2019. 4. 2. ①

중간상
- Reciprocal vector 재정의. , Brass condition & Laue condition.
- Translation 이전 ③
- BCC.

수업.
- FCC
- XRD refinement. - prefer orientation
  microstrain
  size
  background fn.
  R.
  refine peak 좁히기

과제2 → 4.9. (XRD, TGA., 콘크리트 bond 종류. → 에너지 - 힘.) ← XRD 결과 토의. Glass
과제3 → 4.16 steel restraint. , phase diagram.
과제3 → 4.23 시험

Translation of $\vec{G}$

$\vec{G}$: a set of reciprocal lattice vectors

이전 Note ③

Flourier Analysis of the Basis

- Scattering amplitude., F_G for N cells.

$$F_G = N \int_{cell} dV\, n(\vec{r}) \exp(-i \vec{G}\cdot\vec{r}) = N S_G$$

$n(\vec{r})$: electron concentration.

$\exp(-i\vec{G}\cdot\vec{r})$ (=) Structure factor.

Note; Previously Intensity $\propto \left| \int_{\vec{r}} n(\vec{r})\, e^{i(\vec{k}-\vec{k}')\vec{r}} \right|^2$.

$$S_G = \int_{cell} dV\, n(\vec{r}) \exp(-i\vec{G}\cdot\vec{r}) \quad \rightarrow \text{for one cell.}$$

④

$$= \sum_j \int dV\, n_j(\vec{r}-r_j) \exp(-i\vec{G}\cdot\vec{r}) \quad \rightarrow \text{for all basis } j \text{ in one cell}$$

$$= \sum_j \exp(-i\vec{G}\cdot r_j) \int dV\, n_j(\vec{\rho}) \exp(-i\vec{G}\cdot\vec{\rho}) \quad \text{where } \vec{\rho} = \vec{r} - r_j$$

f_j = atomic form factor. (원자 종류 (전자갯수))

$$\Rightarrow S_G = \sum_j f_j \exp(-i\vec{G}\cdot r_j)$$

if $r_j = x_j a_1 + y_j a_2 + z_j a_3$

$\vec{G} = \nu_1 b_1 + \nu_2 b_2 + \nu_3 b_3$, then

$$\vec{G}\cdot r_j = (\nu_1 b_1 + \nu_2 b_2 + \nu_3 b_3)\cdot(x_j a_1 + y_j a_2 + z_j a_3)$$

$$= 2\pi(\nu_1 x_j + \nu_2 y_j + \nu_3 z_j) \qquad (a_i b_j = 2\pi\delta_{ij})$$

Also,

$$S_G = \sum_j f_j \exp[-i2\pi(\nu_1 x_j + \nu_2 y_j + \nu_3 z_j)]$$

Example BCC

BCC = SC + 2 basis $\begin{cases} x_1 = y_1 = z_1 = 0 & \text{atom \#1} \\ x_2 = y_2 = z_2 = \frac{1}{2} & \text{atom \#2.} \end{cases}$

$$S_G = f_1 \exp[-i2\pi(0)]$$

$$+ f_2 \exp[-i2\pi(\tfrac{1}{2}\nu_1 + \tfrac{1}{2}\nu_2 + \tfrac{1}{2}\nu_3)]$$

$$\left(\text{if } f_1 = f_2 = f,\right) = f[1 + \exp[-i\pi(\nu_1 + \nu_2 + \nu_3)]]$$

$\Rightarrow S_G = 0$, when $\nu_1 + \nu_2 + \nu_3 =$ odd

$S_G = 2f$, when " = even

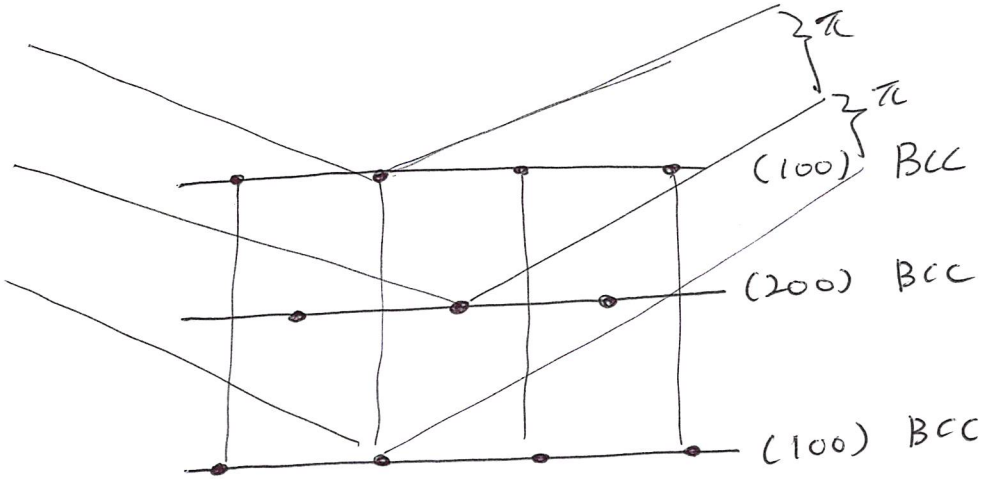
cf.) $e^{-ix} = \cos x - i\sin x$.

$x =$ even, $e^{-ix\pi} = 1$

(100), (300), (111) or (221) → No peaks

(200), (110), (222) → peaks present

Note: (V_1, V_2, V_3) indices are refered to a cubic cell.
conventional lattice
(h, k, ℓ)
(= primitive SC)



$K = \frac{2\pi}{\lambda}$; (100) 차이는 2π → constructive interference 보강간섭

(100), (200) π → destructive " 상쇄간섭

~~Example KU~~ ,

Example FCC.

↳ SSP KCl, KBr 예제 참고.

$$(x_j, y_j, z_j)$$

FCC = SC + 4 basis $\begin{cases} (0,0,0) \\ (0,\frac{1}{2},\frac{1}{2}) \\ (\frac{1}{2},0,\frac{1}{2}) \\ (\frac{1}{2},\frac{1}{2},0) \end{cases}$

$$S_G = f\left[1 + \exp[-i\pi(\nu_2+\nu_3)] + \exp[-i\pi(\nu_1+\nu_3)] + \exp[-i\pi(\nu_1+\nu_2)]\right]$$

All even → $S_G = 4f$

All odd → 〃

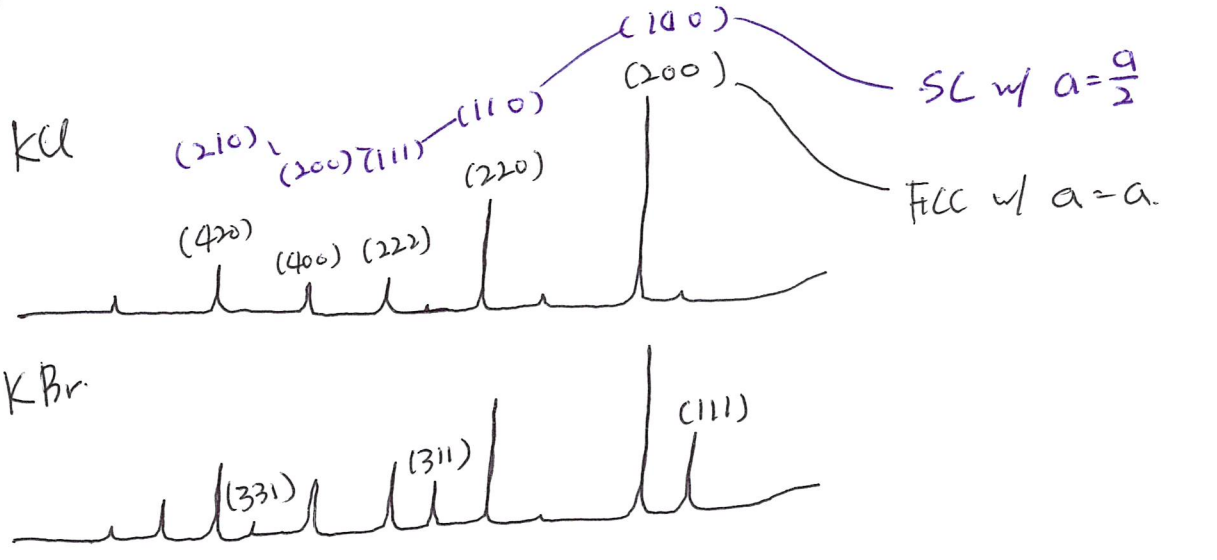
one even → 0

one odd → 0

Br 35번 전자-35개.
K 19번 전자-19개
Cl 17번 전자-17개.

e.g.) KCl ⇒ $K^+ + Cl^-$ (Ionic bond), FCC; $f(K^+) \approx f(Cl^-)$

KBr ⇒ $K^+ + Br^-$ (〃), 〃), $f(K^+) \not\approx f(Br^-)$

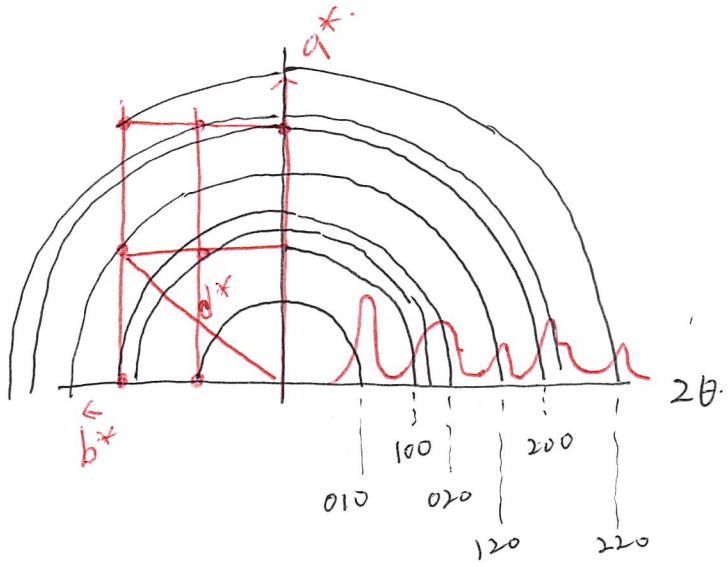


Summary

(h, k, l) → crystal system

position $(2\theta, d, \phi)$ → lattice parameter.

Intensity → type (bond, atomic, $n(\vec{\rho})$)



Classification of Methods.

Quantitative Analysis.

	Profile fitting	Whole-pattern decomposition	Rietveld refinement
Aim of analysis	Pattern decomposition	Pattern decomposition and refinement of unit cell parameters	Structure refinement
Range of analysis	Local peaks or peak clusters	whole pattern	Whole pattern
Peak position	Independent parameters	Function of unit cell parameters.	=
Integrated intensities (profile area)	//	=	Function of structural parameters
Initial parameters required to start refinement	Nil	Approximate unit cell parameters.	Initial structural parameters (structural models)

Profile shape functions

Intensity

Gaussian $G = I_0 \exp\left\{-\ln 2\left(\frac{2\theta - 2\theta_0}{w}\right)^2\right\}$

Lorentzian $L = I_0 \left\{1 + \left(\frac{2\theta - 2\theta_0}{w}\right)^2\right\}^{-n}$; $n = 1; 1.5; 2$

Pseudo-Voigt $V = \eta L + (1-\eta) G$; $(0 \le \eta \le 1)$

Pearson VII $P = I_0 \left\{1 + \left(\frac{2\theta - 2\theta_0}{m a^2}\right)^2\right\}^{-m}$

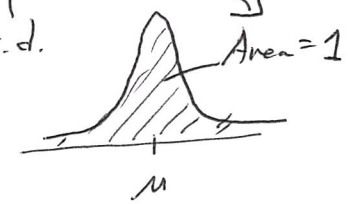
$2\theta_0$ = peak position.
I_0 = peak intensity
w = FWHM / 2.
m = shape parameter.

Note; $(FWHM)_k = U \tan^2\theta_k + V \tan\theta_k + W$

Note; Gaussian distribution (Normal)

$$f(x \mid \mu, \sigma^2) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

mean, s.d.



Definition of R-indices. = goodness of fit

$$R_F = \frac{\sum \left| (I_k(obs))^{1/2} - (I_k(calc))^{1/2} \right|}{\sum (I_k(obs))^{1/2}}$$

$$R_B = \frac{\sum \left| (I_k(obs)) - (I_k(calc)) \right|}{\sum I_k(obs)}$$

$$R_p = \frac{\sum \left| y_i(obs) - \left(\frac{1}{c}\right) y_i(calc) \right|}{\sum y_i(obs)}$$

$$R_{wp} = \left[\frac{\sum w_i \left(y_i(obs) - \left(\frac{1}{c}\right) y_i(calc)\right)^2}{\sum w_i (y_i(obs))^2} \right]^{1/2}$$