Indexing an X-ray diffraction pattern

Just one example, but indexing problems all follow the same pattern.

June 2010, Q.1(a): Bragg reflections take place off a crystal of CaO, which has a cubic structure, at values of $\sin\theta = 0.400$, 0.462 and 0.653. Find the Miller indices of the planes likely to be responsible for these three reflections.

Solution: I would normally work in terms of the $\boldsymbol{G}$ vector of the reflection, where $\boldsymbol{G} = \boldsymbol{k}' - \boldsymbol{k}$. The angle between $\boldsymbol{k}'$ and $\boldsymbol{k}$ is 2θ, so [see note at end]

$$\tfrac{1}{2}|\boldsymbol{G}| = |\boldsymbol{k}| \sin\theta \,. \tag{1}$$

Now, the crystal is cubic, so $\boldsymbol{G} = (p_1\, p_2\, p_3) \times 2\pi/a$, where a is the cubic lattice parameter. So (1) shows that

$$\sin\theta \propto |\boldsymbol{G}| \propto \sqrt{p_1^2 + p_2^2 + p_3^2}\,,$$

or, more conveniently for "index-spotting",

$$\sin^2\theta \propto p_1^2 + p_2^2 + p_3^2\,.$$

From the given values of $\sin\theta$, the values of $\sin^2\theta$ are 0.160, 0.213 and 0.426. These are in the ratio $3:4:8$, which strongly suggests that the indices are $(p_1\, p_2\, p_3) = (1\,1\,1)$, $(2\,0\,0)$ and $(2\,2\,0)$.

For me, the above would be a satisfactory solution to the indexing problem—we have found vectors $\boldsymbol{G}$ that the reflections are likely to correspond to. However, as a reminder of how this relates to the Miller indices of lattice planes, you might want to read on.

If the crystal had the simple cubic lattice (as in the caesium chloride *structure*), we would say that there was first-order diffraction from the $(1\,1\,1)$ planes and second-order diffraction from the $(1\,0\,0)$ and $(1\,1\,0)$ planes: these "Miller indices" are just the values $(p_1\, p_2\, p_3)$ with any common integer factor removed; and the common integer factor is the order of reflection, i.e., the value of n that appears in the Bragg equation.

Actually, there is strong evidence from the data that the lattice is not *simple* cubic: if it were simple cubic, we'd expect to see the $(2\,1\,0)$ and $(2\,1\,1)$ reflections at angles intermediate between those for $(2\,0\,0)$ and $(2\,2\,0)$. The values of the p_i we found earlier were either all odd (in one case) or all even (in the other two cases). And this suggests that the reciprocal lattice is *body-centered*, so that the crystal lattice itself is *face-centered*. [There is a good diagram in the Wikipedia article on calcium oxide; the crystal structure is the same as for rocksalt/halite.]

Note: Make sure you can draw the vector diagram that leads to (1). In lectures, we derived the Bragg (or Bragg–Wulff) equation $n\lambda = 2d\sin\theta$ from (1); the Bragg equation is an equally good starting point for solving indexing problems, provided you remember a formula for interplanar spacings in a cubic crystal,

$$d_{p_1p_2p_3} = \frac{a}{\sqrt{p_1^2 + p_2^2 + p_3^2}}\,.$$

If you need to *derive* the last result, the quickest way is probably via the reciprocal lattice vectors, as these are the wave vectors of waves which have the same periodicity as the crystal lattice. You can easily verify that, in the cubic case, the wavelength $2\pi/|\boldsymbol{G}|$ is equal to the expression for $d_{p_1p_2p_3}$ given above.