

Each small cube has atoms at alternate corners [Fig. 1(a)]. In all, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedron. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total. Each of the eight small cubes have one void in one unit cell of *ccp* structure. We know that *ccp* structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.

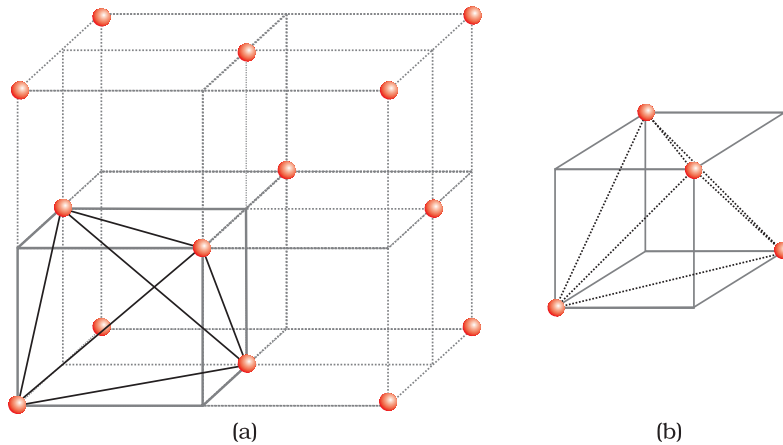


Fig. 1: (a) Eight tetrahedral voids per unit cell of *ccp* structure
(b) one tetrahedral void showing the geometry.

(b) Locating Octahedral Voids

Let us again consider a unit cell of *ccp* or *fcc* lattice [Fig. 2(a)]. The body centre of the cube, C is not occupied but it is surrounded by six atoms on face centres. If these face centres are joined, an octahedron is generated. Thus, this unit cell has one octahedral void at the body centre of the cube.

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges [Fig. 2(b)]. It is surrounded by six atoms, four belonging to the same unit cell (2 on the corners and 2 on face centre) and two belonging to two adjacent unit cells. Since each edge of the cube is shared between four adjacent unit cells, so is the octahedral void located on it. Only $\frac{1}{4}$ th of each void belongs to a particular unit cell.

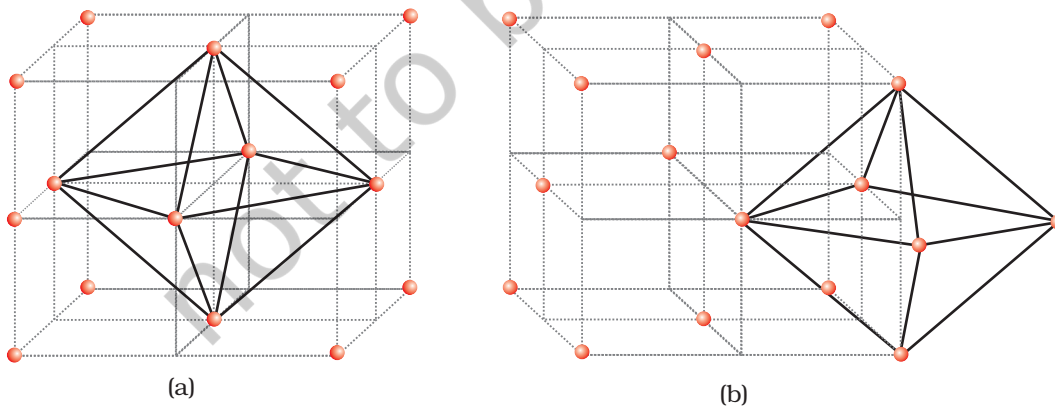


Fig. 2: Location of octahedral voids per unit cell of *ccp* or *fcc* lattice (a) at the body centre of the cube and (b) at the centre of each edge (only one such void is shown).

Thus in *cubic close packed structure*:

Octahedral void at the body-centre of the cube = 1

12 octahedral voids located at each edge and shared between four unit cells

$$= 12 \times \frac{1}{4} = 3$$

∴ Total number of octahedral voids = 4

We know that in ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

1.7 Packing Efficiency

In whatever way the constituent particles (atoms, molecules or ions) are packed, there is always some free space in the form of voids. **Packing efficiency** is the percentage of total space filled by the particles. Let us calculate the packing efficiency in different types of structures.

1.7.1 Packing Efficiency in hcp and ccp Structures

Both types of close packing (*hcp* and *ccp*) are equally efficient. Let us calculate the efficiency of packing in ccp structure. In Fig. 1.24 let the unit cell edge length be 'a' and face diagonal AC = b.

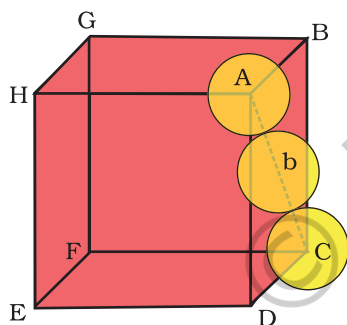


Fig. 1.24: Cubic close packing other sides are not provided with spheres for sake of clarity.

In ΔABC

$$AC^2 = b^2 = BC^2 + AB^2$$

$$= a^2 + a^2 = 2a^2 \text{ or}$$

$$b = \sqrt{2}a$$

If r is the radius of the sphere, we find

$$b = 4r = \sqrt{2}a$$

$$\text{or } a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$$

(we can also write, $r = \frac{a}{2\sqrt{2}}$)

We know, that each unit cell in ccp structure, has effectively 4 spheres. Total volume of four spheres is equal to $4 \times (4/3)\pi r^3$ and volume of the cube is a^3 or $(2\sqrt{2}r)^3$.

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}} \%$$

$$= \frac{4 \times (4/3)\pi r^3 \times 100}{(2\sqrt{2}r)^3} \%$$

$$= \frac{(16/3)\pi r^3 \times 100}{16\sqrt{2}r^3} \% = 74\%$$

1.7.2 Efficiency of Packing in Body-Centred Cubic Structures

From Fig. 1.25, it is clear that the atom at the centre will be in touch with the other two atoms diagonally arranged.

$$\begin{aligned} \text{In } \triangle EFD, \\ b^2 &= a^2 + a^2 = 2a^2 \\ b &= \sqrt{2}a \end{aligned}$$

$$\begin{aligned} \text{Now in } \triangle AFD \\ c^2 &= a^2 + b^2 = a^2 + 2a^2 = 3a^2 \\ c &= \sqrt{3}a \end{aligned}$$

The length of the body diagonal c is equal to $4r$, where r is the radius of the sphere (atom), as all the three spheres along the diagonal touch each other.

$$\text{Therefore, } \sqrt{3}a = 4r$$

$$a = \frac{4r}{\sqrt{3}}$$

$$\text{Also we can write, } r = \frac{\sqrt{3}}{4} a$$

In this type of structure, total number of atoms is 2 and their volume is $2 \times \left(\frac{4}{3}\right)\pi r^3$.

$$\text{Volume of the cube, } a^3 \text{ will be equal to } \left(\frac{4}{\sqrt{3}} r\right)^3 \text{ or } a^3 = \left(\frac{4}{\sqrt{3}} r\right)^3.$$

Therefore,

$$\begin{aligned} \text{Packing efficiency} &= \frac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}} \% \\ &= \frac{2 \times \left(\frac{4}{3}\right)\pi r^3 \times 100}{\left[\left(\frac{4}{\sqrt{3}} r\right)^3\right]} \% \\ &= \frac{(8/3)\pi r^3 \times 100}{64/(3\sqrt{3})r^3} \% = 68\% \end{aligned}$$

1.7.3 Packing Efficiency in Simple Cubic Lattice

In a simple cubic lattice the atoms are located only on the corners of the cube. The particles touch each other along the edge (Fig. 1.26).

Thus, the edge length or side of the cube 'a', and the radius of each particle, r are related as

$$a = 2r$$

$$\text{The volume of the cubic unit cell} = a^3 = (2r)^3 = 8r^3$$

Since a simple cubic unit cell contains only 1 atom

$$\text{The volume of the occupied space} = \frac{4}{3}\pi r^3$$

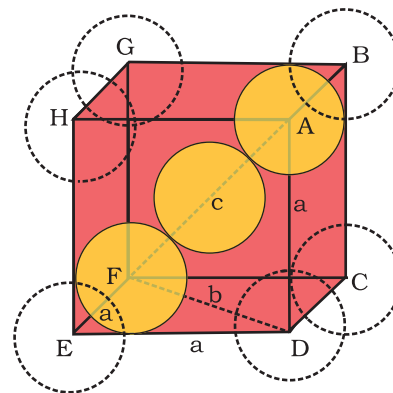
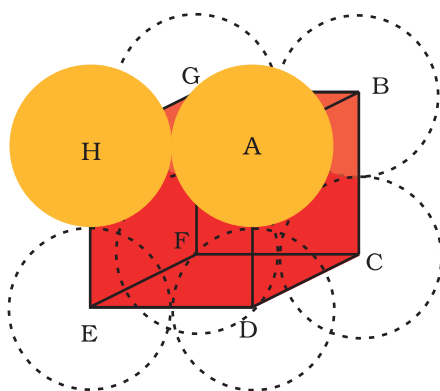


Fig. 1.25: Body-centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries).

Fig. 1.26
Simple cubic unit cell.
The spheres are in contact with each other along the edge of the cube.



∴ Packing efficiency

$$\begin{aligned}
 &= \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\% \\
 &= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100 \\
 &= 52.36\% = 52.4\%
 \end{aligned}$$

Thus, we may conclude that *ccp* and *hcp* structures have maximum packing efficiency.

1.8 Calculations Involving Unit Cell Dimensions

From the unit cell dimensions, it is possible to calculate the volume of the unit cell. Knowing the density of the metal, we can calculate the mass of the atoms in the unit cell. The determination of the mass of a single atom gives an accurate method of determination of **Avogadro constant**. Suppose, edge length of a unit cell of a cubic crystal determined by X-ray diffraction is a , d the density of the solid substance and M the molar mass. In case of cubic crystal:

$$\text{Volume of a unit cell} = a^3$$

Mass of the unit cell

$$= \text{number of atoms in unit cell} \times \text{mass of each atom} = z \times m$$

(Here z is the number of atoms present in one unit cell and m is the mass of a single atom)

Mass of an atom present in the unit cell:

$$m = \frac{M}{N_A} \quad (M \text{ is molar mass})$$

Therefore, density of the unit cell

$$\begin{aligned}
 &= \frac{\text{mass of unit cell}}{\text{volume of unit cell}} \\
 &= \frac{z \cdot m}{a^3} = \frac{z \cdot M}{a^3 \cdot N_A} \quad \text{or} \quad d = \frac{zM}{a^3 N_A}
 \end{aligned}$$

Remember, the density of the unit cell is the same as the density of the substance. The density of the solid can always be determined by other methods. Out of the five parameters (d , z , M , a and N_A), if any four are known, we can determine the fifth.

Example 1.3 An element has a body-centred cubic (*bcc*) structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm³. How many atoms are present in 208 g of the element?

Solution Volume of the unit cell = (288 pm)³
 $= (288 \times 10^{-12} \text{ m})^3 = (288 \times 10^{-10} \text{ cm})^3$
 $= 2.39 \times 10^{-23} \text{ cm}^3$

Volume of 208 g of the element

$$= \frac{\text{mass}}{\text{density}} = \frac{208\text{g}}{7.2\text{g cm}^{-3}} = 28.88\text{ cm}^3$$

Number of unit cells in this volume

$$= \frac{28.88\text{cm}^3}{2.39 \times 10^{-23}\text{ cm}^3 / \text{unit cell}} = 12.08 \times 10^{23} \text{ unit cells}$$

Since each *bcc* cubic unit cell contains 2 atoms, therefore, the total number of atoms in 208 g = 2 (atoms/unit cell) \times 12.08×10^{23} unit cells
= 24.16×10^{23} atoms

X-ray diffraction studies show that copper crystallises in an *fcc* unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3 , calculate the atomic mass of copper.

[Example 1.4](#)

In case of *fcc* lattice, number of atoms per unit cell, $z = 4$ atoms

[Solution](#)

$$\text{Therefore, } M = \frac{d N_A a^3}{z}$$

$$= \frac{8.92\text{ g cm}^{-3} \times 6.022 \times 10^{23} \text{ atoms mol}^{-1} \times (3.608 \times 10^{-8}\text{cm})^3}{4 \text{ atoms}}$$

$$= 63.1\text{ g/mol}$$

Atomic mass of copper = 63.1 u

Silver forms *ccp* lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass = 107.9 u).

[Example 1.5](#)

Since the lattice is *ccp*, the number of silver atoms per unit cell = $z = 4$

[Solution](#)

$$\text{Molar mass of silver} = 107.9\text{ g mol}^{-1} = 107.9 \times 10^{-3}\text{ kg mol}^{-1}$$

$$\text{Edge length of unit cell} = a = 408.6\text{ pm} = 408.6 \times 10^{-12}\text{ m}$$

$$\text{Density, } d = \frac{z.M}{a^3 \cdot N_A}$$

$$= \frac{4 \times (107.9 \times 10^{-3}\text{ kg mol}^{-1})}{(408.6 \times 10^{-12}\text{ m})^3 (6.022 \times 10^{23}\text{ mol}^{-1})} = 10.5 \times 10^3\text{ kg m}^{-3}$$
$$= 10.5\text{ g cm}^{-3}$$

Intext Questions

- 1.14** What is the two dimensional coordination number of a molecule in *square close-packed* layer?
- 1.15** A compound forms *hexagonal close-packed* structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

- 1.16 A compound is formed by two elements M and N. The element N forms *ccp* and atoms of M occupy $\frac{1}{3}$ rd of tetrahedral voids. What is the formula of the compound?
- 1.17 Which of the following lattices has the highest packing efficiency (i) simple cubic (ii) body-centred cubic and (iii) hexagonal close-packed lattice?
- 1.18 An element with molar mass 2.7×10^{-2} kg mol⁻¹ forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^3 kg m⁻³, what is the nature of the cubic unit cell?

1.9 Imperfections in Solids

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects. The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, *point defects* and *line defects*. **Point defects** are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the **line defects** are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called *crystal defects*. We shall confine our discussion to point defects only.

1.9.1 Types of Point Defects

Point defects can be classified into three types : (i) stoichiometric defects (ii) impurity defects and (iii) non-stoichiometric defects.

(a) Stoichiometric Defects

These are the point defects that do not disturb the stoichiometry of the solid. They are also called *intrinsic* or **thermodynamic defects**. Basically these are of two types, vacancy defects and interstitial defects.

(i) *Vacancy Defect*: When some of the lattice sites are vacant, the crystal is said to have **vacancy defect** (Fig. 1.27). This results in decrease in density of the substance. This defect can also develop when a substance is heated.

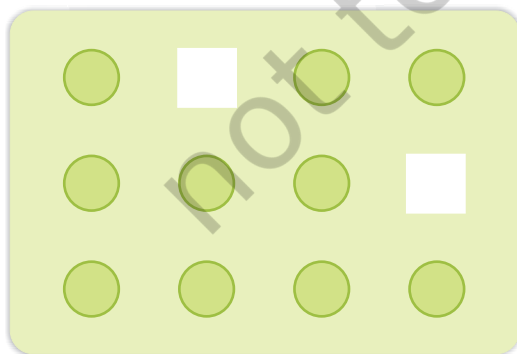


Fig. 1.27: Vacancy defects

(ii) *Interstitial Defect*: When some constituent particles (atoms or molecules) occupy an **interstitial** site, the crystal is said to have **interstitial defect** (Fig. 1.28). This defect increases the density of the substance.

Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as **Frenkel and Schottky defects**.

- (iii) **Frenkel Defect:** This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site (Fig. 1.29). It creates a *vacancy defect* at its original site and an **interstitial defect** at its new location.

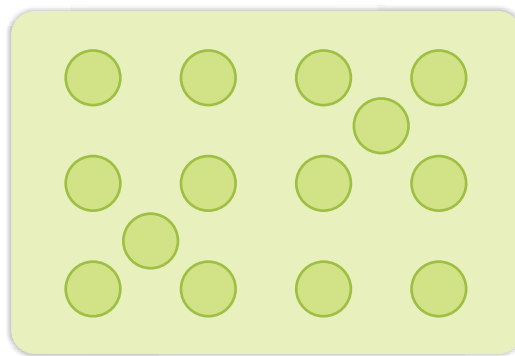


Fig. 1.28: Interstitial defects

Frenkel defect is also called **dislocation defect**.

It does not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions.

- (iv) **Schottky Defect:** It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (Fig. 1.30).

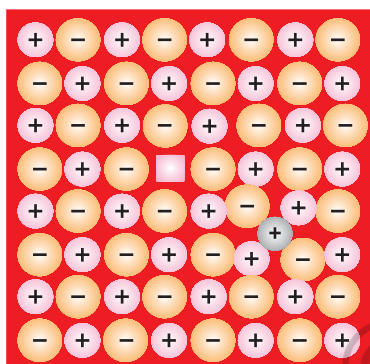


Fig. 1.29: Frenkel defects

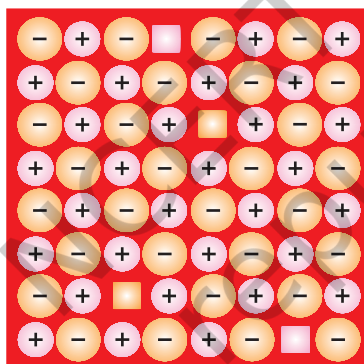


Fig. 1.30: Schottky defects

Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions. Schottky defect is shown by ionic substances in which the

cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

(b) Impurity Defects

If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} (Fig.1.31). Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Another similar example is the solid solution of $CdCl_2$ and AgCl.

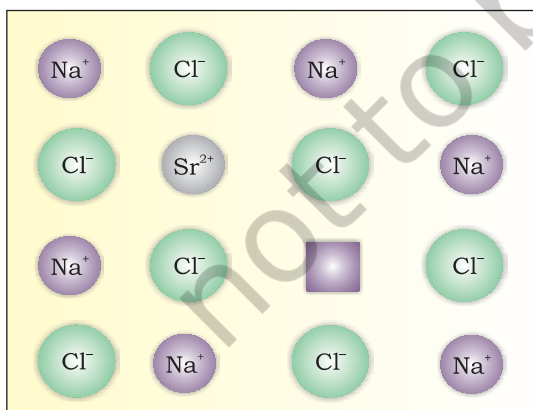


Fig. 1.31: Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}

(c) Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) Metal Excess Defect

- *Metal excess defect due to anionic vacancies:* Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl⁻ ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na⁺ ions. The released electrons diffuse into the crystal and occupy anionic sites (Fig. 1.32). As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called *F-centres* (from the German word *Farbenzenter* for colour centre). They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

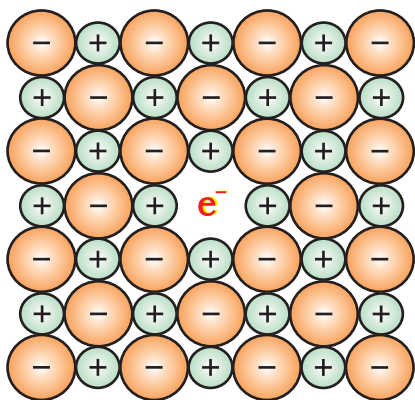
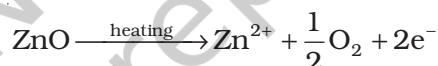


Fig. 1.32: An F-centre in a crystal

- *Metal excess defect due to the presence of extra cations at interstitial sites:* Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.



Now there is excess of zinc in the crystal and its formula becomes Zn_{1+x}O. The excess Zn²⁺ ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(ii) Metal Deficiency Defect

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of Fe_{0.95}O. It may actually range from Fe_{0.93}O to Fe_{0.96}O. In crystals of FeO some Fe²⁺ cations are missing and the loss of positive charge is made up by the presence of required number of Fe³⁺ ions.

1.10 Electrical Properties

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from 10⁻²⁰ to 10⁷ ohm⁻¹ m⁻¹. Solids can be classified into three types on the basis of their conductivities.

- (i) *Conductors:* The solids with conductivities ranging between 10⁴ to 10⁷ ohm⁻¹ m⁻¹ are called conductors. Metals have conductivities in the order of 10⁷ ohm⁻¹ m⁻¹ are good conductors.