18.4 The origin of the defect is due to that a small portion of the iron is Fe(III) instead of Fe(II). For a pair of Fe(III) ions to appear, an O\(^{2-}\) would be missed from its lattice site to compensate the charge difference.

One of the most studied and best understood defect systems is wüsite, Fe\(_{1-x}\)O: \(0 \leq x \leq 0.1\). Stoichiometric FeO has the rock salt structure with Fe\(^{2+}\) ions on octahedral sites. Density measurements show that non-stoichiometric Fe\(_{1-x}\)O contains a deficiency of iron rather than an excess of oxygen, relative to stoichiometric FeO. Using ideas of point defects, one would anticipate that non-stoichiometric Fe\(_{1-x}\)O would have the structural formula Fe\(^{2+}\)\(_{x}\)Fe\(^{3+}\)\(_{2x}\)V\(_x\)O in which Fe\(^{2+}\), Fe\(^{3+}\) and cation vacancies were distributed at random over the octahedral sites in the ccpp oxide ion array. The defect structure is different, however, since neutron and X-ray diffraction studies have shown that Fe\(^{3+}\) ions are in tetrahedral sites and that defect clusters appear to form. The structure of one possibility, the so-called Koch cluster, is shown in Fig. 5.9. The oxygen ions are ccpp throughout and the cluster involves all the cation sites in a cube the size of the normal fcc rock salt unit cell. The twelve edge centre and one body centre octahedral sites are all empty; four of the eight possible tetrahedral sites contain Fe\(^{3+}\) ions (dividing the cube into eight smaller cubes, these tetrahedral sites occupy the body centres of the small cubes). This cluster has a net charge of 14—since there are thirteen vacant M\(^{2+}\) sites (26 —) and only four interstitial Fe\(^{3+}\) ions (12 +). Extra Fe\(^{3+}\) ions are distributed over octahedral sites around the clusters to preserve electroneutrality. The concentration of these Koch clusters increases with x and hence the average separation between clusters decreases. Evidence from diffuse neutron scattering indicates that the clusters order into a regularly repeating pattern resulting in a superstructure for wüsite.

The introduction of Li$_2$O into NiO places Li$^+$ in Ni$^{2+}$ sites, the system balances the charge by oxidation of one Ni$^{2+}$ to Ni$^{3+}$ for each Li$^+$ ion present. This process introduces holes near the valance band of NiO and the conductivity increases greatly as a p-type semiconductor.

For Cr$^{3+}$ in the O$_h$ site, the three d-electrons are filled in $t_{2g}$ orbitals. The dark green color of Cr$_2$O$_3$ is due to the absorption of red light of incident white light by its 3d electron.

When small amount of Cr$^{3+}$ doped into the alumina matrix, the Cr$^{3+}$ ion replaced Al$^{3+}$ in O$_h$ site. The Cr$^{3+}$ was compressed by the O$^{2-}$ ligands because the diameter of Al$^{3+}$ is smaller than that of Cr$^{3+}$. The compression increases the ligand-field splitting parameter and shifts the first-allowed d-d band to higher energy. Therefore, the red color of ruby is due to the absorption of violet and green light of incident white light by the 3d electron of Cr$^{3+}$ doped in the alumina matrix.

The mechanism of phosphorescence was described in the textbook.

For normal spinel, the formula is A$^{II}$[B$^{III}$]$_2$O$_4$, where A$^{II}$ and B$^{III}$ are occupied in the T$_d$ and O$_h$ sites, respectively. The occupation factor, $\delta$, of a spinel is the faction of B$^{III}$ cations in the tetrahedral sites. Thus, $\delta = (B^{III})_{Td}/(B^{III})_{Total}$. $\delta = 0$ for normal spinel, and $\delta = 0.5$ for an inverse spinel B$^{III}$[A$^{II}$B$^{III}$]O$_4$, where A$^{II}$ is in the O$_h$ sites and a half of the B$^{III}$ ions are occupied in the T$_d$ and another half in O$_h$ sites.

(a) Fe$_3$O$_4$

In octahedral (O$_h$) symmetry, the ligand field stabilized energy (LFSE) of Fe$^{3+}$ in high spin state (or in weak ligand field) is $0 \Delta \sigma$.

In tetrahedral (T$_d$) symmetry, the LFSE of Fe$^{3+}$ is also $0 \Delta \sigma$.

Define $\Delta$LFSE = (LFSE)$_{Oh}$ - (LFSE)$_{Td}$. If $\Delta$LFSE < 0, Oh site is more stable than Td site.

Since the LFSEs of Fe$^{3+}$ in T$_d$ and O$_h$ sites are the same, $\Delta$LFSE = 0, the Fe$^{3+}$ ion can be in either sites.

For Fe$^{2+}$, electron configuration is 3d$^6$. $\Delta$LFSE = [4(-0.4 $\Delta \sigma$) + 2(0.6) $\Delta \sigma$] - [3(-0.6) + 3(0.4) $\Delta t$] = (-0.4 $\Delta \sigma$) - (-0.6 $\Delta t$) = (-0.4 $\Delta \sigma$) - (-0.6 x 4/9 $\Delta \sigma$) = -0.13 $\Delta \sigma$

Fe$^{2+}$ in Oh site is more stable than in Td site.

Thus, Fe$_3$O$_4$ is inverse spinel structure and its $\delta$ is 0.5.
(b) Cr$_3$O$_4$.
For Cr$^{3+}$, electron configuration is 3d$^3$. $\Delta$LFSE = [3(-0.4 $\Delta$o)] – [2(-0.6)+(0.4) $\Delta$t] = [-1.2 $\Delta$o- (-0.8) $\Delta$t] = -1.2 $\Delta$o.
For Cr$^{2+}$, electron configuration is 3d$^4$. $\Delta$LFSE = [3(-0.4 $\Delta$o) +(0.6) $\Delta$o] – [2(-0.6)+2(0.4) $\Delta$t] = [-0.6 $\Delta$o- (-0.4) $\Delta$t] = -0.6 $\Delta$o.
Cr$^{3+}$ prefers in Oh site more than Cr$^{2+}$.
Thus, Cr$_3$O$_4$ is normal spinel structure.

(c) Mn$_3$O$_4$
For Mn$^{3+}$, electron configuration is 3d$^4$. $\Delta$LFSE = [3(-0.4 $\Delta$o) + (0.6) $\Delta$o] – [2(-0.6) + 2(0.4) $\Delta$t] = -0.6 $\Delta$o.
For Mn$^{2+}$, electron configuration is 3d$^5$. $\Delta$LFSE = [3(-0.4 $\Delta$o) + 2(0.6) $\Delta$o] – [2(-0.6)+3(0.4) $\Delta$t] = 0.
Mn$^{3+}$ prefers in Oh site and no difference for Mn$^{2+}$.
Thus, Mn$_3$O$_4$ is normal spinel structure.

Additional problems
1. The inter-facial angles of the unit cell are defined to be:
   $\alpha$: angle between edges b and c.
   $\beta$: angle between edges a and c.
   $\gamma$: angle between edges a and b.
In 3D, non-primitive cells are of three kinds:
End-centered : an extra lattice point is centered in each of two opposing faces of the cell.
Face-centered : an extra lattice point is centered in every face of the cell.
Body-centered : an extra lattice point is centered in the exact middle of the cell.

Correction for question 1(a):
There is no unit cell as “end-centered tetragonal”. It can be simplified to “primary tetragonal”. The end-centered unit cells only occur in “orthorhombic” and in “monoclinic” as shown below.
2.

- **CUBIC**
  \[ a = b = c \]
  \[ \alpha = \beta = \gamma = 90^\circ \]

- **TETRAGONAL**
  \[ a = b = c \]
  \[ \alpha = \beta = \gamma = 90^\circ \]

- **ORTHORHOMBIC**
  \[ a \neq b \neq c \]
  \[ \alpha = \beta = \gamma = 90^\circ \]

- **HEXAGONAL**
  \[ a \neq b = c \]
  \[ \alpha = \beta = 90^\circ \]
  \[ \gamma = 120^\circ \]

- **MONOCLINIC**
  \[ a \neq b \neq c \]
  \[ \alpha = \gamma = 90^\circ \]
  \[ \beta \neq 120^\circ \]

- **TRICLINIC**
  \[ a \neq b \neq c \]
  \[ \alpha \neq \beta \neq \gamma \neq 90^\circ \]

4 Types of Unit Cell
- P = Primitive
- I = Body-Centred
- F = Face-Centred
- C = Side-Centred

7 Crystal Classes
\[ \rightarrow 14 \text{ Bravais Lattices} \]

Angle = 90 degree
3. The space group $P2_1/c$ means

(a) $P$: primitive cell.
$2_1$: translate 1/2, and then rotate 180°.
$/$: c-glide plane is perpendicular to $2_1$ screw axis

C: axial glide plane, translate c/2 alone z-axis and then reflect through ac-plane or bc-plane.

(b) 4 lattice points.