

Structure and Properties of Functional Materials

Exercise Set 2

Friday, 18 January, 2013

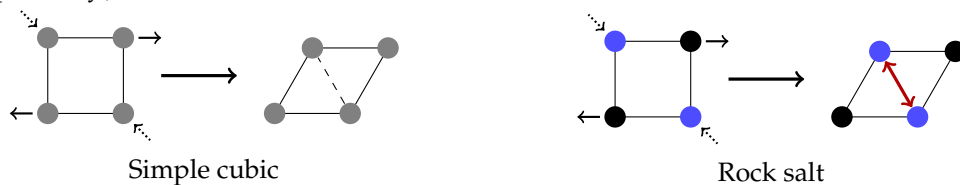
1. For discussion:

- (a) Explain why the simple cubic structure is rare, but the rock salt structure very common.

Solution: The simple cubic structure, where all atoms are identical, is unstable with respect to shearing in the $\{100\}$ planes (or, equivalently, to tension along the $\langle 110 \rangle$ directions). This is because this strain doesn't change the existing nearest-neighbour distances, but brings more atoms closer together, resulting in an energetic benefit.

On the other hand, in the rock salt structure, the ions brought closer together by shearing have the same charge and repel one another. Thus this structure is stable to shear strain. The crucial difference is that there are long-range repulsive interactions in typical solids with the rock-salt structure, but none in the simple cubic.

This is illustrated in the figures below. (As a side point of interest, the solid and dotted arrows represent the two ways of looking at this deformation: as shear or tensile strain respectively.)



- (b) Explain why we say that the rock-salt structure is based on a face-centred cubic lattice, not a simple cubic lattice.

Solution: Certainly if we imagined that every atom was identical, we would have a simple cubic lattice. But in fact we have two different sorts of atom in the rock-salt structure. Since every point in a lattice must be identical, we construct this by combining a motif of two atoms (one of each type) with an appropriate lattice. Focusing on just one type of atom shows that this lattice is in fact face-centred cubic. (An appropriate motif is, e.g., A at $(0, 0, 0)$, B at $(\frac{1}{2}, 0, 0)$.)

2. (a) Find the number of nearest neighbours and distance to these nearest neighbours (in terms of the cell parameter a) for an atom in each of the following structures: simple cubic, body-centred cubic, face-centred cubic, diamond.
- (b) Repeat the calculation, but this time for *second*-nearest neighbours.
- (c) Finally calculate the ratio between the second-nearest and nearest neighbour distances. For which structure is this ratio the lowest?

Solution:

Structure	Nearest neighbours		Second-nearest neighbours		Ratio
	Number	Distance	Number	Distance	
Simple cubic	6	a	12	$\sqrt{2}a$	$\sqrt{2} = 1.414$
Body-centred cubic	8	$\sqrt{3}/2a$	6	a	$2/3\sqrt{3} = 1.155$
Face-centred cubic	12	$\sqrt{2}/2a$	6	a	$\sqrt{2} = 1.414$
Diamond	4	$\sqrt{3}/4a$	12	$\sqrt{2}/2a$	$2/3\sqrt{6} = 1.633$

The ratio is lowest by far for the bcc structure, in which nearest and second-nearest neighbours are almost the same distance apart. This is one reason why this structure is common for metals even though it is not closest packed.

3. Cadmium telluride, CdTe, is an important material for photovoltaic manufacture. It has the cubic zinc blende structure. At room temperature, the lattice parameter is $a = 6.48 \text{ \AA}$.

- (a) Calculate the X-ray structure factors $F(111)$, $F(200)$, and $F(733)$ and hence the intensities $|F|^2$ one would observe in experiment for each of these peaks. The X-ray form factors for Cd and Te are given below. Ignore the effects of thermal motion.

Solution: The basic equation we need here is

$$F = \sum f \exp(2\pi i(hx + ky + lz))$$

(ignoring thermal motion). The atomic positions (x, y, z) are given (from the cheat sheet) by

$$\text{Cd: } (0, 0, 0) \quad \left(\frac{1}{2}, \frac{1}{2}, 0\right) \quad \left(\frac{1}{2}, 0, \frac{1}{2}\right) \quad \left(0, \frac{1}{2}, \frac{1}{2}\right)$$

$$\text{Te: } \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right) \quad \left(\frac{3}{4}, \frac{3}{4}, \frac{1}{4}\right) \quad \left(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}\right) \quad \left(\frac{1}{4}, \frac{3}{4}, \frac{3}{4}\right)$$

The form factors f can be read from the diagram once we know the value of $\sin \theta / \lambda$, which we get from $Q = 4\pi \sin \theta / \lambda$. Indeed, since CdTe has a cubic structure,

$$\frac{\sin \theta}{\lambda} = \frac{Q}{4\pi} = \frac{\sqrt{h^2 + k^2 + l^2}}{4\pi} a^* = \frac{\sqrt{h^2 + k^2 + l^2}}{2a}$$

Putting this all together for (111) gives

$$\frac{\sin \theta}{\lambda} = \frac{\sqrt{1^2 + 1^2 + 1^2}}{2(6.48)} = 0.134 \text{ \AA}^{-1} \quad f_{\text{Cd}} \approx 43 \quad f_{\text{Te}} \approx 46$$

and hence

$$\begin{aligned} F(111) &= 43 \left(\exp(2\pi i(1 \cdot 0 + 1 \cdot 0 + 1 \cdot 0)) + \exp(2\pi i(1 \cdot \frac{1}{2} + 1 \cdot \frac{1}{2} + 1 \cdot 0)) \right. \\ &\quad \left. + \exp(2\pi i(1 \cdot \frac{1}{2} + 1 \cdot 0 + 1 \cdot \frac{1}{2})) + \exp(2\pi i(1 \cdot 0 + 1 \cdot \frac{1}{2} + 1 \cdot \frac{1}{2})) \right) \\ &\quad + 46 \left(\exp(2\pi i(1 \cdot \frac{1}{4} + 1 \cdot \frac{1}{4} + 1 \cdot \frac{1}{4})) + \exp(2\pi i(1 \cdot \frac{3}{4} + 1 \cdot \frac{3}{4} + 1 \cdot \frac{1}{4})) \right. \\ &\quad \left. + \exp(2\pi i(1 \cdot \frac{3}{4} + 1 \cdot \frac{1}{4} + 1 \cdot \frac{3}{4})) + \exp(2\pi i(1 \cdot \frac{1}{4} + 1 \cdot \frac{3}{4} + 1 \cdot \frac{3}{4})) \right) \\ &= 43(1 + 1 + 1 + 1) + 46(-i - i - i - i) = 172 - 184i \end{aligned}$$

$$\text{so } |F(111)|^2 = 172^2 + 184^2 = 6.3 \times 10^4.$$

Similarly, for (200), $\sin \theta / \lambda = 0.154 \text{ \AA}^{-1}$ so $f_{\text{Cd}} \approx 42$ and $f_{\text{Te}} \approx 45$, giving $F(200) = 168 - 180 = -12$ and $|F(200)|^2 = 1.4 \times 10^2$.

For (733), $\sin \theta / \lambda = 0.631 \text{ \AA}^{-1}$ so $f_{\text{Cd}} \approx 24$ and $f_{\text{Te}} \approx 22$, giving $F(733) = 96 + 88i$ and $|F(733)|^2 = 1.7 \times 10^4$.

- (b) Why is $|F(733)|^2$ smaller than $|F(111)|^2$? Would $|F(733)|^2$ still be much smaller than $|F(111)|^2$ if neutron instead of X radiation were used? Why or why not?

Solution: The main difference between $F(733)$ and $F(111)$ is that the atomic form factors f are substantially lower for (733) since $\sin \theta / \lambda$ is higher. Since neutron scattering lengths do not change appreciably with angle (because the nucleus is so much smaller than the electron cloud), we would expect $F(733)$ and $F(111)$ to be closer in magnitude in this case.

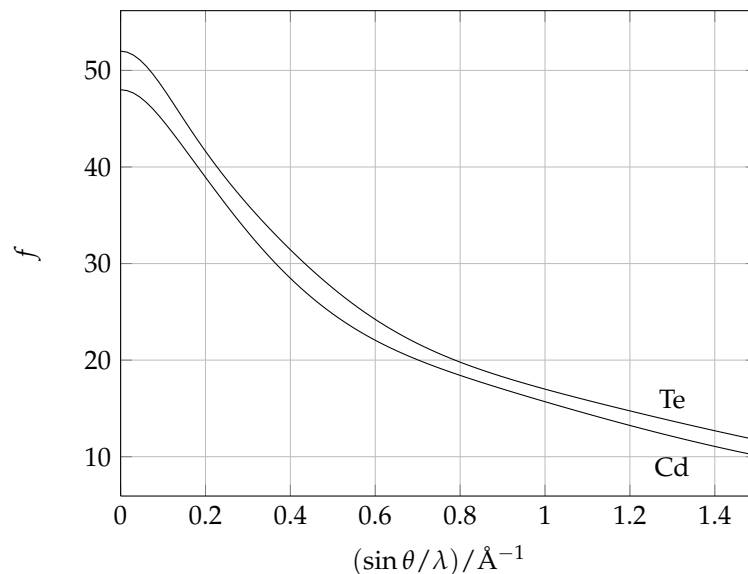
- (c) Why is $|F(200)|^2$ smaller than $|F(111)|^2$? Would $|F(200)|^2$ still be much smaller than $|F(111)|^2$ if neutron instead of X radiation were used? Why or why not?

Solution: As can be shown by drawing the (200) planes, in this peak there is destructive interference between layers of Cd atoms and layers of Te atoms. Since these have almost the same form factor, the destructive interference is almost complete, leaving very low observed intensity. (In the limit as the form factors become identical, we have the diamond structure, for which the (200) peak is systematically absent – see next week’s lectures!)

The reason the form factors are similar is that Cd and Te have almost the same number of electrons. Since neutron scattering lengths do not vary systematically with number of electrons in the same way as X-ray form factors, the neutron scattering lengths of Cd and Te are likely to be more different, lessening the effect of the destructive interference and again making $F(111)$ and $F(200)$ more similar in magnitude. (In fact, the naturally occurring distribution of Te has scattering length 5.8 fm while the common isotope ^{114}Cd (natural abundance 28.7%) has scattering length 7.5 fm. See below for why it would be necessary to control the isotopic composition of the Cd.)

- (d) Why would it be difficult to investigate this structure using neutron diffraction?

Solution: Isotopic substitution of the Cd would be required, since naturally occurring Cd absorbs neutrons very effectively (which is why cadmium rods are used in nuclear reactors). The culprit is the isotope ^{113}Cd .



4. The following lattices are, by convention, not used to describe crystal structures. In each case explain why not.

(a) Body-centred triclinic

Solution: There's no point in having the centring at all – it doesn't emphasise any symmetry, because there is none! Just use a primitive triclinic cell.

(b) Base-centred cubic

Solution: Base-centred cells have an extra lattice point at the centre of a single face. This would break the cubic symmetry which says that every face has to be the same (they are related by the compulsory threefold axes). This is not a cubic lattice at all but a primitive tetragonal lattice.

(c) Face-centred tetragonal

Solution: We can redraw this as a smaller body-centred tetragonal lattice with lattice vectors $(\frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}, \frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b}, \mathbf{c})$ – draw this to see how it works.