy

$$\left(\frac{\partial U_{tot}}{\partial R}\right)_{R^*} = 0 \qquad \text{but} \qquad \left(\frac{\partial^2 U_{tot}}{\partial R^2}\right)_{R^*} \neq 0$$

↳ elastic constant 와 관련

· Mechanical Properties $\quad G = \dfrac{E}{2(1+\nu)}$, $\boxed{K}$, C_{ij}

· 

isotropic loading

uniform dilation (expansion) or contraction

$$\cancel{\partial U = -P\,\partial V}$$

$$\cancel{P = -\left(\frac{\partial U}{\partial V}\right)}$$

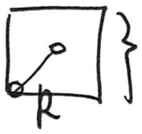
$$\cancel{B = -V\left(\frac{\partial P}{\partial V}\right)_T = +V\left(\frac{\partial^2 U}{\partial V^2}\right)}$$

$$\cancel{P = -\frac{\partial U}{\partial V}}$$

$$\cancel{B = -V\left(\frac{\partial P}{\partial V}\right)_T = +V\left(\frac{\partial^2 U}{\partial V^2}\right)}$$

- $P = -\dfrac{\partial U_{TOTAL}}{\partial V}$ — 대문자

$$B \equiv -V\left(\frac{\partial P}{\partial V}\right)_T = +V\left(\frac{\partial^2 U_{TOTAL}}{\partial V^2}\right)$$ — 대문자.

- FCC case.  $\}\ a$, $V = a^3$, $N = 4$, $v = \dfrac{V}{N} = \dfrac{a^3}{4} = \dfrac{R^3}{\sqrt{2}}$

$R = \dfrac{a}{\sqrt{2}}$

$$B = \cancel{N}\cdot v\left(\frac{\partial^2 U_{TOTAL}/N}{\partial v^2}\right)$$

$$\frac{\partial v}{\partial R} = \frac{3}{\sqrt{2}}R^2$$

$$= \frac{R^3}{\sqrt{2}}\,\frac{\partial^2}{\partial v^2}\left(U_{TOT}/N\right)$$

$$\frac{\partial}{\partial v} = \frac{\partial R}{\partial v}\cdot\frac{\partial}{\partial R} = \frac{\sqrt{2}}{3}\,\frac{1}{R^2}\,\frac{\partial}{\partial R}$$

$u_{TOTAL} = U_{TOTAL}/N$

$$= \frac{R^3}{\sqrt{2}}\cdot\frac{\sqrt{2}}{3}\cdot\frac{1}{R^2}\cdot\frac{\partial}{\partial R}\left\{\frac{\sqrt{2}}{3}\cdot\frac{1}{R^2}\,\frac{\partial}{\partial R}(u_{TOT})\right\}$$

if $R = R^*$

$$\frac{\partial}{\partial R}\left\{\frac{1}{R^2}\,\frac{\partial}{\partial R}(u_{TOT})\right\} = -\frac{2}{R^3}\,\underbrace{\frac{\partial u_{TOT}}{\partial R}}_{\to\,0} + \frac{1}{R^2}\,\frac{\partial^2 u_{TOT}}{\partial R^2}$$

$$= \frac{\sqrt{2}}{9R^*}\left(\frac{\partial^2 u_{TOT}}{\partial R^2}\right)_{R^*}$$

모든 FCC 구조의 Bulk modulus는 위 식을 만족한다.

Elastic Strains

- Hooke's Law (small strains)

$$\varepsilon_{xx} = \frac{\partial u}{\partial x} \; ; \; \varepsilon_{yy} = \frac{\partial v}{\partial y} \; ; \; \varepsilon_{zz} = \frac{\partial w}{\partial z}$$

- Strain component in xy: $\varepsilon_{yx} + \varepsilon_{xy} = \dfrac{\partial u}{\partial y} + \dfrac{\partial v}{\partial x}$;

  in yz: $\varepsilon_{zy} + \varepsilon_{yz} = \dfrac{\partial v}{\partial z} + \dfrac{\partial w}{\partial y}$;

  in zx: $\varepsilon_{zx} + \varepsilon_{xz} = \dfrac{\partial u}{\partial z} + \dfrac{\partial w}{\partial x}$.

- Dilation (increase / decrease of volume)

$$x' \cdot y' \times z' = \begin{vmatrix} 1+\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & 1+\varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & 1+\varepsilon_{zz} \end{vmatrix} \cong 1 + \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}.$$

determinant

$$\delta \equiv \frac{V' - V}{V} \cong \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}.$$

Elastic Stiffness Constants

$\updownarrow$

Compliance.

$$X_x = C_{11} e_{xx} + C_{12} e_{yy} + C_{13} e_{zz} + C_{14} e_{yz} + C_{15} e_{zx} + C_{16} e_{xy}$$

direction of force

normal to the plane to which the force is applied.

$$\vdots$$

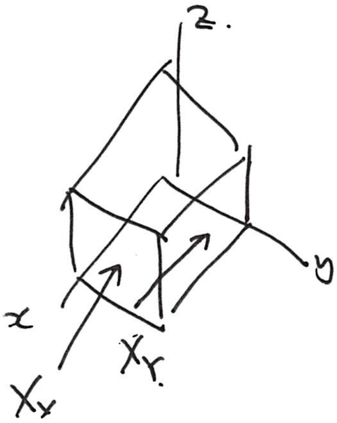
$$X_y = C_{61} e_{xx} + C_{62} e_{yy} + C_{63} e_{zz} + C_{64} e_{yz} + C_{65} e_{zx} + C_{66} e_{xy}$$

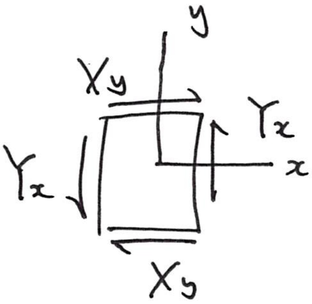
where $1 \equiv xx$, $2 \equiv yy$, $3 \equiv zz$

$4 \equiv yz$, $5 \equiv zx$, $6 \equiv xy$

- Elastic compliance.

$$e_{xx} = S_{11} X_x + S_{12} Y_y + S_{13} Z_z + S_{14} Y_z + S_{15} Z_x + S_{16} X_y$$





$$C_{14} = C_{41} \quad ; \quad C_{ij} \quad \text{if } i \neq j$$

$$1 \le i, j \le 6$$

Hooke

$kx = F$

F  $U = \frac{1}{2} F \cdot x$

x $= \frac{1}{2} kx^2.$

- Elastic Energy

$$U = \frac{1}{2} \sum_{i=1}^{6} \sum_{j=1}^{6} C_{ij} e_i e_j$$

$$X_x = \frac{\partial U}{\partial e_{xx}} \equiv \frac{\partial U}{\partial e_1} = C_{11} e_1 + \frac{1}{2} \sum_{j=2}^{6} (C_{1j} + C_{j1}) e_j$$

→ ~~[illegible]~~

- Cubic case

	e_{xx}	e_{yy}	e_{zz}	e_{yz}	e_{zx}	e_{xy}
X_x	C_{11}	C_{12}	C_{12}			
Y_y	C_{12}	C_{11}	C_{12}			
Z_z	C_{12}	C_{12}	C_{11}			
Y_z				C_{44}		
Z_x					C_{44}	
X_y						C_{44}

- ~~He~~ Hexagonal. ($a=b\neq c$, $\alpha=\beta=90$, $\gamma=120$)

$$\begin{Bmatrix} C_{11} & C_{12} & C_{13} & & & \\ \cdot & C_{11} & C_{13} & & & \\ \cdot & \cdot & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{44} & \\ & & & & & C_{66} \end{Bmatrix}$$

- Rhombohedral ($a=b=c$, $\alpha=\beta=\gamma$.)

$$\begin{Bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & & \\ \cdot & C_{11} & C_{13} & -C_{14} & & \\ \cdot & \cdot & C_{33} & & & \\ \cdot & & & C_{44} & & \\ & & & & C_{44} & C_{14} \\ & & & & \cdot & C_{66} \end{Bmatrix}$$

- Orthorhombic ($a\neq b\neq c$, $\alpha=\beta=\gamma=90$)

$$\begin{Bmatrix} C_{11} & C_{12} & C_{13} & & & \\ \cdot & C_{22} & C_{23} & & & \\ \cdot & \cdot & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{55} & \\ & & & & & C_{66} \end{Bmatrix}$$

- Triclinic ($a\neq b\neq c$, $\alpha\neq\beta\neq\gamma\neq 90$)

$$\begin{Bmatrix} \\ \text{All.} \\ \\ \end{Bmatrix}$$

Moon et. al.
CCR 2015.

· Bulk modulus $\quad B \equiv -V\left(\frac{\partial P}{\partial V}\right)_T$

· Cubic case. ($C_{11}, C_{12}, C_{44} \neq 0$)

· Another definition of B.

$$U = \frac{1}{2} B \delta^2 \quad : \delta = \text{volumetric strain.}$$

∴ Isotropic pressure condition ($\underset{1}{e_{xx}} = \underset{2}{e_{yy}} = \underset{3}{e_{zz}} = \frac{1}{3}\delta$)

$$U = \frac{1}{2} \sum_{i=1}^{6} \sum_{j=1}^{6} C_{ij} e_i e_j$$

$$= \frac{1}{6}(C_{11} + 2C_{12})\delta^2.$$

숙제

No.

뒷장에

$$\therefore \quad B = \frac{1}{3}(C_{11} + 2C_{12})$$

cf. B from u_{tot} $\Rightarrow$ $B = \frac{\sqrt{2}}{9R^*}\left(\frac{\partial^2 u_{tot}}{\partial R^2}\right)_{R^*}$

(FCC)

차이 설명.

$B \leftarrow U$ 두번 미분 V or R.

(u_{tot}) B가 원자간 거리의 bond 에서 부터 구한 식

$B \leftarrow$ isotropic pressure condition ($e_1 = e_2 = e_3 = \frac{1}{3}\delta$)

(C_{ij}) 로부터 구한 식

$$\frac{1}{2}\left\{\begin{array}{cccccc}
\boxed{C_{11}e_1e_1} & \cancel{C_{21}e_2e_1} & \cancel{C_{31}} & \cancel{C_{41}} & \cancel{C_{51}} & \cancel{C_{61}} \\
C_{12}e_1e_2 & \boxed{C_{22}e_2e_2} & & & 0 & \\
C_{13}e_1e_3 & & \boxed{C_{33}e_3e_3} & & & \\
C_{14}e_1e_4 & & & \boxed{C_{44}e_4e_4} & & \\
C_{15}e_1e_5 & 0 & 0 & & \boxed{C_{55}e_5e_5} & \\
C_{16}e_1e_6 & & & & & \boxed{C_{66}e_6e_6}
\end{array}\right\}$$

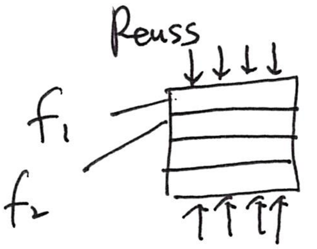
$\frac{1}{2}$

$$\frac{1}{2}\cdot 3\cdot C_{11}\cdot\left(\frac{1}{9}\delta^2\right) + \frac{1}{2}\cdot 6\cdot C_{12}\left(\frac{1}{9}\delta^3\right)$$

$$=\left(\frac{1}{6}C_{11} + \frac{2}{6}C_{12}\right)\delta^2$$

· Avg. Technique (Effective Medium Theories)

· Reuss - Voigt bound~~ary~~s

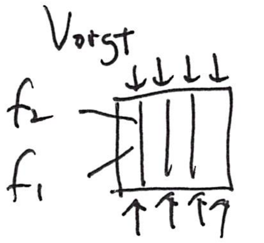


equal stress. $\hat{E} = \frac{\hat{\sigma}}{\hat{\varepsilon}} = \frac{\hat{\sigma}}{\Sigma f_i \varepsilon_i} = \frac{\hat{\sigma}}{\Sigma f_i \left(\frac{\hat{\sigma}}{E_i}\right)}$

<Lower>

$\Rightarrow \frac{1}{\hat{E}} = \Sigma \frac{f_i}{E_i}$

↳ isostress situation (perfect for fluid mixture)



equal strain $\hat{E} = \frac{\hat{\sigma}}{\hat{\varepsilon}} = \frac{\Sigma f_i \sigma_i}{\hat{\varepsilon}} = \frac{\Sigma f_i (\hat{\varepsilon} E_i)}{\hat{\varepsilon}}$

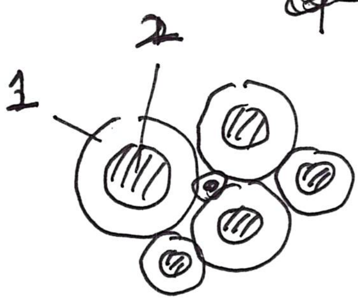
<upper>

$\Rightarrow \hat{E} = \Sigma f_i E_i$

· Hashin - Strikman bounds. (narrower than RV bound)

$$\cancel{K^{HS} = K_1 + \frac{f_2}{(K_2-K_1)^{-1} + f_1\left(K_1+\frac{4}{3}G_1\right)^{-1}}}$$

$$K_1 + \frac{f_2}{\frac{1}{K_2-K_1} + \frac{f_1}{K_1+\frac{4}{3}G_1}} \leq \hat{K} \leq K_2 + \frac{f_1}{\frac{1}{K_1-K_2} + \frac{f_2}{K_2+\frac{4}{3}G_2}}$$

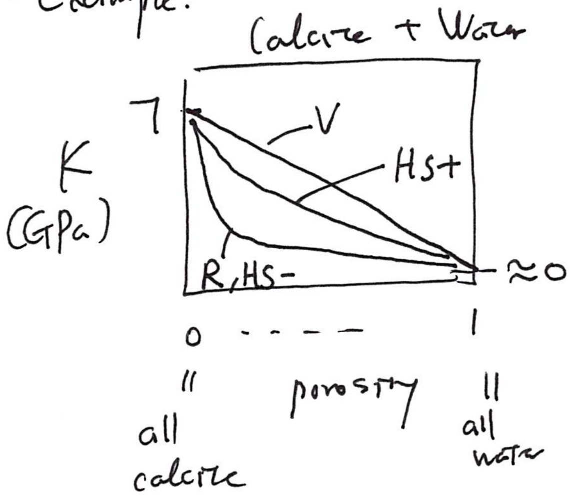


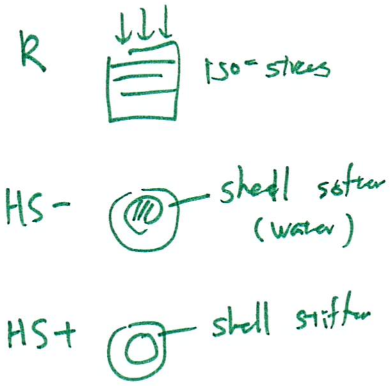
$$G_1 + \frac{f_2}{\frac{1}{G_2-G_1} + \frac{6(K_1+2G_1)f_1}{5(3K_1+4G_1)G_1}} \leq \hat{G} \leq G_2 + \frac{f_1}{\frac{1}{G_1-G_2} + \frac{6(K_2+2G_2)f_2}{5(3K_2+4G_2)G_2}}$$

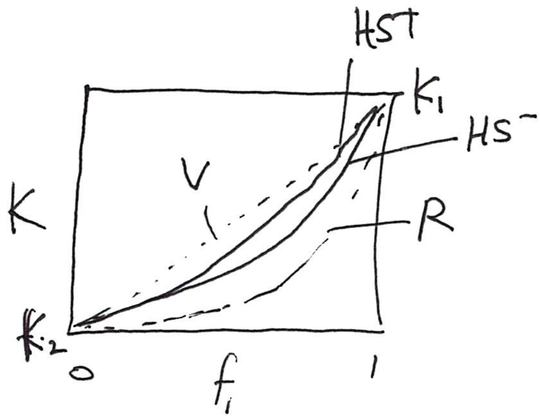
~~If shell is stiffer, <upper> $(K_1, G_1) > (K_2, G_2)$ <lower> (shell is softer)~~

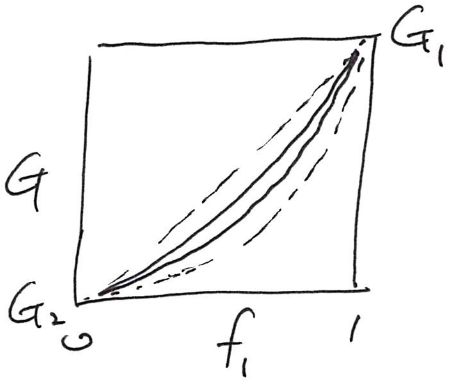
<lower> shell softer <upper> shell stiffer

· Example.









wideness depends on relative stiffness of material, shape of components, porosity

K or G (similarity / difference)

Metal : Iron-carbon systems

· Solid phases in the Fe-Fe_3C Phase diagram.

ferrite(α) : interstitial solid solution of carbon in BCC iron crystal.
carbon is only slightly soluble in ~~α~~ ferrite (α)
max. solubility of 0.02 % at 723°C

same

ferrite (δ) (delta iron) : ______________________
but with a greater lattice constant.
max. solubility of 0.09 % at 1465°C.

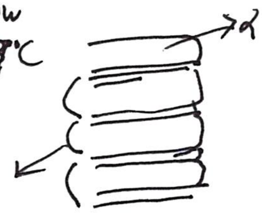
higher solubility

Austenite (γ) : " FCC "
higher solubility of 2.08 % at 1148°C
↓
0.8 % at 723°C

Cementite (Fe_3C) : Intermetallic compound Fe_3C.
6.67 % C + 93.3 % Fe.
hard and brittle.

perlite

$\gamma \rightarrow \alpha + Fe_3C$.
below 723°C



C diffuses from γ to Fe_3C

Fe diffuses from γ to α.

· Mechanical properties

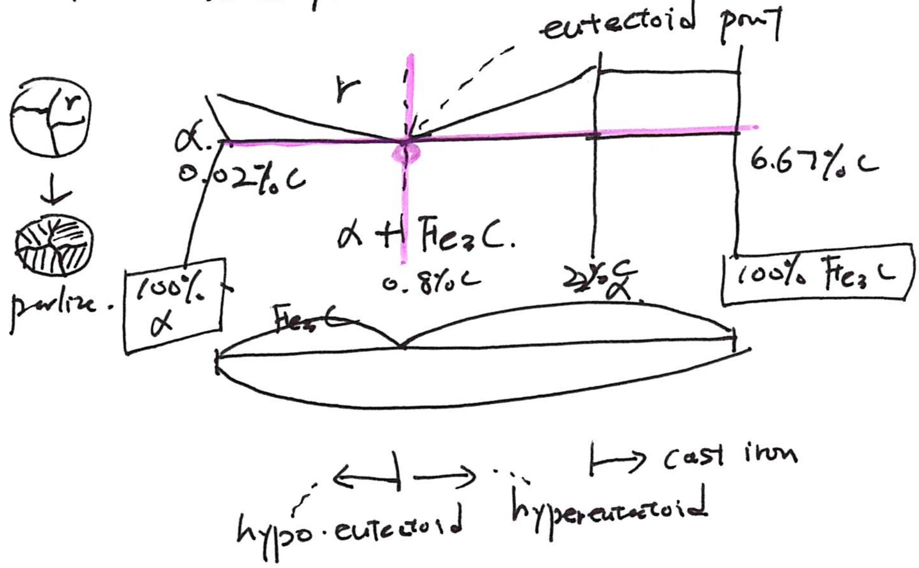
		Strength	Ductility
low C%	 perlite, α.	↓	↑
high C%	 perlite, Fe_3C	↑	↓

Example #1

just below

A 0.8 % C plain-carbon steel cooled from 750 → 723°C.

γ → α + ferrite.
(100% pearlite)



$$\alpha\% = \frac{6.67-0.8}{6.67-0.02}\times 100$$

$$= 88.3\%$$

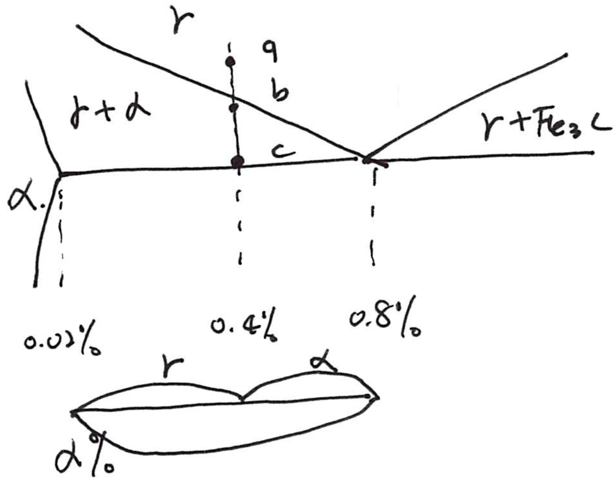
$$Fe_3C\% = \frac{0.8-0.02}{6.67-0.02}\times 100$$

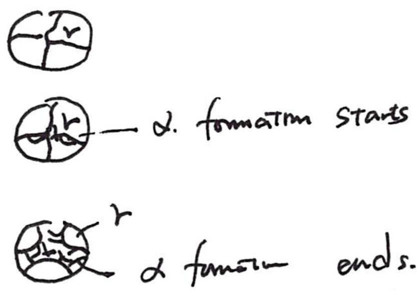
$$= 11.7\%$$

1.2% 속께 α 대신 Fe₃C 만 나오게.

Example #2.

A 0.4 % C plain-carbon steel cooled from 940°C → just above 723°C

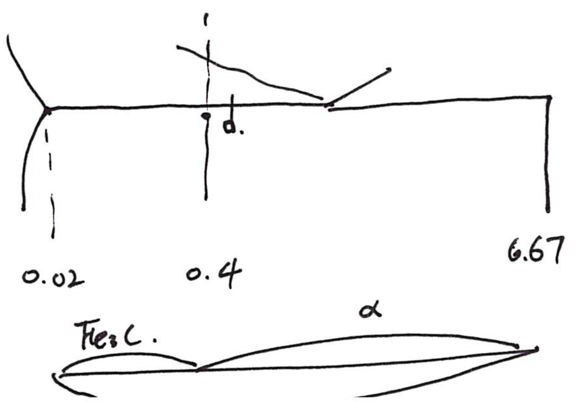




$$\alpha\% = \frac{0.8-0.4}{0.8-0.02}\times 100 = 50\%$$

$$\gamma = \frac{0.4-0.02}{0.8-0.02}\times 100 = 50\%$$

Same steel → just below 723 °C



$$\alpha\% = \frac{6.67-0.4}{6.67-0.02}\times 100 = 94.3\%$$

⇒ total α.

$$Fe_3C = \frac{0.4-0.02}{6.67-0.02}\times 100 = 5.7\%$$

α in pearlite = 94.3% − 50% = 44.3%