1) \[ (R+r)^2 + (R+r)^2 = 4R^2 \]
\[ 2(R+r)^2 = 4R^2 \]
\[ R+r = \sqrt{2}R \]
\[ r = (\sqrt{2}-1)R \]
\[ \frac{r}{R} = \sqrt{2}-1 \approx 0.414 \]

2) In center (100) (200) (110) (111)

\[ \sqrt{2}a \]

Note: does not cut through center.
3) odd octants look like

\[
\frac{1}{2}a
\]

\[
\frac{\sqrt{3}}{2}a
\]

\[
O = F^-
\]

\[
O = Ca^{2+}
\]

Consider red triangle

\[
\frac{1}{2}a + \frac{\sqrt{3}}{2}a = (2R_{Ca} + 2R_F)^2
\]

\[
\frac{3}{4}a^2 = (2R_{Ca} + 2R_F)^2
\]

\[
\frac{\sqrt{3}}{2}a = 2R_{Ca} + 2R_F
\]

\[
\frac{\sqrt{3}}{4}a = R_{Ca} + R_F \Rightarrow a = (0.1 + 0.132) \text{nm} \cdot \frac{4}{\sqrt{3}} = 0.538 \text{nm}
\]

Other way to get \(a\)

Ca is at coordinate \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a\)

\[
R_{Ca} + R_F = \sqrt{\left(\frac{1}{4}a\right)^2 + \left(\frac{1}{4}a\right)^2 + \left(\frac{1}{4}a\right)^2}
\]

\[
0.233 \text{nm} = \frac{\sqrt{3}}{4}a
\]

\[
a = 0.538 \text{nm}
\]

\[
\text{APF} = \frac{\text{Vol atoms}}{\text{Vol cell}} = \frac{4 \cdot V_{Ca} + 8 \cdot V_F}{a^3} = \frac{\frac{4}{3} \pi \left(4 \cdot 0.1 \text{nm}^3 + 8 \cdot (0.132 \text{nm})^3\right)}{0.538 \text{nm}^3} = 0.614
\]

\[
\text{Mass} \left(4 \cdot \text{Ca} + 8 \cdot \text{F}\right) = 4 \cdot 40.078 \text{amu} + 8 \cdot 18.978 \text{amu} = 200.6 \text{amu} = \frac{200.6 \text{amu}}{\text{nm}^3} = \frac{3.33 \text{ g}}{\text{cm}^3}
\]
4) Basal plane

- Oxygen anions
- $\cdot$ = Octahedral site
- $\circ$ = Atom on next plane up (tetrahedral site underneath)

Within one plane, there are 3 octahedral sites touching each $O^{2-}$, each shared with 3 $O^{2-}$: $\frac{1}{3} \cdot 3 = 1$ site/anion

Or if you include prior planes as well, 6 sites shared with 6 anions: $\frac{1}{6} \cdot 6 = 1$

$$\frac{2 \ Al^{3+} \cdot 10^{-2}}{3 \ O^{2-} \ \text{oct. site}} = \frac{\frac{2}{3} \ Al^{3+}}{\text{site}}$$

2 of octahedral sites are full of $Al^{3+}$

Shade in $\frac{2}{3}$ in a regular pattern

Octahedral sites are where next plane atoms are not.

4bii) $Al^{3+} = 53.5 \ pm = 0.38 = \text{tetrahedral predicted, but close to threshold for octahedral}$

Prediction is wrong because Atoms are not hard spheres, $Al-O$ is partly covalent bond, so has some directionalality. Model only works well for highly ionic bonds.
4e) Multiple answers. Important thing is to maintain charge balance.

<table>
<thead>
<tr>
<th>Possibilities</th>
<th>Effective charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}^{3+}$ interstitial</td>
<td>+3</td>
</tr>
<tr>
<td>$\text{Al}^{3+}$ vacancy</td>
<td>-3</td>
</tr>
<tr>
<td>$\text{O}^{2-}$ interstitial</td>
<td>-2 ( \leq ) very high energy = unlikely</td>
</tr>
<tr>
<td>$\text{O}^{2-}$ vacancy</td>
<td>+2</td>
</tr>
<tr>
<td>Schottky pair (O and Al vacancy)</td>
<td>-1 ( \leq ) high energy = unlikely</td>
</tr>
</tbody>
</table>

and more:

if $\text{Ti}^{4+}$ subs $\text{Al}^{3+}$, effective charge of +1

1 $\text{Al}^{3+}$ vacancy per 3 substitutions

if $\text{Mg}^{2+}$ subs $\text{Al}^{3+}$, effective charge -1

1 $\text{Al}^{3+}$ interstitial per 3 subs

1 $\text{O}^{2-}$ vacancy per 2 subs

if $\text{Cr}^{3+}$ subs $\text{Al}^{3+}$, effective charge 0

no compensation needed
5) No. Anions are very large, so there is a large amount of bond/lattice strain needed to accommodate an anion interstitial and anion vacancy pair.

In other words, $Q$ for this defect would be very large.

6) \[
\frac{N_S}{N} = \exp\left(\frac{-Q}{k_B T}\right) \rightarrow 2.8 \times 10^{-22} = \exp\left(\frac{-Q}{k_B \times 298K}\right)
\]

\[
Q = -k_B \times 298K \times \ln(2.8 \times 10^{-22}) = -0.026eV \times \ln(2.8 \times 10^{-22})
\]

\[
Q = +1.57eV
\]

\[
\frac{N_S}{N} = \exp\left(\frac{-1.52eV}{k_B \times (1250+273)K}\right)
\]

\[
= \sqrt[6.4]{10^{-6}}
\]

Whether this is "per ion" or "per anion cation" pair is ambiguous and should have been specified in the problem.