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SEMICONDUCTORS

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XXII CORSO

a cura di R. A. SMITH
Direttore del Corso

VARENNA SUL LAGO DI COMO

VILLA MONASTERO

17 LUGLIO - 5 AGOSTO 1961

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PROCEEDINGS
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« ENRICO FERMI »

COURSE XXII

edited by R. A. SMITH
Director of the Course

VARENNA ON LAKE COMO
VILLA MONASTERO
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Introductory Lecture.

R. A. SMITH

Royal Radar Establishment - Malvern, Worcestershire

The purpose of this introductory lecture is to explain the arrangements of the Semiconductor Course. To-day the field of semiconductor physics is an extremely wide one and it is quite impossible to cover more than a small part of it in a three-week's course. I have therefore, tried to choose one or two of the most important areas and to have them dealt with rather more thoroughly, instead of trying to touch slightly on nearly everything. There are, naturally, some unfortunate omissions. Some of these are inevitable because of lack of space for them in the course. Others planned for inclusion have had to be dropped since some of the lecturers had to call off at the last minute. Perhaps the most serious omission is that there are now no lectures on the theory of recombination processes. This important subject was included in the original plan for the course, but two invited lectures dropped out and it has not been possible to include it. Some mention of recombination processes will, however, be made in other lectures.

Most of the students attending the course have already a certain amount of experience in semiconductor physics but a number, although experienced physicists, are hoping to use the course as an advanced introduction to the subject with a view, perhaps, to transferring their field of research activity to this area. For those and for others less experienced, the course will open with a series of lectures by Dr. L. PINCHERLE on the basic concepts of semiconductor physics and, in particular, on the energy-band structure of semiconductors. In this way we hope that all students on the course will «learn the language» of the subject. Dr. PINCHERLE will then follow this introduction with a few lectures on the more advanced aspects of the theory and calculation of band structures. After all, the most fundamental of all properties of semiconductors is their band structure. We have indeed used many semiconductors in a practical way without detailed knowledge of their band structure but no one could deny that many of the more interesting and subtle developments with Ge and Si have come about since we knew the form of the

energy bands, Our knowledge of the band structure of all but a very few semiconductors is very rudimentary and one of the most needed developments in the subject lies in finding more powerful methods, both theoretical and experimental, for determining the form of the energy bands in some detail. That such methods are beginning to open up is now clear and we shall later in the course be concerned with the experimental approach to this subject, particularly through the use of optical and microwave techniques associated with powerful magnetic fields. In addition, Dr. T. P. McLEAN will lecture on the effective-mass approximation, a concept which forms the basis of most theoretical discussions of the properties of semiconductors.

From an experimental point of view the most extensively studied and practically most important characteristics of semiconductors are their transport properties and no course on semiconductors would make sense without a large section being devoted to this subject. It is their unique properties as conductors of electricity that have made semiconductors of such great importance technologically, and this, in turn, has led to a great deal of research effort being devoted to transport problems. I have therefore included, as one of the main series in the course, a set of lectures by Dr. A. F. GIBSON on transport properties of semiconductors. The approach in this case will be mainly from an experimental point of view. The first few lectures will be introductory, leading to more advanced concepts; the series will end with a discussion of some of the outstanding problems in this field and will deal, in particular, with some interesting new phenomena associated with nonequilibrium electron distribution in high electric fields, popularly known as «hot electrons». These aspects will be illustrated by a number of seminars dealing with recent work in this area including that of Dr. GIBSON himself and his research staff.

Another field of research which has contributed greatly to our understanding of semiconductors has been a study of their optical properties, first through investigations of photoconductivity and more recently through observation of optical absorption spectra. The use of strong magnetic fields in conjunction with the latter has added greatly to the power of the technique. After a brief introduction by myself, the subject will be treated in a series of lectures by Dr. B. LAX who will deal in particular with optical properties of semiconductors in a magnetic field, including some of the more recent work by himself and his research staff. (Another series will include lectures dealing with optical absorption due to lattice vibrations, see below.)

These two subjects, transport and optical properties of semiconductors, are, in my opinion, perhaps the most important and so I have chosen to devote these two main series of lectures to them. Other properties, such as magnetic and thermo-magnetic behaviour, have added a great deal of supplementary information and discussions of these have been added as shorter supplementary series of lectures by Prof. C. ENZ and Prof. L. SOSNOWSKI.

The marked success of semiconductor research in the past decade has largely been due to the availability in pure form and as single crystals of the materials for investigation. Much of the early work in semiconductors was bedevilled by unreproducibility and uncertainty owing to the presence of uncontrolled impurities and to the effects of boundaries between micro-crystals in the polycrystalline samples which were generally used. The remarkable purity and control which can now be achieved has resulted only from a great deal of hard work and from an understanding of the physical chemistry and metallurgy of the processes involved. It therefore seems to me to be quite appropriate, and indeed very desirable, to devote quite a substantial portion of this course to the physical chemistry and metallurgy of semiconductors and to the problems of specimen preparation. A series of lectures lasting right through the course will be devoted to this subject being given first of all by Dr. H. J. VINK and later by Dr. N. B. HANNAY. Dr. VINK's lectures will deal with the thermodynamics of imperfections in crystals and with other basic phenomena associated with crystal growth and Dr. Hannay will discuss the theory and practice of obtaining crystals with desired impurity concentrations.

The above lectures constitute what I might call the main structure of the course. In addition I have decided to include a series of lectures on one aspect of semiconductor physics in which, in my opinion, outstanding progress has recently been made. This will give those attending the course an opportunity to hear at first hand a detailed account of work on one of the vigorous growing points of the subject by those responsible for its growth. For this subject I have chosen lattice vibrations. A series of lectures will be given on the theory of lattice vibrations by Dr. W. COCHRAN, who has made outstanding contributions to this subject, and was to be followed by some lectures by Dr. F. A. JOHNSON whose measurements of the lattice vibration bands of a number of semiconductors has been one of the outstanding recent advances in the experimental investigation of the properties of crystalline solids. Unfortunately Dr. Johnson is unable to come and I shall do my best to describe some of his work.

These lectures will be supplemented by a number of lectures and seminars on special topics given by some of the lecturers and by distinguished visitors to the school. For example, Dr. HANNAY will give two lectures on recent work on oxide and organic semiconductors, Professor H. WELKER will give two seminars on the magneto-resistance of InSb in high magnetic fields and Dr. S. H. KOENIG will give two seminars on the effect of stresses on the band structure of Ge. In addition, a number of short papers will be given by students of the course in the seminars, describing some of their own research work. The opportunity which this will afford for them to discuss their work with more experienced research workers is one of the more important features of the school.

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Band Structure of Semiconductors.

L. PINCHERLE

Bedford College, University of London - London

1. - The foundations of band theory.

It is assumed that students are already familiar with the fundamental notions about semiconductors, and the present lectures are meant to provide a wider picture of the theoretical framework.

The band theory of solids is a model for the study of the electronic properties of crystals; it is based on that point of view which considers a crystal as a single very large molecule in which it has no meaning to associate an electron to a given atom. Rather all the electrons are assumed to move through the whole crystal, and an electron has the same probability of being at equivalent points in the crystal.

The alternative point of view, which starts by considering each electron as bound to a given nucleus is also useful, for instance for the discussion of types of bonding, and in those substances in which conduction occurs through a « hopping » motion. It corresponds to the Heitler-London approach for molecules. In general, however, the first picture, analogous to the method of molecular orbitals in molecules, has proved more fruitful, though, of course, electrons of deep shells and sometimes *d*-electrons in transition metals are better treated as localized, and the Heitler-London approach must, of course, be the correct one when the interatomic separation becomes very large.

From the start one makes in band theory the very important approximation of assigning an individual wave function to each electron. The problem being a many-body one, one ought to consider a single wavefunction Ψ being a function of $3N$ ($4N$ if spin is included) co-ordinates, N being the total number of electrons. But to deal with such $3N$ -dimensional Ψ is far too difficult and one must then resort to approximations of the type

$$\Psi(x_1 y_1 z_1 \dots x_N y_N z_N) = \psi_1(x_1 y_1 z_1) \dots \psi_N(x_N y_N z_N)$$

in which one considers individual wave functions depending on the co-ordinates

of a single electron. Correspondingly, the total energy is the sum of the energies of the individual electrons. More complicated combinations of the ψ_i may be taken, to make Ψ a completely antisymmetrical function, and in this way interaction effects may be taken into consideration. One should note that the classification of these interactions into exchange, correlation, etc., arises because of the use of the approximation of individual wave functions.

The name « band theory » arises because of the striking fact that in the model the energy levels allowed for the electrons group themselves into bands, often separated by intervals of energy in which normal levels are forbidden. That every atomic level must, on the assumption that the motion of each electron extends to the whole solid, broaden very considerably, can be under-

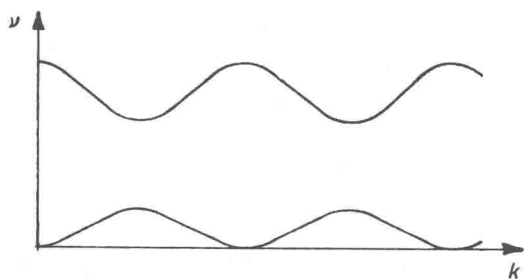


Fig. 1. — a) Second band of allowed frequencies; b) Forbidden gap; c) Fiss band of allowed frequencies.

stood by a simple application of the uncertainty principle, since the electron spends only a short time orbiting around each atom. But the existence of bands is better understood adopting the wave picture of the electron, since bands of allowed and forbidden frequencies exist

in the case of any wave propagation in a periodic structure (for electrons the frequency ν of the De Broglie waves is not an observable quantity and one considers instead the energy $E = h\nu$). In all such cases it is found that the dispersion relation, that is the relation between frequency ν and wave number k is, taking for simplicity a one-dimensional problem, of the type indicated schematically in Fig. 1. Its main features are:

- 1) ν is a periodic function of k ;
- 2) for any given k there are generally a number of possible frequencies;
- 3) values of ν within certain frequency intervals are not found for any value of k .

Yet another useful way of visualizing how the energy bands arise is to start with a « crystal » with two atoms and add successively more atoms. As is well known from the example of the H_2 molecule, when two like atoms come together, each atomic level splits into two molecular levels. Adding a third atom gives three molecular orbitals with energies grouped about the original atomic level. Each addition of a new atom adds one more energy level and

in the limit for N very large one gets bands, each containing N levels, each band deriving in a sense from an atomic level, though this statement requires qualification. The N levels are so close together, that in practice one may consider them as a continuum and introduce a density of states dn_s/dE , being the number of levels per unit volume of the crystal per unit energy interval.

In what follows, complete validity of the band model will be assumed. Yet one may wonder how a one-particle approximation can be valid when the electrons interact with strong long-range forces. However it has been shown in the last few years, chiefly from the work of GELL-MANN, KOHN and others, that a many-body system such as the electrons in a crystal, is capable of single particle excitations, as well as of other excitations such as collective oscillations which are not easily described by a single-particle model and for which the interaction between the excited particles is important. Now the single-particle excitations in which one is interested in solids have energies much lower than that of the lowest collective motion. In such cases, and as long as one is not interested in interactions between excited particles and between excited particles and holes, the single-particle excitations are described by energy bands specified by functions $E(\mathbf{k})$. Under the usual experimental conditions, all complicated many-electron effects are completely contained in $E(\mathbf{k})$ and in the dielectric constant and magnetic susceptibility of the material. It has been proved that the energy bands defined in this way are the same as those obtained from the Hartree-Fock self-consistent equations in the one-particle model. It may be remarked in this context that there are many experimental indications that the basic ideas of the one-particle approximation are applicable to metals. A well defined Fermi surface, enclosing the occupied region of \mathbf{k} -space for the one-particle functions, exists in metals and its detailed characteristics can be determined. It is clear that the approximation is even more legitimate in the case of semiconductors where the number of carriers involved in transport processes is usually small. In conclusion, the three major approximations of the band model are:

1) the action of other electrons on the electron under study can be replaced by a periodic potential;

2) anything in the nature of multiplet structure can be neglected, treating the problem like, in the case of atoms, that of one electron outside closed shells; there are phenomena where this does not hold, for instance in the case of the exciton resulting from the interaction between an electron and a hole;

3) one can calculate the energy bands assuming fixed nuclei. The interaction with the lattice vibrations is introduced later as a perturbation and in many cases, particularly at low temperatures, it simply increases the effective mass of the carriers. When the interaction is very strong, as in ionic crystals, it is not yet certain whether the perturbation approach is justified.

2. - Form of the individual wave functions.

The crystal is a periodic structure, thus the potential $U(\mathbf{r})$ to be inserted into Schrödinger's equation for the determination of the one-electron energies and wave functions is also periodic: from this simple fact follow many far-reaching properties. U includes the field of the nuclei and of all the electrons except the one under investigation. Now the solution of the equation

$$(2.1) \quad \nabla^2 \psi(\mathbf{r}) + 2m/\hbar^2 [E - U(\mathbf{r})] \psi(\mathbf{r}) = 0$$

can be proved (Floquet's theorem) to have the form

$$(2.2) \quad \psi = \exp[i\mathbf{k} \cdot \mathbf{r}] u(\mathbf{r}),$$

where $u(\mathbf{r})$ is periodic with the periodicity of the lattice. Functions of the type (2.2) are sometimes called Bloch functions. The vector \mathbf{k} plays the role of a set of three quantum numbers and can take any real value. (2.2) can be justified from a physical point of view by observing that, according to our hypotheses, $|\psi|^2$ must be periodic with the periodicity of the lattice and thus, if \mathbf{R}_i is any fundamental translation of the lattice, $|\psi(\mathbf{r} + \mathbf{R}_i)|^2 = |\psi(\mathbf{r})|^2$, from which $\psi(\mathbf{r} + \mathbf{R}_i) = \exp[i\theta] \psi(\mathbf{r})$. To determine the form of the phase shift θ , observe that \mathbf{R}_i (Section 3) is $l\mathbf{a} + m\mathbf{b} + n\mathbf{c}$, where \mathbf{a} , \mathbf{b} , \mathbf{c} are the primitive vectors of the lattice. One can then introduce an arbitrary real vector \mathbf{k} such that the constant by which ψ is multiplied under the translation \mathbf{a} is $\exp[i\mathbf{k} \cdot \mathbf{a}]$, under \mathbf{b} it is $\exp[i\mathbf{k} \cdot \mathbf{b}]$, under \mathbf{c} it is $\exp[i\mathbf{k} \cdot \mathbf{c}]$. If now we make the translation \mathbf{R}_i , where the index i indicates the set of integers l, m, n , ψ becomes multiplied by $\exp[i\mathbf{k} \cdot \mathbf{R}_i]$. The relation $\psi(\mathbf{r} + \mathbf{R}_i) = \exp[i\mathbf{k} \cdot \mathbf{R}_i] \psi(\mathbf{r})$ is the fundamental periodicity relation for the wave functions. Indicating by T_i the operation of translating by \mathbf{R}_i , (2.3) becomes $T_i \psi_{\mathbf{k}} = \exp[i\mathbf{k} \cdot \mathbf{R}_i] \psi_{\mathbf{k}}$ and may be interpreted as showing that $\psi_{\mathbf{k}}$ is an eigenfunction of the operator T_i belonging to the eigenvalue $\exp[i\mathbf{k} \cdot \mathbf{R}_i]$, which is a constant of the motion. The Hamiltonian commutes with all translations T_i , which also all commute with each other. Writing now $u(\mathbf{r}) = \exp[-i\mathbf{k} \cdot \mathbf{r}] \psi(\mathbf{r})$, we have

$$u(\mathbf{r} + \mathbf{R}_i) = \exp[-i\mathbf{k} \cdot (\mathbf{r} + \mathbf{R}_i)] \psi(\mathbf{r} + \mathbf{R}_i) = \exp[-i\mathbf{k} \cdot \mathbf{r}] \psi(\mathbf{r}) = u(\mathbf{r}),$$

that is, u has the periodicity of the lattice and (2.2) is justified. The rigorous proof can only be indicated in an incomplete form. It is necessary to assume periodic boundary conditions, that is that the wave function repeats itself after a very large number of lattice points along any chosen direction along which the lattice spacing is a . As before $\psi(x+a) = C\psi(x)$, where C is a com-

plex constant. Then $\psi(x+Na) = C^N \psi(x) = \psi(x)$, that is $C^N = 1$, or

$$C = \exp[2\pi mi/N] \quad m = 0, 1, \dots, N-1.$$

This is satisfied if ψ has the form $\psi(x) = \exp[2\pi mi x/Na]u(x)$ with $u(x)$ periodic; writing now $k = 2\pi m/Na$, the theorem is proved (since the direction considered is arbitrary). As $N \rightarrow \infty$, k becomes a continuous variable.

If the potential is constant, it may be taken as zero and the solution of (2.1) is $\psi = \exp[i\mathbf{k} \cdot \mathbf{r}]$ with $E = \hbar^2 k^2/2m$. $\hbar\mathbf{k}$ is in this case just the momentum of the electron. It will be proved in Section 4 that also in the general case $\hbar\mathbf{k}$ has many of the properties of momentum and can thus be called « crystal momentum ». It is not equal, though, to the average value of momentum. The energy of a state $\psi_{\mathbf{k}}$ is to all intents and purposes a continuous function of \mathbf{k} and a particular dispersion relation $E(\mathbf{k})$ characterizes each band. Such relation is one of the most important properties of a material. It enters in a fundamental way in any calculation of the electrical, optical, thermal, etc., properties of the substance.

It should be remarked that, although energy bands are characteristic of periodic structures, they are not confined to these structures. It is still useful to talk about bands in a disordered material (as broadened atomic levels), provided there is enough overlapping between atomic orbitals centred on neighbouring atoms. It is still possible to consider an $E - \mathbf{k}$ relation, but the wave functions have not in general the form 2.2. These considerations are in line with the experimental fact that often no great discontinuities of the electrical and other properties of metals and semiconductors occur at the melting point.

More precisely it is found that in general the loss of long-range order has not a great effect on the electrical properties, and thus presumably on the band structure, provided the short-range order is preserved, that is, provided the co-ordination corresponding to the solid phase is preserved in the liquid one. Thus, when a metal with a close-packed structure melts, hardly any discontinuity occurs. On the other hand, fusion must have a marked effect in substances with directed bonds which must necessarily be broken at the melting point. This occurs, for instance, in Ge and InSb, their density increasing considerably at the melting point, the structure of the liquid approaching that of a close-packed metal. Correspondingly, the conductivity increases by a factor of the order of 10, due to a marked reduction of the energy gap.

The system of electronic bands in a liquid depends on the average distance between atoms and on the fluctuations from this average. The problem of evaluating the band structure is a complicated one, and is probably best tackled by the approach which considers the electrons as bound to individual atoms, rather than by an extension of the band model. The possibility of conduction

by positive holes remains, though the bases of the concept of positive hole are then somewhat different from those holding in the case of a crystal.

3. - Representation in reciprocal space. Brillouin zone.

A crystal lattice has several periods. One chooses periods \mathbf{a} , \mathbf{b} , \mathbf{c} such that

$|\mathbf{a}|$ is the shortest period in the lattice (or one of several equal shortest ones);

\mathbf{b} is the shortest not parallel to \mathbf{a} ;

\mathbf{c} is the shortest not coplanar to \mathbf{a} and \mathbf{b} ;

then any period \mathbf{R} of the lattice is given by

$$\mathbf{R} = l\mathbf{a} + m\mathbf{b} + n\mathbf{c} \quad l, m, n \text{ integers.}$$

The lattice so defined is called the Bravais lattice of the crystal to which it belongs. The crystal is entirely described if the content of one parallelepiped of sides \mathbf{a} , \mathbf{b} , \mathbf{c} is known. This unit is called a primitive cell of the crystal

(Fig. 2 shows the primitive cell for the face-centred cubic lattice; the volume of this cell is one quarter that of the fundamental cube) and it may contain any number of atoms. It is proved in crystallography that there are just 14 different Bravais lattices, *e.g.* the hexagonal, the simple cubic, the face-centred and the body-centred cubic lattices. In each case the primitive cell may be filled in a number of different ways having different symmetry and in this way the 14 Bravais

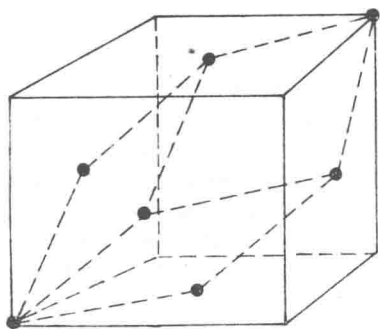


Fig. 2.

lattices become diversified into 230 complete space groups. Each of these groups can be the symmetry type of several different crystal structures. Figure 3 gives three structures having the face-centred cubic Bravais lattice, that is the monatomic face-centred structure (Al), the NaCl structure, the diamond structure (Si, Ge) and the zincblende structure (most III-V intermetallic semiconductors). In the last three structures, there are two atoms per fundamental cell: they are made up of two interpenetrating face-centred lattices.

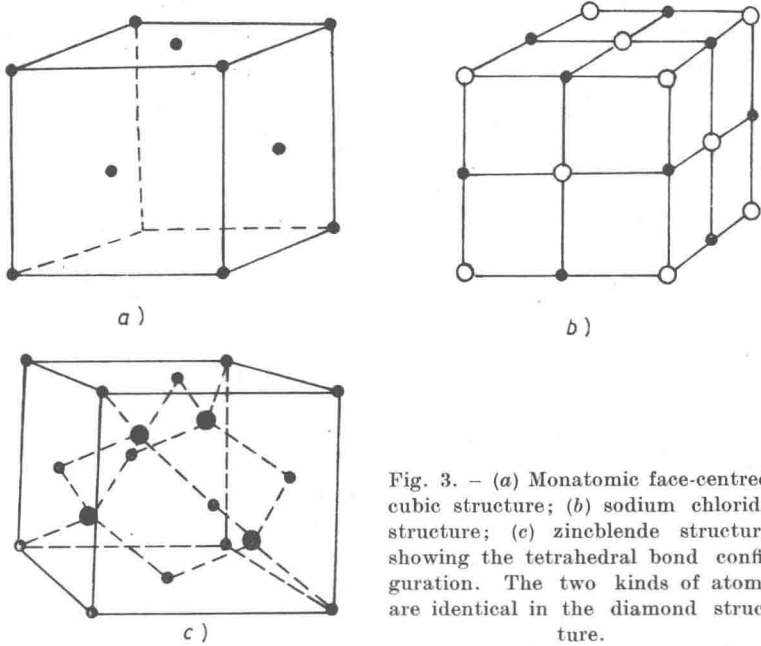


Fig. 3. - (a) Monatomic face-centred cubic structure; (b) sodium chloride structure; (c) zincblende structure showing the tetrahedral bond configuration. The two kinds of atoms are identical in the diamond structure.

Some of the rotational symmetries of the Bravais lattice are not present in the crystal, or retained in a modified form, *e.g.* a rotation about a certain axis which is a symmetry element of the Bravais lattice must be combined with a translation along the axis of rotation by a fraction of a lattice displacement. Thus in the diamond structure the normal cubic fourfold symmetry becomes a screw symmetry (Fig. 4: the screw axis lies in the centre of the squares one of which is outlined). The presence of screw axes, or glide planes, has a more important effect on the band structure than the number of atoms per primitive cell. Again, the centre of inversion present in the Bravais face-centred lattice is missing in the zincblende structure.

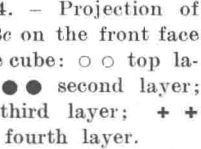


Fig. 4. - Projection of Fig. 3c on the front face of the cube: $\circ \circ$ top layer; $\bullet \bullet$ second layer; $\times \times$ third layer; $++$ fourth layer.

Now, given a lattice with basis vectors a, b, c , one defines as its reciprocal space that generated by

three basic vectors α, β, γ , satisfying

$$(3.1) \quad \begin{cases} \alpha \cdot a = 2\pi; & \beta \cdot a = 0; & \gamma \cdot a = 0, \\ \alpha \cdot b = 0; & \beta \cdot b = 2\pi; & \gamma \cdot b = 0, \\ \alpha \cdot c = 0; & \beta \cdot c = 0; & \gamma \cdot c = 2\pi, \end{cases}$$

so that the co-ordinate axes in reciprocal space are perpendicular to the co-ordinate planes of the direct lattice. Solving the eqs. (3.1)

$$\alpha = \frac{2\pi\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}; \quad \beta = \frac{2\pi\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}; \quad \gamma = \frac{2\pi\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}.$$

The relation between any reciprocal vector $\mathbf{K}_n = p\alpha + q\beta + r\gamma$ (p, q, r integers) and any direct lattice vector $\mathbf{R}_i = la + mb + nc$ is

$$(3.2) \quad \mathbf{l}_n \cdot \mathbf{R}_i = 2\pi(pl + qm + rn) = 2\pi g \quad (g \text{ an integer}).$$

The vectors \mathbf{K}_n are introduced in perhaps the most natural way by expanding the potential $V(\mathbf{r})$, which is periodic with the periodicity of the lattice in a Fourier series $V(\mathbf{r}) = \sum_{\mathbf{K}_n} V(\mathbf{K}_n) \exp[i\mathbf{K}_n \cdot \mathbf{r}]$. The \mathbf{K}_n as defined are the only « frequencies » which lead to the correct periodicity.

The volume of the primitive cell of the reciprocal lattice is $8\pi^3$ divided by the volume of the primitive cell of the direct lattice. By its definition each vector \mathbf{K}_n is perpendicular to a set of planes of atoms in the crystal and the spacing of these planes is $2\pi/K_n$. This is made use of in the theory of the diffraction of X-rays by crystals.

It is easily seen that the reciprocal lattice of a simple cubic lattice is also simple cubic, and that the reciprocal lattice of a face-centred cubic lattice is body-centred and viceversa.

Consider now two waves that differ from each other by a fundamental vector of the reciprocal lattice, \mathbf{K}_n . Take two corresponding points \mathbf{r} and $\mathbf{r} + \mathbf{R}_i$ in the direct lattice. Let the phase difference between the two waves at \mathbf{r} be φ . Then the phase difference at $\mathbf{r} + \mathbf{R}_i$ is $\varphi + (\mathbf{k} + \mathbf{K}_n) \cdot \mathbf{R}_i - \mathbf{k} \cdot \mathbf{R}_i = \varphi + 2\pi g$ (because of (3.2)). The phase difference is thus the same at equivalent points. From the point of view of the Bravais lattice the two waves may be said to be equivalent, since, although they differ from each other within a primitive cell, they behave equivalently from cell to cell. It is unnecessary to consider more than one of all the equivalent waves of wave vector $\mathbf{k} + \mathbf{K}_n$ and thus wave vectors are reduced to their smallest possible value which can be obtained by subtracting vectors of the reciprocal lattice. The end points of all reduced wave vectors fill a region around the origin of reciprocal space which is called the first Brillouin zone: it contains all nonequivalent \mathbf{k} -vectors. Since for our purpose we shall not require the other zones that may be constructed outside the first, we shall call it simply and somewhat improperly just the Brillouin zone (BZ). Having chosen one reciprocal lattice site as origin of \mathbf{k} -space, the BZ is by its definition the polyhedron whose faces bisect perpendicularly the lines joining the chosen lattice point to its near neighbours. The

BZ for the direct face-centred cubic lattice, whose reciprocal lattice is body-centred, is the truncated octahedron of Fig. 5. The hexagonal faces are the planes bisecting perpendicularly the lines joining the central lattice point to its eight nearest neighbours along the $(1, 1, 1)$ and equivalent directions; the

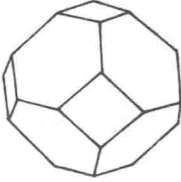


Fig. 5.

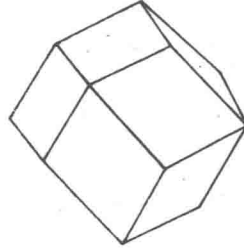


Fig. 6.

square faces bisect the lines joining it to its six second nearest neighbours along the $(1, 0, 0)$ and equivalent directions. The BZ of the body-centred cubic lattice, whose reciprocal lattice is face-centred, is the rhombododecahedron of Fig. 6. For the simple cubic lattice the BZ is a cube; for the hexagonal lattice it is a hexagonal prism.

The shape of the BZ is determined only by the type of the Bravais lattice, not by the particular crystal structure. There are thus just 14 BZ and, for instance, the BZ of Al, NaCl, Si, InSb are all the truncated octahedron of Fig. 5. However, the classification of the various energy bands and, of course, the ordering of the bands, depend on the particular structure.

When the wave is modulated by the periodic function u as in (2.2), it is still true that the « wave vector » \mathbf{k} can always be reduced (by subtracting a suitable reciprocal lattice fundamental vector \mathbf{K}_n) to give a \mathbf{k}' lying in the first Brillouin zone, while still preserving the form (2.2) of the wave function; in fact

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}) &= \exp[i\mathbf{k}\cdot\mathbf{r}]u_{\mathbf{k}}(\mathbf{r}) = \exp[i(\mathbf{k} - \mathbf{K}_n)\cdot\mathbf{r}]u_{\mathbf{k}}(\mathbf{r}) \exp[i\mathbf{K}_n\cdot\mathbf{r}] = \\ &= \exp[i\mathbf{k}'\cdot\mathbf{r}]u_{\mathbf{k}}(\mathbf{r}), \end{aligned}$$

since $\exp[i\mathbf{K}_n\cdot\mathbf{r}]$ has, like u , the periodicity of the lattice.

Thus the one-electron wave functions of a solid are periodic in reciprocal, or \mathbf{k} -space, and then also the eigenvalues $E(\mathbf{k})$ must be periodic functions of \mathbf{k} , with the periodicity of the reciprocal lattice. Fundamentally this is still a consequence of the fact that the Hamiltonian commutes with all the translations T_i of the lattice. Therefore it is necessary to study the dispersion relation only within the BZ. This scheme in which all vectors are considered