Chapter 6: X-ray diffraction and related methods

6.1(a) First, identify from Figure 6.3 the two 'arcs' which correspond to the (2,0,0) reflections on the powder photograph. Measure the separation between these (in mm) and convert to degrees, remembering that 1mm = 1 degree.

This gives a total separation of 117mm and hence 117° angular separation: since this equates to 4θ, $\theta = 29.25°$, the Bragg angle for this diffraction.

(b) Use the Bragg equation ($n\lambda = 2d\sin\theta$) to derive d, the separation of the layers of ions giving this reflection. Since $n = 1$, $\lambda = 0.154$ *nm*, and $\sin\theta = 0.489$, we can calculate d as 0.157 *nm.*

Since this distance refers to the separation between the layers giving the 2,0,0 reflection, this corresponds to a distance between the planes of $a/2$ where a is the
unit cell side (for a cubic system, $d_{hkl} = a/\sqrt{(h^2+k^2+l^2)}$)
Thus $a = 2 \times 0.157$, i.e. 0.314 nm.

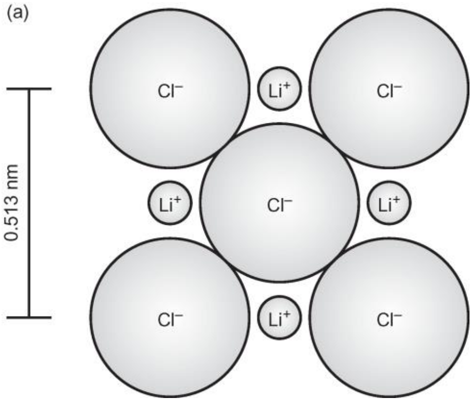
6.2(a) First calculate the value of θ for one layer of lines (e.g. for $n = 2$) by measuring y (the vertical distance between n = 0 and n = 2 for the spots on layers) and utilizing the equation 6.2 given on page 135 ($\tan\varphi = y/R$), where R is the film radius. Measuring y as 19 mm, and with R = 29 mm gives θ as 33.23°

Now use the equation $n\lambda = d\sin\theta$ (see page 134) to derive d, given $n = 2$, $\lambda = 0.154$ nm with θ 33.23°; hence $\sin\theta$ is 0.549; this gives d as 0.56 nm, 5.6 Å. This is the length of the side of the unit cell.

6.2(b) For the n = 2 reflections, there will be two wavelengths' difference between the rays from the layers: ions in *intermediate layers* (with half the spacing) will give a diffraction in phase with these.

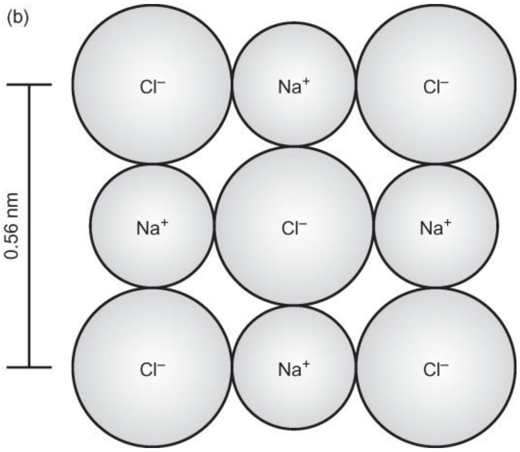
For the n = 1 reflection, with a single wavelength difference between the diffracted beams, the interstitial layers will produce reflections exactly out of phase, resulting in a weak reflection overall.

6.3(a) Given the length of the side of the unit cell for lithium chloride (0.513nm), we need to calculate the length of the diagonal which should correspond to the total of 4 times the ionic radius of Cl^- (since the chloride ions are assumed to touch).



Calculation using Pythagoras' Theorem gives the length of the diagonal as 0.725 nm, which gives the atomic radius r_{Cl^-} as 0.18 nm (1.8 Å).

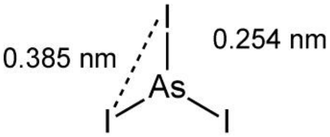
6.3(b) If we assume that, in NaCl, the ions (Na^+ and Cl^-) touch each other on each *side* of the cube, then the cell-side of 0.56 nm equals twice the sum of the Na^+ and Cl^- radii. This leads to a value of 0.10 nm, 10.0 Å) for Na^+

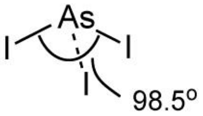


6.4 For LiCl, there will be much less scattering from the Li^+ ions because these are much smaller than the Cl^- ions, and with much less electron density (which is responsible for the scattering). There will be little interference of the in-phase scattering from layers of Cl^- by the Li^+ ions.

6.5 The molecule must be highly symmetric, with either a planar or pyramidal structure (all three iodines equivalent).

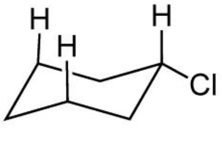
The plan view is thus:





Trigonometric analysis then rules out a planar structure and yields an angle of 98.5° for I -As-I.

6.6 The answer is that chlorine occupies the equatorial position, where there is less steric interaction (repulsion). In the axial position, there is destabilizing repulsion between the chlorine and the (vertical) hydrogen atoms in the 3-positions of the ring.



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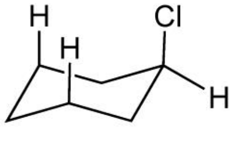

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