

PRACTICAL EXAM, SECTION A

DISCLAIMER

This guide is based on the syllabus written in the 2024/25 Earth Sciences Course Guide, and the 2023-2025 past papers. Course content and syllabus styles may change with time, so keep that in mind.

I have included 'model' answers to the past two years of the practical exam, and my own interpretations to some parts of the crystallography tables which I found to be confusing when I learnt about it. While this has been proofread, there is still a high likelihood of at least some error, so take them with a grain of salt. Nevertheless, I have shared them here; I hope you find them useful.

PREFACE

The key to the practical exam is that you are allowed to annotate your own copy of DHZ and bring it into the practical exam. If you care about your grade, do utilize this opportunity.

For section A the entire mineralogy section (including optical mineralogy, though it hasn't been tested yet) is on the table. Note that I am not explicitly encouraging you to copy down all the relevant information, but there are very few downsides to doing so. Recommended sections of the course to 'write short notes' on are:

- vector calculation formulae (if you have zero physics background like me),
- how to interpret space group tables,
- vacancy rules for different lattice types,
- X-ray diffraction,
- the biaxial optical indicatrix and what each section looks like under the Bertrand lens,
- miscellaneous formulas that you think might get tested.

CRYSTALLOGRAPHY AND POINT GROUPS

Historically, the first part of this section has tested how you can derive the properties of space groups from reading the tables. The second part is often on other miscellaneous bits of the mineralogy course which are difficult to test using essay writing.

If the examiner is having a bad day, you can even be tested on deriving properties from the space group name itself. Therefore, it is very important not only to know how to read the space group tables but understand the principles behind the groups.

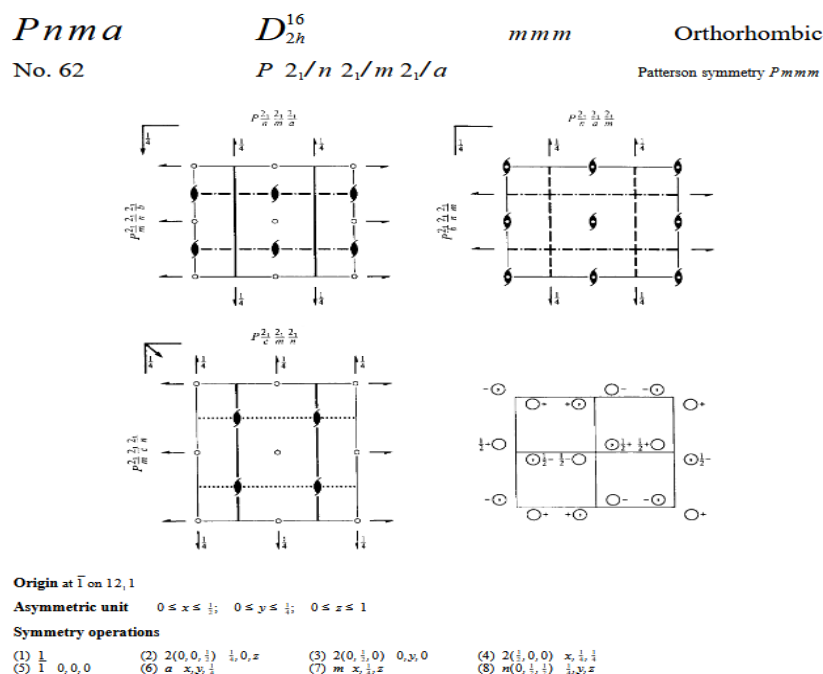
A point group is a mathematical group of symmetry operations that have a fixed point in common. In other words, it's a list of all the ways in which the orientation of a crystal can be changed without seeming to change the positions of its atoms. Each molecule has its own set of symmetry operations that fit this criteria; the total set is the point group.

Molecules do not have an infinitely repeating structure and therefore do not possess translational symmetry. However, when considering crystal lattices, we model them as infinitely translatable objects. Therefore, translational symmetry must also be considered. The addition of translational symmetry elements to the existing rotational and reflectional symmetry elements gives the space group of a crystal lattice.

For the mathematically inclined, an IUCR-published explanation of the ITC tables is given [here](#). (I wish I had found this while preparing for exams!) If there are any errors in my document, please refer to this one instead (and let me know).

With that in mind, let's start interpreting space group tables.

International Tables for Crystallography (2006). Vol. A, Space group 62, pp. 298–299.



This is the first page of the table for the space group $Pnma$ – long form $P\ 2_1/n\ 2_1/m\ 2_1/a$. The equivalent name in Schoenflies notation is D_{2h}^{16} – used in Chemistry A. You can ignore the Patterson symmetry – outside the scope of this course.

In Hermann-Mauguin notation, symmetry operations are represented as follows:

Letter	Symmetry operation
1	Identity
$\bar{1}$, or /	Center of inversion
2, 3, 4, 6	Axis of rotation of $360/n^\circ$
m	Mirror plane
a, b, c, d, n	Glide plane: translation + reflection. <ul style="list-style-type: none"> - a, b, and c glide planes involve translations of $a/2$, $b/2$ and $c/2$, respectively. - n glide planes (diagonal glide) involve translations of the type $(a/2 + b/2)$, $(a/2 + c/2)$, $(b/2 + c/2)$, or $(a/2 + b/2 + c/2)$. - d glide planes (diamond glide) involve translations of the type $(a/4 + b/4)$, $(a/4 + c/4)$, $(b/4 + c/4)$, or $(a/4 + b/4 + c/4)$.
n_m (where both are numbers)	Screw axis: translation + rotation of order $360/n^\circ$ followed by a translation of m/n of the unit cell repeat along the axis.

The first letter of the space group symbol always represents the type of lattice. The lattice types and their XRD selection rules are given below:

Letter	Lattice type	Absences
P	Primitive	None
I	Body-centered	$h+k+l = \text{odd}$ (e.g. [111])
F	Face-centered	h, k, l mix of odd/even (e.g. [201])
C	C-centered	$h+k$ odd (e.g. [110])

The short form space group symbol *Pnma* can be interpreted as follows:

Letter	Information from the letter
P	Primitive lattice type
n	Diagonal glide
m	Mirror plane (about c)
a	Glide about a

However, we should be vigilant that the shortened form leaves out symmetry elements that are implicitly present. For example, there are 3 2_1 -screw axes along each crystallographic direction (as given in the long form name). Therefore, you should also use your own judgement when deriving the symmetry operations from the name.

The list of symmetry operations are also listed in full at the bottom of the point group table. You can ignore the 'x,y,z' information given here next to each operation as there are more important (and easy to interpret) information on the next page.

The first page also gives three "floor-plan" images which are a schematic of how these symmetry operations are arranged in 3D space,, from the POV of a, b, c direction respectively. For more information, click [here](#).

The range of the asymmetric unit is also given: it is the subset of the unit cell which can be used to generate the complete unit cell via symmetry operations of the space group.

CONTINUED

No. 62

*Pnma***Generators selected** (1); $\tau(1, 0, 0)$; $\tau(0, 1, 0)$; $\tau(0, 0, 1)$; (2); (3); (5)**Positions**Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

General:

8	<i>d</i>	1	(1) x, y, z	(2) $\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$	(3) $\bar{x}, y + \frac{1}{2}, \bar{z}$	(4) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$
			(5) \bar{x}, y, \bar{z}	(6) $x + \frac{1}{2}, y, z + \frac{1}{2}$	(7) $x, y + \frac{1}{2}, z$	(8) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$

 $0kl : k + l = 2n$
 $hk0 : h = 2n$
 $h00 : h = 2n$
 $0k0 : k = 2n$
 $00l : l = 2n$

Special: as above, plus

4	<i>c</i>	$\bar{1}$	$x, \frac{1}{2}, z$	$\bar{x} + \frac{1}{2}, \frac{1}{2}, z + \frac{1}{2}$	$\bar{x}, \frac{1}{2}, \bar{z}$	$x + \frac{1}{2}, \frac{1}{2}, \bar{z} + \frac{1}{2}$
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no extra conditions

4	<i>b</i>	$\bar{1}$	$0, 0, \frac{1}{2}$	$\frac{1}{2}, 0, 0$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 0$
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 $hkl : h + l, k = 2n$

4	<i>a</i>	$\bar{1}$	$0, 0, 0$	$\frac{1}{2}, 0, \frac{1}{2}$	$0, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
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 $hkl : h + l, k = 2n$ **Symmetry of special projections**Along [001] $p2gm$ $a' = \frac{1}{2}a$ $b' = b$ Origin at $0, 0, z$ Along [100] $c2mm$ $a' = b$ $b' = c$ Origin at $x, \frac{1}{2}, \frac{1}{2}$ Along [010] $p2gg$ $a' = c$ $b' = a$ Origin at $0, y, 0$ **Maximal non-isomorphic subgroups**

I	[2] $Pn2_1a$ ($Pna2_1$, 33)	1; 3; 6; 8
	[2] $Pnm2_1$ ($Pmn2_1$, 31)	1; 2; 7; 8
	[2] $P2_1ma$ ($Pmc2_1$, 26)	1; 4; 6; 7
	[2] $P2_12_12_1$ (19)	1; 2; 3; 4
	[2] $P112/a$ ($P2/c$, 14)	1; 2; 5; 6
	[2] $P2/n11$ ($P2/c$, 14)	1; 4; 5; 8
	[2] $P12/m1$ ($P2/m$, 11)	1; 3; 5; 7

IIa none**IIb** none**Maximal isomorphic subgroups of lowest index****IIc** [3] $Pnma$ ($a' = 3a$) (62); [3] $Pnma$ ($b' = 3b$) (62); [3] $Pnma$ ($c' = 3c$) (62)**Minimal non-isomorphic supergroups****I** none**II** [2] $Amma$ ($Cmcm$, 63); [2] $Bbmm$ ($Cmcm$, 63); [2] $Ccme$ ($Cmce$, 64); [2] $Imma$ (74); [2] $Pcma$ ($b' = \frac{1}{2}b$) ($Pbam$, 55); [2] $Pbma$ ($c' = \frac{1}{2}c$) ($Pbcm$, 57); [2] $Pnmm$ ($a' = \frac{1}{2}a$) ($Pmnn$, 59)

This is page two. The 'generators selected' are the minimal set of symmetry operations that can generate the entire space group when combined. The full set of symmetry operations of the space group can be obtained by taking all possible products (compositions) of these generators and their inverses. Not too useful, but worth noting.

Then, a table involving different symmetry-equivalent sites and their coordinates are given below. This is the most important bit of the space group table to understand.

From the table, there are 4 symmetrically distinguishable sites in the group *Pnma*. Each site has its own set of symmetry operations, that when applied, generate geometrically indistinguishable points of the same symmetry.

Multiplicity is the number of symmetrically equivalent points of a particular site. E.g. for a multiplicity 8 site, if I use any symmetry operation valid to this point, I will generate 8 other sites in the unit cell with the same set of valid symmetry operations as my origin.

Wyckoff letter is a label (a, b, c, d, ...) assigned to Wyckoff positions, ordered by decreasing site symmetry and decreasing multiplicity for equal symmetry.

Site symmetry is the subset of space group symmetry operations that leave a specific point unmoved. Atoms must lie *on* symmetry elements (mirror planes, rotation axes, etc.) to have non-identity site symmetry: these are *special* positions. Atoms which do not lie on symmetry elements have identity site symmetry (1) and are *general* positions.

The **coordinates** given to the right of the site symmetry label tell you what type of symmetrically distinguishable site it is. For example, the point (0.69, 0.25, 0.42) has a format of (x, $\frac{1}{4}$, z) and thus belongs to Wyckoff site *c* with multiplicity 4.

Whether a site is special or general may have an impact on the set of **reflection conditions** they obey. (This is because glide planes and screw axes cause systematic absences.) They are given on the right of the table and are self-explanatory. For example, the reflection condition “00l, l=2n” means if l is even, it will be observed in the diffraction pattern, so [002] is observed while [001] isn't. If a point does not meet any reflection condition, it will not be observed in the diffraction pattern.

The rest of the table is not relevant for this examination. Nevertheless, I have included physical explanations for those who are interested in this subject. **Take them with a grain of salt.**

Symmetry of special projections: the plane (2D) point group that is obtained if the three-dimensional point group is projected along a crystallographic axis. This may help with interpreting diffraction patterns.

Maximal non-isomorphic subgroups: lower-symmetry variants of *Pnma*. (e.g. if a site containing Fe^{2+} was substituted with Mg^{2+} , the lattice would have a lower symmetry).

Maximal isomorphic subgroups: variants with identical symmetry to *Pnma*, but with a new basis of crystallographic vectors. (Basically just means larger unit cells.)

Minimal non-isomorphic supergroups: variants with higher symmetry than *Pnma*. Useful for interpreting phase transitions and computer modelling of crystal lattices.

MINERALOGY (OTHER)

I have included some other useful formulae here:

Diffraction: $n\lambda = 2d_{hkl} \sin(\theta)$

Weiss Zone Law: if $[UVW] // (hkl)$, $hU + kV + lW = 0$

Angle between 2 lattice vectors: $\vec{t}_1 \cdot \vec{t}_2 = t_1 t_2 \cos(\theta)$

Boltzmann distribution: $\frac{n_i}{n} = \frac{1}{q} e^{-\frac{E_i}{kT}}$

Also, check that you know how stereograms of point groups work.

You now know enough to do the Tripos questions. Suggested answers are given in red.

2023

SECTION A

You are provided below on pages 4 and 5 with a section of the International Tables for Crystallography describing Space Group 62 (Pnma).

1. Based on the information contained within the tables answer the following questions about space group Pnma:

a) What crystal system does this space group belong to? **Orthorhombic**

b) What lattice type does this space group belong to? **Primitive**

c) What constraints does this space group place on the shape of the unit cell?
 $a \neq b \neq c, \alpha = \gamma = \beta = 90^\circ$ (as it is orthorhombic)

d) What types of symmetry operation are present in this space group?
Identity; Inversion; Mirror plane (m); Screw axes (2_1); Glide plane (n, a).

e) How are those symmetry operations arranged in the unit cell?
Just copy the three projections from the first page onto your answer sheet. Label the element symbols with what they represent, such that the examiner knows you know the content (instead of just copying it down). Symbol meanings are given [here](#).

f) What general conditions do the lattice type and symmetry operations place on which lattice planes would be present in an X-ray or electron diffraction pattern?
0kl: $k + l = 2n$, hk0: $h = 2n$, h00: $h = 2n$, 0k0: $k = 2n$, 00l: $l = 2n$ (Copy the table). Other points are invalid and will not appear.

2. A mineral crystallises with the space group Pnma. To generate the structure of the mineral, atoms are placed at the following positions within the unit cell: For each atom, state whether this is a general or a special position within the unit cell, give the Wykoff label, the multiplicity of the site and the site symmetry.

Determine the total number of each type of atom in the unit cell. Hence determine the chemical formula of the mineral and the number of formula units per unit cell. Suggest a potential name for the mineral. [20 minutes]

Position	Type	Mul.	Label	Site symmetry	Chemical formula of mineral = <i>Mg₂SiO₄</i> Name = Forsterite
Mg at 0, 0, 0	Special	4	a	-1	
Mg at 0.2776, 0.25, 0.9896	Special	4	c	.m.	
O at 0.0918, 0.25, 0.7667	Special	4	c	.m.	
O at 0.4477, 0.25, 0.2203	Special	4	c	.m.	
O at 0.1633, 0.0337, 0.2781	General	8	d	1	
Si at 0.0945, 0.25, 0.4266	Special	4	c	.m.	

3. An electron diffraction pattern is obtained in the transmission electron microscope from a thin foil of this mineral. The electron beam is oriented parallel to the [001] direction of the mineral. The diffraction pattern obtained is a projection of the reciprocal lattice of the mineral. Each spot in the reciprocal lattice corresponds to a lattice plane (hkl) that is parallel to the electron beam direction. The lattice parameters of the mineral are $a = 10.225 \text{ \AA}$, $b = 5.994 \text{ \AA}$ and $c = 4.762 \text{ \AA}$.

a) Using the Weiss Zone Law, write down two different (i.e., intersecting) lattice planes that lie parallel to the [001] electron beam.

$hU + kV + lW = 0$; $W = 1$ so all planes with $l = 0$ are valid, i.e. (hk0) // [001]

The most logical choice of planes are (100) and (010) as they are orthogonal, so they intersect

b) Calculate the d-spacings of the two planes you have chosen, and the angle between the planes.

$$\overrightarrow{d_{100}} = 10.225 \text{ \AA}, \overrightarrow{d_{010}} = 5.994 \text{ \AA}, \angle = 90^\circ$$

c) Calculate the length of the reciprocal lattice vector of the two planes. Recall lattice vector properties $a_i b_j c_k =$

δ_{ijk} if vectors orthogonal (in orthorhombic, yes)

$$\overrightarrow{t_{hkl}^*} \cdot \overrightarrow{t_{hkl}^*} = (h\overrightarrow{a^*} + k\overrightarrow{b^*} + l\overrightarrow{c^*})^2 = h^2\overrightarrow{a^{*2}} + k^2\overrightarrow{b^{*2}} + l^2\overrightarrow{c^{*2}}$$

$$\overrightarrow{t_{100}^*} = \sqrt{1 \times \left(\frac{1}{10.225}\right)^2} = \frac{1}{10.225} = 0.09779 \text{ \AA}^{-1}$$

$$\overrightarrow{t_{010}^*} = \frac{1}{5.994} = 0.16683 \text{ \AA}^{-1}$$

d) Hence, sketch the electron diffraction pattern that would be observed in this orientation out to $h = \pm 4$ and $k = \pm 2$, taking into account the General Reflection Conditions listed in the International Tables.

The reciprocal lattice is the diffraction pattern (Fourier transform) of the lattice. We should be looking down on the hk plane. A grid with h - h distances of 0.09779 units and k - k distances of 0.16683 units, with absences according to the General Reflection Conditions.

From earlier: $hk0$: $h = 2n$, $h00$: $h = 2n$, $0k0$: $k = 2n$

Spots with odd h and odd k are gone, but if $h = 2n$, k can be odd as well. (I think)

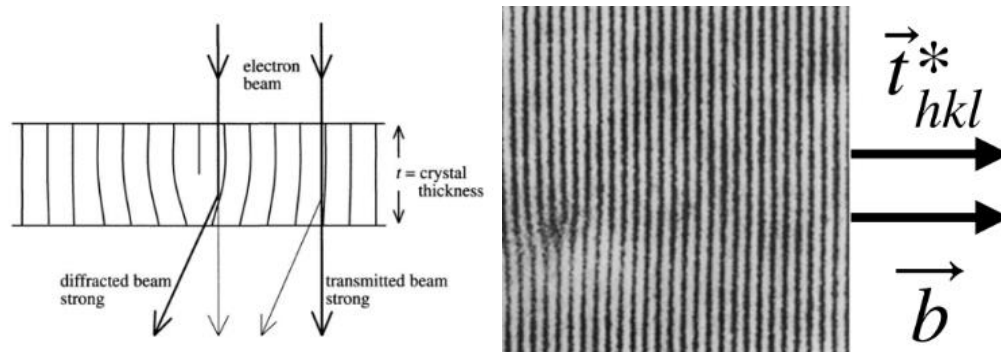
e) This mineral deforms via the movement of dislocations that have Burgers vectors parallel to either $[100]$ or $[010]$. A highly deformed sample is imaged in the transmission electron microscope. Explain why we would expect such a sample to show a higher density of dislocations relative to an undeformed sample.

Burger vectors = atomic displacement caused by dislocations, which move on a preferred glide plane.

During deformation, a stress is applied, leading atomic planes to slip past each other; dislocations occur to accommodate excessive strain.

f) An image of the sample is obtained using selected diffracted electron beams. For each of the diffracted beams below, state whether the dislocations would be present or absent from the image:

A set of planes with reciprocal lattice vector // Burger's vector is strongly deformed and are visible.



$$\therefore \text{Visible if } \vec{t}_{hkl}^* \cdot \vec{b} \neq 0$$

Note that in the diffraction pattern, the indices (hkl) correspond to the reciprocal lattice vector $[\vec{t}_{hkl}^*]$ because this is an orthorhombic system.

i) (110) $hU + kV + lW$ for $[110] \cdot [100] = 1$ and $[110] \cdot [010] = 1$ so both are present.

ii) (011) $[011] \cdot [100] = 0$ and $[011] \cdot [010] = 1$ so only $\vec{b} = [010]$ is present

iii) (101) $[101] \cdot [100] = 1$ and $[101] \cdot [010] = 0$ so only $\vec{b} = [100]$ is present

iv) (001) $[001] \cdot [100] = 0$ and $[001] \cdot [010] = 0$ so both are not present

2024

SECTION A

You are provided with a section from the International Tables for Crystallography describing Space Groups 167 ($R\bar{3}c$) and 148 ($R\bar{3}$). Both space groups belong to the trigonal crystal system, and are referenced to a set of crystallographic axes with $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.

1. Based on the information in the Tables, answer the following questions about space group $R\bar{3}c$:

a) What types of symmetry operation are present in this space group?

Rotoinversion ($\bar{3}$) (which includes rotation 3 and inversion i)

Glide plane (c) along the c axis.

b) How are those symmetry operations arranged in the unit cell?

$\bar{3}$ axis runs along c .

Glide plane contains c and translations parallel to c .

c) What general conditions do the lattice type and symmetry operations place on the lattice planes that are represented in an X-ray or electron diffraction pattern?

These planes described by the conditions are the ones that get diffracted and are visible under XRD.

2. Mineral A has the space group $R\bar{3}c$. Atoms are present at the following positions in the unit cell:

Fe at 0, 0, 0.3553

O at 0.3059, 0, 0.25

a) For each atom, state whether this is a general or a special position in the unit cell, give the Wyckoff label, the multiplicity of the site and the site symmetry.

Fe: Special, (0,0,z) so 12, c , 3.

O: Special, (x,0,1/4) so 18, 2, . 2

(Only 36f is general because its site symmetry is 1, indicating only the identity operation leaves it unchanged. Hence it does not sit on any (other) symmetry elements)

b) Determine the total number of each type of atom in the unit cell. Hence determine the chemical formula of the mineral and the number of formula units per unit cell. Suggest a potential name for mineral A.

12x Fe and 18x O gives Fe_2O_3 , with 6 formula units per unit cell. This is **haematite**.

c) What is the valence state of Fe in Mineral A?

Fe(III), 3+

3. Mineral B forms with a closely related structure that has similar lattice

parameters and space group 148 $R\bar{3}$.

Atoms are found at the following positions in the unit cell:

Fe at 0, 0, 0.35537

Ti at 0, 0, 0.1464

O at 0.31743, 0.02332, 0.245

a) For each atom, state whether this is a general or a special position in the unit cell, give the Wykoff label, the multiplicity of the site and the site symmetry.

Fe: Special, (0,0,z) so 6, c, 3.

Ti: Special, (0,0,z) so 6, c, 3.

O: General, (x,y,z) so 18, f, 1

b) Determine the total number of each type of atom in the unit cell. Hence, determine the chemical formula of the mineral and the number of formula units per unit cell. Suggest a potential name for mineral B.

6x Fe, 6x Ti, 18x O. FeTiO_3 . This is **ilmenite**.

c) What is the valence state of Fe in Mineral B?

Fe(II), 2+ (because Ti prefers 4+)

4. Write down the z coordinates of the Fe and Ti atoms in Minerals A and B that lie along the c axis of the unit cell, i.e. for all atoms that have coordinates of the form (0, 0, z). Sketch and compare the arrangement of atoms along the c axis in each structure.

Fe z = 0.35537 and -0.35537; Ti z = 0.1464

A rudimentary sketch of the c axis is given below where 1 dash corresponds to 0.15 unit

-ve -----(-1)-Ti-Fe----- (0)-Ti-Fe----- (1)-Ti-Fe--- +ve (for haematite)
-ve ---Fe-Ti-(-1)-Ti-Fe---Fe-Ti-(0)-Ti-Fe---Fe-Ti-(1)-Ti-Fe--- +ve (for ilmenite)

5. A complete solid solution between Mineral A and Mineral B forms.

a) For a solid solution containing a mole fraction (1-X) of Mineral A and X of Mineral B, write down the chemical formula of the solid solution.

$\text{A}_{(1-x)}\text{B}_{(x)}$, so $\text{Fe}_{2-2x}\text{O}_{3-3x}\text{Fe}_x\text{Ti}_x\text{O}_{3x} = \text{Fe}_{2-x}\text{Ti}_x\text{O}_3$

b) Based on the given structures of the Mineral A and B end members, describe how the arrangement of Fe and Ti atoms along the z axis in the solid solution might differ for the following cases, explaining your reasoning:

i) B-rich solid solution at low temperatures.

Ordered arrangement of (Fe, Ti) rich regions with rare Fe^{3+} regions mixed in between.

ii) B-rich solid solution at high temperatures.

Fully disordered arrangement

iii) A-rich solid solution at low temperatures.

Ordered arrangement of Fe^{3+} rich regions with rare (Fe, Ti) regions mixed in between.

iv) A-rich solid solution at high temperatures.

Fully disordered arrangement

This is assuming that w is +ve; i.e. energy associated with pairs of cations $W_{\text{Fe(III)}-\text{(Fe(II), Ti)}} < W_{\text{Fe(III)}-\text{Fe(III)}} \text{ \& } W_{\text{(Fe(II), Ti)}-\text{Fe(II), Ti}}$. In other words, Fe(III)-Fe(III) pairs are more preferred than Fe(III)-Fe(II) or Fe(III)-Ti(IV) bonds.

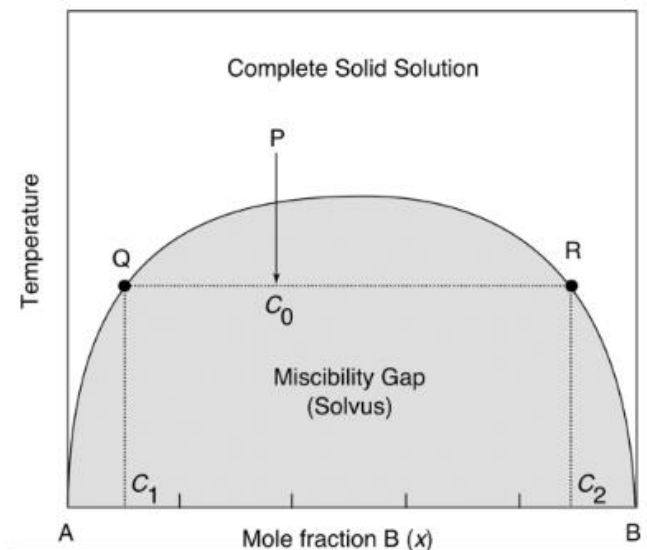
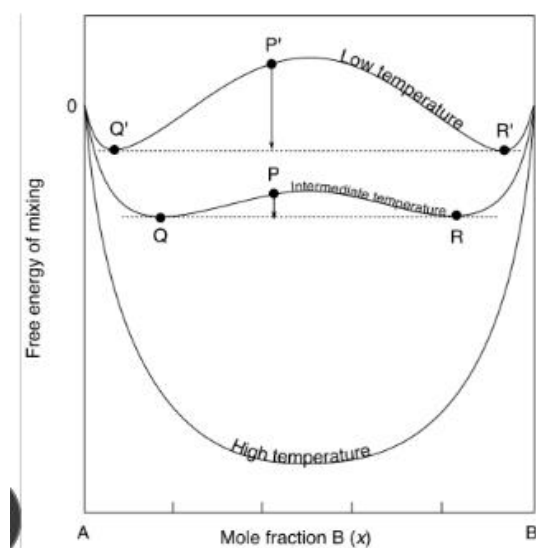
If w is -ve, order-disorder phase transition occurs at low temperatures, and we have alternating ordered/antiphase regions of cations.

6. The cation radii of Fe^{3+} and Ti^{4+} are 63 pm and 74.5 pm, respectively. Based purely on size considerations, would you expect the enthalpy of mixing for the solid solution to be positive, negative, or zero?

Ionic radii mismatch of 11.5 pm (>15% difference) causes lattice strain when substitution occurs. This increases the enthalpy. Hence $\Delta H_{\text{mix}} > 0$

7. Based on your answers to questions 4, 5 and 6, sketch the form of the binary phase diagram for the A-B solid solution, explaining your reasoning.

Locus of phase compositions in equilibrium: solvus



[10 minutes]

8. Samples of B-rich solid solution are cooled quickly from high temperatures to a temperature of 800 °C, held for a short period of time (0.1 hours, 1 hours, 10 hours, or 100 hours) and then cooled quickly to room temperature. Dark-field TEM images of each samples are given in Fig. 1 below. Each image is formed using the (003) diffraction spot from the electron diffraction pattern. Taking into account your answers to 1c and 7, discuss the likely origin of the microstructures observed. What processes account for the variations in microstructure with annealing time? What constraints do the microstructural observations place on the phase diagram sketched in answer to question 7?

(003) diffraction spots typically don't occur in A-rich regions as we need (006). Therefore the diffraction spots show grain boundaries, or B-rich regions. Walls are round with little preferential orientation.

Hence, the images are showing ordering/antiphase domains.

0.1 hr: high density of boundaries

100 hr: only two boundaries observed

∴ Boundary density decreases as more time is allowed for boundaries to merge after cooling has taken place. The system evolves to minimize free energy by reducing interfacial area. (reduce surface area / volume ratio) As a result, boundaries merge or disappear, decreasing their number.

This is because there is an energy penalty associated with each boundary which arises from the incorrect neighbour pairs of ions. Rearrangement of ions such that the amount of boundary interfaces decrease is thermodynamically favourable, but takes time.

(Ostwald ripening)

Constraint: Composition must be within the spinode where $\frac{d^2G}{dx^2} < 0$ [11 minutes]