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THEORY OF CERTAIN ENERGY SURFACES AND BRILLOUIN ZONES

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INTRODUCTION

The general purpose of this project is the investigation of the relations between the shapes of energy surfaces and of Brillouin zones in solids. The reasons why this investigation is important and the proposed methods for carrying out the investigation are discussed in detail in the introduction to Quarterly Progress Report No. 1[1], hereafter referred to as Q.P.R. No. 1.

The project is divided into three phases. The first phase is an investigation of the shape of higher Brillouin zones for the more important crystal structures. Both drawings and models of these zones will be made. The second phase is an investigation of the shape of the energy surfaces in reciprocal space (k-space). This is to be done by extending the nearly-free-electron approximation and by using results already published in the literature. The third phase is an application of the results of the first two phases to certain problems in the theory of metals and alloys and to the appearance of energy gaps due to faint superstructures.

The work during the first three months of this project was devoted almost entirely to extending the nearly-free-electron approximation. The results were reported in Q.P.R. No. 1. The work during this second quarter has been on the construction of some higher Brillouin zones of the simple, face-centered, and body-centered cubic structures.

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[1]Air Research and Development Command Contract AF 18(600)-750, Project No. R-355-40-10, September, 1953. This report was erroneously labeled No. V instead of No. 1

BRILLOUIN ZONES

Summary of Known Results

There are several different definitions of Brillouin zones in use in the literature. In order to see the significance of the different definitions we will review briefly the general theory of electrons in a periodic lattice.

An electron moving in a periodic potential is described by a Bloch wave function

$$\Psi_{n,\vec{k}}(\vec{r}) = e^{2\pi i \vec{k}\cdot\vec{r}} U_{n,\vec{k}}(\vec{r})$$

where $\vec{k}$ is called the wave vector and n is a quantum number which labels different functions with the same $\vec{k}$. The energy of the electron is a periodic function in k-space:

$$E_n(\vec{k} + \vec{m}) = E_n(\vec{k}),$$

where $\vec{m}$ is a vector to a lattice point of the reciprocal lattice (defined below). Since $\Psi_{n,\vec{k}+\vec{m}} = \Psi_{n,\vec{k}}$, the wave vector $\vec{k} + \vec{m}$ describes the same physical state as the vector $\vec{k}$. Thus all physically different states with the quantum number n are described by any set of points in k-space which fill a (possibly multiply connected) region in k-space that has the following properties:

(i) For every interior point $\vec{k}$ in the region the point $\vec{k} + \vec{m}$ lies outside of the region for all reciprocal lattice vectors $\vec{m}$.

(ii) For every boundary point $\vec{k}$ of the region there is at least one other boundary point $\vec{k}'$ such that $\vec{k}' = \vec{k} + \vec{m}$ for some reciprocal lattice vector $\vec{m}$.

Which particular fundamental region in k-space with the properties (i) and (ii) is chosen is purely a matter of convenience for the problem being studied.

The different energy levels $E_n(\vec{k})$ are usually considered in one of two different ways. In the reduced zone scheme only $\vec{k}$ vectors in one region or zone are used; and the energy is considered to be a multivalued function in the zone, the different energy values being specified by n. In the expanded zone scheme all the k-space is divided up into an infinite number of different zones. Because of the periodicity of E, a different energy

band (different n) can be assigned to each zone, making the energy a single-valued but discontinuous function in all the k-space. By convention the different energy bands are assigned to the zones in such a way that, if the perturbative periodic potential vanished, the energy would go over to the energy of a free electron, which is $(h^2/2m)\,k^2$.

The three most important definitions of the Brillouin zones are described in the following paragraphs. Throughout this project, unless expressly stated to the contrary, we use L. Brillouin's definition of the Brillouin zones.

Brillouin's Definition[2]. Brillouin's definition is a purely geometrical one based on the concept of the reciprocal lattice. The direct lattice can be considered to be built up from the periodic repetition of a unit cell. In what follows we must choose any one of the unit cells which has the smallest possible volume. The direct lattice is made up by translations of this unit cell by integral multiples of three basic vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$. The basic vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ of the reciprocal lattice are defined by the following relations:

$$\vec{a}_i \cdot \vec{b}_j = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} .$$

The reciprocal lattice is defined to be the point lattice obtained by translating the point at the origin through the lattice vectors $\vec{m}$:

$$\vec{m} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3 ,$$

where m_1, m_2, and m_3 are integers. A more complete discussion of the reciprocal lattice can be found in almost any book on solid-state physics or on the diffraction of x-rays.

According to Brillouin the zones are defined in the following way. The perpendicularly bisecting planes of each of the lattice vectors $\vec{m}$ are constructed. These divide all the reciprocal space into polyhedrons. The polyhedron containing the origin is the first zone. The set of polyhedrons next to the faces of this zone form the second zone, and so forth. The set of zones thus defined has the following remarkable properties.

(a) The first zone is a unit cell of the reciprocal lattice.

(b) All zones have equal volume. Each higher zone can be cut up so that each part can be brought by one and only one

[2] Brillouin, L., J. Phys. Radium 1, 377 (1930).
_____, Wave Propagation in Periodic Structures, Dover Publications, Inc., 1953.

translation $\vec{m}$ to the inside of the first zone, and these parts then just fill the first zone without any overlapping of the parts.

It follows from these properties that each Brillouin zone can be taken to be a fundamental region of k-space. This definition of an extended zone scheme is particularly suitable for use in the nearly-free-electron approximation.

It should be noted that the simple hexagonal and the hexagonal close-packed structures have the same unit cell and hence the same reciprocal lattice. Therefore, according to Brillouin's definition the sets of Brillouin zones for the two structures are identical. Similarly, the sets of Brillouin zones for the diamond cubic and face-centered cubic structures are identical.

Group-Theoretical Definition[3]. It can be shown by group-theoretical methods that, just because the potential energy function of the electron has a certain symmetry, the energy surfaces in different energy bands may touch for k vectors which lie in certain symmetry points, lines, and planes of the reciprocal lattice.

It is desirable that whenever possible such points should lie on the surface of a zone. When precisely formulated, this criterion determines the complete zone boundary only for simple cases. For other cases this criterion requires that the surface contain only certain points, lines, and parts of planes. The remainder of the zone boundary can be completed by almost arbitrarily shaped curved surfaces, subject to the condition that the zone must satisfy the requirements of a fundamental region in k-space. By taking the arbitrary surfaces to be parts of suitable planes, the zones as defined by Brillouin are obtained.

Other Definitions. In a perturbation calculation of energy bands the natural choice for the surfaces not uniquely determined by the symmetry criterion mentioned above is that they be surfaces on which there is degeneracy of the unperturbed energy bands. Thus, in the nearly-free-electron approximation the natural choice is to take the plane faces of Brillouin's scheme. Seitz[4] has shown that there exist other perturbation methods for which the zone boundaries should contain certain curved surfaces on which there is degeneracy of the unperturbed energy bands.

It is possible, according to Seitz[4], to define in a purely geometrical way a set of zones which differs from Brillouin's set. Under some conditions this set is geometrically simpler than Brillouin's.

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[3]Bouckaert, L.P., Smoluchowski, R., and Wigner, E., Phys. Rev. 50, 58 (1936). Herring, C., Phys. Rev. 52, 361, 365 (1937).

[4]Seitz, F., The Modern Theory of Solids, McGraw-Hill Book Co., New York, 1940, Sections 61 and 63.

All the different zone schemes discussed in the preceding paragraphs can be made to coincide with Brillouin's scheme by suitably cutting up the zones and translating the parts by lattice vectors of the reciprocal lattice. Because of the periodicity of the energy, this cutting and translating operation has no physical significance, so that all the different zone schemes discussed up to now are equivalent.

Practical Definition. The practical definition is based on a consideration of the energy gap between adjacent parts of different zones in the extended zone scheme. In many substances the number of electrons per unit volume is such that the energy levels are occupied in one or more complete Brillouin zones and in parts of one or more additional Brillouin zones. Just which parts of the higher zones are filled depends both on the shape of the energy surface within the Brillouin zones and on the energy gaps between the Brillouin zones, and thus cannot be determined accurately without a complete solution of the problem of the energy levels of the periodic structure. However, it is often possible to make a reasonable guess as to the filled part, since the filling of the higher zones will usually start where the energy gap is small and will not take place where the energy gap is large. Thus, it is convenient to speak of a region in k-space which is surrounded by a large energy gap as the first "zone" and of the neighboring region across the gap as the second "zone". These zones are of great importance in determining the electronic properties of the substance. However, these zones are usually made up from parts of several Brillouin zones, and hence, they do not satisfy the first property of a fundamental region in k-space and do not have the properties (a) and (b) of zones as defined by Brillouin. Unfortunately, the practical zones are usually called "Brillouin zones" in the literature, which has led to some confusion. For example, the practical first zones of the hexagonal close-packed and diamond cubic structures are different from the first Brillouin zones of these structures.

It is hoped that knowledge obtained from this project of the exact shape of the higher zones and of the extension of the nearly-free-electron approximation will aid in a more accurate determination of the practical zones and the energy gap between them.

Some New Results

Work during this second quarter has been on the construction of Brillouin zones for the simple, face-centered, and body-centered cubic structures. The shapes of, say, the $(n + 1)$th zone is determined by adding suitable caps to the faces of the nth zone. The edges of these caps are parts of lines of intersection of the planes which perpendicularly bisect the lattice vectors of the reciprocal lattice. These lines can be determined by using simple geometrical theorems or by vectorial methods. For the latter method we have computed the perpendicular vector to the line of intersection, called the critical vector $\vec{k}_c$ in the Q.P.R. No. 1, and a vector parallel to

the line of intersection. It is believed that the general features of the method of construction of the Brillouin zones together with the volume check (all zones have equal volume), give a unique check on the correctness of the zone.

At the present time sketches have been made of the first six Brillouin zones of the face-centered cubic structure and of the first eight zones of the body-centered cubic structure. The complexity of the higher zones is evident from the following table.

BODY-CENTERED CUBIC STRUCTURE

Zone	1	2	3	4	5	6	7	8
Number of Faces	12	48	30	72	216	240	156	312
Number of Edges	24	72	48	120	336	384	264	480
Number of Corners	14	26	20	50	122	146	110	170

It is interesting to note the simplifications which occur for the third and seventh zones. It was found that the second zone of the body-centered cubic structure which is pictured in Seitz[4] and Kittel[5] is incorrect.

To aid in visualizing the shape of the Brillouin zones, solid models are being constructed of wood. The surface of each model is the outer surface of a Brillouin zone. Thus, the surface of the model of the nth zone is the outer surface of the nth zone, and the solid interior contains all zones up to and including the nth. Various methods of construction were investigated. Large power tools are of some use on the lower-ordered zones. The higher-ordered zones have so many small faces that the best method seems to be the combination of hand carving and the use of model-maker's tools powered by a flexible shaft. At present we have models of the first four zones of the simple cubic structure, of the first four zones of the face-centered cubic structure, and of the first three zones of the body-centered cubic structure.

When work on the cubic structures has been completed, both line drawings of the Brillouin zones and photographs of the models will be

[5]Kittel, C., Introduction to Solid State Physics, John Wiley and Sons, New York, 1953.

published. We gratefully acknowledge the assistance of Mr. Conrade C. Hinds, who is constructing the models of the higher-ordered zones.

PLANS FOR FUTURE WORK

The construction of models of higher Brillouin zones is being continued. At present it is planned to investigate the zones of the hexagonal close-packed structure in addition to the three cubic structures. Other structures will be investigated if time permits. Work on the nearly-free-electron approximation and on the Fourier coefficients of the potential, discussed in the Q.P.R. No. 1, will be resumed shortly.