Condensed Matter Physics

Problem Set 3

Crystal Structure, Reciprocal Lattice, and Scattering

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3.1 Crystal structure

This is a face-centred cubic (FCC) lattice with a basis:

$$\begin{aligned} \text{Zn} &: [0,0,0] \\ &: [1/2,0,1/2] \\ &: [0,1/2,1/2] \\ &: [1/2,1/2,0] \\ \text{S} &: [1/4,1/4,3/4] \\ &: [3/4,3/4,3/4] \\ &: [3/4,1/4,1/4] \\ &: [1/4,3/4,1/4] \end{aligned} \tag{1}$$

By simple geometry, the closest distances are:

$$\begin{aligned} d_{\text{Zn-Zn}} &= \frac{\sqrt{2}}{2}a \\ d_{\text{Zn-S}} &= \frac{\sqrt{3}}{4}a \\ d_{\text{S-S}} &= \frac{\sqrt{2}}{2}a \end{aligned} \tag{2}$$

The spacing between (210) planes is $d_{[210]} = \sqrt{5}a/10$.

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3.2 Directions and spacings of crystal planes

The direction $[hkl]$ is defined by the vector:

$$\mathbf{v} = h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3 \tag{3}$$

where as the plane (hkl) is defined by the equation:

$$\mathbf{r} \cdot \mathbf{G} = \mathbf{r} \cdot (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) = 2\pi m \tag{4}$$

Since we have $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$, we substitute $\mathbf{r} \to \mathbf{v}$:

$$\begin{aligned}\mathbf{v}\cdot\mathbf{G} &= h^2\mathbf{a}_1\cdot\mathbf{b}_1 + k^2\mathbf{a}_2\cdot\mathbf{b}_2 + l\mathbf{a}_3\cdot\mathbf{b}_3 \\ &= 2\pi(h+k+l)\end{aligned} \tag{5}$$

which satisfies the condition for the (hkl) plane, i.e. vector $\mathbf{v}$ is perpendicular to the (hkl) plane.

The same holds true for an orthorhombic lattice, where the (reciprocal) lattice vectors are orthogonal to each other.

The spacing between (hkl) planes is:

$$\begin{aligned}d &= \frac{2\pi}{|\mathbf{G}|} \\ &= \frac{2\pi}{\sqrt{(2\pi/a)^2(h^2+k^2+l^2)}} \\ &= \frac{a}{\sqrt{h^2+k^2+l^2}}\end{aligned} \tag{6}$$

To generalize this to an orthorhombic lattice, we have:

$$\begin{aligned}d &= \frac{2\pi}{|\mathbf{G}|} \\ &= \frac{2\pi}{\sqrt{(2\pi h/a)^2+(2\pi k/b)^2+(2\pi l/c)^2}} \\ &= \frac{1}{\sqrt{(h/a)^2+(k/b)^2+(l/c)^2}}\end{aligned} \tag{7}$$

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3.3 Reciprocal lattice

(b) Consider the given expressions for the reciprocal lattice vectors. We have:

$$\begin{aligned}\mathbf{a}_1\cdot\mathbf{b}_1 &= 2\pi\frac{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3} = 2\pi \\ \mathbf{a}_1\cdot\mathbf{b}_2 &= 2\pi\frac{\mathbf{a}_1\cdot\mathbf{a}_3\times\mathbf{a}_1}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3} = 0 \\ \mathbf{a}_1\cdot\mathbf{b}_3 &= 2\pi\frac{\mathbf{a}_1\cdot\mathbf{a}_1\times\mathbf{a}_2}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3} = 0\end{aligned} \tag{8}$$

where the last two expressions are zero because $\mathbf{a}_1$ is orthogonal to $\mathbf{a}_3 \times \mathbf{a}_1$ and $\mathbf{a}_1 \times \mathbf{a}_2$. A similar argument can be made for the other reciprocal lattice vectors.

(c) Tetragonal lattice has two of the three sides equal at 90°, whereas orthorhombic lattice has all three sides unequal at 90°. For orthorhombic lattice, a lattice vector can be written as:

$$\mathbf{R} = ha_1\hat{\mathbf{x}} + ka_2\hat{\mathbf{y}} + la_3\hat{\mathbf{z}} \tag{9}$$

The vectors are already orthogonal so we choose $\mathbf{b}_i = 2\pi\hat{\mathbf{i}}/a_i$. The length of a reciprocal lattice vector is:

$$\begin{aligned} |\mathbf{G}| &= |h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3| \\ &= \sqrt{h^2\left(\frac{2\pi}{a_1}\right)^2 + k^2\left(\frac{2\pi}{a_2}\right)^2 + l^2\left(\frac{2\pi}{a_3}\right)^2} \\ &= 2\pi\sqrt{\frac{h^2}{a_1^2} + \frac{k^2}{a_2^2} + \frac{l^2}{a_3^2}} \\ &= 2\pi/d \end{aligned} \tag{10}$$

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3.4 Reciprocal lattice and diffraction

The (210) planes cut the x-axis at $x = a/2$, y-axis at $y = a$. The reciprocal lattice vector is thus $\mathbf{G} = 4\pi/a_1\hat{\mathbf{x}} + 2\pi/a_2\hat{\mathbf{y}}$. Now consider the relation:

$$\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k} = \mathbf{G} \tag{11}$$

The two wave vectors have the same magnitude so the difference has the length $\Delta k = 2k\sin\theta$. But the length of $\mathbf{G}$ is $2\pi/d$ so we arrive at the Laue condition:

$$\lambda = 2d\sin\theta \tag{12}$$

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3.5 Scattering from a crystal lattice

The X-ray structure factor for $(00l)$ Bragg reflection is:

$$\begin{aligned} S_{00l} &= f_{Ba} + f_{Ti}\exp\left\{2\pi i(00l)[\frac{1}{2}\frac{1}{2}\frac{1}{2}]\right\} \\ &\quad + f_O\left[\exp\left\{2\pi i(00l)[\frac{1}{2}\frac{1}{2}0]\right\} + \exp\left\{2\pi i(00l)[\frac{1}{2}0\frac{1}{2}]\right\} + \exp\left\{2\pi i(00l)[0\frac{1}{2}\frac{1}{2}]\right\}\right] \\ &= f_{Ba} + f_{Ti}\exp\{2\pi il\} + f_O\left[1 + 2\exp\{2\pi il\}\right] \\ &= f_{Ba} + (-1)^l f_{Ti} + \left[1 + 2(-1)^l\right] f_O \end{aligned} \tag{13}$$

We have the intensity ratio:

$$\begin{aligned} \frac{I_{002}}{I_{001}} &= \frac{(f_{Ba} + f_{Ti} + 3f_O)^2}{(f_{Ba} + f_{Ti} - f_O)^2} \\ &= \left(\frac{Z_{Ba} + Z_{Ti} + 3Z_O}{Z_{Ba} + Z_{Ti} - Z_O}\right)^2 \\ &= 15.4 \end{aligned} \tag{14}$$

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3.6 X-ray scattering and systematic absences

(b) For BCC lattice, we have the basis:

$$\begin{aligned} X &: [0,0,0] \\ &: [1/2,1/2,1/2] \end{aligned} \tag{15}$$

Then the structure factor is:

$$\begin{aligned} S_{hkl} &= f_X\left[\exp\{2\pi i(hkl)[000]\} + \exp\left\{2\pi i(hkl)[\frac{1}{2}\frac{1}{2}\frac{1}{2}]\right\}\right] \\ &= f_X\left[1 + (-1)^{h+k+l}\right] \end{aligned} \tag{16}$$

which is $2f_X$ for $h+k+l$ even and zero otherwise.

For FCC lattice, we have the basis:

$$\begin{aligned} X &: [0,0,0] \\ &: [1/2,0,1/2] \\ &: [0,1/2,1/2] \\ &: [1/2,1/2,0] \end{aligned} \tag{17}$$

Then the structure factor is:

$$S_{hkl} = f_X \left[1 + (-1)^{h+k} + (-1)^{k+l} + (-1)^{l+h}\right] \tag{18}$$

which is $4f_X$ if h, k, and l are all even or all odd, and zero otherwise.

Thus (110) reflection is allowed for BCC lattice and forbidden for FCC lattice.

(c) The overall structure factor is a multiplication of the lattice factor and the basis factor. Thus, as long as the lattice is BCC or FCC, the selection rules apply regardless of the basis.

(d) Consider the following data:

2θ	d	$(d_1/d)^2$	3	$N = h^2+k^2+l^2$	hkl	$a = d\sqrt{h^2+k^2+l^2}$
42.3	0.2245	1	3	3	111	0.389
49.2	0.1945	1.331	3.99	4	200	0.389
72.2	0.1374	2.667	8	8	220	0.389
87.4	0.1172	3.667	11	11	311	0.389
92.3	0.1123	3.995	11.98	12	222	0.389

Thus the lattice is FCC with $a = 0.389$ nm.

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3.7 Neutron scattering

(a) If we have a NaCl lattice, the structure factor is:

$$\begin{aligned} S_{hkl} &= S^{\text{FCC}} \times S^{\text{basis}} \\ &= \left[1 + (-1)^{h+k} + (-1)^{k+l} + (-1)^{l+h}\right] \times \left[f_{Na} + f_H \exp\left\{2\pi i (hkl)[\frac{1}{4}\frac{1}{4}\frac{1}{4}]\right\}\right] \end{aligned} \tag{19}$$

Substituting $(hkl) = (111)$ and $(hkl) = (200)$, we have:

$$\begin{aligned} S_{111} &= 4(f_{Na} - if_H) \\ S_{200} &= 4(f_{Na} - f_H) \end{aligned} \tag{20}$$

If we have a ZnS lattice, the structure factor is:

$$\begin{aligned} S_{hkl} &= S^{\text{BCC}} \times S^{\text{basis}} \\ &= \left[1 + (-1)^{h+k+l}\right] \times \left[f_{Zn} + f_S \exp\left\{2\pi i(hkl)[\frac{1}{2}\frac{1}{2}\frac{1}{2}]\right\}\right] \end{aligned} \tag{21}$$

Substituting $(hkl) = (111)$ and $(hkl) = (200)$, we have:

$$\begin{aligned} S_{111} &= 0 \\ S_{200} &= 2(f_{Zn} - f_S) \end{aligned} \tag{22}$$

For (111) reflection to be much stronger than (200) reflection, we need NaCl lattice.

The difference between X-ray and neutron scattering lies mainly in the scattering intensity. For neutrons we may typically assume that the scatter length is independent of scattering angle, whereas the form factor for X-rays is angle-dependent.

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