

## Problem Sheet 2

Michaelmas 2016

### 1. Powder diffraction crystal structure solution

USi crystallises in an orthorhombic space group with lattice parameters  $a = 0.565\text{nm}$ ,  $b = 0.765\text{nm}$ ,  $c = 0.390\text{nm}$ . There are four USi ‘formula units’ per crystallographic unit cell ( $Z = 4$ ). The general equivalent positions of the space group are

$$\begin{array}{l} x, y, z \quad x, y, \frac{1}{2} - z \quad \frac{1}{2} + x, \frac{1}{2} - y, \bar{z} \quad \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z \\ \bar{x}, \bar{y}, \bar{z} \quad \bar{x}, \bar{y}, \frac{1}{2} + z \quad \frac{1}{2} - x, \frac{1}{2} + y, z \quad \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z \end{array}$$

Given that all four U atoms have  $z = \pm\frac{1}{4}$ , show that the four U atoms lie at the positions

$$\pm \left[ x, y, \frac{1}{4} \right] \quad \text{and} \quad \pm \left[ \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4} \right]$$

(a) Show that the structure factor for the U atoms alone and for a general  $hkl$  is given by.

$$F_{hkl} = 4f_U \cos 2\pi \left[ hx_U - \left( \frac{h+k}{4} \right) \right] \cos 2\pi \left[ ky_U + \left( \frac{h+k+l}{4} \right) \right] \quad (1)$$

(b) We are now interested in using diffraction data to determine the exact location of the U atoms. Because of the arbitrariness in the choice of the origin, it is sufficient to limit our search to the range  $x < \frac{1}{4}$  and  $y < \frac{1}{4}$ . Given that the (200) and (040) reflections have zero intensities, would measuring the intensities of the (111) and (231) reflections be sufficient to determine  $x$  and  $y$  uniquely?

(c) A powder diffraction experiment is performed on USi using copper  $K_\alpha$  radiation (1.542 Å). Determine the multiplicity of the reflections (111), (200), (211), (040), and (231). From the measured intensity data below (which has been corrected for Lorentz, polarisation, and absorption factors), determine approximate values for the positions  $x_U$  and  $y_U$  (the Si contributions can be neglected — why is this?). In the table,  $f_U$  is the uranium form factor at the appropriate value of  $|\mathbf{Q}|$ .

$hkl$	111	200	211	040	231
$I$	457	$\sim 0$	221	$\sim 0$	630
$2\theta$ (deg.)	30.12	31.6	40.09	47.41	53.70
$f_U( \mathbf{Q} )$	81	79	75	71	69

(d) Draw to scale the positions of the U atoms in the unit cell projected on (001). Calculate and mark on your diagram the shortest U-U distance in  $\text{nm}$ .

### 2. Friedel’s Law

A crystal contains two atoms at general positions in the unit cell. Suppose one of them has a real atomic form factor  $f_1$ , while the second has atomic form factor  $f_2 = f' + if''$  with real and imaginary components. Write down the structure factor for the  $hkl$  and  $\bar{h}\bar{k}\bar{l}$  reflections, showing that in this case Friedel’s law is untrue, i.e. show that  $I(hkl) \neq I(\bar{h}\bar{k}\bar{l})$ . Illustrate your answer on an Argand diagram.

### 3. Measurements of phonons by triple-axis neutron scattering

The phonon dispersion relations of a primitive tetragonal crystal ( $a = 3.87 \text{ \AA}$ ,  $c = 9.49 \text{ \AA}$ ) are measured via inelastic scattering of monochromatic neutrons ( $E_i = 25 \text{ meV}$ ) using a triple-axis spectrometer. The crystal is aligned with the  $c$ -axis vertical, normal to the horizontal scattering plane of the instrument, and can be rotated around the  $c$ -axis. One of the optical phonon modes has energy  $E = 12 \text{ meV}$  at the zone-boundary point  $X(1/2, 0, 0)$ .

- (a) Draw a diagram of the  $a^*b^*$  reciprocal space plane of the crystal and indicate all symmetry-equivalent points to  $X$  in the 1<sup>st</sup> Brillouin zone (1<sup>st</sup> Wigner-Seitz unit cell) and also the  $X$  points in the next set of Wigner-Seitz unit cells further out.
- (b) Consider processes whereby neutrons scatter inelastically by exciting a phonon (energy loss scattering); show that such processes cannot occur to excite the above optical phonon mode at  $(1/2, 0, 0)$ . Show, however, that the above phonon mode can be observed by inelastic neutron scattering at  $(1, 1/2, 0)$ , an  $X$  point in a further out Wigner-Seitz cell. In this case, find the total scattering angle  $\gamma$  and the (right-handed) rotation angle of the crystal around the  $c$ -axis required to observe this excitation, assuming that the neutron beam is initially along the  $a$ -axis. [Hint: consider the conservation of energy and momentum, and use the convention for the scattering vector  $-\mathbf{Q} = \mathbf{k}_{\text{phonon}} = \mathbf{k}_i - \mathbf{k}_f$ ].
- (c) Could the phonon mode at  $(1/2, 0, 0)$  be observed in energy gain scattering, i.e. neutrons scattering by absorbing energy from a phonon? What should the temperature of the crystal be for such scattering processes to have sizeable intensity?

### 4. Ferroelectric phase transitions

Barium titanate ( $\text{BaTiO}_3$ ) becomes ferroelectric below  $T_C = 395 \text{ K}$ , and undergoes the following sequence of structural phase transitions on cooling:



The different phases are related by small distortions of the lattice. The table below gives the directions of the unit cell axes for the above ferroelectric phases in terms of the Cartesian axes of the cubic phase.

$P4mm$	$[100]$	$[010]$	$[001]$
$Cm2m$	$[110]$	$[\bar{1}10]$	$[001]$

- (a) Explain what is meant by *ferroelectricity*. State the symmetry requirement for a crystal to be ferroelectric.
- (b) For each of the two ferroelectric phases,
  - i) explain the meaning of the space group symbol, identify the point group, and draw a stereographic projection showing the point group symmetries;
  - ii) deduce the direction of the ferroelectric polarization relative to the cubic axes, explaining your reasoning;

- iii) determine how many distinct ferroelectric domains can exist [Hint: consider all the possible directions of the polarisation with respect to the original cubic axes].
- (c) Explain how you might detect the structural change from cubic to tetragonal space groups using x-ray powder diffraction data. Explain why no net ferroelectric polarization is observed when a single crystal of BaTiO<sub>3</sub> is cooled through  $T_C$ ?

### 5. Landau theory of phase transitions

Consider the first phase transition in BaTiO<sub>3</sub>. Below the phase transition certain ions are displaced parallel to each other from sites of high symmetry to form an electrically polar material with spontaneous polarisation denoted  $P$ . Above the phase transition the ionic displacements are zero, i.e.  $P = 0$ . The spontaneous polarisation for such a transition can be considered as the *order parameter* for the transition. According to the Landau theory of phase transitions, the free energy in the high-temperature phase can be expanded in terms of a power series in  $P$ , thus:

$$F = F_0 + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots$$

- (a) Explain why there are no odd powers in this expansion.
- (b) Assume that the coefficient  $a$  is temperature-dependent approximating to

$$a = a'(T - T_0)$$

and that  $b > 0$  and is temperature-independent. Let all terms higher than  $P^4$  be taken to be zero. Now, by minimising with respect to the *order parameter*, show that there are the following solutions to the free energy equation:

$$P = 0$$

$$P = \pm \left(\frac{a'}{b}\right)^{\frac{1}{2}} (T_0 - T)^{\frac{1}{2}}$$

- (c) Explain the physical meaning of these solutions. Sketch the graph of  $P$  against temperature and  $F - F_0$  against  $P^2$  for different temperature regimes and state whether the phase transition is 1st or 2nd order.
- (d) Derive formulae for the temperature behaviour of the inverse dielectric susceptibility,  $\chi^{-1}$ , below and above  $T_0$ .
- (e) For  $b < 0$ , sketch the graph of  $F - F_0$  against  $P^2$  for different temperature regimes, and sketch the graph of  $P$  against temperature. State whether the phase transition is 1st or 2nd order.
- (f) In practice, the spontaneous polarisation  $P$  is accompanied by a corresponding change in lattice strain  $\epsilon$ , so that the free energy expansion can be modified to

$$F = F_0 + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{2}\lambda\epsilon P^2 + \frac{1}{2}C_{el}\epsilon^2 \dots$$

$\lambda$  represents the amount of coupling between polarisation and strain, and  $C_{el}$  is an elastic constant. Show that the free energy expression can be recast as

$$F = F_0 + \frac{1}{2}aP^2 + \frac{1}{4} \left( b - \frac{\lambda^2}{2C_{el}} \right) P^4 + \dots$$

and discuss how strain-coupling can change the phase transition order.