STATE UNIVERSITY OF NEW YORK AT BUFFALO

Department of Mechanical and Aerospace Engineering

MEA 589 Diffraction, Microscopy and Spectroscopy Techniques

Prof. D.D.L. Chung

February 5, 2004

HOMEWORK NO. 3
SOLUTION

Problem 1 (30%)

(i) The cubic system

$$\vec{a_1} = a(1,0,0) \qquad \vec{b_1} = \frac{2\pi}{a}(1,0,0)$$

$$\vec{a_2} = a(0,1,0) \qquad \vec{b_2} = \frac{2\pi}{a}(0,1,0)$$

$$\vec{a_3} = a(0,0,1) \qquad \vec{b_3} = \frac{2\pi}{a}(0,0,1)$$

$$\vec{G_m} = m_1\vec{b_1} + m_2\vec{b_2} + m_3\vec{b_3}$$

$$= \frac{2\pi}{a}(m_1, m_2, m_3)$$

$$|\vec{G_m}| = \frac{2\pi}{a}\sqrt{m_1^2+m_2^2+m_3^2}$$

$$\Delta d = \frac{2\pi}{|\vec{G_m}|} = \frac{a}{\sqrt{m_1^2+m_2^2+m_3^2}}$$

(ii) The tetragonal system

$$\vec{a_1} = a(1,0,0) \qquad \vec{b_1} = \frac{2\pi}{a}(1,0,0)$$

$$\vec{a_2} = a(0,1,0) \qquad \vec{b_2} = \frac{2\pi}{a}(0,1,0)$$

$$\vec{a_3} = c(0,0,1) \qquad \vec{b_3} = \frac{2\pi}{c}(0,0,1)$$

$$\vec{G_m} = m_1\vec{b_1} + m_2\vec{b_2} + m_3\vec{b_3}$$
$$= \left(\frac{2\pi}{a} m_1 , \frac{2\pi}{a} m_2 , \frac{2\pi}{c} m_3\right)$$
$$= 2\pi\left(\frac{m_1}{a} , \frac{m_2}{a} , \frac{m_3}{c}\right)$$

$$|\vec{G_m}| = 2\pi\sqrt{\left(\frac{m_1}{a}\right)^2+\left(\frac{m_2}{a}\right)^2+\left(\frac{m_3}{c}\right)^2} = 2\pi\sqrt{\frac{m_1^2+m_2^2}{a^2}+\frac{m_3^2}{c^2}}$$

$$\Delta d = \frac{2\pi}{|\vec{G_m}|} = \underline{\underline{\left(\frac{m_1^2+m_2^2}{a^2}+\frac{m_3^2}{c^2}\right)^{-\frac{1}{2}}}}$$

(iii) <u>The orthorhombic system</u>

$$\vec{a_1} = a\,(1,0,0) \qquad \vec{b_1} = \frac{2\pi}{a}\,(1,0,0)$$
$$\vec{a_2} = b\,(0,1,0) \qquad \vec{b_2} = \frac{2\pi}{b}\,(0,1,0)$$
$$\vec{a_3} = c\,(0,0,1) \qquad \vec{b_3} = \frac{2\pi}{c}\,(0,0,1)$$

$$\vec{G_m} = m_1\vec{b_1} + m_2\vec{b_2} + m_3\vec{b_3}$$
$$= 2\pi\left(\frac{m_1}{a}, \frac{m_2}{b}, \frac{m_3}{c}\right)$$

$$|\vec{G_m}| = 2\pi\sqrt{\left(\frac{m_1}{a}\right)^2+\left(\frac{m_2}{b}\right)^2+\left(\frac{m_3}{c}\right)^2}$$

$$\Delta d = \frac{2\pi}{|\vec{G_m}|} = \underline{\underline{\left(\frac{m_1^2}{a^2}+\frac{m_2^2}{b^2}+\frac{m_3^2}{c^2}\right)^{-\frac{1}{2}}}}$$

(iv) The hexagonal system

For the hexagonal system, we can choose the fundamental translation vectors in direct space to be

$$\vec{a}_1 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0\right)$$

$$\vec{a}_2 = a\left(\frac{\sqrt{3}}{2}, +\frac{1}{2}, 0\right)$$

$$\vec{a}_3 = c\,(0, 0, 1).$$

By inspection, we obtain the corresponding fundamental translation vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ as

$$\vec{b}_1 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, -1, 0\right)$$

$$\vec{b}_2 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, +1, 0\right)$$

$$\vec{b}_3 = \frac{2\pi}{c}\,(0, 0, 1).$$

Note that

$$|\vec{b}_1| = |\vec{b}_2| = \frac{2\pi}{a}\frac{2}{\sqrt{3}}$$

and

$$|\vec{b}_3| = \frac{2\pi}{c}.$$

A reciprocal lattice vector $\vec{G}_m$ is given by

$$\vec{G}_m = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$$

$$= \left(\frac{2\pi}{\sqrt{3}\,a}(m_1 + m_2),\ \frac{2\pi}{a}(-m_1 + m_2),\ \frac{2\pi}{c}m_3\right)$$

Thus,

$$|\vec{G}_m| = \left\{ \left[\frac{2\pi}{\sqrt{3}a}(m_1+m_2)\right]^2 + \left[\frac{2\pi}{a}(-m_1+m_2)\right]^2 + \left(\frac{2\pi}{c}m_3\right)^2 \right\}^{\frac{1}{2}}$$

$$|\vec{G}_m| = \left[\frac{4\pi^2}{3a^2}(m_1^2+2m_1m_2+m_2^2) + \frac{4\pi^2}{a^2}(m_1^2-2m_1m_2+m_2^2) + \frac{4\pi^2}{c^2}m_3^2\right]^{\frac{1}{2}}$$

$$= 2\pi\left[\frac{4}{3}\frac{m_1^2}{a^2} - \frac{4}{3}\frac{m_1m_2}{a^2} + \frac{4}{3}\frac{m_2^2}{a^2} + \frac{m_3^2}{c^2}\right]^{\frac{1}{2}}$$

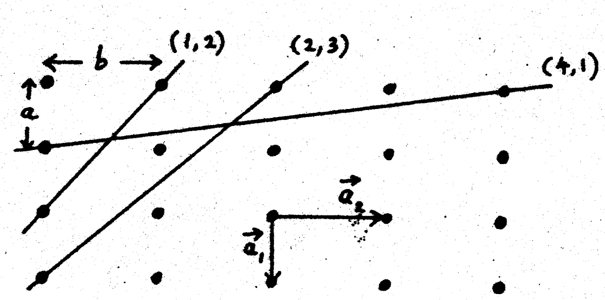
$$= 2\pi\left[\frac{4}{3}\frac{(m_1^2-m_1m_2+m_2^2)}{a^2} + \frac{m_3^2}{c^2}\right]^{\frac{1}{2}}$$

Provided that m_1, m_2 and m_3 have no factors in common the spacing between adjacent lattice planes perpendicular to $\vec{G}_m$ is

$$\Delta d = \frac{2\pi}{|\vec{G}_m|} = \underline{\underline{\left[\frac{4}{3}\frac{(m_1^2-m_1m_2+m_2^2)}{a^2} + \frac{m_3^2}{c^2}\right]^{-\frac{1}{2}}}}$$

<u>Problem 2</u> (30 %)

(a)



(b) $\vec{G}_m = 2\vec{b}_1 + 3\vec{b}_2$,

where $\vec{b}_1$ and $\vec{b}_2$ are the fundamental translation vectors of the reciprocal lattice corresponding to the direct lattice defined by

$$\vec{a}_1 = a(1,0)$$
$$\vec{a}_2 = b(0,1).$$

Thus,

$$\vec{b}_1 = \frac{2\pi}{a}(1,0)$$
$$\vec{b}_2 = \frac{2\pi}{b}(0,1).$$

(c) $\vec{G}_m = m_1\vec{b}_1 + m_2\vec{b}_2$

(d) For the (2,3) plane,

$$\vec{G}_{(2,3)} = 2\vec{b}_1 + 3\vec{b}_2$$
$$= \frac{4\pi}{a}(1,0) + \frac{6\pi}{b}(1,0)$$
$$= \left(\frac{4\pi}{a}, \frac{6\pi}{b}\right)$$

For the (1,2) plane,

$$\vec{G}_{(1,2)} = \vec{b}_1 + 2\vec{b}_2$$
$$= \left(\frac{2\pi}{a}, \frac{4\pi}{b}\right)$$

Taking the dot product of the normals to the two planes,

$$\vec{G}_{(2,3)} \cdot \vec{G}_{(1,2)} = \frac{8\pi^2}{a^2} + \frac{24\pi^2}{b^2} = 8\pi^2\left(\frac{1}{a^2} + \frac{3}{b^2}\right).$$

Let θ be the angle between the two planes. Then,

$$\cos\theta = \frac{\vec{G}_{(2,3)} \cdot \vec{G}_{(1,2)}}{|\vec{G}_{(2,3)}|\ |\vec{G}_{(1,2)}|}$$

$$|\vec{G}_{(2,3)}| = \sqrt{\left(\frac{4\pi}{a}\right)^2 + \left(\frac{6\pi}{b}\right)^2} = \pi\sqrt{\frac{16}{a^2} + \frac{36}{b^2}}$$

$$|\vec{G}_{(1,2)}| = \sqrt{\left(\frac{2\pi}{a}\right)^2 + \left(\frac{4\pi}{b}\right)^2} = \pi\sqrt{\frac{4}{a^2} + \frac{16}{b^2}}$$

Hence,

$$\cos\theta = \frac{8\pi^2\left(\frac{1}{a^2} + \frac{3}{b^2}\right)}{\pi^2\sqrt{\left(\frac{16}{a^2} + \frac{36}{b^2}\right)\left(\frac{4}{a^2} + \frac{16}{b^2}\right)}}$$

$$= \underline{\underline{\frac{2(b^2+3a^2)}{\sqrt{(4b^2+9a^2)(b^2+4a^2)}}}}$$

(e) For the $(4,1)$ plane, $\vec{G}_{(4,1)} = 4\vec{b}_1 + \vec{b}_2 = \left(\frac{8\pi}{a}, \frac{2\pi}{b}\right)$

As found before, $\vec{G}_{(1,2)} = \left(\frac{2\pi}{a}, \frac{4\pi}{b}\right)$

Let θ be the angle between the $(4,1)$ plane and the $(1,2)$ plane.

$$\cos\theta = \frac{\vec{G}_{(1,2)} \cdot \vec{G}_{(4,1)}}{|\vec{G}_{(1,2)}|\,|\vec{G}_{(4,1)}|}$$

$$= \frac{\dfrac{16\pi^2}{a^2} + \dfrac{8\pi^2}{b^2}}{\sqrt{\left[\left(\dfrac{4\pi^2}{a^2} + \dfrac{16\pi^2}{b^2}\right)\left(\dfrac{64\pi^2}{a^2} + \dfrac{4\pi^2}{b^2}\right)\right]}}$$

$$= \frac{4b^2 + 2a^2}{\sqrt{[(16b^2 + a^2)(b^2 + 4a^2)]}}$$

(f) For the (1,2) plane, $\vec{G_m} = \vec{b_1} + 2\vec{b_2} = \left(\frac{2\pi}{a}, \frac{4\pi}{b}\right)$.
Since 1 and 2 have no factors in common,

$$\Delta d = \frac{2\pi}{|\vec{G_m}|}.$$

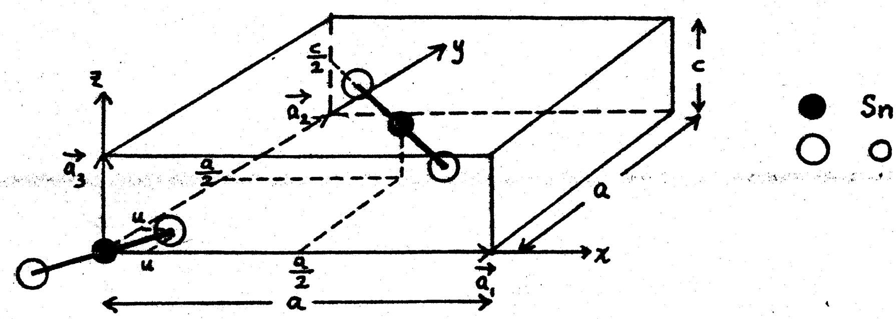
$$|\vec{G_m}| = \sqrt{\frac{4\pi^2}{a^2} + \frac{16\pi^2}{b^2}}$$

Therefore,

$$\Delta d = \frac{2\pi}{\sqrt{\dfrac{4\pi^2}{a^2} + \dfrac{16\pi^2}{b^2}}} = \frac{1}{\sqrt{\dfrac{1}{a^2} + \dfrac{4}{b^2}}}$$

Problem 3 (40%)

The primitive unit cell for SnO_2 is shown below.



(a) The fundamental translation vector for the primitive unit cell are

$$\vec{a_1} = a(1,0,0)$$
$$\vec{a_2} = a(0,1,0)$$
$$\vec{a_3} = c(0,0,1)$$

The positions of the Sn atoms are $(0,0,0)$, $(\frac{a}{2},\frac{a}{2},\frac{c}{2})$.
The positions of the O atoms are $(u,u,0)$, $(\bar{u},\bar{u},0)$, $(\frac{a}{2}-u, \frac{a}{2}+u, \frac{c}{2})$, $(\frac{a}{2}+u, \frac{a}{2}-u, \frac{c}{2})$,

where u = projection of bond length between Sn and O atoms on the x and y axes.

(b)

$$\vec{b}_1 = \frac{2\pi}{a}(1,0,0)$$

$$\vec{b}_2 = \frac{2\pi}{a}(0,1,0)$$

$$\vec{b}_3 = \frac{2\pi}{c}(0,0,1)$$

(c) $$f(\vec{r}) = \sum_j C_j \, \delta(\vec{r}-\vec{r}_j)$$

$$F_{\vec{G}_m} = \frac{1}{\Omega}\int_{\text{unit cell}} d^3r \, f(\vec{r})\, e^{-i\vec{G}_m\cdot\vec{r}}$$

$$= \frac{1}{\Omega}\int_{\text{unit cell}} d^3r \sum_j C_j \, \delta(\vec{r}-\vec{r}_j)\, e^{-i\vec{G}_m\cdot\vec{r}} ,$$

where $\vec{r} = x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3$
and $\vec{G}_m = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$.

<u>For $\vec{G}_m = (1,1,1)$</u> $= \vec{b}_1+\vec{b}_2+\vec{b}_3 = 2\pi\left(\frac{1}{a},\frac{1}{a},\frac{1}{c}\right)$.

$$F_{\vec{G}_m} = \frac{1}{\Omega}\int_{\text{unit cell}} d^3r \sum_j C_j \, \delta(\vec{r}-\vec{r}_j)\, e^{-i\,2\pi(x_1+x_2+x_3)}$$

$$F_{\vec{G}_m} = \frac{1}{\Omega}\Big\{A + (-A) + B\Big[e^{-i2\pi\left(\frac{u}{a}+\frac{u}{a}\right)} + e^{-i2\pi\left(-\frac{u}{a},-\frac{u}{a}\right)}$$

$$+ e^{-i2\pi\left(\frac{1}{2}-\frac{u}{a}+\frac{1}{2}+\frac{u}{a}+\frac{1}{2}\right)} + e^{-i2\pi\left(\frac{1}{2}+\frac{u}{a}+\frac{1}{2}-\frac{u}{a}+\frac{1}{2}\right)}\Big]$$

$$F_{\vec{G}_m} = \frac{B}{\Omega}\left[e^{-i2\pi\frac{2u}{a}} + e^{+i2\pi\frac{2u}{a}} - 2\right]$$

$$= \frac{B}{\Omega}\left(2\cos\frac{4u\pi}{a} - 2\right)$$

$$= \frac{2B}{\Omega}\left(\cos\frac{4\pi u}{a} - 1\right)$$

$$= \frac{2B}{\Omega}\left(-2\sin^2\frac{2\pi u}{a}\right)$$

Therefore,

$$F_{\vec{G}_m} = 0 \quad \text{when} \quad \sin\frac{2\pi u}{a} = 0$$

$$\text{or} \quad \frac{u}{a} = \frac{1}{2}, 1, \frac{3}{2}, \cdots$$

This crystal structure requires that $u < \frac{a}{2}$, so $F_{\vec{G}_m} \neq 0$.

For $\vec{G}_m = (1,0,2)$

$$F_{\vec{G}_m} = \frac{1}{\Omega} \int_{\substack{\text{unit}\\ \text{cell}}} d^3r \sum_j C_j \, \delta(\vec{r}-\vec{r}_j) \, e^{-i\left(\frac{x_1}{a} + \frac{2x_3}{c}\right)2\pi}$$

$$F_{\vec{G}_m} = \frac{1}{\Omega}\left\{A - A + B\left[e^{-i2\pi\left(\frac{u}{a}\right)} + e^{-i2\pi\left(-\frac{u}{a}\right)} + e^{-i\left(\frac{1}{2}-\frac{u}{a}+1\right)2\pi} + e^{-i\left(\frac{1}{2}+\frac{u}{a}+1\right)2\pi}\right]\right.$$

$$= \frac{B}{\Omega}\left[2\cos\frac{2\pi u}{a} + e^{-i\left(-\frac{u}{a}+\frac{3}{2}\right)2\pi} + e^{-i\left(\frac{u}{a}+\frac{3}{2}\right)2\pi}\right]$$

$$= \frac{2B}{\Omega}\left(\cos\frac{2\pi u}{a} - \cos\frac{2\pi u}{a}\right)$$

$$= 0 \quad \text{for all } u.$$

For $\vec{G}_m = (1,1,0)$

$$F_{\vec{G}_m} = \frac{1}{\Omega} \int_{\substack{\text{unit}\\ \text{cell}}} d^3r \sum_j C_j \, \delta(\vec{r}-\vec{r}_j) \, e^{-i\left(\frac{x_1}{a} + \frac{x_2}{a}\right)2\pi}$$

$$= \frac{1}{\Omega}\Big\{ A + A + B\Big[e^{-i2\pi\left(\frac{2u}{a}\right)} + e^{i2\pi\left(\frac{2u}{a}\right)} + e^{-i2\pi\left(\frac{1}{2}-\frac{u}{a}+\frac{1}{2}+\frac{u}{a}\right)} + e^{-i2\pi\left(\frac{1}{2}+\frac{u}{a}+\frac{1}{2}-\frac{u}{a}\right)}\Big]$$

$$= \frac{1}{\Omega}\Big[2A + B\Big(2\cos\frac{4\pi u}{a} + 2\Big)\Big]$$

$$= \frac{2}{\Omega}\Big(A + 2B\cos^2\frac{2\pi u}{a}\Big)$$

$F_{\vec{G}_m} = 0$ when $\cos^2\frac{2\pi u}{a} = -\frac{A}{2B}$

This is impossible if $A, B > 0$.

Thus, $F_{\vec{G}_m} \neq 0$ for all u

Conclusion

$F_{\vec{G}_m}$ vanishes for $\vec{G}_m = (1,0,2)$ for all u

This means that $f(\vec{r}) = \sum_{\vec{G}_m} F_{\vec{G}_m} e^{-i\vec{G}_m\cdot\vec{r}}$, when decomposed into a sum over $\vec{G}_m$ of waves travelling in the $\vec{G}_m$ direction, has no component for $\vec{G}_m = (1,0,2)$.