

# Physics of Functional Materials

Hasse Fredriksson and Ulla Åkerlind

 WILEY

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# Physics of Functional Materials

# Preface

The basic idea and the initial aim of this book, *Physics of Functional Materials*, was to provide the necessary knowledge in physics for a deeper interpretation of many of the solidification and crystallization processes that are treated in the book *Materials Processing during Casting*, written for the university undergraduate level and published in March 2006. The present book fulfils this requirement and is at such a mathematical level that a basic knowledge of mathematics at university level is sufficient.

However, the book *Physics of Functional Materials* has a very wide and general character. It is by no means designed only for the purpose described above. On the contrary, this book may be useful and suitable for students in various sciences at the Master's and PhD level, who have not taken mathematics and physics as major subjects. Examples of such sciences are materials science, chemistry, metallurgy and many other scientific and technical fields where a basic knowledge of the foundations of modern physics and/or properties of materials is necessary or desirable as a basis and a background for higher studies.

Fundamental properties of different materials such as diffusion, viscosity, heat capacity and thermal and electrical conduction are examined more extensively in the present book than in available physics books of today. This book will fill a gap between the demand for and supply of such knowledge.

The atomistic view of matter requires a genuine background of modern physics from atoms via molecules to solid-state physics, primarily the modern band theory of solids, and the nature of bonds and crystal structure in solids. These topics are treated in Chapters 1–3 and are applied in later chapters, particularly in Chapter 7.

The three first chapters on modern physics are followed by applications of classical physics of material properties. Basic thermodynamics, properties of gases, including the kinetic theory of gases and the Boltzmann distributions of velocity and energy of molecules, transformation kinetics including chemical reactions and diffusion in solids, mechanical, thermal and magnetic properties of matter including ferromagnetism, are treated in Chapters 4–6.

Chapter 7 deals with thermal and electrical conduction in solids and their optical properties, particularly electrical conduction in metals and semiconductors. Polarization phenomena in crystals and optical activity in solids and liquids are discussed. In the last chapter, a short survey of the material properties of liquids is given.

*Physics of Functional Materials* contains solved examples in the text and exercises for students at the end of each chapter. Answers to all the exercises are given at the end of the book.

## Acknowledgements

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We are most grateful for financial support from The Iron Masters Association in Sweden. Finally and in particular we want to express our sincere gratitude to Karin Fredriksson and Lars Åkerlind. Without their constant support and great patience through the years this book would never have been written.

**Hasse Fredriksson**

**Ulla Åkerlind**

Stockholm, Sweden

March 2008

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# 1

## Structures of Melts and Solids

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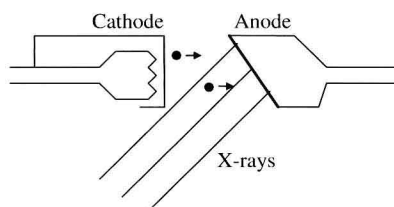
### 1.1 Introduction

Crystallization is the process of transferring a material from a liquid or a gas phase into a solid state of regular order. The three aggregation states have widely different atomic structures and properties. In order to understand crystallization processes, it is essential to have a thorough knowledge of the atomic structure of both the melt or gas and of the new solid phase.

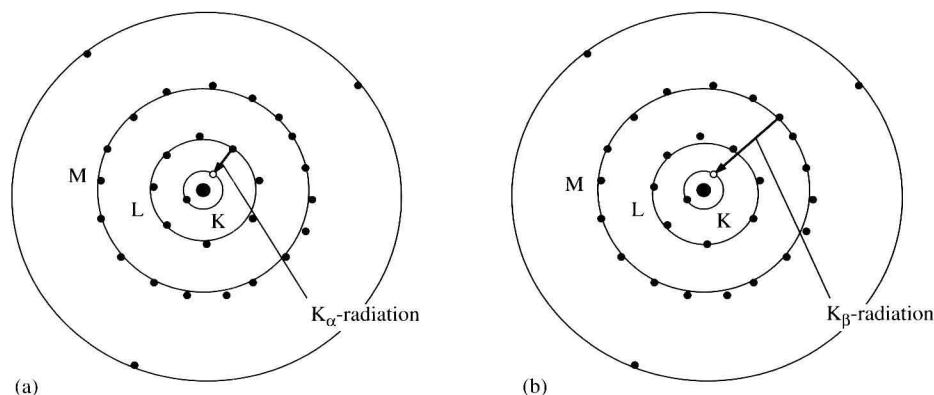
In this chapter, the atomic structures of melts and various solid phases will be examined. The structures of pure elements and of alloys and chemical compounds will be discussed. The chapter starts with a short introduction to X-ray analysis, which is a very important tool for investigating atomic structures.

## 1.2 X-ray Analysis

The energetic X-radiation was discovered in 1901 by the German physicist W. K. Roentgen. The source was an evacuated tube where electrons, accelerated by an electric field, hit a metal target (Figure 1.1). When the electrons suddenly lost their kinetic energy, continuous X-ray radiation was emitted together with a few discrete X-ray wavelengths characteristic of the target atoms (Figure 1.2).



**Figure 1.1** The principle of an X-ray tube. Electrons are accelerated in a strong electric field between an anode and an indirectly heated cathode, hit the anode and lose their kinetic energy successively during numerous collisions. Their kinetic energies are transformed into continuous X-radiation. The whole equipment is included in a highly evacuated tube.



**Figure 1.2** (a) The origin of the characteristic X-radiation: When a high-speed electron hits an electron in an inner shell of a target atom, both electrons leave the atom and a vacancy is left in its inner shell. The rest of the process is described in (b). (b) The vacancy is filled by an electron from an outer shell of the atom and an X-ray photon with a wavelength characteristic for the anode material is emitted. There are several alternative wavelengths, depending on the shell from which the jumping electron emanates. The X-ray lines  $K_{\alpha}$  and  $K_{\beta}$  shown in (a) and (b) appear simultaneously as numerous such processes occur at the same time.

X-ray analysis of materials has been used since the beginning of the 20th century to investigate the construction and structure of materials. Measurements, calculations and interpretations of the results were made by hand for many decades. Today, completely automatic computer-based X-ray spectrometers, which perform both the experiments and the analysis of the results, are commercially available. However, it is necessary to understand the principles of their function, which are described briefly below.

### 1.2.1 Methods of X-ray Examination of Solid Materials

A very important method to provide information on the structure of materials is X-ray diffraction measurements. In solid crystalline materials, the diffraction pattern is caused by the atoms in the crystal lattice (Figure 1.3). If a crystal surface is

exposed to parallel monoenergetic X-radiation with a known angle of incidence, Bragg's law gives the condition for coherence (in phase) of the diffracted waves:

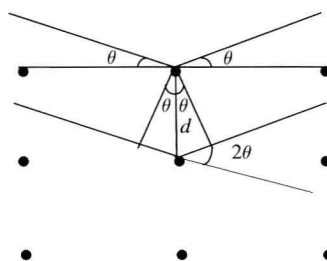


Figure 1.3 X-ray diffraction in a crystal.

$$2d \sin \theta = p\lambda \quad (1.1)$$

where

$d$  = distance between the atomic planes

$\theta$  = angle between the incident ray and the atomic plane

$\lambda$  = wavelength of the monoenergetic X-ray

$p$  = an integer  $\neq 0$ .

If  $\lambda$  is known and  $\theta$  can be measured, Bragg's law can be used to determine the distance  $d$  between the atomic planes in the crystal lattice.

An X-ray crystallographic examination of a single crystal will in principle be performed as described in Figure 1.4.

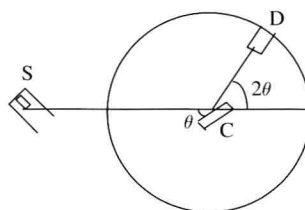


Figure 1.4 The principle of an X-ray spectrometer.

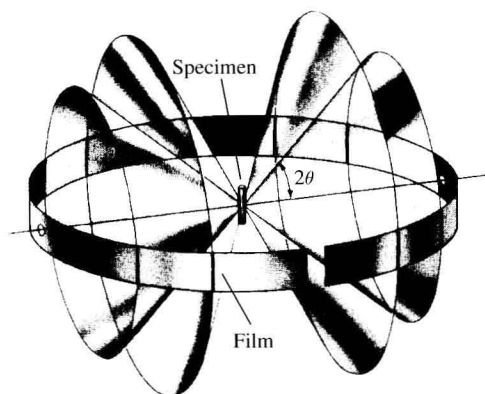
The radiation from an X-ray tube S falls on a turnable single crystal C. The angle between the incident and diffracted rays is  $2\theta$ . The crystal is tilted stepwise. For every angle of incidence  $\theta$  the detector D is placed at the corresponding angle of diffraction  $2\theta$  and the intensity of the diffracted radiation is measured. In this way, the intensity as a function of  $\theta$  is obtained and the whole X-ray spectrum of the solid material can be obtained.

The method described above is time consuming. If the single crystal is replaced with a powder compound, consisting of small crystals of the solid material, it is no longer necessary to tilt the specimen to find high-intensity angles. All possible crystallographic directions are present in the powder compound.

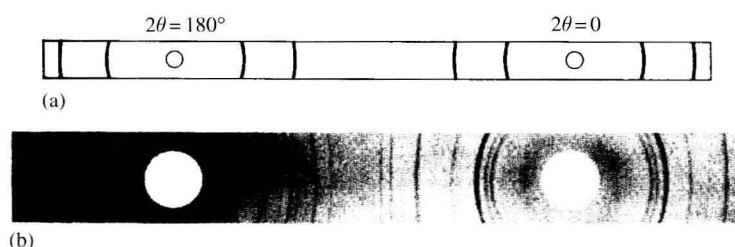
In practice, the Debye-Scherrer method of X-ray crystallographic investigations on metallic or other crystalline materials is the most common one. The principle is the same as that described in Figure 1.4. The apparatus used is shown in Figure 1.5. The detector consists of a cylinder-shaped photographic film. The monoenergetic radiation from the X-ray tube passes through a narrow vertical slit and then the specimen, a thin powder compound, placed at the centre of the cylinder.

The diffracted radiation with the highest intensity has the angle of scattering  $2\theta$  (Figure 1.7). The diffracted radiation has a cone-shaped form. The radiation is registered on the photographic film as four slightly curved lines. These lines are characteristic of the solid material and will appear symmetrically around the direct beam when the film is developed. Figure 1.6b shows the appearance of the diffraction pattern of zinc.

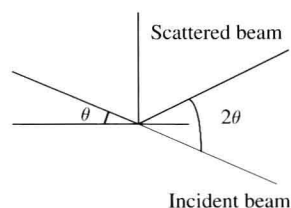
The positions of the lines are measured. The pattern on the film is analysed and the various distances between the atomic planes in the crystals are calculated. In this way, the structure of the solid material can be derived.



**Figure 1.5** X-ray examination according to the Debye–Sherrer method. Reproduced with permission from B. D. Cullity, *Elements of X-Ray Diffraction*, © Addison-Wesley Publishing Company, Inc. (now under Pearson Education).



**Figure 1.6** (a) The appearance of a Debye–Sherrer pattern. (b) Debye–Sherrer pattern of zinc. Reproduced with permission from B. D. Cullity, *Elements of X-Ray Diffraction*, © Addison-Wesley Publishing Company, Inc. (now under Pearson Education).



**Figure 1.7** The angle  $2\theta$  of scattering is the angle between the incident and scattered beams.

### 1.2.2 X-ray Examination and Structures of Metal Melts

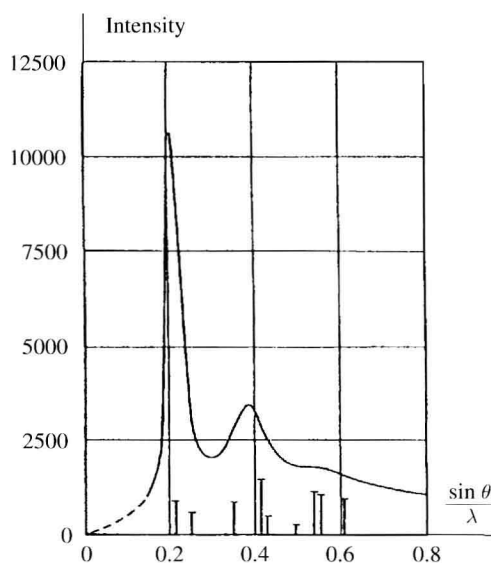
By replacing the powder compound by a metal melt at constant temperature, the corresponding Debye–Sherrer measurements can be made on a liquid metal.

The results deviate very much from those obtained for crystalline powders. Instead of a few sharp, well-defined lines one obtains several wide, unsharp maxima and minima. The resulting patterns can be analysed and fairly detailed information on the structures of the melts can be obtained. This is illustrated below by two examples.

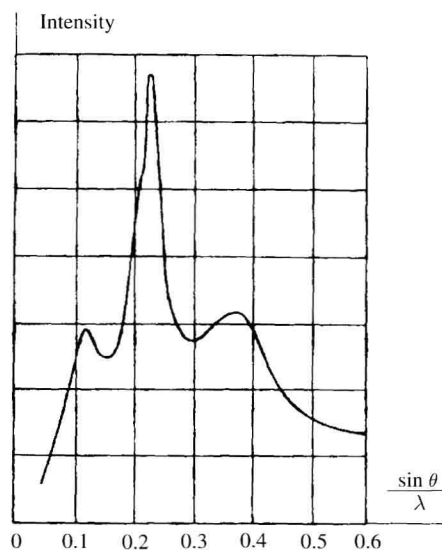
#### Structures of Pure Metal Melts

The X-ray pattern of liquid gold at  $1100^\circ\text{C}$  is shown in Figure 1.8. The intensity of the diffracted radiation is plotted versus  $\sin \theta/\lambda$ , where  $\theta$  is half the scattering angle and  $\lambda$  is the X-ray wavelength. In Figure 1.8, the main peak is found to the left and a series of subsidiary peaks to the right.

The short vertical lines in Figure 1.8 show the corresponding X-ray pattern of crystalline gold. The intensities of the diffracted waves are indicated by the heights of the lines. There is a clear correspondence between the positions along the horizontal axis of the main peaks of liquid gold and the main lines of crystalline gold.



**Figure 1.8** The intensity of scattered X-radiation as a function of  $\sin \theta / \lambda$ . The curve originates from scattering in liquid gold at  $1100^{\circ}\text{C}$ . The vertical lines originate from scattering in crystalline gold. Reproduced with permission from N. S. Gingrich, The diffraction of X-rays by liquid elements, *Rev. Mod. Phys.* **15**, 90–100. © 1943 The American Physical Society.



**Figure 1.9** The intensity of scattered X-radiation as a function of  $\sin \theta / \lambda$ . The curve originates from scattering in liquid zinc at  $460^{\circ}\text{C}$ . Reproduced with permission from N. S. Gingrich, The diffraction of X-rays by liquid elements, *Rev. Mod. Phys.* **15**, 90–100. © 1943 The American Physical Society.

An X-ray intensity spectrum such as those in Figures 1.8 and 1.9 supply the necessary basis to obtain information concerning the structure of a liquid or solid metal. However, to interpret an intensity diagram and obtain information from it, such as type of structure and atomic distances, it is necessary to transform the X-ray spectrum into another type of diagram. The background of this is given in next section.

### From X-ray Plots to Atomic Distribution Diagrams

We consider the distribution of atoms around an arbitrary atom anywhere in the liquid and choose this atom as the origin.

The probability of finding another atom in a unit volume at a distance  $r$  from the origin is called  $w_r$ . The average probability of finding another atom in any randomly selected unit volume is called  $w_0$ .

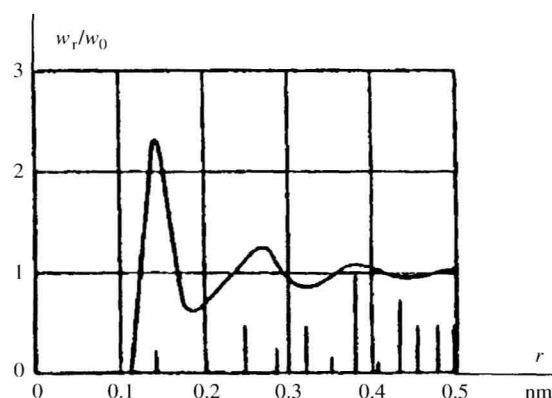
The probability of finding the next atom within the volume element  $dV$  at a distance  $r$  from the origin atom equals the product of  $dV$  and  $w_r$ . If we choose a spherical shell with radius  $r$  and thickness  $dr$  as volume element, the probability  $dW_r$  of finding another atom within the spherical shell will be given by the expression

$$dW_r = w_r dV = w_r 4\pi r^2 dr \quad (1.2)$$

It is possible to derive the probability  $w_r$  as a function of the X-ray intensity theoretically. When this function is known, it is possible to draw *atomic distribution diagrams* on the basis of X-ray intensity diagrams such as those in Figures 1.8 and 1.9. By plotting  $4\pi r^2 w_r$  as a function of the radius  $r$  we obtain the atomic distribution diagram of the metal melt in question.

The ratio  $w_r/w_0$  is plotted as a function of  $r$  for liquid and solid crystalline gold in Figure 1.10. It shows the relative probability of finding gold atoms in a unit volume at various places and distances from the origin. In analogy with Figure 1.8, the vertical lines represent the values for solid gold. Their heights, relative to the right-hand scale, give the number of atoms per unit volume at the indicated distance.

At infinity, the probability  $w_r$  equals the probability  $w_0$  and the ratio equals 1.



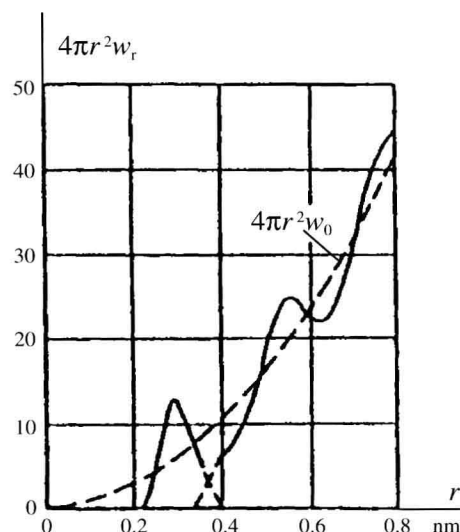
**Figure 1.10** The relative probability  $w_r/w_0$  of finding an atom in a unit volume in liquid gold at a distance  $r$  from the origin is a function of  $r$ . The vertical peaks correspond to crystalline gold. Reproduced with permission from F. D. Richardson, *Physical Chemistry of Melts in Metallurgy*, Vol. 1. © 1974 Academic Press Inc. (London) Ltd (now by Elsevier).

### Interpretation of Atomic Distribution Diagrams. Nearest Neighbour Distances, Coordination Shells and Coordination Numbers

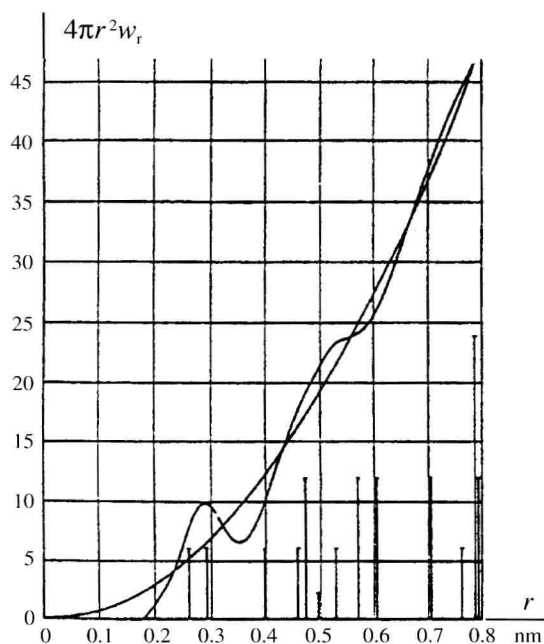
Figures 1.11 and 1.12 are the atomic distribution diagrams for gold and zinc, corresponding to Figures 1.8 and 1.9, respectively. Each curve can be regarded as a product of two functions of  $r$ , the probability  $w_r$  (Figure 1.10) and  $4\pi r^2$ , which is a parabola. Both figures show the same characteristics.

The first peak of the atomic distribution function gives the most probable distance between nearest neighbour atoms and is called the *nearest neighbour distance*. The peak appears close to the same position as the nearest neighbour distance in the solid crystalline metal.

The subsiding peaks at larger distances also show some correspondence with peaks in the solid metals but this decreases with increasing distance. A very likely explanation is that the melt still possesses some of its short-range order of the solid crystal but has lost its long-range regularity.



**Figure 1.11** Atomic distribution diagrams of liquid gold at 1100°C and of gold crystals. The probability of finding an atom within a spherical shell with the radius  $r$  is a function of  $r$ . The curve corresponds to liquid gold. Reproduced with permission from F. D. Richardson, *Physical Chemistry of Melts in Metallurgy*, Vol. 1. © 1974 Academic Press Inc. (London) Ltd (now by Elsevier).



**Figure 1.12** Atomic distribution diagrams of liquid zinc at 460°C and of zinc crystals. The probability of finding an atom within a spherical shell with the radius  $r$  is a function of  $r$ . The curve corresponds to liquid zinc and the vertical peaks to crystalline zinc. Reproduced with permission from F. D. Richardson, *Physical Chemistry of Melts in Metallurgy*, Vol. 1. © 1974 Academic Press Inc. (London) Ltd (now by Elsevier).

The curves in Figures 1.11 and 1.12 drop steeply to the left and become zero for a characteristic small  $r$  value in both cases. This value corresponds to the nearest possible spacing between a pair of atoms owing to their mutual resistance to interpenetration. The characteristic distance is 0.22 nm for liquid gold.

The vertical peaks for solid gold and zinc are interpreted as *coordination shells* in the crystal structure. The maximum number of atoms, that can be included within a coordination shell is called the *coordination number* of the shell. These atomic concepts can be applied to both liquids and solids.

From diffraction data, it is possible to derive values of the coordination numbers for the first and sometimes also for the second coordination shell. This can be done graphically in the following way. To explain the method, we concentrate on the atomic distribution diagram for gold.

We consider the number of atoms in a spherical shell between radius  $r$  and  $r + \Delta r$ . It equals  $w_r \times 4\pi r^2 \Delta r$  and is called *the radial distribution function*.

The radial distribution function  $4\pi r^2 w_r$  for liquid gold is plotted in Figure 1.11 as a function of  $r$  together with the function  $4\pi r^2 w_0$ . The latter curve represents the number of atoms in the shell volume  $4\pi r^2 \Delta r$  in a fictional space with equally distributed atoms, i.e. no coordination shells. The area under the parabola curve represents the total number of atoms within a sphere with radius  $r$ .

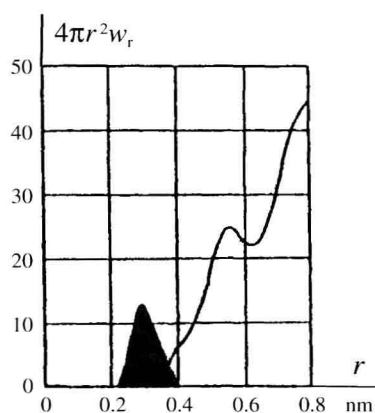
The real curve for liquid gold in Figure 1.11 has the same type of peaks as the corresponding curve in Figure 1.10. The liquid gold curve in Figure 1.11 can be interpreted as the sum of a series of separate curves, which arise from each coordination shell and start from the horizontal axis as indicated by dotted lines. These extrapolations can be done fairly accurately for the first and sometimes also for the second peak. The area under each peak gives approximately the number of atoms in the coordination shell:

$$\text{Number of atoms in coordination shell} = \int_{r_0}^{r_{\min}} 4\pi r^2 w_r dr \quad (1.3)$$

where  $r_0$  and  $r_{\min}$  are the limiting  $r$  values of the peak.

Estimations of the area under the first peak in Figure 1.13 indicate that there are about 8.5 atoms in the first coordination shell of liquid gold. The values for the second peak are too uncertain for any worthwhile calculations.

Increasing temperature causes the amplitudes of vibration of the atoms to increase and the fluctuations around their equilibrium positions become more violent. This affects the diffraction patterns of liquid metals and the peaks of the curves in Figures 1.11 and 1.12 become lower and wider when the temperature increases.



**Figure 1.13** Radial distribution function of liquid gold plotted versus the distance  $r$  from the origin. Reproduced with permission from F. D. Richardson, *Physical Chemistry of Melts in Metallurgy*, Vol. 1. © 1974 Academic Press Inc. (London) Ltd (now by Elsevier).

### Example 1.1

The atomic distribution diagram of zinc is given in Figure 1.12 on page 7. Use this diagram to answer the following questions:

- Does the smooth parabola have any physical significance?
- What is the smallest possible distance between two atoms in liquid zinc at  $460^\circ\text{C}$ ?
- What is the nearest neighbour distance in crystalline zinc?
- What is the reason for claiming that there is a short-range order in molten zinc?

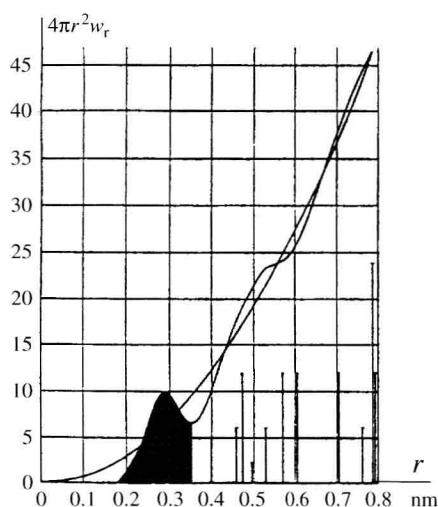


- (e) What is the coordination number in the first shell of solid crystalline zinc?  
 (f) What is the coordination number in the first shell of liquid zinc at 460°C?

**Solution:**

- (a) The smooth curve represents the number of atoms in a spherical shell at a distance  $r$  from the origin atom provided that the probability of finding an atom in unit volume is equal everywhere. This is not the case and therefore the answer to the question is 'no'.  
 (b) The distance is found at the intersection of the curve and the  $r$  axis.  $r = 0.18$  nm.  
 (c) The nearest neighbour distance is the  $r$  value of the first 'crystalline' peak.  $r = 0.26$  nm.  
 (d) The  $r$  values of the first two 'crystalline' peaks are very close to the most probable distance in molten zinc, the  $r$  value of the first top.  
 (e) The coordination number of the first shell is the sum of the number of the atoms in the first two sub-shells, i.e.  $6 + 6 = 12$ .  
 (f) The probability of finding an atom within a spherical shell with the radius  $r$  can be written as

$$dW_r = 4\pi r^2 w_r dr \quad (1')$$



We obtain the number of atoms by integration of the function (1'):

$$W_r = \int_{r_0}^{r_{\min}} 4\pi r^2 w_r dr$$

where  $r_0 = 0.18$  nm and  $r_{\min}$  equals the  $r$  value of the first minimum of the curve. It is 0.36 nm as shown in the figure.

As we have no analytical function of  $w_r$ , we have to integrate graphically. The dark area under the curve represents the demanded number of atoms. Its area is calculated as 11.

**Answer:**

- (a) No.  
 (b)  $r = 0.18$  nm.  
 (c)  $r = 0.26$  nm.  
 (d) The  $r$  values of the first two 'crystalline' peaks are very close to the most probable distance in molten zinc.  
 (e) 12.  
 (f) 11.