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# DEFECTS IN SOLIDS

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Richard J. D. Tilley

Emeritus Professor, University of Cardiff, Wales



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*To Professor F. S. Stone  
who engendered a unique research group spirit  
and my contemporaries in the University of Bristol,  
who augmented it.*





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## **PREFACE**

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During the course of the last century, it was realized that many properties of solids are controlled not so much by the chemical composition or the chemical bonds linking the constituent atoms in the crystal but by faults or defects in the structure. Over the course of time the subject has, if anything, increased in importance. Indeed, there is no aspect of the physics and chemistry of solids that is not decisively influenced by the defects that occur in the material under consideration. The whole of the modern silicon-based computer industry is founded upon the introduction of precise amounts of specific impurities into extremely pure crystals. Solid-state lasers function because of the activity of impurity atoms. Battery science, solid oxide fuel cells, hydrogen storage, displays, all rest upon an understanding of defects in the solid matrix.

As the way in which defects modify the properties of a solid has been gradually understood, the concept of a defect has undergone considerable evolution. The earliest and perhaps simplest concept of a defect in a solid was that of a wrong atom, or impurity, in place of a normal atom in a crystal—a so-called point defect. Not long after the recognition of point defects, the concept of linear defects, dislocations, was invoked to explain a number of diverse features including the mechanical properties of metals and the growth of crystals. In recent years it has become apparent that defect interactions, aggregation, or clustering is of vital importance.

The advance in understanding of defects has been made hand in hand with the spectacular development of sophisticated experimental techniques. The initial breakthrough was in X-ray diffraction—a technique that still remains as the foundation of most studies. A further change came with the development of transmission electron microscopy that was able, for the first time, to produce images of defects at an atomic scale of resolution. Since then, advances in computing techniques, together with the availability of powerful graphics, have thrown quite new light on the defect structure of materials.

Besides the multiplicity of defects that can be envisaged, there is also a wide range of solid phases within which such defects can reside. The differences between an alloy, a metallic sulfide, a crystalline fluoride, a silicate glass, or an amorphous polymer are significant. Moreover, developments in crystal growth and the production of nanoparticles have changed the perspective of earlier studies, which were usually made on polycrystalline solids, sometimes with uncertain degrees of impurity present.

All of these changes have meant that the view of defects in solids has changed considerably over the last 20 years or so. This book is aimed at presenting an

overview of this information. However, the topic encompasses a huge subject area, and selection has been inevitable. Moreover, courses about defects in solids, whether to undergraduate or postgraduate students in chemistry, physics, geology, materials science, or engineering, are usually constrained to a relatively small part of the curriculum. Nevertheless, the material included in this book has been chosen so that not only basics are covered but also aspects of recent research where exciting frontiers lie. Unfortunately, the influence of defects upon mechanical properties is mostly excluded, and the important area of surfaces and surface defects is only mentioned in passing. Similarly, the area of studies prefixed by nano- has been bypassed. This is because the literature here is growing at an enormous rate, and time was not available to sift through this mountain of data. Although these omissions are regrettable, they leave scope for future volumes in this series. Finally, it must be mentioned that most emphasis has been placed upon principles, leaving little space for description of important experimental details. This is a pity, but within the constraints of time and space, became inevitable. Again, a future volume could correct this shortcoming.

The first four chapters introduce basic concepts that are developed to build up a framework for understanding defect chemistry and physics. Thereafter, chapters focus rather more on properties related to applications. Chapter 5 describes diffusion in solids; Chapter 6, ionic conductivity; Chapters 7 and 8 the important topics of electronic conductivity, both intrinsic (Chapter 7) and extrinsic (Chapter 8). The final chapter gives a selected account of magnetic and optical defects.

To assist in understanding, each chapter has been prefaced with three “introductory questions” that focus the reader upon some of the important points to be raised in the following text. These are answered at the end of each chapter. In addition, end-of-chapter questions aid understanding of the preceding material. The first set of these consists of multiple choice questions—a “quick quiz,” to test knowledge of terms and principles. This is followed by a number of more traditional problems and calculations to build skills and understanding in more depth. In addition, supplementary material covering the fundamentals of relevant topics such as crystallography and band theory are included so that, in the first instance, a reader will not have to look elsewhere for this information.

Each chapter contains a short list of additional sources that expand or give a different perspective on the material in the preceding chapter. Most of these are books or original scientific literature, and only a few web sources are listed. The Internet provides a data bank of considerable power but has two drawbacks: It is easy to become swamped by detail (often a simple search will throw up a million or more allegedly relevant pages), and much of the information located has an ephemeral nature. Rather than list a large number of sites, the reader is encouraged to use a search engine and keywords such as “magnetic defects,” which will open an alternative perspective on the subject to that presented in this book.

I have been particularly helped in the compilation of this book by family, friends, and colleagues. Professor R. B. King first suggested the project, and Drs. E. E. M. Tyler, G. J. Tilley, and R. D. Tilley made suggestions about contents and scope. Professor F. S. Stone offered encouragement and kindly offered to read sections in

draft form, resulting in invaluable advice and comment that added substantially to the clarity and balance. Mr. A. Coughlin was constantly encouraging and gave assistance when mathematical discussions of topics such as polynomials or random walks became opaque and provided valued help into the proofs. The staff of the Trevithick Library, University of Cardiff, have been helpful at all times and continually located obscure references. The staff at Wiley, gave constant advice, help, and encouragement. Dr. John Hutchison, University of Oxford, provided stunning micrographs for which I am greatly indebted. Finally, my gratitude to my wife Anne cannot be understated. Her tolerance of my neglect and her continued encouragement has allowed this project to reach a conclusion.

Comments and queries will be gratefully received and can be sent to [tilleyrj@cardiff.ac.uk](mailto:tilleyrj@cardiff.ac.uk) or [rjdtalley@yahoo.co.uk](mailto:rjdtalley@yahoo.co.uk).

R. J. D. TILLEY



# Point Defects

*What is a point defect?*

*What is the “effective charge” on a defect?*

*What is an antisite defect?*

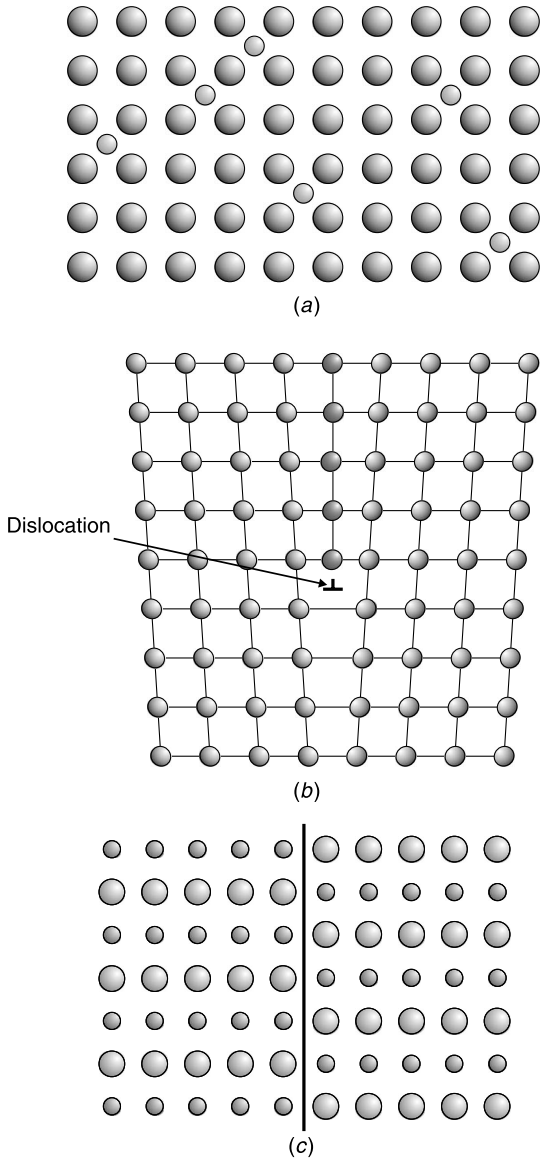
## 1.1 INTRODUCTION

Defects play an important part in both the chemical and physical behavior of solids, and much of modern science and technology centers upon the exploitation or suppression of the properties that defects confer upon a solid. Batteries, fuel cells, displays, data storage, and computer memories all directly utilize, or have evolved from, an understanding and manipulation of defects in inorganic materials. This technology has been developed over some 80–100 years and started with the simplest concepts. However, as the effect of defects upon the properties of the solid gradually became appreciated, the concept of a defect has undergone considerable evolution. The simplest notion of a defect in a solid was the idea of a mistake such as a missing atom or an impurity in place of a normal atom. These structurally simple defects are called point defects. Not long after the recognition of point defects, the concept of more complex structural defects, such as linear defects termed dislocations, was invoked to explain the mechanical properties of metals. In the same period it became apparent that planar defects, including surfaces and grain boundaries, and volume defects such as rods, tubes, or precipitates, have important roles to play in influencing the physical and chemical properties of a solid.

Defects can thus be arranged in a dimensional hierarchy (Fig. 1.1*a–1.1d*):

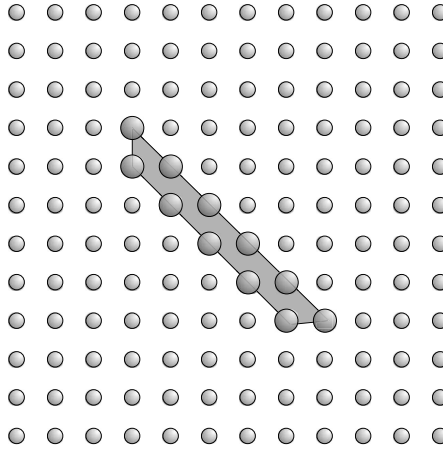
1. Zero-dimensional defects—point defects
2. One-dimensional (linear) defects—dislocations
3. Two-dimensional (planar) defects—external and internal surfaces
4. Three-dimensional (volume) defects—point defect clusters, voids, precipitates.

This and the following chapter are concerned with point defects.

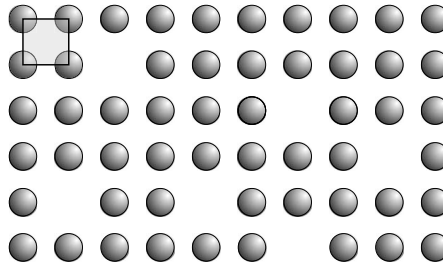


**Figure 1.1** Defects in crystalline solids: (a) point defects (interstitials); (b) a linear defect (edge dislocation); (c) a planar defect (antiphase boundary); (d) a volume defect (precipitate); (e) unit cell (filled) of a structure containing point defects (vacancies); and (f) unit cell (filled) of a defect-free structure containing “ordered vacancies.”

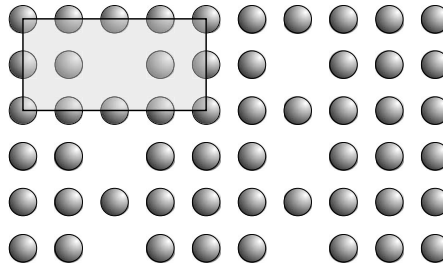
In addition to the defects listed above, which may be termed structural defects, there are also electronic defects. The first of these are electrons that are in excess of those required for chemical bonding and that, in certain circumstances, constitute charged defects that can carry current. In addition, current in some materials is carried by particles



(d)



(e)



(f)

**Figure 1.1** (Continued).

that behave rather like positive electrons, and these form the second type of electronic defect.<sup>1</sup> They are called electron holes, positive holes, or more often just holes.

Besides the multiplicity of defects that can be envisaged, there is a wide range of host solid phases within which such defects can reside. The differences between an alloy, a metallic sulfide, a crystalline fluoride, or a silicate glass are significant from

<sup>1</sup>These are not the positive equivalent of an electron, a positron, because such a particle would be eliminated instantaneously by combination with an ordinary electron, but are virtual particles equivalent to the absence of an electron. They can be considered to be analogs of a vacancy, which is the absence of an atom.

both a chemical or physical viewpoint. By default, defects have come to be associated with crystalline solids because a crystal has a regular repetition of atoms throughout its volume.<sup>2</sup> A disturbance of this regularity then constitutes the defect (Fig. 1.1a–1.1d). In this sense, the nature of a defect in, for example, a glass or amorphous polymer, is more difficult to picture.

When circumstances permit, defects can order. This may happen at low temperatures, for example, when defect interactions overcome the disordering effect due to temperature. From a diffraction point of view the ordered sample no longer contains defects, as the characteristic signs disappear. For example, in X-ray analysis broadened diffraction spots and diffuse scattering, both characteristic of disordered crystals, disappear, to be replaced by additional sharp reflections. In such cases the defects are incorporated or assimilated into the crystal structure and so effectively vanish. The original unit cell of the defect-containing phase is replaced by a new unit cell in which the original “defects” are now integral components of the structure (Fig. 1.1e and 1.1f).

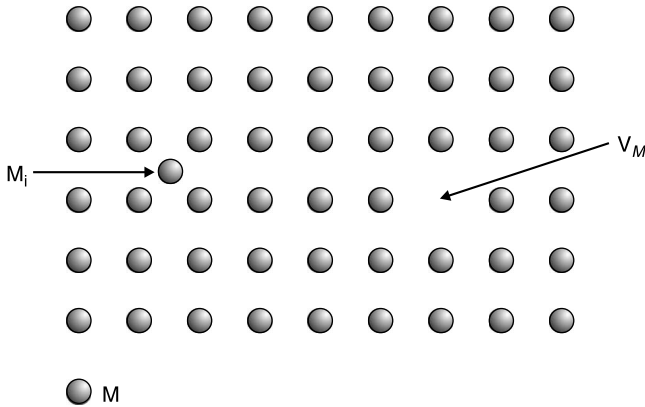
## 1.2 POINT AND ELECTRONIC DEFECTS IN CRYSTALLINE SOLIDS

The simplest localized defect in a crystal is a mistake at a single atom site in a pure monatomic crystal, such as silicon or iron. Such a defect is called a point defect. Two different types of simple point defect can occur in a pure crystal of an element, M. An atom can be imagined to be absent from a normally occupied position, to leave a vacancy, given the symbol  $V_M$  (Fig. 1.2). This may occur, for instance, during crystal growth. A second defect can also be envisaged; namely an extra atom incorporated into the structure, again, say, during crystallization. This extra atom is forced to take up a position in the crystal that is not a normally occupied site: it is called an interstitial site, and the atom is called an interstitial atom (or more often simply an interstitial), given the symbol  $M_i$ , (Fig. 1.2). If it is necessary to stress that the interstitial atom is the same as the normal atoms in the structure, it is called a self-interstitial atom.

The various point defects present in a crystal as grown, for example, vacancies, interstitials, excess electrons, holes, and other arrangements, are called *native defects*. These native defects can arise in several ways. They can be introduced during crystal growth, as mentioned above, especially if this is rapid and crystallization is far removed from equilibrium. Defects can also form after the crystal is developed if the crystal is subjected to irradiation by high-energy particles or other forms of radiation. Defects that result from such processes are called *induced defects*. When a pure crystal is heated at a moderate temperature for a long period, a process called annealing, the number of native defects will gradually change. However, no matter how long the sample is annealed, a population of point defects will always remain, even in the purest crystal. These point defects are in thermodynamic equilibrium

<sup>2</sup>An introduction to crystal structures and nomenclature is given in the Supplementary Material Section S1.





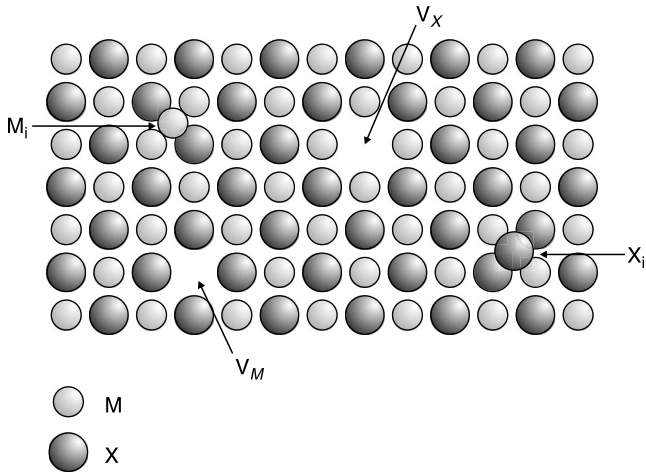
**Figure 1.2** Point defects in a pure monatomic crystal of an element  $M$ , a vacancy,  $V_M$ , and a self-interstitial,  $M_i$ .

(Chapter 2) and cannot be eliminated from the solid. They are called *intrinsic* point defects. This residual population is also temperature dependent, and, as treated later (Chapter 2), heating at progressively higher temperature increases the number of defects present.

As well as these intrinsic structural defect populations, electronic defects (excess electrons and holes) will always be found. These are also intrinsic defects and are present even in the purest material. When the equilibria among defects are considered, it is necessary to include both structural and electronic defects.

Turning to pure *compounds*, such as  $\text{CaO}$ ,  $\text{MgAl}_2\text{O}_4$ , or  $\text{FeS}$ , the same intrinsic defects as described above can occur, but in these cases there is more than one set of atoms that can be affected. For example, in a crystal of formula  $\text{MX}$ , vacancies might occur on metal atom positions, written  $V_M$ , or on nonmetal atom positions, given the symbol  $V_X$ , or both. Similarly, it is possible to imagine that interstitial metal atoms, written  $M_i$ , or nonmetal atoms, written  $X_i$ , might occur (Fig. 1.3). The different sets of atom types are frequently called a sublattice, so that one might speak of vacancies on the metal sublattice or on the nonmetal sublattice.

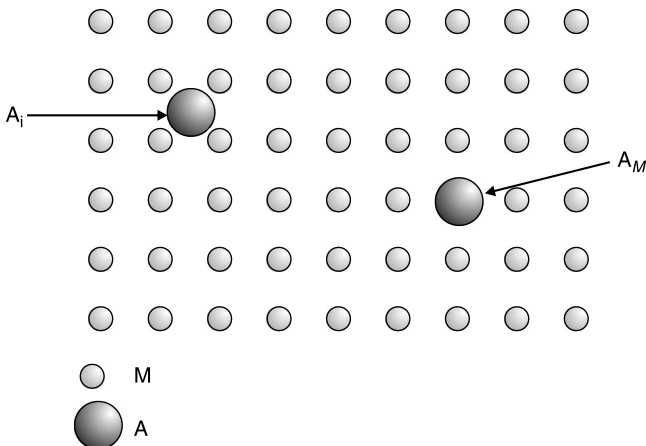
No material is completely pure, and some foreign atoms will invariably be present. If these are undesirable or accidental, they are termed impurities, but if they have been added deliberately, to change the properties of the material on purpose, they are called dopant atoms. Impurities can form point defects when present in low concentrations, the simplest of which are analogs of vacancies and interstitials. For example, an impurity atom  $A$  in a crystal of a metal  $M$  can occupy atom sites normally occupied by the parent atoms, to form substitutional point defects, written  $A_M$ , or can occupy interstitial sites, to form interstitial point defects, written  $A_i$  (Fig. 1.4). The doping of aluminum into silicon creates substitutional point defects as the aluminum atoms occupy sites normally filled by silicon atoms. In compounds, the impurities can affect one or all sublattices. For instance, natural sodium chloride often contains



**Figure 1.3** Point defects in a crystal of a pure compound,  $MX$ ,  $V_M$ , a metal vacancy;  $V_X$  a nonmetal vacancy;  $M_i$ , a metal (self-)interstitial; and  $X_i$  a nonmetal (self-)interstitial.

potassium impurities as substitutional defects on sites normally occupied by sodium ions, written  $K_{Na}$ , that is, the impurities are associated with the metal sublattice. Impurities are called extrinsic defects. In principle, extrinsic defects can be removed by careful processing, but in practice this is very difficult to achieve completely.

Impurities can carry a charge relative to the host structure, as, for example, with a  $Ca^{2+}$  ion substituted on a  $Na^+$  site in  $NaCl$  or  $F^-$  substituted for  $O^{2-}$  in  $CaO$ . In essence, this means that the impurity carries a different chemical valence, that is,



**Figure 1.4** Impurity or dopant (A) point defects in a crystal of material M, substitutional,  $A_M$ ; interstitial,  $A_i$ .

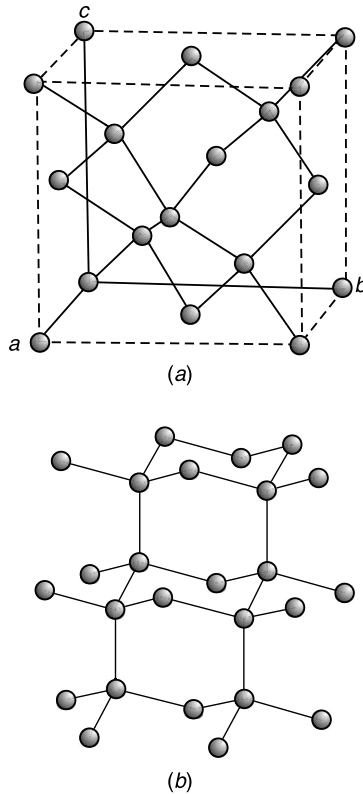
it comes from a different group of the periodic table than the host atoms. Deliberate introduction of such impurities is called aliovalent or altrivalent doping. The introduction of charged impurities will upset the charge neutrality of the solid, and this must be balanced in some way so as to restore the electronic neutrality of the crystal. One way in which this compensation can be achieved is by the incorporation of other vacancies or interstitial atoms that carry a balancing charge. The substitution of a  $\text{Ca}^{2+}$  ion for  $\text{Na}^+$  in  $\text{NaCl}$  can be balanced, for example, by the introduction at the same time, of a sodium ion vacancy,  $V_{\text{Na}}$ , at the same time. This mechanism is called ionic compensation, structural compensation, or less often self-compensation. However, compensation can also take place electronically by the introduction of appropriate numbers of electrons or holes. For example, the substitution of  $\text{F}^-$  for  $\text{O}^{2-}$  in  $\text{CaO}$  could be balanced by the introduction of an equivalent number of electrons, one per added  $\text{F}^-$ . Impurities that are compensated by excess electrons in this way are called donors or donor impurities, while those that are compensated by addition of holes are called acceptors or acceptor impurities. One consequence of these alternatives is that the electrons and holes present in the solid must be included in the overall accounting system used for assessing the defects present in a solid.

The importance of point defects in a crystal cannot be overstated. They can change the physical properties of a solid significantly. To introduce the range of changes possible, Sections 1.3–1.6 outline some of the physical properties that are influenced in this way.

### 1.3 ELECTRONIC PROPERTIES: DOPED SILICON AND GERMANIUM AS EXAMPLES

Silicon, Si, lies at the heart of most current electronic devices. Both silicon and the similar semiconductor element germanium, Ge, crystallize with the diamond structure (Fig. 1.5). In this structure each atom is surrounded by four others arranged at the corners of a tetrahedron. Each atom has four outer electrons available for chemical bonding, and these are completely taken up by creating a network of tetrahedrally oriented  $sp^3$ -hybrid bonds. Although pure silicon and germanium are intrinsic semiconductors, these properties are inadequate for the creation of sophisticated electronic materials for which selected impurity doping is necessary. The resulting materials are called extrinsic semiconductors because of the extrinsic nature of the defects that give rise to the important conductivity changes.

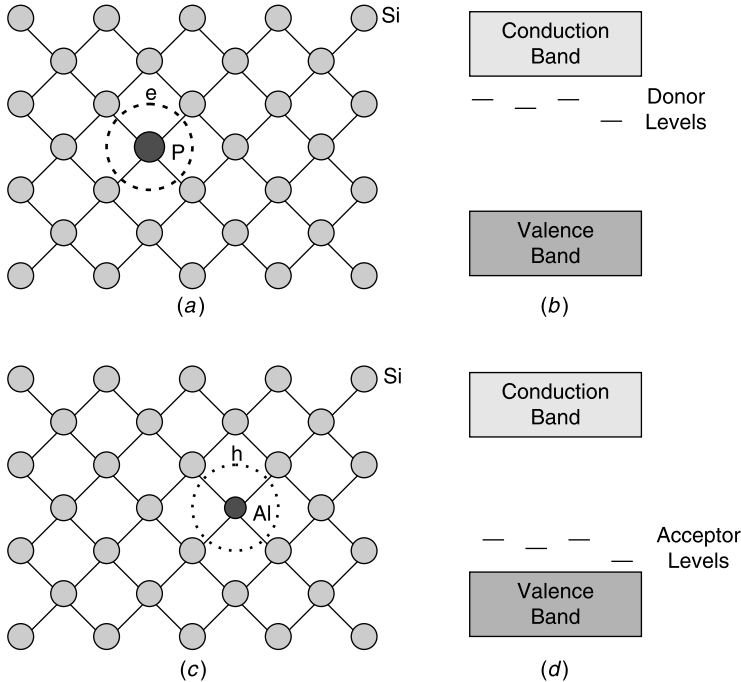
Impurity atoms will upset the orderly arrangement of bonding electrons and this changes the electronic properties. Doping with a very small amount of an impurity from the next *higher* neighboring group of the periodic table, phosphorus (P), arsenic (As), or antimony (Sb), results in the formation of substitutional point defects in which the impurities occupy normal sites, for example, a phosphorus atom on a site normally occupied by a silicon atom,  $\text{P}_{\text{Si}}$  (Fig. 1.6a). Each of these atoms has five valence electrons available for bonding, and after using four to form the four  $sp^3$ -hybrid bonds, one electron per impurity atom is left over. These electrons are easily liberated from the impurity atoms by thermal energy and are



**Figure 1.5** Diamond structure: (a) unit cell and (b) viewed with [111] vertical.

then (more or less) free to move through the crystal under the influence of an external electric field. Each dopant atom contributes one extra electron to the crystal. They are defects, and are given the symbol  $e'$  (the superscript indicates a single negative charge relative to the surroundings) to differentiate them from ordinary electrons. The doped material conducts mainly using these electrons, and, as they are negatively charged, the solid is called an  $n$ -type semiconductor. The atoms P, As, or Sb in silicon or germanium are called donors as they donate extra electrons to the crystal. In terms of band theory they are said to occupy states in the conduction band (Supplementary Material S2), the donors themselves being represented by localized energy levels just below the conduction band in the crystal (Fig. 1.6b).

An analogous situation arises on doping silicon or germanium with elements from the next *lower* neighboring periodic table group, aluminum (Al), gallium (Ga), and indium (In). The impurity atoms again form substitutional defects, such as  $Al_{Si}$  (Fig. 1.6c). In this case the impurities have only three outer bonding electrons available, which are not sufficient to complete four bonds to the surrounding atoms. One bond is an electron short. It simplifies understanding if the missing electron is regarded as a hole, represented by the symbol  $h^\bullet$ . The superscript indicates that the hole carries a



**Figure 1.6** (a) Donor impurity ( $P_{Si}$ ) in a silicon crystal. (b) Donor energy levels below the conduction band. (c) Acceptor impurity ( $Al_{Si}$ ) in a silicon crystal. (d) Acceptor energy levels above the valence band.

positive charge relative to the surroundings. Each impurity atom introduces one positive hole into the array of bonds within the crystal. Thermal energy is sufficient to allow the holes to leave the impurity atom, and these can also move quite freely throughout the crystal. The doped material conducts mainly using these holes, and, as they are positively charged, the solid is called a *p*-type semiconductor. The impurities are termed acceptors because they can be thought of as accepting electrons from the otherwise full valence band. On an energy band diagram the acceptors are represented by normally vacant energy levels just above the top of the valence band (Fig. 1.6*d*), which become occupied by electrons from that band on thermal excitation. The holes thereby created in the valence band provide the means for conductivity.

The idea of a hole is widely used throughout electronics, but its exact definition varies with circumstances. It is frequently convenient to think of a hole as a real particle able to move throughout the crystal, a sort of positive electron. It is equally possible to think of a hole as an electron missing from a localized site such as an atom or a covalent bond. Thus a metal cation  $M^{2+}$  could be regarded as a metal atom plus two localized holes ( $M + 2 h^{\bullet}$ ). In band theory, a hole is generally regarded as an electron missing from the top of the valence band. All of these designations are more or less equivalent, and the most convenient of them will be adopted in any particular case.

The unique electronic properties of semiconductor devices arise at the regions where  $p$ -type and  $n$ -type materials are in close proximity, as in  $p$ - $n$  junctions. Typical impurity levels are about 0.0001 at %, and their inclusion and distribution need to be very strictly controlled during preparation. Without these deliberately introduced point defects, semiconductor devices of the type now commonly available would not be possible.

## 1.4 OPTICAL PROPERTIES: F CENTERS AND RUBY AS EXAMPLES

Point defects can have a profound effect upon the optical properties of solids. The most important of these in everyday life is color,<sup>3</sup> and the transformation of transparent ionic solids into richly colored materials by F centers, described below, provided one of the first demonstrations of the existence of point defects in solids.

Defects can impart color to an otherwise transparent solid if they interact with white light. In general the interaction between a defect and the incident light is via electrons or holes. These may pick up some specific frequency of the incident illumination and in so doing are excited from the low-energy ground state,  $E_0$ , to one or more higher energy excited states  $E_1$ ,  $E_2$ ,  $E_3$  (Fig. 1.7a). The light that leaves the crystal is thus depleted in some frequencies and appears a different color to the incident light. The reverse also happens. When electrons drop from the excited states to the ground state  $E_0$ , they release this energy and the same light frequencies will be emitted (Fig. 1.7b). The relationship between the energy gained or lost,  $\Delta E_n$ , and the frequency,  $\nu$ , or the wavelength,  $\lambda$ , of the light absorbed or emitted, is

$$E_n - E_0 = \Delta E_n = h\nu_n = \frac{hc}{\lambda_n}$$

where  $E_n$  is the energy of the higher energy level ( $n = 1, 2, 3, \dots$ ),  $h$  is Planck's constant, and  $c$  is the speed of light.

The first experiments that connected color with defects were carried out in the 1920s and 1930s by Pohl, who studied synthetic alkali halide crystals. A number of ways were discovered by which the colorless starting materials could be made to display intense colors. These included irradiation by X rays, electrolysis (with color moving into the crystal from the cathode), or heating the crystals at high temperatures in the vapor of an alkali metal. Pohl was a strict empiricist who did not openly speculate upon the mechanics of color formation, which he simply attributed to the presence of Farbzentren (lit. color centers), later abbreviated to F centers.

Leading theoreticians were, however, attracted to the phenomenon and soon suggested models for F centers. In 1930 Frenkel suggested that an F center was an electron trapped in a distorted region of crystal structure, an idea that was incorrect in this instance but led directly to development of the concepts of excitons and

<sup>3</sup>Color is the name given to the perception of radiation in the electromagnetic spectrum with a wavelength of between 400 and 700 nm, for an average eye. If all wavelengths in this range are present in a distribution similar to that of radiation from the sun, the light is called white light.