15. <u>Indexing Diffraction Patterns</u>

Allowed reflections
Here is a summary of what we found for cubic systems: For sc, we can have any integer set of Miller indices $hk\ell$. For bcc, the only allowed reflections have $h+k+\ell$ even; the rest are absent. For fcc, we must $hk\ell$ either all even or all odd. It seems like the loss of some reflections should cause an increase somewhere else.

h	k	ℓ	$h^2+k^2+\ell^2$	sc	bcc	fcc
1	0	0	1	√		
1	1	0	2	√	√	
1	1	1	3	√		√
2	0	0	4	√	√	√
2	1	0	5	√		
2	1	1	6	√	√	
2	2	0	8	√	√	√
2	2	1	9	√		
2	2	2	12	√	√	√
3	0	0	9	√		
3	1	0	10	√	√	
3	1	1	11	√		√
3	2	0	13	√		
3	2	1	14	√	√	
3	2	2	17	√		
3	3	0	18	√	√	
3	3	1	19	√		√
3	3	2	22	√	√	
3	3	3	27	√		√
4	0	0	16	√	√	√
4	1	0	17	√		
4	1	1	18	√	√	
4	2	0	20	√	√	√
4	2	1	21	√		
4	2	2	24	√	√	√
4	3	0	25	√		
4	3	1	26	√	√	
4	3	2	29	√		
4	3	3	34	√	√	

For one thing, notice that when some reflections are absent, the structure factors of the rest are larger. For bcc, half of the possible $hk\ell$ values correspond to absent reflections, but the $F_{hk\ell}$ for the rest are twice as big (compared to sc). Likewise, for fcc, only one-fourth of all possible sets of $hk\ell$ values are all even or all odd, but the $F_{hk\ell}$ are four times bigger.

Another way to compare is in terms of nearest-neighbor distances. For sc, atoms are only on the corners:

$$d_{\text{n-n}} = a$$

For bcc, it's half of the body-diagonal distance, so

$$d_{\text{n-n}} = \sqrt{3}a/2 = 0.87a$$

For fcc, it's half of the face-diagonal distance, so

$$d_{\text{n-n}} = a/\sqrt{2} = 0.71a$$

For sc, the atomic concentration is

$$\rho = 1/a^3 = 1/d_{\text{n-n}}^3$$

For bcc, it's:

$$\rho = 2/a^3 = 3\sqrt{3}/8d_{\text{n-n}}^3 = 0.65/d_{\text{n-n}}^3$$

And for fcc, it's:

$$\rho = 4/a^3 = \sqrt{2}/d_{\text{n-n}}^3 = 1.41/d_{\text{n-n}}^3$$

If spherical atoms are packed in these arrangements so that they are just touching, the highest density (closest-packed) arrangement is fcc.

The zone axis

Take an arbitrary direct lattice vector:

$$\mathbf{r}_{uvw} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$$

An an RLV:

$$\mathbf{g}_{hk\ell} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3$$

The RLV is perpendicular to $[uvw]$ if:

$$\mathbf{g}_{hk\ell} \cdot \mathbf{r}_{uvw} = hu + kv + \ell w = 0$$

The vector $\mathbf{g}_{hk\ell} = \mathbf{g}_{hk\ell} - \mathbf{0}$ points from the reciprocal-space origin to the reciprocal-lattice point $hk\ell$. So $hk\ell$ is in the ZOLZ for the zone axis $[uvw]$. In other words, Laue zones are planes in the reciprocal lattice, which can be specified by the direct-lattice vector that they are perpendicular to.
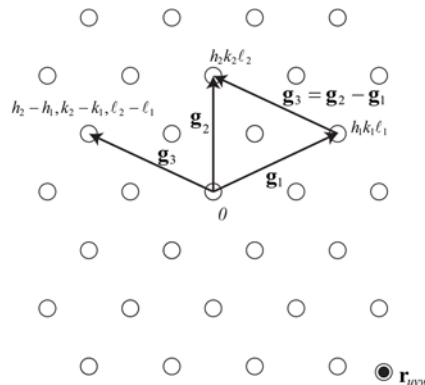
Take any two non-parallel RLVs, $\mathbf{g}_1$ and $\mathbf{g}_2$, perpendicular to $[uvw]$ ($\mathbf{g}_1 \cdot \mathbf{r}_{uvw} = 0$ and $\mathbf{g}_2 \cdot \mathbf{r}_{uvw} = 0$). Now consider their difference vector:

$$(\mathbf{g}_2 - \mathbf{g}_1) \cdot \mathbf{r}_{uvw} = 0$$

So $\mathbf{g}_2 - \mathbf{g}_1$ is also perpendicular to $[uvw]$. Furthermore, if the corresponding indices are $h_1 k_1 \ell_1$ and $h_2 k_2 \ell_2$, then $\mathbf{g}_2 - \mathbf{g}_1 = (h_2 - h_1)\mathbf{b}_1 + (k_2 - k_1)\mathbf{b}_2 + (\ell_2 - \ell_1)\mathbf{b}_3$, so the reciprocal-lattice point $h_2 - h_1, k_2 - k_1, \ell_2 - \ell_1$ is also in the $[uvw]$ ZOLZ.

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Finding the zone axis

Again consider two non-parallel RLVs, $\mathbf{g}_1$ and $\mathbf{g}_2$, perpendicular to $[uvw]$. The cross-product $\mathbf{g}_1 \times \mathbf{g}_2$ must be parallel (or anti-parallel) to $[uvw]$. By convention, the zone axis vector points out of the page, towards the viewer (opposite to the direction of the incident beam.) When we take the cross-product of two RLVs, we will encounter the cross-products of the reciprocal-lattice basis vectors. This generates weird combinations that involve all three direct-lattice basis vectors:

$$(\mathbf{a}_i \times \mathbf{a}_j) \times (\mathbf{a}_j \times \mathbf{a}_k) = [(\mathbf{a}_i \times \mathbf{a}_j) \cdot \mathbf{a}_k] \mathbf{a}_j = V \mathbf{a}_j$$

We end up with:

$$\mathbf{b}_2 \times \mathbf{b}_3 = \frac{\mathbf{a}_1}{V}, \ \mathbf{b}_3 \times \mathbf{b}_1 = \frac{\mathbf{a}_2}{V}, \text{ and } \mathbf{b}_1 \times \mathbf{b}_2 = \frac{\mathbf{a}_3}{V}$$

So we can write the cross-product of the RLVs fairly easily in terms of the direct-lattice basis vectors:

$$\mathbf{g}_1 \times \mathbf{g}_2 = \frac{1}{V} \begin{vmatrix} \mathbf{a}_1 & \mathbf{a}_2 & \mathbf{a}_3 \\ h_1 & k_1 & \ell_1 \\ h_2 & k_2 & \ell_2 \end{vmatrix}$$

If we only want to know the zone axis for a ZOLZ, we can take any two reflections that are not on a line containing 0, and evaluate:

$$[uvw] \| [k_1 \ell_2 - \ell_1 k_2, \ell_1 h_2 - h_1 \ell_2, h_1 k_2 - k_1 h_2]$$

Determining orientation

If we know the structure type, but not the lattice parameter, we can still figure out the orientation of a selected-area diffraction pattern (which consists almost entirely of ZOLZ reflections), index the ZOLZ reflections, and then deduce the lattice parameter. Say we know the structure for the pattern below is fcc:
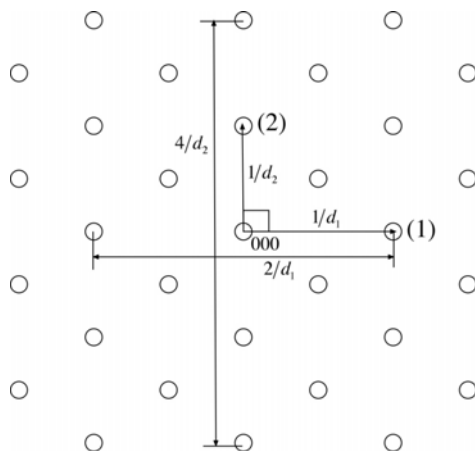
It helps to measure the angles between at least two rows of reflections. We usually know which spot is 0. (It must be there somewhere if it is a ZOLZ.) In this case, we see a horizontal row and a vertical row that are perpendicular to one another. Find the $2/d$ values for the longest $\mathbf{g}$ vectors on the pattern that can be measured reliably. Then back out the d values for the lowest-order reflection in that row. For example, call the lowest-order horizontal reflection 1 and the lowest-order vertical reflection 2. We measure $2/d_1$ and find $d_1 = 0.208 \text{ nm}$. Then we measure $4/d_2$ and find $d_2 = 0.293 \text{ nm}$.

We know it's fcc, wo we take the ratio and square, knowing that, for cubic crystals, the squared ratio should be a rational fraction. So we try to assign Miller indices consistent with the fraction:

$$\left(\frac{d_2}{d_1}\right)^2 = 1.98 \approx \frac{h_1^2 + k_1^2 + \ell_1^2}{h_2^2 + k_2^2 + \ell_2^2} = \frac{\cancel{2}}{\cancel{1}} = \frac{\cancel{4}}{\cancel{2}} = \frac{\cancel{6}}{\cancel{3}} = \frac{8}{4} = \frac{2^2 + 2^2 + 0^2}{2^2 + 0^2 + 0^2}$$

Now we can say that the horizontal reflection is a {220} and the vertical reflection is a {200}. We need to find particular Miller indices consistent with these that lie in the same ZOLZ. In this case, $\mathbf{g}_1 \cdot \mathbf{g}_2 = 0$, so we assign: $2\bar{2}0$ for reflection 1 and 002 for reflection 2.

Now we can find the zone axis. No need to keep extra factors of 2:

$$[uvw] = [\bar{1} \cdot 1 - 0 \cdot 0, 1 \cdot 0 - 1 \cdot 1, 1 \cdot 0 - 0 \cdot 1] = [\bar{1}\,\bar{1}0]$$

Our zone axis is then $\mathbf{B} = [\bar{1}\,\bar{1}0]$

I would prefer not to have the double negative in the indices. Let's reconsider this choice:

Revise and index

Let's make the change in indices $2\bar{2}0 \rightarrow \bar{2}20$. Now the zone axis is found using:

$$[uvw] = [1 \cdot 1 - 0 \cdot 0, 0 \cdot 0 - 1 \cdot \bar{1}, \bar{1} \cdot 0 - 0 \cdot 1] = [110]$$

So $\mathbf{B} = [110]$, which I like better.

Let's fill out some more indices, and try a few tricks. There is a spot halfway between 002 and $\bar{2}20$:
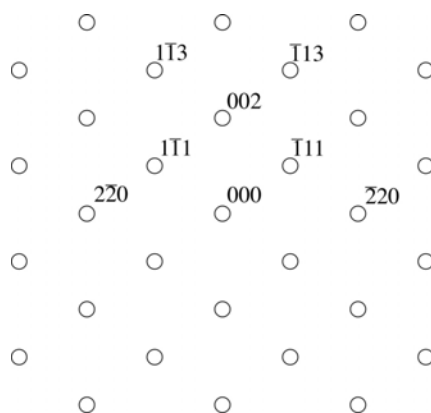
$$\frac{1}{2}[(002) + (\bar{2}20)] = (\bar{1}11)$$

Another spot is displaced from this new spot, $(\bar{1}11)$, by the vector connecting 0 to (002):

$$(\bar{1}11) + [(002) - (000)] = (\bar{1}13)$$

And so on and so forth, until we are satisfied. What is the spot opposite to $(2\bar{2}0)$?

$$(000) - [(2\bar{2}0) - (000)] = (\bar{2}20)$$

We don't always have to write (000), but it sometimes helps to keep track of what we are doing, especially when we get to indexing HOLZs!
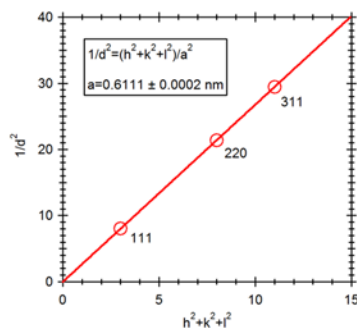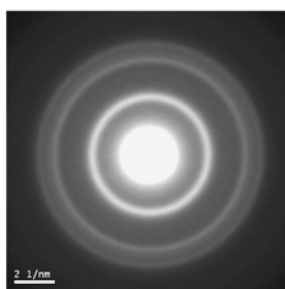

We can figure out the lattice parameter now. For example, we know $d_2 = d_{002} = a/2$. So

$$a = 2d_{002} = 0.586 \text{ nm}$$

Ah, yes. This is InP.

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Powder pattern (I): CdSe

Powder patterns show rings instead of spots, so we can't rely as much on symmetry, but the measurements can be simpler. Take a ring pattern from a powder:

List the rings, measure $2/d$ for each, then find the d spacings. (It's just usually a good idea.)

ring	$2/d$ (1/nm)	d (nm)
1	5.677	0.352
2	9.251	0.216
3	10.858	0.1842

If we think it is cubic, we may want to measure the lattice parameter. We need to know some indices first. The squared ratios should be rational fractions:

$$\left(\frac{d_2}{d_1}\right)^2 = 2.66 \approx \frac{8}{3} = \frac{2^2 + 2^2 + 0^2}{1^2 + 1^2 + 1^2} , \quad \left(\frac{d_3}{d_1}\right)^2 = 3.66 \approx \frac{11}{3} = \frac{3^2 + 1^2 + 1^2}{1^2 + 1^2 + 1^2}$$

So it looks like the indices are 1: 111, 2: 220, and 3: 311. This is consistent with fcc. For cubic, we know $\frac{1}{d} = \frac{\sqrt{h^2 + k^2 + \ell^2}}{a}$

We can plot $1/d^2$ vs. $h^2 + k^2 + \ell^2$ and perform a least-squares fit. The lattice parameter should be the square root of the inverse of the slope.

Powder pattern (II): Gd$_2$Ti$_2$O$_7$

Here is another example, also with an fcc lattice. The structure is a bit more complicated, and the crystallites are bigger, so the pattern is spotty. It can be useful to take a rotational average around the center of the pattern. This time, I just fit $1/d$ as a function of $(h^2 + k^2 + \ell^2)^{1/2}$.
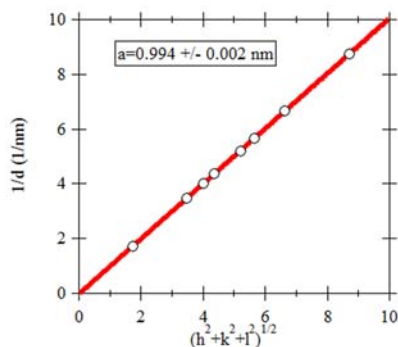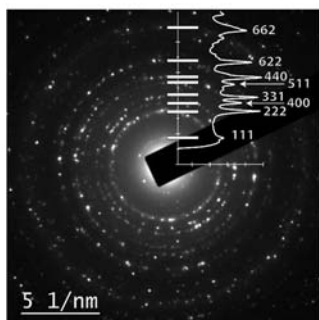
Structure factor and intensity

We saw that centered cubic lattices have missing reflections (systematic absences). How can adding extra atoms reduce the intensities of some diffraction peaks?
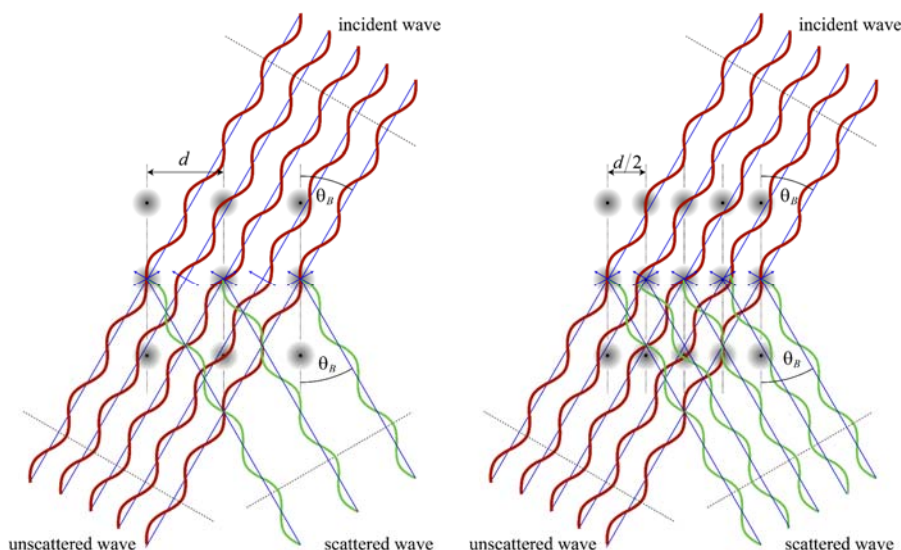
Say we set up the Bragg condition for some set of planes. The path length difference between two adjacent planes is exactly one wavelength λ, giving constructive interference and a strong diffraction peak or spot. If this unit cell has only one atom, with form factor f, we might say the structure factor for this reflection is

$$F_{\mathbf{g}} = f$$

Now we insert an extra, identical plane (though, in principle, it could be shifted laterally to any position parallel to the plane), between every pair of adjacent planes of the original structure. At the same crystal orientation, waves scattered from the the inserted planes have a path length differences of $\lambda/2$. So the interference is destructive and we observe no peak. This is revealed in the structure factor:

$$F_{\mathbf{g}} = f \cdot (1 + e^{\pi i}) = 0$$