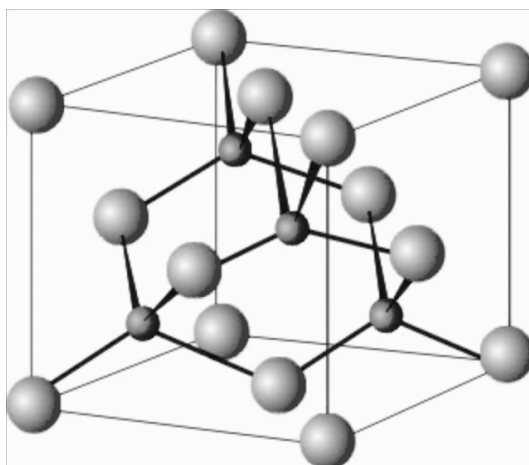


Marks
5

- The cubic form of boron nitride (borazon) is the second-hardest material after diamond and it crystallizes with the structure shown below. The large spheres represent the nitrogen atoms and the smaller spheres represent boron atoms.



From the unit-cell shown above, determine the empirical formula of boron nitride.

There are N atoms on the corners and on the faces of the unit cell:

- There are 8 N atoms on the corners. These contribute $1/8$ to the unit cell giving a total of $8 \times 1/8 = 1$ N atom.**
- There are 6 N atoms on the faces. These contribute $1/2$ to the unit cell giving a total of $6 \times 1/2 = 3$ N atoms.**
- There are a total of $1 + 3 = 4$ N atoms in the unit cell.**

There are B atoms inside the unit cell:

- There are 4 B atoms completely inside the cell. These contribute only to this unit cell giving a total of $4 \times 1 = 4$ B atoms.**

The formula is therefore B_4N_4 which simplifies to BN.

Answer: **BN**

Determine the oxidation state of the boron atoms.

Nitrogen has an oxidation number of $-III$ (or -3) to complete its octet. To ensure neutrality, boron must be $+III$ (or $+3$).

Answer: **+III (or +3)**

ANSWER CONTINUES ON THE NEXT PAGE

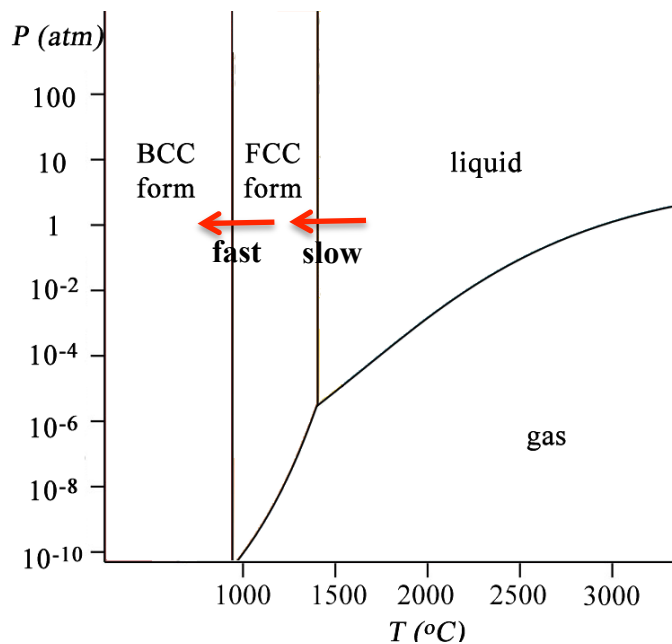
The cubic form of boron nitride is more thermally stable in air than diamond. Provide a reasonable explanation for this observation.

Boron and nitrogen have different electronegativities, with N more electronegative than B. This leads to partial δ^+ and δ^- charges on B and N respectively. These charges give the bonds partial ionic character and this acts to increase the strength of the bonds.

A protective layer of B_2O_3 forms on the surface of BN in the presence of air. For diamond, gaseous CO_2 forms at high temperatures which leads to thermal degradation rather than protection.

- A simplified phase diagram for iron is shown below, with the solid part divided into the body-centred cubic (BCC) and face-centred cubic (FCC) phases.

Marks
5



Which form of iron is stable at room temperature and pressure?

BCC form

If molten iron is cooled slowly to around 1200 °C and then cooled rapidly to room temperature, the FCC form is obtained. Draw arrows on the phase diagram to indicate this process and explain why it leads to the FCC form as a metastable phase.

The slow cooling leads to the most stable form at 1200 °C – the FCC form. Fast cooling to room temperature does not allow the atoms to re-arrange; they are stuck in the FCC form as considerable re-arrangement is needed to turn this in the BCC form.

The structure is stuck in the FCC arrangement even though BCC is more stable.

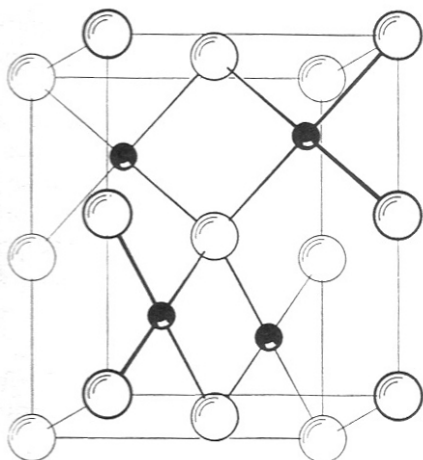
The line dividing the BCC and FCC forms is almost, but not quite vertical. Predict which way this line slopes and explain your answer.

BCC is less dense than FCC – the latter is a close packed structure so has the maximum possible density whereas the former is not closed packed.

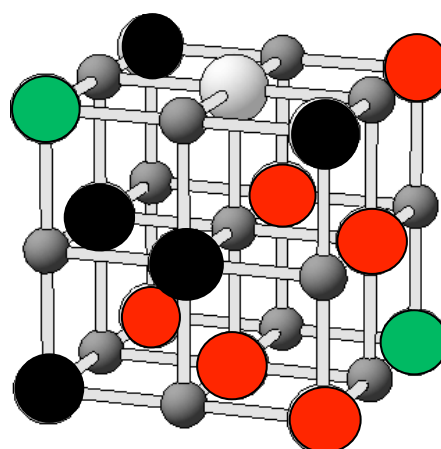
Applying pressure will favour the more dense structure as it takes up less space. Increasing pressure therefore favours the FCC structure. The line between BCC and FCC has a negative slope (\searrow). If the system is on the line and the pressure is increased, the system moves into the FCC region.

Marks
8

- PdO is used as a hydrogenation catalyst and it crystallizes with the tetragonal structure shown below. NiO has a variety of uses and crystallizes with the rocksalt structure. The large spheres represent the oxygen atoms and the smaller spheres represent palladium or nickel atoms.



palladium(II) oxide, PdO



nickel(II) oxide, NiO

Show the structure on the left is consistent with the formula PdO.

In the unit cell there are:

4 Pd atoms

1 O atom in the centre

$2 \times \frac{1}{2} = 1$ O atom at the top and bottom faces

$4 \times \frac{1}{4} = 1$ O atom at the equatorial edges

$8 \times \frac{1}{8} = 1$ O atom at the corners

This gives unit cell formula of Pd₄O₄ and thus empirical formula of PdO.

What is the coordination number about each metal atom?

Pd: **4**

Ni: **6**

The radius of the Pd²⁺ ion is 86 pm, that of the Ni²⁺ ion is 69 pm. Give a reason why the larger ion has a smaller coordination number.

Pd²⁺ (*d*⁸) prefers square planar coordination and thus has a lower coordination number than Ni²⁺. The ionic model would predict that the larger Pd²⁺ ion would have a higher coordination than Ni²⁺. The preference of Pd²⁺ for square planar coordination overrides this.

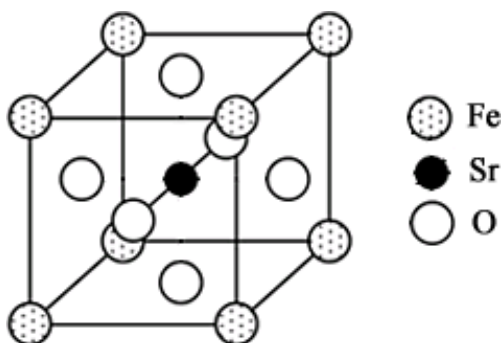
Does either structure contain a close-packed arrangement of O²⁻ ions?

PdO: YES / NO

NiO: YES / NO

If YES, indicate the layers on the unit cell(s) above. See coloured layers above

- SrFeO_3 crystallises with the perovskite structure, shown below. The structure is cubic with iron atoms on each corner, oxygen atoms at the centre of each face and a strontium atom at the centre of the cube. Mixed metal oxides such as this are of current research interest because of their magnetic and possible superconducting properties.



Show the structure is consistent with the formula SrFeO_3 and give the coordination numbers of the Sr, Fe and O atoms.

There is a Fe atom on each of the 8 corners, each of which is shared between 8 cells so contribute 1/8 to each: number of Fe atoms = $8 \times 1/8 = 1$.

There is a O atom on each of the 6 faces, each of which is shared between 2 cells so contribute 1/2 to each: number of O atoms = $6 \times 1/2 = 3$.

There is a single Sr atom which is at the centre and is unshared: number of Sr atoms = 1.

The formula is thus FeSrO_3 .

Each Fe atom is surrounded by 12 O atoms: it has a coordination number of 12.

Each Sr atom is surrounded by 6 O atoms: it has a coordination number of 6.

Each O atom is surrounded by 2 Sr atoms, at a distance of $0.5a$, and 4 Fe atoms, at a distance of $0.707a$. As coordination number is defined as the number of nearest neighbours, it is 2.

Using the box notation to represent atomic orbitals, work out how many unpaired electrons are present on the iron cation in this compound.

As Sr^{2+} and 3O^{2-} are present, iron must have an oxidation number of +4. As iron has 8 valence electrons, Fe^{4+} has $(8 - 4) = 4$ valence electrons and a d^4 configuration. These are arranged in the five d orbitals to minimise repulsion by maximising the number of unpaired spins:



There are 4 unpaired electrons

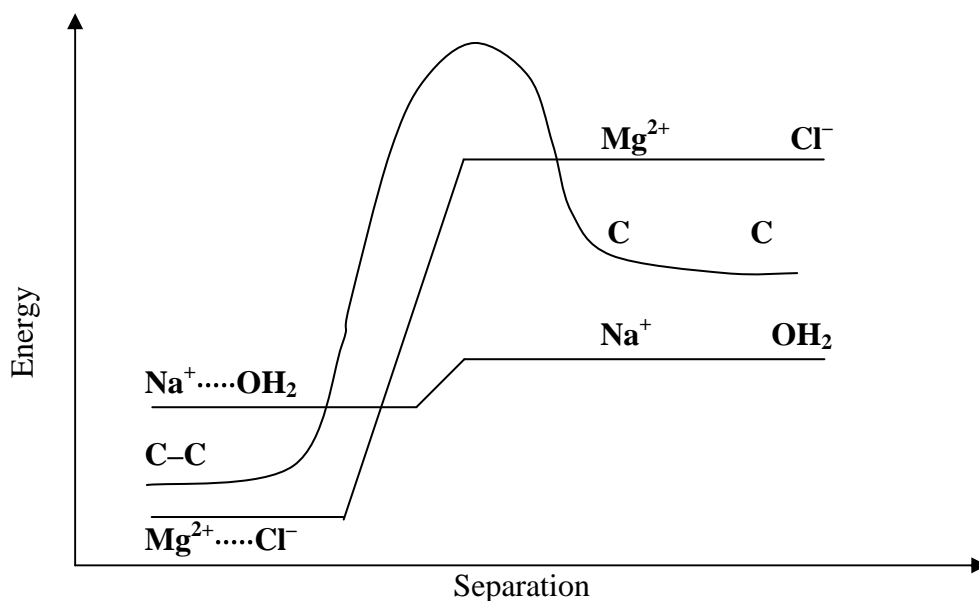
It is possible to substitute the Sr^{2+} ions at the centre of the unit cell by La^{3+} ions to make a series of compounds with the formula $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ with $0 \leq x \leq 1$. Suggest why this substitution is achieved without significant change to the unit cell dimensions and describe how charge balance is achieved in these compounds.

La^{3+} has a similar size to Sr^{2+} as they are diagonally related on the Periodic Table. La^{3+} has an extra shell but has a higher charge. As a result, La^{3+} is able to occupy the same position in the unit cell as Sr^{2+} without the unit cell being strained.

Each time a La^{3+} replaces a Sr^{2+} , a Fe^{4+} is reduced to Fe^{3+} to ensure charge balance is maintained.

- Shown below is the energy profile for the separation of Na^+ from H_2O . Draw energy profiles for the separation of Mg^{2+} from Cl^- and for the breaking of the C–C bond in ethane to the same scales (approximately).

Marks
6



There is an activation energy (barrier) for the breaking of a covalent bond. For an ionic bond and an ion-dipole interaction, the energy just increases with separation. Due to the charges, the ion-ion interaction is harder to break than the ion-dipole interaction.

Name the inter- or intra-molecular forces involved in each of these three interactions.

Na^+ OH_2

ion - dipole

Mg^{2+} Cl^-

ion – ion (ionic bond)

C C

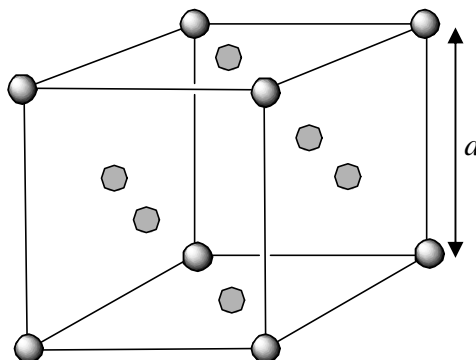
covalent bond

Explain why bonds such as C–C are generally considered to be stronger than interactions such as that between Mg^{2+} and Cl^- .

The covalent bond has a large energy barrier (activation energy) that must be overcome to break the bond. Ionic bonds do not have this barrier, but have a larger overall ΔH .

Marks
5

- The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces. The unit cell dimension (edge length, a) for this alloy is 0.36 nm.



What is the chemical formula of the alloy?

There are 8 Au atoms on the corners. Each of these contribute 1/8 to the unit cell:

$$\text{number of Au atoms} = 8 \times 1/8 = 1$$

There are 6 Cu atoms on the face. Each of these contribute 1/2 to the unit cell:

$$\text{number of Cu atoms} = 6 \times 1/2 = 3$$

The ratio of Cu to Au atoms is therefore 3 : 1 and the formula is Cu₃Au.

Answer: **Cu₃Au**

Given that pure gold is 24 carat and gold alloyed with 25% by weight of another metal is termed 18 carat gold, what carat gold is this alloy?

The molar mass of Cu₃Au is:

$$\text{molar mass} = (3 \times 63.55 \text{ (Cu)} + 1 \times 196.97 \text{ (Au)}) \text{ g mol}^{-1} = 387.62 \text{ g mol}^{-1}.$$

As 1 mol of Cu₃Au contains 1 mol of Au, the percentage by weight of gold in Cu₃Au is:

$$\text{percentage by weight} = \frac{197.67}{387.62} \times 100 \% = 50 \%$$

As a 100 % alloy is 24 carat and a 75% alloy is 18 carat, a 50 % alloy is 12 carat.

Answer: **12 carat**

What is the volume of the unit cell?

As the unit cell is cubic:

$$\text{volume} = (\text{side length})^3 = a^3 = (0.36 \times 10^{-9} \text{ m})^3 = 4.7 \times 10^{-29} \text{ m}^3$$

Answer: **$4.7 \times 10^{-29} \text{ m}^3$**

ANSWER CONTINUES ON THE NEXT PAGE

What is the density of the alloy?

From above, the unit cell contains 1 Au atom and 3 Cu atoms:

$$\text{mass of gold} = 196.97 \text{ g mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1} = 3.271 \times 10^{-22} \text{ g}$$

$$\text{mass of copper} = 3 \times 63.55 \text{ g mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1} = 3.166 \times 10^{-22} \text{ g}$$

$$\text{mass of unit cell} = (3.271 \times 10^{-22} + 3.166 \times 10^{-22}) \text{ g} = 6.437 \times 10^{-22} \text{ g}$$

The density is therefore:

$$\text{density} = \text{mass} / \text{volume}$$

$$= 6.437 \times 10^{-22} \text{ g} / 4.7 \times 10^{-29} \text{ m}^3 = 1.4 \times 10^7 \text{ g m}^{-3}$$

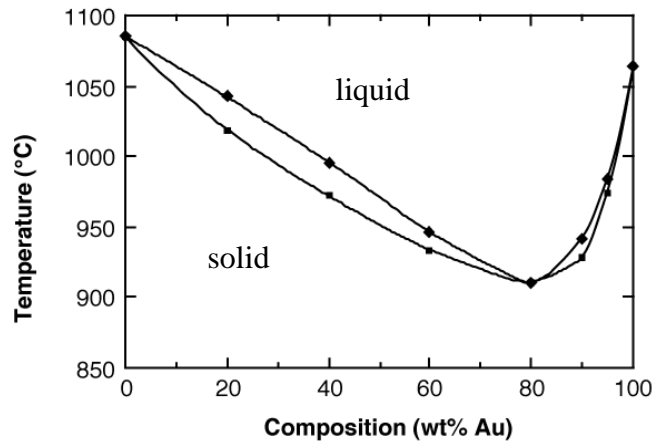
As 1 m = 100 cm, 1 m³ = (100)³ cm³ = 10⁵ cm³:

$$\text{density} = 14 \text{ g cm}^{-3}$$

Answer: 14 g cm⁻³

Shown below is the phase diagram for the Cu/Au system. Describe what would be seen as a sample of the alloy is heated from 900 to 1100 °C.

Marks
3



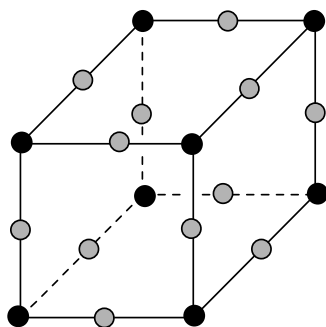
The solid would warm to 950 °C where melting would begin.

From 950 - 960 °C, the solid and liquid phases would co-exist. This should be compared to the behaviour of a pure substance where there is no increase in temperature whilst the solid melts.

Above 960 °C, only liquid is present.

- The diagram below shows the structure of an oxide of rhenium. The unit cell is cubic with rhenium at each of the corners and oxygen in the centre of each of the edges.

Marks
5



What is the chemical formula of this oxide?

There are 8 Re atoms on the corners, each contributing 1/8 to the unit cell: total number of Re atoms = $8 \times 1/8 = 1$.

There are 12 O atoms on the edges, each contributing 1/4 to the unit cell: total number of O atoms = $12 \times 1/4 = 3$.

The formula is thus ReO_3 .

Answer: **ReO_3**

What are the coordination numbers of rhenium and oxygen in this compound?

Re: **6 (octahedral)**

O: **2 (linear)**

There is a large hole at the centre of the cell that in some compounds is occupied by a cation. What is the coordination number of a cation occupying this site?

12 coordinate.

Given that the density of this oxide is 7.1 g cm^{-3} , calculate the length of the cell edge. (The structure is cubic.)

The unit cell contains one formula unit of ReO_3 .

The formula mass of ReO_3 is $(186.2 \text{ (Re)} + 3 \times 16.00 \text{ (O)}) = 234.2 \text{ g mol}^{-1}$.

This is the mass of 1 mol. The mass of 1 formula unit is therefore:

$$\text{mass} = 234.2 \text{ g mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1} = 3.889 \times 10^{-22} \text{ g}$$

ANSWER CONTINUES ON THE NEXT PAGE

As density = mass / volume,

$$\text{volume} = \text{mass} / \text{density} = (3.889 \times 10^{-32} \text{ g}) / (7.1 \text{ g cm}^{-3}) = 5.48 \times 10^{-23} \text{ cm}^3$$

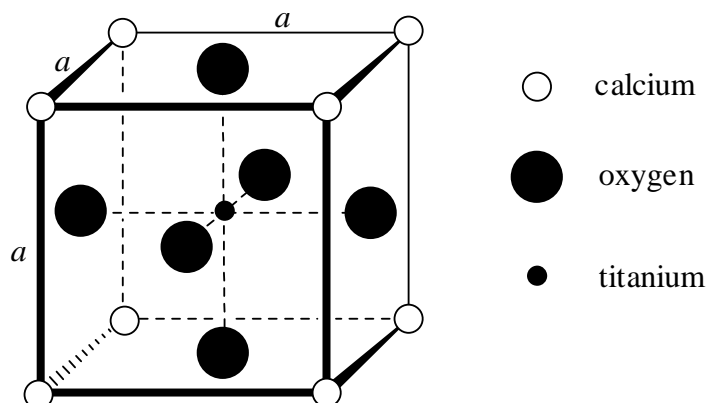
As the cell is cubic, if the side length is a , the volume is a^3 and,

$$a = (5.48 \times 10^{-23} \text{ cm}^3)^{1/3} = 3.8 \times 10^{-8} \text{ cm} = 3.8 \times 10^{-10} \text{ m or } 380 \text{ pm.}$$

Answer: **380 pm**

Marks
5

- The diagram below shows the structure of perovskite, a mineral made up of calcium (at each of the corners), oxygen (in the centre of each of the faces), and titanium (at the centre of the cube). The unit cell dimension (edge length, a) for perovskite is 0.38 nm.



What is the chemical formula of perovskite?

There are eight Ca^{2+} ions on the corners of the cube. These are each shared between eight unit cells: number of Ca^{2+} ions = $8 \times 1/8 = 1$.

There is a single, unshared Ti^{4+} ion at the cube centre.

There are six O^{2-} ions at the centres of the faces of the cube. These are each shared between two cubes: number of O^{2-} ions = $6 \times 1/2 = 3$.

Overall, $\text{Ca}^{2+} : \text{Ti}^{4+} : \text{O}^{2-} = 1 : 1 : 3$. The formula is CaTiO_3 .

Answer: **CaTiO_3**

What is the volume of the unit cell?

The length of the side of the cube = $a = 0.38$ nm. As $V = a^3$,

$$V = (0.38 \times 10^{-9} \text{ m})^3 = 5.5 \times 10^{-29} \text{ m}^3$$

Answer: **$5.5 \times 10^{-29} \text{ m}^3$**

What is the density of perovskite? Give your answer in g cm^{-3} .

As the atomic mass is the mass of a mole, the mass of one atom is $\frac{M}{N_a}$. From above, each unit cell contains 1 Ca^{2+} , 1 Ti^{4+} and 3 O^{2-} . The mass of one cell is therefore:

$$\begin{aligned}\text{mass of cell} &= \frac{M_{\text{Ca}}}{N_a} + \frac{M_{\text{Ti}}}{N_a} + 3\frac{M_{\text{O}}}{N_a} = \frac{1}{N_a} (40.08 + 47.88 + 16.00) \text{ g} \\ &= \frac{1}{N_a} \times 135.96 \text{ g} = 2.258 \times 10^{-22} \text{ g}\end{aligned}$$

As $1 \text{ cm} = 0.01 \text{ m}$, $1 \text{ cm}^3 = (0.01)^3 \text{ m}^3 = 1 \times 10^{-6} \text{ m}^3$. From above, $V = 5.5 \times 10^{-29} \text{ m}^3$ so,

$$\text{volume} = 5.5 \times 10^{-29} / 1 \times 10^{-6} \text{ cm}^3 = 5.5 \times 10^{-23} \text{ cm}^3.$$

Hence,

$$\text{density} = \frac{\text{mass (g)}}{\text{volume (cm}^3\text{)}} = \frac{2.258 \times 10^{-22} \text{ g}}{5.5 \times 10^{-23} \text{ cm}^3} = 4.1 \text{ g cm}^{-3}$$

Answer: 4.1 g cm^{-3}

ANSWER CONTINUES ON THE NEXT PAGE

What is the density of perovskite? Give your answer in g cm^{-3} .

As the atomic mass is the mass of a mole, the mass of one atom is $\frac{M}{N_a}$. From above, each unit cell contains 1 Ca^{2+} , 1 Ti^{4+} and 3 O^{2-} . The mass of one cell is therefore:

$$\begin{aligned}\text{mass of cell} &= \frac{M_{\text{Ca}}}{N_a} + \frac{M_{\text{Ti}}}{N_a} + 3\frac{M_{\text{O}}}{N_a} = \frac{1}{N_a} (40.08 + 47.88 + 16.00) \text{ g} \\ &= \frac{1}{N_a} \times 135.96 \text{ g} = 2.258 \times 10^{-22} \text{ g}\end{aligned}$$

As $1 \text{ cm} = 0.01 \text{ m}$, $1 \text{ cm}^3 = (0.01)^3 \text{ m}^3 = 1 \times 10^{-6} \text{ m}^3$. From above, $V = 5.5 \times 10^{-29} \text{ m}^3$ so,

$$\text{volume} = 5.5 \times 10^{-29} / 1 \times 10^{-6} \text{ cm}^3 = 5.5 \times 10^{-23} \text{ cm}^3.$$

Hence,

$$\text{density} = \frac{\text{mass (g)}}{\text{volume (cm}^3\text{)}} = \frac{2.258 \times 10^{-22} \text{ g}}{5.5 \times 10^{-23} \text{ cm}^3} = 4.1 \text{ g cm}^{-3}$$

Answer: 4.1 g cm^{-3}

- Many elemental metals crystallise in one of three cubic forms, either with a face-centred cubic, a body-centred cubic or a simple cubic unit cell. Explain the main differences and similarities between these different crystalline forms.

All three are based on a cubic unit cell:

- **The simple cubic form has atoms on each corner so that the atoms are stacked directly one on top of the other. As the 8 atoms are shared with eight other cubes, each contributes $1/8$ to the cell so that the cell contains $8 \times 1/8 = 1$ atom. The atoms touch along the edges of the cube.**
- **The body centred cubic form has an additional atom in the cube centre, giving a total of 2 atoms in the cell. The atoms touch along the cube diagonal.**
- **The face centred cubic form has atoms on each corner and atoms at the centre of each face (with no atom at the centre of the cube). The atoms on the face centres are shared with two other cubes and so contribute $1/2$ to the cell. The cell contains $8 \times 1/8$ (corner) + $6 \times 1/2$ (face) = 4. The atoms touch along the face diagonals.**
- **The face centred cubic form is the only close packed structure and is the most dense.**
- **In a face centred cubic structure, 74% of the space is occupied. In a body centred cubic, 68% is occupied. In a simple cubic structure, 52% is occupied.**