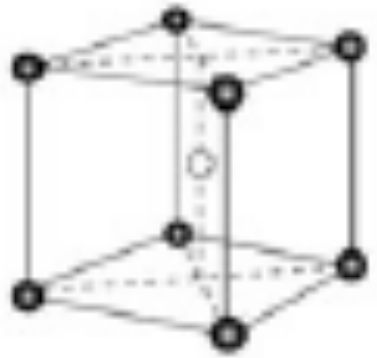
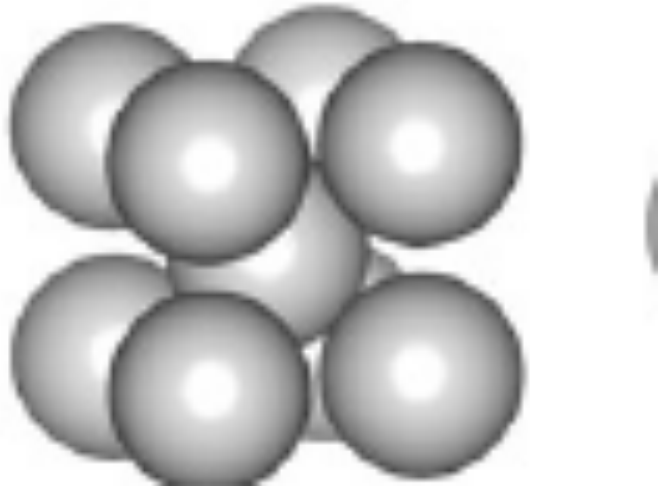
EXAMPLES

Question: Answer the following questions about body-centered cubic (bcc) structure with the lattice parameter "a."

(1) Obtain the volume of void, supposing the case where the spherical atoms of radius r_A are arranged in each lattice point. Calculate also the porosity and packing fraction.





In body-centered cubic (bcc) structure, atoms contacting each other are seen on diagonals and then we obtain the following relationship:

$$4 \times r_{\mathrm{A}} = a\sqrt{3}$$

$$r_{\mathrm{A}} = \frac{\sqrt{3}}{4}a$$

In a unit cell of bcc structure, there are two atoms: one atom at eight corners ($8 \times 1/8 = 1$) and one atom at the center. Therefore, the volume V_{A} occupied by atoms is described by

$$V_{\mathrm{A}} = 2 \times \frac{4}{3}\pi \left(\frac{\sqrt{3}}{4}a\right)^3 = \frac{\sqrt{3}\pi}{8}a^3.$$

The unit cell volume is expressed by a^3, so that the void volume V_H is as follows:

$$V_H = a^3 - V_A = \left(1 - \frac{\sqrt{3}}{8}\pi\right) a^3.$$

The porosity in the bcc lattice is given in the following:

$$\left(\frac{V_H}{a^3}\right) = \left(1 - \frac{\sqrt{3}}{8}\pi\right)^3 = 0.32.$$

At 278 K, iron (Fe) is found to show bcc structure with a lattice parameter of 0.2866 nm. Obtain the density of iron from this information.

The bcc structure includes two atoms per unit cell. If Avogadro's number
is NA, one mole of iron includes NA/2 unit cells. Therefore, the volume V per
mole of Fe (atomic volume) is given by

$$V = \frac{(0.2866 \times 10^{-9})^3}{0.6022 \times 10^{24}/2}.$$

The atomic weight M (molar mass) per 1 mol of Fe is 55.845 g is obtained from. Therefore, from the relationship of V= M/ρ, we can estimate the density value of as follows:

$$\rho = \frac{55.845 \times 2}{(0.2866 \times 10^{-9})^3 \times 0.6022 \times 10^{24}} = 7.88 \times 10^6\ \mathrm{g/m^3}.$$

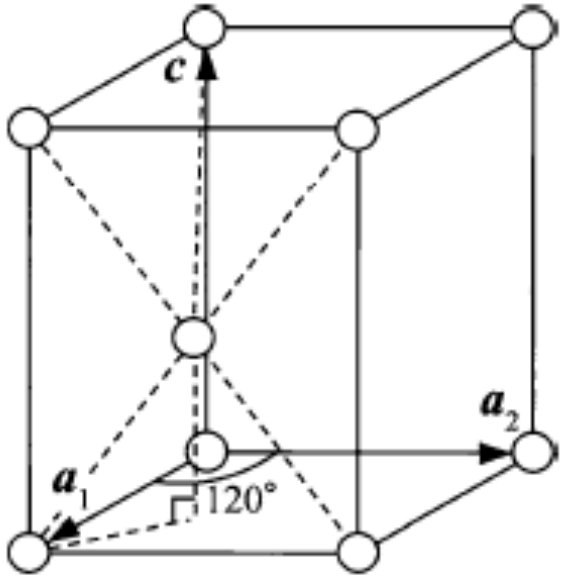
Beryllium (Be) mineral is expressed by a chemical formula (3BeO.Al2O3 6SiO2), and it is revealed that the structure is hexagonal with the lattice parameters a = 0.9215 nm and c = 0.9169 nm, and density
2.68 *10^6 g/m3. Obtain the numbers of molecules contained in a unit cell.

At first, we obtain the molecular weight of beryllium mineral using a chemical formula from the molecular weight per 1 mol of the individual oxide component:

$$BeO = 25.01\,g, \qquad Al_2O_3 = 101.96\,g, \qquad SiO_2 = 60.08\,g$$

$$3BeO + Al_2O_3 + 6SiO_2 = 537.47\,g/mol$$

If this molecular weight is divided by Avogadro's number, one obtain the value equivalent to the weight of one beryllium mineral molecule.



Next, we estimate the volume of a unit cell for beryllium mineral from the given values of lattice parameters. As readily seen in Fig. 1, in a unit cell of hexagonal system, the value of c is given by twice the height of $\left(\sqrt{\frac{2}{3}}a\right)$ for the regular tetrahedron of length a of one side, and the area of the parallelogram which corresponds to the base is given by $\left(\sqrt{\frac{3}{4}}a^2\right)$.Therefore, the volume V of a unit cell of hexagonal system is given in the following equation (see also Appendix A.6):

$$V = \frac{\sqrt{3}}{2}a^2c = 0.866a^2c$$
$$= 0.866 \times (0.9215 \times 10^{-9})^2 \times (0.9169 \times 10^{-9}) = 0.6743 \times 10^{-27}\ [\mathrm{m}^3].$$

The product of the volume of a unit cell and the density corresponds to the weight of one beryllium mineral molecule, so that if this value is compared with the value calculated from molecular weight and Avogadro's number, the number of molecules in a unit cell will be obtained:

$$\frac{0.6743 \times 10^{-27} \times 2.68 \times 10^{6}}{\left(\frac{537.47}{0.6022 \times 10^{24}}\right)} = 2.02.$$

Thus, the number of molecules in a unit cell is estimated to be two.

The atomic weight per 1 mol of copper (Cu) with face-centered cubic (fcc) structure and the density at 298K are 63.54 g and $8.89*10^6$ g/m^3, respectively. Estimate the nearest-neighbor distance of Cu atoms.

In the fcc lattice, four atoms are known to be included in a unit cell.
When Avogadro's number is denoted by NA, 1 mol Cu (63.54 g) includes NA/4 unit cells.

If the lattice parameter is set as "a," the volume of 1 mol Cu (=the atomic volume) V can be expressed as $V = a^3NA/4$.

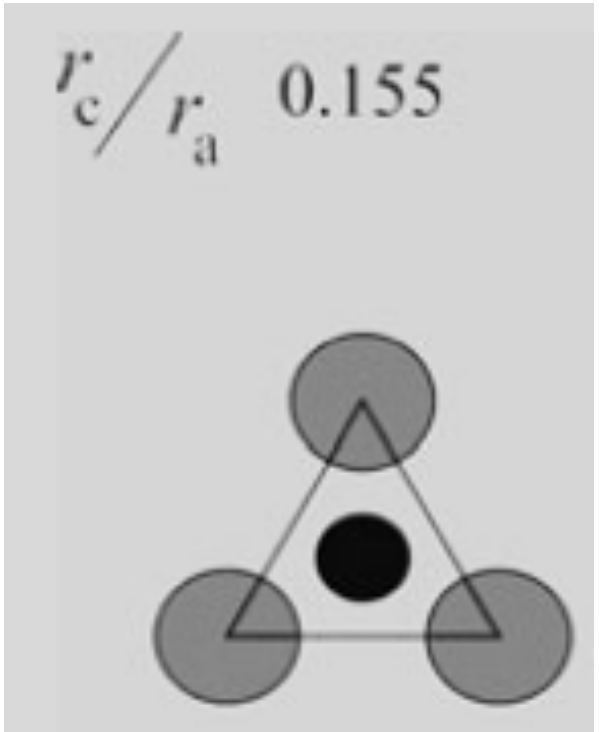
On the other hand, we obtain the relationship of $a^3NA/4 = M/\rho$ using the atomic weight M and ρ density , the lattice parameter can be estimated as follows:

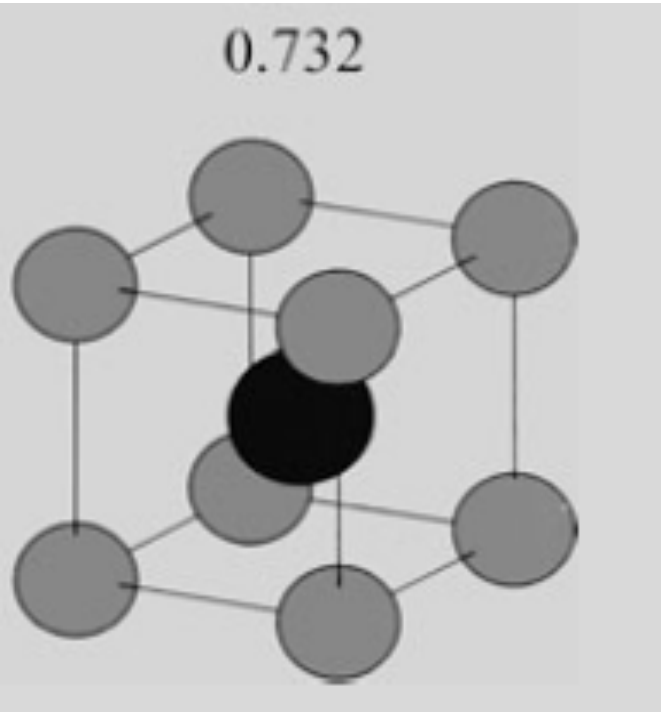
$$a^3 = \frac{4 \times 63.54}{0.6022 \times 10^{24} \times 8.89 \times 10^6} \qquad a = 3.621 \times 10^{-10}\,\text{m}.$$

The nearest-neighbor distance r of Cu atoms can be calculated since Cu atoms are in contact along the diagonal line of a cell face in the fcc structure:

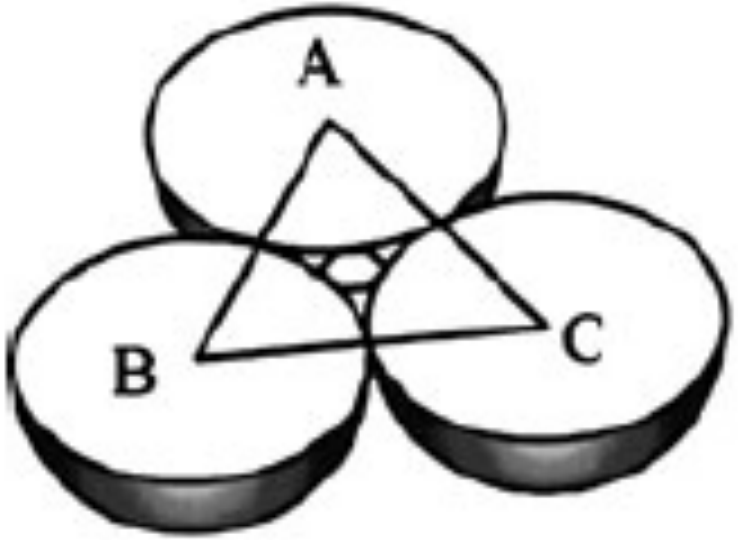
$$r = a/\sqrt{2} = 2.560 \times 10^{-10}\,\text{m} = 0.2560\,\text{nm}.$$

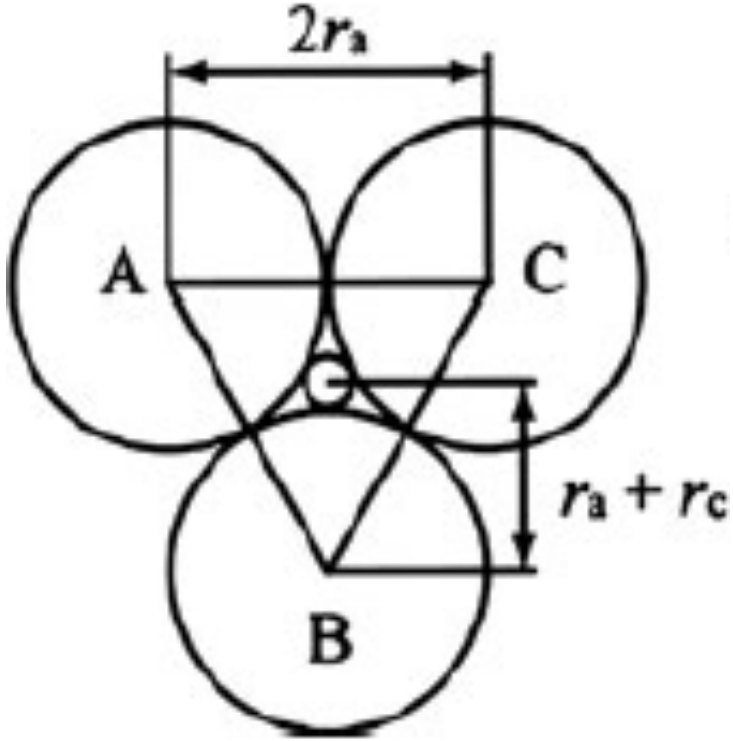
In ionic crystals, anions of the relatively larger size are densely arranged so as to avoid their direct contact, whereas cations of relatively smaller size occupy the positions equivalent to the vacant space produced by anions. For this reason, if the radii of cation and anion are described by rc and ra, respectively, some correlations are recognized between the coordination numbers and the size ratio of rc/ra. Estimate the specific values of rc/ra for cases that cations are surround by anions with the coordination numbers of 3 and 8.





(1) When the coordination number is 3, a cation is likely to occupy the position equivalent to the center of an equilateral triangle of ABC formed by three anions as shown in Fig. 1. The height and the center of gravity for the equilateral triangle with its one edge being $2r_a$ are given by $\sqrt{3}r_a$ and the height $\times \frac{2}{3}$, respectively. Then, the value of $\frac{2}{3} \times \sqrt{3}r_a$ is exactly equivalent to $r_a + r_c$





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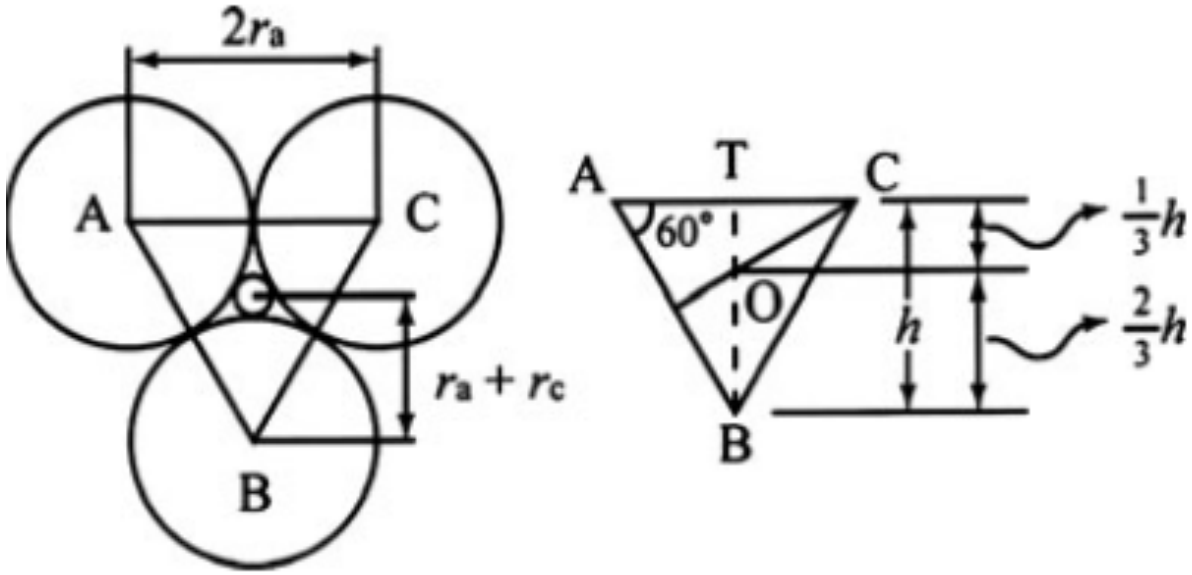
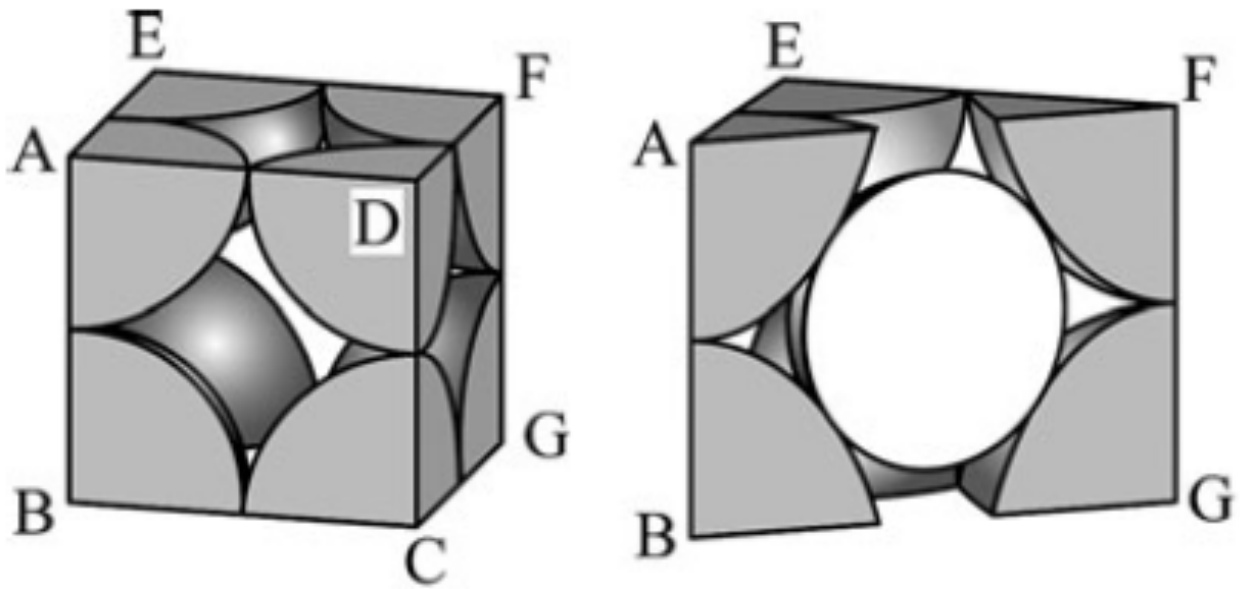
$$r_a + r_c = \frac{2\sqrt{3}}{3} \times r_a \quad \Rightarrow \quad r_c = \left(\frac{2\sqrt{3}}{3} - 1\right) r_a \qquad \frac{r_c}{r_a} = \frac{2\sqrt{3}}{3} - 1 = 0.155$$



For 8-coordination, it is difficult to visualize the cation in the vacant space of a polyhedron formed by anions. Nevertheless, if the appropriate value of r_c/r_a is given, one can obtain the ionic arrangements in which a cation is located at a center of body-centered cubic (bcc) lattice formed by eight anions. In this case, the diagonal line of the cross-sectional view of ABGF portion of bcc lattice with one edge of $2r_a$ just corresponds to twice the value of $(r_a + r_c)$ as readily seen in Fig. 3. Here, the lengths of each edge of square ABGF are $2r_a$ and $2\sqrt{2}r_a$, respectively. Therefore,



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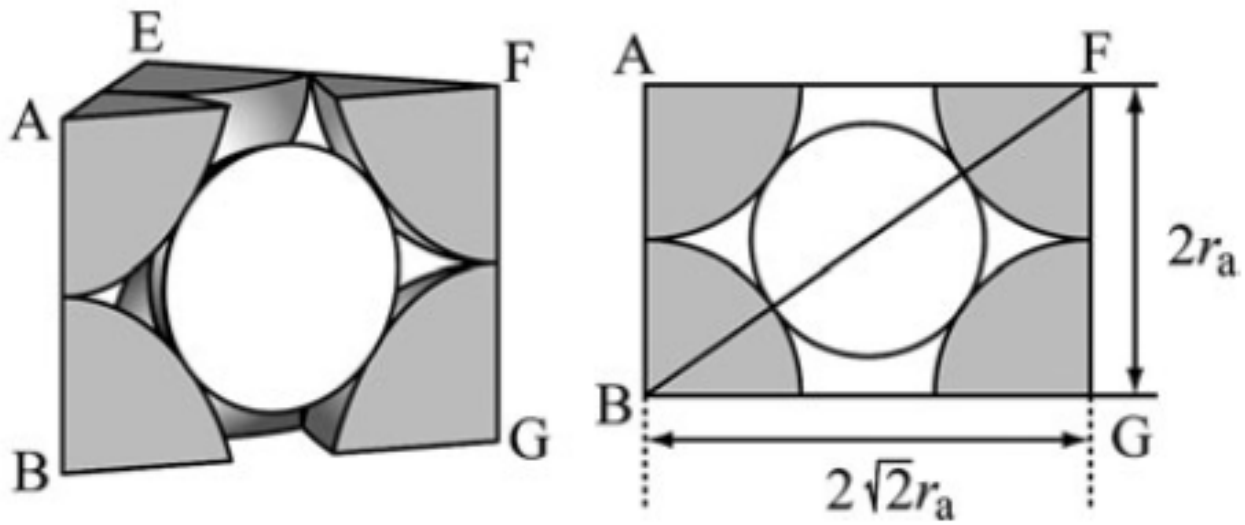
$$2(r_a + r_c) = \sqrt{3} \times (2r_a) \qquad r_a + r_c = \sqrt{3}r_a \quad \Rightarrow \quad r_c = (\sqrt{3} - 1)r_a$$



$$\frac{r_c}{r_a} = \sqrt{3} - 1 = 0.732$$