Advanced Physical Chemistry II
HW Part III

王石嵘
161240065

January 11, 2020

29 Solids and Surface Chemistry

1,2,3,5,9,13,14,15,16,18,21,24,
25,27,29,37,38,43,46,51,53,54,55,
57,58,61,65,68

29-1

$$\rho = \frac{m}{V} = \frac{M}{a^3 N_\mathrm{A}} = \frac{209\,\mathrm{g/mol}}{(334.7\times 10^{-10}\,\mathrm{cm})^3\times N_\mathrm{A}} = 9.26\,\mathrm{g/cm^3} \tag{29.1}$$

29-2

a) Primitive cubic:
$a = 2R$ is obvious.

$$f = \frac{\frac{4}{3}\pi R^3}{(2R)^3} = \frac{\pi}{6} \tag{29.2}$$

b) Face-centered cubic:

$$4R = \sqrt{2}a \Rightarrow a = \frac{4R}{\sqrt{2}} \tag{29.3}$$

$$f = \frac{4\times\frac{4}{3}\pi R^3}{\left(\frac{4R}{\sqrt{2}}\right)^3} = \frac{16\pi/3}{32/\sqrt{2}} = \frac{\sqrt{2}\pi}{6} \tag{29.4}$$

b) Body-centered cubic:

$$4R = \sqrt{3}a \Rightarrow a = \frac{4R}{\sqrt{3}} \tag{29.5}$$

$$f = \frac{2\times\frac{4}{3}\pi R^3}{\left(\frac{4R}{\sqrt{3}}\right)^3} = \frac{8\pi/3}{64/3\sqrt{3}} = \frac{\sqrt{3}\pi}{8} \tag{29.6}$$

29-3

$$r = \frac{\sqrt{3}a}{4} = 143.0\,\mathrm{pm} \tag{29.7}$$

29-5

$$a = \frac{4r}{\sqrt{2}} = 361.5\,\mathrm{pm} \tag{29.8}$$

$$\rho = \frac{NM}{a^3 N_\mathrm{A}} = \frac{4 \times 63.55\,\mathrm{g/mol}}{(361.5 \times 10^{-10}\,\mathrm{cm})^3 \times N_\mathrm{A}} = 8.94\,\mathrm{g/cm^3} \tag{29.9}$$

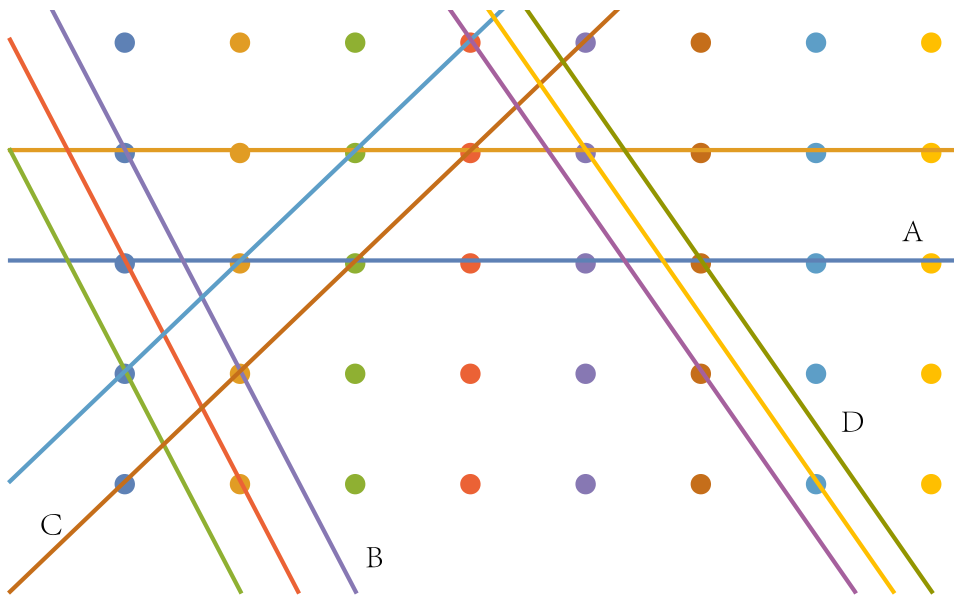
29-9

$$N = \frac{\rho a^3 N_\mathrm{A}}{M} = \frac{2.75 \times (654 \times 10^{-10})^3 \times 6.022 \times 10^{23}}{119.0} = 3.9 \tag{29.10}$$

thus there's 4 formula units of KBr in a unit cell.
The unit cell has a NaCl structure.

29-13
A: $1\bar{3}$
B: 11
C: 01
D: 32

29-14



29-15 They are perpendicular to each other

29-16 They are equivalent.

29-18
A: 111
B: 110
C: 54 10
D: $22\bar{4}$

29-21

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \tag{29.11}$$

thus

$$d(100) = \frac{529.8}{1} = 529.8\,\mathrm{pm} \tag{29.12}$$
$$d(111) = \frac{529.8}{\sqrt{3}} = 305.9\,\mathrm{pm} \tag{29.13}$$
$$d(12\bar{1}) = \frac{529.8}{\sqrt{6}} = 216.3\,\mathrm{pm} \tag{29.14}$$

29-24

$$a = V^{1/3} = \left(\frac{M}{N_\mathrm{A}\rho}\right)^{1/3} = \left(\frac{2\times 51.996\,\mathrm{g/mol}}{N_\mathrm{A}\times 7.20\,\mathrm{g/cm^3}}\right)^{1/3} = 288.4\,\mathrm{pm} \tag{29.15}$$

thus

$$d(110) = \frac{288.4}{\sqrt{2}} = 203.9\,\mathrm{pm} \tag{29.16}$$
$$d(200) = \frac{288.4}{2} = 144.2\,\mathrm{pm} \tag{29.17}$$
$$d(111) = \frac{288.4}{\sqrt{3}} = 166.5\,\mathrm{pm} \tag{29.18}$$

29-25

$$\tan\alpha = \frac{52.0}{14.8} \Rightarrow \alpha = 74.11^\circ \tag{29.19}$$
$$a = \frac{h\lambda}{\cos\alpha} = 564.1\,\mathrm{pm} \tag{29.20}$$

29-27

$$\cos\alpha_0 = \cos\alpha - \frac{h\lambda}{a} = \cos 18.79^\circ - \frac{154.433}{380.5} = 0.5408 \tag{29.21}$$
$$\Rightarrow \alpha_0 = 57.26^\circ \tag{29.22}$$
$$\cos\beta_0 = \cos\beta - \frac{k\lambda}{b} = \cos 0^\circ - \frac{154.433}{380.5} = 0.5941 \tag{29.23}$$
$$\Rightarrow \beta_0 = 53.55^\circ \tag{29.24}$$
$$\cos\gamma_0 = \cos\gamma - \frac{l\lambda}{c} = \cos 0^\circ - \frac{154.433}{380.5} = 0.5941 \tag{29.25}$$
$$\Rightarrow \gamma_0 = 53.55^\circ \tag{29.26}$$

29-29 Since

$$PQ = QR = d\sin\theta \tag{29.27}$$

$\therefore$

$$PQR = 2d\sin\theta \tag{29.28}$$

When constructive interference occur, the waves must in same phase, thus $2d\sin\theta = nd$.

29-37

a) primitive
lattice points: $(0,0,0), (1,0,0), (0,1,0), (0,0,1), (1,1,0), (1,0,1), (0,1,1), (1,1,1)$.

$$\begin{aligned} F(hkl) &= \frac{1}{8}f[\mathrm{e}^{2\pi(0)} + \mathrm{e}^{2\pi(h)} + \mathrm{e}^{2\pi(k)} + \mathrm{e}^{2\pi(l)} + \mathrm{e}^{2\pi(h+k)} + \mathrm{e}^{2\pi(h+l)} + \mathrm{e}^{2\pi(k+l)} + \mathrm{e}^{2\pi(h+k+l)}] \\ &= \frac{1}{8}f(1 + 1^h + 1^k + 1^l + 1^{h+k} + 1^{h+l} + 1^{k+l} + 1^{h+k+l}) \\ &= f \end{aligned} \tag{29.29}$$

i.e. all integer values of h, k, l gives reflection.

b) face-centered
lattice points: $(0,0,0),(1,0,0),(0,1,0),(0,0,1),(1,1,0),(1,0,1),(0,1,1),(1,1,1)$
$(1/2,1/2,1),(1,1/2,1/2),(1/2,1,1/2),(1/2,1/2,0),(0,1/2,1/2),(1/2,0,1/2)$.

$$
\begin{aligned}
F(hkl) &= f + \frac{1}{2}f[\mathrm{e}^{2\pi(h/2+k/2)} + \mathrm{e}^{2\pi(h/2+l/2)} + \mathrm{e}^{2\pi(k/2+l/2)} + \mathrm{e}^{2\pi(h/2+k/2+l)} + \mathrm{e}^{2\pi(h/2+k+l/2)} + \mathrm{e}^{2\pi(h+k/2+l/2)}] \\
&= f + \frac{1}{2}f[(-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l} + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}] \\
&= f + f[(-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}] \qquad (29.30)
\end{aligned}
$$

If h,k,l are all odd or all even, $F(hkl) = 4f$, either, $F(hkl) = 0$.

29-43

$$
\cos\phi = \frac{Na}{2a} = \frac{N}{2} \qquad (29.31)
$$

Since $-1 \leq \cos\phi \leq 1$, N must be $-2,-1,0,1,2$.
Thus ϕ can only be $180°, 120°, 90°, 60°, 360°$.