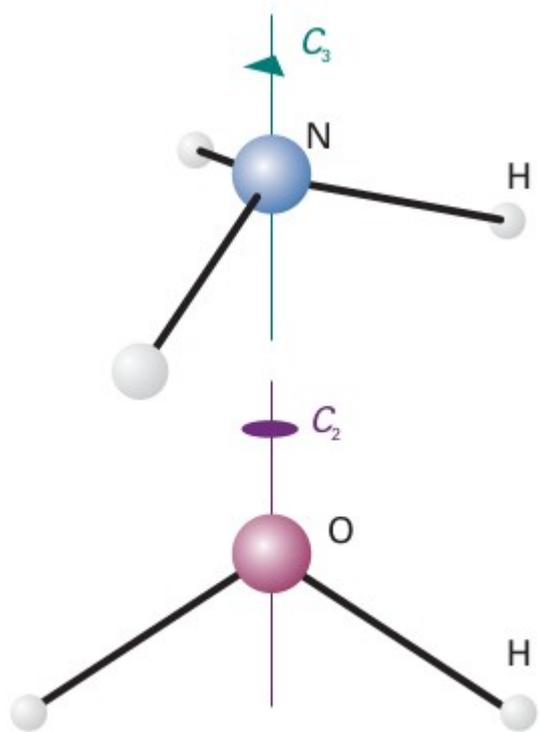


Кристаллохимия

Хохлов Даниил Витальевич

Олимпиадный сезон 2020-21

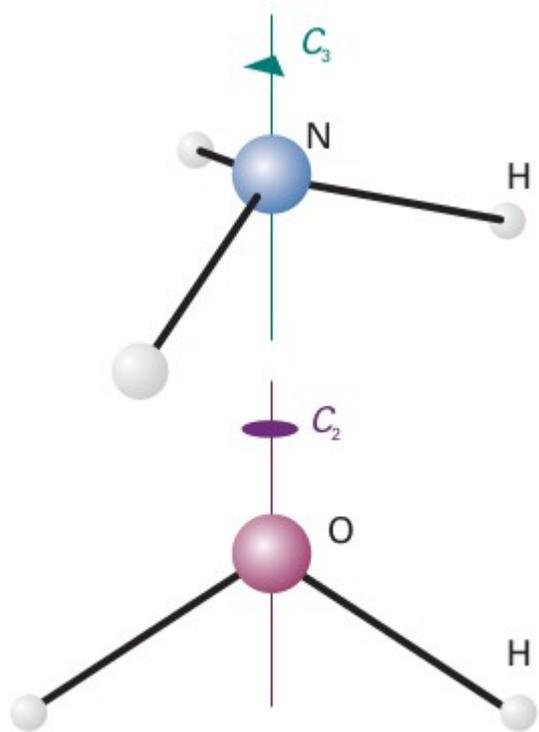
Элементы симметрии



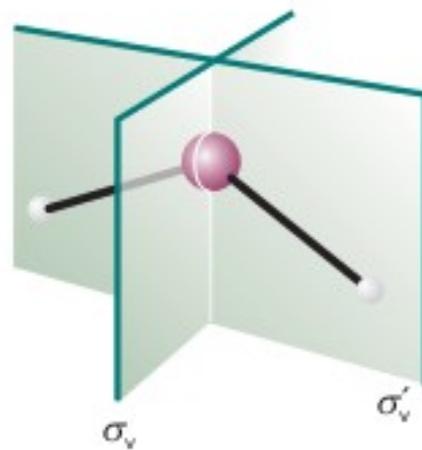
Поворотная ось C_n



Элементы симметрии



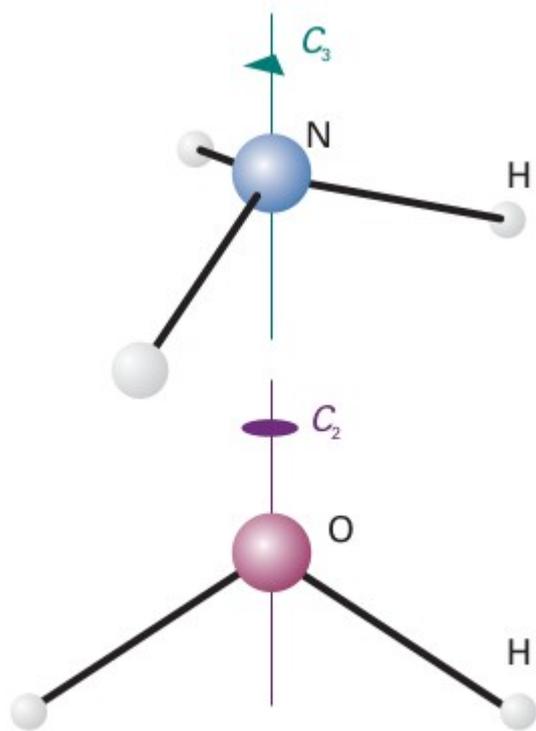
Поворотная ось C_n



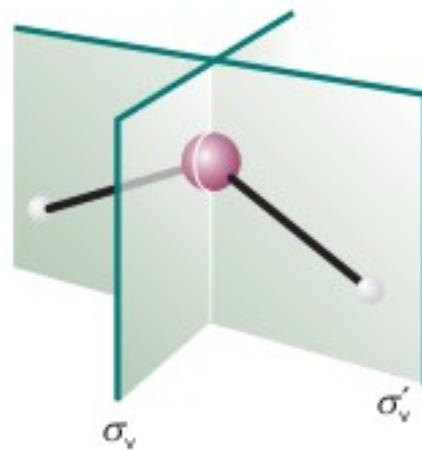
Плоскость симметрии σ



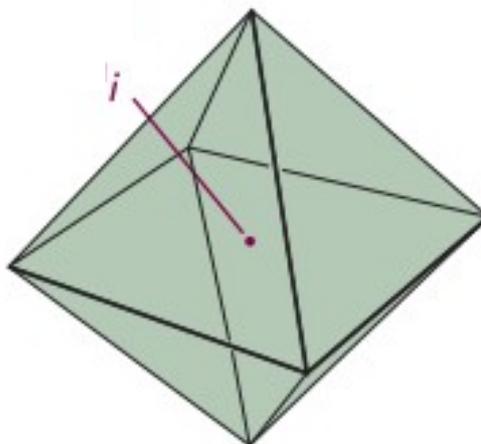
Элементы симметрии



Поворотная ось C_n



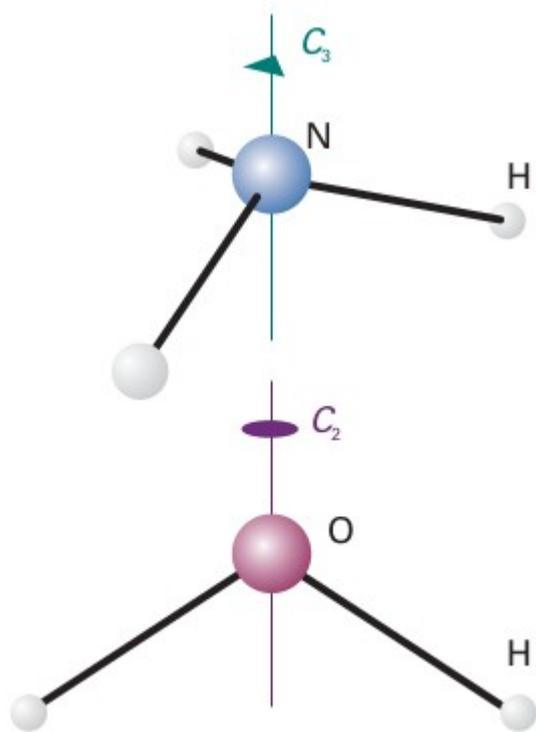
Плоскость симметрии σ



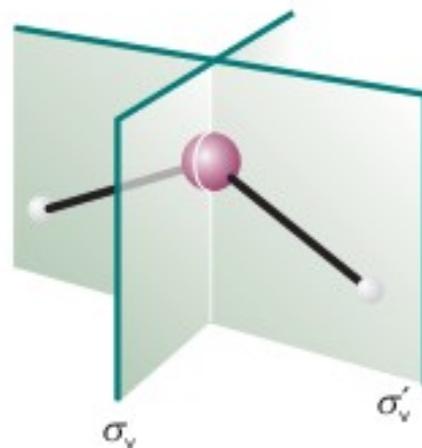
Центр инверсии i



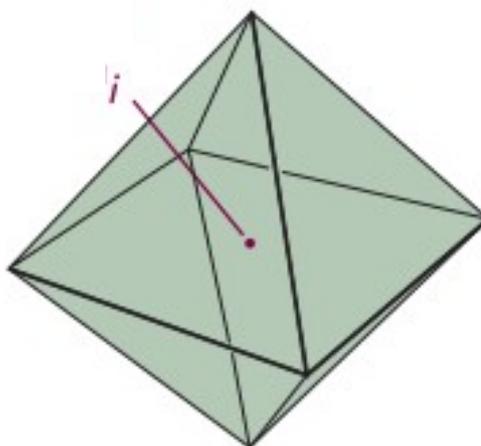
Элементы симметрии



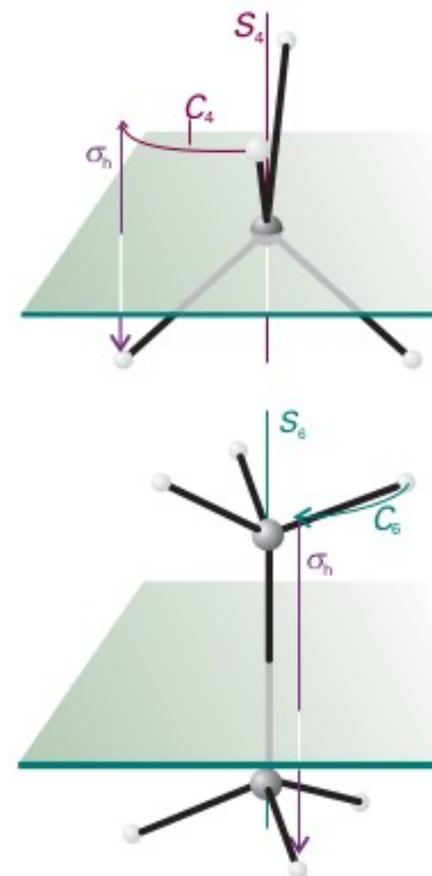
Поворотная ось C_n



Плоскость симметрии σ



Центр инверсии i



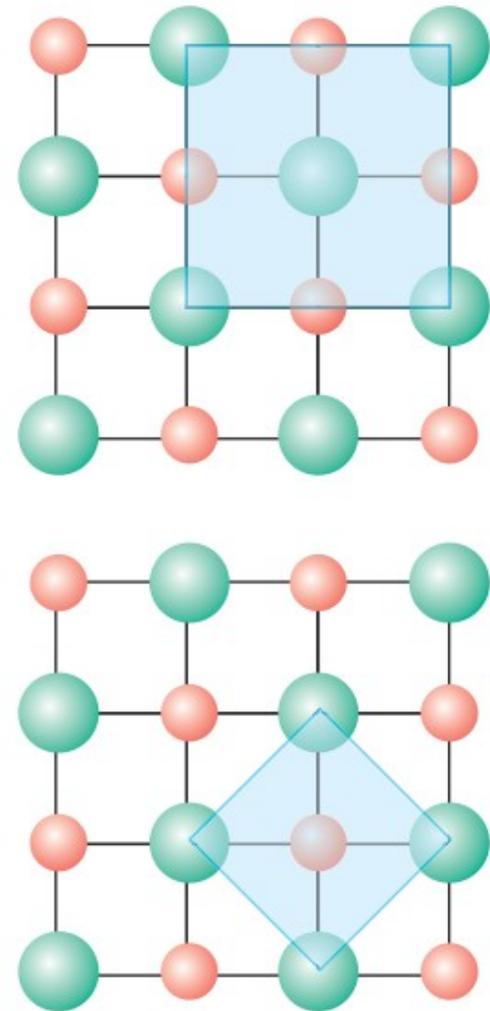
Зеркально-поворотная ось S_n



Кристалл

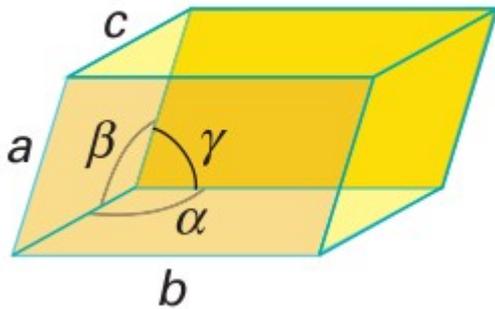
Элементарная ячейка:

- позволяет построить кристалл целиком только на основе трансляций
- имеет наименьший возможный объем



Сингонии

$$a \neq b \neq c$$
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

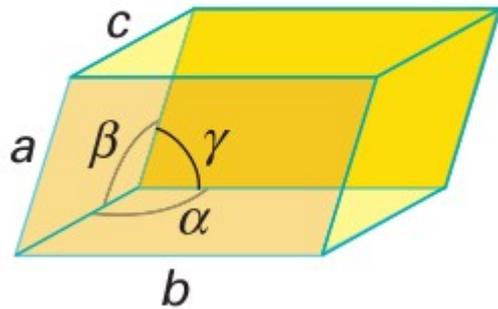


Триклинная



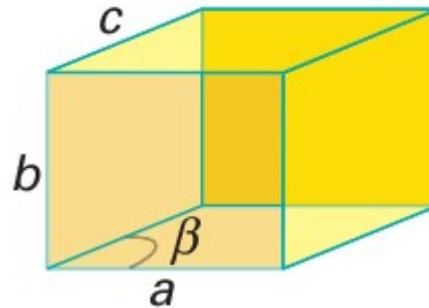
Сингонии

$$a \neq b \neq c$$
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



Триклинная

$$a \neq b \neq c$$
$$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$$

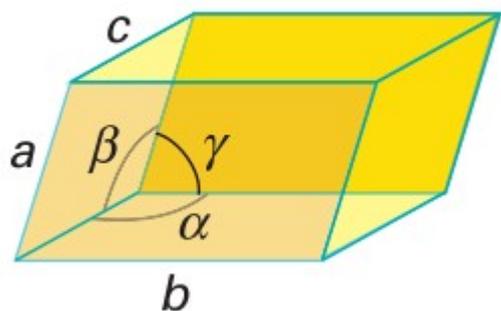


Моноклинная



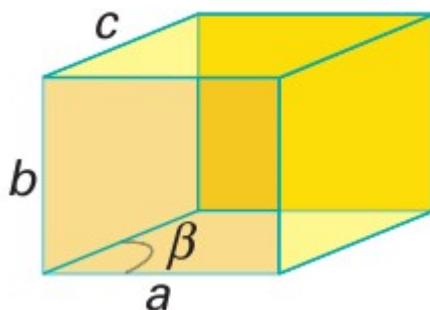
Сингонии

$$a \neq b \neq c$$
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



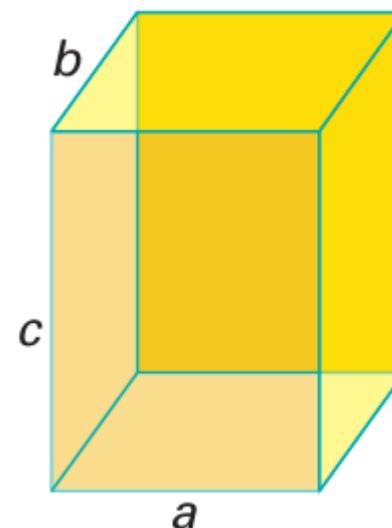
Триклинная

$$a \neq b \neq c$$
$$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$$



Моноклинная

$$a \neq b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$

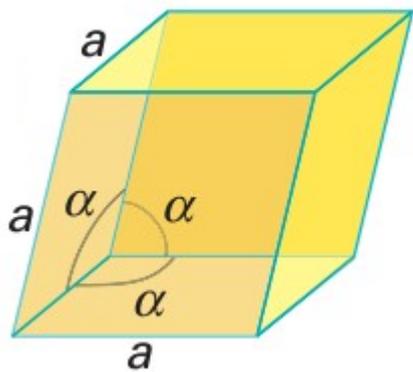


Ромбическая



Сингонии

$$a = b = c$$
$$\alpha = \beta = \gamma \neq 90^\circ$$

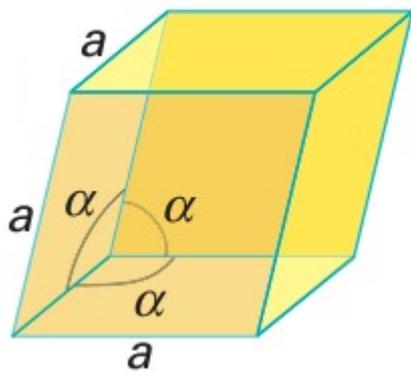


Ромбоэдрическая



Сингонии

$$a = b = c$$
$$\alpha = \beta = \gamma \neq 90^\circ$$

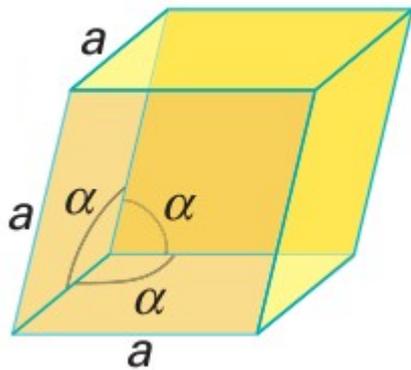


Ромбоэдрическая



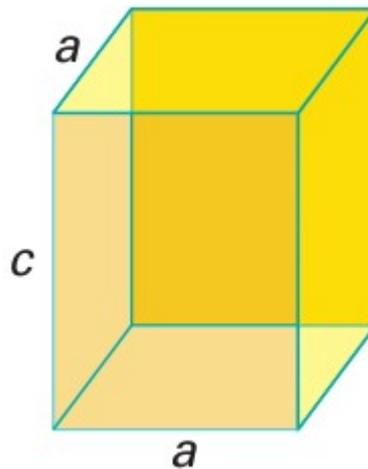
Сингонии

$$a = b = c$$
$$\alpha = \beta = \gamma \neq 90^\circ$$



Ромбоэдрическая

$$a = b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$

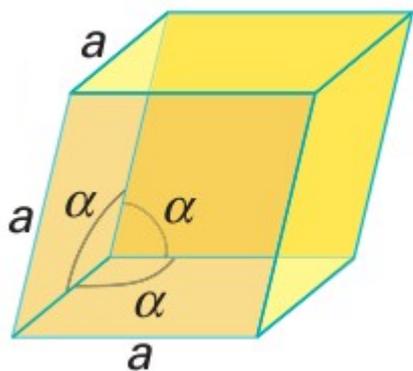


Тетрагональная



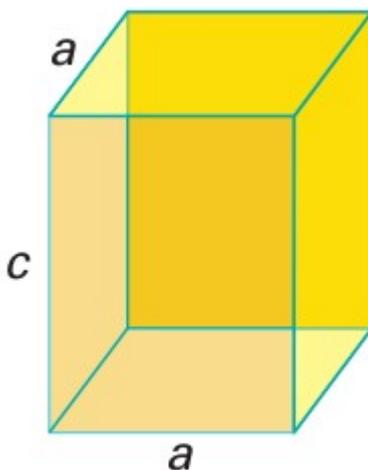
Сингонии

$$a = b = c$$
$$\alpha = \beta = \gamma \neq 90^\circ$$



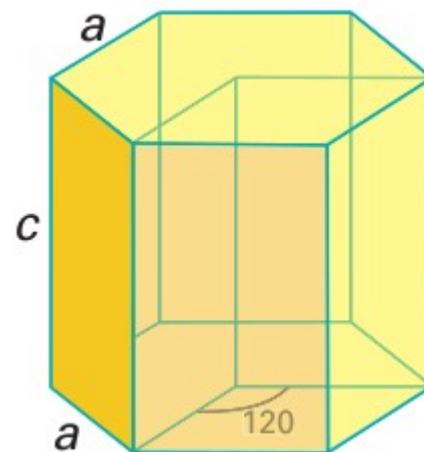
Ромбоэдрическая

$$a = b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$



Тетрагональная

$$a = b \neq c$$
$$\alpha = \beta = 90^\circ, \gamma = 120^\circ$$

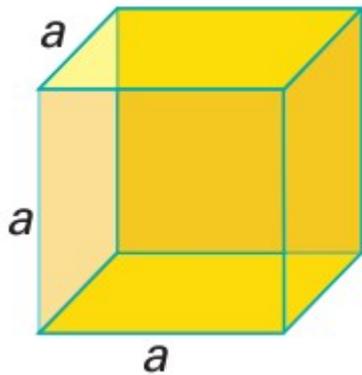


Гексагональная



Сингонии

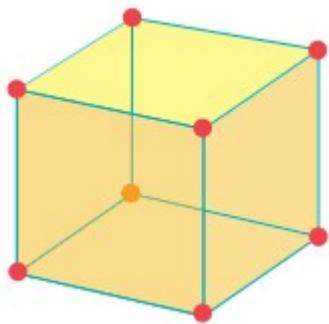
$$a = b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$



Кубическая



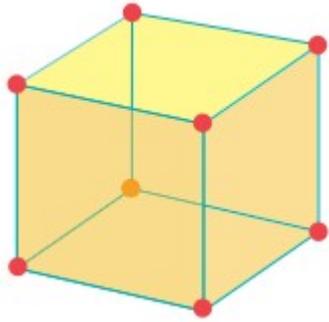
Центрировки



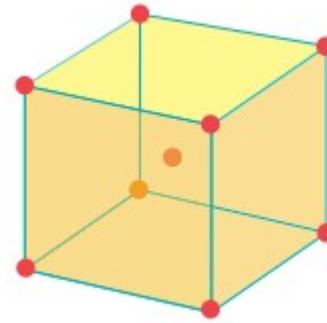
Примитивная



Центрировки



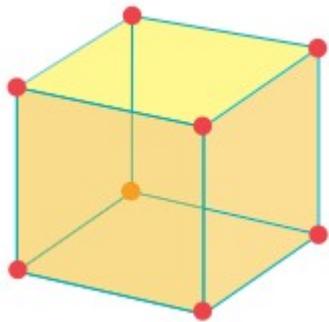
Примитивная



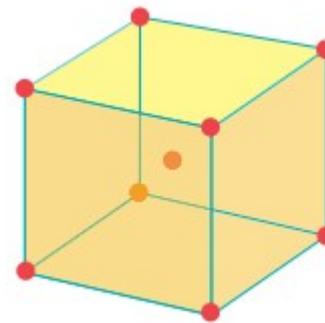
Объемноцентрированная



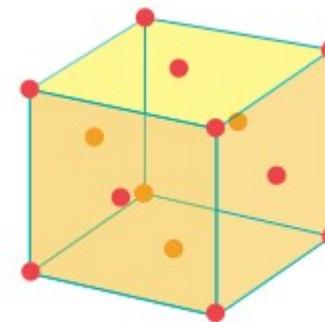
Центрировки



Примитивная



Объемноцентрированная



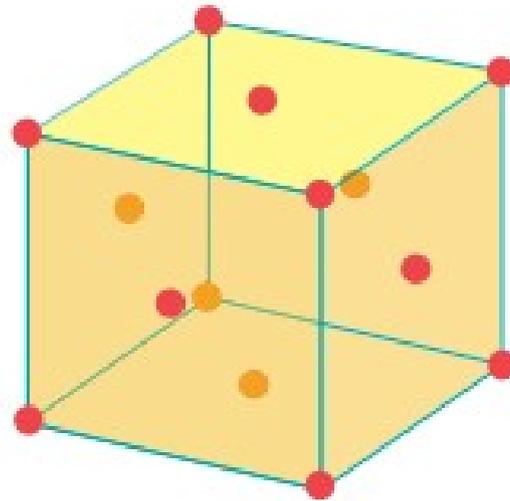
Гранецентрированная



Число атомов в ячейке

Атомы принадлежат не только одной ячейке!

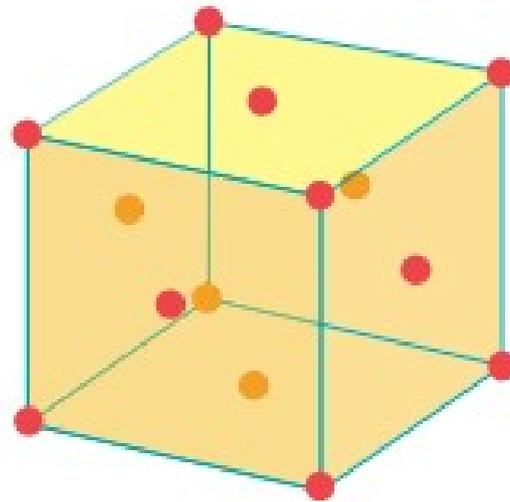
- Внутри ячейки $N = 1$
- На грани ячейки $N = 1/2$
- На ребре ячейки $N = 1/4$
- На вершине $N = 1/8$



Число атомов в ячейке

Атомы принадлежат не только одной ячейке!

- Внутри ячейки $N = 1$
- На грани ячейки $N = 1/2$
- На ребре ячейки $N = 1/4$
- На вершине $N = 1/8$



В ГЦК в одной ячейке $N = 8 \cdot 1/8 + 6 \cdot 1/2 = 4$



Плотность упаковки

- ПК

$$\eta = \frac{V_{\text{ат}}}{V_{\text{яч}}} = \frac{1 \cdot 4/3 \pi r^3}{(2r)^3} = \frac{\pi}{6}$$



Плотность упаковки

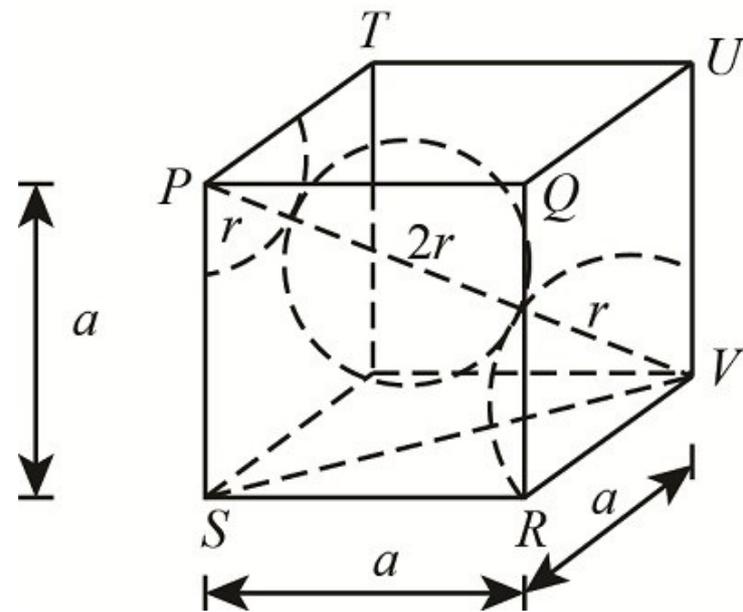
- ПК

$$\eta = \frac{V_{\text{ат}}}{V_{\text{яч}}} = \frac{1 \cdot \frac{4}{3} \pi r^3}{(2r)^3} = \frac{\pi}{6}$$

- ОЦК

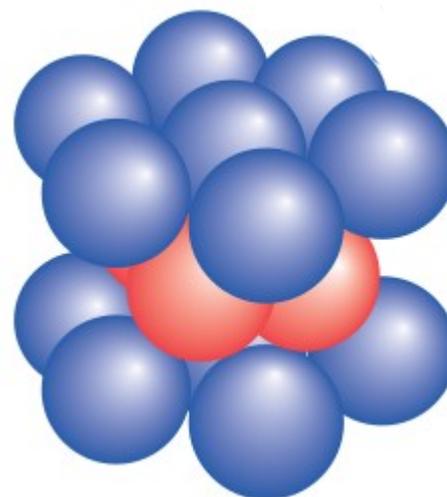
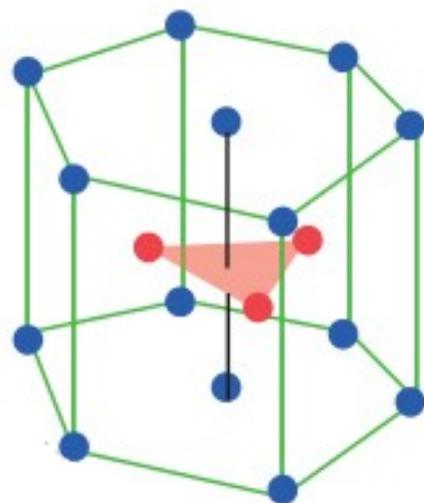
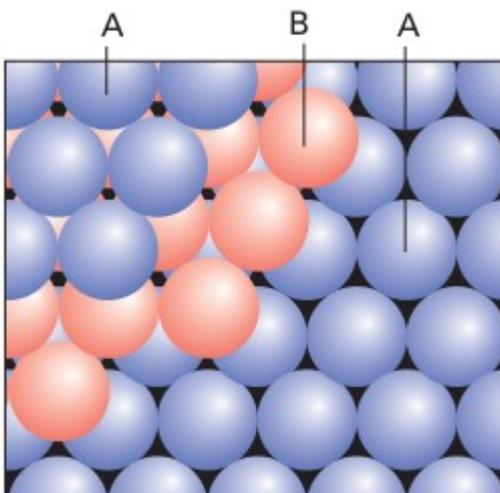
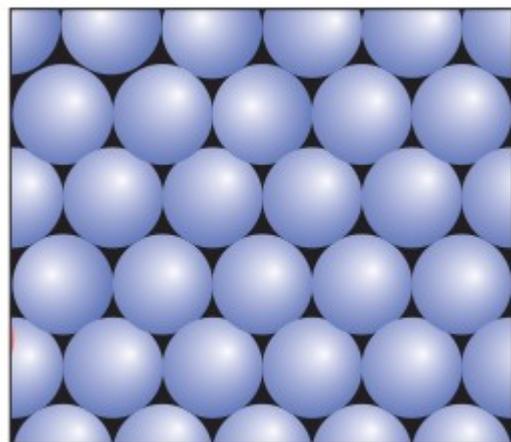
$$\eta = \frac{V_{\text{ат}}}{V_{\text{яч}}} = \frac{2 \cdot \frac{4}{3} \pi r^3}{(a)^3}$$

$$3a^2 = (4r)^2 \Rightarrow a = \frac{4r}{\sqrt{3}}$$



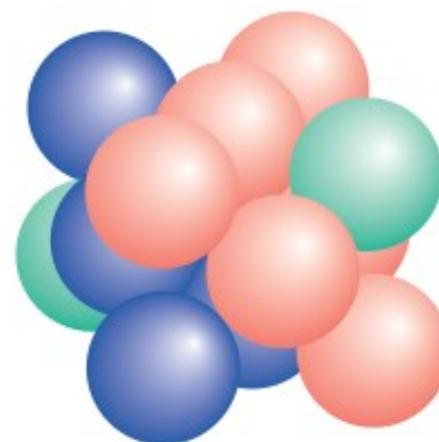
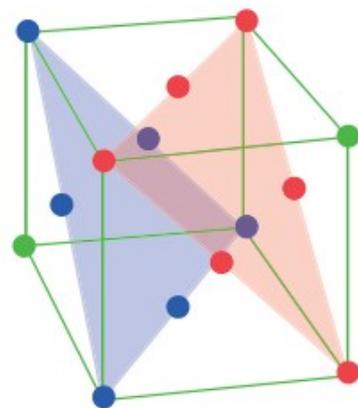
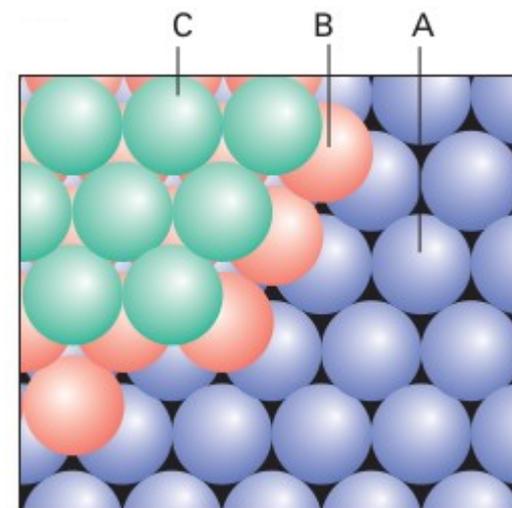
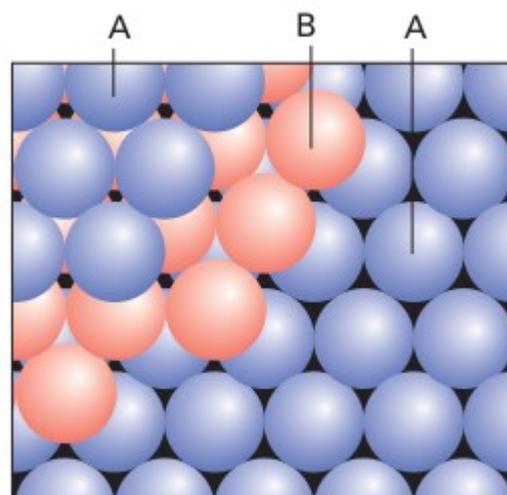
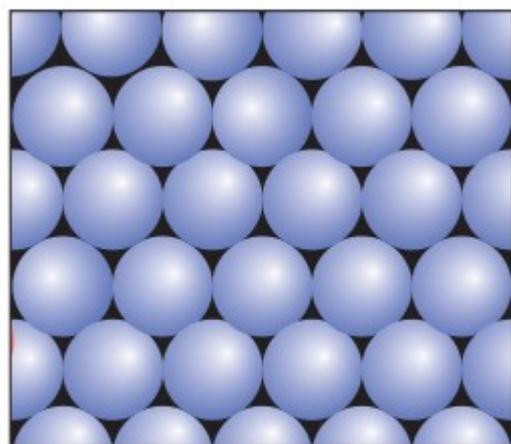
Плотнейшие упаковки

Гексагональная ПУ

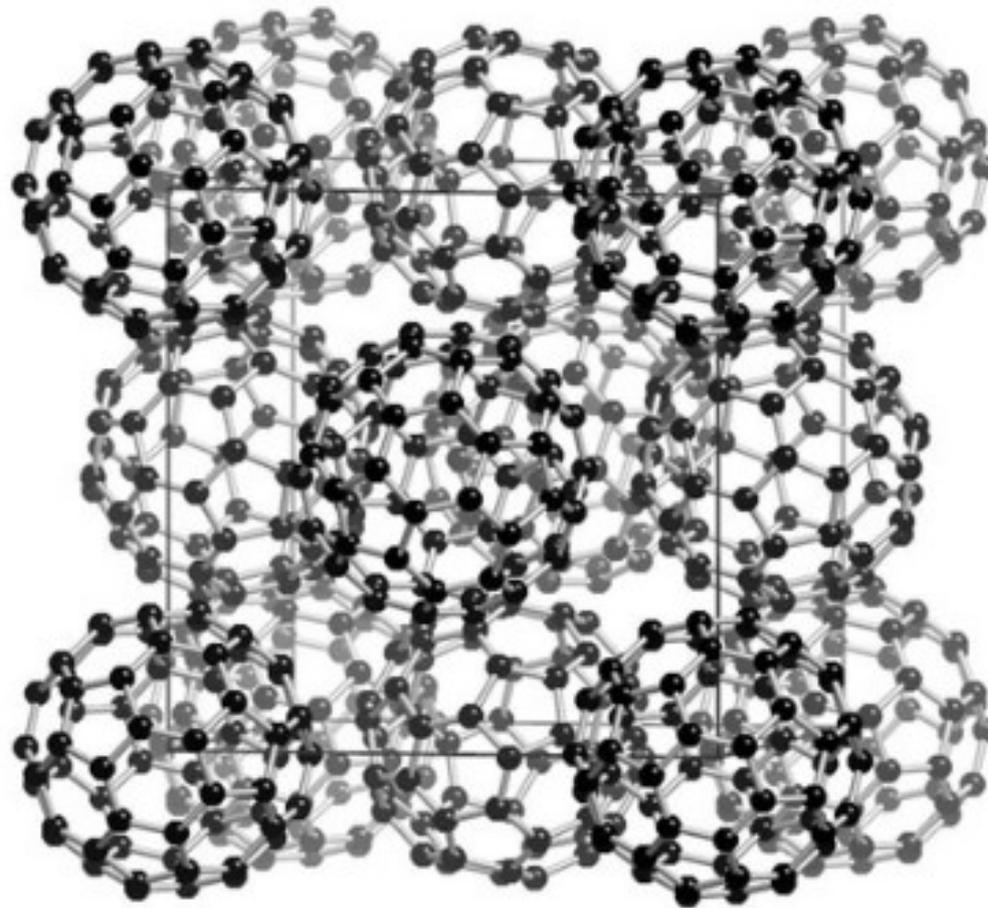


Плотнейшие упаковки

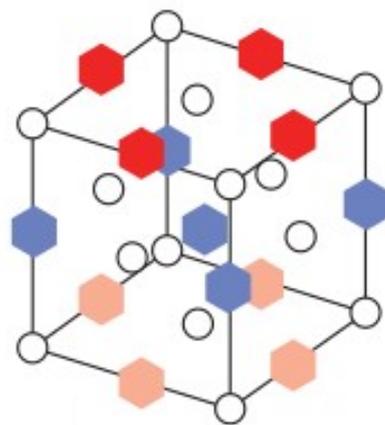
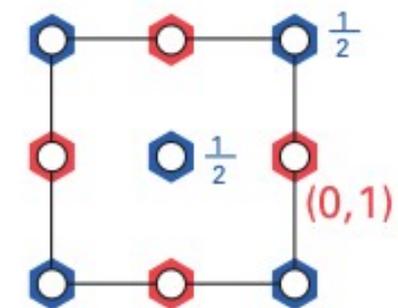
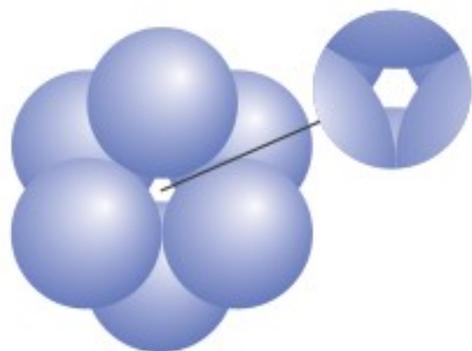
Кубическая ПУ



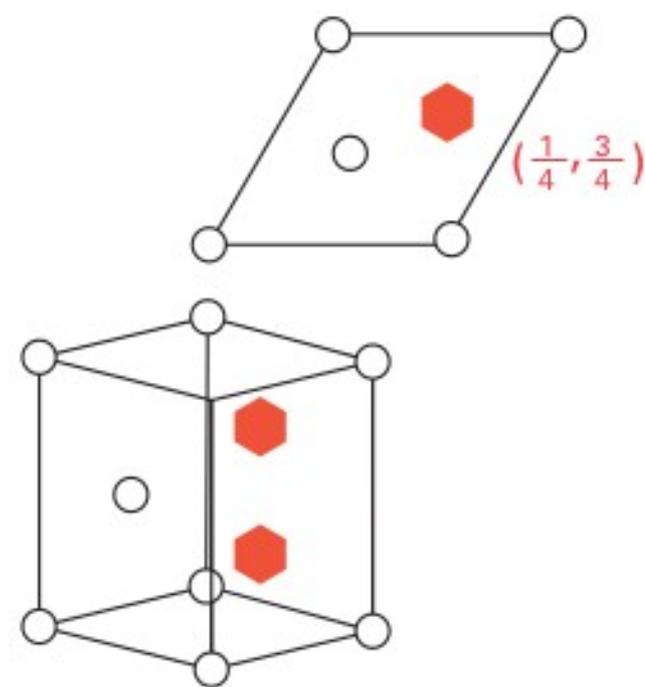
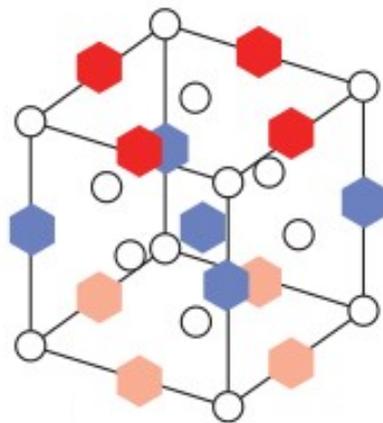
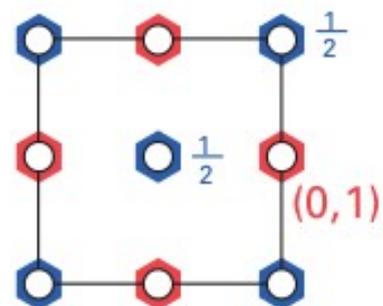
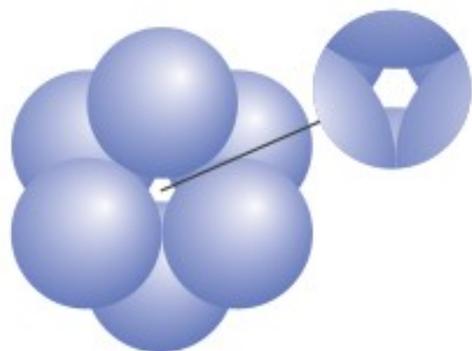
Фуллерен C_{60}



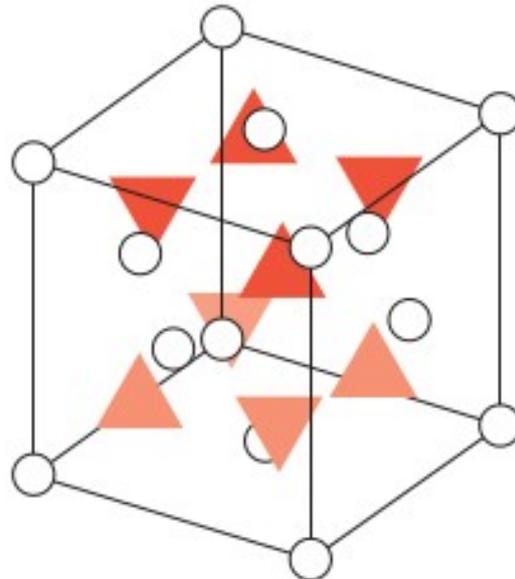
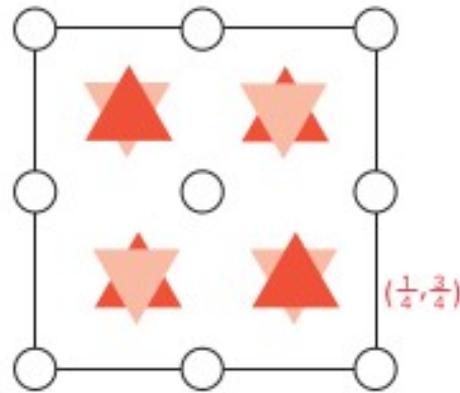
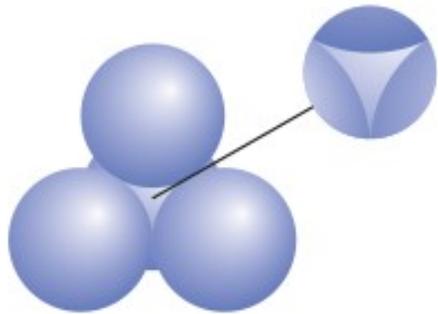
Пустоты



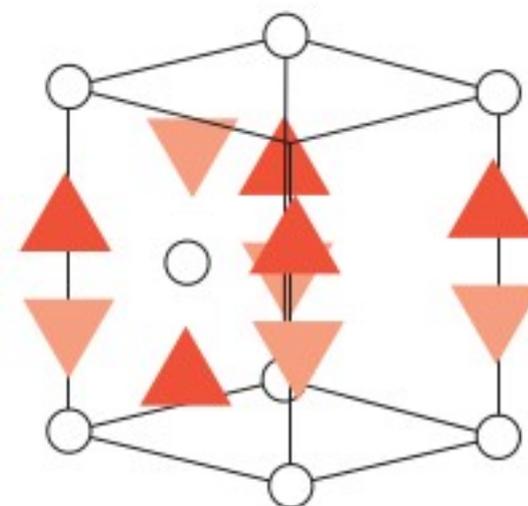
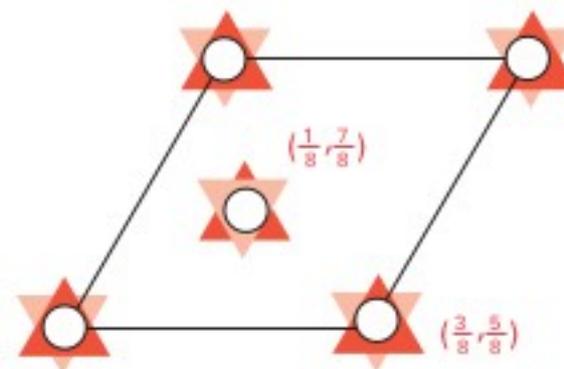
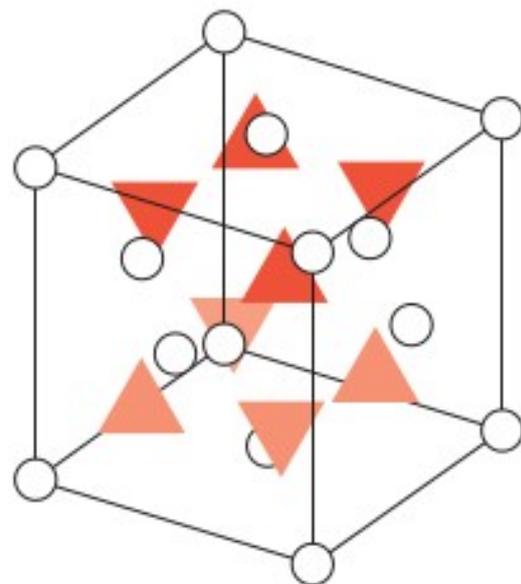
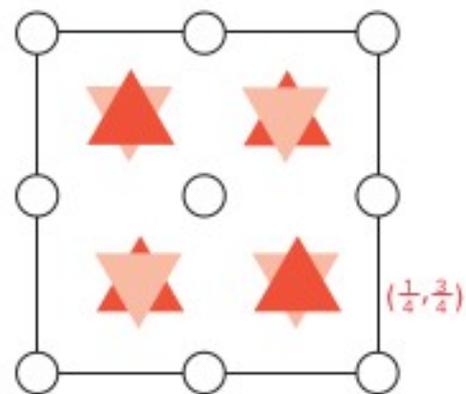
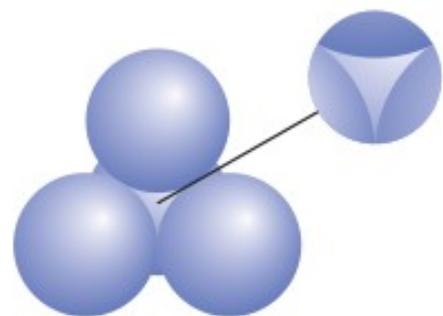
Пустоты



Пустоты: тетраэдрические



Пустоты

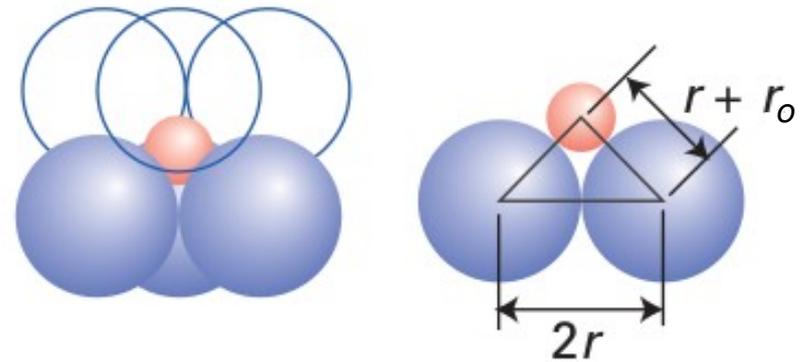


Размер пустот

Октаэдрические пустоты

$$(2r)^2 = 2(r+r_o)^2 \Rightarrow 2r = \sqrt{2}(r+r_o)$$

$$r_o = (\sqrt{2} - 1)r$$

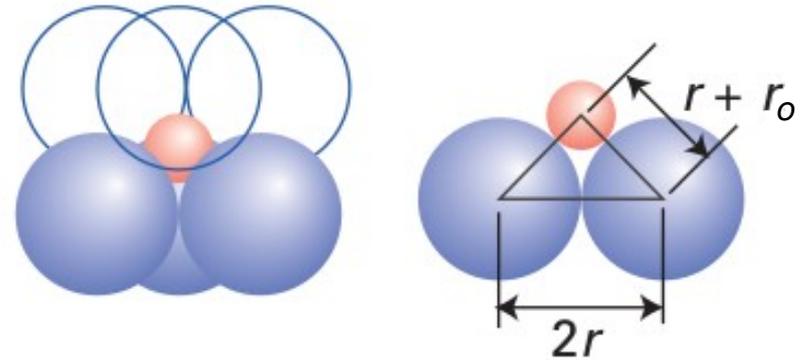


Размер пустот

Октаэдрические пустоты

$$(2r)^2 = 2(r+r_o)^2 \Rightarrow 2r = \sqrt{2}(r+r_o)$$

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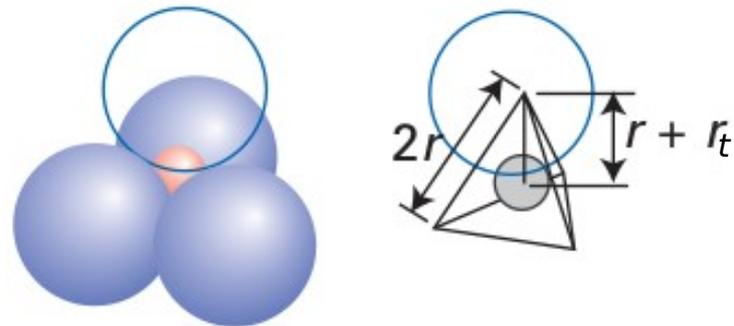


Тетраэдрические пустоты

$$(2r)^2 = 2(r+r_t)^2 - 2(r+r_t)^2 \cos[109^\circ 28']$$

$$2r = (r+r_t)(2 - 2\cos[109^\circ 28'])^{1/2}$$

$$r_t = 0.225r$$

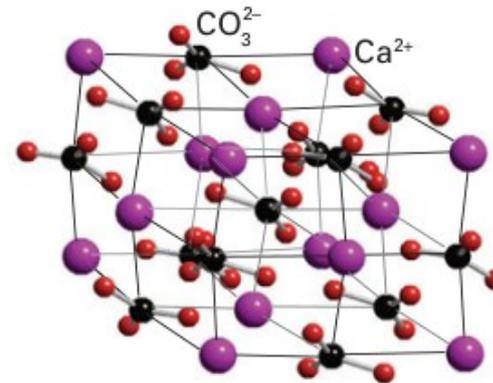
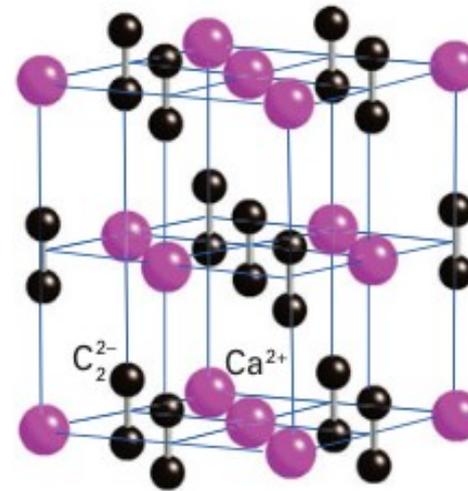
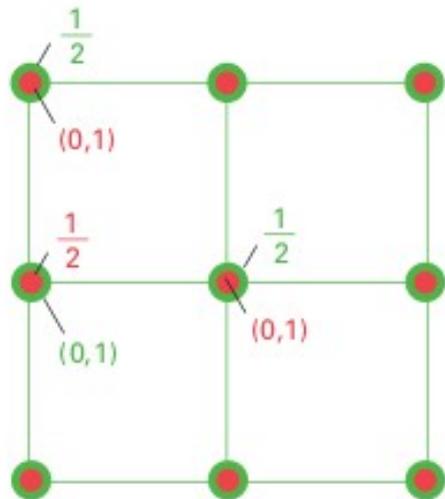
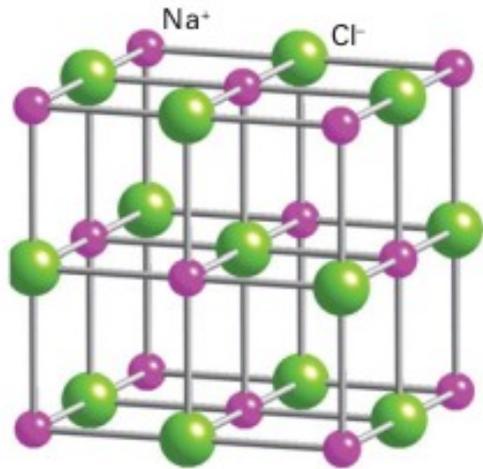


Ионные соединения

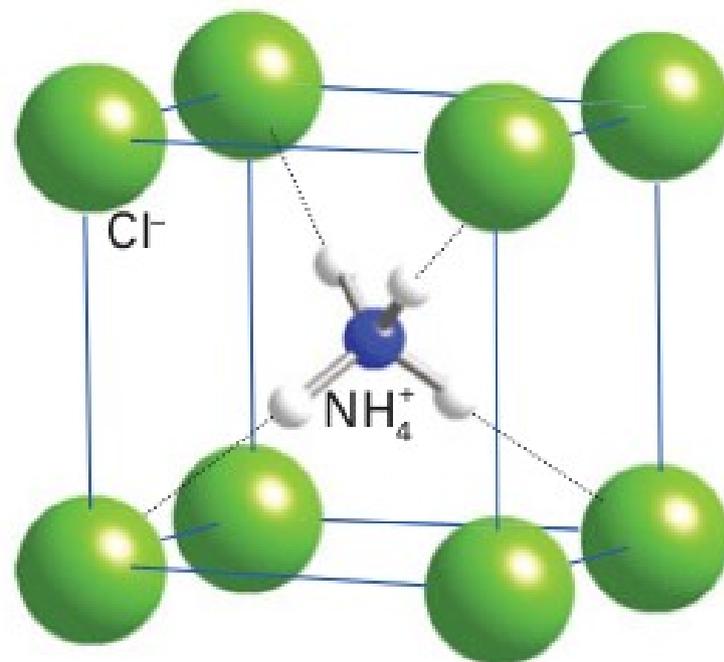
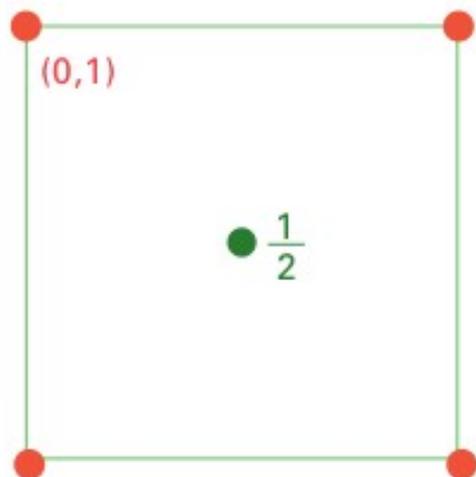
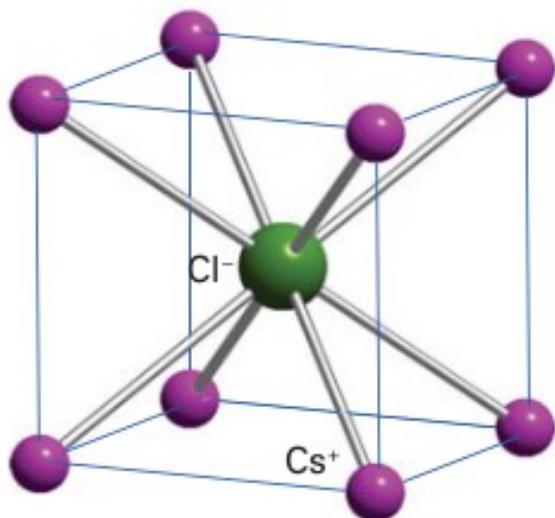
Структура	Вещества
Антифлюорит	K_2O, K_2S, Na_2O, Na_2S
Хлорид цезия	TlI, CsAu, NbO
Флюорит	UO_2, HgF_2, PbO_2
Арсенид никеля	NiS, FeS, CoS
Хлорид натрия	KBr, AgCl, CaO, NiO
Рутил	MnO_2, WO_2, MgF_2
Сфалерит	CuCl, HgS, GaP
Вюрцит	ZnO, Mns, AgI



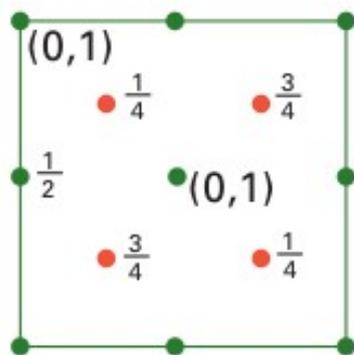
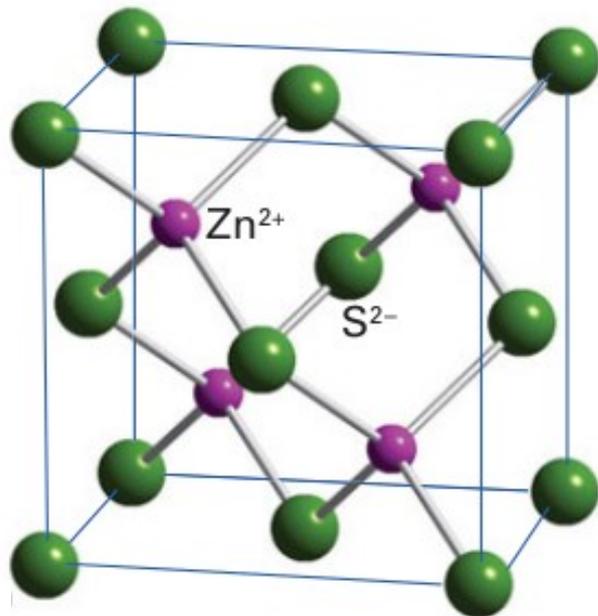
Структурный тип NaCl



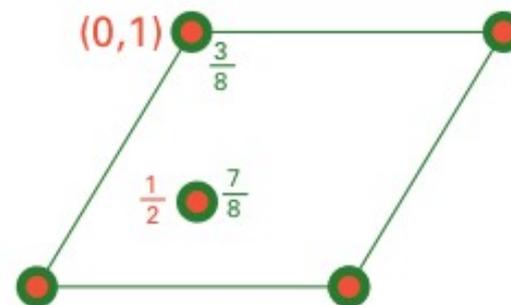
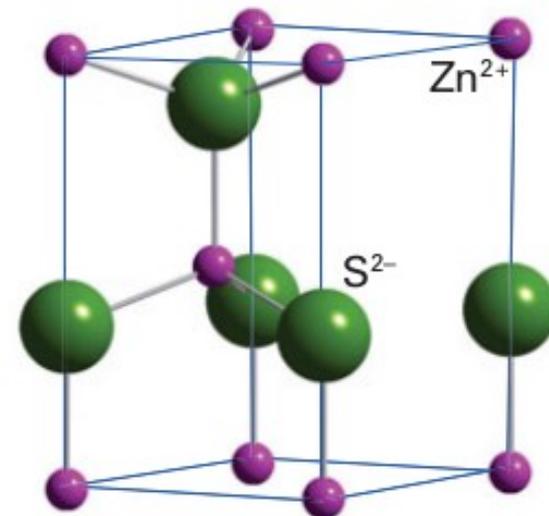
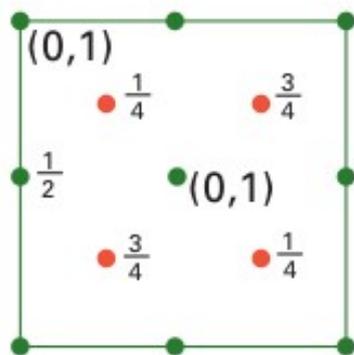
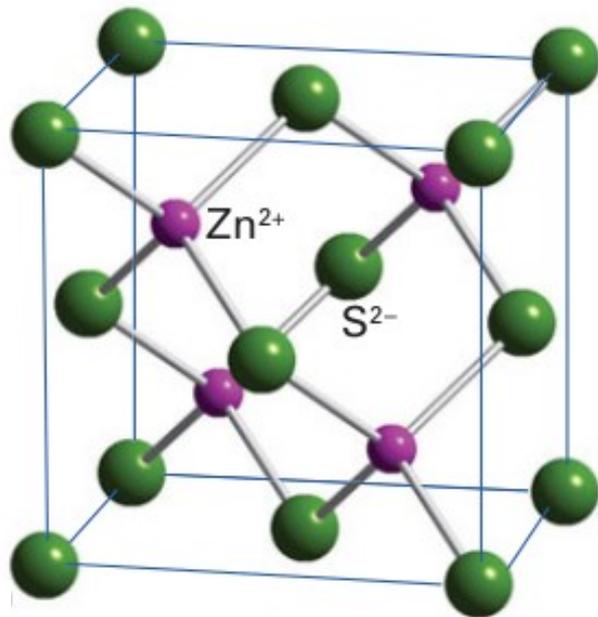
Структурный тип CsCl



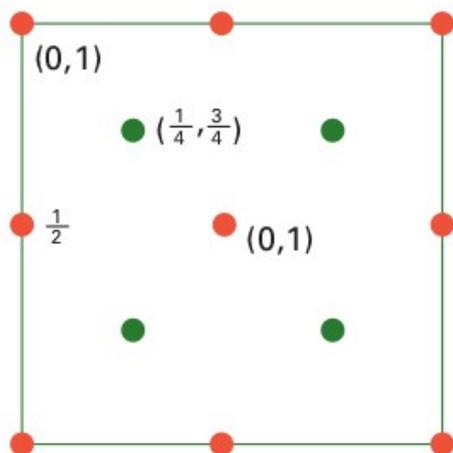
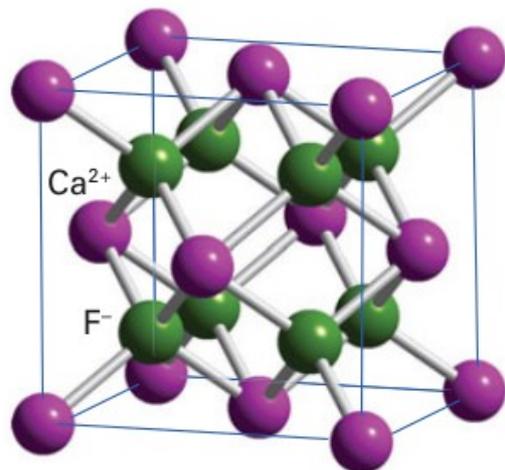
Структурные типы ZnS: сфалерит и вюрцит



Структурные типы ZnS: сфалерит и вюрцит



Структурный тип CaF_2



$$KЧ(\text{Ca}) = 8$$

$$KЧ(\text{F}) = 4$$

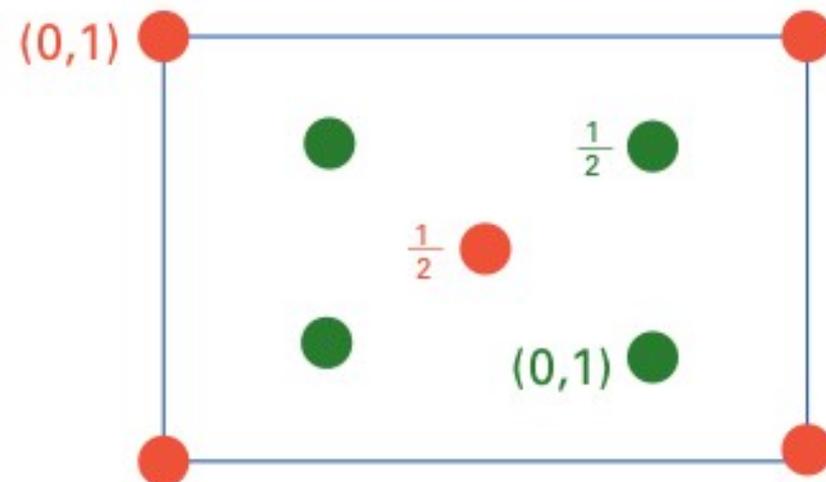
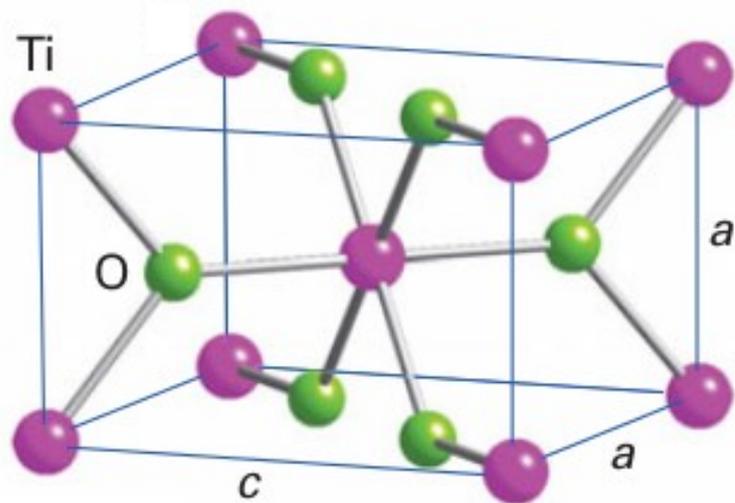
В общем случае для $A_x B_y$

$$x \cdot KЧ(A) = y \cdot KЧ(B)$$

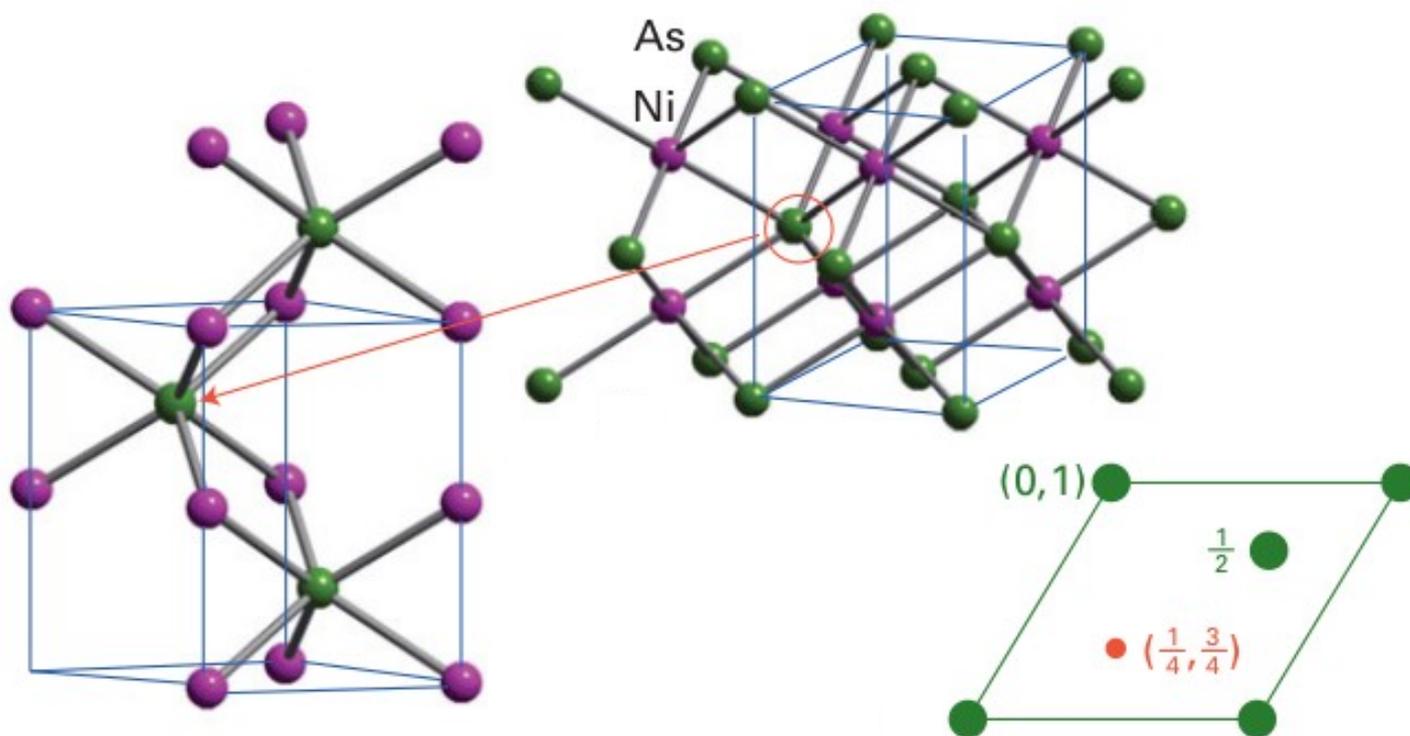
Антифлюорит - Li_2O



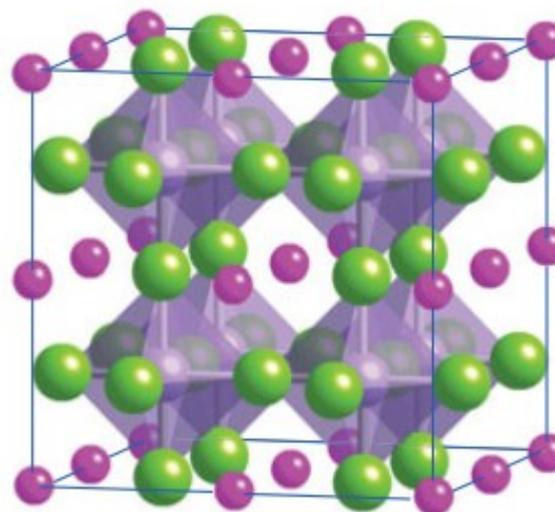
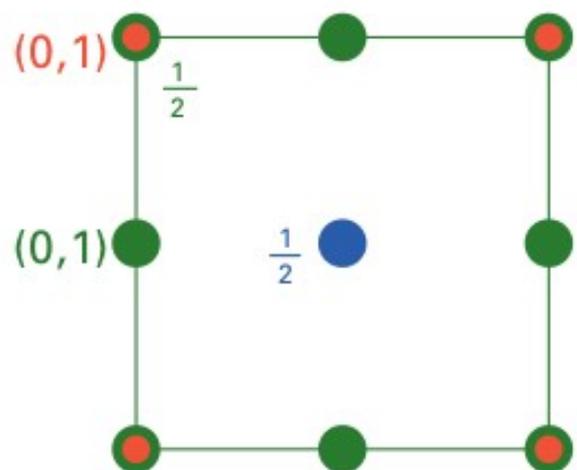
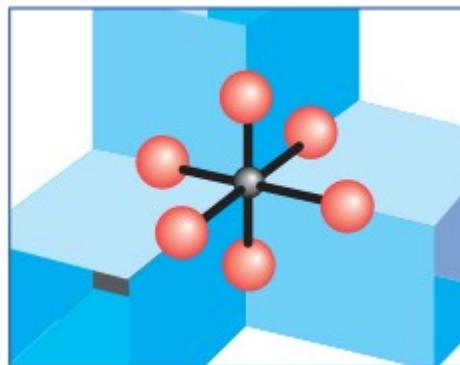
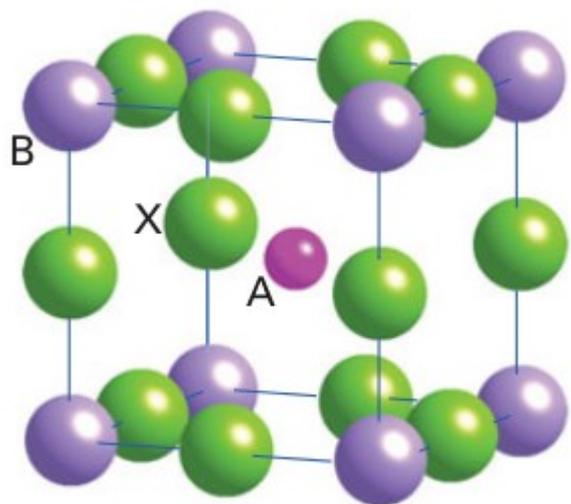
Структурный тип TiO_2



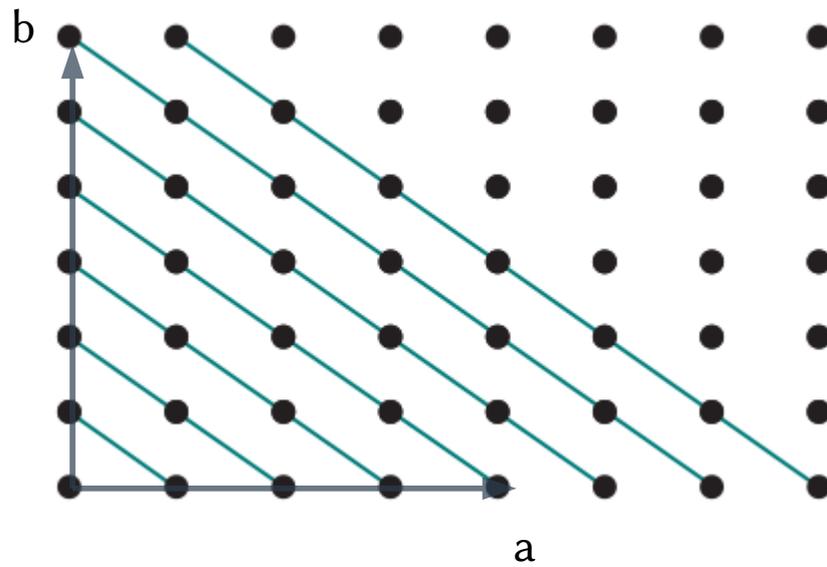
Структурный тип NiAs



Структурный тип перовскита (ABX_3)



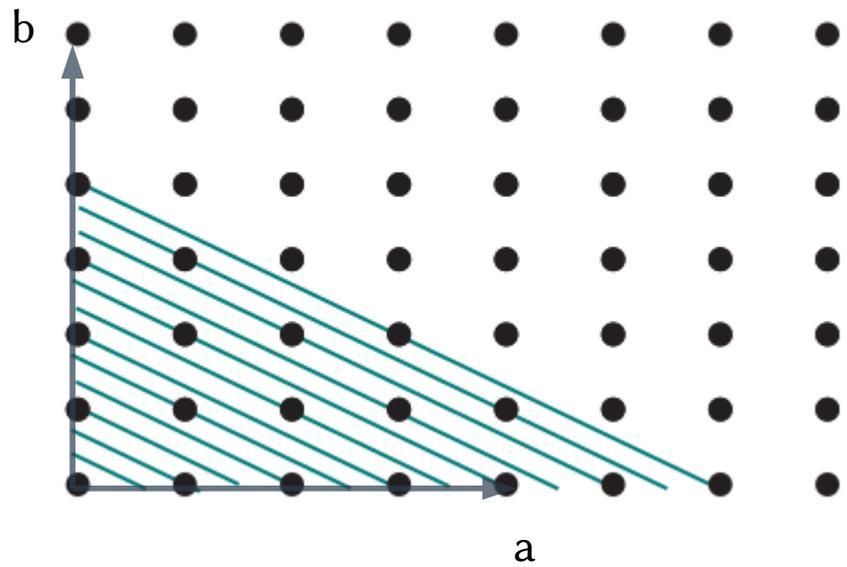
Плоскости в кристаллах



$$(1a, 1b) \rightarrow (1, 1)$$



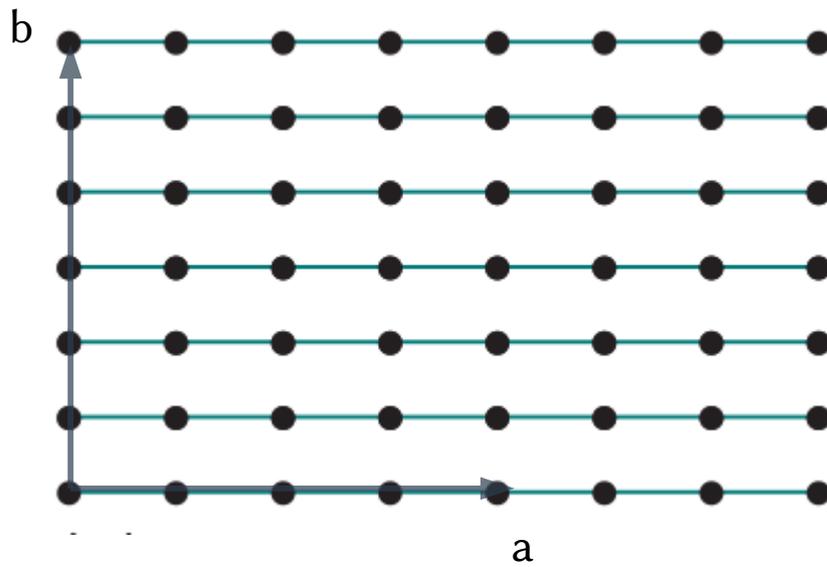
Плоскости в кристаллах



$$(a/2, b/3) \rightarrow (1/2, 1/3)$$



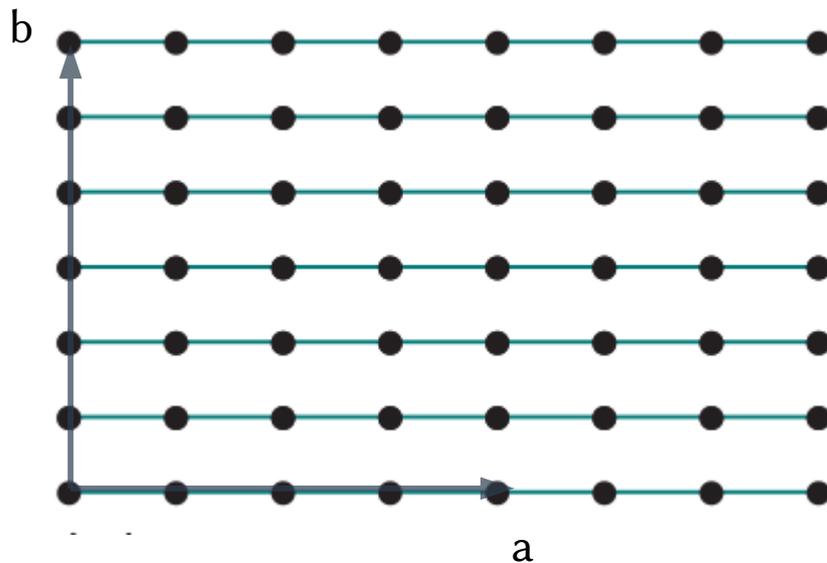
Плоскости в кристаллах



$$(\infty a, 1b) \rightarrow (\infty, 1)$$



Индексы Миллера



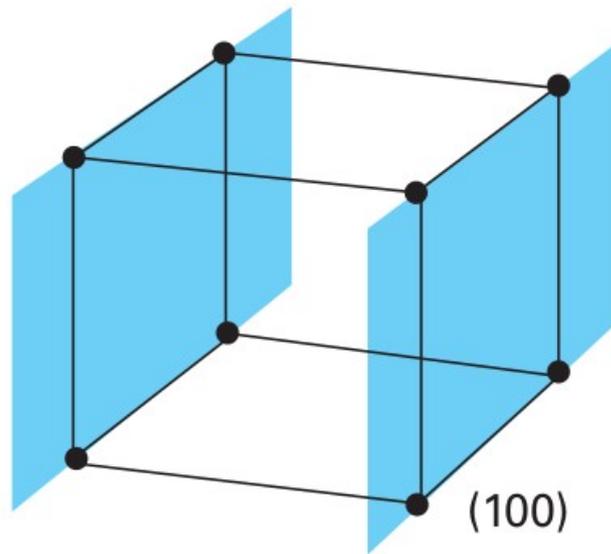
$$(1,1) \rightarrow (1,1)$$

$$(1/2, 1/3) \rightarrow (2,3)$$

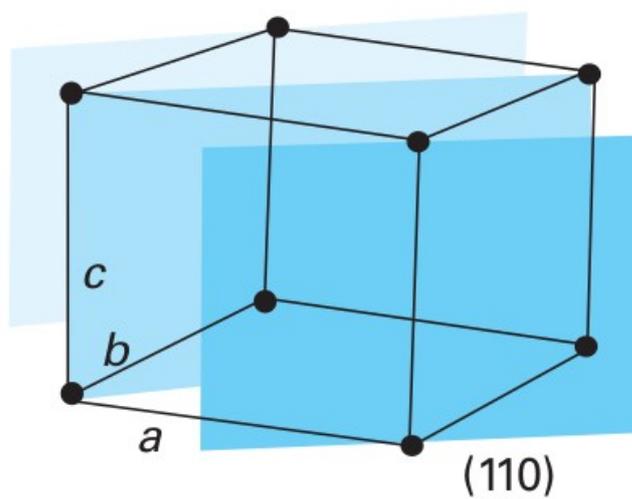
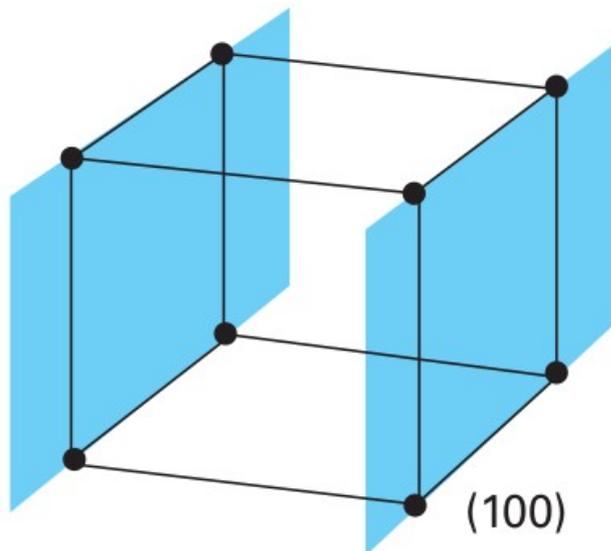
$$(\infty, 1) \rightarrow (0,1)$$



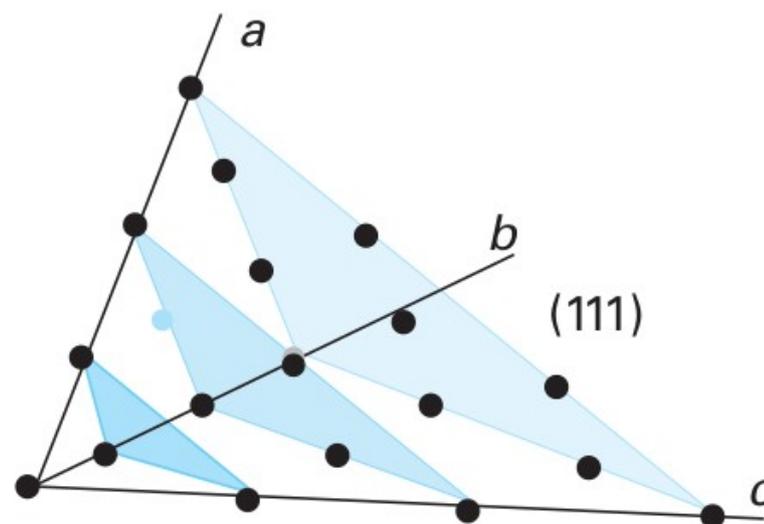
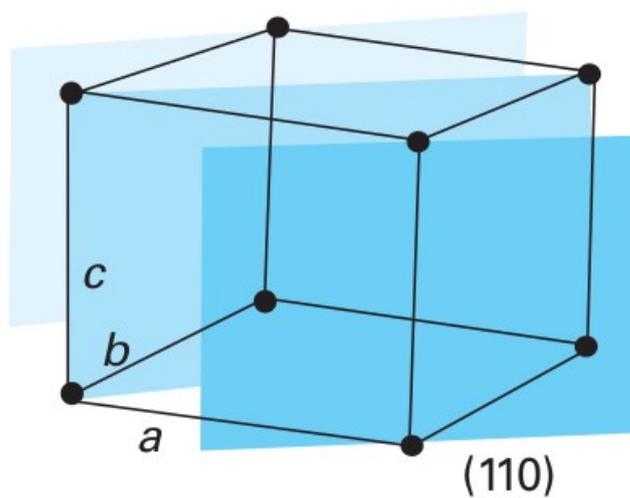
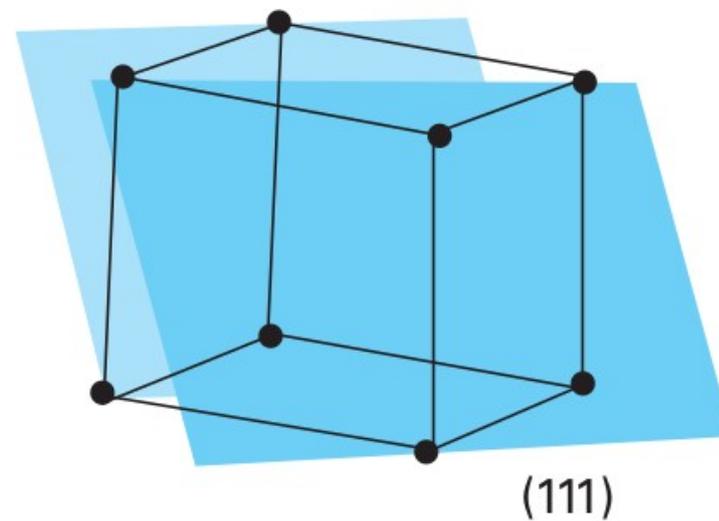
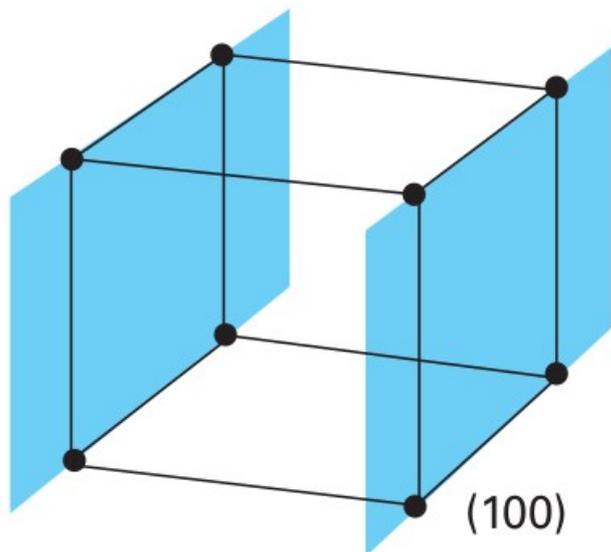
Индексы Миллера (hkl)



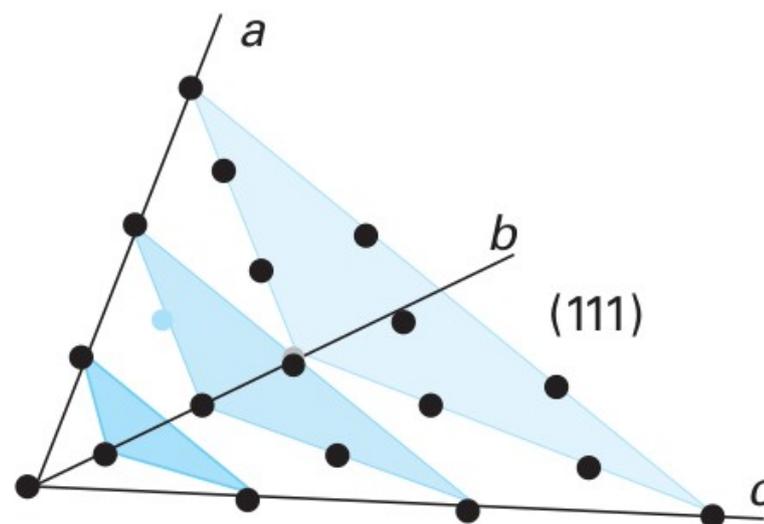
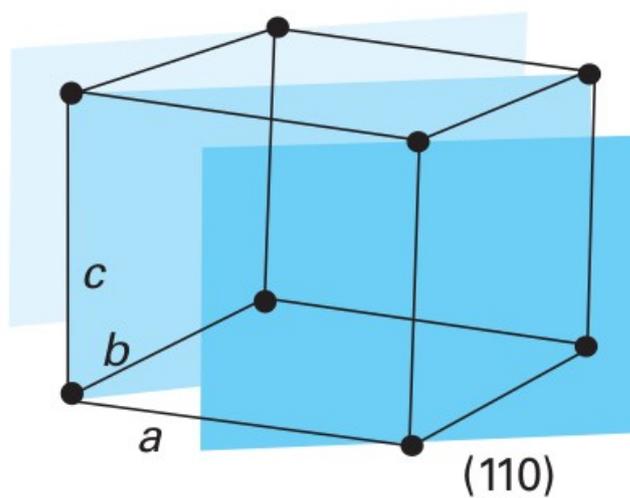
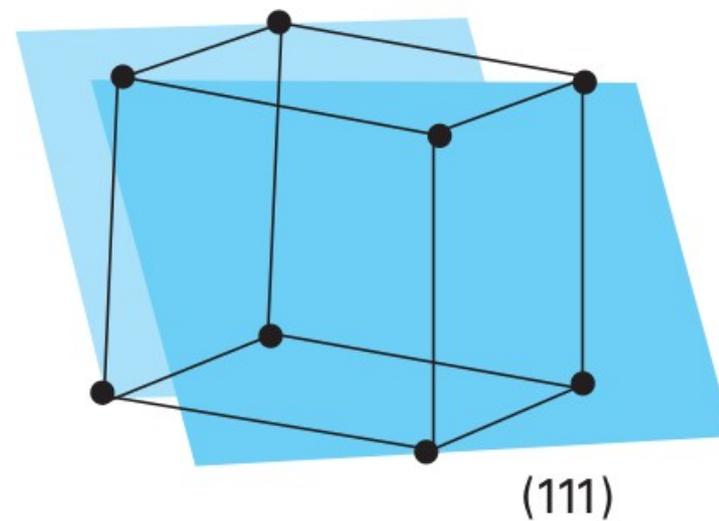
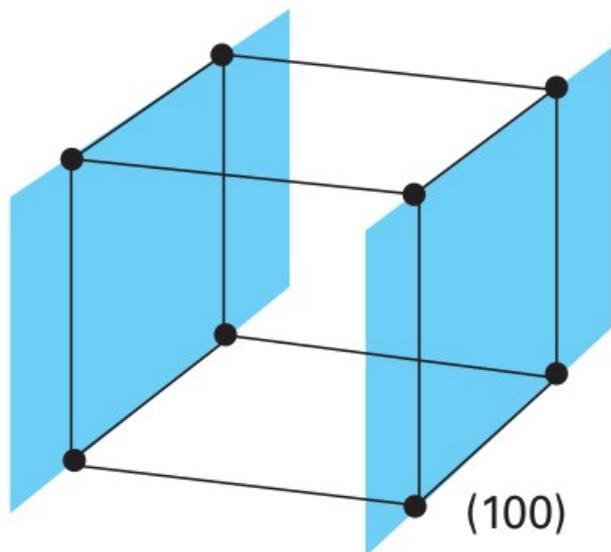
Индексы Миллера (hkl)



Индексы Миллера (hkl)

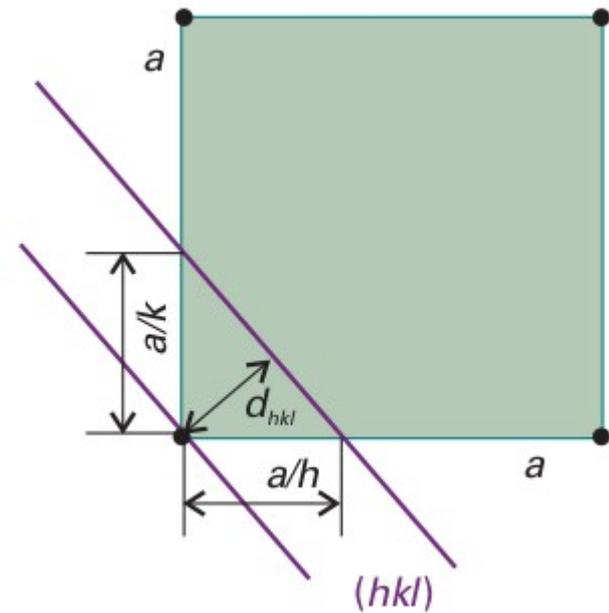


Индексы Миллера (hkl)



Межплоскостные расстояния

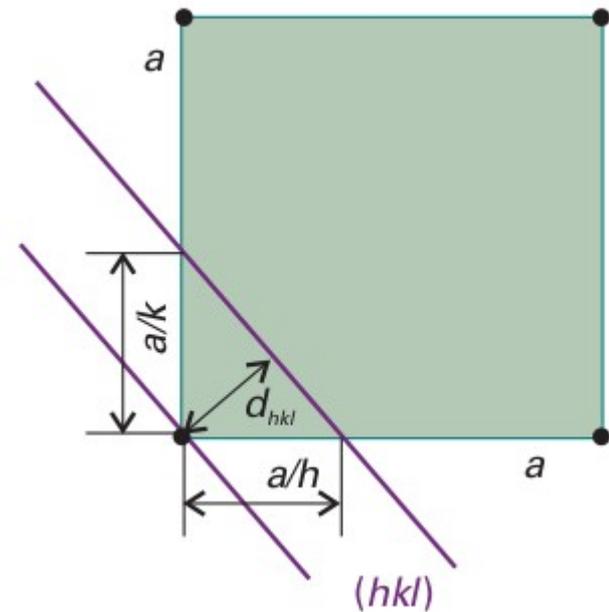
$$2d_{hk0}^2 = \frac{a^2}{h^2} + \frac{a^2}{k^2} \Rightarrow d_{hk0} = \frac{a}{(h^2 + k^2)^{1/2}}$$



Межплоскостные расстояния

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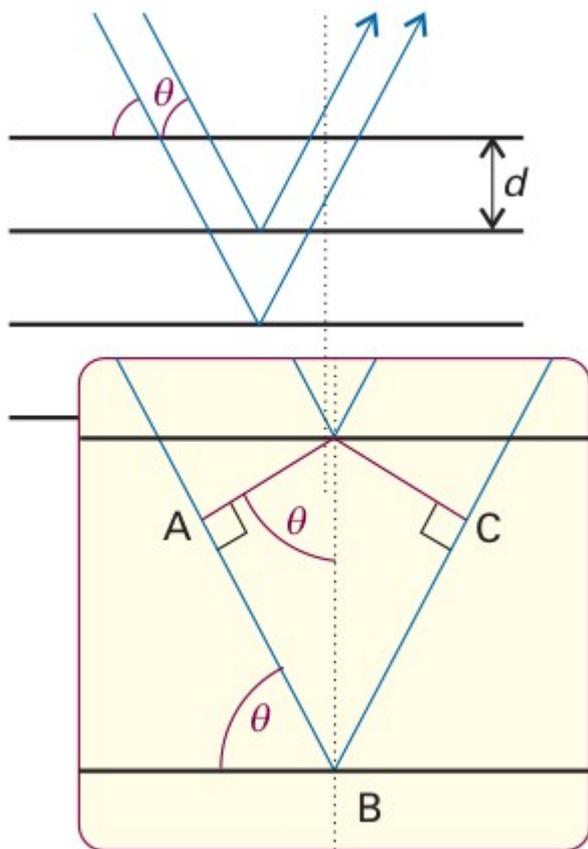
$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$



Рентгеноструктурный анализ

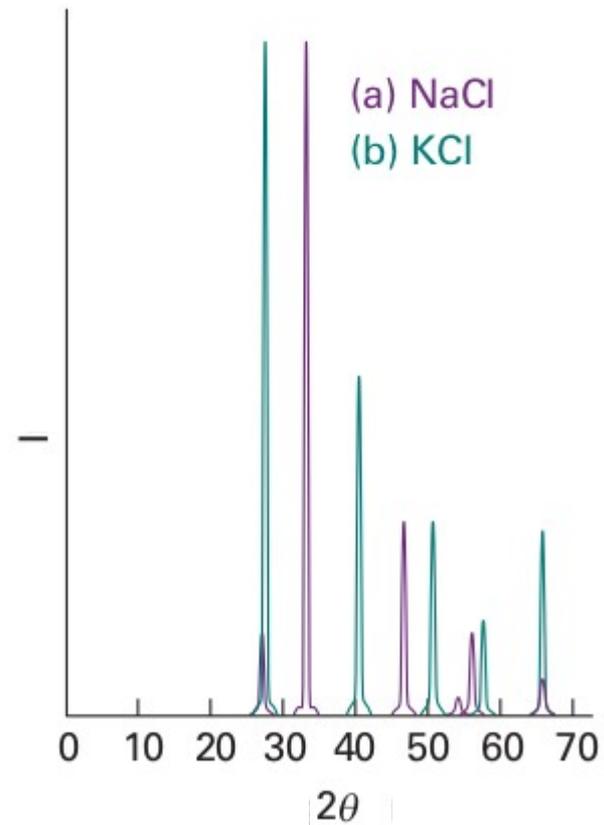
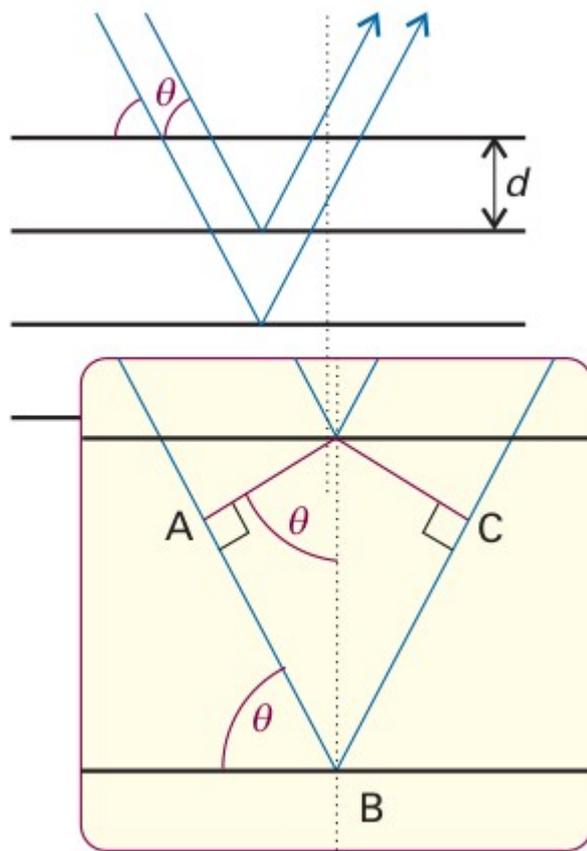
$$n \lambda = AB + BC = 2 d \sin \theta$$

$$n \lambda = 2 d \sin \theta, d = \frac{a}{(h^2 + k^2 + l^2)}$$



Рентгеноструктурный анализ

$$n\lambda = 2d \sin \theta$$



Пример 1

Минимальный угол дифракции пучка монохроматического рентгеновского излучения равен 11.5° . Исходя из этого, определите при каком угле наблюдается дифракция второго порядка от той же плоскости кристалла.

$$\lambda = d \sin 11.5^\circ$$

$$2\lambda = d \sin \theta$$

$$\theta = \arcsin 2 \sin 11.5^\circ = 23.5^\circ$$



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Минимальный угол дифракции пучка монохроматического рентгеновского излучения равен 11.5° . Исходя из этого, определите при каком угле наблюдается дифракция второго порядка от той же плоскости кристалла.

$$\lambda = d \sin 11.5^\circ$$

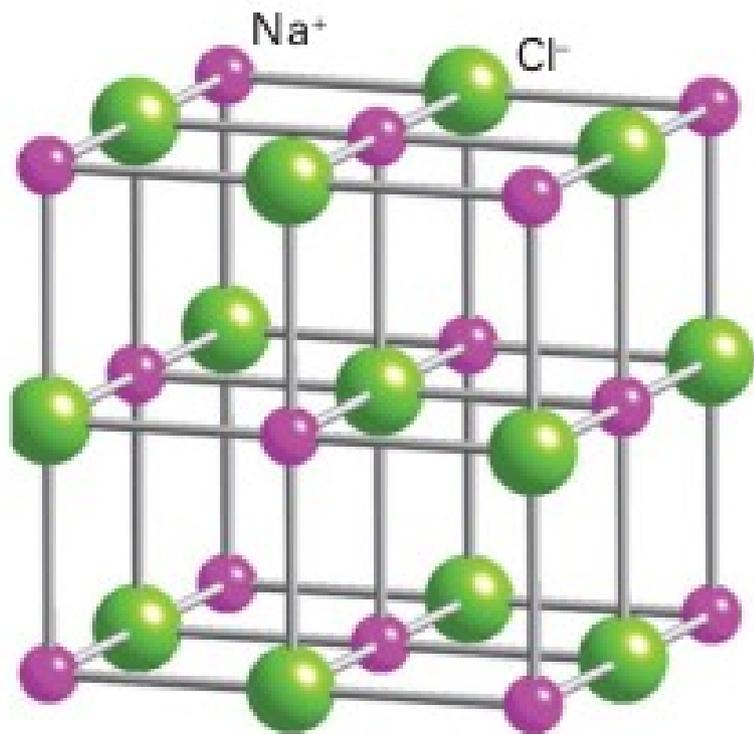
$$2\lambda = d \sin \theta$$

$$\theta = \arcsin 2 \sin 11.5^\circ = 23.5^\circ$$

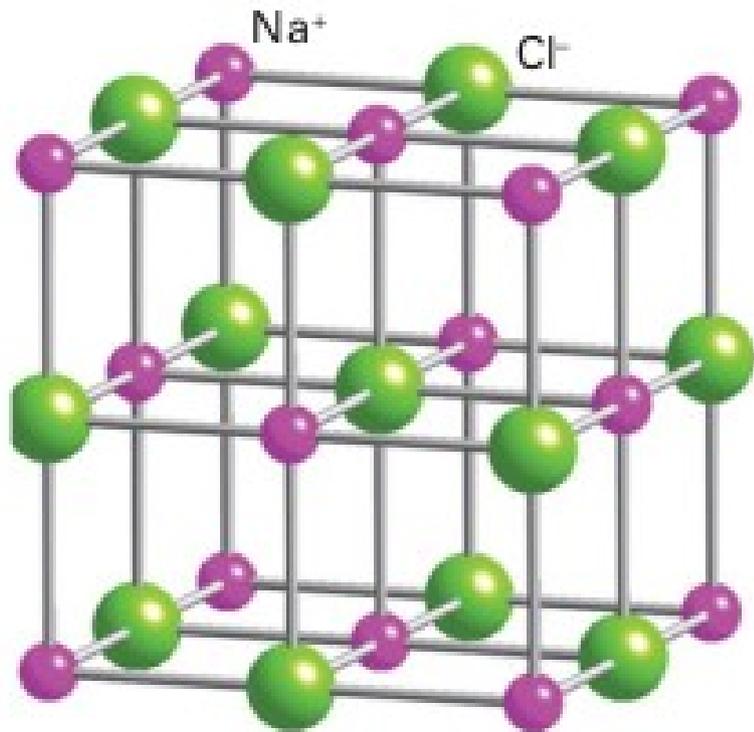


Пример 2: плотность

$r(\text{Na}^+) = 102 \text{ пм}$, $r(\text{Cl}^-) = 181 \text{ пм}$



Пример 2: плотность



$$r(\text{Na}^+) = 102 \text{ пм}, r(\text{Cl}^-) = 181 \text{ пм}$$

$$\rho = \frac{m_{\text{яч}}}{V_{\text{яч}}} = \frac{Z M}{N_a V_{\text{яч}}} =$$

$$\rho = \frac{4 \cdot 58.5 \cdot 10^{-3}}{6.02 \cdot 10^{23} (2(102 + 181) \cdot 10^{-12})^3} =$$

$$\rho = 2140 \text{ кг/м}^3$$

