

### ***ICHO Montréal 1997 (Prep. Prob.)***

A gold single crystal has a cubic shape and the dimension of the cube is a cm = 1 000. When irradiated with Cu  $K_{\alpha 1}$  X-rays ( $\lambda = 154.05$  pm) at the angle ( $\theta$ ) of  $10.89^\circ$  it gives a well-defined first-order diffraction pattern.

- How many gold atoms are in the cube?
- What is the mass of the unit cell of gold?
- What is the density of gold?

### ***ICHO Montréal 1997 (Prep. Prob.)***

A gold thin film is deposited on a square piece of mica having the dimension of  $a = 1.000$  cm. The gold film forms an ideal (100) surface structure. Such prepared gold layer and a gold wire are immersed in  $10.000$  cm<sup>3</sup> of aqueous electrolyte containing  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_4$ ; the molar concentrations of the salts are  $c_{\text{CuSO}_4} = 0.100$  mM and  $c_{\text{Na}_2\text{SO}_4} = 0.100$  M, respectively. A constant potential is applied between the two electrodes; the gold (100) layer acts as a cathode and the gold wire as an anode. An epitaxial layer of Cu having 100 atomic monolayers is deposited on the Au(100) substrate. Gold has the face centered cubic (fcc) crystallographic structure and its lattice constant equals  $4.077 \cdot 10^{-8}$  cm.

What is the concentration of  $\text{CuSO}_4$  in the electrolyte after deposition of the Cu epitaxial layer?

### ***ICHO Montréal 1997***

Iron metal melts at 1811 K. Between room temperature and its melting point, iron metal can exist in different allotropic or crystalline forms. From room temperature to 1185 K, the crystal structure of iron metal exists as a body-centered cubic (bcc) lattice known as  $\alpha$ -iron. From 1185 K to 1667 K, the structure becomes face-centered cubic (fcc) and is called  $\gamma$ -iron. Above 1667 K, and up to its melting point, iron reverts to a bcc structure similar to that of  $\alpha$ -iron. The latter phase is called  $\delta$ -iron.

Given that the density of pure iron metal is  $7.874$  g·cm<sup>-3</sup> at 293 K,

- Calculate the atomic radius of iron (expressed in cm)
- Calculate its density (expressed in g·cm<sup>-3</sup>) at 1250 K

Notes: Ignore the small effects due to the thermal expansion of the metal.

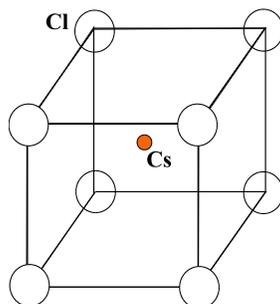
Clearly define any symbols which you use, e.g.  $r$  = atomic radius of Fe

Steel is an alloy of iron and carbon in which some of the interstitial spaces ("holes") of the crystal lattice (iron) are occupied by small atoms (carbon). Its carbon content typically ranges from 0.1% to 4.0%. In a blast-furnace, the melting of iron is facilitated when it contains 4.3% of carbon by mass. If this mixture is cooled too rapidly the carbon atoms remain dispersed within the  $\alpha$ -iron phase. This new solid, called martensite, is extremely hard and brittle. Although it is slightly distorted, the size of the unit cell of this solid (martensite) is the same as that of  $\alpha$ -iron (bcc).

Assuming that the carbon atoms are evenly distributed in the iron structure,

- Calculate the average number of carbon atoms per unit cell of  $\alpha$ -iron in martensite containing 4.3% C by mass.
- Calculate the density (expressed in g·cm<sup>-3</sup>) of this material.

**IChO Bangkok 1999 (Prep. Prob.)**



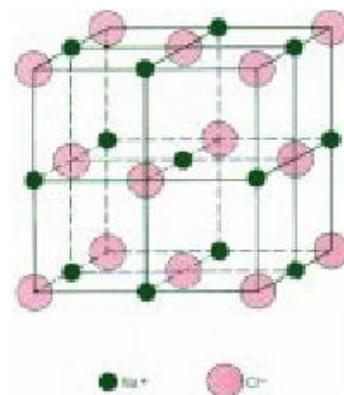
- What type of Bravais lattices, P, I, F or C ( P = primitive , I = inner or body centered , C = end or side or C - centered) of the structure depicted in the Figure?
- What is the empirical formula of this structure?
- What is the coordination number of Cs ion?
- In an experiment using this compound it is found that the first order reflection from the (100) plane is detected when the planes are indicated at  $10.78^\circ$  to the x-ray beam of wavelength  $1.542 \text{ \AA}$ . Given that the unit cell is cubic, calculate the volume.
- Calculate the density of this solid.
- Calculate the ionic radius of  $\text{Cs}^+$ , assuming that the ion touch along a diagonal through the unit cell and the ion radius of  $\text{Cl}^-$  is  $1.81 \text{ \AA}$ .

**IChO Mumbai 2001 (Prep. Prob.)**

Modern methods of structural analysis using X-rays provide valuable information about the three dimensional arrangement of atoms, molecules or ions in a given crystal structure.

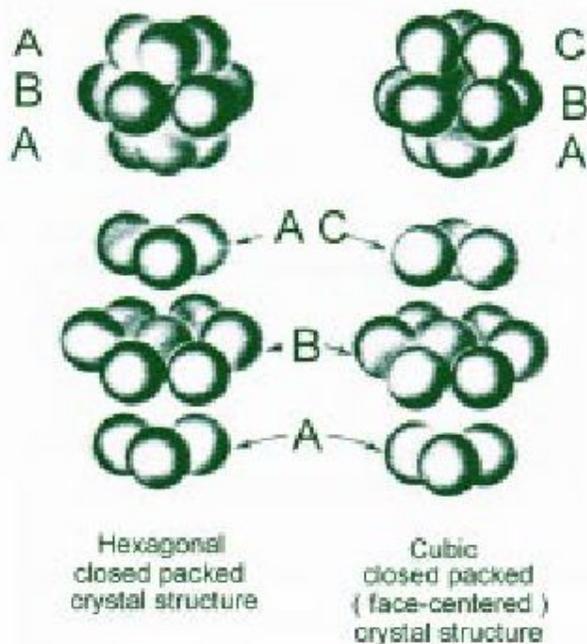
I. Crystal structure of rock salt (NaCl) is given below.

- What is the type of crystal lattice presented in the diagram?
- What is the coordination number of a sodium ion in this structure?
- What is the number of formula units of NaCl per unit cell?
- Calculate the  $r_{\text{Na}^+} / r_{\text{Cl}^-}$  limiting radius ratio for this structure.
- Why is the array of chloride ions slightly expanded, with the nearest Cl-Cl distance being  $400 \text{ pm}$ , compared to the close packed value of  $362 \text{ pm}$ ?
- What happens when the cation radius in the structure shown above is progressively increased till the cation/anion radius ratio reaches a value of  $0.732$ ?
- What is the range of cation/anion radius ratio for which the structure like that of NaCl is stable?



- II. The  $\text{Cu} - \text{K}_\alpha$  X-ray ( $\lambda = 154 \text{ pm}$ ) reflection from (200) planes of sodium chloride crystal is observed at  $15.8^\circ$ . Given that the radius of the chloride ion is  $181 \text{ pm}$ , calculate
- the separation between adjacent 200 planes of NaCl.
  - the length of the unit cell edge (lattice constant) of NaCl.
  - the radius of the sodium ion.

III. The diagram of a cubic close packing (ccp) and a hexagonal close packing (hcp) lattice arrangement (assuming rigid sphere model) is given below.



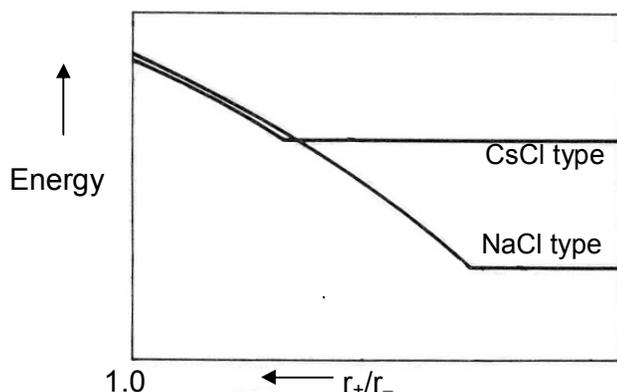
- Describe the difference between the ccp and hcp lattice arrangements.
- Calculate the packing fraction for a ccp arrangement.
- Will the coordination number, and the packing fraction in a hcp arrangement be the same as that in a ccp arrangement?

**IV.** Nickel (at.wt. 58.69) crystallizes in the ccp structure. X-ray diffraction studies indicate that its unit cell edge length is 352.4 pm. Given that the density of Nickel is  $8.902 \text{ g cm}^{-3}$ , calculate

- the radius of the nickel atom.
- the volume of the unit cell.
- the Avogadro number.

**ICHO Mumbai 2001**

X-ray crystallography reveals many aspects of the structure of metal halides. The radius ratio ( $r_+/r_-$ ) is a useful parameter to rationalize their structure and stability. A table of radius ratio ( $r_+/r_-$ ) for some alkali halides is given below. The variation of the electrostatic component of lattice energy of alkali halides with radius ratio ( $r_-$  kept constant) is shown schematically for NaCl-type and CsCl-type crystal structures.



	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$
$\text{Cl}^-$	0.33	0.52	0.74	0.82	0.93
$\text{Br}^-$	0.31	0.49	0.68	0.76	0.87
$\text{I}^-$	0.28	0.44	0.62	0.69	0.78

a) For a given anion, the graph for NaCl-type structure levels off at low  $r_+/r_-$  values because of

- (a) cation–cation contact along the face diagonal.
- (b) anion–anion contact along the face diagonal.
- (c) cation–anion contact along the cell edge.


b) Which among the halides LiBr, NaBr and RbBr is likely to undergo phase transition from NaCl type to CsCl-type structure with change of temperature and /or pressure?

c) Show by calculation the radius ratio ( $r_+/r_-$ ) at which the energy of CsCl-type structure levels off.

d) Using Cu  $K\alpha$  X-rays ( $\lambda = 154$  pm), diffraction by a KCl crystal (fcc structure) is observed at an angle ( $\theta$ ) of  $14.2^\circ$ . Given that (i) diffraction takes place from the planes with  $h^2 + k^2 + l^2 = 4$ , (ii) in a cubic crystal  $d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}$ , where 'd' is the distance between adjacent hkl planes and 'a' is the lattice parameter, and (iii) reflections in an fcc structure can occur only from planes with 'all odd' or 'all even' hkl (Miller) indices, calculate the lattice parameter 'a' for KCl.

e) Indicate in the table given below the required information for the 2<sup>nd</sup> and 3<sup>rd</sup> nearest neighbours of a  $K^+$  ion in the KCl lattice.

2 <sup>nd</sup> nearest neighbours			3 <sup>rd</sup> nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)

f) Determine the lowest value of diffraction angle  $\theta$  possible for the KCl structure.

***ICHO Groningen 2002 (Prep. Prob.)***

BP (boron phosphite) is a valuable wear-resistant hard coating that is produced by the reaction of boron tribromide and phosphorus tribromide under a hydrogen atmosphere at high temperature ( $>750^\circ\text{C}$ ) This ceramic material is used as a protecting thin film on metal surfaces. BP crystallizes in a cubic-close-packed structure with tetrahedral surrounding.

- a) Give the equation for the formation of BP.
- b) Draw the Lewis structures of boron tribromide and phosphorus tribromide.
- c) Draw the structure of BP in the crystalline state.
- d) Give the overall composition of the unit cell corresponding with the formula BP.
- e) Calculate the density of BP when the lattice parameter of the unit cell is  $4.78 \text{ \AA}$ .
- f) Calculate the distance between a boron and a phosphorus atom in BP.

The Born-Landé formula given below can be used to calculate the lattice energy:

$$U_{\text{lattice}} = -f \frac{Z_+ Z_- A e^2}{r_+ + r_-} \left( 1 - \frac{1}{n} \right)$$

The factor  $f e^2$  amounts to 1390 when the ionic radii  $r_+$  and  $r_-$  are given in Å. The Madelung constant is 1.638. The Born exponent is  $n$  is 7. The charges of ions  $Z_+$  and  $Z_-$  are integer numbers.

g) Calculate the lattice energy of BP.

### **ICHO Athens 2003 (Prep. Prob.)**

The crystalline form of iron, known as  $\alpha$ -Fe, has a *body centered cubic* (bcc) unit cell with an edge length of 2.87 Å. Its density at 25 °C is 7.86 g/cm<sup>3</sup>. Another – higher temperature - crystalline form, known as  $\gamma$ -Fe, has a *face centered cubic* (fcc) unit cell with an edge length of 3.59 Å.

a) Calculate the atomic radius of iron in  $\alpha$ -Fe and use the above facts to estimate Avogadro's number, assuming that the atoms in  $\alpha$ -Fe touch each other *along the body diagonal*.

b) Calculate the atomic radius of iron in  $\gamma$ -Fe as well as the density of  $\gamma$ -Fe, assuming that the atoms touch each other *along the face diagonal*.

c) Assume that an interstitial atom (other than Fe) fits perfectly *at the center of  $\alpha$ -Fe cube face* [i.e., a position with fractional coordinates ( $\frac{1}{2}$ , 0,  $\frac{1}{2}$ )], hence it just touches the surface of an iron atom at the center of the unit cell. What is the radius of the interstitial atom?

d) In a similar manner as in c), calculate the radius of a perfectly fitted interstitial atom *at the center of the  $\gamma$ -Fe unit cell*.

e) How much oversize is a carbon atom, having a radius of 0.077 nm, as compared with the interstitial atoms in questions c) and d)?

f) The (200) lattice planes of a cubic structure coincide with the faces of the unit cell as well as those planes that cut the axis at half of the cell edge (see figure). Suppose that a monochromatic X-ray beam, incident on a  $\alpha$ -Fe crystal, is diffracted on these planes at an angle of 32.6°. Calculate the wavelength of the X-ray beam.

### **VV1999**

Üks olulisemaid pooljuhte Ge on teemandi tüüpi võreaga, mille kristallograafiline struktuur on kujutatud joonisel: (puudub)

a) Määrake kindlaks võre elementaarrakku moodustavate aatomite koordinaadid.

b) Tehke kindlaks Ge koordinatsiooniarv ning nimetage koordinatsiooniline hulktahukas.

c) Tehke kindlaks (arvutage), mitu aatomit kuulub elementaarrakku.

d) Leidke Ge võrekonstant teades, et Ge tihedus  $\rho = 5.32 \text{ g/cm}^3$  ja molaarmass  $M = 72.69 \text{ g/mol}$ .

e) Leidke, milline on Ge (100) tasandi peegeldusnurk  $\theta$ , kui on teada, et kasutatava röntgenkiirguse lainepikkus  $\lambda = 71.07 \text{ pm}$  (röntgenkiirguse allikana kasutatakse MO  $K_\alpha$ -allikat).

f) Arvutage Ge-Ge sideme pikkus ideaalses Ge kristallis ning Ge aatomiraadius eeldusel, et tegemist on ..... tiheda pakendiga (st. täpsustage, millise tiheda pakendiga on Ge korral tegemist).

h) Arvutage Ge ruumitäitumis- (ehk pakkimis-) koefitsient.

i) Millega Te seletate Ge pooljuhi omadusi ja tema suhteliselt suurt kõvadust?