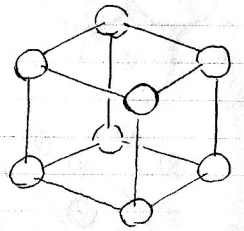
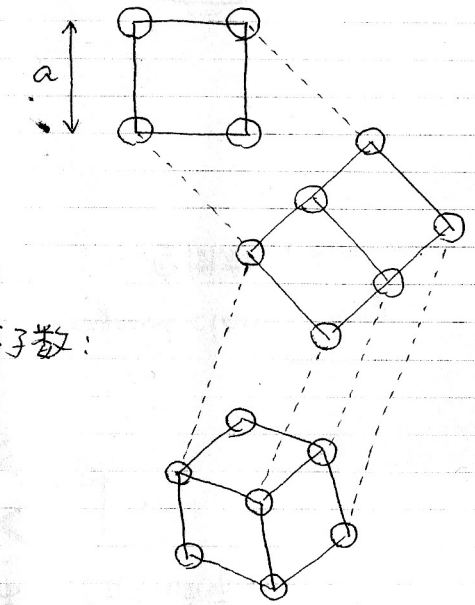
固体化学 資料

1. 単体の結晶構造

1-1 単純立方構造 simple cubic

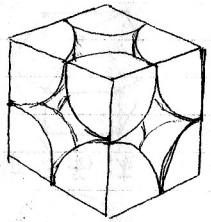


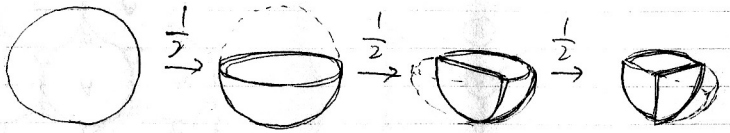


空間群：$Pm\bar{3}m$

単位格子内の原子数：

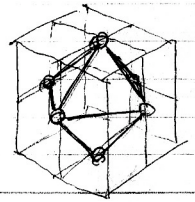
$\frac{1}{8} \times 8 = 1$



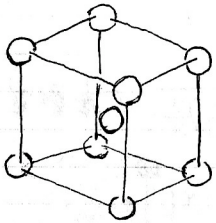


充填率：$\frac{\frac{\pi}{6}a^3}{a^3} = \frac{\pi}{6} = 0.523599\cdots$

配位多面体：正八面体
(六配位)



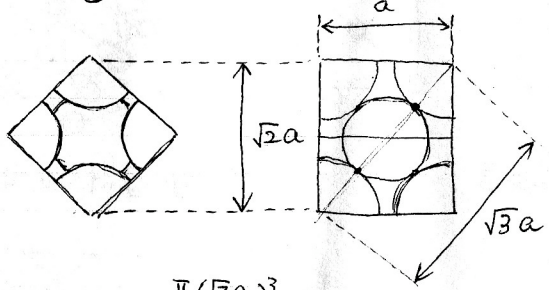
1-2 体心立方構造 body center cubic



空間群：$Im\bar{3}m$

単位格子あたりの原子数：

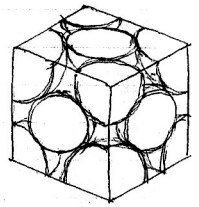
$\frac{1}{8} \times 8 + 1 = 2$

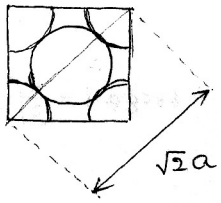


充填率：$\frac{\frac{\pi}{6}\left(\frac{\sqrt{3}a}{2}\right)^3 \times 2}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.680175\cdots$

1-3 面心立方構造 face center cubic
立方最密充填 cubic close packing

空間群：$Fm\bar{3}m$

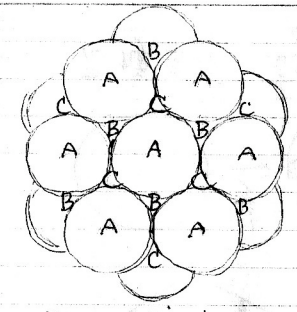


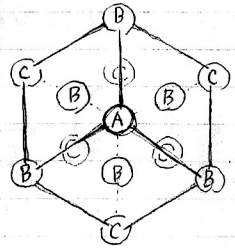


単位格子あたりの原子数：

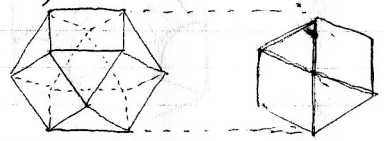
$\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

充填率 $\frac{\frac{\pi}{6}\left(\frac{a}{\sqrt{2}}\right)^3 \times 4}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.740480\cdots$





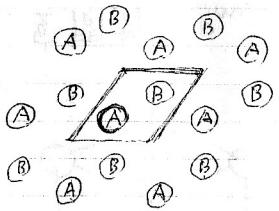
配位多面体 ： 十四面体 (立方八面体 cuboctahedron)

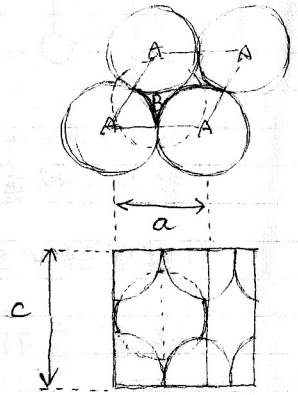


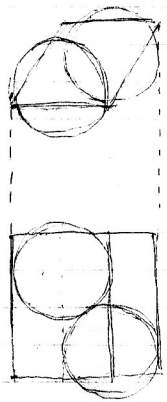
配位数 12

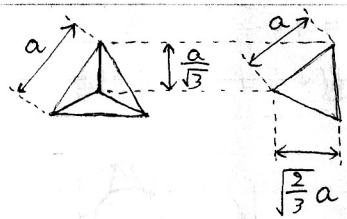
1-4 六方最密充填構造 hexagonal close packing

空間群 $P6_3/mmc$







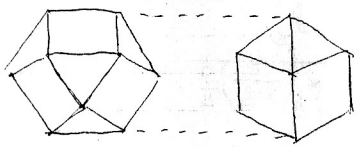


軸比

$$\frac{c}{a} = 2\sqrt{\frac{2}{3}} = 1.63299\cdots$$

充填率 $\dfrac{\frac{\pi}{6}a^3 \times 2}{a \times a \times \frac{\sqrt{3}}{2} \times c} = \dfrac{\pi}{3\sqrt{2}} = 0.740480\cdots$

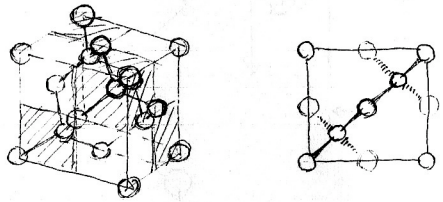
配位多面体 ： 十四面体



配位数 12

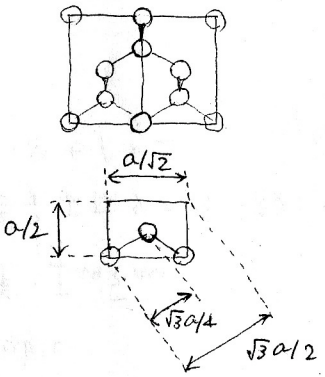
1-5 ダイヤモンド型構造

空間群 $Fd\bar{3}m$



充填率 ： $\dfrac{\frac{\pi}{6}\left(\frac{\sqrt{3}a}{4}\right)^3 \times 8}{a^3} = \dfrac{\sqrt{3}\pi}{16}$

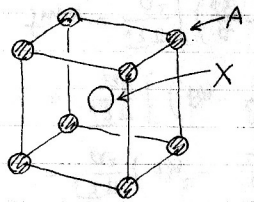
$= 0.340087\cdots$



2. 二元系の結晶構造

2-1 塩化セシウム型構造
CsCl 型

空間群 $Pm\bar{3}m$



充填率： $f = \dfrac{\frac{\pi}{6}D_A^3 + \frac{\pi}{6}D_X^3}{a^3} = \dfrac{\pi}{6a^3}(D_A^3 + D_X^3)$

$$\begin{cases} 0 < D_A \leq a \\ 0 < D_X \leq a \\ D_X + D_A = \sqrt{3}a \end{cases}$$

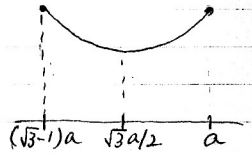
$$f = \frac{\pi}{6a^3}\left[D_A^3 + (\sqrt{3}a - D_A)^3\right] = \frac{\pi}{6a^3}\left(3\sqrt{3}a^3 - 9a^2 D_A + 3\sqrt{3}a D_A^2\right)$$

$$= \frac{\sqrt{3}\pi}{2a^2}\left(D_A^2 - \sqrt{3}a D_A + a^2\right) = \frac{\sqrt{3}\pi}{2a^2}\left[\left(D_A - \frac{\sqrt{3}a}{2}\right)^2 - \frac{3a^2}{4} + a^2\right]$$

$$= \frac{\sqrt{3}\pi}{2a^2}\left[\left(D_A - \frac{\sqrt{3}a}{2}\right)^2 + \frac{a^2}{4}\right]$$

$$\begin{cases} 0 < D_A \leq a \\ 0 < \sqrt{3}a - D_A \leq a \end{cases}$$

$$\Rightarrow (\sqrt{3}-1)a \leq D_A \leq a$$

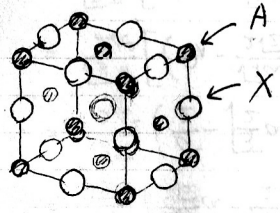


最大 $f_{max} = \dfrac{\sqrt{3}\pi}{2}\left[\left(1 - \frac{\sqrt{2}}{2}\right)^2 + \frac{1}{4}\right] = \dfrac{\sqrt{3}\pi}{2}\left(1 - \sqrt{3} + \frac{3}{4} + \frac{1}{4}\right)$

$$= \frac{\sqrt{3}(2-\sqrt{3})\pi}{2} = \frac{(2\sqrt{3}-3)\pi}{2} = 0.\times\times 9090\ldots$$

2-2 岩塩型構造
rock salt
NaCl 型

空間群 $Fm\bar{3}m$



充填率： $f = \dfrac{\frac{\pi}{6}D_A^3 \times 4 + \frac{\pi}{6}D_X^3 \times 4}{a^3} = \dfrac{2\pi}{3a^3}(D_A^3 + D_X^3)$

$$\begin{cases} 0 < D_A \leq a/\sqrt{2}, \quad 0 < D_X \leq a/\sqrt{2} \\ D_A + D_X = a \end{cases}$$

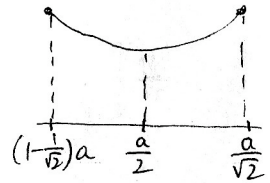
$$f = \frac{2\pi}{3a^3}\left[D_A^3 + (a - D_A)^3\right] = \frac{2\pi}{3a^3}\left(a^3 - 3a^2 D_A + 3a D_A^2\right)$$

$$= \frac{2\pi}{a^2}\left(D_A^2 - a D_A + \frac{a^2}{3}\right) = \frac{2\pi}{a^2}\left[\left(D_A - \frac{a}{2}\right)^2 - \frac{a^2}{4} + \frac{a^2}{3}\right]$$

$$= \frac{2\pi}{a^2}\left[\left(D_A - \frac{a}{2}\right)^2 + \frac{a^2}{12}\right]$$

$$\begin{cases} 0 < D_A \leq a/\sqrt{2} \\ 0 < a - D_A \leq a/\sqrt{2} \end{cases}$$

$$\Rightarrow (1 - 1/\sqrt{2})a \leq D_A \leq a/\sqrt{2}$$



最大 $f_{max} = 2\pi\left[\left(\frac{1}{\sqrt{2}} - \frac{1}{2}\right)^2 + \frac{1}{12}\right]$

$$= 2\pi\left(\frac{1}{2} - \frac{1}{\sqrt{2}} + \frac{1}{4} + \frac{1}{12}\right) = \left(\frac{5}{3} - \sqrt{2}\right)\pi$$

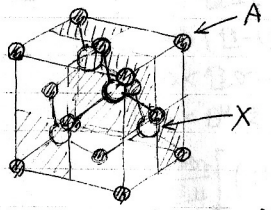
$$= 0.793105\ldots$$

2-3 閃亜鉛鉱型構造

Zinc blende

ZnS 型

空間群 $F\bar{4}3m$

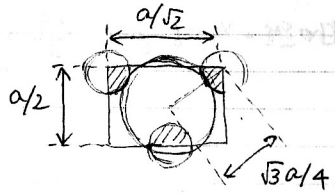


充填率 $f = \dfrac{\frac{\pi}{6}\Phi_A^3 \times 4 + \frac{\pi}{6}\Phi_X^3 \times 4}{a^3} = \dfrac{2\pi}{3a^3}(\Phi_A^3 + \Phi_X^3)$

$$\begin{cases} 0 < \Phi_A \leqq a/\sqrt{2} \\ 0 < \Phi_X \leqq a/\sqrt{2} \\ \Phi_A + \Phi_X = \sqrt{3}a/2 \end{cases}$$

$$\Rightarrow \begin{cases} 0 < \Phi_A \leqq a/\sqrt{2} \\ 0 < \sqrt{3}a/2 - \Phi_A \leqq a/\sqrt{2} \end{cases}$$

$$\Rightarrow (\sqrt{3}/2 - 1/\sqrt{2})a \leqq \Phi_A \leqq a/\sqrt{2}$$



$$f = \frac{2\pi}{3a^3}\left[\Phi_A^3 + \left(\frac{\sqrt{3}a}{2} - \Phi_A\right)^3\right] = \frac{2\pi}{3a^3}\left(\frac{3\sqrt{3}a^3}{8} - \frac{9a^2\Phi_A}{4} + \frac{3\sqrt{3}a}{2}\Phi_A^2\right)$$

$$= \frac{\sqrt{3}\pi}{a^2}\left(\Phi_A^2 - \frac{\sqrt{3}a}{2}\Phi_A + \frac{a^2}{4}\right) = \frac{\sqrt{3}\pi}{a^2}\left[\left(\Phi_A - \frac{\sqrt{3}a}{4}\right)^2 - \frac{3a^2}{16} + \frac{a^2}{4}\right]$$

$$= \frac{\sqrt{3}\pi}{a^2}\left[\left(\Phi_A - \frac{\sqrt{3}a}{4}\right)^2 + \frac{a^2}{16}\right]$$

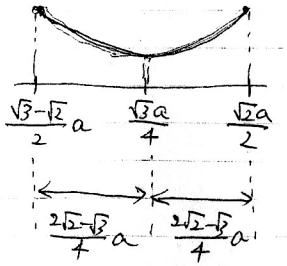
$$f_{max} = \frac{\sqrt{3}\pi}{a^2}\left[\left(\frac{a}{\sqrt{2}} - \frac{\sqrt{3}a}{4}\right)^2 + \frac{a^2}{16}\right]$$

$$= \sqrt{3}\pi\left(\frac{1}{2} - \frac{\sqrt{3}}{2\sqrt{2}} + \frac{3}{16} + \frac{1}{16}\right)$$

$$= \sqrt{3}\left(\frac{3}{4} - \frac{\sqrt{3}}{2\sqrt{2}}\right)\pi$$

$$= \left(\frac{3\sqrt{3}}{4} - \frac{3}{2\sqrt{2}}\right)\pi$$

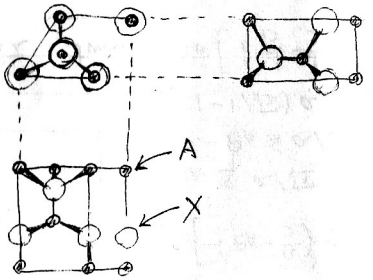
$$= \frac{3}{2}\left(\frac{\sqrt{3}}{2} - \frac{1}{\sqrt{2}}\right)\pi = 0.748860\cdots$$

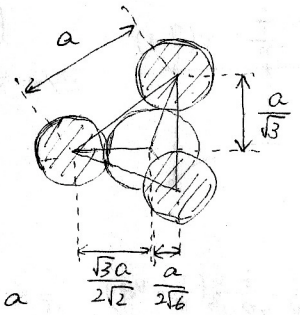


2-4 ウルツ鉱型構造

Wurtzite

空間群 $P6_3mc$





$$\begin{cases} 0 < \Phi_A \leqq a \\ 0 < \Phi_X \leqq a \\ \Phi_A + \Phi_X = \sqrt{3/2}\,a \end{cases} \Rightarrow \begin{cases} 0 < \Phi_A \leqq a \\ 0 < \sqrt{3/2}\,a - \Phi_A \leqq a \end{cases}$$

$$\Rightarrow (\sqrt{3/2} - 1)a \leqq \Phi_A \leqq a$$

$$f = \frac{\frac{\pi}{6}\Phi_A^3 \times 2 + \frac{\pi}{6}\Phi_X^3 \times 2}{\sqrt{2}a^3} = \frac{\pi}{3\sqrt{2}a^3}(\Phi_A^3 + \Phi_X^3)$$

$$= \frac{\pi}{3\sqrt{2}a^3}\left[\Phi_A^3 + (\sqrt{3/2}\,a - \Phi_A)^3\right]$$

$$= \frac{\pi}{3\sqrt{2}a^3}\left(\frac{3\sqrt{3}}{2\sqrt{2}}a^3 - \frac{9a^2}{2}\Phi_A + \frac{3\sqrt{3}}{\sqrt{2}}a\Phi_A^2\right)$$

$$= \frac{\sqrt{3}\pi}{2a^2}\left(\frac{a^2}{2} - \sqrt{\frac{3}{2}}a\Phi_A + \Phi_A^2\right)$$

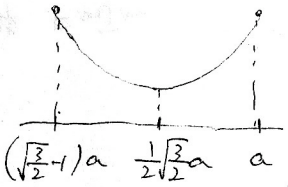
$$= \frac{\sqrt{3}\pi}{2a^2}\left[\left(\Phi_A - \frac{\sqrt{3}a}{2\sqrt{2}}\right)^2 - \frac{3a^2}{8} + \frac{a^2}{2}\right]$$

$$= \frac{\sqrt{3}\pi}{2a^2}\left[\left(\Phi_A - \frac{\sqrt{3}a}{2\sqrt{2}}\right)^2 + \frac{a^2}{8}\right]$$

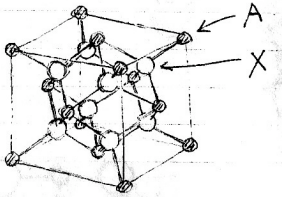
$$\longrightarrow \frac{\sqrt{3}\pi}{2}\left[\left(1 - \frac{\sqrt{3}}{2\sqrt{2}}\right)^2 + \frac{1}{8}\right]$$

$$= \frac{\sqrt{3}\pi}{2}\left(1 - \frac{\sqrt{3}}{\sqrt{2}} + \frac{3}{8} + \frac{1}{8}\right)$$

$$= \frac{\sqrt{3}\pi}{2}\left(\frac{3}{2} - \frac{\sqrt{3}}{\sqrt{2}}\right) = \frac{3}{2}\left(\frac{\sqrt{3}}{2} - \frac{1}{\sqrt{2}}\right)\pi \fallingdotseq 0.748860\cdots$$

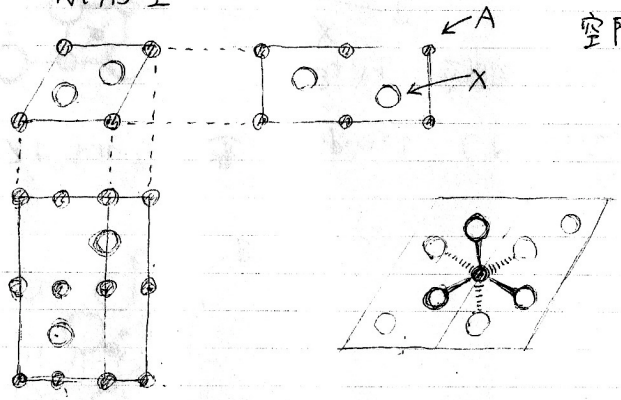


2-5 螢石(ホタルイシ)型構造
CaF_2 型



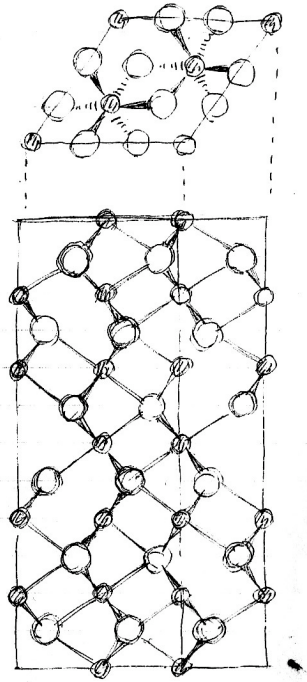
空間群：$Fm\bar{3}m$

2-6 ヒ化ニッケル型構造
NiAs 型

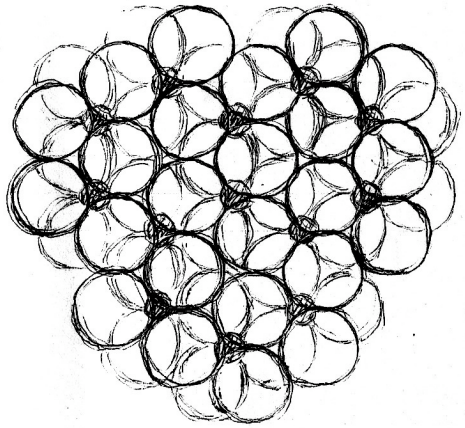


空間群 $P6_3/mmc$

2-7 コランダム構造 corundum



空間群 $R\bar{3}c$



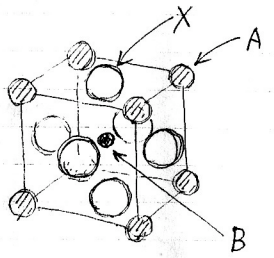
No. 11
Date

3. 三元系の構造

3-1 ペロブスカイト型構造　perovskite ($CaTiO_3$)

ABX_3

空間群 $Pm\bar{3}m$



3-2 スピネル型構造　spinel ($MgAl_2O_4$)

AB_2X_4　空間群 $Fd3m$