Assignment 4 : Solution

1. Show the Fourier transformation of face centered cubic direct lattice is a body centered lattice in the reciprocal space.
   Solution:
   As we know, the Fourier transform of a lattice gives the reciprocal lattice which, means to prove that the Fourier transform of the face-centered cubic direct lattice is a body-centered lattice in the reciprocal space we just need to find the basis vectors in reciprocal space. Take $\vec{a}_1, \vec{a}_2, \vec{a}_3$, as the direct lattice primitive basis vectors of the face centered cubic lattice, which are:

$$\begin{aligned} \vec{a} &= \frac{a}{2}(\hat{j} + \hat{k}) \\ \vec{b} &= \frac{a}{2}(\hat{i} + \hat{k}) \\ \vec{c} &= \frac{a}{2}(\hat{i} + \hat{j}) \end{aligned} \tag{1}$$

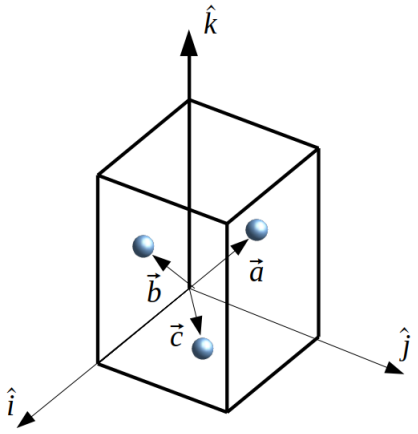


Figure 1: Face Centered Direct Lattice

Take $\vec{a}^*, \vec{b}^*, \vec{c}^*$, as the basis vectors in reciprocal space. To find these basis vectors we

can use the following equations with $\Omega = \vec{a}.\vec{b} \times \vec{c}$

$$\begin{aligned} \vec{a}^* &= 2\pi \frac{\vec{b} \times \vec{c}}{\Omega} \\ \vec{b}^* &= 2\pi \frac{\vec{c} \times \vec{a}}{\Omega} \\ \vec{c}^* &= 2\pi \frac{\vec{a} \times \vec{b}}{\Omega} \end{aligned} \tag{2}$$

Now,

$$\vec{a}.(\vec{b} \times \vec{c}) = \frac{a^3}{8} \begin{vmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{vmatrix} = \frac{a^3}{4} \tag{3}$$

$$\begin{aligned} \vec{a}^* &= \frac{8\pi}{a^3} . \frac{a^2}{4} \begin{vmatrix} \hat{i} & \hat{k} & \hat{k} \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{vmatrix} = \frac{2\pi}{a}(-\hat{i} + \hat{j} + \hat{k}) \\ \vec{b}^* &= \frac{8\pi}{a^3} . \frac{a^2}{4} \begin{vmatrix} \hat{i} & \hat{k} & \hat{k} \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{vmatrix} = \frac{2\pi}{a}(\hat{i} - \hat{j} + \hat{k}) \\ \vec{c}^* &= \frac{8\pi}{a^3} . \frac{a^2}{4} \begin{vmatrix} \hat{i} & \hat{k} & \hat{k} \\ 0 & 1 & 1 \\ 1 & 0 & 1 \end{vmatrix} = \frac{2\pi}{a}(\hat{i} + \hat{j} - \hat{k}) \end{aligned} \tag{4}$$

Noted that these lattice vectors are the primitive lattice vectors of a body-centered lattice. Hence, Fourier transformation of face-centered cubic direct lattice is a body-centered lattice in the reciprocal space.

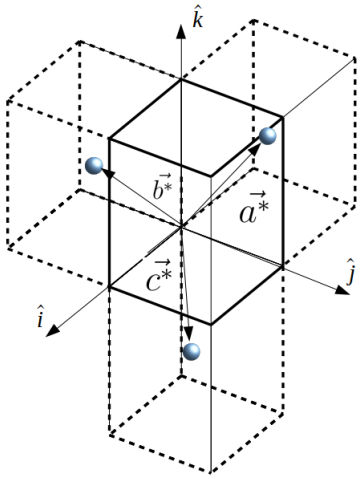


Figure 2: Face Centered Direct Lattice

2. (a) Show clearly, with all steps, that the Fourier transformation of a direct lattice is indeed the reciprocal lattice.

Solution:

Consider a 1D direct lattice because it's easy to start by thinking in one dimension. Direct lattice can be represented by a set of delta functions:

$$\mathcal{L}(x) = \sum_n \delta(x - an) \tag{5}$$

These delta functions describe the density of each point in 1D. Fourier transformation of this function gives:

$$\begin{aligned} \mathcal{F}(\mathcal{L}(x)) &= \int dx e^{ikx} \mathcal{L}(x) \\ &= \sum_n \int dx e^{ikx} \delta(x - an) = \sum_n e^{ikan} \end{aligned} \tag{6}$$

Now in class, we proved the following

$$\sum_m e^{\frac{-2\pi m x}{p}} = p \sum_n \delta(x - an) \tag{7}$$

which can be inserted to Eq.(6) yielding

$$\mathcal{F}(\mathcal{L}(x)) = \frac{2\pi}{a} \sum_n \delta\left(k - n\frac{2\pi}{a}\right) \tag{8}$$

Note that $\frac{2\pi}{a}$ is the length of a reciprocal vector $\vec{G}$ in 1D. This result can be extended to three dimensions

$$\mathcal{F}(\mathcal{L}(r)) = \frac{2\pi}{V} \sum_G \delta^3\left(\vec{k} - \vec{G}\right) \tag{9}$$

We obtain the delta peaks at the positions of reciprocal lattice which show that Fourier transformation of the direct lattice is reciprocal lattice.

(b) Prove the shift theorem used in Fourier theory, i.e., if in 1D,

$$\begin{aligned} \mathcal{F}(f(x)) &= \hat{F}(k) \\ \mathcal{F}(f(x - a)) &= \hat{F}(k) e^{-ika} \end{aligned}$$

Solution:

Fourier transformation of a function $f(x)$ and $f(x - a)$:

$$\begin{aligned} \mathcal{F}(f(x)) &= \int dx f(x) e^{-ikx} \\ \mathcal{F}(f(x - a)) &= \int dx f(x - a) e^{-ik(x)} \end{aligned} \tag{10}$$

Let take $y = x - a$ which gives $dy = dy$ then equation (6b) becomes,

$$\mathcal{F}(f(y)) = \int dx f(y) e^{-ik(y+a)} = e^{-ika} \int dx f(y) e^{-iky} \tag{11}$$

Last integral is same as in equation (6a) so we can use the given equation $\mathcal{F}(f(x)) = \hat{F}(k)$ just replacing x with y, we get:

$$\begin{aligned} \mathcal{F}(f(y)) &= e^{-ika}\hat{F}(k) \\ \mathcal{F}(f(x-a)) &= e^{-ika}\hat{F}(k) \end{aligned} \tag{12}$$

3. Cs and CsCl are both simple primitive Bravais lattices. In each case:

   (a) Identify the basis.
   Solution:
   For Cs, basis comprises Cs atom at $[0, 0, 0]$
   For $CsCl$, basis comprises C_5 at $[0, 0, 0]$ and Cl at $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$.

   (b) Find the structure factor $S(hkl)$.
   Solution:
   Let's first find the structure factor for the lattice. For any primitive lattice

$$S_{lattice}(hkl) = e^{i(h.0+k.0+l.0)} = 1. \tag{13}$$

   Now for the basis, the structure factor for (hkl) is:

$$S_{(hkl)} = \sum_j f_j e^{i\vec{G}.\vec{d_j}} \tag{14}$$

   where, $\vec{d_j}$ is the location of the jth atom in the basis.
   Cs has one atom in the basis, its basis structure factor will be:

$$\begin{aligned} S_{(hkl)} &= f_{Cs} e^{i\vec{G}.[0\vec{a}+0\vec{b}+0\vec{c}]} \\ &= f_{Cs} e^{i2\pi(h\vec{a}^*+k\vec{b}^*+l\vec{c}^*).(0)} \\ &= f_{Cs} \end{aligned} \tag{15}$$

$$\begin{aligned} S_{Cs}(hkl) &= S_{lattice}(hkl) S_{basis}(hkl) \\ &= 1.f_{Cs} \\ &= f_{Cs} \end{aligned} \tag{16}$$

   Similarly, for $CsCl$, the lattice structure factor does not change, for the basis it does.

$$\begin{aligned} S_{basis}(hkl) &= f_{Cs} e^{i(0)} + f_{Cl} e^{i2\pi(h\vec{a}^*+k\vec{b}^*+l\vec{c}^*).[\frac{\vec{a}}{2}\frac{\vec{b}}{2}\frac{\vec{c}}{2}]} \\ &= f_{Cs} + f_{Cl} e^{i\pi(h+k+l)}. \end{aligned} \tag{17}$$

   So,

$$S_{CsCl}(hkl) = S_{lattice}(hkl) S_{basis}(hkl) = f_{Cs} + f_{Cl} e^{i\pi(h+k+l)}. \tag{18}$$

(c) Mention a few planes which give/do not give scattered intensities.
Solution:
For bath Cs and $CsCl$, there are no systematic absences. No combination of (hkl) can yield zero structure factor. All planes will scatter X-rays.

4. Consider the accompanying figure showing scattering of X-rays of wavelength λ from a one-dimensional crystal with monoatomic basis and spacing a. The vector $\vec{s}_o$ and $\vec{s}$ are incident and scattered directions. Note the vector $\vec{a}$ and angle α_o and β_o.

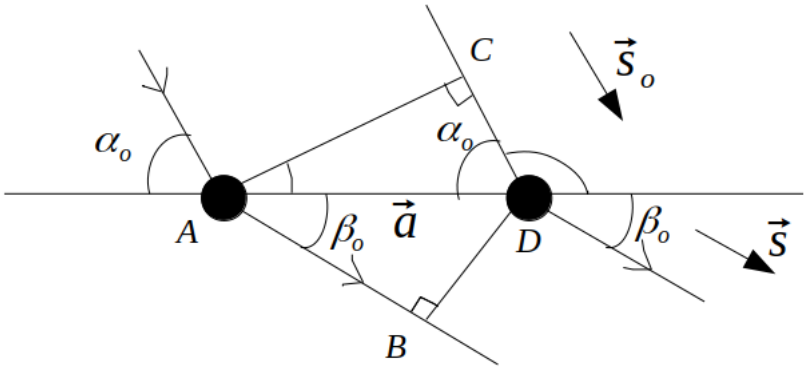


Figure 3

(a) Scattering takes place when the path difference is an integral number of wavelength, $n_x\lambda$. What is the path difference between the two scattered X-rays?
Solution:
Consider the figure showing right angle triangles ACD and ABD. In figure shown that path difference between the two scattered X-rays is:

$$\Delta = \overline{AB} - \overline{CD}$$
$$\Delta = acos\beta_o - acos\alpha_o$$

(b) Show that in vectorial form

$$\vec{a}.(\vec{s} - \vec{s}_o) = n_x\lambda \tag{19}$$

Solution:
Now $a\cos\beta_o = \vec{a}.\vec{s}$ and $a\cos\alpha_o = \vec{a}.\vec{s}_o$ where $\vec{s}$ and $\vec{s}_o$ are unit vectors. Therefore, it immediately follow that for constructive interference to occur,

$$\vec{a}.\vec{s} - \vec{a}.\vec{s}_o = \vec{a}.(\vec{s} - \vec{s}_o) = n_x\lambda. \tag{20}$$

From part (a),

$$acos\beta_o - acos\alpha_o = n_x\lambda \tag{21}$$

(c) Write similar vectorial equations for the x, y, z directions in a 3D crystal, i.e.

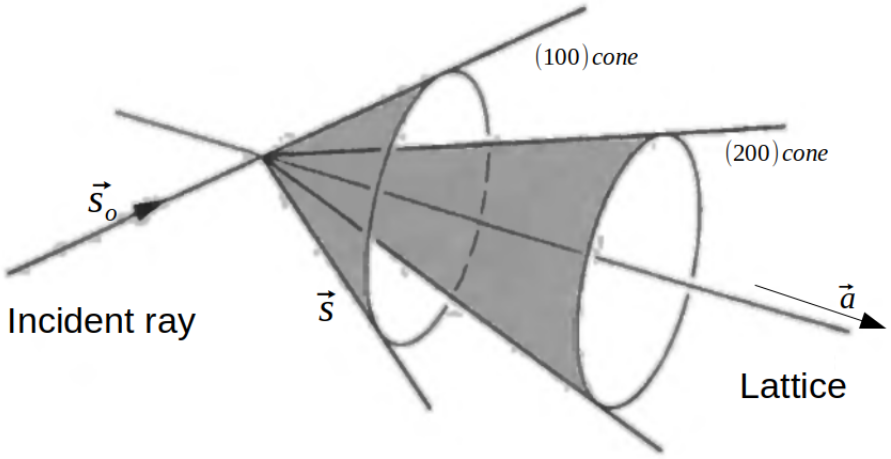
$$\vec{b}.(\vec{s}-\vec{s_o}) = n_y\lambda \tag{22}$$
$$\vec{c}.(\vec{s}-\vec{s_o}) = n_z\lambda \tag{23}$$

Solution:
Take the other axis and follow the same procedure we did in previous part.

(d) Show graphically that Eq. 1 results in scattering along the surface of a cone. What is the axis of this cone?
Solution:
Figure shows the cones for first order (100) and second order (200). The axis of the cones are along $\vec{a}$. All points on the surface of the cone satisfy

$$\vec{a}.(\vec{s}-\vec{s_o}) = n_x\lambda$$

Similarly, cones can be drawn along $\vec{b}$ and $\vec{c}$ axes. The actual diffracted rays are along the intersections of these cones



(e) The figure 1 is called the Laue formulation. By the equivalence of Lane and Bragg formulation, show the n_x, n_y and n_z in Eqs. 1-3 are Miller indices of the Miller planes.
Solution:
From the Laue formula:

$$\vec{a}.(\vec{s}-\vec{s_o}) = n_x\lambda \tag{24}$$

From the Bragg's formula:

$$\begin{aligned} \vec{k}-\vec{k_o} &= \vec{G} \\ \frac{2\pi}{\lambda}\vec{s}-\vec{s_o} &= \vec{G} \end{aligned} \tag{25}$$

From (24) and (25)

$$\begin{aligned} n_x\lambda = \vec{a}.(\vec{s}-\vec{s}_o) &= \frac{\lambda}{2\pi}\vec{a}.\vec{G} \\ &= \frac{\lambda}{2\pi}\vec{a}.h\vec{a^*} + k\vec{b^*} + l\vec{c^*} \\ &= \lambda h \end{aligned}$$

which shows that $n_x = h$. Likewise, we can show that $n_y = k$ and $n_x = l$.

5. The length of a reciprocal lattice vector normal to an (hkl) plane is

$$|\vec{d^*_{hkl}}| = \frac{2\pi}{d_{hkl}},$$

where d_{hkl} is the inter planar spacing.

(a) Show that for an orthogonal crystal system

$$\frac{1}{d_{hkl}} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{\frac{1}{2}} \tag{26}$$

In this part, I require you to use the formula for a vector length and the definition of the reciprocal lattice vectors $(\vec{a^*}, \vec{b^*}, \vec{c^*})$. How does this formula look when we have a cubic crystal system?

Solution:

Reciprocal lattice vector:

$$\vec{G} = h\vec{a^*} + k\vec{b^*} + l\vec{c^*}. \tag{27}$$

Using vector length formula:

$$|\vec{d^*}_{hkl}| = \sqrt{h^2(\vec{a^*})^2 + k^2(\vec{b^*})^2 + l^2(\vec{c^*})^2}. \tag{28}$$

For orthogonal system,

$$|\vec{a^*}| = \frac{2\pi}{a}, \qquad |\vec{b^*}| = \frac{2\pi}{b}, \qquad |\vec{c^*}| = \frac{2\pi}{b}.$$

$$|\vec{d^*}_{hkl}| = 2\pi\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}.$$

$$\frac{2\pi}{|\vec{d}_{hkl}|} = 2\pi\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}.$$

$$\frac{1}{d_{hkl}} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{\frac{1}{2}}.$$

6. $BaTiO_3$ is $Pm\bar{3}m$. The basis is:

$$\begin{array}{ll} Ba & [0,0,0] \\ Ti & \left[\frac{1}{2},\frac{1}{2},\frac{1}{2}\right] \\ O & \left[\frac{1}{2},\frac{1}{2},0\right], \left[\frac{1}{2},0,\frac{1}{2}\right], \left[0,\frac{1}{2},\frac{1}{2}\right]. \end{array}$$

(a) Sketch the unit cell.
Solution:

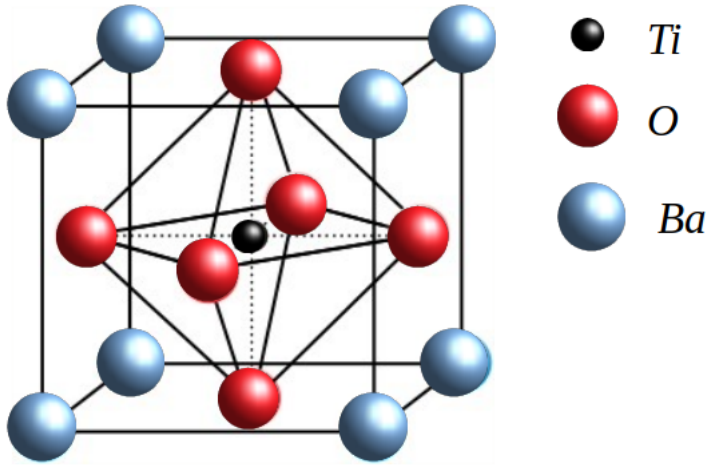


Figure 4

(b) Find $S(001)$ where the atomic form factors are f_{Ba}, f_{Ti}, f_O, i.e. find $S(hkl)$ for $h=0, k=0, l=1$. You are required to find the structure factors for both the lattice and the basis. Then multiply the two together.
Solution:
Structure factor for the lattice is unity since its a primitive lattice. Structure factor for basis:

$$\begin{aligned} S_{basis(}hkl)^{Basis} =& f_{Ba}e^{i2\pi(0)} + f_{Ti}e^{i2\pi(\frac{h}{2}\frac{k}{2}\frac{l}{2})} \\ &+ f_O(e^{i2\pi(\frac{h}{2}\frac{k}{2})} + e^{i2\pi(\frac{h}{2}\frac{l}{2})} + e^{i2\pi(\frac{k}{2}0\frac{l}{2})}). \end{aligned} \tag{29}$$

For $(hkl) = (001)$,

$$S_{basis}(hkl) = f_{Ba} - f_{Ti} - f_O(1-1-1) = f_{Ba} - f_{Ti} - f_O. \tag{30}$$

The overall, structure factor will be

$$\begin{aligned} S(hkl) &= S_{lattice}(hkl) \times S_{basis}(hkl), \\ &= f_{Ba} - f_{Ti} - f_O. \end{aligned} \tag{31}$$

7. Copper ($Fm\bar{3}m$) is shone with X-rays ($\lambda = 154pm$).

   (a) Show that for the scattering angle θ,

   $$sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2) = \frac{\lambda^2}{4a^2}N = A \times N.$$

   where $N = h^2 + k^2 + l^2$ must be an integer.

   (b) A real experiment yields the scattering directions tabulated in the given table. Complete the table and in the process verify that the crystal system is cubic and find the unit cell size.

Solution:

(a) For the cubic system,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \tag{32}$$

According to Bragg's law $d = \frac{\lambda}{2sin\theta}$. Inserting into the above equation, becomes,

$$\begin{aligned} \frac{4sin^2\theta}{\lambda^2} &= \frac{h^2 + k^2 + l^2}{a^2} \\ sin^2\theta &= \left(\frac{\lambda^2}{4a^2}\right)(h^2 + k^2 + l^2) = AN, \end{aligned}$$

where N is an integer.

(b) Therefore each value of $sin^2\theta$ be decomposable as a constant A and an integer. Now consider the accompany table as our first trial, we choose $N = 1$ and the top most row with the smallest value of $sin^2\theta$. Now $sin^2\theta/N = A = 0.1335/1 = 0.1365$. For successive rows,

$$\frac{sin^2\theta}{A} = \frac{0.1820}{0.1365}, \frac{0.3640}{0.1356}, \frac{0.5005}{0.1356}..... = 1.33, 2.66, 3.66, ...,$$

which are not integers. Hence $N = 1$ is not a solution for $sin^2\theta = 0.1365$. Let's repeat the procedure for $N = 2$, yielding $A = \frac{0.1365}{2} = 0.15825$. Applying this A to successive rows results in,

$$\frac{sin^2\theta}{A} = \frac{0.1820}{0.15825}, \frac{0.3640}{0.15825}, \frac{0.5005}{0.15825}..... = 1.15, 2.30, 3.16, ...,$$

$sin^2\theta$	N	h	k	l
0.1365	3	1	1	1
0.1820	4	2	0	0
0.3640	8	2	2	0
0.5005	11	3	1	1
0.5460	12	2	2	2
0.7280	16	4	0	0
0.8645	19	3	3	1
0.9100	20	4	2	0

Once again the results are not integers, so we try $N = 3$. With $N = 3$, our trial A becomes $\frac{0.1365}{3} = 0.0455$ and the application of A to successive rows results in,

$$\frac{sin^2\theta}{A} = \frac{0.1820}{0.0455}, \frac{0.3640}{0.0455}, \frac{0.5005}{0.0455}..... = 4, 8, 11, ...,$$

which are indeed integers. Hence $A = 0.0455 = \frac{\lambda^2}{4a^2}$ gives us the unit cell size $a = \sqrt{\frac{\lambda^2}{4\times 0.045}} = 361pm = 0.36nm$.
With $A = 0.0455$, the complete table is shown.

8. Find the systematic absences in the diamond $Fd\bar{3}m$ crystal structure.
Solution:
Let's first derive the structure factor (S) for the face centered cubic lattice.

$$\vec{R}_1 = (0, 0, 0)$$
$$\vec{R}_2 = (\frac{1}{2}, \frac{1}{2}, 0)$$
$$\vec{R}_3 = (\frac{1}{2}, 0, \frac{1}{2})$$
$$\vec{R}_4 = (0, \frac{1}{2}, \frac{1}{2})$$

$$\begin{aligned} S_{lattice}(hkl) &= e^{(i0)} + e^{i2\pi(\frac{h}{2}+\frac{k}{2})} + e^{i2\pi(\frac{h}{2}+\frac{l}{2})} + e^{i2\pi(\frac{k}{2}+\frac{l}{2})} \\ &= 1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)} \end{aligned}$$

If each of h, k and l is even, $S_{lattice} = 4$.
If each of h, k and l is odd, $S_{lattice} = 4$.
If h, k and l are mixed even and odd, $S_{lattice} = 0$.
Therefore planes such (100), (123), (243) etc will not scatter X-rays for all structure

h	k	l	$h+k+l$
0	0	0	0
1	1	1	3
2	0	0	2
2	2	0	4
2	2	2	6
3	1	1	5
3	3	1	7
3	3	3	9

with an underlying face centered cubic lattice.
The basis comprises C atoms at

$$\vec{d_1} = (0,0,0)$$
$$\vec{d_2} = (\frac{1}{4},\frac{1}{4},\frac{1}{4})$$

$$\begin{aligned} S_{basis}(hkl) &= f_C(e^{i0} + e^{i2\pi(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}))} \\ &= f_C(1 + e^{i\frac{\pi}{2}(h+k+l)}) \end{aligned}$$

The face centered cubic lattice are: So, $h+k+l = n(someinteger)$. If
$h+k+l = 4n+1$, e.g $1,5,9,...$ then $S_{basis}(hkl) = f_C(1+i)$
$h+k+l = 4n+3$, e.g $3,7,11,...$ then $S_{basis}(hkl) = f_C(1-i)$
$h+k+l = 4n$, e.g $0,4,8,...$ then $S_{basis}(hkl) = 2f_C$
$h+k+l = 4n+2$, e.g $2,6,10,...$ then $S_{basis}(hkl) = 0$

$$\begin{aligned} &S_{basis}(hkl) = f_C(1+i) && if && h+k+l = 4n+1 \\ &S_{basis}(hkl) = f_C(1-i) && if && h+k+l = 4n+3 \\ &S_{basis}(hkl) = 2f_C && if && h+k+l = 4n \\ &S_{basis}(hkl) = 0 && if && h+k+l = 4n+2 \end{aligned}$$

Plane such as (100), (123), (243), (200),(222) will be systematic absences.