gap semiconductors where the gap occurs at a specific point on the boarder of the Brillouin zone. Semiconductors, in which the two above-mentioned extrema occur at different k values in the Brillouin zone have an indirect gap or are called indirect semiconductors. The reason for this terminology comes from optical transitions between the band extrema. A photon with an energy equivalent to the typical width of a semiconductor band gap has (almost) vanishing momentum on the scale of the first Brillouin zone. Optical transitions are in this sense vertical in a $E(k)$ relation. If the band extrema occur at the same point in k-space, a transition between the extrema is directly possible by absorption (or emission) of a photon. In the other case this transition is forbidden by the k-conservation law and only indirect transitions are possible, which also involve the absorption or emission of a phonon for momentum conservation.

We shall see examples for both cases in Sect. 8.8.

8.3   An Overview of Semiconducting Materials

We now understand that semiconductors are solids that have at $T = 0\,\mathrm{K}$ a series of completely filled valence bands. The uppermost band is separated by an energy gap $E_\mathrm{g} \lesssim 4\,\mathrm{eV}$ from the empty conduction bands.

Since a crystal can be considered a huge molecule, we should also give the terms used in chemistry. The uppermost valence band is known in this scientific discipline as highest occupied molecular orbital (HOMO). The lowest conduction band is called consequently the lowest unoccupied molecular orbital (LUMO). If not stated explicitly otherwise, when we use in the following the terms valence and conduction band we always mean the highest and lowest ones, respectively.

Presently more than 600 element and compound semiconductors are known. They are listed with their propeties in the volumes by Landolt–Börnstein ([82L1] of Chap. 1).

With the help of the periodic Table 8.1 we try to localize the most important semiconductors. In the first two lines we give the current internationally recommended numbering system for the columns used by chemists, which runs from 1 to 18, and the old one, which we and most other semiconductor physicists use. It runs from I to VIII and has subclassifications such as II^A and II^B.

The technically most important semiconductor is Si. It is found in column IV^A. Conduction and valence bands are formed from the antibonding and bonding sp^3 hybrid orbitals. See Fig. 8.14 below. The binding is completely covalent and E_g is around 1.1 eV at room temperature. See, e.g., Table 8.2 where we give some data, which we partly explain later. Silicon crystallizes in the diamond structure with point group 0_h. The modification diamond of carbon is a semiconductor as well as Ge.

Tin is usually a metal, but there exists a modification, which is a semimetal namely grey tin, which also crystallizes in the diamond structure. Lead, finally, is a metal.

Table 8.1 Periodic table of the elements. The names of elements 104–110 might change and others may be discovered in the future

Iᵃ	IIᵃ	IIIᵇ	IVᵇ	Vᵇ	VIᵇ	VIIᵇ		VIIIᵇ		Iᵇ	IIᵇ	IIIᵃ	IVᵃ	Vᵃ	VIᵃ	VIIᵃ	VIIIᵃ
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mb	43 Tc	44 Ru	45 Rh	46 PoL	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118

90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

We can already see a general trend, namely that the width of the band gap decreases if one goes down the columns. SiC also belongs to the group IV semiconductors. SiC is notorious for forming many different polytypes. The indirect band gaps of all of them are around 3 eV, i.e., they lie between the gaps of diamond and Si.

Carbon has further modification [08S1] namely graphite, graphene [09N1], nanotubes and fullerene (C_{60}). Graphite is a semimetal with rather strong covalent sp^2 hybrid binding within the hexagonal layers and weak van der Waals binding between the layers. C_{60} is a semiconductor with $E_g \approx 2.2$ eV. Graphene and nanotubes can be semiconductors, semimetals or metals.

In the diamond structure every atom is tetrahedrally surrounded by its nearest neighbors. See Fig. 7.2. We can now replace, e.g., the Ge atoms on one sublattice by Ga, which has one outer electron less, and the others by As, which has one electron

Table 8.2 Values of the band gap energy of some group IV, III–V, II–VI and I–VII semiconductors (SC) at low temperature ($T \lesssim 10$ K), Sy: Symmetry (point group) (According to [82L1] of Chap. 1 and [01V1, 04A1])

| Group IV | | | | Group III–V | | | | Group II–VI | | | | Group I–VII | | | |
SC	Sy	E_g (eV)	dir/indir	SC	Sy	E_g (eV)	dir/indir	SC	Sy	E_g (eV)	dir/indir	SC	Sy	E_g (eV)	dir/indir
C	O_h	5.48	i	AlN	C_{6v}	6.28	d	ZnO	C_{6v}	3.437	d	CuCl	T_d	3.395	d
Si	O_h	1.17	i	AlP	T_d	2.53	i	ZnS	C_{6v}	3.91	d	CuBr	T_d	3.077	d
Ge	O_h	0.744	i	AlAs	T_d	2.228	i	ZnS	T_d	3.78	d	CuI	T_d	3.115	d
Grey Sn	O_h	0	Semimetal	AlSb	T_d	1.696	i	ZnSe	T_d	2.82	d	AgCl	T_d	3.249	i
				GaN	C_{6v}	3.503	d	ZnTe	T_d	2.391	d	AgBr	T_d	2.684	i
				GaP	T_d	2.350	i	CdO	O_h	0.8	i	AgI	C_{6v}	3.024	d
				GaAs	T_d	1.518	d	CdS	C_{6v}	2.583	d				
				GaSb	T_d	0.812	d	CdSe	C_{6v}	1.841	d				
				InN	C_{6v}	0.67[a]	d	CdTe	T_d	1.60	d				
				InP	T_d	1.424	d	HgS	T_d	0	d				
				InAs	T_d	0.418	d	HgSe	T_d	0	d				
				InSb	T_d	0.237	d	HgTe	T_d	0	d				

[a]New data, see [02D1, 02K2]

more than Ge, leaving the total number of electrons per unit unchanged, but adding a little bit of ionic binding to the still dominant covalent one. This procedure leads to the so-called zincblende type crystal structure with point group T_d and to the group of III–V semiconductors. To this group of semiconductors belong the compounds of B, Al, Ga or In with N, P, As or Sb. We see again the general trend of the band gaps within the columns of the periodic table with BN being an insulator, AlN, GaN being wide gap semiconductors while InSb is a narrow gap semiconductor.

The group III nitrides crystallize preferentially in the hexagonal wurtzite type structure (point group C_{6v}). In this case every atom of one type is still tetrahedrally surrounded by the others, but the arrangement of the next-nearest neighbours is such, that a hexagonal structure evolves (see Fig. 7.2).

If we repeat this step, which leads from the group IV semiconductors to the III–V compounds, once more or even twice more, we come to the II–VI (more precisely II^B–VI^A) and I–VII (more precisely I^B–VII^A) semiconductors, with increasing and finally dominating ionic binding, but still generally tetrahedral coordination. The II^A–VI^A and I^A–VII^A components are usually insulators and crystallize frequently in the rock-salt and CsCl structures.

The II–VI semiconductors comprise the compounds of Zn, Cd or Hg with O, S, Se or Te. The gap generally decreases again when going down the columns ZnS, ZnO and CdS are wide gap semiconductors, while the mercury compounds are usually semimetals. The II–VI semiconductors usually crystallize in zincblende or wurtzite type structures with a few exceptions. Both structures are partly possible with only minor energetic differences, as is the case for ZnS.

Some compounds have other structures like CdO (rocksalt structure), HgO (rhombohedral). HgS is a semimetal in the zincblende structure but a semiconductor with a gap around 2.2 eV in the trigonal modification (red cinnabar).

The main I–VII compounds are listed in Table 8.2. The most investigated ones are the Cu-halides and the Ag-halides, with the exception of the fluorides. Not much is known about the fluorides or the Au^+ halides concerning their properties as semiconductors.

Until now the list included only elements or binary compounds. In a similar way as above one can come to ternary semiconductors like $CuGaSe_2$ or even to quaternary ones like Ag_2CdGeS_4.

Furthermore, some of the elements and many of the binary compounds form alloys partly even without a miscibility gap like $Si_{1-x}Ge_x$, $Ga_{1-y}Al_yAs$, $CdS_{1-x}Se_x$, $ZnSe_{1-x}Te_x$ or $Cd_{1-y}Hg_yTe$. In an alloy one still has, in principle, nice crystals with a periodic lattice structure, but the lattice sites of one sublattice are randomly occupied by the two different atoms ($Si_{1-x}Ge_x$), anions (e.g., $CdS_{1-x}Se_x$) or cations (e.g., $Ga_{1-y}Al_yAs$). However, on a microscopic scale, the concentration fluctuations of the composition x introduce some disorder.

Some alloys tend to form ordered structures for compositions close to 0.5 like $Ga_{0.5}In_{0.5}P$ adopting the so-called CuPt structure [95C1].

Alloying is also possible on both sublattices like in $Ga_{1-y}In_yN_xAs_{1-x}$.

Most of the examples in the rest of this book will be taken from these more common semiconductors, but there are many more, some of which we mention below.

The IV–VI compounds (also known as lead salts) include the compounds of Pb or Sn with S, Se and Te. They serve partly as IR laser diodes. PbSe has e.g. a direct gap of 0.3 eV [07Z1].

There are further elemental semiconductors like S, Se, Te some modifications of P or I (As and Sb are considered semimetals). There exist various oxides as semiconductors apart from the group II^B oxides like GeO_2, SnO_2 (SiO_2 = quartz is an insulator); Cu_2O (see Sect. 13.2); TiO_2 in its various modifications (anatase, rutil, brookit) or the highly poisonous Tl–halides. To conclude this section we mention organic semiconductors like crystals of anthracene ($C_{14}H_{10}$), pentacene ($C_{22}H_{14}$), dibenzothiophene $C_{12}H_8S$ or hexathiophene. Organic semiconductors do not fall within the focus of this book, but we will occasionally give examples of their optical properties.

There is a general trend that the band gap of semiconductors decreases with increasing temperature. The decrease $E_g(T = 0) - E_g(T) = \Delta E_g(T)$ tends to vary quadratically with temperature at lower temperatures ($T \leq 100$ K) and linearly above. This behavior is often described by the Varshni formula [67V1]

$$\Delta E_g(T) = \frac{\alpha T^2}{\beta + \gamma T}. \qquad (8.8a)$$

More complex formula were recently suggested, e.g., in [94A1, 99P1, 00L1, 02G1, 03G1, 03S1, 06H1] and references therein. In [99P1] e.g. the following (8.8b) has been given

$$\Delta E_g(T) = \frac{\alpha \theta_p}{2} \left[\sqrt[P]{1 + \frac{2T}{\Theta_p}} - 1 \right] \qquad (8.8b)$$

with Θ_p being an effective Phonon temperature, α a high temperature limit of the entropy and P a third material specific parameter.

There are two main contributions to $\Delta E_g(T)$ namely the carrier-phonon coupling, which depends on the phonon occupation, and the temperature dependence of the lattice constant, since the band gap depends on this quantity via the deformation potentials introduced below with (8.21).

Some semiconductors like CuCl or some lead salts also show an increase in E_g with increasing temperature, for some others like CuBr $E_g(T)$ goes through a maximum with increasing temperature. For data see, e.g., in [82L1] of Chap. 1 and references therein.

8.4   Electrons and Holes in Crystals as New Quasiparticles

As we shall see later, the optical properties of the electronic system of semiconductors are largely determined by transitions of electrons between the upper valence bands and the lower conduction bands.

Table 8.3 Properties of a hole in the valence band compared to the properties of the electron that has been removed from the valence band to create the hole

Property	Hole	Removed electron
Electric charge q	q_h	$= -q_{re}, q_{re} \approx -1.6 \times 10^{-19}$ As
Wave vector	$\boldsymbol{k}_h$	$= -\boldsymbol{k}_{re}$
Spin	σ_h	$= -\sigma_{re}$
Eff. mass	$m_h > 0$	$= -m_{re}, m_{re} < 0$

The bandstructure as presented until now, i.e., in connection with Figs. 8.1–8.5, describes the so-called $N \pm 1$ particle problem in the following sense: if we consider a semiconductor with a completely filled valence band containing N electrons per cm^3

$$N \simeq 10^{22} - 10^{23} \text{ cm}^{-3} \tag{8.9}$$

and a completely empty conduction band and add one more electron, we find that this electron can be placed into exactly the conduction band states. If we remove one of the N electrons and ask from which state it came, we find the valence band states.

An obvious step now is to consider the one or few electrons in an otherwise empty conduction band (CB). For an almost filled valence band, however, it is easier to consider the few empty states and their properties instead of the many occupied ones. This idea leads to the concept of "defect-electrons" or "holes". The properties of the hole are connected in the following way (Table 8.3) with the properties of the electron that has been removed from the valence band (VB).

From Table 8.3 we see that the hole has a positive charge and that its wave vector and spin are opposite to those of the electron removed from the valence band. The two latter statements are easy to understand. A semiconductor with a completely filled valence band has total momentum and spin equal to zero. If we take one particle out, the remainder acquires for the above quantities values exactly opposite to those of the removed particle. For clarity Figs. 8.6a, b show the bandstructure containing one electron in the conduction band and one hole in the valence band, respectively. The states are equidistant in $\boldsymbol{k}$ (see Sect. 2.6) but we should note that there are usually 10^{22}–10^{23} states in each band per cm^3 and not only the few shown in Fig. 8.6.

The electrons and holes in a semiconductor crystal are quasi-particles. They can exist only in the crystal and not in vacuum, in contrast to normal electrons and positrons with which they have a lot in common, except the magnitude of the energy gap which is $\simeq 1$ MeV for normal electrons and positrons i.e., twice the rest mass of 511 keV $= m_0 c^2$. The dispersion relations of electrons and holes are different from those of free electrons and positrons which for the non-relativistic case are given by

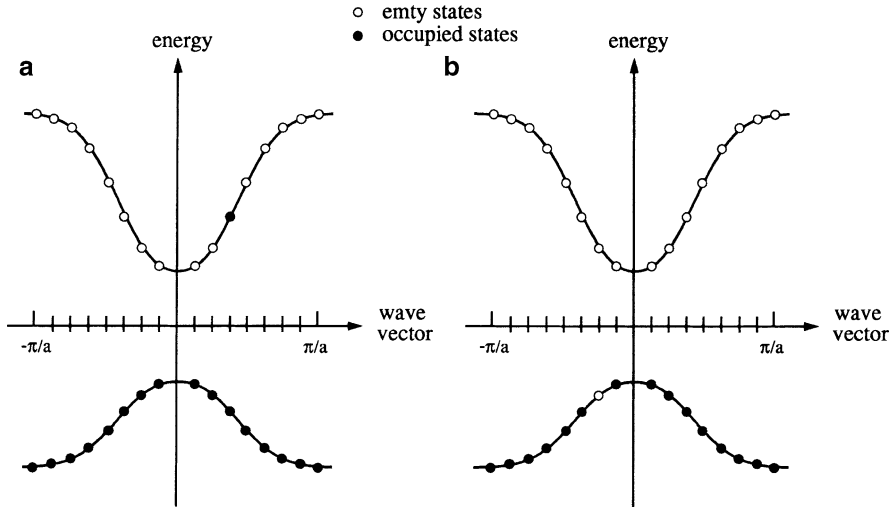$$E_{e,p} = \pm \left(m_0 c^2 + \frac{\hbar^2 k^2}{2m_0} \right), \tag{8.10}$$

Fig. 8.6 One electron in the conduction band (**a**) and one hole in the valence band (**b**) representing the $N \pm 1$ particle problem of (8.9). *Full circles:* occupied states; *open circles:* empty states

where m_0 is the free electron mass.

The quantity $\hbar k_{\mathrm{e,h}}$ of crystal electron and hole is a quasi-momentum, since it is conserved only modulo reciprocal lattice vectors – see (8.4) and (8.5) – and since the Bloch waves of (8.2) and (8.3) are not proper eigenstates of the momentum operator $\frac{\hbar}{\mathrm{i}}\nabla$. For more details of the concept of quasi-momentum see [98B1] of Chap. 5.

One should note that the energy of a hole increases if it is brought deeper into the valence band.

8.5   The Effective-Mass Concept

If we want to describe the motion of an electron or hole in a semiconductor under the influence of an external field (e.g., an electric or magnetic field) it is intuitively clear that we ought to consider a wave packet rather than the infinitely extended Bloch waves. To describe such a wave packet we superpose Bloch waves of a certain range of k-vectors around a k_0 as described schematically in (8.11)

$$\phi_{k_0}(\boldsymbol{r}) = \sum_k a_k\, \mathrm{e}^{\mathrm{i}k\cdot r}\, u_k(\boldsymbol{r}). \tag{8.11}$$

These types of wave packet are known as Wannier-functions. In order to keep the k-vector reasonably well defined, we localize the wavefunction only to a volume larger than a unit cell. Due to the uncertainty relation we would need wavefunctions