Experimental analysis of the electronic structure of metals

EXPERIMENTAL ANALYSIS OF THE ELECTRONIC STRUCTURE OF METALS

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Abstract. After a short résumé of the general ideas and assumptions of the independent-particle model of a metal, an account is given of the experimental methods which have been, or may be, used to determine the details of the model for any given metal, with special reference to the shape of the Fermi surface and the electronic velocity at all points on the Fermi surface. Particular attention is paid to the exposition of the theory underlying each method, and as far as possible only simple mathematical and physical ideas are used. The conditions of application of the methods are discussed, and at the end examples are given of the results so far obtained by their use, with special emphasis on the analysis of the electronic structure of copper. The methods discussed are the following: Magneto-resistance, de Haas–van Alphen and Schubnikov effects, anomalous skin effect, cyclotron resonance, ultrasonic attenuation and magneto-acoustic effects, size effects.

§ 1. Introduction

The subject of this review is the use of experiment in obtaining as accurate as possible a description of a real metal, so that its properties, particularly those concerned with the transport of electrical charge and of thermal energy, may ultimately be understood more exactly than at present. It should, of course, be appreciated from the outset that no strictly exact description is possible. Even under the most ideal conditions, with electrons moving in a perfectly ordered ionic lattice at the absolute zero, exact specification involves writing down the ground state wave function of the assembly of electrons and nuclei—an impossible task. But fortunately this is not what is required. If there were any serious doubt about whether in principle the laws of quantum mechanics are adequate to account for the observed properties of metals one might have to consider questions of this sort. The task, however, is not to see

whether the fundamental laws give a correct description, but to discover a mental technique which will avoid as far as possible the necessity of referring to fundamental laws—to find a model whose properties can be apprehended instinctively, so that any calculations of these properties can be seen in their proper perspective, as more precise statements of what the physical imagination is prepared to accept as qualitatively intelligible. One cannot hope that the model will reproduce every detail of the experimental truth, but one may aim at a reasonable compromise ; a model not so elaborate as to bemuse the imagination, yet close enough to the truth to act as an acceptable substitute for it, above all one whose limits of validity are understood. Just how good a model one may expect to devise is a matter for speculation—certainly nothing like a satisfactory solution has been found yet, as can be seen from the tables comparing theoretical prediction with experimental results, to be found in any standard text on the theory of metals. Yet the limitations of existing models may not lie so much in the basic assumptions as in the introduction of simplifying approximations to make them analytically tractable. There is, in fact, a real need for the analysis, by numerical methods if all else fails, of models more generally formulated than some which have been studied in the past. But if the lack of such analysis is to be imputed a fault on the part of the theoreticians, the experimenters for their part cannot escape blame ; for in spite of the huge mass of information on almost every conceivable metallic property, it does not appear to be sufficient to allow an adequate model of a metal to be synthesized from it. The history of the development of metal physics has been one of invention, on theoretical grounds, of successively more plausible models, whose success has been gauged by comparison with experiment ; rarely has experiment led directly to an improvement in the model. The reason for this is to be found in the complexity of the problem, the properties which are most easily studied being determined by a large number of different parameters of the model, so that it is hard to make any definite statement about the values of these parameters by an examination of the data. In the last few years the situation has improved somewhat by the discovery of phenomena which are dependent on only a few parameters, and there is now some hope that a model of a metal may be synthesized on the basis of experiment and some rather general theoretical ideas. It is these phenomena with which we shall be concerned.

Underlying the whole treatment that follows is one great simplifying assumption, which certainly must lead to errors, but which it may be hoped will not be disastrous. This assumption is that the dynamics of the conduction electrons in the metal may be reduced to the quantum dynamics of individual particles, as if there were no interactions between the electrons. We shall not discuss in detail the measure of *a priori* justification which can be given to this assumption, but shall indicate briefly why it may be expected to work fairly well. In this discussion, as in the whole of what follows, we shall often adopt another approximation which, though perhaps unnecessary, may be regarded as a simplification of thought, especially by experimental physicists ; as far as possible we shall avoid the formalism of quantum mechanics and adhere to the representation of semi-classical mechanics, such as is associated with the names of Bohr, Sommerfeld and Wilson ; that is, the conceptual framework of classical mechanics patched up as necessary by empirical rules of quantization. It is desirable to emphasize that

this attitude is envisaged as a convenience and an aid to the imagination; it is only adopted when it is believed that the errors involved are negligible.

The simplest model of a metal is the free-electron model; the electrons are treated as if they formed a perfect gas of non-interacting particles moving in a rectangular box in which the potential is uniform. Since electrons are fermions the many-particle wave function is a determinant whose elements are individual plane wave functions, each of which is interpreted semi-classically as an individual unlocalized particle having well-defined momentum. Alternatively, by forming linear combinations of the plane waves, wave packets may be constructed to represent partially localized electrons whose momentum is correspondingly uncertain. Now in reality the electrons interact with one another through the long-range Coulomb potential e^2/r. Even although the mean electronic charge is neutralized by the positive lattice charge, local fluctuations in electron density set up fields which influence the whole assembly. So strong is this effect, indeed, that attempts to allow for it by perturbation methods fail through divergence of the distant interaction. A more powerful method of attack, due principally to Bohm and Pines (Pines 1955), analyses the fluctuations of density into their Fourier components, introducing collective variables for the electron assembly in a manner analogous to Debye's use of lattice vibration coordinates to describe the motion of the strongly interacting atoms of a solid. Each Fourier component of charge fluctuation (*plasma mode*) is a fairly independent entity with a characteristic frequency of oscillation $\omega_p = (4\pi Ne^2/m)^{1/2}$, where e is the electronic charge in e.s.u. To a first approximation all plasma modes have the same frequency. The quantum energy associated with a plasma oscillation, $\hbar\omega_p$, is many volts for most metals, so that at normal temperatures these oscillations are unexcited. If then we neglect the zero point plasma oscillations as of no account, we are led to believe that the spontaneous motions of the electrons are so linked as to set up no fluctuations in charge density. This is, however, true only as concerns fluctuations over distances rather larger than the mean distance between electrons, since there is a lower limit to the permissible wavelength for a plasma oscillation. In effect, then, the motions of electrons can be thought of as essentially uncorrelated, except in so far as they arrange to screen the long-range part of the Coulomb interaction, that is, their motions are correlated to the extent that no long-range variations of charge density occur, and in effect their interaction potential instead of being e^2/r approximates to the form $(e^2/r)\,\mathrm{e}^{-\kappa r}$, vanishing rapidly at large distances. The total number of permitted plasma modes is rather small compared with the number of electrons, and this means that the number of degrees of freedom described by independent collective modes is a small proportion of the total, and the restriction to freedom of movement of the particles fairly slight. In this respect there is a marked contrast to the Debye solid, in which all motions can be described in terms of independent oscillations, and the strongly interacting atoms of the solid may be replaced by a gas of phonons, quasi-particles whose motions are practically independent, but whose character is totally different from that of the atoms composing the solid. But in the metal the quasi-particles may be considered to resemble electrons very closely. It is probably not significant to enquire precisely how many quasi-particles there are, for, being fermions, they are nearly all packed down into the lowest-lying energy levels, one to each level in accord with the

Pauli exclusion principle, and the only ones that take part in transport and related properties are those lying within a few kT of the highest occupied energy level, the *Fermi level.* These properties are in fact determined by the wave number $\mathbf{k}$ of a quasi-particle at the Fermi level, and by the relation between energy and wave number for quasi-particles excited above the Fermi level and for holes left below the Fermi level by such excitations. There is no real need in discussing these properties to consider in any detail the precise description of the ground state of the assembly ; it is enough to know that the excitations are particle-like, and to know the relation between energy and wave number and the interactions between them. Since, however, they are particle-like it may be convenient to relate the quasi-particle picture to the model of non-interacting electrons, as we have just done by imagining the ground state to consist of an assembly of independent particles packed into the lowest states, the relation between ϵ and $\mathbf{k}$ at the Fermi level being chosen to correspond to the properties of the excitations. To take the quasi-particles as entirely independent is perhaps to go a little too far, since the screened Coulomb interaction is by no means obviously negligible. We must discuss what effect it is likely to have on the behaviour of the quasi-particles, in order to show that it is probably only a minor influence.

The intervention of the exclusion principle is of paramount importance in restricting the effect of electron–electron interactions. If the electrons (as we shall now refer to the quasi-particles) were not fermions and had a cross section for collision determined by the screened Coulomb potential, the mean free path between collisions of an electron in a metal would be only a few ångströms, the lifetime being correspondingly about 10^{-16} seconds. According to the uncertainty principle the energy of the single-particle state would be indeterminate to the extent of about 10 volts, and we should be unable to think of the electrons as even approximately independent unless we were considering phenomena involving energy interchanges of at least 10 volts. When we take account of the exclusion principle, however, everything is changed. In the collision of two electrons energy and momentum are conserved, and the states into which the electrons are scattered must both be unoccupied—in effect they must be states near or above the Fermi level. Thus if energy is to be conserved the only electrons which are already present and can collide are those lying in the thermally excited region near the Fermi surface. As a result any one electron belonging to this region cannot collide with each of the N electrons present, but only with something like NkT/ϵ_0, where ϵ_0 is the Fermi energy. Moreover, even if the two electrons come from the permitted region, not all collisions which conserve energy and momentum are permitted. For if one electron gains more than a few kT of energy the other will find itself with that much less, and no unoccupied state in which to fall. This requirement of no energy exchange exceeding a few kT imposes another factor of the order kT/ϵ_0 on the scattering probability. As a result the mean free path is not a few ångströms but something like $(\epsilon_0/kT)^2$ ångströms, say 10^{-4} cm at room temperature, 10 cm at 1°K. The energy uncertainty corresponding to this free path is smaller than the thermal spread of electron energies by a factor of about T/T_0, where T_0 is the degeneracy temperature ϵ_0/k, say 50 000°K. There is thus no serious bar at ordinary temperatures to treating the particles as independent for the purpose of thermodynamical

calculations. Moreover, at no ordinary temperatures does the probability of electron–electron collision approach that of electron–phonon or, at the lowest temperatures, electron–impurity collision. In discussing transport phenomena we may therefore regard the electrons as virtually independent particles suffering collision with thermally excited phonons or with static imperfections of the lattice. There is experimental confirmation of this view in comparisons between electrical conductivity σ and thermal conductivity κ of the same samples. If the dominant mechanism of electron scattering is elastic collisions with static imperfections, as at very low temperatures, the Wiedemann–Franz law is expected to hold under rather general conditions, the ratio $\kappa/\sigma T$ taking the value $\frac{1}{3}\pi^2 k^2/e^2$. Now the destruction of an electric current involves the transfer of momentum to the lattice, and electron–electron collisions do nothing to aid this, while conversely the destruction of a thermal current only involves a rearrangement of energy among the electrons, such as can be effected by electron–electron collisions as well as by electron–lattice collisions. The experimental verification of the Wiedemann–Franz law, even in extremely pure metals, with the correct numerical value of the ratio, shows that the probability of electron–electron collision is much less than that of electron–lattice collision.

By arguments of this sort, which have been given detailed treatment only for the over-idealized free electron model, we may support the conviction that it is worth while adopting the independent-particle hypothesis in discussing the electronic structure of real metals, in which the assumption of a uniform potential is certainly inadequate. It may be that experiments will ultimately show that no consistent independent-particle model can be devised, but this has not yet happened. It seems likely that, for most of the phenomena which we shall treat, the discrepancies attributable to electron–electron interactions will be quite small. If this should turn out to be a false hope, the model will have failed and more elaborate models will need to be devised ; there is little point in attempting to meet this situation yet.

Finally, one more simplifying assumption must be mentioned, the neglect of electron–lattice interactions of the type now known to be responsible for superconductivity. Although it seems certain that these interactions are strong enough in many metals to reverse the sign of the short-range interelectronic forces between electrons close to the Fermi energy, and to lead to a collective interaction at low enough temperatures, we shall assume that so long as a metal is not superconducting the independent-particle picture is still adequate, though it must be remembered that the electron–lattice interaction may play its part in determining the dynamical properties of electrons near the Fermi level. One might expect that all effects due to this interaction would show some dependence on M, the isotopic mass of the nucleus—for example, the superconducting transition temperature varies as $M^{-1/2}$—and the small amount of evidence that the electronic specific heat in the normal (non-superconducting) state is independent of the isotopic mass gives support to our neglect of the interaction. Present theories of superconductivity assume that in the normal state an independent-particle model is adequate, and that in the superconducting state the excitations have something of the character of the single particles in the normal state. If the present feeling of optimism about these theories should continue to be justified

by more detailed experimental confirmation, perhaps this will be the surest support for the independent-particle model of a normal metal, for all types of electron–electron and electron–lattice interactions contribute in an important measure to the structure of the superconducting state.

§ 2. The Independent-particle Model

The independent-particle model in its primitive form, as initiated by Sommerfeld and Bloch, disregards interactions between the electrons, except in so far as the mean Coulomb field may contribute to the potential in which each electron is moving independently. Under this assumption the problem of determining the properties of the metal is well defined, in the sense that a specification of the periodic potential determines the permitted energy states for the electrons, and from this all the properties follow in principle. We shall not concern ourselves here with an account of the elaborate techniques which have been devised to carry out this programme in specific instances (Herman 1958, Reitz 1955, Slater 1956), but shall confine our attention to those aspects of the problem which are common to all models of this type, and which are particularly relevant to the special topics under review.

We consider a particle moving in a periodic potential $V(\mathbf{r})$, having the property that $V(\mathbf{r}+l\mathbf{a}+m\mathbf{b}+n\mathbf{c}) = V(\mathbf{r})$, where l, m, n are integers, and $\mathbf{a}, \mathbf{b}, \mathbf{c}$ vectors defining the parallelepipedal unit cell which, replicated through all space, generates the periodic potential. The wave equation for the particle in such a potential has solutions which are analogous to the plane wave solutions for a particle moving in a uniform potential. The wave function takes the same form in each cell, but the phase of the function varies from cell to cell in a linear manner with position of the cell. Thus if $\mathbf{R}$ represents a point in a cell, measured from an origin in the cell, the wave function may be written

$$\psi(\mathbf{r}) = U(\mathbf{R})\,\mathrm{e}^{-i\mathbf{k}.(l\mathbf{a}+m\mathbf{b}+n\mathbf{c})}$$

where

$$\mathbf{r} = \mathbf{R}+l\mathbf{a}+m\mathbf{b}+n\mathbf{c}. \qquad \ldots\ldots(1)$$

Clearly by the substitution $U(\mathbf{R})\,\mathrm{e}^{i\mathbf{k}.\mathbf{R}} \equiv u(\mathbf{R})$, this can be re-expressed in a way which accentuates the similarity to a plane wave

$$\psi(\mathbf{r}) = u(\mathbf{R})\,\mathrm{e}^{-i\mathbf{k}.\mathbf{r}}. \qquad \ldots\ldots(2)$$

If $V(\mathbf{r})$ were constant, all solutions would have $u(\mathbf{R}) =$ constant; the nature of the periodic potential reveals itself in the form of $u(\mathbf{R})$ for any given $\mathbf{k}$, as well as in the energy of the particle whose wave function is characterized by $\mathbf{k}$.

The representation of $\psi(\mathbf{r})$ as a function $u(\mathbf{R})$ and a phase factor $\mathrm{e}^{-i\mathbf{k}.\mathbf{r}}$, as in (2), is not unique; for we may write

$$\psi(\mathbf{r}) = u(\mathbf{R})\,\mathrm{e}^{-i\mathbf{k}.\mathbf{r}} = u'(\mathbf{R})\,\mathrm{e}^{-i(\mathbf{k}+\mathbf{K}).\mathbf{r}},$$

provided that $\mathrm{e}^{-i\mathbf{K}.\mathbf{r}}$ is a function of $\mathbf{R}$ alone, so that $u'(\mathbf{R})\,\mathrm{e}^{-i\mathbf{K}.\mathbf{r}} = u(\mathbf{R})$. This implies, from (1), that

$$\mathrm{e}^{-i\mathbf{K}.(l\mathbf{a}+m\mathbf{b}+n\mathbf{c})} = \text{constant}. \qquad \ldots\ldots(3)$$

The constant can only be unity, and the vectors $\mathbf{K}$ which satisfy the equation form the *reciprocal lattice*. To construct this, consider the three vectors $\mathbf{K}_a$, $\mathbf{K}_b$ and $\mathbf{K}_c$ having the properties

$$\mathbf{K}_a.\mathbf{a} = 2\pi, \quad \mathbf{K}_a.\mathbf{b} = \mathbf{K}_a.\mathbf{c} = 0, \qquad \ldots\ldots(4)$$

and similarly for the other two. Then it is clear that if $\mathbf{K}$ is a sum of integral multiples of $\mathbf{K}_a$, $\mathbf{K}_b$ and $\mathbf{K}_c$ the exponent in (3) is an integral multiple of $2\pi i$, and (3) is satisfied.

As an example of this construction consider a crystal structure which is common in metals, the face-centred cubic lattice of figure 1. This may be derived from a unit cell containing one atom, whose vectors are $a_0(-1, 1, 0)$, $a_0(-1, -1, 0)$ and $a_0(1, 0, 1)$, where $2a_0$ is the cube side. It is easy to see that

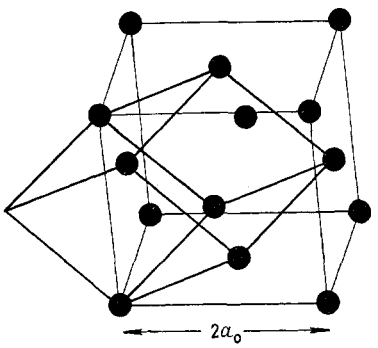

Figure 1. The face-centred cubic lattice, showing unit cell containing one lattice point.

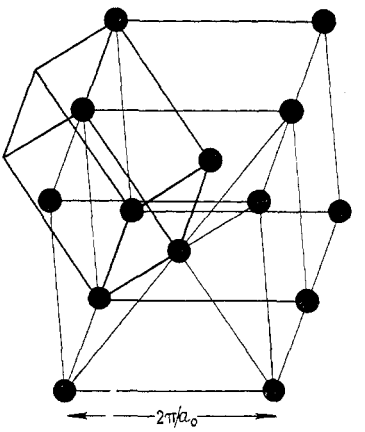

Figure 2. The body-centred cubic lattice, showing unit cell containing one lattice point.

the reciprocal lattice vectors which satisfy (4) are $(\pi/a_0)(-1, 1, 1)$, $(\pi/a_0)(-1, -1, 1)$ and $(\pi/a_0)(0, 0, 2)$; these define a cell which on repetition generates the body-centred cubic lattice, as in figure 2. Any vector $\mathbf{K}$ joining two points of this lattice may be added to $\mathbf{k}$ in (2) to give (with suitable modification of $u(\mathbf{R})$) an equivalent expression for $\psi(\mathbf{r})$. Thus the energy of an electron may be represented as a periodic function of $\mathbf{k}$; if $\epsilon(\mathbf{k})$ is known within one unit cell of the reciprocal lattice, it is known for all $\mathbf{k}$. As a matter of convenience it is usual to redefine the unit cell so as to exhibit more clearly its cubic symmetry; any dissection of the cell in figure 2, with reconstruction after translation of some of its parts through a reciprocal lattice vector, is a permissible redefinition, and the cell of figure 4 may be considered to arise in this way. It contains one lattice point as its centre, and by repetition fills all space and generates the body-centred cubic lattice. An equivalent construction for the face-centred cubic lattice is shown in figure 3. If the metallic lattice is face-centred cubic, figure 3 is the *atomic polyhedron* and figure 4 the *first Brillouin zone* in reciprocal space; while for a body-centred cubic lattice the diagrams are reversed, the atomic polyhedron having the form of figure 4 and the Brillouin zone the form of figure 3.

We have seen that a specification of $\epsilon(\mathbf{k})$ within the Brillouin zone provides complete information about the solution of the wave equation, but it must be realized that for a given potential $V(\mathbf{r})$ there is an infinite number of solutions corresponding to each $\mathbf{k}$, having different energies and different $u(\mathbf{R})$. This is

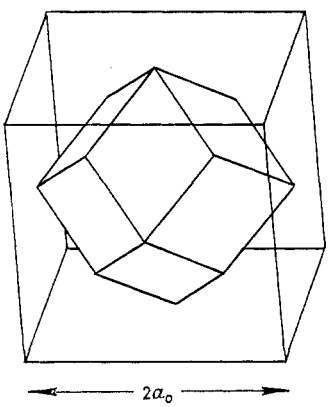

Figure 3. The atomic polyhedron for a face-centred cubic lattice.

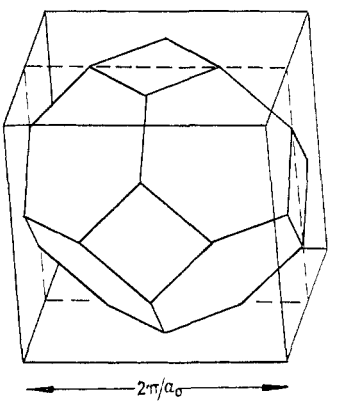

Figure 4. The first Brillouin zone for a face-centred cubic lattice.

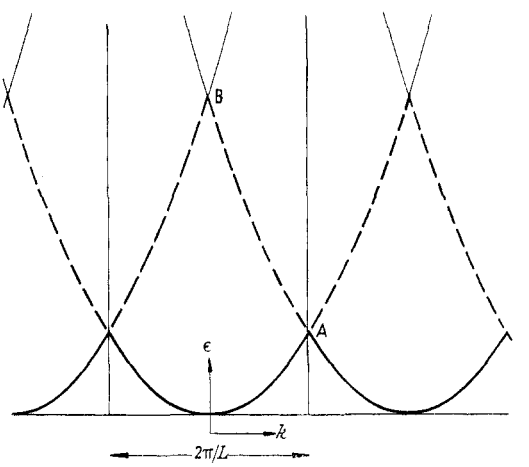

Figure 5. $\epsilon(k)$ for free electron in one dimension, with artificial zone structure imposed.

simply illustrated by an almost trivial one-dimensional example, a particle moving on a line in a uniform potential so that $\epsilon = \hbar^2 k^2/2m$. Let us now divide the line into segments of length L, thus artificially defining a cellular structure ; a typical solution of the wave equation may now be written

$$\psi(x) = \mathrm{e}^{-ikx} = \mathrm{e}^{2\pi i X/L}\,\mathrm{e}^{-i(k+2\pi/L)\,x} \quad \text{etc.},$$

in which the variation of $\psi(x)$ in a single cell, $u(X)$, takes the successive forms $1, \mathrm{e}^{2\pi i X/L}, \ldots, \mathrm{e}^{2\pi n i X/L}, \ldots$, and the value of k is correspondingly changed by multiples of the reciprocal lattice vector $2\pi/L$. The curves of $\epsilon(k)$ are shown in figure 5. The different parabolae correspond to different choices of K $(= 2\pi n/L)$,

and the thickened and broken curves are the lowest two branches of the $\epsilon(k)$ relation in the periodic k-space.

Let us now see what happens when $V(x)$ is not constant, but varies periodically with period L. Then the two degenerate solutions at the point A may have their degeneracy removed if their wave functions combine with the periodic potential to produce a non-vanishing matrix element. For this to be so it is only necessary, since the two solutions at A are simple sine waves differing in wave number by $2\pi/L$, that $V(x)$ shall have a Fourier component of wave number $2\pi/L$, and this will commonly be the case unless the form of $V(x)$ specifically excludes this particular component. Similarly the degeneracy at B is removed by a Fourier component of wave number $4\pi/L$. The effect of a small periodic potential is illustrated in figure 6, from which it will be seen that the periodic branches have now separated and become continuous and differentiable functions,

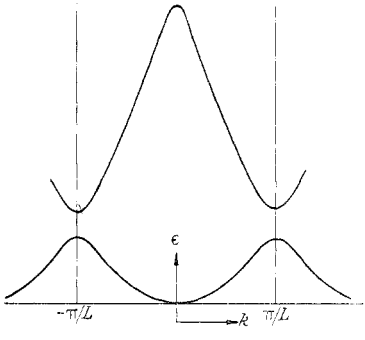

Figure 6. $\epsilon(k)$ for electron in one dimension, with small periodic potential, illustrating reduced and periodically extended zone schemes.

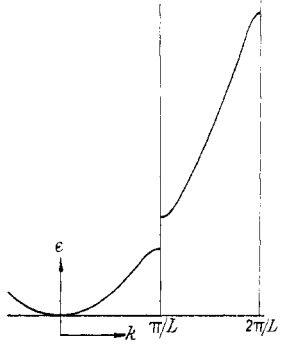

Figure 7. As figure 6, but displayed in extended zone scheme.

while the original smooth parabolas have broken, so that there are energy gaps between the branches at all points. It is worth observing that the transition from figure 5 to figure 6 primarily involves a change of connectivity rather than the appearance of discontinuities—in both diagrams the curves are analytic but of quite different form. In order to give in graphical form a complete specification of $\epsilon(k)$, only the portion of figure 6 lying within $\pm\pi/L$ is necessary ; this is known as the *reduced zone scheme.* Alternatively, it may be convenient, especially if the $\epsilon(k)$ curve can thereby be made to approximate to a parabola, to allow k to run between $\pm\infty$ and to display $\epsilon(k)$ as a single-valued function, as in figure 7 ; this is the *extended zone scheme.* Finally, it will be useful to bear in mind that the reduced zone scheme may be repeated at will, as is begun in the lower curve of figure 6, to produce a multi-valued function $\epsilon(k)$ extending over all values of k ; this is the *periodically extended zone scheme.*

The change in connectivity of the $\epsilon(k)$ curves, resulting from the removal of degeneracies at the edges of the Brillouin zone, can make considerable differences to the form of the lines and surfaces of constant energy when we treat the motion of a particle in two- and three-dimensional lattices. As an example, consider a square two-dimensional lattice as in figure 8, whose reciprocal lattice is the square

lattice of figure 9. It is not difficult to see that, in general, any reciprocal lattice vector **K** represents a possible component present in the Fourier analysis of the corresponding lattice potential $V(\mathbf{r})$ into components of the type $e^{-i\mathbf{K}.\mathbf{r}}$. For it is necessary, if this component is to be present, that $(1/N)\Sigma e^{-i\mathbf{K}.(l\mathbf{a}+m\mathbf{b}+n\mathbf{c})}$, summed over all N lattice points, shall not vanish ; this is clearly ensured by the definition of the reciprocal lattice. It should be mentioned, though we shall pursue this matter no further, that this is not a sufficient condition for the occurrence of a

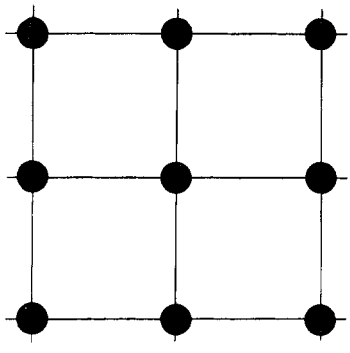

Figure 8. Two-dimensional square lattice.

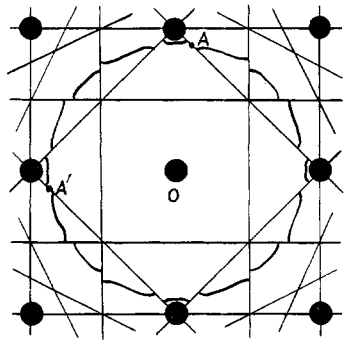

Figure 9. Reciprocal lattice of figure 8, showing construction of zone boundaries, and a typical line of constant energy (for small periodic potential).

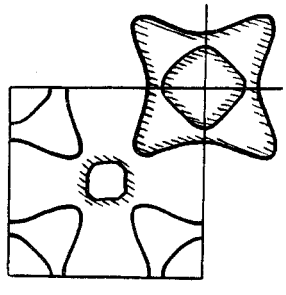

Figure 10. Lines of constant energy in figure 9 remapped into reduced and (top right-hand corner) periodically extended zone scheme. Regions of lower energy are indicated by shading.

given Fourier component. For the present example we assume that all Fourier components defined by the reciprocal lattice are present.

Now, taking one reciprocal lattice point as origin, draw the perpendicular bisectors of all lines joining it to other reciprocal lattice points, as in figure 9. Then, from the construction, any point A on one of these lines (which are the boundaries of higher-order Brillouin zones) may be associated with a point A′ such that AA′ is a reciprocal lattice vector and $OA = OA'$. Thus electrons whose wave vectors are $\overrightarrow{OA}$ and $\overrightarrow{OA'}$ have the same energy if $V(\mathbf{r})$ is constant, and are capable of having their degeneracy removed by the lattice potential when this is taken into account. If the lattice potential is only very small the separation of originally degenerate levels will also be very small, so that a line of constant energy, originally a circle, is only slightly deformed as it crosses the Brillouin

zone boundaries. The new line of constant energy may be remapped into the first Brillouin zone to give a reduced zone picture, as shown in figure 10, of which one corner shows the beginning of the periodic extension of the diagram. In this way it will be seen how the removal of degeneracy breaks up the line of constant energy into three separate branches, which are to be regarded as contours on three distinct sheets of the function $\epsilon(\mathbf{k})$. Moreover, as the shadings reveal, in two of these branches the regions of lower energy lie within the closed curves, as in the original circle, while in the third they lie outside.

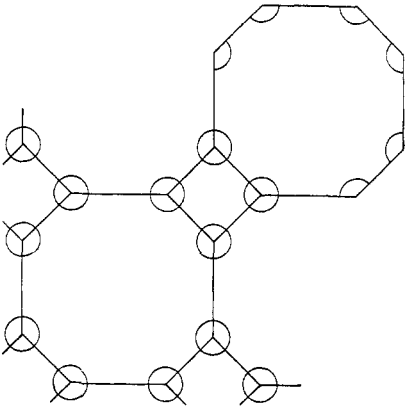

Figure 11. Section of periodically extended zone scheme for face-centred cubic lattice, showing energy surface near corners of the Brillouin zone. The section shown is indicated by a broken line in figure 4.

In three dimensions, the variety of possible forms of energy surface is even greater. If the surface is closed and wholly within the first Brillouin zone, the periodically extended zone scheme merely repeats it as a lattice of isolated closed surfaces. If the surface lies near the corners of the first Brillouin zone, as in figure 11, periodic extension again produces a lattice of isolated closed surfaces (in this case six to every unit cell of the body-centred reciprocal lattice); and if in figure 11 the states of lower energy lie closer to the centre of the zone, then each little closed surface in the extended scheme encloses states of higher energy. A third possibility, which is particularly to be expected with lattices having a high axial ratio, is shown in figure 12, the extended zone scheme giving an array of tubes. And lastly, a multiply-connected surface may arise from contacts with the zone boundary; a simple example may be seen in figure 14. Just as in figures 9 and 10 a very small lattice perturbation of the circular energy curve could result in quite a complex picture in the extended zone scheme, so a repetition of the construction for a three-dimensional lattice gives a remarkable variety of constant energy surfaces. A particular case has been discussed by Gold (1958), the remapping (with rounding-off of corners) of the sphere which in figure 4 would have a volume just equal to the cube, and which therefore lies entirely outside the first Brillouin zone. One of the resulting surfaces in the extended scheme is shown in figure 13.

In the preceding discussion we have assumed that ϵ is a continuous function of $\mathbf{k}$, and indeed for most purposes this is a reasonable assumption. Strictly,

however, in a finite sample, only discrete values of **k** are permitted, such as will allow the wave function to satisfy boundary conditions at the sides of the sample. If we employ the conventional periodic boundary conditions, and a rectangular sample, the permitted values of **k** are such that an integral number of wavelengths

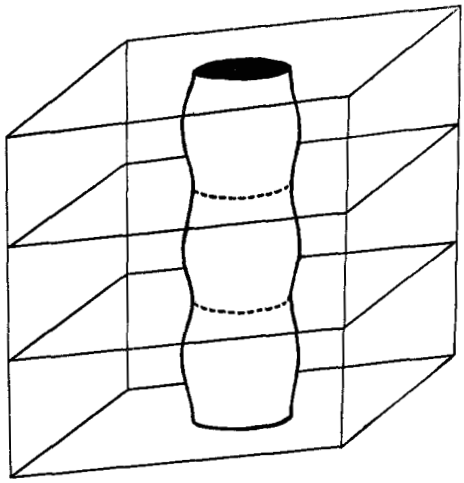

Figure 12. Tubular energy surface in periodically extended zone scheme.

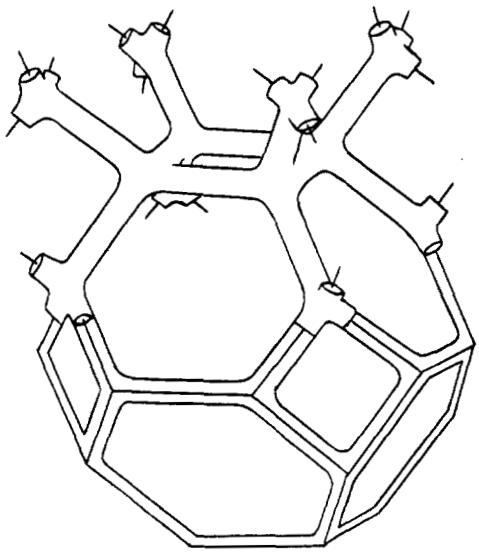

Figure 13. Tubular lattice, suggested by Gold as possible energy surface for lead. (*After* Gold 1958.)

will fit into the sample. For a sample of sides A, B and C, we must have $k_x A = 2n_x\pi, k_y B = 2n_y\pi, k_z C = 2n_z\pi$, and this implies that in reciprocal space the permitted values of **k** form a rectangular lattice, whose unit cell has volume $8\pi^3/V$, where $V = ABC$, the volume of the sample. The exclusion principle allows each of the states represented by a lattice point to be occupied by not more than two electrons (one of each spin), so that the maximum permitted density of

occupation is $V/4\pi^3$ electrons per unit volume of reciprocal space. From figure 4 it will be seen that the volume of the Brillouin zone for a face-centred cubic lattice is $4\pi^3/a_0^3$, so that the zone will hold V/a_0^3 electrons. Now in a volume V, from figure 3, there are $\frac{1}{2}V/a_0^3$ atoms; therefore the Brillouin zone will hold two electrons per atom. This is a general result for those structures whose unit cell holds only one atom. More complex structures (such as that of tin) need more careful discussion, but we shall confine our attention to metals of simpler form.

At the absolute zero the conduction electrons occupy the lowest available energy states, and therefore fill all levels up to a certain energy, the *Fermi energy*, such that the number of states contained within the corresponding energy surface (*Fermi surface*) is just equal to the number of conduction electrons. For one-electron atoms, such as the alkalis and noble metals (if we assume that the core electrons can be ignored), the Fermi surface encloses a volume equal to one-half the volume of the Brillouin zone. We might therefore hope that it would be a fairly simple closed surface lying within the zone; we shall see that this hope is probably not realized in some at least of the metals of this group. For no other metals can we reasonably expect any simplicity of this sort, and our previous discussion leads us to believe that the form of the Fermi surface may be very strange, probably breaking up into several separate sheets of which some may have complex connectivity in the periodically extended scheme. It is this expectation which makes doubtful the value of attempts to discuss the properties of real metals in terms of model $\epsilon(\mathbf{k})$ relations which are easy to handle analytically, such as the two-band model in which the Fermi surface consists of two sets of ellipsoids. Detailed analysis of these models is certainly of value in developing and comparing mathematical methods which may be applied to more difficult situations, but very little meaning can usually be attached to the parameters which are chosen to fit a particular set of experimental data.

At temperatures above the absolute zero those electrons with energy within a few times kT of the Fermi energy will be thermally excited, the probability of occupation of a given energy state being expressed by the Fermi distribution function $\{\exp(\epsilon-\zeta)/kT+1\}^{-1}$, in which ζ is chosen so that the total number of occupied states is equal to the number of electrons. For most purposes the distinction between ζ and the Fermi energy ϵ_0 is negligible. It is clear from this distribution function that the thermal energy is proportional to the number of electronic states per unit energy range at the Fermi surface; if this is written as N_0, the number of empty states below the Fermi surface is of the order $N_0 kT$, the electrons which occupied them at 0°K having been excited by energies of the order kT, so that the thermal energy is roughly $N_0 k^2 T^2$ (the true value, obtained by integrating the Fermi distribution, is $\frac{1}{3}\pi^2 N_0 k^2 T^2$). Thus the specific heat of the electrons is proportional to the temperature, $C=\gamma T$, the constant γ being $\frac{2}{3}\pi^2 N_0 k^2$. Measurements of γ, for which reliable data now exist for many metals, enable N_0 to be computed. In the independent-electron model N_0 may be related to the velocities of electrons on the Fermi surface, in the way we shall now discuss.

We have so far concerned ourselves only with individual electronic states, represented by plane waves of definite wave number $\mathbf{k}$ and frequency ω $(=\epsilon/\hbar)$. The picture can be made to resemble a classical particle-picture by constructing wave-packets out of a group of plane waves centred on a particular value of $\mathbf{k}$.

This group moves through the metal with a group-velocity $\mathrm{grad}_k\,\omega$, e.g. the x-component of the velocity is $(1/\hbar)\partial\epsilon/\partial k_x$.† The motion of the group determines the motion of the electron which it describes, so that it is permissible to say that an electron described by a wave vector $\mathbf{k}$ is travelling through the metal with velocity $\mathbf{v}(\mathbf{k}) = \hbar^{-1}\,\mathrm{grad}_k\,\epsilon$, contributing to the current an amount $e\hbar^{-1}\,\mathrm{grad}_k\,\epsilon$ and to the momentum $m\hbar^{-1}\,\mathrm{grad}_k\,\epsilon$. In general, one must distinguish between the real momentum $m\hbar^{-1}\,\mathrm{grad}_k\,\epsilon$ which can be detected in principle by macroscopic ballistic methods, and the quasi-momentum (crystal momentum) $\hbar\mathbf{k}$ which is a formal construction based on analogy with de Broglie's relation for free particles. It will be seen that the electronic velocity, being proportional to $\mathrm{grad}_k\,\epsilon$, is directed normal to a surface of constant energy and is inversely proportional to the separation of neighbouring energy surfaces. In this way it is immediately related to the density of states. For if dS is an element of area of the Fermi surface, construct a right cylinder having base dS; then the volume of this cylinder contained between the Fermi surface and the surface of energy $d\epsilon$ greater will be $dS/|\mathrm{grad}_k\,\epsilon|\,d\epsilon$, and since for a sample of volume V there are $V/4\pi^3$ states per unit volume of reciprocal space, the cylinder contains $VdSd\epsilon/[4\pi^3|\,\mathrm{grad}_k\,\epsilon\,|]$ states. Hence, by integration over all parts of the Fermi surface, we have that

$$\frac{N_0}{V} = \frac{1}{4\pi^3}\int\frac{dS}{|\mathrm{grad}_k\,\epsilon|} = \frac{S}{4\pi^3\hbar}\left(\overline{\frac{1}{v_0}}\right), \qquad \ldots\ldots(5)$$

where $\overline{(1/v_0)}$ is the average value of the reciprocal of the *Fermi velocity* (the velocity of an electron at the Fermi surface), and S is the total area of the Fermi surface.

The wave-packet picture of an electron in motion enables us to see immediately, by classical analysis, how the electron reacts to applied electric and magnetic fields. In a uniform electric field $\mathbf{E}$ the rate of transfer of energy from the source of the field to the electron is $e\mathbf{v}.\mathbf{E}$; since $\dot{\epsilon}$ can be written as $\dot{\mathbf{k}}.\mathrm{grad}_k\,\epsilon$, it follows that

$$\dot{\mathbf{k}}.\mathrm{grad}_k\,\epsilon = (e/\hbar)\,\mathbf{E}.\mathrm{grad}_k\,\epsilon,$$

which is satisfied if $\hbar\dot{\mathbf{k}} = e\mathbf{E}$, the rate of change of crystal momentum being equal to the force on the electron. Thus every electron is affected in the same way by an electric field, and the distribution of occupied states in reciprocal space is simply shifted uniformly at a rate $\dot{\mathbf{k}} = e\mathbf{E}/\hbar$. One may allow for zone boundary effects by plotting the occupied states in the periodically extended zone scheme, and allowing the whole diagram, except the zone boundaries, to shift uniformly, while only taking account of those occupied states which lie within the first zone. From this it is obvious that the distribution in a completely filled zone is unchanged by a field, and therefore contributes nothing to the current. If the zone is not filled it is easy to write down an expression for the rate of increase of current density under the influence of a uniform field. Consider a small area $d\mathbf{S}$ of the

† To demonstrate this we observe that the phase of a plane wave at $(t, \mathbf{r})$ is given by the expression $\phi = \omega t - \mathbf{k}.\mathbf{r}$. Now any recognizable feature of the wave group owes its character to the particular phase-relationship existing between the various plane-wave components, and if we move through the lattice at such a velocity $\mathbf{v}$ that this relationship is maintained we shall keep in step with the group. To effect this $\mathbf{v}$ must be such that when $\mathbf{r} = \mathbf{v}t$, $\mathrm{grad}_k\,\phi$ does not change with time, i.e.

$$\mathrm{grad}_k\,(\omega - \mathbf{k}.\mathbf{v}) = 0.$$

Since $\mathrm{grad}_k\,(\mathbf{k}.\mathbf{v}) = \mathbf{v}$, $\mathbf{v} = \mathrm{grad}_k\,\omega$.

Fermi surface, imagined, as at 0°K, to be a sharp division between occupied and unoccupied states. After time dt the boundary of occupation has shifted by $e\mathbf{E}dt/\hbar$, so that a new element of occupied volume $edt\mathbf{E}.d\mathbf{S}/\hbar$ has appeared, containing $edt\mathbf{E}.d\mathbf{S}/(4\pi^3\hbar)$ electrons per unit volume of metal. Since each electron moves with velocity $\hbar^{-1}\operatorname{grad}_k \epsilon$, the contribution of this element to the current density is $e^2\,dt\mathbf{E}.d\mathbf{S}\operatorname{grad}_k \epsilon/(4\pi^3\hbar^2)$, so that we may write for the rate of increase of the total current density

$$\mathbf{j} = \frac{e^2}{4\pi^3\hbar^2}\int(\operatorname{grad}_k \epsilon)\,\mathbf{E}.d\mathbf{S}, \qquad \ldots\ldots(6)$$

the integral being taken over the whole Fermi surface. For a crystal of cubic symmetry this expression must be independent of the orientation of $\mathbf{E}$, and is therefore unchanged by averaging over all orientations of $\mathbf{E}$ relative to the crystal axes. From this averaging it follows immediately that

$$\mathbf{j} = \frac{e^2\mathbf{E}}{12\pi^3\hbar^2}\int|\operatorname{grad}_k \epsilon|\,dS = \frac{e^2\,\mathbf{E}S\overline{v_0}}{12\pi^3\hbar}. \qquad \ldots\ldots(7)$$

This expression may also be used with reasonable accuracy for a polycrystalline sample of a non-cubic metal. It may be observed that for a quasi-free-electron model of a metal, having N electrons per unit volume, and with ϵ given by $\hbar^2k^2/(2m^*)$, m^* being the *effective mass*, the radius of the Fermi sphere, k_0, is $(3\pi^2N)^{1/3}$, $S = 4\pi(3\pi^2N)^{2/3}$, $v_0 = \hbar(3\pi^2N)^{1/3}/m^*$, and therefore $\mathbf{j} = Ne^2\mathbf{E}/m^*$.

The steady increase of current does not continue indefinitely in a real metal on account of collisions between the electrons and lattice imperfections, e.g. impurity atoms or lattice waves. As a result the displacement at any region of the Fermi surface ultimately reaches a steady limit, and it is not uncommon to assume for convenience that the approach to the limit is exponential; at a time t after application of the field the displacement $\Delta\mathbf{k}$ is given by $\Delta\mathbf{k}_\infty(1-e^{-t/\tau})$, where $\Delta\mathbf{k}_\infty$ is the limiting value and τ the relaxation time, which may vary with position on the Fermi surface. If this law is obeyed, it is clear that the initial rate of increase of $\Delta\mathbf{k}$ is just $\Delta\mathbf{k}_\infty/\tau$, so that we may immediately modify (6) to give an expression for the steady current

$$\mathbf{J} = \frac{e^2}{4\pi^3\hbar^2}\int(\tau\operatorname{grad}_k \epsilon)\,\mathbf{E}.d\mathbf{S}. \qquad \ldots\ldots(8)$$

For a cubic or polycrystalline metal the conductivity takes the form, from (7),

$$\sigma \equiv \mathbf{J}/\mathbf{E} = \frac{e^2\,S\overline{v_0\tau}}{12\pi^3\hbar} = \frac{e^2\,S\bar{l}}{12\pi^3\hbar}. \qquad \ldots\ldots(9)$$

Here l, which may vary with position on the Fermi surface, is the mean free path, defined as $v_0\tau$, and $\bar{l}$ is its average value taken over the Fermi surface. We shall return later to a somewhat fuller discussion of the relaxation process.

In a magnetic field the classical interpretation of the wave-packet leads us to expect a Lorentz force $e\mathbf{H}\times\mathbf{v}$† on an electron, and this expectation is more or less (though perhaps not perfectly) justified by detailed quantal analysis. Since the velocity $\mathbf{v}$ is directed normally to a surface of constant energy, the Lorentz force always acts tangentially to such a surface, so that the energy remains

† From now on we shall work in electromagnetic units.

unchanged by the magnetic field. But the crystal momentum $\hbar\mathbf{k}$ changes at a rate equal to the Lorentz force, so that $\mathbf{k}$ travels around the orbit in reciprocal space defined by the intersection of the constant energy surface with a plane normal to $\mathbf{H}$, i.e. k_z = constant if $\mathbf{H}$ is taken parallel to the z-axis. Correspondingly, in real space the electron describes an orbit, which bears a very simple relationship to the orbit in reciprocal space. For we may write the equation of motion

$$\dot{\mathbf{k}} = (e/\hbar)\,\mathbf{H} \times \dot{\mathbf{r}}, \qquad \ldots\ldots(10)$$

from which it follows that the variations of the position vector $\mathbf{r}$ (strictly, the components of $\mathbf{r}$ in the plane z = constant) are related to those of $\mathbf{k}$ by a factor $\hbar/(eH)$, constant in constant field, and by a rotation through $\pi/2$. Thus the orbit in real space, projected on a plane normal to $\mathbf{H}$, has the same shape as the $\mathbf{k}$-orbit, but is larger by a factor $\hbar/(eH)$ and rotated through $\pi/2$. This result says nothing about the z-component of the motion, parallel to $\mathbf{H}$, which may in general be quite a complicated periodic function superposed on a mean drift; by following the variation of the z-component of $\mathbf{v}$ around the $\mathbf{k}$-orbit the nature of this motion may be elucidated in any particular case. If the energy surfaces are spherical or, more generally, axially symmetric about the z-axis, the drift velocity is constant and the electron describes a regular helix.

Since the motion in a magnetic field is periodic in the plane z = constant we may expect quantization to occur. An exact treatment for electrons in a periodic lattice has not been given, but the rigorous theory of free electrons finds a simple interpretation in the Bohr–Sommerfeld quantum theory, which can be extended heuristically (Onsager 1952) to the more general case to give results of considerable interest and value. What is involved here is an evaluation of the phase integral

$$\oint p\,dq,$$

which is set equal to a multiple of h or to $(n+\varphi)h$ where φ is an undetermined phase factor. In the phase integral the proper momentum conjugate to the position vector $\mathbf{r}$ is not $\hbar\mathbf{k}$ but $\hbar\mathbf{k}-e\mathbf{A}$, where $\operatorname{curl}\mathbf{A} = \mathbf{H}$. If now we take $\boldsymbol{\kappa}$ and $\boldsymbol{\rho}$, measured from equivalent origins, as the components of $\mathbf{k}$ and $\mathbf{r}$ in the plane normal to $\mathbf{H}$, (10) may be integrated to take the form $\hbar\boldsymbol{\kappa} = e\mathbf{H}\times\boldsymbol{\rho}$, so that the phase integral becomes

$$\oint (\hbar\boldsymbol{\kappa} - e\mathbf{A}).\,d\boldsymbol{\rho},$$

which may be rewritten as $\oint [e\mathbf{H}.(\boldsymbol{\rho}\times d\boldsymbol{\rho}) - e\mathbf{A}.d\boldsymbol{\rho}]$.

Since

$$\oint \boldsymbol{\rho}\times d\boldsymbol{\rho}$$

is twice the projected area of the orbit in real space and

$$\oint \mathbf{A}.d\boldsymbol{\rho}$$

is Φ, the flux contained within the orbit, we see that

$$\oint p\,dq = e\Phi = (n+\varphi)h.$$

This defines the permitted orbits, whose projected areas may only be $(n+\varphi)$ times $h/(eH)$; correspondingly, in reciprocal space the only permitted regions of the energy surfaces are those intersections with planes k_z = constant having areas $\mathscr{A}$ in accordance with the expression

$$\mathscr{A} = (n+\varphi)\,2\pi eH/\hbar. \qquad \ldots\ldots(11)$$

This result, which we shall call Onsager's theorem, holds the clue to the understanding of the de Haas–van Alphen effect which we shall consider in detail later. For the present, however, we note that for many purposes, particularly in the discussion of transport phenomena, it appears to be possible to distinguish features which owe their existence to quantization from those which are uninfluenced by it.

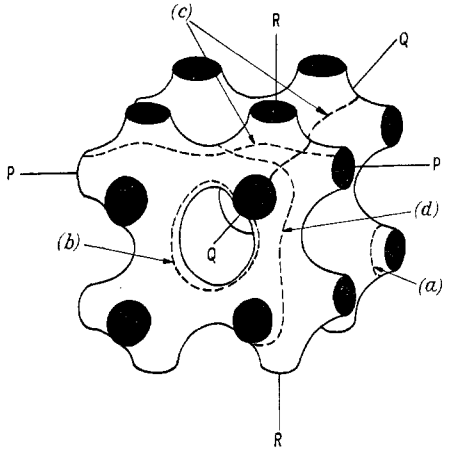

Figure 14. Multiply connected energy surface in periodically extended zone scheme showing: (*a*) electron orbit, (*b*) hole orbit, (*c*) open orbits, (*d*) extended orbit: P, Q, R, axes of open orbits.

The geometrical similarity of the orbits in real and reciprocal space enables us to discuss their principal features with reference to reciprocal space only, and to observe that (with one exception, which occurs when two bands are degenerate at the same value of **k**, and with which we shall not concern ourselves) all types of orbit are described in terms of sections of the periodically extended zone structure by planes normal to **H**. Thus orbits may be closed, open or extended, as illustrated in figure 14. Closed orbits may be of two types, the electron orbit (14(*a*)) which encloses states of lower energy, so that the velocity vector is directed outwards, and the hole orbit (14(*b*)) which encloses states of higher energy so that the velocity vector is directed inwards. If one looks along the direction of **H** (from South to North) an electron in an electron orbit is seen to rotate clockwise, while an electron in a hole orbit rotates anti-clockwise, as if it were positively charged. An electron in an open orbit (if orbit is the right word) describes a wavy path whose general direction is straight (14(*c*)). An extended orbit (14(*d*)) is one which extends in reciprocal space over a region which cannot be contained in one Brillouin zone, however this is placed. It should be noted, therefore, that an orbit such as 14(*b*), although it may cross the boundary of the Brillouin zone whose centre is the origin of **k**, is not an extended orbit according to our definition,

since by shifting the centre of the zone the orbit can be wholly enclosed. It is also worth noting that when the energy surface in the extended scheme is multiply-connected, as in figure 14, it is not possible to ascribe ' electron-like ' or ' hole-like ' character to any part of the energy surface. The same point may, with different orientations of the magnetic field, belong to electron or hole orbits, or to extended or open orbits.

Before leaving the topic of orbits let us calculate the frequency of rotation in the orbit, the *cyclotron frequency* of the particular orbit. Consider two orbits in reciprocal space, in the same section normal to **H**, being sections of the energy surfaces ϵ and $\epsilon + d\epsilon$. At any point their distance apart is $d\epsilon/|\mathrm{grad}_k\,\epsilon|$ or $d\epsilon/(\hbar v)$; so that if $d\kappa$ is an increment of length measured along the orbit, the area of the annulus between the orbits is

$$\frac{d\epsilon}{\hbar}\oint\frac{d\kappa}{v}.$$

Thus

$$\frac{d\mathscr{A}}{d\epsilon}=\frac{1}{\hbar}\oint\frac{d\kappa}{v}.$$

Now the Lorentz force on the electron is evH, so that the time taken to traverse the element $d\kappa$ is $\hbar d\kappa/evH$, and the periodic time of the orbit is

$$\frac{\hbar}{eH}\oint\frac{d\kappa}{v}\quad\text{or}\quad\frac{\hbar^2}{eH}\frac{d\mathscr{A}}{d\epsilon}.$$

We have therefore an expression for the cyclotron frequency

$$\omega_c=\frac{2\pi eH}{\hbar^2}\left(\frac{d\mathscr{A}}{d\epsilon}\right)^{-1}.$$

For free electrons having a component of wave number k in the plane normal to **H**, $\mathscr{A}=\pi k^2$ and $\epsilon=\hbar^2k^2/2m=\hbar^2\mathscr{A}/2\pi m$; so that $\omega_c=eH/m$, which is independent of the energy of the electron. In general, however, ω_c is different for each orbit. If we define the *cyclotron mass* of a given orbit by the equation $m_c^*=(\hbar^2/2\pi)(d\mathscr{A}/d\epsilon)$ we may write, analogously to the free electron case,

$$\omega_c=\frac{e}{m_c^*}H. \qquad \ldots\ldots(12)$$

It is interesting to compare (11) and (12): if the quantum number in (11) is reasonably large so that only a small fractional change of ϵ is involved in changing from one permitted level to the next, we may treat m_c^* as sensibly constant and determine the energy difference between two levels, corresponding to $\Delta\mathscr{A}$ being equal to $2\pi eH/\hbar$,

$$\Delta\epsilon=\frac{\hbar^2\omega_c}{2\pi eH}\Delta\mathscr{A}=\hbar\omega_c.$$

An oscillatory field in resonance with the orbit has thus a quantum energy which is just right for exciting a transition between permitted levels. This result, which is precisely paralleled by the Bohr orbits of hydrogen-like atoms when the quantum number is high, is a good example of the correspondence principle, and shows how, as we remarked earlier, it is often permissible to neglect quantization of orbits and to treat the problem classically.

§ 3. Transport Phenomena

3.1. *The Method of Trajectories*

It is necessary now to consider in a little more detail the process of attainment of equilibrium under the influence of electric and magnetic fields. A complete discussion of all the points involved would be too long for the present article, and we shall do little more than develop the particular point of view which will be most useful here. At any instant the electron distribution is described by the distribution function $f(\mathbf{r}, \mathbf{k})$, which specifies the fraction of available states actually occupied by electrons of position coordinate around $\mathbf{r}$ and wave number around $\mathbf{k}$. In general, when electric fields are present $f(\mathbf{r}, \mathbf{k})$ varies with position, and from a quantal point of view there is a limit to the degree of precision with which the variation of $f(\mathbf{r}, \mathbf{k})$ can be specified, in accordance with the uncertainty principle. If, for example, we wish to describe a situation in which $f(\mathbf{r}, \mathbf{k})$ is a rather rapid function of position, we must be able to confine the wave function of one electron to a rather small region, and this implies the construction of a wave packet from a considerable range of wave numbers. Thus we have lost the right to specify the wave number with precision, and this may lead to difficulties, particularly at very low temperatures where $f(\mathbf{r}, \mathbf{k})$ changes from unity to zero over a very small range of $\mathbf{k}$ across the Fermi surface. A complete resolution of this problem is far from straightforward, but it appears to be permissible in most cases to ignore it and treat the electrons as classical particles except in so far as they obey Fermi rather than Boltzmann statistics. A not unrelated difficulty arises, as already mentioned, in a magnetic field which is strong enough that the energy separation of the permitted orbits given by (11) is comparable with kT, and again we ignore it for the present.

We proceed then on the assumption that the electrons may be pictured as particles. In the absence of collisions of the electrons with each other or with lattice defects, Liouville's theorem is applicable, the distribution function in the neighbourhood of any electron remaining constant as the electron moves under the influence of the applied fields. Since the value of f around any one electron is a function of $\mathbf{r}$, $\mathbf{k}$ and t, we have, in general,

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t}\right)_{\mathbf{r},\mathbf{k}} + \dot{\mathbf{r}}.\operatorname{grad}_r f + \dot{\mathbf{k}}.\operatorname{grad}_k f$$

so that in the absence of collisions, when $df/dt = 0$

$$\begin{aligned}\left(\frac{\partial f}{\partial t}\right)_{\mathbf{r},\mathbf{k}} &= -\dot{\mathbf{r}}.\operatorname{grad}_r f - \dot{\mathbf{k}}.\operatorname{grad}_k f \\ &= -\mathbf{v}.\operatorname{grad}_r f - \frac{e}{\hbar}(\mathbf{E} + \mathbf{v}\times\mathbf{H}).\operatorname{grad}_k f\end{aligned}$$

since $\hbar\dot{\mathbf{k}}$ is equal to the force on the electron. If the electrons are capable of colliding with impurities or with one another, there is an additional contribution to the rate of change of f, which may be written $[\partial f/\partial t]_{\text{coll}}$, so that the equation for $f(\mathbf{r}, \mathbf{k}, t)$ takes the form

$$\left(\frac{\partial f}{\partial t}\right)_{\mathbf{r},\mathbf{k}} + \mathbf{v}.\operatorname{grad}_r f + \frac{e}{\hbar}(\mathbf{E} + \mathbf{v}\times\mathbf{H}).\operatorname{grad}_k f = [\partial f/\partial t]_{\text{coll}}.$$

This is the Boltzmann transport equation in the form suitable for transport problems in metals. If it can be solved for given applied fields the electric and thermal currents immediately follow from the form of $f(\mathbf{r}, \mathbf{k}, t)$.

The Boltzmann equation is the starting point for what may be called the conventional approach to transport problems, and undoubtedly it is the best method when the collision term $[\partial f/\partial t]_{\text{coll}}$ is complicated in form. Often enough, however, a simplified form of $[\partial f/\partial t]_{\text{coll}}$ is assumed, especially when the spatial variations of **E** and **H** are sufficient in themselves to create severe mathematical difficulties, and it may then be more revealing to abandon the Boltzmann equation and go back to first principles (Shockley 1950, Chambers 1952 a). We may illustrate this by a rather special case which happens to be particularly useful for the present discussion; we consider the situation where the temperature is uniform and we are only concerned to evaluate the electric current density, on the assumption that at every point on the Fermi surface a relaxation time is definable. By this we imply that if in the absence of fields $f = f_0$, then $[\partial f/\partial t]_{\text{coll}} = -(f-f_0)/\tau$, τ being the relaxation time. Let us now follow a group of electrons through the metal, taking as our sample those electrons whose values of **k** cover a small area of the Fermi surface and have a sufficient spread of energy that the whole tail of the Fermi distribution is represented. We shall assume that the range of velocities involved is small enough for the group to spread very little, so that each electron in the group has effectively the same history. The effect of **H** is to cause the group to describe a curved trajectory, which may be calculated in principle, but not to change the energy of any electron; thus the Fermi distribution is not perturbed. Along this trajectory, however, the electrons may experience an electric field which changes their energy, and so perturbs the distribution. Consider such a perturbation $p\mathbf{E}$, caused by a field **E** at a time t_0; at a later time $t_0 + t$ collisions will have reduced this perturbation to $p\mathbf{E}\,e^{-t/\tau}$. Just the same result would have occurred if the field had had magnitude $\mathbf{E}\,e^{-t/\tau}$ and there had been no collisions. It is therefore possible to allow for the effects of collisions by a modification of the applied electric field so as to reproduce the destruction of information. Next, consider the calculation of the current density contributed by this group of electrons. Since the unperturbed distribution function f_0 carries no current, we need only consider the current due to the perturbation. Now each electron in the group suffers the same history, and therefore the effect of **E** is to shift the Fermi tail to a different energy, but otherwise leave it unaltered. Of course, groups of electrons taken from different parts of the Fermi surface will have traversed different trajectories and experienced different fields, so that the shift will vary with position on the Fermi surface. At any point the equilibrium and disturbed distributions will look as in figure 15, in which f is plotted against k_n, the component of **k** normal to the Fermi surface. If the displacement is Δ the area between the curves is independent of the shape of the Fermi tail. Thus the calculation could equally well have been carried out by assuming that the Fermi surface marked a sharp division between filled and unfilled states, as at 0°K. Since the density of states is $1/(4\pi^3)$ per unit volume of real and reciprocal spaces, the normal displacement Δ of an area dS of Fermi surface is equivalent to an increment of $\Delta dS/(4\pi^3)$ electrons per unit volume of real space, moving with the

Fermi velocity $\mathbf{v}_0$. Thus the increment of current density is $e\mathbf{v}_0\Delta dS/4\pi^3$ and

$$\mathbf{J} = \frac{e}{4\pi^3}\int \mathbf{v}_0\,\Delta dS. \qquad \ldots\ldots(13)$$

Before considering applications of this result, one comment is perhaps useful. The method of trajectories need not be specialized to the degree we have used here ; it is, for example, quite straightforward to allow τ to be a function of energy

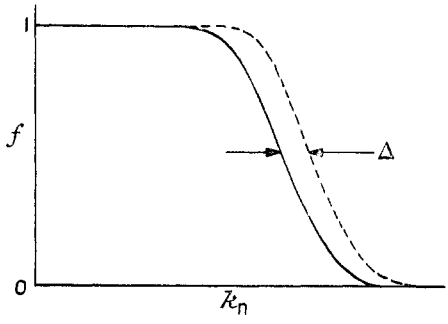

Figure 15. Displaced Fermi distribution.

as well as of position on the Fermi surface, and to consider thermal as well as electrical effects, thus deriving rather general expressions for thermal conduction and other phenomena under conditions which vary in time and space. In discussions of this *method of trajectories* (sometimes misleadingly called the *kinetic method*, as if the use of the Boltzmann equation did not involve the same kinetic principles) it is sometimes implied that the method is an approximation only suitable for rough calculations. This is true so far as concerns the assumption of a rather special form of collision term ; but within the framework of this assumption the results obtained are correct integrals of the Boltzmann equation.

3.2. *Spatially Varying Electric Fields*

The use of the special form of the method of trajectories suitable for isothermal electrical conduction (which we shall call the *hard Fermi surface method*) may be illustrated by solving a problem which is relevant to much of the discussion in the following pages. Consider an infinite sample of metal within which is established a periodic electric field of frequency ω and wave number ν, having the form

$$E_i = E_{0i}\,\mathrm{e}^{i(\omega t-\nu z)}.$$

The field will produce a current density $\mathbf{J}$ with the same periodicity, so that we may write

$$J_i = \sigma_{ij}(\omega,\nu)\,E_j. \qquad \ldots\ldots(14)$$

There is no difficulty in writing down a general expression for σ_{ij} in terms of the geometrical form of the Fermi surface and other relevant parameters, but we shall only consider here some rather specialized cases, particularly concentrating on the behaviour under such conditions that the mean free path is much greater than the spatial period of the field, i.e. $\nu l \gg 1$. A further simplification is effected, once the z-axis has been fixed with respect to the crystallographic axes, by choosing the x and y axes to be the principal axes in their plane. Then $\sigma_{xy} = 0$, and we need

consider only components of the types σ_{xx}, σ_{xz} and σ_{zz}. Let us take σ_{xx} first, letting **E** be directed along the x-axis, and for the moment taking ω as zero, so that $E_x = E_{0x}\,e^{-i\nu z}$. Then a typical electron at the Fermi surface passes through an alternating field, and if the free path is long, experiences very little resultant change of velocity. To calculate the change for an electron at (z_0, t_0) we note that at time t its z-coordinate was $z_0 + v_z(t-t_0)$, so that it was accelerated by an effective field

$$E_{\text{eff}}(t) = E_{0x}\exp\left\{-i(\nu z_0 + \nu v_z[t-t_0]) + \frac{t-t_0}{\tau}\right\}.$$

Hence, from the rate of change of the x-component of momentum, eE_{eff}, we derive an equation for the rate of displacement of the Fermi surface in the x-direction

$$\hbar\dot{\Delta}_x = eE_{0x}\exp\left\{-i(\nu z_0 + \nu v_z[t-t_0]) + \frac{t-t_0}{\tau}\right\},$$

which on integrating from $-\infty$ to t_0 yields the equilibrium displacement

$$\hbar\Delta_x(z_0) = \frac{e\tau}{1-i\nu v_z\tau}E_x(z_0). \qquad \ldots\ldots(15)$$

From (15) it is clear that when $\nu v_0\tau$, i.e. $\nu l \gg 1$, the only contributions of significance to the current are from electrons moving nearly normal to z, when $v_z \ll v_0$. Thus for any section of the Fermi surface by a plane normal to the y-axis, as in figure 16, it is possible to delineate the effective points P, P′ as those

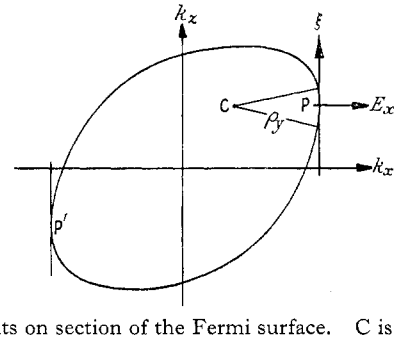

Figure 16. Effective points on section of the Fermi surface. C is the centre of curvature at P.

whose tangents are parallel to the z-axis. Only points in the near neighbourhood of the effective points have significant displacements Δ_x, and to a good approximation (which becomes exact as $\nu l \to \infty$), we may consider only this region and write $v_z = v_x\,\xi/\rho_y$, in which ξ is the coordinate k_z measured from an effective point, and ρ_y is the radius of curvature of the y-section of the Fermi surface at the effective point. The displaced area, $\int\Delta_x\,d\xi$, is now easily calculated from (15) as $\pi eE_{0x}|\rho_y|/(\hbar v_x\nu)$. If the thickness of the plane section is dk_y, the displaced area contains $eE_{0x}|\rho_y|\,dk_y/(4\pi^2\hbar v_x\nu)$ electrons for unit volume of metal, and each electron is moving in the x-direction with velocity v_x. Hence we find the current density and the conductivity component for wave number ν

$$\mathop{\mathscr{L}}_{\nu l\to\infty}\sigma_{xx}(\nu) = \frac{e^2}{4\pi^2\hbar\nu}\oint|\rho_y|\,dk_y, \qquad \ldots\ldots(16)$$

the integral being taken along the locus of effective points on the Fermi surface or surfaces. It will be seen that the expression is independent of l and v_0, and depends only on a geometrical property of the Fermi surface (Pippard 1954 a).

So long as νl is so large that the region around an effective point may be represented as having constant curvature the current is by symmetry precisely parallel to the x-axis, and $\sigma_{zx} = 0$. This result does not hold when variations of curvature are important at lower values of νl, but we may expect when νl is reasonably large that the ratio σ_{zx}/σ_{xx} will be very small. It is easy to see that as νl tends to infinity σ_{zz} also vanishes, for the only effective electrons have a negligible velocity component in the z-direction. We have thus demonstrated that in the limit of long free paths the z-axis is a principal axis of $\sigma_{ij}(\nu)$, which may be diagonalized so that only the terms σ_{xx} and σ_{yy} remain, and that these terms depend only on the geometry of the Fermi surface. These results enable the theory of the anomalous skin effect to take a very simple form, as we discuss later, and thus make the effect useful as an analytical tool.

If we do not take ω as zero the results are slightly altered in a way which is easily understood qualitatively. As an electron moves through the metal the phase of the oscillatory field changes, so that movement normal to z does not ensure a constant field. Since, however, the phase variation is that of a wave moving in the z-direction with velocity ω/ν, there will be an effective region centred about such points on the Fermi surface that $v_z = \omega/\nu$. So long, therefore, as ω is much less than $v_0\nu$, the form of the theory is hardly altered, and (16) is correct provided that ρ_y is taken at the genuine effective points. But when ω is greater than $v_0\nu$ the simplicity of the analysis fails, since there is no dominant effective region, and all parts of the Fermi surface contribute with comparable weight. It should also be remarked that the argument for the vanishing of σ_{zx} loses its validity as soon as $\nu v_0/\omega$ is significantly large.

3.3. *Galvanomagnetic Effects*

As a second example of conduction calculations relevant to our general study we consider the problem of the Hall effect and magneto-resistance, that is, uniform conduction in a magnetic field, with particular emphasis on the case when **J** and **H** are normal to one another. It is convenient to separate the effects due to electric and magnetic fields, and this can be achieved by the simple device of analysing the steady electric field into a time-sequence of impulses. We illustrate this by the free-electron model having spherical Fermi surface and constant relaxation time. Let the magnetic field be applied to an infinite sample along the z-direction, and between times $t = 0$ and $t = dt$ apply a uniform electric field E_x. This will set up a current density $dJ_x(0)$ according to the equation

$$dJ_x(0) = \frac{Ne^2}{m} E_x\, dt,$$

the whole spherical Fermi distribution being shifted in the x-direction. Now because of the field H_z the disturbed distribution precesses uniformly about the z-axis with the cyclotron frequency ω_c $(= eH/m)$, and at the same time reverts exponentially to its undisturbed form with relaxation time τ.

Thus we may write

$$\left.\begin{aligned} dJ_x(t) &= \frac{Ne^2 E_x\, dt}{m} \cos \omega_c t\, e^{-t/\tau}, \\ dJ_y(t) &= \frac{Ne^2 E_x\, dt}{m} \sin \omega_c t\, e^{-t/\tau}. \end{aligned}\right\} \quad \ldots\ldots(17)$$

If we have a steady electric field, we have a superposition of contributions of the type (17) at all epochs t, so that we obtain the steady values of J_x and J_y by integration

$$\left.\begin{aligned} J_x &= \int_{t=0}^{\infty} dJ_x(t) = \frac{Ne^2\tau}{m(1+\omega_c^2\tau^2)} E_x = \frac{\sigma E_x}{1+\omega_c^2\tau^2}, \\ J_y &= \int_{t=0}^{\infty} dJ_y(t) = \frac{Ne^2\omega_c\tau^2}{m(1+\omega_c^2\tau^2)} E_x = \frac{\omega_c\tau\sigma E_x}{1+\omega_c^2\tau^2}. \end{aligned}\right\} \quad \ldots\ldots(18)$$

The relation between **J** and **E** is shown in figure 17, in which ϕ, the *Hall angle* between **J** and **E**, is $\tan^{-1}(\omega_c\tau)$. Moreover, the triangle defined by $\sigma\mathbf{E}$ and **J** is

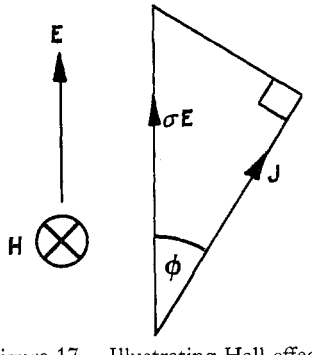

Figure 17. Illustrating Hall effect.

right-angled. In a typical experiment to measure the transverse magneto-resistance of a metal it is the direction of current flow that is determined by the geometry of the sample, rather than the direction of **E**. From figure 17 it is clear that as **H** and ϕ increase, the component of **E** in the direction of **J** remains constant at J/σ, so that there is no magneto-resistance effect in this case. The component of **E** normal to the current flow is $J/\sigma\tan\phi$ or JH/Ne, so that if we define the Hall coefficient R by the equation

$$\text{normal component of } \mathbf{E} = RHJ,$$

we see that R is simply $1/Ne$.

The vanishing of the magneto-resistance effect and the constancy of the Hall coefficient are peculiarities of the free-electron model, not observed in practice, though the nearest approximation to them occurs with sodium for which there is some evidence that the free-electron model is not a bad approximation. If we extend this analysis to more general types of Fermi surface we observe the following generalizations to be necessary :

(1) different orbits may have different cyclotron frequencies ;
(2) electron and hole orbits must be treated as having opposite signs of ω_c ;
(3) open orbits show no periodicities ;

(4) the oscillatory terms in (17) must be supplemented by harmonics of the fundamental frequency ω_c, since the disturbed distribution need not precess unchanged ; in the absence of collisions it will return after each revolution to its original form ;

(5) the relaxation time may vary over the Fermi surface ; in general, indeed, a relaxation time will not be definable.

If all these effects are taken into account the resulting expressions are complex and unrewarding, but it is easy to demonstrate some typical properties by a simple extension of the free-electron model. We assume the Fermi surface to consist of two spherical sheets, one containing N_- electrons and the other N_+ holes, each having the same mass m and relaxation time τ, but with equal and opposite cyclotron frequencies $\pm\omega_c$. The analogues of (18) may now be written

$$J_x = \frac{\sigma E_x}{1+\omega_c^2\tau^2}, \quad J_y = \frac{N_- - N_+}{N_- + N_+}\frac{\sigma\omega_c\tau E_x}{1+\omega_c^2\tau^2},$$

from which it follows that the resistivity, determined by the component of **E** parallel to **J**, takes the form

$$\rho = \frac{1+\omega_c^2\tau^2}{\sigma}\left\{1+\left(\frac{N_- - N_+}{N_- + N_+}\right)^2\omega_c^2\tau^2\right\}^{-1}, \qquad \ldots\ldots(19)$$

and the Hall coefficient the form

$$R = \frac{(N_- - N_+)(1+\omega_c^2\tau^2)}{e\{(N_- + N_+)^2 + (N_- - N_+)^2\omega_c^2\tau^2\}}, \qquad \ldots\ldots(20)$$

in which σ is the conductivity in zero field, $(N_- + N_+)e^2\tau/m$. As the magnetic field, and consequently ω_c, is increased, ρ increases quadratically at first and then more slowly, finally levelling off at the value $\sigma^{-1}(N_- + N_+)^2/(N_- - N_+)^2$. At the same time the Hall coefficient changes from $e^{-1}(N_- - N_+)/(N_- + N_+)^2$ to $[(N_- - N_+)e]^{-1}$. It is clear that the saturation of the magneto-resistance and the Hall coefficient is possible only if the numbers of electrons and holes are different, and that if this is so the value of the field strength at which saturation begins to be complete is determined by the condition

$$\omega_c\tau \gg \left|\frac{N_- + N_+}{N_- - N_+}\right|. \qquad \ldots\ldots(21)$$

The particular results we have deduced concerning saturation and the limiting value of the Hall coefficient are of very wide validity, as we shall now demonstrate.

Let the Fermi surface be such that for the particular direction chosen for **H** (taken as the z-axis) no orbits are open. If we consider a particular section k_z = constant and apply an impulsive field **E***dt* in an arbitrary direction, the displaced distribution in its subsequent precession may be expected to contribute currents of which no component need vanish. In the absence of collisions the current in any direction may be resolved into three parts

$$dJ_i = \left\{C_{ij} + \sum_n a_{ij}^{(n)} \sin n\omega_c t + \sum_n b_{ij}^{(n)} \cos n\omega_c t\right\} E_j\, dt. \qquad \ldots\ldots(22)$$

Because of collisions there will be a steady decrement of dJ_i, which may take a complicated form if the decrement in one period is large, for then differences in

relaxation at different points on the Fermi surface will show themselves. If, however, we have **H** so large that the decrement in one period is small, we may as a good approximation define a mean relaxation time $\bar{\tau}$ for the whole orbit, and hence, multiplying (22) by $e^{-t/\bar{\tau}}$ and integrating from $t = 0$ to $t = \infty$, obtain for the conductivity tensor in a steady field

$$\Delta\sigma_{ij} = \Delta J_i/E_j = C_{ij}\bar{\tau} + \sum_n \frac{a_{ij}^{(n)} n\omega_c \bar{\tau}^2}{1 + n^2\omega_c^2\bar{\tau}^2} + \sum_n \frac{b_{ij}^{(n)}\bar{\tau}}{1 + n^2\omega_c^2\bar{\tau}^2}. \qquad \ldots\ldots(23)$$

This is, of course, the contribution of one section of the Fermi surface. The complete conductivity tensor σ_{ij} involves a summation over all sections, with due account of variations in $\bar{\tau}, \omega_c$ and the coefficients of the various terms. For the present purpose fortunately we do not need to consider the form of (23) in detail, but only to observe that when $\omega_c\bar{\tau} \gg 1$ the three terms are respectively proportional to ω_c^0, ω_c^{-1} and ω_c^{-2}, that is to H^0, H^{-1}, H^{-2}. We now examine which of these terms may be present in each of the components of σ_{ij}, and here it is helpful to use the reciprocity relation of irreversible thermodynamics, that $\sigma_{ij}(H) = \sigma_{ji}(-H)$.† This shows immediately that there are no terms in H^{-1} in the diagonal elements of σ_{ij}, i.e. that sine terms are absent in (22) for the diagonal elements. There is no such restriction on the non-diagonal elements, in fact our analysis of the spherical model leads us to expect them. As for the constant term C_{ij}, this can only appear in the element σ_{zz}, for the following reason. As a consequence of (10) the projection of the motion of an electron on the plane $z =$ constant is a closed orbit in the absence of an electric field, provided that the orbit is closed in reciprocal space, and so no impulsive field can establish a disturbed distribution which has other than oscillatory terms in J_x or J_y. Hence the constant term vanishes in σ_{xx}, σ_{xy}, σ_{xz}, σ_{yx}, σ_{yy} and σ_{yz}, and by reciprocity in σ_{zx} and σ_{zy}. Thus if we retain only the terms of lowest order in $1/H$, as appropriate to the limiting behaviour in high fields, the form of σ_{ij} may be written

$$\sigma_{ij} = \begin{Vmatrix} A/H^2 & B/H & C/H \\ -B/H & D/H^2 & E/H \\ -C/H & -E/H & F \end{Vmatrix}. \qquad \ldots\ldots(24)$$

This is sufficient to ensure the saturation of the magneto-resistance and the Hall effect. To prove this we need to invert the conductivity tensor, since with the current direction fixed (as the x-direction) by the experimental arrangement, the measured resistivity is ρ_{xx} $(= E_x/J_x)$ and the Hall coefficient is ρ_{xy}/H $(= E_y/HJ_x)$. The result of this inversion is that

$$\rho_{xx} = \frac{\sigma_{yy}\sigma_{zz} + \sigma_{yz}^2}{\sigma_{xx}\sigma_{yy}\sigma_{zz} + \sigma_{xx}\sigma_{yz}^2 + \sigma_{yy}\sigma_{xz}^2 + \sigma_{zz}\sigma_{xy}^2} \to \frac{DF + E^2}{FB^2} \quad \text{as } H \to \infty;$$

$$\rho_{xy} = \frac{\sigma_{xy}\sigma_{zz} + \sigma_{xz}\sigma_{yz}}{\sigma_{xx}\sigma_{yy}\sigma_{zz} + \sigma_{xx}\sigma_{yz}^2 + \sigma_{yy}\sigma_{xz}^2 + \sigma_{zz}\sigma_{xy}^2} \to \frac{H}{B}, \quad \text{i.e. } \sigma_{xy}^{-1}, \quad \text{as } H \to \infty.$$

† It is not difficult by analysing an orbit in detail to demonstrate this result, so that this appeal to reciprocity need be regarded only as a means of avoiding thought.

It follows then that the resistance and Hall coefficient tend to a constant value in this general case, provided that there are no open orbits.

To calculate the limiting value of the Hall coefficient, consider a thin section of the Fermi surface bounded by parallel planes normal to **H**, and let there be s states per unit area of the section. In the presence of steady fields H_z and E_x the rate of change of energy of an electron may be written

$$\dot{\epsilon} = -ev_x E_x = \frac{E_x}{H_z}\hbar\dot{k}_y, \quad \text{since } \hbar\dot{k}_y = ev_x H_z.$$

Thus the electron does not describe in reciprocal space an orbit at constant energy ϵ_0, but one in which the energy is $\epsilon_0 + (E_x/H_z)\hbar k_y$. This second term defines the shift of the Fermi surface from equilibrium, from which the current contributed by the whole section may be written down. In particular, the y-component takes the form

$$\Delta J_y = \pm \frac{sE_x e}{H_z} \oint k_y \, dk_x,$$

in which the positive sign is to be taken if the orbit is an electron orbit, and the negative sign if it is a hole orbit. Since the integral is simply the area of the orbit, it is clear that ΔJ_y is just eE_x/H_z times the number of electrons or holes in the section, and that therefore

$$J_y = (N_- - N_+)\, eE_x/H_z,$$

so that the limiting value of the Hall coefficient is $[(N_- - N_+)\, e]^{-1}$.

This result indicates that a certain amount of information about the structure of the Fermi surface may be obtained from high-field measurements of the Hall effect, while at the same time a complete picture is unlikely to emerge. If, for example, all surfaces are closed, the numbers N_- and N_+ are independent of orientation, so that the limiting value of the Hall coefficient should be isotropic. Thus the presence of closed Fermi surfaces and something about their volumes are disclosed, but no details about their shape. It is likely that the situation in which all surfaces are closed arises most frequently with metals of even valency, in which a Brillouin zone may be nearly filled, and the next higher zone contains a few electrons ; in this case $N_- = N_+$ and no saturation of the magneto-resistance is to be expected. Another, more interesting, case is that in which there is limited contact of the Fermi surface with the zone boundaries and the extended surface is multiply connected, as in figure 14. Even for those orientations which yield no open orbits the numbers of electrons and holes are likely to vary with direction of the magnetic field. The observation of a saturating magneto-resistance combined with a variable saturating Hall coefficient may prove useful in elucidating the topography of the Fermi surface, particularly in the monovalent metals which may be taken to have only one sheet to their Fermi surfaces. But the multiply-connected Fermi surface may yield highly extended and open orbits, and one must be careful not to be misled by these into misinterpretation of the results. It is worth devoting a little space to this matter, to show the influence of open orbits on the magneto-resistance and Hall coefficient.

The important thing to appreciate is that the open orbit is rather a rarity.†

† *Note added in proof.* This is not true. A fuller discussion will be found in the note at the end of this article.

An electron in an open orbit describes a path in reciprocal space which waves periodically about a straight line ; the direction of this line will be called the axis of the orbit. It is easy to delineate all possible axes as those straight lines which can pass indefinitely through the periodically extended reciprocal space without intersecting the Fermi surface. Three such lines are shown as P, Q and R in figure 14 ; it is clear that the axis is well defined and will usually coincide with a crystallographic axis of low index. This method of constructing the axis provides a necessary condition which they must satisfy, but not a sufficient condition—even if the plane normal to **H** contains one of the axes, there may still be no open orbits, as may be seen immediately from the figure. It is clear then that we can expect to find open orbits only when **H** lies in a plane normal to one of the orbit axes, and not always then. Moreover, the possibility of having simultaneously open orbits with two different axes is confined to one particular direction of **H**, normal to both ; for the surface of figure 14 this does not occur at all, since if **H** lies along the direction of P the two sets of axes of open orbits R and Q intersect and small closed orbits form in the interstices of their intersections.

We now consider the limiting behaviour in high fields when open orbits having a single axis are present. As the electron moves through reciprocal space in the general direction of the axis, it moves in real space along a similar perpendicular path. The greater the field, the less important the effects of collisions, and in the limit the direction of electron motion is strictly confined to the plane normal to the orbit axis. In this plane the response of the electrons to the electric field becomes independent of **H**. Thus the electrons describing open orbits tend to become strictly two-dimensional conductors. At the same time the components of σ_{ij} contributed by other electrons moving in closed orbits tend to zero as H^{-1} or H^{-2} (except for σ_{zz}) and the conductivity tensor has a limiting form

$$\mathop{\mathscr{L}}_{H\to\infty} \sigma_{ij} = \begin{Vmatrix} a\sin^2\theta & a\sin\theta\cos\theta & 0 \\ a\sin\theta\cos\theta & a\cos^2\theta & 0 \\ 0 & 0 & b \end{Vmatrix},$$

in which θ is the angle between **E** and the orbit axis. The resistivity ρ_{xx} tends to infinity, as expected from the physical argument, except when $\theta = \pi/2$; more detailed analysis shows that ρ_{xx} increases as H^2. This is the same law as may be expected in the other non-saturating case, $N_- = N_+$; the two cases may possibly be distinguished experimentally through the behaviour of the Hall coefficient, but we shall not develop the argument here.

If the orientation is such that the plane normal to **H** does not quite contain any orbit axes, we may expect to find highly extended rather than completely open orbits. These will only behave differently when **H** is so large as to allow complete revolutions of the extended orbits between collisions, and under these circumstances the magneto-resistance will probably increase to a large value before finally saturating in very high fields indeed. A similar sort of effect may also occur if the collision probability is highly anisotropic. The circumstances in which this is particularly likely occur when there is rather small contact between the Fermi surface and the zone boundary, so that the connecting links between

neighbouring regions of periodically extended reciprocal space are thin. It is then possible for scattering which changes **k** by only a little to move an electron from an electron orbit to a hole orbit, and so to alter its motion completely. This possibility has not been examined in detail, but it seems likely on these grounds that an electron may have difficulty in completing an orbit which runs close to such a critical region, and we shall term such orbits *non-viable*. They may not exist, but their possible existence should be borne in mind in view of the influence they may have on delaying saturation of the magneto-resistance until exceedingly high fields have been reached. It may be pointed out that small regions of high scattering probability are difficult to detect in ordinary conductivity measurements, since the major part of the conductivity is contributed by large regions of low scattering probability. But when magnetic fields are present such small regions become much more important since they affect all electrons whose orbits pass through them.

Experimentally the situation is fairly clear, so far as the facts go, but puzzling ; for many comparatively simple metals, like copper, have a magneto-resistance which, after an initial quadratic variation, settles down to a linear variation with field which continues, apparently indefinitely, well beyond the point where saturation might have been expected (Kapitza 1929). Unfortunately, almost all the work has been done with polycrystalline samples, and it has recently been conjectured (Ziman 1958) that this is the origin of the effect, which represents an average between orientations which saturate at different values of the field as well as some which do not saturate at all because of open orbits. To justify this conjecture rigorously demands an analysis of the behaviour of a polycrystal in which each crystallite exhibits a different anisotropic conductivity, and it is probably easier to study single crystals experimentally than to carry through this analysis. In any case the information which is potentially available from such a study is far greater than anything a polycrystal can yield. It is pleasing to note that a serious experimental programme along these lines has apparently begun recently (Alekseevski, Brandt and Kostina 1958, Alekseevski and Gaidukov 1958).

It must be remembered that the whole of the foregoing analysis has been based on the semi-classical wave-packet picture, and that this is particularly suspect in high magnetic fields, where the quantization of the orbits reveals itself in the magnetic behaviour of the metal. We have seen that the condition for saturation of the magneto-resistance is that $\omega_c \tau \gg 1$; since $\Delta\epsilon$, the separation of neighbouring quantized orbits, is $\hbar\omega_c$, the condition for saturation is simply that $\Delta\epsilon \gg \hbar/\tau$, which can be seen by reference to the uncertainty principle to imply that collision broadening of the levels is small in comparison with their spacing. The condition for saturation is thus the condition for breakdown of any obvious justification for the semi-classical approach. It is probable, however, that the results of the semi-classical method have still a certain validity. A great many of the observations on magneto-resistance have been made at such temperatures that $\Delta\epsilon \ll kT$, so that through thermal excitation the characteristic oscillatory effects of quantization are not apparent in the thermodynamic properties nor in the resistance and Hall effect. When the conditions are such that $\Delta\epsilon \gtrsim kT$, the oscillatory effects (Schubnikov, de Haas–van Alphen, etc.) may appear in the magnetic and transport properties, being particularly noticeable in bismuth and graphite but detectable

in other, more typical, metals. The oscillations in resistance are, however, superposed on a general trend which appears to be of the type we have been discussing, and it seems that a clear empirical separation is possible between effects which are and are not essentially dependent on the quantization of the orbit. This conclusion may be justified theoretically, as will be indicated briefly later (see p. 214).

Many of the outstanding problems in the interpretation of the galvanomagnetic effects might well be resolved by a detailed study of high-field magnetoresistance and Hall effects in single crystals of a metal whose Fermi surface has been determined by other methods. If the observed behaviour should turn out to be intelligible by semi-classical arguments, as one would hope, the way will be open for an attempt to interpret the far more involved effects at moderate field strengths, where the detailed shape of the Fermi surface and the variation over it of velocity and relaxation time all play their parts.

§ 4. Analysis of Special Phenomena

4.1. *Introduction*

We have devoted some space to the galvanomagnetic effects because they are among the simplest transport phenomena which appear to be capable of yielding fairly specific information on the electronic structure of metals. Many other phenomena have from time to time been invoked as evidence supporting or refuting particular theories, and we may mention in this category the following : electronic specific heat, soft x-ray spectra, optical and infra-red absorptivity, electrical and thermal conductivities, thermo-electric effects.

The recent analysis by Heine and Cohen (1958) of the monovalent metals may be cited as an example of the use to which this type of information may be put ; it may enable one to conclude that the Fermi surface of a given metal does or does not touch the zone boundary, but it hardly goes further than this. It is to be hoped that other methods, including galvanomagnetic effects, may in the course of time make unnecessary such nice weighing of indirect evidence, and we therefore devote no more space to the topics listed above, but pass straight on to the potential sources of more direct information.

The experimental methods which we shall proceed to analyse in some detail are the following :

(1) de Haas–van Alphen and related effects ; variation with magnetic field of magnetic susceptibility, electrical and thermal conductivity, Hall effect, etc., which are periodic in H^{-1} and associated with the quantization of orbits in a magnetic field.

(2) Anomalous skin effect ; high-frequency conductivity of a pure metal when the mean free path is much greater than the skin depth.

(3) Cyclotron resonance ; the skin effect in a magnetic field, particularly under such conditions that the high-frequency field is in synchronism with the electron orbits.

(4) Magneto-acoustic effects ; variations in absorption of ultrasonic waves in a magnetic field, associated with the relative sizes of the wavelength and the electron orbits, or with resonance between electron orbits and acoustic vibrations.

Of these effects the last three may be understood in quasi-classical terms, that is, classical ideas supplemented by the exclusion principle ; we have, indeed, already laid the foundations of our discussion in the analysis leading up to equation (16). Only for the first group of effects must the quasi-classical approach be abandoned for the semi-classical in the sense of the type of argument used to prove Onsager's theorem. In the following discussion the effects will necessarily have to be taken one at a time, and it may be overlooked that they have one feature in common. Each has this characteristic, that the observed behaviour, under ideal conditions, depends on the properties of a small group of electrons, the particular group being selected by crystal orientation, magnetic field direction or other controllable parameters. Moreover, the behaviour depends in a comparatively simple way on

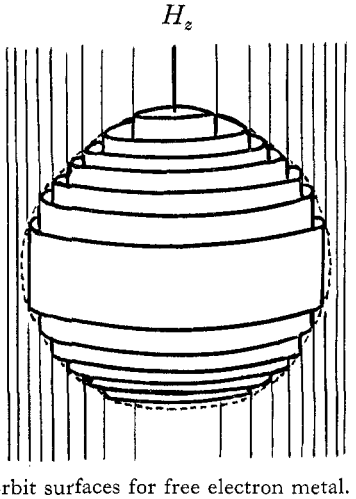

Figure 18. Permitted orbit surfaces for free electron metal. (*After* Chambers 1956 b.)

the properties of this group, so that by patient amassing and interpretation of data it becomes feasible to build up a fairly detailed picture of the variation in reciprocal space of the properties concerned. In (1), (2) and (4), for example, the property is the actual shape of the Fermi surface, $\epsilon_0(\mathbf{k})$; in (3) (and in (1) also) it is the velocity and its variation over the Fermi surface.

4.2. *The de Haas–van Alphen and Related Effects*

The de Haas–van Alphen effect has been reviewed fully by Shoenberg (1957) and Chambers (1956 b), and we shall not discuss it in great detail. Following the semi-classical approach we construct on each plane in reciprocal space normal to **H** those curves of constant energy which are permitted orbits, having areas given by equation (11), in which we shall take the phase factor φ to be $\frac{1}{2}$, being the correct value for a free-electron gas. The full diagram of permitted energy surfaces (orbit surfaces) will then consist of a set of tubes of, in general, variable cross-sectional form. Only in simple cases like the free-electron model will the tubes be cylindrical, and parallel to **H**, as in figure 18. If, for example, the energy surfaces are ellipsoidal, the orbit surfaces are elliptical cylinders, inclined in general to **H**. The degeneracy of the orbital states is such that the mean density of

states in reciprocal space is unchanged by the field. There is thus no gross change in the electronic energy with field, as is clear experimentally from the very small diamagnetism of most metals. There are, however, small changes associated with the relative dispositions of the permitted orbits and the Fermi surface. In order to show how this comes about we shall treat a not-uncommon special case, in which the surface concerned contains only a small fraction of the conduction electrons. Under these conditions the other electrons serve to maintain a constant Fermi energy, supplying or abstracting electrons as necessary so that at the absolute zero the orbit-surfaces are filled up to the points at which they coincide with the

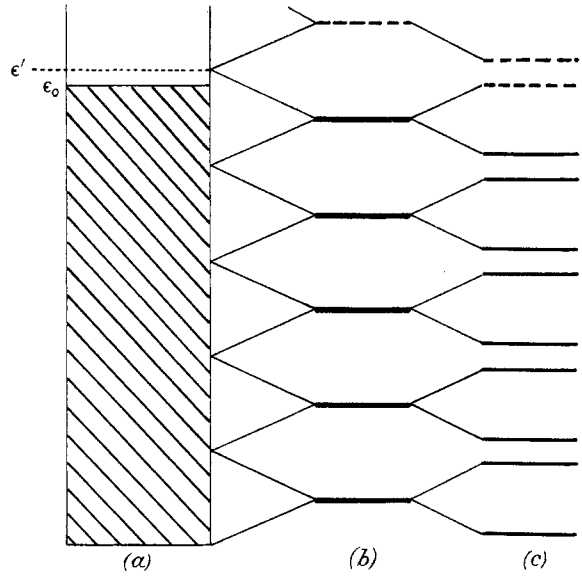

Figure 19. Energy levels in a magnetic field ; (*a*) continuum in zero field, (*b*) collapse of orbital levels into highly degenerate discrete spectrum (spin neglected), (*c*) splitting of levels by spin. The levels above ϵ_0 are empty and are indicated by broken lines.

Fermi surface in zero field. If the Fermi energy is unable to stay constant the difference in behaviour is small enough that we need not discuss it here.

Consider then a section of thickness dk_z cut normal to **H**. The energy levels allowed to the electrons in this section form a fairly evenly spaced succession as in figure 19 and are just sufficiently degenerate to hold the electrons which occupy the same energy range in the absence of the field. Each of the levels is split into two by the electron spin interaction with the field, but we shall for the moment ignore this, as it is easier to correct the result for the effects of spin at the end. Since all the levels below the Fermi energy ϵ_0 are occupied, and all above are empty, the energy of the electrons in this slice amounts in all to the same as if in the absence of a field the Fermi level were at the point ϵ' ; ϵ' is determined as that point, half-way between two permitted levels, which lies nearest to ϵ_0. If ϵ' and ϵ_0 coincide, the energy of the section is the same as in zero field, but otherwise it is greater. For if $\epsilon' > \epsilon_0$, the reservoir must supply electrons at energy ϵ_0 whose energy must be raised by an average amount of $\frac{1}{2}(\epsilon' - \epsilon_0)$ each, while if $\epsilon' < \epsilon_0$,

the section can hold less than its zero-field quota, the rejected electrons with energy less than ϵ_0 being raised by $\frac{1}{2}(\epsilon_0 - \epsilon')$ on the average in order to enter the reservoir. Thus the effect of quantization of the orbits is to raise the mean energy of the electron assembly as well as to cause it to oscillate. The increase of mean energy is easily seen to be proportional to H^2 and since the magnetic moment M is $-d\mathscr{E}/dH$, $\mathscr{E}$ being the total energy, the average of M is negative and proportional to H, i.e. there is a steady diamagnetism, which in fact is temperature-independent. If we use this argument to calculate the *Landau diamagnetism* we arrive at the correct value for a free-electron gas, but apparently not otherwise, as pointed out by Chambers (1956 b). To take proper account of the ionic lattice is a difficult matter, and we say no more about it. There is no reason to doubt the essential applicability of the semi-classical method to the periodic terms which are what really concern us.

To return to the section dk_z, let its area in zero field be $\mathscr{A}_0$, so that for unit volume of metal it contains $\mathscr{A}_0\, dk_z/4\pi^3$ electrons. From (11) the permitted orbits have area $(n+\frac{1}{2})\,2\pi eH/\hbar$. Therefore coincidence of ϵ' and ϵ_0 occurs whenever $\mathscr{A}_0 = n \times 2\pi eH/\hbar$, or

$$\frac{1}{H} = n \times \frac{2\pi e}{\hbar \mathscr{A}_0}. \qquad \ldots\ldots(25)$$

This result shows that the variations in number and energy of the electrons in the section have a constant period when plotted against $1/H$, as is accurately verified by experiment. It is instructive to examine the order of magnitude of the periodicity predicted by (25). Since from now on we shall on several occasions wish to quote typical values of the parameters involved in particular experiments, we shall do so with reference to a hypothetical ' standard metal ' whose definition and properties are described in the Appendix. For this metal (25) takes the form

$$1/H = 2{\cdot}1 \times 10^{-9}\, n.$$

This means that in a field of 10^5 gauss, n is about 4800, so that there are 4800 permitted levels below the Fermi level. If the electrons are free, the levels are equally spaced, and the spacing is $2{\cdot}1 \times 10^{-4}\epsilon_0$, which corresponds to a temperature of 13°K. This can also be seen by remembering that the separation is $\hbar\omega_c$, where ω_c is the cyclotron frequency, $1{\cdot}8 \times 10^{12}$ radians/sec in the present example. If the surface is small, containing only 10^{-3} electrons per atom, $\mathscr{A}_0$ is one hundred times smaller, and n is about 48. If the effective mass of the electrons is still the free electron mass, the separation of levels is still about 13°K in a field of 10^5 gauss. Since the oscillatory effects depend for their observation on this separation being greater than the spread of electron energy due to thermal excitation, it is clear that they are likely to be observed only at rather low temperatures ; this is indeed so, although when the effective cyclotron mass is small, as often happens on small Fermi surfaces, the temperature effect may not be so restrictive.

If n is fairly large, the oscillations will be reasonably evenly periodic when plotted against H, the period (i.e. the change in H which changes n by unity) being $2\pi eH^2/\hbar\mathscr{A}_0$. In figure 20 are plotted the periodic variations of the relevant properties of the section dk_z. Figure 20(a) shows ΔN, the variations in the number of electrons in the section ; this varies linearly with H, with sharp breaks as an orbit crosses the Fermi level and suddenly empties into the reservoir. Since

each level contains as many states as a volume of $2\pi eHdk_z/\hbar$ would contain in zero field, the discontinuity in ΔN is $eHdk_z/2\pi^2\hbar$. At integral values of n the energy takes its minimum value, varying parabolically, as in figure 20(b), except for discontinuities of gradient at half-integral values of n. At such points the excess number of electrons in the section is $\pm eHdk_z/4\pi^2\hbar$, with an average excess energy of $\pm\frac{1}{4}\hbar\omega_c$ each. Hence, from (12), the range of variation of $\Delta\mathscr{E}$ is $e^2H^2dk_z/[8\pi\hbar^2(d\mathscr{A}/d\epsilon)_0]$, the derivative being taken at the Fermi surface. The

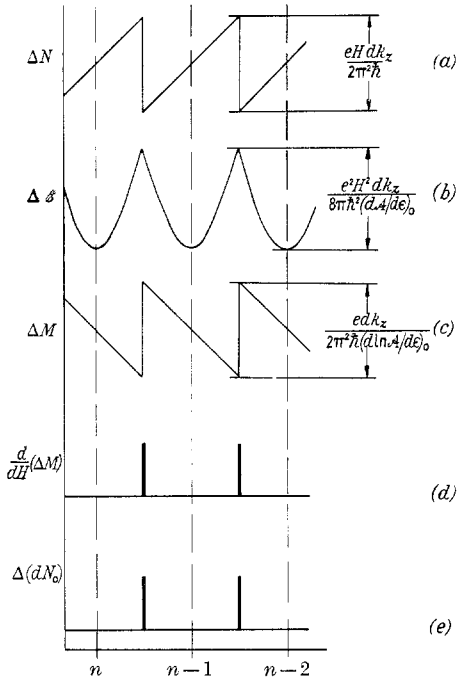

Figure 20. Illustrating origin of de Haas–van Alphen and Schubnikov effects as a consequence of the variation with H of different properties of electrons in a plane section. The vertical broken lines indicate the field strengths at which (25) is satisfied by integral values of n.

magnetic moment ΔM, being $-d\mathscr{E}/dH$, is, like ΔN, a linear function of H with discontinuities of $edk_z/[2\pi^2\hbar(d\ln\mathscr{A}/d\epsilon)_0]$, and is shown in figure 20(c). The other two curves do not concern us yet.

The saw tooth oscillations of ΔM owe their asperity to the sharp cut-off of the Fermi distribution at 0°K. At any other temperature thermal excitation rounds off the variations in a way which can be most easily described in terms of the Fourier components of ΔM. The amplitude of the rth harmonic must be multiplied by $X/\sinh X$, in which X is written for $2\pi^2rT/T'$, kT' being the energy separation of successive levels, i.e. $\hbar\omega_c$. For the standard metal in a field of 10^5 gauss, for which we found T' to be 13°K, the factor at 1°K is about $1{\cdot}5r/\sinh(1{\cdot}5r)$, i.e. 0·71, 0·30 and 0·10 for the fundamental, second and third harmonics respectively. A good deal of the harmonic content is thus eliminated, though a certain departure from strictly sinusoidal wave-form may still be observable, but only at rather low temperatures.

It is clear from figure 20(*c*) that the fundamental of the oscillation is of the form $\sin(\hbar\mathscr{A}_0/eH)$, so that we may take $\hbar\mathscr{A}_0/eH$ as the phase ϕ of the contribution to ΔM by the section considered. Now $\sin\phi$ is a very rapid function of $\mathscr{A}_0$, while the amplitude of the contribution, being proportional to $(d\ln\mathscr{A}/d\epsilon)_0^{-1}$, is a slow function. This enables us to sum the contributions of all sections very easily. For to a large extent they cancel one another out, except in regions where $\mathscr{A}_0$ is locally stationary with respect to k_z, i.e. where the cross section normal to **H** passes through an extremum. Such a region makes a relatively large contribution at a constant phase. The contributions of various sections at a given value of H are readily summed by means of a phase–amplitude diagram. If we measure k_z from a point where ϕ has an extremal value ϕ_0 (say a maximum), we may write $\phi = \phi_0 - ck_z^2$, where c is a constant. Since ϕ varies by many cycles in a short range of k_z, we may take $(d\ln\mathscr{A}/d\epsilon)_0$ to be substantially constant, and take as an element of the phase–amplitude diagram a vector ds of length dk_z and phase $\phi_0 - ck_z^2$. But this we know to be the construction which yields Cornu's spiral, so that we can immediately infer that the resultant of all sections is the closing vector of the spiral, and this lags in phase behind the central vector by $\pi/4$. Since, therefore, the phase of the resultant is uniquely linked to the phase of the central vector, the oscillations of ΔM for the whole surface will have the periodicity characteristic of the maximal area. If there are several extrema (maxima or minima) there will be a corresponding number of periodicities. It is not necessary that the extremal areas shall enclose filled states—extremal hole orbits should contribute equally with electron orbits to the de Haas–van Alphen effect, as should extended orbits in principle, though these may be expected to give very short periods and low amplitudes, and be very hard to observe.

We shall say little here about the techniques of observation of the effect, since they are fully discussed by Shoenberg (1957). The impulsive method which he has developed is particularly suited to observations in fields of about 10^5 gauss. The specimen, in the form of a fine monocrystalline wire, is placed in a solenoid through which is passed a heavy discharge from a bank of condensers. The field rises to about 10^5 gauss and then decays again, the whole discharge occupying about 20 milliseconds. While the field varies smoothly, the magnetic moment of the specimen oscillates very rapidly if the de Haas–van Alphen effect is present, and the oscillations may be detected by a search coil surrounding the specimen. A typical oscillogram of the signal is shown in figure 21. Two frequencies are present, but other crystals and other orientations of the same crystal may give one or three or more, depending on the number and topography of the Fermi surfaces.

The discussion of the periodicity of the de Haas–van Alphen effect has been straightforward; the amplitude is not so simple. The factors which are known to contribute to determining the amplitude in a given field are as follows:

(1) The curvature $d^2\mathscr{A}_0/dk_z^2$ at the extremum: the smaller this is, the larger the expected amplitude.

(2) The temperature: as already mentioned, this contributes to the amplitude of the fundamental frequency a factor $X/\sinh X$, where $X = 2\pi^2 kT/\hbar\omega_c$.

(3) Collision broadening of the levels: for the effect to be appreciable, the electron must have a reasonable chance of completing the orbit. If $\bar{\tau}$ is the average relaxation time around the orbit the contribution to the amplitude is a factor

$\exp(-2\pi/\omega_c\bar{\tau})$. It is, of course, important to remember that the average value of τ around an orbit may be quite different from the average over the whole Fermi surface, particularly if we are right in our supposition that near points of contact with the zone boundary there may be regions of high scattering probability. Non-viable orbits contribute no de Haas–van Alphen effect, and it would be erroneous to infer from the absence of an observable effect in any particular direction that the topography of the Fermi surface is such as to exclude closed extremal orbits.

(4) Lattice broadening of the levels : this is likely to be important only in very special orientations for which the extremal orbit has rather sharp corners as it runs close to a zone boundary. The discussions which have been given of this point

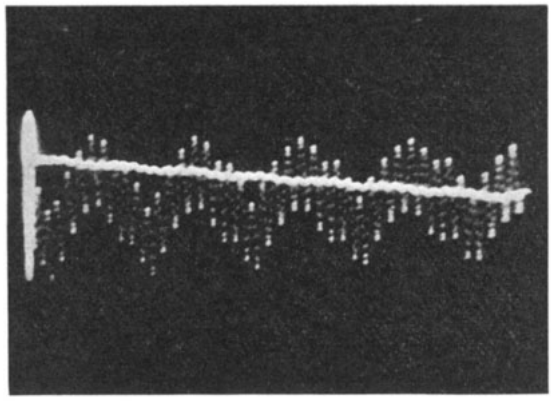

Figure 21. Oscillogram of de Haas–van Alphen effect in lead. The heavy slanting line is a trace of the variation of H. (*After* Gold 1958.)

(Harper 1955, Brailsford 1957) are physically rather obscure, but it appears that the effect may be interpreted semi-classically in the spirit of Onsager's (1952) approach. What is neglected in the latter is the fact that the form of $\epsilon(\mathbf{k})$ is determined by a specific lattice periodicity, and the electrons are not moving in a uniform background potential. The degenerate levels of the free-electron theory correspond to similar orbits around different centres in real space, and in the periodic lattice these different centres may be differently situated in the unit cell. Now the wave function of the electron is not sharply localized, so that the influence of the centring of the orbit should not be very marked. It will, however, be most marked when the orbit has sharp corners, for in the neighbourhood of these the wave packet describing the electrons becomes particularly small in real space.

(5) Electron spin : the effect of spin is to double all the levels, so that instead of a set whose energy separation is $eH\hbar/m_c^*$ we have two similar sets shifted by $geH\hbar/m$, m being the real electron mass, and g a splitting factor to allow for the possibility that spin–orbit coupling may modify the effective spin moment. The degeneracy of each set is half the degeneracy we have hitherto assumed, neglecting spin ; and since each contributes the same fundamental frequency but with a phase difference of $2\pi gm_c^*/m$, the effect is to introduce an amplitude factor $\cos(\pi gm_c^*/m)$. For the rth harmonic the factor is $\cos(r\pi gm_c^*/m)$. Very little is

known about the values of g in real metals, but it appears that in some semiconductors and in bismuth it may become very large, so that even although m_c^* may be extremely small, gm_c^*/m may be of the order of unity. This has been adduced by Cohen and Blount (1960) as an explanation for the anomalous phases of the de Haas–van Alphen oscillations in bismuth.

These are the principal theoretical contributions to the amplitude, so far as is known. There are also experimental influences which tend to reduce the amplitude, such as mosaic structure of the specimen and inhomogeneity of the field. The consequence of all this is that at present little information can be extracted from the absolute amplitude of the effect. This does not prevent the temperature variation from being used to determine m_c^*, on the assumption that the other causes of amplitude reduction are constant. The de Haas–van Alphen effect is therefore able to determine the angular variations of both the extremal cross sections and their derivatives with respect to energy. The former may be used

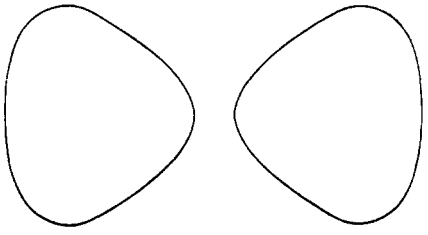

Figure 22. Fermi surface having no central extremal area.

under favourable conditions to deduce the shape of the Fermi surface uniquely, and the latter the variation of electron velocity over the Fermi surface. Lifshitz and Pogorelov (1954) have shown that if the surface is centro-symmetric and convex, so that in each orientation there is only one extremal section, passing through the centre of symmetry, there is a unique procedure for deducing the shape from the variations of periodicity, and under similar restrictions the same holds for the determination of the velocity. This is a very valuable result, but even so it does not guarantee that there will be no ambiguity of interpretation, for one cannot normally be sure that the Fermi surface satisfies the conditions of the theorem. This is especially true for a situation such as that shown in figure 22, where the Fermi surface, though centro-symmetric when considered as a whole, is split into two mirror images, neither of which has central symmetry. For any orientation of field each contributes the same periodicity, and there is no way of telling that there is not just one surface of a different shape. One could, for example, probably devise pseudo-spheres, like smoothed tetrahedra, whose extremal areas were independent of orientation, and which could occur in pairs and be indistinguishable from a single spherical surface. A second example of a surface not satisfying the conditions of the theorem of Lifshitz and Pogorelov is shown in figure 23, which is to be pictured as a dumb-bell-shaped surface of revolution. For magnetic fields in the plane of the diagram, the variation of cross section with orientation is sketched in figure 24, the branch (*a*) being the central section, and (*b*) the non-central section. At P they coalesce, since in this case there is a range of angles for which there is only a central extremum. This

situation should not be difficult to recognize in practice, especially as at the point of coalescence the second derivative $d^2\mathscr{A}_0/dk_z^2$ vanishes, and the oscillations ought to have a particularly large amplitude. Thus although the formal method of Lifshitz and Pogorelov may be inapplicable here, it should not be impossible to reconstruct the surface from the data. As a final example of ambiguity of interpretation, consider a cylindrical Fermi surface, such as might occur in a highly anisotropic metal like graphite. For a field inclined at an angle θ to the axis, the area of all sections is $\mathscr{A}_n \sec\theta$, where $\mathscr{A}_n$ is the normal cross section; rotation about the axis produces no change, and the cross-sectional shape of the cylinder is indeterminate. With these examples we leave the de Haas–van Alphen effect for the present, but shall return later to discuss some of the results which have been obtained by its use.

Closely related to the oscillations of magnetic moment are the oscillations in the transport coefficients, first observed as resistance oscillations in bismuth by

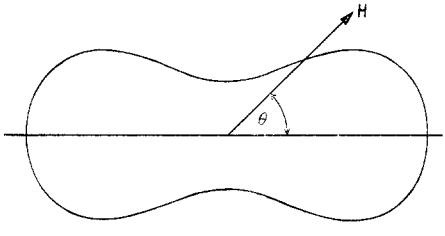

Figure 23. Dumb-bell-shaped surface having more than one extremal area.

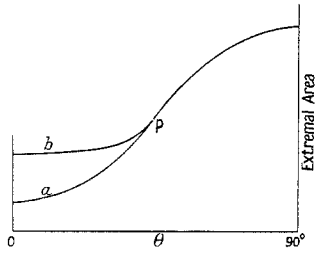

Figure 24. Variation of extremal areas with field orientation for surface of figure 23.

Schubnikov and de Haas (1930), and later observed in both transverse and longitudinal magneto-resistance, Hall effect, thermal conductivity and thermoelectric effects in a variety of substances.† Wherever comparison between any of these effects and the de Haas–van Alphen effect has been possible, the periods of the oscillations have been found to be in complete accord. We shall discuss the connection between the effects by reference in particular to the transverse magneto-resistance and Hall effect, making use of the impulsive electric field method as before. The electronic states in the magnetic field form a discrete spectrum of levels, and when the impulsive electric field Edt is applied it causes a certain number of transitions to higher states. Typically, an electron in a certain stationary state has its wave function modified so that after the impulse it has an admixture of neighbouring stationary state wave functions. In the free-electron metal only states differing in energy by one unit of $\hbar\omega_c$ will combine, and the resulting wave function describes a current-carrying state in which the current density is $Ne^2 Edt/m$,

† The following list, which is probably incomplete, indicates the variety of observations made:
Bismuth: Hall effect and magneto-resistance (Gerritsen and de Haas 1940, Alers and Webber 1953, Reynolds, Hemstreet, Leinhardt and Triantos 1954, Connell and Marcus 1957). Thermal conductivity and thermoelectric power (Steele and Babiskin 1955).
Graphite: Hall effect and magneto-resistance (Berlincourt and Steele 1955, Soule 1958 a).
Zinc: Electrical and thermal magneto-resistance (Alers 1956).
Indium arsenide: Magneto-resistance (Sladek 1958).
Note also the related oscillatory magneto-absorption of light in semiconductors (Zwerdling, Lax and Roth 1957, Lax, Roth and Zwerdling 1959).

rotating about the z-axis with frequency ω_c. In any other case the behaviour is more complex. The immediate response of the system to a sharp pulse Edt is the same as for the free-electron model, a current density Ne^2Edt/m. But this will result from the combining with the original state of many levels, some of which belong to different energy bands and give rise to very high-frequency rotational terms in the current density. If the separation of levels just above ϵ_0 is small in comparison with the band gap the contributions of inter-band transitions may be readily separated from those due to small-energy transitions, and if the former are ignored the initial current density and its subsequent oscillations are the same as given by the semi-classical calculation and expressed in the form of (22). That is to say, the discrete quantization of the levels is not in itself responsible for any significant change in the transport properties. The origin of the periodic changes in resistivity and Hall effect is to be found principally in two rather subsidiary effects of quantization, change in the number of electrons in a band and change in the relaxation time. A great deal of highly complex matter has been published on these effects, which appear to be basically simple.

The treatment which follows is an elementary analysis in the spirit of Lifshitz' (1958) approach to the problem, which seeks to display the parallelism between the Schubnikov and the de Haas–van Alphen effects. The results differ significantly from those of Lifshitz, who appears to ignore the oscillations of relaxation time which are the dominant cause of resistance oscillations. Argyres' (1958 a) calculations of the transverse effects agree substantially with Lifshitz' and are presumably open to the same criticism, although no such fault can be found with his analysis (1958 b) of longitudinal oscillatory magneto-resistance. The most recent treatment, by Adams and Holstein (1959), provides elaborate justification for the earlier results of Davydov and Pomeranchuk (1940), and for the semi-classical approach which we present here. It should be remarked that the disagreements between various workers are not concerned with the frequency of the oscillations and its relation to the Fermi surface, but only with the amplitude. The difference between Adams and Holstein on the one hand, and Lifshitz on the other, is between an oscillatory variation of resistance which is observable with difficulty and one which lies well below observability. We believe the former to represent the true state of affairs.

As with the de Haas–van Alphen effect, we consider for simplicity an assembly of electrons whose Fermi energy is maintained constant, so that the number of electrons within a section dk_z is a periodic function of field, as in figure 20(a), being related to the variations of magnetic moment by the expression

$$\Delta N = -H\left(\frac{d\ln\mathscr{A}}{d\epsilon}\right)_0 \Delta M. \qquad \ldots\ldots(26)$$

The contributions to the conductivity tensor by this section thus fluctuate as if in the absence of a magnetic field the Fermi energy were changing so as to give the variations expressed by (26). We may define an effective mobility μ_{ij} for the electrons in this section by considering the change of conductivity consequent upon a change in the number of electrons it contains, and write

$$\mu_{ij} = \partial\sigma_{ij}/\partial N.$$

This definition takes care of conductivity changes arising both directly from changes in N and indirectly from the possible variation of free path with N, but it assumes that all parts of the Fermi surface other than the section considered remain unchanged. We may now write for the variations of the contribution of the section to the conductivity from this cause

$$\Delta\sigma_{ij}^{(1)} = -H\mu_{ij}\left(\frac{d\ln\mathscr{A}}{d\epsilon}\right)_0 \Delta M. \qquad \ldots\ldots(27)$$

By the same arguments as before, most sections will contribute oscillations which cancel each other, and anything observed will arise at extremal cross sections. Thus the actually observed variations of ΔM and $\Delta\sigma_{ij}^{(1)}$ will be related by the value of the coefficient in (27) which is appropriate to an extremum. For each extremum

$$\Delta\sigma_{ij}^{(1)} = -H\Delta M(\mu_{ij}\, d\ln\mathscr{A}/d\epsilon)_{\text{ext}}. \qquad \ldots\ldots(28)$$

This is not the whole story, however, for the other parts of the Fermi surface do not remain unchanged. In particular, the density of states, taken over the whole Fermi surface, shows variations, and these are reflected in the conductivity since the probability of scattering of a given electron is proportional to the number of vacant states into which it may be scattered. A full treatment of this effect is complicated, but the general principle may be understood if we suppose that the mechanism of scattering is by impurities which scatter essentially isotropically. This means that the probability of scattering of any electron at the Fermi surface is changed in the same proportion, and this is the relative change in the total density of states. Now when the levels are quantized in a magnetic field the only permitted states just above the Fermi level are those which lie on the orbit surfaces as they cut the Fermi surface. The contribution dN_0 of a thin section dk_z to the density of states N_0 is thus zero for most values of field, since usually the area of dk_z will not be such as to allow an orbit surface. Periodically, however, the area will satisfy (11) and then dN_0 will be enormous ; in fact, dN_0 will vary with H as shown in figure 20(*e*). The area under each δ-function is readily calculated from the fact that the average density of states is only slightly variable, so that the average value of dN_0 may be taken as field-independent. Hence for each cycle,

$$\int \Delta(dN_0)\, dH = \frac{2\pi eH^2}{\hbar\mathscr{A}_0}\overline{dN_0} = \frac{eH^2}{2\pi^2\hbar}\left(\frac{d\ln\mathscr{A}}{d\epsilon}\right)_0 dk_z. \qquad \ldots\ldots(29)$$

This behaviour may be compared with that of $d(\Delta M)/dH$, which can be seen from figure 20(*d*) to take precisely the same form, the area under each δ-function being just the discontinuity in ΔM in figure 20(*c*), i.e. $edk_z/[2\pi^2\hbar(d\ln\mathscr{A}/d\epsilon)_0]$.

Hence
$$\Delta(dN_0) = H^2\left(\frac{d\ln\mathscr{A}}{d\epsilon}\right)_0^2 \frac{d}{dH}(\Delta M). \qquad \ldots\ldots(30)$$

By the same argument as before we relate the observed variations to the extremum, and write for each oscillatory component due to this cause

$$\Delta N_0 = H^2\left(\frac{d\ln\mathscr{A}}{d\epsilon}\right)_{\text{ext}}^2 \frac{d}{dH}(\Delta M). \qquad \ldots\ldots(31)$$

Now the dependence of any component of σ_{ij} on ΔN_0 is governed by its dependence on the relaxation time. Since to observe oscillatory effects we need $\omega_c\bar{\tau}$ to be at least comparable with unity we may reasonably consider only the leading terms in the high field limit of σ_{ij} as given by (24). Reference to (23) shows that the off-diagonal terms, varying as H^{-1}, are independent of $\bar{\tau}$, while σ_{xx} and σ_{yy} vary as $\bar{\tau}^{-1}$ and σ_{zz} as $\bar{\tau}$. If then the leading term varies as H^α, it varies as $\bar{\tau}^{\alpha+1}$ and as $N_0^{-(\alpha+1)}$. The oscillatory components of σ_{ij} therefore take the form

$$\frac{\Delta\sigma_{ij}^{(2)}}{\sigma_{ij}} = -(\alpha+1)\frac{\Delta N_0}{N_0} = -(\alpha+1)\frac{H^2}{N_0}\left(\frac{d\ln\mathscr{A}}{d\epsilon}\right)^2_{\text{ext}}\frac{d}{dH}(\Delta M). \qquad \ldots\ldots(32)$$

In general, we may expect contributions of the types (28) and (32), though if there are several sheets to the Fermi surface there may be complicated interactions, since ϵ_0 will not stay constant and account must be taken of scattering from one sheet to another. If there is only one band, ϵ_0 certainly does not stay constant, but the total number of electrons does; we then expect no contribution $\Delta\sigma_{ij}^{(1)}$ (or at most a small one from the energy variation of free path) and only a contribution $\Delta\sigma_{ij}^{(2)}$. In any case, as may be seen by substituting the appropriate values for a free electron gas into (28) and (32), the ratio $\Delta\sigma_{ii}^{(2)}/\Delta\sigma_{ii}^{(1)}$ is of the order of the phase of the oscillation, which we have found to be very large indeed for Fermi surfaces holding anything approaching one electron per atom. We shall therefore concentrate on $\Delta\sigma_{ij}^{(2)}$ as giving an estimate of the magnitude of the effect which may be expected.

To estimate the magnitude of the fundamental frequency contained in ΔN_0 at the absolute zero it is convenient to work from first principles rather than to use (31). We note first that for any section dk_z the variation $\Delta(dN_0)$ is a δ-function whose fundamental has thus an amplitude equal to twice the mean value, i.e. $2\overline{dN_0}$, where $\overline{dN_0}$ is the contribution of the section to N_0 in zero magnetic field. Next we observe that, when we use the Cornu spiral to sum the contributions of all sections, the resultant has the same amplitude as if a certain central section all oscillated in phase, all other regions being neglected. The appropriate effective central section is that lying between the two planes which contribute oscillations differing in phase from the extremal oscillation by $\pi/4$. To make the matter explicit consider a spherical Fermi surface of radius k_0, so that the phase due to the extremal (central) section is $\pi\hbar k_0^2/(eH)$. The effective central section is bounded by planes $\pm k_z$ such that $\pi\hbar k_z^2/(eH) = \pi/4$, i.e. $k_z = \frac{1}{2}(eH/\hbar)^{1/2}$. The surface area of the central section is $2\pi k_0(eH/\hbar)^{1/2}$, a fraction $(eH/\hbar)^{1/2}/(2k_0)$ of the total surface area. It follows then from the foregoing argument that the relative amplitude of the fundamental oscillation is twice this, i.e.

$$\frac{\Delta N_0}{N_0} = \frac{1}{k_0}\left(\frac{eH}{\hbar}\right)^{1/2} = (2n)^{-1/2}, \qquad \ldots\ldots(33)$$

where n is the order of the oscillation as defined in (25). For the standard metal (see Appendix) n was found to be about 4800 in a field of 100 kG. We should expect the oscillations of σ_{ii} to amount to about $\pm 1\%$ if there were no factors, such as temperature or mosaic structure, reducing the effect. It is clear, therefore, that for this sort of metal we cannot expect a very striking phenomenon.

The effect is also in practice very weak in metals such as tin and zinc where the value of n is much lower. This is presumably because the oscillations are due to small portions of the Fermi surface whose total contribution to N_0 is in any case small. Where the effect really becomes marked is in semi-metals like bismuth

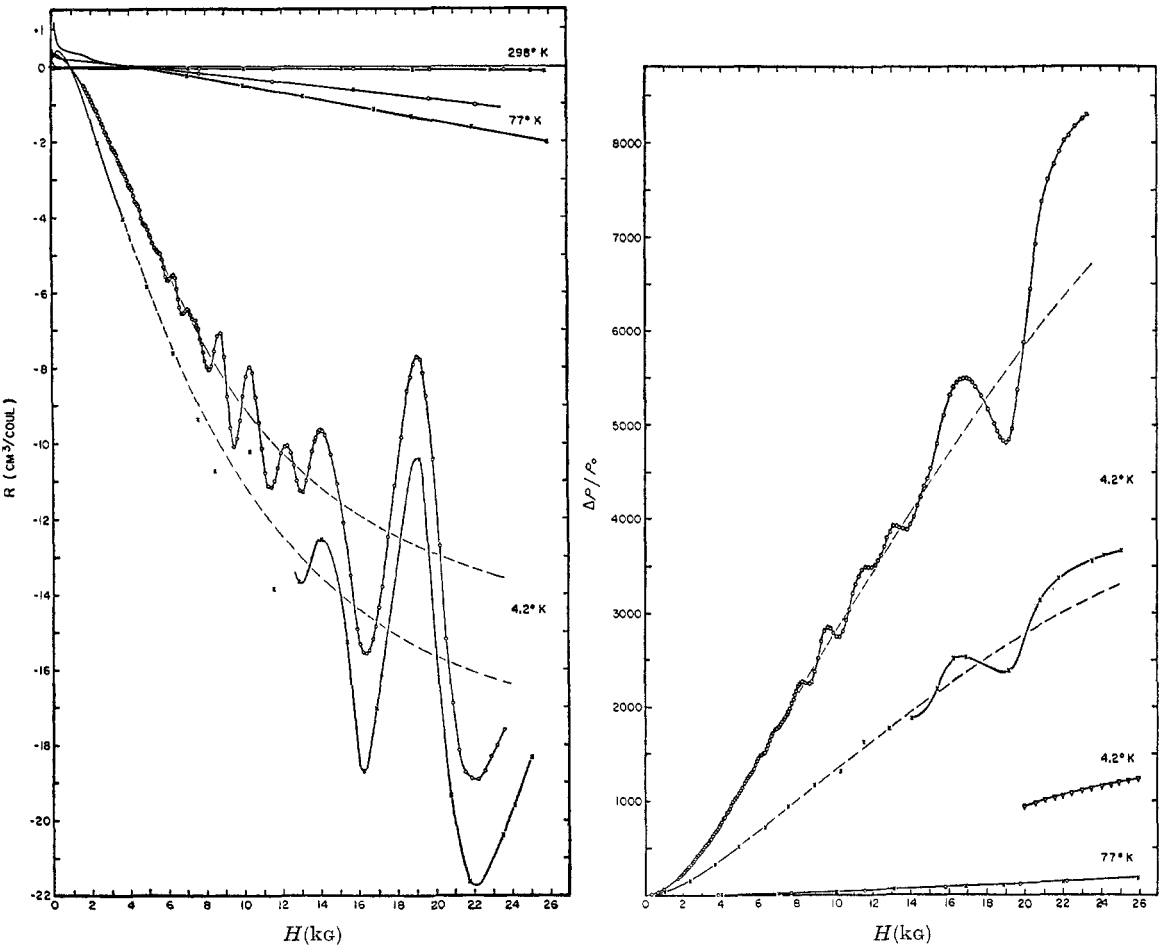

Figure 25. Field variation of (*a*) Hall coefficient and (*b*) transverse magneto-resistance in different specimens of graphite at various temperatures. The field is parallel to the *c*-axis. (*After* Soule 1958 a.)

and graphite and degenerate semiconductors like InAs and InSb where all Fermi surfaces are small. An example of the oscillations of resistivity and Hall coefficient in graphite is shown in figure 25. It will be recollected that the measured coefficients are components of the resistivity tensor ρ_{ij}, not σ_{ij}, and both diagonal and non-diagonal elements of σ_{ij} participate in the oscillatory effects.

Since the oscillations in ρ_{ij} are so intimately related to those of magnetic moment it is not to be expected that the information obtained from each should differ, and the question of which is to be preferred is solely a matter of convenience

and ease of observation. The Schubnikov effect has never been observed for any Fermi surface containing something approaching one electron per atom, perhaps only because no attempt has been made to observe it with such patience as has been lavished on the de Haas–van Alphen effect. It is possible that it may come into its own in the study of whiskers, which have already been shown by Shoenberg (1959) to be especially valuable for studying the de Haas–van Alphen effect in the large Fermi surface of copper. If whiskers of diameter as large as 0·01 cm are unobtainable, the magnetic observations become very difficult, but this limitation should not apply to resistance measurements. Since the radius of an electronic orbit in a field of 100 kG is about 10^{-4} cm, it is probably only in whiskers less than 10^{-3} cm in diameter that level broadening by collision with the surface becomes serious.

4.3. *The Anomalous Skin Effect*

The anomalous skin effect has been reviewed up to 1954 by Pippard (1954 c), and we shall adopt here a rather different point of view which is particularly suited to the present need, and which justifies and supersedes a heuristic procedure known as the *ineffectiveness concept*. Since this procedure yields the correct answer but apparently bewilders some rigorists, the sooner it is justified and abandoned the better.

We shall concern ourselves only with conduction in the surface layer, normal to the z-axis, of a plane semi-infinite slab of metal, all quantities varying with angular frequency ω, so that $\partial/\partial x = \partial/\partial y = 0$, $\partial/\partial t = i\omega$. Then Maxwell's equations give as the relation between E and J (both directed along the x-axis)

$$\partial^2 E/\partial z^2 = 4\pi i\omega J. \qquad \ldots\ldots(34)$$

If the metal is isotropic there are no other components of E and J; we make this simplifying assumption for the present. We shall analyse the field variables into their Fourier components, writing, for example,

$$E(z) = \int_{-\infty}^{\infty} E_\nu \, e^{-i\nu z}\, d\nu, \quad \text{where} \quad E_\nu = \frac{1}{2\pi}\int_{-\infty}^{\infty} E\, e^{i\nu z}\, dz,$$

so that (34) takes the form

$$\nu^2 E_\nu + 4\pi i\omega J_\nu^{\text{tot}} = 0, \qquad \ldots\ldots(35)$$

in which J_ν^{tot} has contributions from all current sources. In order to find the field distribution in the metal we require an expression for the current density produced by a given field, and this also may be written formally in terms of the Fourier components

$$J_\nu = \sigma_\nu E_\nu, \quad \text{with} \quad \sigma_\nu(-\nu) = \sigma_\nu(\nu). \qquad \ldots\ldots(36)$$

This equation defines the conductivity component σ_ν in the same way as in (14). Such a definition is immediately useful only if the metal sample is infinite in extent, and we must consider how to allow for the surface of the actual sample. A particularly simple treatment is based on one first given by Klein (1944), which is applicable when the surface is a perfect reflector of electrons. Any electron leaving the surface after a collision with it has k_x and k_y unaltered while k_z is reversed in sign. Its condition is exactly as if it had passed through a field on the

other side of the surface which was a mirror image of the field in the metal. We may therefore replace the actual problem by one in which an infinite sample of metal is subjected to a field having the property that $E(-z) = E(z)$. Such a field may be set up by a current sheet confined to the plane $z = 0$.

We therefore suppose that there is a current I per unit width on the origin plane, having a Fourier spectrum $I_\nu = I/2\pi$. The total current component consists of I_ν and the conduction current J_ν, so that (35) now reads

$$\nu^2 E_\nu + 4\pi i\omega(I/2\pi + J_\nu) = 0.$$

Combining this with (36) we find

$$E_\nu = \frac{-2i\omega I}{\nu^2 + 4\pi i\omega\sigma_\nu},$$

so that

$$E(z) = -4i\omega I \int_0^\infty \frac{\cos \nu z \, d\nu}{\nu^2 + 4\pi i\omega\sigma_\nu}.$$

The field distribution depends on the form of σ_ν; in all the cases we shall be concerned with the form is such that $E(z)$ decreases to zero as z increases, so that the field is confined to a layer near the origin plane. It is clear then that the total conduction current is just equal and opposite to the source current I. To apply this solution to the field configuration at the surface of a semi-infinite slab we can immediately write down the surface impedance Z, which is the ratio of $E(0)$, the field strength at the surface, to the total current per unit length in the skin layer, in this case $-\frac{1}{2}I$. Therefore

$$Z = 8i\omega \int_0^\infty \frac{d\nu}{\nu^2 + 4\pi i\omega\sigma_\nu}. \qquad \ldots\ldots(37)$$

When the electronic free path is so short that for any component contributing to (37) $\nu l \ll 1$, it is permissible to treat σ_ν as constant and equal to the usual d.c. conductivity σ. Under these conditions the *normal skin effect* prevails and (37) may be integrated to yield the well-known result

$$Z_n = (1+i)\sqrt{(2\pi\omega/\sigma)}. \qquad \ldots\ldots(38)$$

If, on the other hand, the free path is so long that for all components of importance in (37) $\nu l \gg 1$, we must use the result which is expressed in its extreme limit by (16), writing

$$Z_\infty = 8i\omega \int_0^\infty \frac{d\nu}{\nu^2 + is^3\nu} = \frac{8\pi\omega}{3^{3/2}s}(1+\sqrt{3}i), \qquad \ldots\ldots(39)$$

where

$$s^3 = \frac{\omega e^2}{\pi\hbar} \int |\rho_y| \, dk_y.$$

This result shows that in the *extreme anomalous limit*, when the limiting form (16) is applicable, the surface impedance is related to the radius of curvature of the Fermi surface around the effective zone, on which the velocity of the electron is parallel to the surface of the sample; Z_∞ is independent of the free path and of the Fermi velocity. The condition of applicability of (16) may be expressed in terms of the *resistive skin depth* δ_r, which is formally defined from Z by the relations

$$\delta \equiv \delta_r + i\delta_i \equiv Z/4\pi\omega. \qquad \ldots\ldots(40)$$

It is easy to see from Maxwell's equations that δ so defined simply measures the value of $E/(dE/dz)$ at the surface, and hence the distance within which the field would fall to zero if it varied linearly with depth. There is no implication in the definition of δ that the field falls exponentially, as it does in the normal skin effect; in fact, in the anomalous skin effect it is not exponential and is rather troublesome to evaluate. For the present, however, we need only note that the values of ν which dominate the integral (39) lie around δ_r^{-1}, so that the condition of applicability of (16) is that $l/\delta_r \gg 1$. For microwave frequencies δ_r in the anomalous limit is of the order of 10^{-5} cm for most metals, so that it is desirable to have l at least as great as 5×10^{-4} cm. This implies the use of pure metals at low temperatures, since typically l is between 10^{-6} and 10^{-5} cm at room temperature. If values of l/δ_r as great as 100 can be achieved the correction needed to obtain the limiting value of Z_∞ is only a few per cent, and can be estimated fairly reliably, as has been shown by Chambers' (1952 b) experimental confirmation of the detailed theory due to Reuter and Sondheimer (1948).

In the foregoing analysis it has been assumed implicitly that **E** and **J** are parallel to one another and to the surface of the metal. This is true for an isotropic metal, but not in general. In the extreme anomalous limit, however, the analysis holds with one simple modification. We saw (see p. 198) that in the limit the tensor $\sigma_{ij}(\nu)$ can be diagonalized, by a suitable choice of x and y axes, and that $\sigma_{zz}(\nu)$ vanishes; moreover, the principal axes depend on the Fermi surface alone and not on ν. In consequence we need not concern ourselves with possible normal components of **E** and **J**, and if we confine our attention to the principal axes in the x–y plane the result (39) is valid. For any plane surface there will be two principal values of Z_∞, which we may label $Z_{\infty x}$ and $Z_{\infty y}$. If the current flow makes an angle ϕ with the x-axis the surface impedance will follow the two-dimensional tensor law

$$Z_\infty(\phi) = Z_{\infty x}\cos^2\phi + Z_{\infty y}\sin^2\phi. \qquad \ldots\ldots(41)$$

These results were first obtained by means of the ineffectiveness concept, which is fully discussed elsewhere (Pippard 1954 a, c) and which assumes that only electrons moving nearly parallel to the surface can carry current. The present analysis justifies the physical idea behind the concept and renders it obsolete.

The assumption of specular reflection of electrons which hit the surface appears from experiment to be unsound, and is indeed theoretically improbable, for irregularities on an atomic scale are sufficient to cause large-angle diffraction of the de Broglie waves. It is almost certainly much nearer the truth to assume completely diffuse scattering at the surface, which is the only other case which has been found mathematically tractable. Even this is of a different order of difficulty from the case of specular reflection, but it has been worked out by Reuter and Sondheimer (1948), again in terms of the Fourier coefficients of the conductivity. The result takes the form

$$Z = 4\pi^2 i\omega \Big/ \int_0^\infty \ln(1 + 4\pi i\omega\sigma_\nu/\nu^2)\, d\nu,$$

and in the extreme anomalous limit

$$Z_\infty = \frac{\sqrt{3}\pi\omega}{s}(1+\sqrt{3}i), \qquad \ldots\ldots(42)$$

which is 9/8 times the expression (39) for specular reflection. It is clear that the limiting value Z_∞ still depends only on the geometry of the Fermi surface and not on the mean free path or Fermi velocity.

One final point in the theory which is worth discussing is the problem of retardation effects. So long as the frequency is low and the mean free path not too long an electron can execute its path while the field is sensibly constant. In normal conduction in a uniform field the breakdown of this condition, when $\omega\tau \sim 1$, leads to a substantial change, the d.c. conductivity being replaced by $\sigma/(1+i\omega\tau)$. This effect does not occur in the extreme anomalous limit. As we have remarked in deriving the form of σ_ν, the criterion for retardation effects to be important is not that $\omega\tau$, but $\omega/v_0\nu$, shall be comparable with unity. This is equivalent in the anomalous skin effect to the statement that no serious modifications are to be expected until the electron is unable to traverse the skin depth normally in a time short compared with the period of oscillation. Since $\delta \sim 10^{-5}$ cm and $v_0 \sim 10^8$ cm/sec, for most metals the critical frequency is about 10^{13} sec^{-1}, some 10^2–10^3 times the frequencies used in practice. The effects of retardation are not negligible, but the correction to be applied amounts to no more than a few per cent. The compensation for retardation effects is managed by a shift in the position of the effective zone, different for each Fourier component of the field, so that at too high a frequency the anomalous skin effect is not governed by a rather precisely defined effective zone, and the usefulness of the phenomenon as an analytic tool is diminished. But at microwave frequencies this limitation will only be felt with semi-metals such as bismuth (Smith 1959), where the Fermi velocity is rather small and the skin depth rather large.

Up to the present the only detailed studies of the anisotropy of the surface resistance are those which have been made on tin (Fawcett 1955) and copper (Pippard 1957 a), both by calorimetric methods. The essence of the method is to let a microwave beam fall on a plane surface of metal which is mounted *in vacuo* in rather loose heat contact with the helium bath surrounding the apparatus. The resulting temperature rise measures the power absorbed and hence the surface resistance. Details of the standardization of the apparatus can be found in the original papers. We shall not discuss the results obtained at this point, but merely comment on one or two general features. First, there is no discrimination of different sheets of the Fermi surface, as in the de Haas–van Alphen effect, so that analysis of a complex metal is virtually impossible by this means alone (though it may prove useful in combination with other methods). Secondly, it is absolutely essential to use well-prepared surfaces, so that the skin layer which carries the current is in all essentials the same as the bulk of the sample. This means that all traces of mechanical strain must be eliminated by etching and electrolytic polishing, and in addition the surface must be left with no asperities on a scale comparable with the skin depth. The major experimental problem is indeed metallurgical—the microwave problems are comparatively trivial. On the other hand, there is not the need here, as in the de Haas–van Alphen effect, to obtain very perfect crystals, since small misalignments of crystallites do nothing to destroy the effect which is being observed. Finally, some comment on the analysis of the results is desirable. The measured quantity is related to an integral of the radius of curvature around the effective zone. An analytical

expression for this property in terms of the equation of the surface is very complicated and virtually useless. The process of constructing a surface which will account for the observations is thus very tedious, and in this respect the method compares rather unfavourably with the de Haas–van Alphen effect. This, indeed, is our general conclusion, but there are exceptional metals, such as copper and silver, which are susceptible to analysis by the anomalous skin effect and which show it to advantage. In a later section we shall compare the results obtained for copper by the two methods so as to display the peculiar merit of the anomalous skin effect in this case. The question of the analysis of the results has been discussed also by Chambers (1956 b) and by Kaganov and Azbel' (1955), making use of a slightly different formulation of the expressions for Z_∞. If the direction of the normal is related to that of the z-axis by the polar angles θ and ϕ, the effective zone of the Fermi surface is characterized as that for which $\theta = \pi/2$. It is not difficult to show that if ϕ is measured from the z–x plane, the two principal values of R_∞ may be written as $\sqrt{3\pi\omega/s}$ (see (42)), the principal values of s^3 being

$$\frac{\omega e^2}{\pi\hbar}\oint\frac{\cos^2\phi\,d\phi}{K(\pi/2,\phi)} \quad \text{and} \quad \frac{\omega e^2}{\pi\hbar}\oint\frac{\sin^2\phi\,d\phi}{K(\pi/2,\phi)}.$$

In these expressions $K(\theta,\phi)$ is the Gaussian curvature at (θ,ϕ), i.e. $(\rho_1\rho_2)^{-1}$, where ρ_1 and ρ_2 are the two principal radii of curvature at that point. From this it can be seen that $\overline{R_\infty^{-3}}$, the mean of $R_{\infty x}^{-3}$ and $R_{\infty y}^{-3}$, gives the mean of s^3, and hence

$$\oint\frac{d\phi}{K(\pi/2,\phi)}.$$

It is now pointed out that the theorem of Lifshitz and Pogorelov, applied to a complete set of data on the variation of this integral with crystal orientation, would enable $K(\theta,\phi)$, and hence the Fermi surface, to be uniquely determined if the Fermi surface were convex and centro-symmetric. It seems to the present author that, as hinted by Chambers, this suggested procedure is of little practical utility. The labour of obtaining complete data would be enormous: the Fermi surfaces to which the method is particularly applicable cannot be relied on to be convex: and finally, by taking the average of $R_{\infty x}^{-3}$ and $R_{\infty y}^{-3}$ a lot of the significant information may be hidden. It may indeed be more generally true that the mathematical beauty of the theorem of Lifshitz and Pogorelov encourages an overestimate of its practical value, and that a quicker way of analysing the data, whether on the anomalous skin effect or the de Haas–van Alphen effect, is by the use of the geometrical imagination and a fair amount of trial and error.

Before leaving the anomalous skin effect let us remark on its use to determine the total area of the Fermi surface. It may be shown, for example from the relation between $\overline{R_\infty^{-3}}$ and the Gaussian curvature, that the mean value of $\overline{R_\infty^{-3}}$, taken over all crystal orientations, is related to the total area S of all sheets of the Fermi surface by the expression

$$\omega^2(\overline{R_\infty^{-3}})_{\text{av}} = \frac{e^2 S}{4\cdot 3^{3/2}\pi^4\hbar}. \qquad \ldots\ldots(43)$$

If the anisotropy of R_∞ is not too great, one may approximate to $(\overline{R_\infty^{-3}})_{\text{av}}$ by $(R_\infty)_{\text{av}}^{-3}$ and thus obtain the value of S by a single measurement on a random polycrystalline sample. A comparison of the value of S with that expected from

simple models may serve as a rough check of these models. For example, if the energy discontinuities at the zone boundaries are small, the Fermi surface, when plotted in the extended reciprocal space, may approximate to a sphere, with small deformations around the regions of intersection with zone boundaries. The total area will be very similar to that of a sphere holding the same number of electrons. It is interesting, though not conclusive, that in aluminium, which Heine (1957 a) has suggested should have rather small discontinuities, the value of S is close to that of a sphere containing three electrons per atom (Chambers 1952 b, Faber and Pippard 1955). For most many-electron metals S is distinctly smaller than the free-electron value, and we may conclude that there are considerable departures from the spherical shape. The value of S may also be used in conjunction with the specific heat constant γ to estimate the mean Fermi velocity, since the density of states at the Fermi surface is $(4\pi^3\hbar)^{-1}\int dS/v_0$, i.e.

$$\gamma = \frac{k^2 S}{12\pi\hbar}\left(\overline{\frac{1}{v_0}}\right). \qquad \ldots\ldots(44)$$

Such an estimate of the Fermi velocity might with advantage be compared with an estimate from the de Haas–van Alphen effect or from cyclotron resonance, for the two types of measurement involve different patterns of excitation ; thermal excitations produce excited electrons and holes all over the Fermi surface, while current-carrying excitations produce excited electrons on one side and holes on the other. If interactions between excited electrons and holes play any significant part in determining the energy spectrum near the Fermi level, one may expect the velocity deduced in the two ways to differ. Thus (44) applied to detailed independent measurements of γ, S and v_0 may serve as a critical check on the assumptions of the independent-particle model.

4.4. *Cyclotron Resonance*

An understanding of cyclotron resonance in metals, which is a more complicated matter than the corresponding effect in semiconductors, involves a consideration of the effect of a magnetic field on the electrons in a metal exhibiting the anomalous skin effect. Two distinct experimental arrangements have been investigated, one in which the magnetic field is applied normally to the metal surface and the other in which it is parallel to the surface. It is the second which is of greater interest in the study of metals ; it was proposed and has been analysed in detail by Azbel' and Kaner (1956, 1958). Their analysis is of very great complexity, to some extent unavoidable since an exact treatment such as they attempt involves real mathematical difficulties, altogether apart from the repellent obscurity occasioned by the generality of their model. Other published treatments of more specialized models are either avowedly (as Heine's (1957 b)) or unwittingly (as Mattis and Dresselhaus' (1958) and Rodriguez' (1958 a)) inexact. For the present we shall follow the latter's lead, since the errors involved do not seriously affect the answers, and their physical interpretation of the phenomenon is sound enough. There is, indeed, no difficulty in understanding how the resonance comes about (see figure 26). If the field is parallel to the surface the electronic orbits can return again and again to the surface layer containing the oscillatory field, provided that $\omega_c\bar{\tau} \gg 1$, and if the successive traverses find the electric

field at the same phase each time, i.e. if ω is an integral multiple of ω_c, the electrons can contribute very effectively to the conduction and the impedance may be expected to take a low value. Since the cyclotron frequency, as given by (12), is proportional to H, successive resonances should be evenly spaced in H^{-1}.

We shall now assume, incorrectly, that the treatment of the anomalous skin effect given in the last section can be taken over unmodified, so that we are concerned only to evaluate the Fourier components of the conductivity, σ_ν. We shall discuss later the errors introduced by this assumption. They are not of great consequence so long as we are interested in the resonance phenomenon, since they are due to an incorrect treatment of surface scattering and the electrons involved in the resonance do not hit the surface. Even with this approximation the evaluation of $\sigma_\nu(H)$ is in general rather lengthy, but by considering only a limiting case we can shorten the work greatly. We therefore

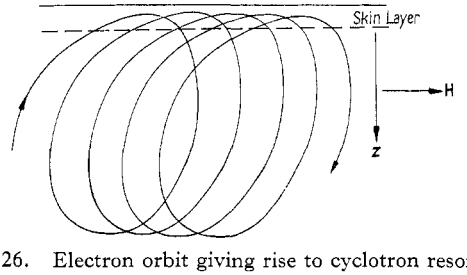

Figure 26. Electron orbit giving rise to cyclotron resonance.

choose the conditions such that the size of the electronic orbit is much larger than the wavelength of the Fourier component of the electric field, and the relaxation time is so long that $\omega_c\bar{\tau} \gg 1$. These are the conditions under which the resonance is most marked.

Take the normal to the surface of the metal as the z-axis, and let the steady magnetic field lie along the x-axis. There are two directions of microwave polarization of interest, the electric field being either parallel or normal to H. We shall consider the latter first, and discuss the behaviour of an electron in a field $E_y = E_0 e^{i(\omega t - \nu z)}$. As the electron goes round its large, not necessarily circular, orbit it suffers a rapidly alternating field from which it acquires practically no change of momentum. Only at the extremal values of z, where its velocity lies in a plane $z =$ constant, does the cancellation of contributions fail. We may therefore concentrate on the region of the orbit where z is minimal, and suppose that in this region the orbit may be represented by a circular arc of radius r; we disregard the x-component of velocity as irrelevant. The phase–amplitude diagram of the electric field acting on the electron in its trajectory forms a Cornu spiral, so that, as on p. 216, we can represent the effect of one traversal of this region by supposing the electron to move in a uniform field for such a length of arc, $\sqrt{(2\pi r/\nu)}$, as lies within one-eighth of a wavelength from the extreme point, the phase of the field being shifted by $\pi/4$ from that at the extreme. Hence if the electron passes its extreme point z at time t we may write for the change in momentum caused by one traversal

$$\hbar v_y \, \delta k_y = eE_0(2\pi r/\nu)^{1/2} e^{i(\omega t - \nu z - \pi/4)}, \qquad \ldots\ldots(45)$$

where v_y is the velocity in the plane normal to H. The previous traversal, at $t-2\pi/\omega_c$, caused a similar displacement $\delta k_y'$, of which a fraction $\exp[-2\pi/(\omega_c\bar{\tau})]$ survived the circuit; the sum of all previous traversals is thus given by the expression

$$\Delta k_y = F\,\delta k_y,$$

where

$$F = \sum_{n=0}^{\infty} \exp\left[-\frac{2\pi n}{\omega_c\bar{\tau}}(1+i\omega\bar{\tau})\right] = \left\{1-\exp\left[-\frac{2\pi}{\omega_c\bar{\tau}}(1+i\omega\bar{\tau})\right]\right\}^{-1}. \quad \ldots\ldots(46)$$

It is the oscillations of the factor F which cause the observed resistance oscillations.

We must now move to reciprocal space to calculate the current at a given point z. Figure 27 shows a typical Fermi surface, of which we select for study a plane section, normal to **H**, of thickness dk_x. On this surface is drawn the effective zone, the locus of points where the normal is parallel to the surface of the metal; the effective zone cuts the section considered at Z. An electron

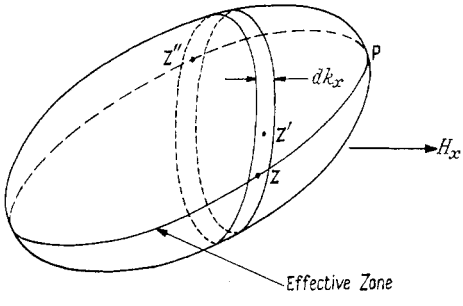

Figure 27. Illustrating calculation of cyclotron resonance.

represented by Z is moving at the extreme of its orbit, and has suffered a displacement Δk_y, as given by (46). An electron at Z' is performing a similar orbit and has suffered a displacement $\Delta k_y'$ which is the same as Δk_y in (46), except that if the electron is represented by Z' when its depth in the metal is z the extreme position of its orbit is not z, and the phase of $\Delta k_y'$ is correspondingly different from that of Δk_y. The phase–amplitude diagram of the contributions of electrons near Z to the current at z is once more a Cornu spiral, and the same rule for summation applies, the effective length of arc in reciprocal space being obtained from the effective length in real space by scaling in proportion to the radii of the orbits in the two representations. Thus the total current is the same as if all electrons in an arc of length $\rho_x(2\pi/\nu r)^{1/2}$ suffered the displacement Δk_y of the electron at Z, ρ_x being the radius of the Fermi surface in the plane of the section, but with a phase shift of $\pi/4$ which removes the phase shift in (45). Hence from (45) and (46), writing $1/4\pi^3$ for the density of states in reciprocal space, we have for the current density

$$dJ_y = d\sigma_{yy}(\nu,H).E_y, \quad \text{where} \quad d\sigma_{yy}(\nu,H) = F\frac{e^2|\rho_x|\,dk_x}{2\pi^2\hbar\nu}. \quad \ldots\ldots(47)$$

In deriving this result we have neglected two contributions to J_y which might appear to be important. First, there is at least one other point besides Z on the section dk_x where the electronic velocity is parallel to the surface, such as Z'' in

figure 27. But if Z represents an electron as near the surface of the metal as it can go, Z'' corresponds to the electron having gone as far into the metal as its orbit allows. If an electron represented by Z'' lies in the skin layer it will be prevented by the surface of the metal from completing its orbit, and it seems reasonable to disregard its contribution to $d\sigma_{yy}(\nu,H)$. Secondly, Z'' may correspond to the other end of an orbit of which Z represents the region near the surface ; in any orbit there are two regions which contribute to J_y and we have taken only one into account. The reason for this is that the relative phase of the two contributions is very sensitive to the exact value of ν since by hypothesis $\nu r \gg 1$. In the actual problem the Fourier components of the field in the skin depth are so phased as to combine constructively near the surface and to annul one another at depths as great as r. It is therefore appropriate to regard $d\sigma_{yy}(\nu,H)$ as an average over a small range of ν, the average contribution from the far end of the orbit being zero. For similar reasons, if the Fermi surface is not wholly convex so that there is more than one effective zone, the value of ρ_x in (47) is to be taken only on that effective zone which has a maximum value of k_y, corresponding to the closest point of approach to the surface of the metal. Bearing in mind that for a convex surface only half the effective zone contributes to $d\sigma_{yy}(\nu,H)$, we see by comparison with (16) that, apart from the resonance factor F, $d\sigma_{yy}(\nu,H)$ is not only independent of H within the range of validity of the calculation, but also takes the same value as in zero field. This should not be taken to mean that $d\sigma_{yy}(\nu,H)$ will be governed solely by the simple factor F in all fields, since our treatment is only valid when $\omega_c\bar{\tau} \gg 1$; in particular, there is a difficult transition region between the high-field situation in which only one side of the effective zone contributes and the zero-field situation in which both sides contribute.

To turn now to the case where the microwave field is parallel to **H**, the calculation is readily modified to yield the result

$$d\sigma_{xx}(\nu,H) = F\frac{e^2|\rho_y|\,dk_y}{2\pi^2\hbar\nu}, \qquad \ldots\ldots(48)$$

where dk_y is the y-component of the length of the effective zone cut off by the section dk_x and ρ_y is the radius of the Fermi surface on the effective zone in a plane normal to the y-axis. Thus for both polarizations of the microwave field the conductivity is the same as without the magnetic field, apart from the resonance factor F.

If the effective mass and cyclotron frequency are constant over the whole Fermi surface, F will take the same value for all electrons. Since in the extreme anomalous limit the surface impedance varies as $\sigma^{-1/3}$, we may write immediately

$$Z_\infty(H) = \alpha Z_\infty(0)\,F^{-1/3}, \qquad \ldots\ldots(49)$$

where $Z_\infty(0)$ is given by (42). The factor α is supplied to make up for the deficiencies of the calculation which arise from taking imperfect account of the surface scattering. According to Azbel' and Kaner (1958), in the resonance region α is to a good approximation 8/9, though there are small oscillatory terms which slightly modify the amplitude of the oscillations of $Z_\infty(H)$. On account of the complex form of $Z_\infty(0)$, which has a factor $(1+\sqrt{3}i)$, the real and imaginary parts of $Z_\infty(H)$ do not exhibit symmetrical oscillations, but are distorted in the way

shown in figure 28. The distortion would hardly be noticeable experimentally for values of $\omega_c \bar{\tau}$ less than 10, but the maxima and minima in F appear somewhat displaced from the expected positions.

To examine the order of magnitude of the quantities involved, so as to find the conditions under which the effect should be observable, let us consider the standard metal (see Appendix) for which, if we use 1 cm microwaves, the fundamental resonance will occur at the quite accessible field of 11 000 gauss, the other resonances being at sub-multiples of this figure. The perimeter of the fundamental orbit is $4{\cdot}7 \times 10^{-3}$ cm, about 10^3 times larger than the skin depth, so that this condition for resonance is easily met. On the other hand, to see several oscillations of the resistance it would be desirable to have the mean free path rather larger than the perimeter of the fundamental orbit, say 10^{-2} cm. With this free path the metal would have a d.c. conductivity 2000 times better than

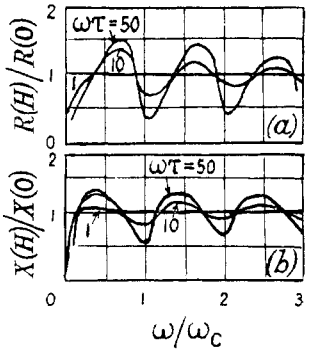

Figure 28. Theoretical variation of R and X with H in free-electron metal, for various values of $\omega_c \tau$. (*After* Azbel' and Kaner 1958.)

copper at room temperature. Such a conductivity is obtainable at the lowest temperatures with a few metals which can be prepared in a state of high purity, but the requirement is rather stringent and at present is something of a limitation to the use of this method as an analytical tool. A significant improvement would be realized by working at rather higher frequencies, since there is still a factor in hand in the ratio of orbit radius to skin depth, which varies as $\omega_c^{-2/3}$; but the magnetic fields required become correspondingly greater, and there are technical difficulties (probably not insuperable) in the use of microwaves of wavelength less than 4 mm, especially if resonant cavities are to be used to measure the surface impedance.

If the Fermi surface is not ellipsoidal and the effective mass is different for different orbits the interpretation of the theory becomes somewhat delicate. Azbel' and Kaner enter into the matter in great detail, but we shall do no more than discuss one or two special points of importance. Let us start with a Fermi surface something like that shown in figure 27, having a centre of symmetry. The variation of ω_c with k_x must be an even function; the point P, where the tangent plane is normal to **H** (an *elliptic limiting point* in the terminology of Azbel' and Kaner), is not especially distinguished so far as the variation of ω_c is concerned, and we may expect around P that $d\omega_c/dk_x$ will be finite and non-vanishing.

The resonance factor F will then be a smooth even function of k_x, and to determine the oscillations of the impedance it is clear from (47) and (48) that we have to evaluate integrals of the type $\int F|\rho_x|\,dk_x$ for $\sigma_{yy}(\nu,H)$ and $\int F|\rho_y|\,dk_y$ for $\sigma_{xx}(\nu,H)$. If we confine our attention to the fundamental oscillation of F (i.e. neglect the distorted form which appears at large values of $\omega_c\bar{\tau}$) the evaluation of these integrals may proceed by the use of a phase–amplitude diagram, in which an element of arc represents the amplitude (ds) and phase (ϕ) of $F|\rho_x|\,dk_x$ on an Argand diagram. The value of ϕ for any strip dk_x is seen from (46) to be $-2\pi\omega/\omega_c$, which may be written in the form

$$\left.\begin{aligned}\phi &= -\alpha/H,\\ \text{where, from (12),}\quad \alpha &= 2\pi\omega m_c^*/e,\end{aligned}\right\} \qquad \ldots\ldots(50)$$

α being a smooth even function of k_x. So far as $\sigma_{yy}(\nu,H)$ is concerned, the behaviour is dominated by the central region of the Fermi surface, around which ϕ varies no more rapidly than as k_x^2, while the contribution of a strip is sensibly proportional to dk_x, since ρ_x is stationary at the centre. The phase–amplitude diagram thus starts with ϕ proportional to s^2, once more the Cornu spiral ; in this

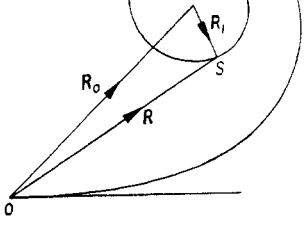

Figure 29. Cornu spiral showing contributions to cyclotron resonance.

particular application of the spiral, however, we cannot suppose that the whole length is realized, since the total difference in ϕ between the centre of the Fermi surface and the limiting point may be quite small. If it amounts to as much as 2π, the resultant oscillatory behaviour of the whole Fermi surface is easily described. Suppose that the phase–amplitude diagram is precisely a portion of the Cornu spiral, as the arc OS in figure 29, which represents **R**, the resultant amplitude of $\sigma_{yy}(\nu,H)$. This resultant may be considered as dissected into two terms, $\mathbf{R}_0$ the limiting vector of the spiral, and $\mathbf{R}_1$ a correction term. Now if S lies farther than about 2π from O, $\mathbf{R}_1$ is very nearly normal to the curve at S, while, of course, $\mathbf{R}_0$ is at $\pi/4$ to the curve at O. As the magnetic field is changed, and with it all the ϕ's, S will move regularly along the spiral, getting farther from O as **H** is reduced, since from (50) $\phi = -\alpha/H$. But the resultant will always have one large term $\mathbf{R}_0$ phase-linked to the spiral at O and another $\mathbf{R}_1$ phase-linked at S. Consequently the oscillations of the conductivity will have one dominant term whose frequency is determined by the value of m_c^* at the centre of the Fermi surface, and one lesser term determined by the value of m_c^* at the limiting point. Actually this situation is rather unrealistic, since the Cornu spiral does not represent the

(s, ϕ) relationship close to the limiting point, but over-estimates the amplitude contributed by this region. The real spiral closes up more sharply, perhaps as in figure 30 ; the secondary contribution, from the limiting point, is then even less important, and apart from small periodic perturbations of phase and amplitude the observed oscillations will be essentially those of the central section of the Fermi surface. It is interesting that the superposition of oscillations involving

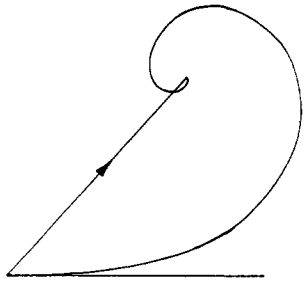

Figure 30. Modified version of figure 29.

only a fairly narrow range of phases yields a resultant in much the same way as in the de Haas–van Alphen effect, where by contrast the range is huge, the dominant role in both being played by the extremal section.

If the microwave field is polarized parallel to the magnetic field, a similar analysis shows that the limiting point contributes the region near the origin of the Cornu spiral, and this is likely to be the dominant oscillation. The central

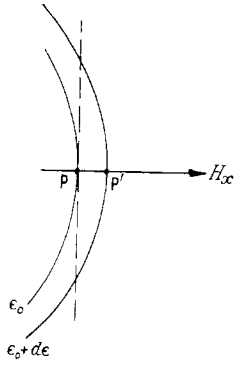

Figure 31. Cyclotron resonance at a limiting point.

section of the Fermi surface may also contribute its characteristic frequency if the magnetic field does not lie along a symmetry axis of the surface. It is not difficult to see that the section of the Fermi surface which makes no contribution is that at which the electron on the effective zone has no velocity component parallel to **H** ; only if this section is also the central section will there be no oscillations from the central extremum. It should clearly be possible by measurements using different polarizations to determine which oscillations are due to limiting points and which to central sections or to other extrema of effective mass which are not located at limiting points. The possibility of singling out a particular

point on the Fermi surface is potentially very valuable, and we shall examine more closely what information it can reveal and under what conditions the effect should be observable. In figure 31 are drawn the sections of two energy surfaces, the Fermi surface ϵ_0 and a neighbouring surface $\epsilon_0+d\epsilon$, with elliptic limiting points P and P′ whose normal separation is $d\epsilon/\hbar v_0$. The tangent plane at P intersects the upper surface in an ellipse whose semi-axes are $(2\rho_{1,2}\,d\epsilon/\hbar v_0)^{1/2}$, where $\rho_{1,2}$ are the principal radii of the surface at P′. Hence the area of the ellipse is $2\pi(\rho_1\rho_2)^{1/2}\,d\epsilon/\hbar v_0$ or $2\pi d\epsilon/K^{1/2}\hbar v_0$, where K is the Gaussian curvature at the limiting point. It follows from (12) that the cyclotron frequency is $eHv_0K^{1/2}/\hbar$. If then by other means, such as anomalous skin effect studies in zero field, the shape of the Fermi surface has been found, K may be calculated; in this way the cyclotron resonance frequency can yield a value for the Fermi velocity at a particular point on the surface at which the normal is parallel to the applied field. The appearance of $K^{1/2}$ in the result emphasizes the fact that only elliptical limiting points reveal themselves, that is points at which both principal curvatures have the same sign. A wholly convex surface should show the effect at all orientations, so that in principle a complete analysis of the variation of Fermi velocity appears possible. Other cases require more care in interpretation, and we refer the interested reader to Azbel' and Kaner's thorough investigation of these points, with the mild warning that some of their suggestions for the application of cyclotron resonance, while theoretically sound enough, seem to an experimenter to be rather over-optimistic in the demands they make for purity, precision and perseverance.

As regards the conditions for observing resonance due to the limiting points, two comments may be made. The first is that one does not of course expect to observe the resonance of the electron actually at the limiting point, since it is essential to the effect that only a small fraction of the orbit shall lie in the skin depth. But if the cyclotron frequency is not an extremely rapid function of k_x there should be sections close to the limiting point having to all intents the same frequency and at the same time giving rise to sizeable orbits, at any rate for the larger Fermi surfaces which are of principal interest. The very size of the orbits, however, leads to the second observation, that between two traverses of the skin layer the electron travels quite a distance (taking $1{\cdot}4\times10^8$ cm sec^{-1} as a typical velocity and 3×10^{-11} second as a typical microwave period we see that this distance is $4{\cdot}2\times10^{-3}$ cm at the fundamental resonance). When a limiting point is being studied the electrons have a component of velocity parallel to **H** which is very nearly the Fermi velocity; thus the paths of the electrons are open helices having the direction of **H** as axis and a pitch of about 4×10^{-3} cm. If **H** is not precisely parallel to the surface of the metal the depths at which successive traverses take place will not be the same, and this will prevent the observation of cyclotron resonance. Since typically the pitch of the helix is 500 times the skin depth, alignment to a few minutes of arc or even better is desirable if the limiting point resonance is to be observed. It should be remembered that the surface impedance is complex, which implies that the phase of the oscillation varies with depth. Even if successive traverses lie well within the skin depth there may still be a displacement of the resonance by this phase shift. The limiting points occur in pairs at opposite ends of the Fermi surface, and have opposite displacements;

lack of exact parallelism may therefore show itself by the appearance of two resonances of equal amplitude beating with one another, or, when this effect is averaged over all contributing orbits, a diminution in the amplitude of the oscillations. The extreme sensitivity of the limiting point resonance to alignment makes it doubtful if it has ever been observed. It is more likely that the recorded resonances are due either to ellipsoidal Fermi surfaces of constant mass, which resonate all of a piece, such as those in bismuth which Aubrey and Chambers (1957) have studied in some detail (figure 32), or to sections of extremal mass in

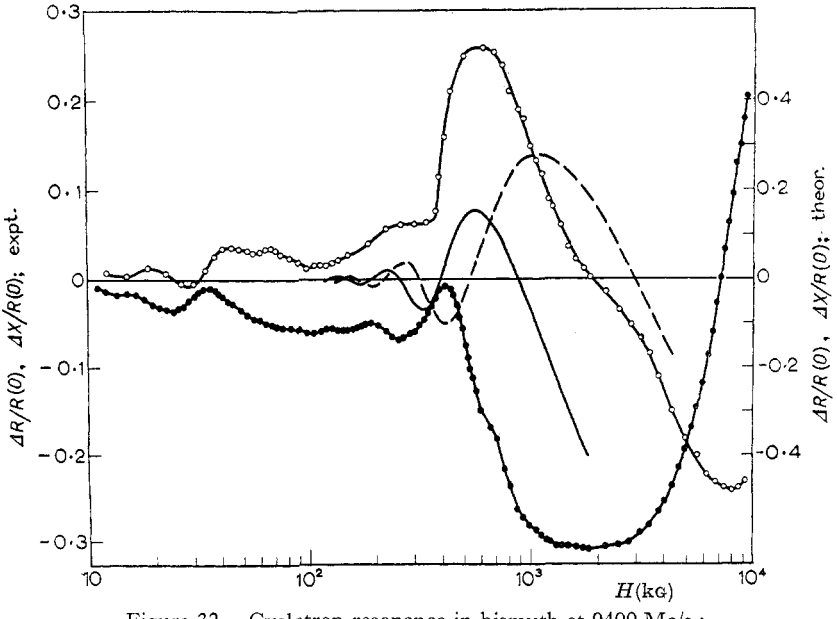

Figure 32. Cyclotron resonance in bismuth at 9400 Mc/s ;
———, ● $\Delta R/R(0)$, — — —, ○ $\Delta X/R(0)$.
The theoretical curves are calculated for $m_c^* = 0{\cdot}11$ electron masses and $\omega\tau = 3$. (*After* Aubrey and Chambers 1957.)

large surfaces, as we venture to interpret the observations on tin (figure 33). This does not mean that the limiting points are of no value, but only that a far more careful investigation is needed before their worth can be assessed. The degree of parallelism required is certainly formidable, especially as strain-free electropolished surfaces are not normally very flat. Central sections, on the other hand, do not demand such a high degree of parallelism, since the mean velocity parallel to **H** is zero. The variation of the resonance with field orientation should prove of value in diagnosing the origin of the resonance. It is, however, rather unprofitable to speculate in detail along these lines until more systematic experimental evidence is available.

The foregoing discussion has been based on the assumption that the whole problem may be treated in terms of the Fourier components of the field and the response of the electrons to them, without explicit reference to the boundary conditions. This proved to be possible in zero magnetic field since in the two cases chosen, specular reflection and diffuse scattering at the surface, the electrons

leaving the surface could be treated as if they had come from the exterior of the metal, having passed through a suitable 'image field'; in the former case the image field was defined by the equation $E(-z) = E(z)$, in the latter $E(-z) = 0$. But when there is a magnetic field present this particular device becomes unworkable. The trajectory of an electron reflected specularly is as shown in figure 34;

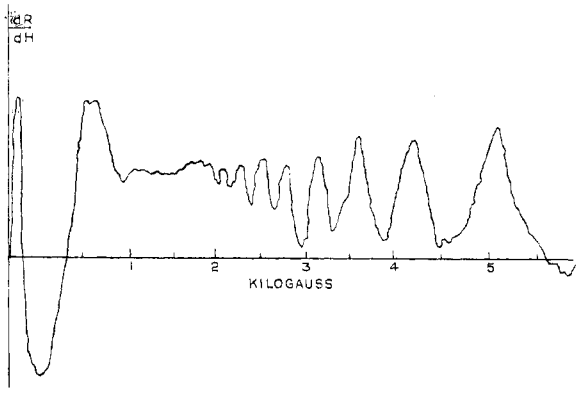

Figure 33. Cyclotron resonance in tin at 24 000 Mc/s. Note that it is dR/dH, not R, which is measured in this experiment. (*After* Kip, Langenberg, Rosenblum and Wagoner 1957.)

if an image field $E(-z) = E(z)$ is supplied to simulate the effect of multiple passages through the actual field, we must at the same time reverse the steady magnetic field, making $\mathbf{H}(-z) = -\mathbf{H}(z)$. This means that some of the important electrons, i.e. those in the skin layer which collide with the surface, cannot be treated as responding to the electric field in the presence of a uniform magnetic field, and the Fourier method in its simple form breaks down. Similarly, if we

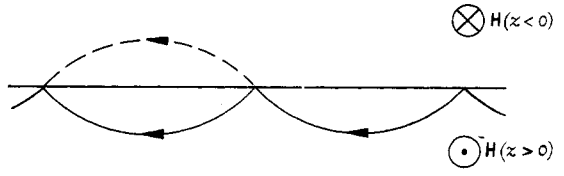

Figure 34. Electron trajectory for specular surface reflection, showing equivalent trajectory in an infinite sample.

replace diffuse boundary scattering by the assumption that $E(-z) = 0$ in an infinite medium, unless at the same time we make $\mathbf{H}(-z)$ vanish, we allow the possibility of multiple traverses between successive collisions of the skin layer by electrons which in fact collide with the surface. It appears, then, that the simple extension of the anomalous skin effect theory which we have adopted is not justified, but fortunately in the resonance region the only errors incurred are of the numerical constants, not the qualitative features, and are in any case quite small. There is, however, a phenomenon which needs the full treatment to find a satisfactory explanation, and this is a drop in surface resistance in quite small fields, as illustrated by figure 35. In this curve the hump is believed to be a rather ill-marked resonance, but the initial fall (which should surely start as H^2 in small enough

fields) is not associated with the resonance. The same effect has been seen in tin at a frequency as low as 3000 Mc/s (Pippard, unpublished), certainly too low for a resonance to be observed in the particular sample used. According to Azbel' and Kaner, whose theory takes explicit account of the surface scattering difficulty, the characteristic field strengths for this effect are those which bend the electron trajectories sufficiently to prevent any free path being completed wholly within the skin layer. Referring back to figure 27, we see that a typical electron moving parallel to the surface is represented by Z, and if the radius of curvature in the plane of the section is ρ_x, the radius of curvature of the orbit in real space will be $\hbar\rho_x/eH$. If a free path of length l having this curvature can just be contained in a layer of thickness δ_r, we must have H equal to $8\delta_r\hbar\rho_x/el^2$.

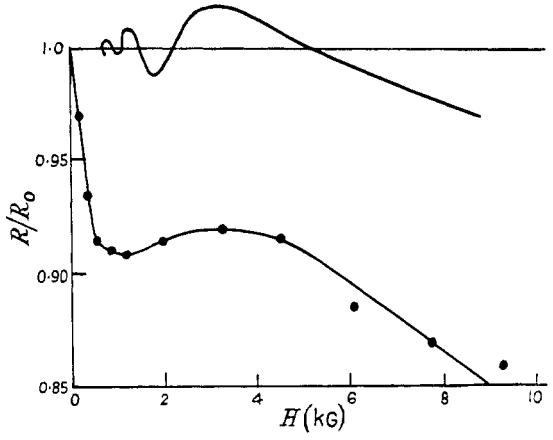

Figure 35. Cyclotron resonance in tin (Fawcett 1956) at 24 000 Mc/s. The upper curve shows the oscillations which might have been expected for the particular value of $\omega\tau$. (*After* Chambers 1956 b.)

Typically at microwave frequencies, this might be about $3 \times 10^{-5}/l^2$ gauss, so that for rather pure copper at the lowest temperatures, where $l \sim 10^{-3}$ cm, a field of 30 gauss is enough to affect the resistance appreciably. For the purest tin available the value of l is nearly 10^{-1} cm, and a field of only 3 milligauss should be sufficient. But this corresponds to an orbit radius of about 250 cm, very much more than local radii of curvature on normal electropolished surfaces ; we may perhaps doubt whether the theory is valid under these circumstances. If, however, the theory may be safely applied when the orbit radius is reasonably small, there seems to be a possibility of making a direct measurement of the mean free path on the effective zone by a systematic application of this effect. Considerable evaluation of the Azbel'–Kaner theory is needed in order to discover the predicted variation of R with H (they give only the initial quadratic variation for a metal with a single ellipsoidal Fermi surface), for it is certain that a careful quantitative comparison between theory and experiment is needed before any results obtained can be regarded as reliable. It would also be of interest to attempt a solution of the theoretical problem with different boundary conditions (e.g. specular reflection), for it is likely that the behaviour is sensitive to the nature of the surface scattering, and it might be possible to use the effect to demonstrate, even more

clearly than does Chambers' (1952 b) careful work, that the surface scattering is in effect completely diffuse.

We must now turn briefly to another phenomenon, also called cyclotron resonance (Galt *et al.* 1955, 1956, 1959), which under rather special conditions can yield information on the effective masses. In this the experimental arrangement is such that the magnetic field is applied normally to the surface of the metal. Let us see what effect such a field can have on the surface impedance of a free-electron metal. It is convenient, both in order to understand the effect and to get the most from it experimentally, to have the microwave field circularly polarized, so that the phase angle of any field component represents the actual orientation of the field, and all field variables rotate about the z-axis. The retardation effects which occur when the free path is so long that $\omega\tau$ is comparable with, or greater than, unity can now be understood in the following way : electrons moving in the plane normal to z continually pick up momentum from the field and hence contribute to the current, but as **E** rotates the current already created does not and so a phase lag results. In fact, if the z-variation of **E** is sufficiently slow to be neglected, the effective conductivity is not σ but $\sigma/(1+i\omega\tau)$, the complex nature of the expression reflecting the phase lag between current and field. In the presence of a magnetic field the whole electronic distribution, and hence the current, is caused to rotate with angular velocity ω_c, and if ω and ω_c have the same sense the phase lag is reduced, the effective conductivity becoming $\sigma/[1+i(\omega-\omega_c)\tau]$. In particular, if the magnetic field is adjusted to the resonant condition, $\omega=\omega_c$, the electronic distribution and the electric field rotate in phase and all retardation effects are eliminated. It might be thought that if $\omega\tau$ is much greater than unity the increase of effective conductivity at resonance would show up as something like a resonant peak in the surface impedance, but this is not so. To continue with the present example, if the z-variation of **E** is slow we may use the normal expression (38) for the surface impedance, and write

$$Z(H)=R+iX=\left\{\frac{4\pi i\omega}{\sigma}[1+i(\omega-\omega_c)\tau]\right\}^{1/2}. \qquad \ldots\ldots(51)$$

The real and imaginary parts of Z are monotonic functions of ω_c, as shown in figure 36 ; only $|Z|$ shows anything like resonant behaviour, and this unfortunately is not easily measured directly. The resistance, which is easiest to measure, shows an inflection at the point of resonance. One would hesitate to lean heavily on the determination of a point of inflection for deriving an important parameter, since such a point may readily be shifted by quite minor secondary effects. If there is more than one Fermi surface, and the normal skin effect theory is still applicable, the behaviour of $R(H)$ may be more complicated and peaks may even appear, as shown by the experimental results for bismuth (figure 37). The positions of the various features of such curves as this may be interpreted in terms of Shoenberg's (1957) ellipsoidal model of the bismuth Fermi surface, but we may be permitted to doubt if this interpretation would have been arrived at without the aid of Shoenberg's very specific model. It is, indeed, a serious criticism of this experiment as an analytical tool that the recognizable features of the curves appear at positions which are determined by an implicit relation between all the different contributing electrons, and that this relation is bad enough for ellipsoidal

Fermi surfaces which represent the most complicated case yet analysed theoretically. It is nevertheless possible, as recent measurements on zinc (Galt, Merritt, Yager and Dail 1959) have shown, to use this experimental arrangement in conjunction with Azbel'–Kaner resonance with advantage. The latter determines the effective mass, and hence the field strength at which resonance should occur in a normal field. If circular polarization is now used, it proves to be possible to see sometimes whether the resonance occurs with positive or negative field, and hence to ascribe the resonance to electron or hole orbits. This is something which is not

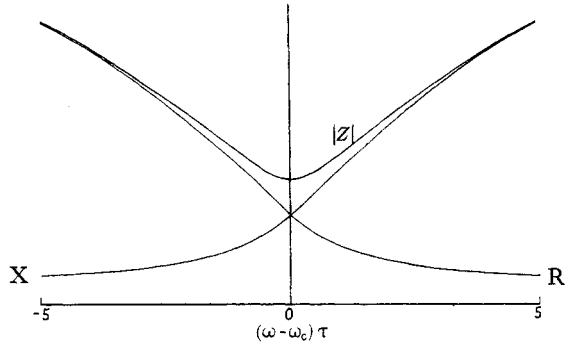

Figure 36. Variation of R, X and $|Z|$ from equation (51).

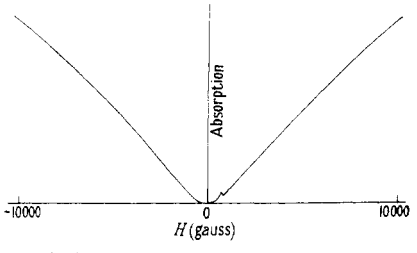

Figure 37. Field variation of absorption due to bismuth in a circularly polarized resonant cavity at 24 000 Mc/s. (*After* Galt, Yager, Merritt, Cetlin and Brailsford 1959.)

revealed directly by any other method, except possibly the Kjeldaas ultrasonic experiment which we discuss later (p. 252), and it would establish normal field resonance as a tool of great utility if there were the possibility of general application.

The method is, however, subject to the serious criticism that the phenomenon may usually be unobservable (Chambers 1956 c). We have seen how at the resonant condition retardation effects are neutralized; the magnitude of the observed effect is thus dependent on the extent to which the impedance in zero field is modified by retardation effects. But when the anomalous skin effect is well-developed, retardation effects are of little importance (see p. 221) in most metals at frequencies less than 10^{12} sec^{-1}. At microwave frequencies, as the field is changed all that happens is that the position of the effective zone shifts slightly so as to bring into prominence those electrons which have the appropriate z-component of velocity to move in phase with the rotating field. We expect to see very little, then, with most metals except at very high, long infra-red frequencies (and in correspondingly high fields of several hundred kilogauss). The

most likely exceptions to this negative conclusion are semi-metals such as bismuth and graphite which even at microwave frequencies show pronounced retardation effects, metals such as zinc in which there are small as well as large sheets to the Fermi surface, the former playing a significant role in conduction, and metals with highly distorted Fermi surfaces for which the complicated orbits in a magnetic field may lead to excessive boundary scattering of the most effective electrons and hence to a modification of the surface impedance. But the theory of the last, which is likely to be rather difficult, has not been worked out. We are therefore inclined to see very little prospect of this method making a significant contribution to the analysis of any but semi-metals and relatively minor portions of metals, and for these the de Haas–van Alphen and related effects seem vastly more powerful, except for distinguishing electrons from holes.

Finally, it should be mentioned that oscillatory skin effects analogous to the Schubnikov effect ought to be observed in the microwave impedance, under conditions suitable for observing oscillations of the d.c. resistance. According to Azbel' (1958) the amplitude of the oscillations should be of the order of ϵ_0/kT greater than the d.c. oscillations. His comparison is made, however, with the theory of Lifshitz (1958), which, as we have already seen (p. 214), predicts oscillations smaller by the same factor than the predictions based on the views of Davydov and Pomeranchuk (1940). It seems therefore that if the latter is correct there is little point in looking for the skin effect oscillations when a d.c. measurement should do as well. We shall therefore not discuss this suggested experiment further.

4.5. *Ultrasonic Attenuation and Magneto-acoustic Effects*

The experiments of Bömmel (1954, 1955) and later workers (see Mason 1958) have revealed that in pure metals at low temperatures a new mechanism of ultrasonic attenuation appears, as a result of a direct interaction between the conduction electrons and the ultrasonic vibrations of the lattice, and that in propitious circumstances the attenuation may be an oscillatory function of the strength of an applied magnetic field. The analysis of these effects leads us to what are potentially the most complicated of all the phenomena to be considered in this review. The general case of the interactions between the lattice vibrations of an anisotropic solid and the electrons lying on an arbitrary Fermi surface, in the presence of a magnetic field, conjures up a vision of almost unlimited complexity. The principal effects can, however, be made clear with the aid of the free-electron model of an elastically isotropic solid, which is the only model so far treated in print. What little has been published on the theory is at times somewhat misleading (Pippard 1955, 1957 b, Steinberg 1958 a, b, c, Rodriguez 1958 b, Kjeldaas 1959, Kjeldaas and Holstein 1959, see also Mason 1958 for other references), while as for the experimental results, they are so suggestive, and yet so tantalizingly scrappy, as to do little more than point to the need for systematic study, with the virtual certainty that something of interest will emerge. It is therefore worth while devoting some space to a detailed discussion of the free-electron model. But before doing this we shall take the opportunity of suggesting a standard notation which will serve to describe any particular experimental arrangement. So long as the metal is isotropic, the disposition of the experiment is defined by

the polarization of the wave and the direction of the applied magnetic field ; if we take a Cartesian system of axes, with unit vectors $\mathbf{i}, \mathbf{j}, \mathbf{k}$, the experiment is defined by two vectors $(\mathbf{X}, \mathbf{Y})$ by which it is to be understood that the wave vector $\mathbf{q}$ is directed parallel to $\mathbf{i}$, the particle velocity $\mathbf{u}$ in the wave parallel to $\mathbf{X}$, and the magnetic field $\mathbf{H}$ parallel to $\mathbf{Y}$. Thus $(\mathbf{j}, \mathbf{k})$ represents a transverse wave in a transverse magnetic field which is normal both to the propagation direction and to the particle velocity ; we shall be concerned primarily with six special cases of interest $(\mathbf{i}, 0)$, $(\mathbf{j}, 0)$, $(\mathbf{i}, \mathbf{j})$, $(\mathbf{j}, \mathbf{j})$, $(\mathbf{j}, \mathbf{k})$ and $(\mathbf{j}, \mathbf{i})$. To deal with real anisotropic metals (and of course even cubic metals may be highly anisotropic elastically as well as in the shape of their Fermi surfaces), the above notation is insufficient. We propose that for such a situation three vectors should be used, referred to specified axes fixed with respect to the crystallographic axis ; the first vector defining the direction of $\mathbf{q}$, the second that of $\mathbf{u}$, and the third that of $\mathbf{H}$. We have at present no occasion to use this more elaborate notation.

To understand how the interaction between acoustic vibrations and the conduction electrons leads to attenuation, let us first suppose that the electrons suffer no collisions with the lattice. We might then picture the wave as affecting only the positive lattice, leaving the electrons at rest with a uniform density. If the wave is longitudinal the density of positive charge will vary periodically, so that in the absence of a compensating variation of negative charge there will be set up powerful longitudinal electric fields, which will force the electrons into motion. In fact, of course, only the minutest degree of charge imbalance is needed to keep the electronic current at the same magnitude as the lattice current (provided that the ultrasonic frequency is much less than the plasma frequency $\omega_p = c(4\pi Ne^2/m)^{1/2}$; since $\omega_p \sim 10^{16}$ sec^{-1} in most metals this condition is easily met). We conclude that a longitudinal electric field is associated with a longitudinal wave, having a magnitude sufficient to keep charge neutrality. If there are collisions between electrons and lattice they also may help to establish the required electronic current, but whatever the mechanism we may divide the current into contributions from the lattice and the electrons, and write

$$\mathbf{J}_{\text{latt}} + \mathbf{J}_{\text{el}} = 0. \qquad \ldots\ldots(52)$$

If the wave is transverse there is no tendency for space charges to be established, but now the movement of lattice without electrons causes a transverse current and hence a magnetic field associated with the wave. By induction an electric field is produced and it is this which pulls the electrons into motion with the lattice. The need for ' current neutrality ' is not nearly so strong as for charge neutrality, the condition being that the frequency shall be much less than that at which the skin depth for alternating fields becomes equal to the wavelength. At lower frequencies than this the skin depth is smaller than the wavelength and each part of the wave is, as it were, screened from the other parts and transmits no magnetic effects ; this can only be achieved if there is no net current. For most metals the critical frequency is around 10^3 Mc/s, so that the ultrasonic frequencies in use at present, up to about 100 Mc/s, are reasonably well within the condition for current neutrality. We shall assume then that (52) holds also for transverse waves, but it should be remembered that a more thorough treatment may be required in special cases (such as bismuth, where the wave velocity is low

and the skin depth high). It is worth remarking that if the frequency is well above the critical value, as with the thermally excited phonons at all but the very lowest temperatures ($< 0{\cdot}1°\text{K}$), the electrons are not drawn into motion with the lattice, and lose their power of attenuating transverse waves.

The electric field which effects current neutrality is the link between lattice and electrons which is responsible for transferring energy from the former to the latter and so attenuating the wave. If the peak value of the electric field is $\mathbf{E}$, the mean rate of increase of energy of the electron assembly, per unit volume, is given by

$$\dot{W} = \tfrac{1}{2}\mathscr{R}(\mathbf{E}^*.\mathbf{J}_{\text{el}}), \qquad \ldots\ldots(53)$$

and because of (52) this is the mean rate of decrease of energy of the lattice. Thus (53) represents the rate at which mechanical energy is converted into excitation energy of the electron assembly. Inelastic collisions transfer this energy back to the lattice as heat, but this part of the process does not concern us—the rate at which it occurs does not affect the attenuation. We must not ignore the possibility that collisions between the lattice and the electrons† may also dissipate the mechanical energy of the wave, though in fact it is easily seen that this is not so provided (52) holds. The reason is that at any point the electronic current, as seen from a frame of reference moving with the lattice, vanishes and with it the total momentum of the electron assembly. The statistical effect of collisions between electrons and scattering centres moving with the lattice is to bring the electron assembly into equilibrium with the moving lattice. Since the equilibrium state is one of zero momentum, there is no net momentum transfer in the collision processes, and hence no force of reaction between the electrons and the lattice, other than that due to the electric field. In calculating the attenuation then, we need only consider the influence of the electric field, as expressed in (53).

If the peak value of the particle velocity in the wave is $\mathbf{u}$, the lattice current density $\mathbf{J}_{\text{el}}$ is $-Ne\mathbf{u}$, where N is the number of free electrons per unit volume, and the energy per unit volume in the wave, W, is $\frac{1}{2}Mu^2$, where M is the density (we shall not concern ourselves with the minute difference between the lattice density and the density of the metal). Thus

$$\frac{\dot{W}}{W} = \frac{Ne}{Mu^2}\mathscr{R}(\mathbf{E}^*.\mathbf{u}), \qquad \ldots\ldots(54)$$

from which it is seen that the characteristic time for loss of mechanical energy is the reciprocal of the right-hand side of (54), and the extinction distance is this multiplied by the wave velocity v_s; alternatively, if the wave takes the form

$$\mathbf{u} \equiv \mathbf{u}\, e^{-\frac{1}{2}\alpha z} e^{i(\omega t - qz)}, \qquad \ldots\ldots(55)$$

the attenuation constant α is the reciprocal of the extinction distance, or

$$\alpha = \frac{Ne}{Mu^2 v_s}\mathscr{R}(\mathbf{E}^*.\mathbf{u}). \qquad \ldots\ldots(56)$$

The problem of calculating α is thus reduced to that of calculating the electric field needed to maintain current neutrality. More precisely, if we take $\mathbf{u}$ as real, we are interested in the real part of β, defined as $E_\parallel/u$, where $E_\parallel$ is the component of $\mathbf{E}$ in the direction of $\mathbf{u}$.

† In all that follows we are thinking particularly of collisions between electrons and impurities, though similar behaviour is to be expected from electron–phonon collisions.

At this point the collisions between electrons and lattice come into prominence, for although they do not directly contribute to the attenuation, they do play an important role in the establishment of the electron current. We must imagine that there is a periodic electric field **E** (all field variables are to be understood as multiplied by $e^{i(\omega t-qz)}$, so that $\partial/\partial t = i\omega$, $\partial/\partial z = -iq$; the attenuation is taken as very small so that $e^{-\frac{1}{2}\alpha z}$ may be put equal to unity in the calculation of **E**) associated with the lattice velocity **u**, and that the electrons move through this field, acquiring momentum from it and from collisions with the moving lattice. If we confine our attention to the case of isotropic elastic scattering, we may suppose that the effect of a collision is to return the electron to some point on the Fermi surface, taking into account the fact that the Fermi surface is centred on the origin with respect to an observer moving with the lattice. This enables us to separate the problem into two parts. First we imagine the lattice at rest, and calculate the current density due to **E** and to collisions with the stationary lattice; then we put **E** = 0 and calculate the current density due to collisions with the moving lattice. To take the second contribution first, it is convenient to replace the effect of collisions with the moving lattice by a fictitious electric field $\mathbf{E}_c$, by the following argument. To calculate the average displacement in reciprocal space suffered by an electron on the Fermi surface we must take a weighted average over its past history. Let us suppose that at an instant t earlier it is moving through a region where the lattice velocity is $\mathbf{u}(t)$; the chance of a collision in the interval dt leading to a change in its velocity by an amount **u** is dt/τ, and the chance that it will survive for a time t without further collision is $e^{-t/\tau}$. Thus the average additional velocity of electrons of this trajectory when $t = 0$ is

$$(1/\tau)\int_0^\infty \mathbf{u}(t)\, e^{-t/\tau}\, dt.$$

If instead of lattice movement we had an electric field $\mathbf{E}_c$ equal to $m\mathbf{u}/e\tau$ the result would be just the same. Both contributions to the current may therefore be calculated at the same time by imagining the lattice to be stationary and the field to be $\mathbf{E} + m\mathbf{u}/e\tau$.

So far what we have said applies both to transverse and to longitudinal waves. It is now convenient to treat them separately, and we take transverse waves first, as being simpler. If the lattice movement is parallel to the unit vector **j**, the electronic current to be established is Neu_j. When there is no magnetic field present, the field needed to establish the current is also parallel to **j**, but in a magnetic field there may be other components. Since, however, the attenuation is determined by the component E_j, we need only concern ourselves with the element $\rho_{jj}(q, \omega)$ of the resistivity tensor appropriate to a periodic field, writing

$$Ne\rho_{jj}u_j = E_j + E_c = E_j + mu_j/e\tau, \qquad \ldots\ldots(57)$$

so that

$$E_j = \frac{m}{e\tau}(\gamma_t - 1)\, u_j,$$

in which $\gamma_t = \sigma\rho_{jj}$ and σ is the d.c. conductivity $Ne^2\tau/m$. Hence from (56)

$$\alpha_{\text{trans}} = \frac{Nm}{Mv_{st}\tau}\mathscr{R}(\gamma_t - 1), \qquad \ldots\ldots(58)$$

in which v_{st} is the velocity of transverse waves. In the absence of a magnetic field ρ_{jj} is simply the reciprocal of the corresponding conductivity σ_{jj}, which may be calculated in the same way as was used in deriving (16). Strictly one should make allowances for the fact that the transverse field is moving with velocity v_{st}, but as for most metals this is much smaller than the Fermi velocity v_0 the error involved in supposing the field to be stationary (i.e. $\omega = 0$) is negligible. The calculation then yields the result

$$\gamma_t = \frac{\frac{2}{3}a^3}{(a^2+1)\tan^{-1}a - a}, \quad \text{where} \quad a = ql, \qquad \ldots\ldots(59)$$

which may be inserted into (58) to give α_{trans}. We shall return later to discuss this result in more detail.

For longitudinal waves it is not permissible to neglect effects arising from the movement of the electric field associated with deformation, because this field is so large (yet so phased as not to contribute to the attenuation) that effects of relative magnitude v_s/v_0 are still large enough (if correctly phased) to make major contributions to the attenuation. To substantiate this statement in more detail let us start by considering the equilibrium of a metal subjected to a static longitudinal deformation ζe^{-iqz}, which results in a periodic dilation $-iq\zeta e^{-iqz}$. In consequence the equilibrium density of electrons and the kinetic energy at the Fermi surface vary according to the laws

$$\frac{\Delta N}{N} = iq\zeta e^{-iqz},$$

$$\frac{\Delta \epsilon_0}{\epsilon_0} = \tfrac{2}{3}iq\zeta e^{-iqz},$$

since for a free electron gas $\epsilon_0 \propto N^{2/3}$. In equilibrium the total Fermi energy is constant, so that there must be developed such space charges as will maintain a periodic potential ϕ so that $\epsilon_0 + e\phi$ is independent of z;

i.e. $$e\phi = -\tfrac{2}{3}iq\zeta\epsilon_0 e^{-iqz} = -\tfrac{1}{3}iq\zeta m v_0^2 e^{-iqz}.$$

The longitudinal electric field E_0, derived from ϕ, is given by the expression

$$eE_0 = iqe\phi = \tfrac{1}{3}q^2\zeta m v_0^2 e^{-iqz}. \qquad \ldots\ldots(60)$$

An electron at the Fermi surface, moving in this statically deformed lattice, remains always on the Fermi surface, which itself varies in size from point to point; there is thus no current associated with E_0. But as soon as we allow the whole pattern of dilation and electric field to move uniformly with velocity v_s, a current is set up. To calculate this current, consider an electron, initially on the Fermi surface, moving with velocity v_0 at an angle θ to the z-axis. In traversing a distance dl it gains kinetic energy $eE_0\,dl\cos\theta$ from the field; meanwhile the field pattern has moved forwards a distance $v_s\,dl/v_0$ and the electron finds itself at a point where its potential energy has not changed by $-iqe\phi dl\cos\theta$, i.e. $-eE_0\,dl\cos\theta$, but by $-eE_0\,dl(\cos\theta - v_s/v_0)$. It has therefore departed from the local Fermi surface to the extent given by the increment of energy $eE_0 v_s\,dl/v_0$. The same effect would be produced if the field pattern were stationary and each electron were subjected to a fictitious force F, of magnitude $eE_0 v_s/v_0$, directed parallel to its motion. We may calculate the resulting current density J_i' produced by this fictitious force in the

usual way, integrating over the trajectories of all electrons at the Fermi surface. If there is no magnetic field present we easily obtain the result

$$J_i' = \tfrac{3}{2}\sigma E_0 (v_s/v_0) \int_{-1}^{1} \frac{x\,dx}{1-iax}.$$

It will be noted that this integral is purely imaginary, so that the current J_i' is in phase quadrature with E_0. It is easy enough to evaluate the integral, but a tidier result is obtained by introducing yet another fictitious field E_i', which is that electric field which would produce the same current J_i' as is produced by F (it should be noted that F acts parallel to each electron trajectory and is not therefore derivable from a potential like E_i'). On carrying out a calculation of the current which would be produced by a stationary field E_i', we derive an equation which determines E_i':

$$J_i' = \tfrac{3}{2}\sigma E_0 (v_s/v_0) \int_{-1}^{1} \frac{x\,dx}{1-iax} = \tfrac{3}{2}\sigma E_i' \int_{-1}^{1} \frac{x^2\,dx}{1-iax},$$

from which, since only the real part of the right-hand integral exists and has the same form as the imaginary part of the left-hand integral, we find

$$E_i' = ia(v_s/v_0) E_0 = i\omega\tau E_0. \qquad \ldots\ldots(61)$$

It is interesting that the same simple result is obtained when there is a magnetic field present, as is shown by Rodriguez' (1958 b) analysis, but we are unable to provide an intuitive physical reason for this. At any rate it enables us to cast the theory into the same form whether or not a magnetic field is applied. Since the lattice velocity u_i is related to displacement ζ by the equation $u_i = i\omega\zeta$, (60) may be used to write the amplitudes of the real and fictitious fields in the form

$$E_0 = -\tfrac{1}{3}iqu_i mv_0^2/ev_s,$$

$$E_i' = \frac{1}{3}\frac{mu_i}{e\tau}a^2.$$

The true field E_0, being in phase quadrature with u_i, contributes nothing to the attenuation and may henceforth be neglected. But E_i' is in phase with u_i, and may be very large when the electronic free path is large, since it is $\frac{1}{3}a^2$ times as great as the fictitious 'collision field' E_c.

We may now repeat for longitudinal waves the treatment of transverse waves already given, writing instead of (57)

$$Ne\rho_{ii}u_i = E_i + E_c + E_i' = E_i + \frac{mu_i}{e\tau}(1+\tfrac{1}{3}a^2), \qquad \ldots\ldots(62)$$

where E_i is the electric field which supplements E_0 and supplies as much of the required current as is not supplied by E_c and E_i'. Since E_i' is introduced when the moving field configuration is replaced by an equivalent stationary field, ρ_{ii} is to be interpreted as the longitudinal resistivity for a stationary field of wave number q. From (56) and (62) we find

$$\alpha_{\text{long}} = \frac{Nm}{Mv_{sl}\tau}\mathscr{R}(\gamma_1 - 1 - \tfrac{1}{3}a^2), \qquad \ldots\ldots(63)$$

in which v_{sl} is the velocity of longitudinal waves and $\gamma_l = \sigma\rho_{ii}$.† In the absence of an applied magnetic field, ρ_{ii} is the reciprocal of σ_{ii}, which is readily calculated to yield the result

$$\gamma_l = \frac{a^3}{3(a-\tan^{-1}a)}. \qquad \ldots\ldots(64)$$

It will be observed that as $a\to\infty$, $\gamma_l\to\frac{1}{3}a^2$. Thus the presence of the term $\frac{1}{3}a^2$ in (63) serves to reduce enormously the attenuation which would be observed in its absence, when the free path is very long. We saw (p. 198) that as $l\to\infty$ the conductivity associated with a periodic longitudinal field tends to zero, in contrast to that for a transverse field, and we might therefore have expected longitudinal ultrasonic waves to be highly attenuated in the range $ql\gg 1$. But in fact under these conditions the current needed for charge neutrality is almost all supplied automatically by the retardation effect which is reflected in the fictitious field E_i', and the attenuation remains finite.

In order to appreciate in more detail the behaviour of α_{trans} and α_{long} in zero magnetic field it is convenient to see the limiting forms at low and high frequencies ($ql\ll 1$ and $ql\gg 1$ respectively), as deduced from (58) and (59) and from (63) and (64):

$$\alpha_{trans} = \frac{Nmv_0 q^2 l}{5Mv_{st}}; \quad ql\ll 1 \qquad \ldots\ldots(65)$$

$$\frac{4Nmv_0 q}{3\pi Mv_{st}}; \quad ql\gg 1 \qquad \ldots\ldots(66)$$

$$\alpha_{long} = \frac{4Nmv_0 q^2 l}{15Mv_{sl}}; \quad ql\ll 1 \qquad \ldots\ldots(67)$$

$$\frac{\pi Nmv_0 q}{6Mv_{sl}}; \quad ql\gg 1. \qquad \ldots\ldots(68)$$

It will be seen that α_{trans} and α_{long} are very similar in behaviour, varying as $q^2 l$ when ql is small, and as q when ql is large. Since for both αl is a function of ql it is convenient to display the full range of behaviour in terms of these parameters, as in figure 38. So far as $l\alpha_{trans}$ is concerned it has been assumed that l is so long that the region in which $ql\gg 1$ is reached well before the frequency has become too high for current neutrality to be maintained. It is clear from (66) and (68) that when $ql\gg 1$, α is independent of l. This is verified experimentally, as can be seen from figure 39, with remarkable precision, which is rather surprising in view of the inadequacy of the free-electron model to describe a complex metal like indium.

The way in which α becomes independent of l recalls the anomalous skin effect, and indeed the explanation is the same in the two cases, with this difference, that with the ultrasonic wave one is in effect exploring the response of the electrons to one Fourier component of the electric field, rather than to a rather wide spectrum of components (as in the anomalous skin effect), all of which behave similarly as regards independence of l. When ql is very great the current carrying ability is

† The foregoing analysis, in terms of fictitious fields, is a not wholly successful attempt to cast the theory in a form which enables the physical content to be appreciated. More conventional analyses may be found in the references cited at the beginning of this section. In view of the assertion by several authors that the expressions for α_{trans} and α_{long}, which are the same as those derived by Pippard (1955), are in error through an inconsistency in the definition of τ, it is worth affirming categorically that this is not so ; the relaxation time which enters here is defined in the same way as that used in conductivity theory.

dominated by a small group of effective electrons moving nearly normal to **q**, whose velocity component parallel to **q** is just the velocity of sound, for these electrons move in a constant field and interact strongly with the acoustic wave. It is interesting to observe that one can reach the same conclusion by starting with the

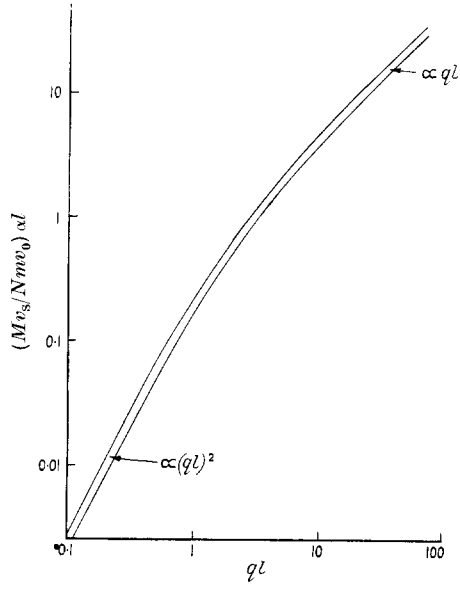

Figure 38. Theoretical attenuation curves for ultrasonic waves, shown as variation of αl with ql. The upper curve is for longitudinal, the lower for transverse, waves.

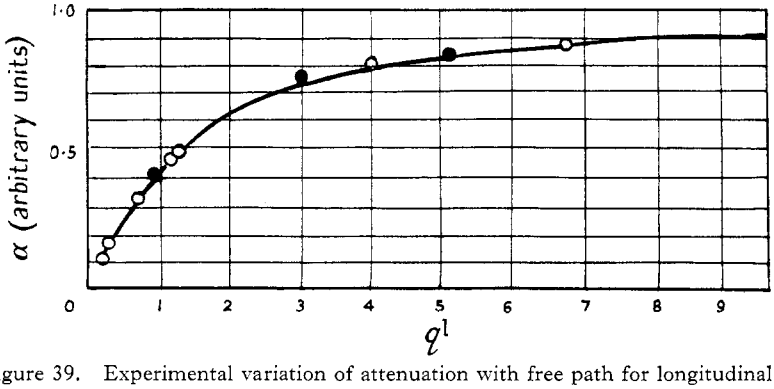

Figure 39. Experimental variation of attenuation with free path for longitudinal waves ; ○ Indium, ● Copper.
The full curve is the theoretical variation. (*After* Morse 1959.)

idea of the acoustic wave as a directed stream of phonons. The process of attenuation is then brought about by an electron–phonon collision which destroys the phonon, whose energy and momentum are taken by the electron. It is easy to show that if the electron wave number **k** is much greater than the phonon wave number **q**, so that the electron is scattered through only a small angle, the only electrons which can take part in the interactions are those which move so as to

keep in phase with the wave. There is, in fact, a very close connection between the semi-classical treatment of ultrasonic absorption given here and the quantal (or semi-quantal) treatment of electron–phonon scattering which is normally applied to conduction problems in metals. In the low frequency limit ($q \ll k$ for an electron on the Fermi surface) they give the same answer, provided $ql \gg 1$.† This suggests that a detailed survey of the attenuation of ultrasonic waves as a function of crystal orientation might be able to supply empirical values for the matrix elements of the electron–phonon interaction, so that a comparison might be made between the high-temperature phonon-dominated resistivity and calculations based on realistic interaction parameters. At the moment, however, no analysis has been made of the way in which the information should be used; moreover there has been no attempt yet to make a detailed survey of the behaviour of any single metal as a function of crystal orientation. The usefulness of this type of study really depends on how much can be inferred about large-angle scattering ($q \sim k$) and Umklapp processes (scattering between two points on the periodically extended Fermi surface, of which only one lies in the first Brillouin zone) from experimental information on small-angle scattering.

The attenuation under conditions such that $ql \ll 1$, as given by (65) and (67), may be derived by a different argument (Morse 1955), which is of value in discussing what can be expected in real metals to which the free-electron model is inapplicable. When $ql \ll 1$ the whole problem may be treated in terms of the local values of the field variables and their first spatial derivatives, and this is equivalent to the calculation of a (complex) elastic modulus. If the appropriate compliance coefficient (reciprocal of elastic modulus) is χ so that the wave velocity may be written as $(\chi M)^{-\frac{1}{2}}$, a complex χ implies a complex v_s and hence attenuation, the attenuation constant as earlier defined being related to the imaginary part of v_s^{-1} by the expression

$$\alpha = -2\omega \mathscr{I}(v_s^{-1}),$$

so that if χ is written as $\chi' - i\chi''$, and $\chi'' \ll \chi'$,

$$\alpha = q\chi''/\chi'. \qquad \ldots\ldots(69)$$

The complex nature of χ can be thought of as originating in a typical relaxation process. When a small sample of the metal is suddenly sheared, as in figure 40, by the application of stresses in the directions indicated, the Fermi surface, originally spherical, is distorted to an ellipsoidal shape; if the sides of the square are multiplied by $1 \pm \delta$, the axes of the ellipse are proportional to $1 \mp \delta$. The changes of **k** suffered by the electrons may be thought of as arising when the electrons are reflected from the moving boundaries. The ellipsoidal shape is of course not the equilibrium form of the Fermi surface, and electron–lattice collisions lead to a re-establishment of the spherical form with characteristic relaxation time τ. Now to produce the deformation the stresses P have in the main to overcome the rigidity of the lattice, but there is a small additional dynamical term due to the pressure created by electronic collisions with the boundary. In equilibrium this takes the well-known value $\frac{1}{3}Nm\overline{v^2}$, which for a degenerate Fermi gas of free electrons is

† If ql is not much greater than 1 a quantal theory is lacking. It may be expected from the semi-classical theory that free path effects will be important in electron–phonon interactions if $ql \sim 1$: this matter has been discussed briefly (Pippard 1957 c), and there is some experimental evidence supporting the conclusions. A more rigorous quantal treatment is most desirable.

$\frac{1}{5}Nmv_0^2$; but when the Fermi surface is deformed into an ellipsoid the velocity components must be appropriately scaled, so that the pressures on different surfaces are unequal. In figure 40 the pressure on the boundaries normal to x and y are $\frac{1}{5}Nmv_0^2(1-2\delta)$ and $\frac{1}{5}Nmv_0^2(1+2\delta)$ respectively. The external stresses required to produce the initial deformation are thus rather larger than are required to maintain it once relaxation has occurred, the difference being $\frac{2}{5}Nmv_0^2\,\delta$. Since

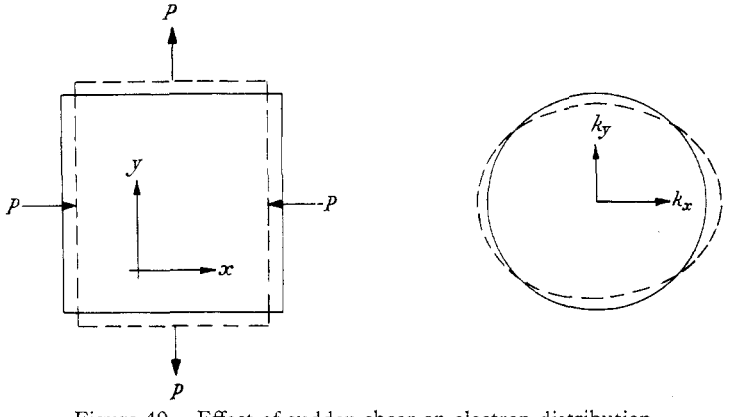

Figure 40. Effect of sudden shear on electron distribution.

the angle of shear in the present case is 2δ, the shear compliance is $2\delta/P$. If then we write χ_0 for the long-term compliance and χ_∞ for the short-term compliance, we have that

$$P = 2\delta/\chi_\infty \quad \text{and} \quad P-\tfrac{2}{5}Nmv_0^2\,\delta = 2\delta/\chi_0,$$

so that

$$\Delta\chi \equiv \chi_0-\chi_\infty = \tfrac{1}{5}Nmv_0^2\chi_0^2. \qquad \ldots\ldots(70)$$

We now make use of a standard result of relaxation theory

$$\chi(\omega) = \chi_\infty + \frac{\Delta\chi}{1+i\omega\tau},$$

so that

$$\chi'(\omega) = \chi_\infty + \frac{\Delta\chi}{1+\omega^2\tau^2}$$

and

$$\chi''(\omega) = \frac{\omega\tau\Delta\chi}{1+\omega^2\tau^2}.$$

Since we are limited to the case when $ql \ll 1$, it follows that $\omega\tau$, which equals $v_s ql/v_0$, is extremely small, so that we may write $\chi'(\omega) = \chi_0$ and $\chi''(\omega) = \omega\tau\Delta\chi$. Hence from (69) and (70), for a transverse wave

$$\alpha_{\text{trans}} = \tfrac{1}{5}Nmv_0^2\chi_0\,q\omega\tau = \frac{Nmv_0\,q^2\,l}{5Mv_{st}},$$

exactly as in (65). We may also reproduce the result for longitudinal waves by recalling that the appropriate elastic modulus is $K+\frac{4}{3}n$, where K is the bulk modulus and n the shear modulus. For a free-electron gas there is no imaginary

part of K, since uniform compression does not destroy equilibrium. The attenuation is thus all attributable to the shear modulus, and α_{long} is obtained from α_{trans} by multiplying by $\frac{4}{3}$ and replacing v_{st} by v_{sl}, as in (67).

By interpreting the attenuation in terms of relaxation processes contributing to the elastic compliance we may investigate qualitatively the types of contribution which may be expected in real metals, where the free electron model is inapplicable, and for which the fuller treatment, valid for arbitrary ql, is complicated and full of pitfalls. As a first example we consider a model in which there is one spherical Fermi surface, but the effective mass is not the same as the real electron mass, i.e. v_0 is written as $\hbar k_0/m^*$. Because the difference between effective and real masses is caused by interaction between the electrons and the ionic lattice it is not safe to use the idea of electron pressure incautiously. Instead we may derive the required result by consideration of the difference in total electron energy between the unrelaxed and relaxed states; since for a given strain the elastic energy is proportional to the elastic modulus, we may use the energy lost as heat in the relaxation process as a measure of $\Delta\chi$, other things being equal. Thus to compare the metal having n electrons of effective mass m^* with one which is identical except for having n electrons of real electronic mass, for a given shear the unrelaxed Fermi surface is the same in both, but the former has an excess electronic energy which is m/m^* times that of the latter. In consequence the attenuation constant, for a given value of τ, is m/m^* times that in the free-electron metal. The results expressed by (65) and (67) represent this more general case if m is replaced by m^*.

It would be unwise to infer from this that the general expressions for α can be so simply modified to allow for departures from the free electron model. Indeed it seems likely that the method of analysis used here is not applicable in general, since there is not the possibility of a unique division of the system into conduction electrons and lattice. A start towards the solution of the problem for arbitrary Fermi surfaces has been made by Blount (1959), which is sufficient to indicate how further progress may be made, but which has not yet yielded any results of wide applicability. We therefore revert to our discussion of such cases as can be treated as local relaxation phenomena.

The process we have analysed, relaxation following a shear deformation, is exactly analogous to viscosity in a liquid, and in fact one of the first explanations (Mason 1955) of the observed high attenuation of ultrasonics in pure metals at low temperatures was in terms of the viscosity of the electron gas. Since the viscosity of a gas is proportional to the free path, we expect as l increases at low temperatures to find a greater viscous damping of the lattice oscillations. This expectation is of course also expressed in (65) and (67) when $ql \ll 1$, and is verified by observation, as shown in figure 41. This figure also shows how the attenuation drops when the metal becomes superconducting. From observations (Bömmel 1955) on well-prepared single crystals it has been made fairly certain that the electronic contribution to α vanishes as the temperature goes to zero. This result has a certain value in the study of the non-superconducting state of the metal, for it enables extraneous sources of attenuation to be allowed for. Thus α does not drop to zero in the superconducting state of a polycrystalline sample, presumably because of scattering at grain boundaries which is unaffected by the superconducting transition. If

one may assume that the residual, non-electronic attenuation is temperature-independent in the range of interest, the electronic part may be determined accurately by subtraction. We shall say nothing more of the behaviour in the superconducting state, which is of great interest but not obviously relevant to the present study.

Once we leave the highly idealized models of metals with one spherical Fermi surface, other effects can come in and make important contributions to the attenuation. With one non-spherical Fermi surface, for example, it is possible

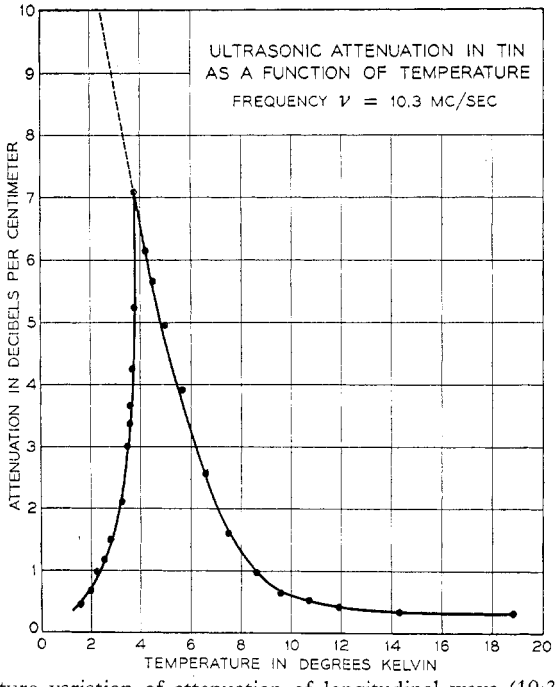

Figure 41. Temperature variation of attenuation of longitudinal wave (10·3 Mc/s) in a very pure single crystal of tin. The superconducting transition occurs at 3·7°K. (*After* Bömmel 1955.)

to have losses associated with pure compression as well as with pure shear, in hydrodynamical terms second as well as first viscosity. It is only necessary that the equilibrium form of the Fermi surface shall depend on the volume of the metal, so that a sudden uniform compression, which produces a uniform expansion in reciprocal space, leaves the Fermi surface in a non-equilibrium state. One would not expect this effect to be important in a metal whose Fermi surface was nearly spherical, but it might well be comparable to the effect of shear in a metal whose Fermi surface is very close to, or just touches, the zone boundary; for the energy gap at the boundary and consequently the degree of contact are probably sensitive functions of the atomic volume. In principle it should be possible to estimate the sensitivity of the Fermi surface to volume changes by measuring the imaginary parts of the bulk modulus, and hence to discover whether there is likely to be contact with the zone boundary. Measurements of the attenuation of longitudinal and transverse waves on the same sample, under conditions such that $ql \ll 1$, appear at first sight promising, but there are difficulties. Since all metals

are elastically anisotropic, the simple concepts of bulk and shear moduli are inapplicable except to a finely polycrystalline sample whose crystallites are small compared to the wavelength. If such samples are used there will probably be grain-boundary attenuation as well as electronic attenuation, and the only method known at present to estimate this is to use the superconducting behaviour already discussed.† Unfortunately the group I metals for which this study would be particularly interesting, being the only metals in which the Fermi surface is likely to have but one sheet, do not become superconducting. It would therefore be necessary to use carefully prepared single crystals, having small residual attenuation, and to measure the attenuation of the different waves in different directions chosen so that the shear processes in each were identical.

When the metal has more than one Fermi surface, additional attenuation may result from the transfer of electrons from one to another. For example, uniform

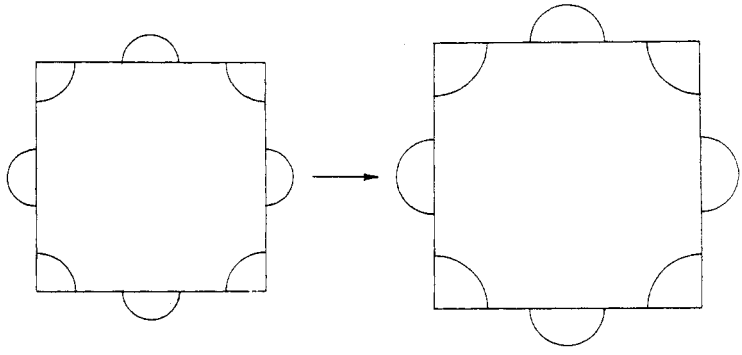

Figure 42. Transfer of electrons between bands as a result of uniform compression.

compression alters the energy discontinuities at the zone boundary and may therefore shift the energy bands in different zones with respect to one another, as illustrated in figure 42 for a hypothetical metal which has just enough electrons to fill the zone, but a small energy overlap so that the Fermi surface occupies two zones. In the cases we have mentioned the calculation of the attenuation constant when $ql \ll 1$ reduces to a calculation of the energy difference between the unrelaxed and relaxed electron distributions, combined with a knowledge of the relaxation time for the appropriate transition. If the shape of the energy surfaces is highly dependent upon deformation, and especially if the effective mass is small so that the transfer of a small number of electrons involves a considerable energy change, the metal may show an abnormally high attenuation in comparison with the free-electron model. Such is presumably the explanation of the fact that α is quite readily measurable in bismuth (Reneker 1959), although the effective number of conduction electrons is extremely small.

When ql is greater than unity, the current which balances the effective lattice current is not carried by all electrons, but more particularly by those whose velocity

† It might be possible to correlate the temperature variation of attenuation with that of electrical resistance and so detect the temperature-invariant part of the attenuation. It is not certain, however, that the phonon-controlled mean free path is the same in the two phenomena. Presumably a careful study of superconducting metals would enable this point to be investigated, so that ultimately some use could be made of polycrystalline non-superconductors.

component in the direction of wave propagation equals the wave velocity. One may expect that the overall sensitivity of the Fermi surface to deformation is still a measure of the effective lattice current, which is to say that one may expect (58) and (63) still to describe qualitatively the variation of α with ql. But there will be quantitative differences depending on the properties of the electrons on the effective zone in relation to the average over the whole Fermi surface. A complete theory has not been worked out, and until it has one should be cautious about the use of the free-electron theory for the quantitative interpretation of results on real metals.

We turn now to the effect of a magnetic field on the attenuation, considering first a free-electron model for which the calculations are straightforward in principle,

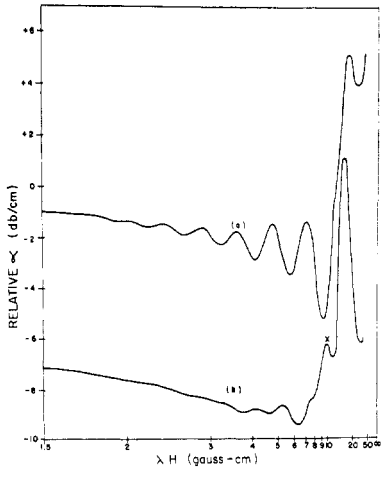

Figure 43. Oscillatory variation of attenuation of longitudinal waves (75 Mc/s) in a very pure single crystal of copper. The wave is propagated along [001] and H is applied along [100]. (*After* Morse and Gavenda 1959.)

even though they may involve a considerable amount of numerical work to evaluate the answer. The general results expressed by (58) and (63) are still valid, and the problem reduces to a calculation of γ. What is found in practice (Bömmel 1955) is that when $ql \gg 1$ the attenuation is an oscillatory function of field strength, as shown in figure 43. A naïve interpretation of this, which appears to agree with the experiments as regards the field strength involved, relates the variations of α to the relative sizes of wavelength and orbit diameter. For example, in the simplest case (**j**, **j**) the orbits and electric fields associated with the wave are represented in figure 44 ; **E** and **u** are parallel and ρ_{jj} is the reciprocal of the conductivity in this direction. If the field varies as $\mathbf{E}\,e^{i(\omega t - qz)}$ and the orbit, centred at z_0, has radius R, the average field strength around the orbit is $\mathbf{E}(z_0)J_0(qR)$. This is an oscillatory function of qR whose absolute amplitude has maxima whenever the orbit diameter is very nearly $(n+\frac{1}{4})$ wavelengths. When we take into account all electrons at one point having a given orbit diameter we must allow for a distribution of centres, which leads to the average field experienced being $E(z_0)\,[J_0(qR)]^2$. If all the electrons had the same orbit diameter their effective conductivity would contain the term $[J_0(qR)]^2$, and so γ and α would be oscillatory, the maxima of

$[J_0(qR)]^2$ corresponding to maximum conductivity and minimum attenuation. Since $R \propto H^{-1}$ we might expect to find α an oscillatory function of H^{-1} with regular period. This is similar to the de Haas–van Alphen effect and cyclotron resonance, but here the effect involves the spatial extensions of orbit and wave, not their periods as in cyclotron resonance. As a result the frequency at which the magneto-acoustic oscillations should occur is of the order of a hundred times less than the cyclotron resonance frequency in the same magnetic field, the ratio being $0{\cdot}26v_0/v_s$. This agrees well with what is found in practice (Morse, Bohm and Gavenda 1958), and it is disturbing therefore to discover that a full working of the theory destroys the predicted effect in this particular case. If the Fermi surface is spherical different electrons on the surface have different orbit radii,

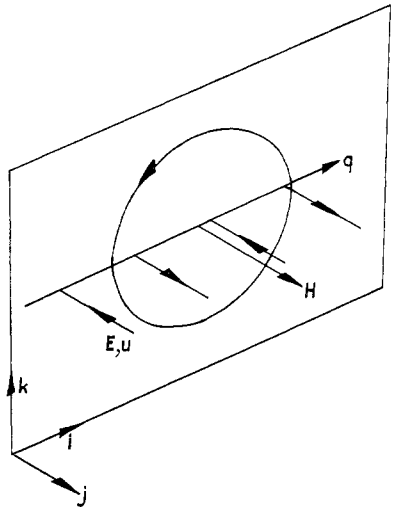

Figure 44. Illustrating fields and an electron orbit in the case (**j**, **j**).

and it is necessary to integrate over all parts of the Fermi surface. The final result is that for a sphere of radius k_0, when $ql \gg 1$,

$$1/\gamma = 3\int_0^1 [J_0(mx)]^2 x\sqrt{(1-x^2)}\,dx, \quad \text{where} \quad m = \hbar k_0 q/eH. \qquad \ldots\ldots(71)$$

The meaning of this expression is clear ; $3x\sqrt{(1-x^2)}\,dx$ is the fraction of electrons lying within a cylindrical shell of radius $k_0 x$ and thickness $k_0\,dx$, having its axis parallel to **H**. When **E** is parallel to **H**, as here, this is the weighting factor to be ascribed to the orbits of radius $hk_0 x/eH$. The vanishing of the weighting factor at the upper limit of integration corresponds to the fact that with this geometry the electrons of largest orbit make a vanishing contribution to the current, for their velocity is normal to the electric field. There is thus no especial orbit size which can dominate the conductivity, and it is not surprising to find on carrying out the integration of (71) that γ is a monotonic function of H. If the Fermi surface is not spherical it may be possible for one particular orbit size to be sufficiently dominant to produce oscillations in γ ; for example a cylindrical Fermi surface, oriented so that its axis is not parallel or normal to **H**, will have

all electrons on the surface executing the same elliptic orbit, and very marked oscillations can be expected. But in less extreme cases one can hardly hope for anything better than a broad spectrum of orbit sizes, so that even if any oscillations are seen they will be confined to one or two cycles only, higher harmonics (orbit diameters of several wavelengths) being smeared out. If this should be the explanation of the oscillations observed, it is of interest as showing the phenomenon to be one which is dependent on the Fermi surface departing from spherical shape in a particularly favourable way. But there are other possibilities of explanation, which we defer until we have discussed the other transverse field geometries (**k**, **j**) and (**i**, **j**).

Here the situation is a little more complex, since it is not sufficient to have **E** and **u** parallel to get **J** and **u** parallel ; both transverse and longitudinal electric fields are needed. In the case (**k**, **j**) we wish to know what field E_k is needed to produce a given J_k, that is we have to substitute in (58) the component of resistivity ρ_{kk} appropriate to a sinusoidal electric field distribution ; in the case (**i**, **j**) we have to substitute ρ_{ii} in (63). Each of these involves calculating the components σ_{kk}, σ_{ii} and σ_{ik} of the conductivity tensor, since for example $\rho_{kk} = \sigma_{ii}/(\sigma_{ii}\sigma_{kk} + \sigma_{ik}^2)$. Expressions have been given by Rodriguez (1958 b), which although correct are unfortunately written in such a form as to mislead him into making a number of erroneous statements about their behaviour, particularly that they are not oscillatory (it is perhaps unnecessary to remark that his physical argument to explain why they are not oscillatory is also quite unsound). For example in the interesting limit $ql \gg 1$ the conductivity component $d\sigma_{kk}$ due to a plane section of the electron assembly, cut normal to **H** ($= H_j$) and containing dN electrons per unit volume, takes the form

$$d\sigma_{kk} = \frac{2e^2\tau dN}{m}[J_1(qR)]^2, \qquad \ldots\ldots(72)$$

which is certainly oscillatory, as are σ_{ik} and σ_{ii} also. In contrast to the case (**j**, **j**), the central section of the Fermi sphere now has considerable weight, for the displacement of the surface of the section carries, as it were, all the inner electrons with it ; alternatively expressed, the central electrons have their velocities in the plane normal to **H** which also contains **E**, and are therefore efficient conductors. In fact when we come to integrate over all sections the situation is like what we found in cyclotron resonance, that the extremal section dominates the average, and the components of the conductivity oscillate with a periodicity characteristic of the extremal section. We thus expect to find an even periodicity when α is plotted against H^{-1}, the separation of neighbouring maxima being $\pi e/\hbar q k_0$. The curve shown in figure 43 exhibits this clearly ; from the number of periods visible one may feel sure that there is no averaging of frequencies involved, but that one group of orbits is dominating the behaviour. It is therefore rather disturbing to find that the value of k_0 deduced from this curve is only 0·8 of what is expected ; the discrepancy is large enough to need explanation.

It is possible that the explanation lies in the non-spherical nature of the Fermi surface of copper—not that it is likely to have any dimension as small as 0·8 times the diameter of the free-electron sphere (see p. 258), but it may be that the theory of the effect in non-spherical surfaces will reveal some unconsidered remedy for the discrepancy. This is not however a very hopeful suggestion ; one would

surely expect the periodicity to be governed by the full extension of the orbit in the direction of **q**, since it is at the extremes of the orbit that the electron spends a significant time in a constant field. If this difficulty can be cleared up the study of magneto-acoustic oscillations† should prove a useful method of determining specific dimensions of the Fermi surface. It is therefore worth examining the conditions which must be satisfied if the oscillations are to be observed. The electronic free path must be long enough for an orbit to be completed between collisions ; one may guess a collision damping factor of the form $e^{-2\pi R/l}$, so that l must be at least as big as the orbit diameter, or perhaps three or four wavelengths, if several cycles of the oscillation are to be observed. For a sound velocity of 2×10^5 cm sec^{-1} and a frequency of 100 Mc/s this implies that l must approach 10^{-2} cm, which is at present achievable only with very few metals. The magnetic fields required are quite modest, of the order of 10 kG, so that the main limitation of this method is the purity of the sample.

The possibility of oscillatory behaviour in the cases (**k**, **j**) and (**i**, **j**) makes one suspicious about the explanation of the oscillations in (**j**, **j**) tentatively advanced above. For the elastic anisotropy of the metals used implies that only along very special directions of high symmetry will the wave be purely transverse or longitudinal. In a polycrystal most crystallites will have electric fields with components not parallel to **H**, and it is possible that these are responsible for the oscillatory behaviour. One cannot be sure of this, but it could be checked by a study of single crystals of copper, as pure as those used by Morse to obtain figure 43, to see whether the oscillations only appear when **q** does not lie along an axis of high symmetry.

One last point to be made in connection with the transverse field effects concerns the limiting behaviour in high magnetic fields, when $qR\ll1$. The different cases have theoretically different limits. For example in (**j**, **j**) the coiling of the orbits into a small space allows lattice collisions to take over entirely the business of establishing the electronic current ; γ tends to unity, and α to zero, as H^{-2}. In the other two cases the combined effect of lattice collisions and magnetic field is to establish a current at right angles to the required direction, and electric fields are still needed. This does not prevent the attenuation going to zero as H^{-2} in the other transverse case (**k**, **j**), but in the longitudinal case (**i**, **j**) α tends to the limit $\frac{1}{15}(nmv_0\,q^2\,l/Mv_{\rm si})$. This has the same form as in zero field, when $ql\ll1$ (see (67)), but with one quarter of the coefficient. Since for observing the oscillations ql must be much greater than unity, the limiting value of α will be several times the value in zero field. It should of course be remembered that this analysis of the limiting behaviour is only valid for a spherical Fermi surface ; magneto-resistance may considerably alter the behaviour in high fields.

The last magneto-acoustic effect to be treated is the case (**j**, **i**) discussed in some detail by Kjeldaas (1959). It is convenient here to think of the transverse wave as circularly polarized, setting up a circularly polarized electric field. Since **H** is parallel to **q** the electrons perform helical paths about **q** as axis, and there is one particular group which have the correct component of velocity parallel to **q** to rotate in their orbits at just the same rate as the field in which they find

† In a short note (Pippard 1957 b) proposing this method of studying metals the effect was referred to as magneto-acoustic *resonance*. This is not a resonance phenomenon in the accepted sense and the term should be dropped. It is as well to point out also that in this note, through faulty reasoning, the condition of minimum attenuation was stated to be one of maximum attenuation.

themselves. These electrons in synchronism with the field are particularly good conductors and when $ql \gg 1$ make a dominant contribution to the real part of the effective conductivity. The phenomenon can be thought of as a cyclotron resonance between the electrons and the ultrasonic wave, but the frequency of the latter is enormously shifted by the Doppler effect of the electronic motion. We shall analyse the problem for a very special simple model in which the Fermi surface has axial symmetry about **q** (see figure 45). An electron at O has cyclotron

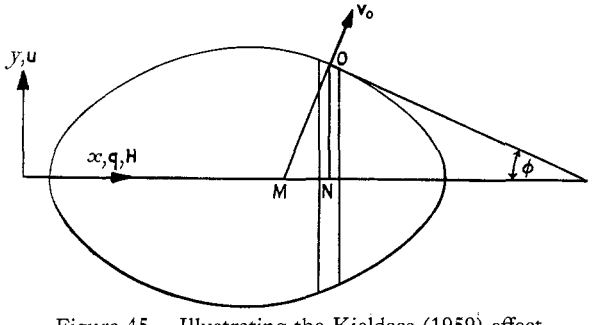

Figure 45. Illustrating the Kjeldaas (1959) effect.

frequency $\omega_c = Hev_0 \cos\phi/(\hbar k_y)$, where k_y is the radius ON, and is moving in the x-direction, parallel to **q**, with velocity $v_0 \sin\phi$. The Doppler-shifted frequency ω' which it experiences is $q(v_0 \sin\phi - v_s)$, and the relative frequency is thus given by the expression

$$\Delta\omega \equiv \omega_c - \omega' = qv_0 \sin\phi(\Gamma/S - 1 + v_s \operatorname{cosec}\phi/v_0), \qquad \ldots\ldots(73)$$

where $\Gamma = eH/(\hbar q)$ and $S = k_y \tan\phi = MN$.

If we neglect the term $v_s \operatorname{cosec}\phi/v_0$, which is equivalent to assuming the wave to be at rest, the resonance condition is seen to be that $\Gamma = S$, S being the sub-normal of the curve at O. As **H** and hence Γ change, different parts of the Fermi surface come into resonance. The calculation of the effective conductivity σ_{eff} is straightforward, since all that is necessary is to forget about **H** and instead to imagine each electron in a uniform electric field which rotates with frequency $\Delta\omega$. A short calculation then shows that

$$1/\gamma_t = \sigma_{\text{eff}}/\sigma = C\int \frac{lk_y \cos\phi}{1 + i\Delta\omega \cdot \tau}\, dk_x, \qquad \ldots\ldots(74)$$

where $$1/C = \int lk_y \cos\phi \, dk_x,$$

$\Delta\omega$ being, of course, a function of k_x, given by (73). We now consider what happens when l and τ are very large. The only significant contribution to the real part of γ_t^{-1} comes from the region around the resonance point where $\Delta\omega = 0$, the rest of the Fermi surface being responsible for the imaginary part of γ_t^{-1}. In evaluating $\mathscr{R}(\gamma_t^{-1})$ we may therefore take $lk_y \cos\phi$ in the integrand as constant, and after a certain amount of manipulation obtain the result

$$\mathscr{R}(\gamma_t^{-1}) = \frac{\pi C}{2q}\left|\frac{d(k_y^4)}{d(S^2)}\right|_{S=\Gamma}, \qquad \ldots\ldots(75)$$

while
$$\mathscr{I}(\gamma_t^{-1}) = -\frac{iC}{2q}\mathscr{P}\int\frac{d(k_y^4)}{d(S^2)}\cdot\frac{dS}{S-\Gamma}, \qquad \ldots\ldots(76)$$

in which $\mathscr{P}$ means that the principal value of the integral is to be taken. It will be observed that except for the field-independent C both parts of γ_t^{-1} are determined by the geometry of the Fermi surface. Now from (58) α depends on $\mathscr{R}(\gamma_t - 1)$, and both $\mathscr{R}(\gamma_t^{-1})$ and $\mathscr{I}(\gamma_t^{-1})$ enter into this. In particular

if
$$\mathscr{R}(\gamma_t^{-1}) \gg \mathscr{I}(\gamma_t^{-1}), \quad \alpha \propto 1/\mathscr{R}(\gamma_t^{-1})$$

if
$$\mathscr{R}(\gamma_t^{-1}) \ll \mathscr{I}(\gamma_t^{-1}), \quad \alpha \propto \mathscr{R}(\gamma_t^{-1})/[\mathscr{I}(\gamma_t^{-1})]^2.$$

If the Fermi surface is a sphere of radius k_0 (75) and (76) are readily evaluated to give
$$\gamma_t^{-1} = \frac{\pi C}{q}(k_0^2 - \Gamma^2) - \frac{iC}{q}\left\{(k_0^2 - \Gamma^2)\ln\frac{1+\Gamma}{1-\Gamma} + 2k_0\Gamma\right\}. \qquad \ldots\ldots(77)$$

The variation of α with Γ, i.e. with **H**, is shown in figure 46. The point of particular interest is the absorption edge which occurs when $\Gamma = k_0$, and which marks the field strength at which there cease to be any electrons which can resonate with

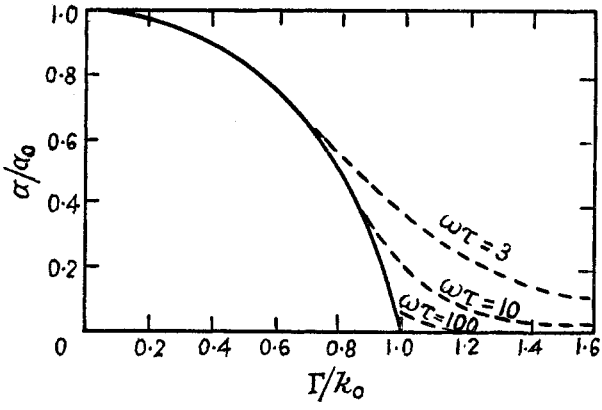

Figure 46. Variation of attenuation with field for various values of $\omega\tau$. (*After* Kjeldaas 1959).

the ultrasonic field. Such an edge may be expected to occur with any elliptic limiting point (in the nomenclature which Azbel' and Kaner use for cyclotron resonance), and it is easy to show that, whether or not the surface is axially symmetric, the value of Γ at the absorption edge is just $K^{-1/2}$, when K is the Gaussian curvature at the limiting point.

At first sight this elegant result appears to offer an attractive opportunity for analysing the Fermi surface, particularly of those metals for which it is difficult to prepare clean surfaces for the study of the anomalous skin effect, or those whose mosaic structure renders them unfit for de Haas–van Alphen studies. But certain reservations must be made. Even if we leave aside the difficulty of obtaining circularly polarized transverse waves,† there still remains the fact that in most

† If linearly polarized waves are used, as is experimentally much easier, the theory is hardly altered, as the wave can be analysed into two circularly polarized waves of opposite sense, which resonate with almost equivalent regions on opposite sides of the Fermi surface. There is, however, a small difference in velocity of the two waves, so that a rotation of polarization of the plane wave is to be expected. This may prove very annoying in practice.

directions of propagation the waves will not be purely transverse. It may be that a longitudinal component will not affect the form of the absorption edge, but this needs careful analysis. Along directions of high symmetry in cubic metals (e.g. (100), (110) and (111)) the present analysis should be valid, and in some cases determination of the curvature of the limiting points in these directions might almost entirely fix the form of the Fermi surface, if there is but one sheet as in the alkali and noble metals. It must also be remembered in making a provisional assessment of the method that the sharpness of the absorption edge is a consequence of a very high value of ql; according to Kjeldaas's calculations, a value of 50 is desirable, and this we have seen involves material of extremely high purity, as well as high acoustic frequencies. Finally we must point out the possibility of

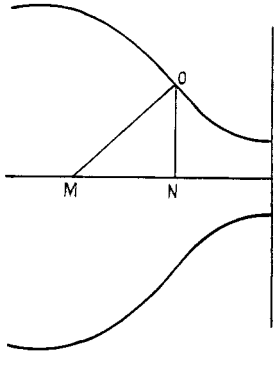

Figure 47. Maximal sub-normal when Fermi surface has no limiting point.

ambiguity in interpretation of the results. If the Fermi surface has no limiting point, because of contact with the zone boundary, it will have another region at which S is maximal (figure 47), and this will give rise to an absorption edge. The behaviour of γ_t^{-1} here is quite different from that at a limiting point, for the real part becomes infinite as $(S_{\max}-\Gamma)^{-1/2}$ while the imaginary part tends to become rather small. The attenuation goes to zero at the absorption edge, but as $(S_{\max}-\Gamma)^{1/2}$, i.e. with a vertical tangent, rather than as $(S_{\max}-\Gamma)$, with a finite slope, as it does if there is a limiting point. In principle the two types of edge can be discriminated, but one might have difficulty unless ql were very high indeed. Nevertheless this experiment promises to have considerable interest, and there is quite a good chance that it will yield information of real value.

4.6. *Size Effects*

It is possible, though difficult, to prepare a thin film or wire in a sufficiently pure state that at low temperatures by far the most potent scattering mechanism is by collision of the electrons with the surface of the sample. Measurement of the conductivity of the film or wire, combined with some assumption about the scattering properties of the surface, enable an estimate to be made in principle of the conductivity of the metal for a known free path (a calculable function now of the direction of the electronic trajectory). In a film for example the dominant electrons are those moving parallel to the surfaces, and the information which might be extracted is to all intents the same as is yielded by the anomalous skin

effect. It seems, however, that the latter is a much easier and more reliable technique, having the advantages that the exact nature of the surface scattering is of only minor importance, and the preparation of clean samples of any crystal orientation is not too difficult. With the film, on the other hand, only certain orientations of single crystals can be made, by epitaxial growth, and it is extremely hard to ensure that they shall be uncontaminated by residual gas in the evaporating oven. Moreover the films made in this way are very liable to vary in thickness and even to have holes in them which greatly obscure the interpretation of the measured resistance. Thin monocrystalline wires are more readily prepared, as whiskers, and may be obtained very pure so that surface scattering is dominant. But they also are limited in the range of orientations possible, and in addition do not yield the specific information about the electronic structure that is yielded by films and the anomalous skin effect, for the electrons moving nearly parallel to the axis are too few in number to play a dominant role. It does not seem therefore that the prospect of using these simple size effects as analytic tools is very promising.

There is more hope that useful information will come out of such measurements in the presence of a magnetic field, though here again the limitations are such as to make it no more than an outside chance. The periodic oscillations of conductivity of a film in a magnetic field normal to its plane, predicted by Sondheimer (1950) but never observed, and the similar effect observed by Babiskin and Siebenmann (1957) in a wire, but not treated theoretically in detail, might possibly yield data on the extension of orbits in a given field. It is rather disheartening to find that even for a free-electron metal with surface scattering completely dominant the predicted oscillations are so highly damped as to be observable for only two or three cycles, for this suggests that there is no one group of electrons which can govern the periodicity as in some of the other phenomena we have analysed. The interpretation of the data for a real metal is therefore likely to be difficult unless the electronic structure is already known.

Finally we may mention the proposal by Azbel' (1958) to study the Schubnikov-like oscillations of the skin resistance (see p. 236) in a rather thick monocrystalline film. He points out that no oscillations will be observed until the field is high enough for the electronic orbit to lie completely within the film, and that the field strength at which any particular oscillation appears determines one dimension of the Fermi surface. We shall not enter into this proposal any further here; a full discussion may well await the performance of the experiment. As this involves the preparation of a thick film ($>10^{-4}$ cm) so perfectly crystalline as to show the oscillations, and so pure that the electron can complete an orbit entirely within the film, we believe that a revolutionary advance in the art of thin films will be necessary before it is worth trying.

§ 5. Applications

We shall not attempt to give a complete survey of the applications made up to the present of the methods we have discussed. It seems more profitable to take the view that these studies are still in their infancy, and to describe a few examples which illustrate the scope and limitations of the methods. We therefore pass over without comment a large amount of work on the de Haas–van Alphen

effect in moderate fields, which has shown the presence in many metals of small inclusions of holes or electrons; a full discussion has been given by Shoenberg (1957). It is not perhaps so justifiable to let pass without discussion a great diversity of valuable work on bismuth, graphite and other semi-metals, in which the Fermi surfaces are all small in extent, and the revealing properties, being capable of examination in moderate magnetic fields, have been studied in some detail. Our excuse for this neglect is that these substances form a special class of their own, and deserve an article to themselves if all that is known about them is to be placed in proper perspective.† By adopting this cavalier attitude we have narrowed down the field sufficiently to permit what is left to be examined at leisure, and we shall concentrate on results obtained for copper and lead.

The analysis of the Fermi surface of copper (Pippard 1957 a) illustrates both the strength and the weakness of the anomalous skin effect for this work. The surface resistance varies in a complicated manner with crystal orientation, the extreme variation amounting to nearly a factor of two. Only moderate precision (about 3%) was needed to reveal the anisotropy of resistance with sufficient accuracy to make detailed analysis worth the considerable effort. There is no need to recapitulate the arguments and numerical procedures which led to a single closed surface whose variations of curvature were able to explain the observations. The surface is derivable from a sphere by pulling it out along the (111) directions and slightly denting it in the (110) directions, the ratio of maximum to minimum radius being 1·16. Although the variations of radius are so small, the high (cubic) symmetry of the surface makes them sufficient to introduce slight concavities, so that there are regions of very large radius of curvature contributing strongly to the effective conductivity. This is how the large anisotropy of resistance comes about, and this is the strength of the method, that small variations of radius can lead to large variations of resistance. The shape of the Fermi surface is thus rather precisely determined, particularly around the flattened parts. The absolute size of the surface can be found no more accurately than the probable error of the readings, and although this would not be of great importance in many cases, it happens that copper is not one of these. The measurements suggest that the surface is of such a size as to hold, within a few per cent, one electron per atom. If we were genuinely dealing with independent electrons we should feel no hesitation about taking this result as confirmation that only the valence electrons occupy unfilled Brillouin zones, and scaling the surface so that it was precisely the size to hold one electron per atom, that is, half the volume of the Brillouin zone. But the quasi-particles are not independent electrons, but only something like electrons, and it is not obvious that the Fermi surface of the quasi-particles should contain as many states as there are electrons. Plausible arguments may be developed in support of this view, but they are not altogether convincing, and although we shall adopt it as the most likely hypothesis it remains a weakness in the chain of reasoning. When the derived surface is scaled to occupy half the zone it is found that it will not quite go in, the (111) extensions causing overlap beyond the zone boundaries. Now it is just at the points of maximum extension that the shape is least securely

† The following papers give some idea of what has been done in this field :
For bismuth ; Abeles and Meiboom (1956), Heine (1956 b).
For graphite ; Soule (1958 b), McClure (1958).

determined, for the radius of curvature is small here, and the contribution to the conductivity correspondingly small. By means of crude arguments it may be contended that the most plausible modification to make the surface fit into the zone is to have positive contact with the boundary, as shown in figure 48, and this is what is proposed as the Fermi surface in copper. It should be emphasized that the extent of the contact, its existence even, is conjectural, but it is almost certain from the data that the deformation of the surface from spherical form is of the type and roughly of the magnitude shown here ; that is, it is pulled out towards the (111) faces, and either touches them over a small area or just fails to touch them. The insensitivity of the experimental results to the form of a critical region like this is a real weakness of the method.

Recently the de Haas–van Alphen effect has been discovered in copper whiskers (Shoenberg 1959), and although the investigation is far from complete it is worth

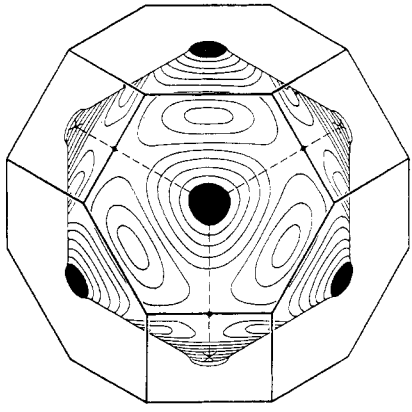

Figure 48. The Fermi surface in copper (redrawn from Pippard 1957 a). The dark patches mark contacts with the zone boundaries.

seeing what might be expected if the proposed Fermi surface is correct. For a considerable range of orientations of the magnetic field around the (100) axes (within a cone of semi-angle about 30°) and around the (111) axes (semi-angle about 15°), the central section normal to the field does not intersect the contact regions, and the section is bounded by a closed electron orbit whose area is nearly equal to that of a free-electron sphere. One would expect the period of the oscillations to vary only by a few per cent. The results up to now, of which figure 49 is typical, indicate that for these orientations only one period is present, and this is nearly independent of orientation, but the oscillations have not been followed more than 8–10° from either axis as the amplitude falls off rapidly. This may be an effect of mosaic structure, which is less deleterious when the crystal is oriented so that by symmetry the period is extremal. If the field lies along or near a (110) axis, the central section cuts four contact regions and in periodically extended reciprocal space the bounding curve is a slightly re-entrant hole orbit whose area is about 60% of the electron orbits we have just considered. There are also non-central extremal (minimal) sections, each enclosing two contact regions, which have distinctly smaller areas still. Oscillations of even longer period should be observed over a wide range of angles, particularly round the (111)

directions, corresponding to orbits enclosing one contact region, but in fact they have never been detected. Nor indeed has an oscillation of any period been found yet in a whisker orientated along (110). It is dangerous to speculate on the meaning of the absence of any particular de Haas–van Alphen oscillation since the factors controlling the amplitude are so little understood, but it is clear that the behaviour around (110) or the long period oscillations, if either can be observed, will prove decisive in the question of whether there is contact with the zone boundary. If the views expressed on p. 204, concerning the non-viability of orbits which pass close to contact regions, should turn out to be correct, it may be impossible to find any oscillations in the critical directions, and the question of contact will remain conjectural. It should not prove impossible to discover whether there are regions of abnormally high scattering probability ; a careful examination

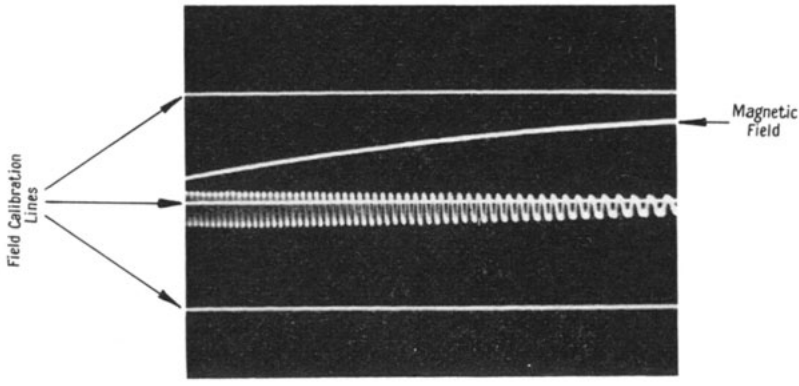

Figure 49. Oscillogram of de Haas–van Alphen oscillations in copper (Shoenberg, unpublished). As the rate of variation of H decreases the oscillations spread out, the period ΔH being virtually constant.

of the magneto-resistance might serve, or, a more elaborate test, a study of the sharpness of the absorption edge in the Kjeldaas ultrasonic experiment when propagation is along a (111) axis. Whether or not these experiments will yield the particular information desired cannot be predicted, but it is certain that there is a strong case for a systematic examination of the properties of copper, by cyclotron resonance, magneto-acoustic effects, high field galvano-magnetic effects, and anything else which might be expected to yield its contribution, however small, to the general picture. The technical problem of preparing good enough samples for these studies has been overcome by several workers, and in other respects copper seems to be almost an ideal metal for a concentrated attack on the elucidation of the electronic structure. It does not seem to be so easy to prepare copper crystals of really low residual resistance as it is with silver or gold, but on the other hand whiskers are more readily produced, and copper surfaces are much more easily electropolished than surfaces of the other noble metals. If the shape of the Fermi surface can be certainly established, systematic measurements on the temperature variation of the de Haas–van Alphen amplitude or on cyclotron resonance (or preferably both) should enable a velocity to be ascribed to every point. If this can be done the way is clear for a serious examination of the properties of copper—

specific heat, transport effects, etc.—to discover the extent to which they are quantitatively intelligible on the basis of a one-particle model.

Between the reasonable expectation of an elucidation of the structure of copper, and the hope for similar success with so much more complex a metal as lead, lies a gulf whose extent can hardly be guessed. It is certainly a measure of the power of the de Haas–van Alphen effect that it can yield any information of value in the latter case; in fact this is to understate what Gold (1958) has achieved. He has shown that the oscillations, of which as many as four might be observed simultaneously, can be analysed into three groups, which he associates with different sheets of the Fermi surface. Not all oscillations are observed over a wide range of angles, and the amplitudes vary considerably and in a complicated manner, all of which is ingeniously incorporated into the interpretation. The form of the Fermi surface is not so much synthesized from the data—it is rather doubtful whether this could be done by a systematic and objective procedure—as adapted by reference to the data from a scheme suggested by the free-electron model. As discussed on p. 186, if a sphere containing 4 electrons per atom is dissected and reconstructed in the various Brillouin zones, a quite remarkable set of surfaces emerges, which with a little smoothing at the corners may be taken to represent what would be expected if the energy discontinuities at the zone boundaries were small. Gold finds that these surfaces account, with comparatively little modification, for most, if not all, of his observations. The first zone is full and therefore contains 2 electrons and contributes no oscillations; the second zone has its maximum energy at the centre, and contains 1.6 electrons, leaving a nearly spherical hole at the centre which gives a rather short period oscillation of isotropic frequency; the third zone is filled only along the edges of the zone, giving in periodically extended reciprocal space the tubular lattice illustrated in figure 13; and lastly the fourth zone has a small number of electrons in each corner which combine in periodically extended space to form a set of cushion-shaped surfaces. There is little comparison with other data possible. The total area may be compared with an estimate based on anomalous skin effect measurements on a polycrystalline sample; even allowing for poor polish on the surface of the latter there seems to be some discrepancy, the total area of Gold's surfaces being distinctly too high. The skin effect measurements certainly need repetition under better conditions before one can conclude that they offer serious objections to Gold's construction. It is also possible to estimate the mean Fermi velocity on each surface from the temperature variation of the amplitude of the oscillations, and hence to calculate the expected value of the specific heat coefficient γ. This comes out about 40% too high, not outside the considerable uncertainty of the estimate.

It is probably not unfair to Gold to characterize his work as an ingenious, not unplausible, but not certainly established delineation of the Fermi surface. It may be that this starting model, the free-electron sphere, is a good approximation to the truth, but if it is not one may doubt whether the data do not contain too many ambiguities of interpretation to make it possible at this stage to proceed further with assurance. In an ideal world one would doubtless settle the monovalent metals first, and then proceed cautiously to investigate the more promising multivalent metals such as beryllium, magnesium, aluminium, etc., in the hope that with increased insight the more difficult metals would yield their secrets. As it is,

however, one can only expect a haphazard attack governed by rather secondary considerations such as the availability of suitable samples. We have tried here to assess the value of various methods, none of which has really been thoroughly tested. It is to be hoped that future work will confirm our general conclusion, that there is now a reasonable expectation of synthesizing from experimental data a valid model of a metal, and will reveal new ways of testing critically the inherent assumptions of the independent-particle model and the theory of transport processes.

APPENDIX

The Standard Metal

We choose as standard a monovalent metal whose atomic volume is 10 cm^3, so that there are 6.0×10^{22} conduction electrons per cm^3. The electrons are assumed to be perfectly free, so that the Fermi surface is a sphere. The magnitudes of the relevant properties are as follows:

Radius of Fermi sphere : $k_0 = 1.21 \times 10^8$ cm^{-1}
Maximal cross-sectional area : $\mathscr{A}_{0,\max} = 4.60 \times 10^{16}$ cm^{-2}
Fermi velocity : $v_0 = 1.40 \times 10^8$ cm sec^{-1}
Cyclotron frequency in a field of H gauss : $\omega_c = 1.76 \times 10^7 H$ radians sec^{-1}
Maximal orbit radius in a field of H gauss : $R = 7.96/H$ cm
Electrical conductivity with free path l cm : $\sigma = 1.21 \times 10^{11} l$ $ohm^{-1}\,cm^{-1}$
Electronic specific heat coefficient per unit volume : $\gamma = 632$ erg $deg^{-2}\,cm^{-3}$
Fermi energy : $\epsilon_0 = 8.93 \times 10^{-12}$ ergs
$= 5.57$ ev
Degeneracy temperature : $T_0 = \epsilon_0/k = 64\,700°\,K$

Acknowledgments

During the preparation of this review I have benefited very greatly from discussions with Dr. V. Heine, Dr. J. M. Ziman, Mr. J. E. Aubrey and Mr. A. R. Mackintosh, and from the critical comments of Dr. R. G. Chambers ; to all of whom I express my warmest thanks, while absolving them from any responsibility for its imperfections.

I also thank the authors and publishers of papers from which diagrams have been reproduced, for their permission for publication.

References

Articles distinguished by an asterisk contain extensive references, not all of which are repeated below.

§ 1. Introduction

*Pines, D., 1955, *Solid State Physics* (ed. Seitz and Turnbull) (New York : Academic Press), **1**, 368.

§ 2. The Independent-particle Model

Gold, A. V., 1958, *Phil. Trans. Roy. Soc.* A, **251**, 85.
*Herman, F., 1958, *Rev. Mod. Phys.*, **30**, 102.
Onsager, L., 1952, *Phil. Mag.*, **43**, 1006.
*Reitz, J. R., 1955, *Solid State Physics*, **1**, 2.
*Slater, J. C., 1956, *Hand. d. Phys.* (ed. S. Flügge) (Berlin : Springer), **19**, 1.

§ 3. Transport Phenomena

3.1. *The Method of Trajectories*

Chambers, R. G., 1952 a, *Proc. Phys. Soc.* A, **65**, 458.
Shockley, W., 1950, *Phys. Rev.*, **79**, 191.

3.2. *Spatially Varying Electric Fields*

Pippard, A. B., 1954 a, *Proc. Roy. Soc.* A, **224**, 273.

3.3. *Galvanomagnetic Effects*

Alekseevski, N. E., Brandt, N. B., and Kostina, T. N., 1958, *J. Exper. Theor. Phys.*, **34**, 1339.
Alekseevski, N. E., and Gaidukov, Yu. P., 1958, *J. Exper. Theor. Phys.*, **35**, 554.
Borovik, E. S., 1954, *J. Exper. Theor. Phys.*, **27**, 355; 1955, *Izv. Akad. Nauk, S.S.S.R.*, **19**, 429.
Chambers, R. G., 1956 a, *Proc. Roy. Soc.* A, **238**, 344.
Kapitza, P., 1929, *Proc. Roy. Soc.* A, **123**, 292.
Lifshitz, I. M., 1956, *J. Exper. Theor. Phys.*, **30**, 814.
Lifshitz, I. M., Azbel', M. Ya., and Kaganov, M. I., 1956 a, *J. Exper. Theor. Phys.*, **30**, 220; 1956 b, *Ibid.*, **31**, 63.
Lüthi, B., 1956, *Helv. Phys. Acta*, **29**, 217.
*MacDonald, D. K. C., and Sarginson, K., 1952, *Rep. Progr. Phys.*, **15**, 249 (London: Physical Society).
Okada, T., 1957, *J. Phys. Soc. Japan*, **12**, 1327.
Olsen, J. L., and Rinderer, L., 1954, *Nature, Lond.*, **173**, 682.
Olson, R., and Rodriguez, S., 1957, *Phys. Rev.*, **108**, 1212.
Ziman, J. M., 1958, *Phil. Mag.*, **3**, 1117.

§ 4. Analysis of Special Phenomena

4.1. *Introduction*

*Chambers, R. G., 1956 b, *Canad. J. Phys.*, **34**, 1395.
*Heine, V., and Cohen, M. H., 1958, *Advanc. Phys.* (*Phil. Mag.*, Suppl.), **7**, 395.
*Lax, B., 1958, *Rev. Mod. Phys.*, **30**, 122.
*Pippard, A. B., 1954 b, *Solvay Conf.*, **10**, 123.

4.2. *The de Haas–van Alphen and Related Effects*

Adams, E. N., and Holstein, T. D., 1959, *J. Phys. Chem. Solids*, **10**, 254.
Alers, P. B., 1956, *Phys. Rev.*, **101**, 41.
Alers, P. B., and Webber, R. T., 1953, *Phys. Rev.*, **91**, 1060.
Argyres, P. N., 1958 a, *Phys. Rev.*, **109**, 1115; 1958 b, *J. Phys. Chem. Solids*, **4**, 19.
Argyres, P. M., and Adams, E. N., 1956, *Phys. Rev.*, **104**, 900.
Berlincourt, T. G., 1954, *Phys. Rev.*, **94**, 1172; 1955, *Ibid.*, **99**, 1716.
Berlincourt, T. G., and Steele, M. C., 1954, *Phys. Rev*, **95**, 1421; 1955, *Ibid.*, **98**, 956.
Brailsford, A. D., 1957, *Proc. Phys. Soc.* A, **70**, 275.
Brodie, L. C., 1954, *Phys. Rev.*, **93**, 935.
Chambers, R. G., 1956 b, *Canad. J. Phys.*, **34**, 1395.
Cohen, M. H., and Blount, E. I., 1960, *Phil. Mag.*, in the press.
Connell, R. A., and Marcus, J. A., 1957, *Phys. Rev.*, **107**, 940.
Davydov, B., and Pomeranchuk, I., 1940, *J. Phys. U.S.S.R.*, **2**, 147.
Dhillon, J. S., and Shoenberg, D., 1955, *Phil. Trans. Roy. Soc.* A, **248**, 1.
Fukuroi, T., and Saito, Y., 1957, *Sci. Rep. Res. Insts Tôhoku Univ.* A, **9**, 273.
Gerritsen, A. N., and de Haas, W. J., 1940, *Physica*, **8**, 802.
Gunnersen, E. M., 1956, *Phil. Trans. Roy. Soc.* A, **249**, 299.
Harper, P. G., 1955, *Proc. Phys. Soc.* A, **68**, 874.
Heine, V., 1956 a, *Proc. Phys. Soc.* A, **69**, 505.
Kosevich, A. M., 1957, *J. Exper. Theor. Phys.*, **33**, 735.
Lax, B., Roth, L. M., and Zwerdling, S., 1959, *J. Phys. Chem. Solids*, **8**, 311.

LIFSHITZ, I. M., 1958, *J. Phys. Chem. Solids*, **4**, 11.
LIFSHITZ, I. M., and KOSEVICH, A. M., 1954, *Dokl. Akad. Nauk, S.S.S.R.*, **96**, 963 ; 1955, *J. Exper. Theor. Phys.*, **29**, 730 ; 1958, *J. Phys. Chem. Solids*, **4**, 1.
LIFSHITZ, I. M., and POGORELOV, A. V., 1954, *Dokl. Akad. Nauk, S.S.S.R.*, **96**, 1143.
OVERTON, W. C., and BERLINCOURT, T. G., 1955, *Phys. Rev.*, **99**, 1165.
REYNOLDS, J. M., HEMSTREET, H. W., LEINHARDT, T. E., and TRIANTOS, D. D., 1954, *Phys. Rev.*, **96**, 1203.
SCHUBNIKOV, L., and DE HAAS, W. J., 1930, *Commun. Phys. Lab. Univ. Leiden*, **207**, 210.
*SHOENBERG, D., 1952, *Phil. Trans. Roy. Soc.* A, **245**, 1 ; *1957, *Progress in Low Temperature Physics* (ed. C. J. Gorter) (Amsterdam : North-Holland), **2**, 226 ; 1959, *Nature, Lond.*, **183**, 171.
SLADEK, R. J., 1958, *Phys. Rev.*, **110**, 817.
SOULE, D. E., 1958 a, *Phys. Rev.*, **112**, 698.
STEELE, M. C., and BABISKIN, J., 1955, *Phys. Rev.*, **98**, 359.
VERKIN, B. I., and DMITRENKO, I. M., 1955, *Izv. Akad. Nauk, S.S.S.R.*, **19**, 409.
VERKIN, B. I., DMITRENKO, I. M., and LAZAREV, B. G., 1956, *J. Exper. Theor. Phys.*, **31**, 538.
VERKIN, B. I., DMITRENKO, I. M., and MIKHAILOV, I. F., 1955, *Dokl. Akad. Nauk, S.S.S.R.*, **101**, 233.
ZWERDLING, S., LAX, B., and ROTH, L. M., 1957, *Phys. Rev.*, **108**, 1402.

4.3. *The Anomalous Skin Effect*

CHAMBERS, R. G., 1952 b, *Proc. Roy. Soc.* A, **215**, 481 ; 1956 a, *Ibid.*, **238**, 344.
FABER, T. E., and PIPPARD, A. B., 1955, *Proc. Roy. Soc.* A, **231**, 336.
FAWCETT, E., 1955, *Proc. Roy. Soc.* A, **232**, 519.
HEINE, V., 1957 a, *Proc. Roy. Soc.* A, **240**, 361.
KAGANOV, M. I., and AZBEL', M. YA., 1955, *Dokl. Akad. Nauk, S.S.S.R.*, **102**, 49.
KLEIN, O., 1944, *Ark. Mat. Astr. Fys.* A, **31**, No. 12.
PIPPARD, A. B., 1954 a, *Proc. Roy. Soc.* A, **224**, 273 ; *1954 c, *Advances in Electronics and Electron Physics* (ed. L. Marton) (New York : Academic Press), **6**, 1 ; 1957 a, *Phil. Trans. Roy. Soc.* A, **250**, 325.
REUTER, G. E. H., and SONDHEIMER, E. H., 1948, *Proc. Roy. Soc.* A, **195**, 336.
SMITH, G. E., 1959, *Phys. Rev.*, **115**, 1561.

4.4. *Cyclotron Resonance*

ANDERSON, P. W., 1955, *Phys. Rev.*, **100**, 749.
AUBREY, J. E., and CHAMBERS, R. G., 1957, *J. Phys. Chem. Solids*, **3**, 128.
AZBEL', M. YA., 1958, *J. Phys. Chem. Solids*, **7**, 105.
AZBEL', M. YA., and KANER, E. A., 1956, *J. Exper. Theor. Phys.*, **30**, 811 ; *1958, *J. Phys. Chem. Solids*, **6**, 113.
BEZUGLYI, P. A., and GALKIN, A. A., 1957, *J. Exper. Theor. Phys.*, **33**, 1076.
CHAMBERS, R. G., 1952 b, *Proc. Roy. Soc.* A, **215**, 481 ; 1956 c, *Phil. Mag.*, **1**, 459.
DONOVAN, B., and SONDHEIMER, E. H., 1953, *Proc. Phys. Soc.* A, **66**, 823.
DAVYDOV, B., and POMERANCHUK, I., 1940, *J. Phys. U.S.S.R.*, **2**, 147.
FAWCETT, E., 1956, *Phys. Rev.*, **103**, 1582.
GALT, J. K., MERRITT, F. R., YAGER, W. A., and DAIL, H. W., 1959, *Phys. Rev. Lett.*, **2**, 292.
GALT, J. K., YAGER, W. A., and DAIL, H. W., 1956, *Phys. Rev.*, **103**, 1586.
GALT, J. K., YAGER, W. A., MERRITT, F. R., CETLIN, B. B., and BRAILSFORD, A. D., 1960, *Phys. Rev.*, **114**, 1396.
GALT, J. K., YAGER, W. A., MERRITT, F. R., CETLIN, B. B., and DAIL, H. W., 1955, *Phys. Rev.*, **100**, 748.
HEINE, V., 1957 b, *Phys. Rev.*, **107**, 431.
KIP, A. F., LANGENBERG, D. N., ROSENBLUM, B., and WAGONER, G., 1957, *Phys. Rev.*, **108**, 494.
MATTIS, D. C., and DRESSELHAUS, G., 1958, *Phys. Rev.*, **111**, 403.
RODRIGUEZ, S., 1958 a, *Phys. Rev.*, **112**, 1616.

4.5. *Ultrasonic Attenuation and Magneto-acoustic Effects*

BLOUNT, E. I., 1959, *Phys. Rev.*, **114**, 418.
BÖMMEL, H. E., 1954, *Phys. Rev.*, **96**, 220 ; 1955, *Ibid.*, **100**, 758.
KITTEL, C., 1955, *Acta Metallurg.*, **3**, 295.
KJELDAAS, T., 1959, *Phys. Rev.*, **113**, 1473.
KJELDAAS, T., and HOLSTEIN, T. D., 1959, *Phys. Rev. Lett.*, **2**, 340.
MACKINNON, L., 1955 a, *Phys. Rev.*, **98**, 1181 ; 1955 b, *Ibid.*, **98**, 1210 ; 1955 c, *Ibid.*, **100**, 655.
MASON, W. P., 1955, *Phys. Rev.*, **97**, 557 ; *1958, *Physical Acoustics and the Properties of Solids* (New York : van Nostrand).
MASON, W. P., and BÖMMEL, H. E., 1956, *J. Acoust. Soc. Amer.*, **28**, 930.
MORSE, R. W., 1955, *Phys. Rev.*, **97**, 1716 ; *1959, *Progress in Cryogenics* (ed. K. Mendelssohn) (London : Heywood), **1**, 219.
MORSE, R. W., and BOHM, H. V., 1957, *Phys. Rev.*, **108**, 1094.
MORSE, R. W., BOHM, H. V., and GAVENDA, J. D., 1958, *Phys. Rev.*, **109**, 1394.
MORSE, R. W., and GAVENDA, J. D., 1959, *Phys. Rev. Lett.*, **2**, 250.
PIPPARD, A. B., 1955, *Phil. Mag.*, **46**, 1104 ; 1957 b, *Ibid.*, **2**, 1147 ; 1957 c, *J. Phys. Chem. Solids*, **3**, 175.
RENEKER, D., 1959, *Phys. Rev.*, **115**, 303.
RODRIGUEZ, S., 1958 b, *Phys. Rev.*, **112**, 80.
STEINBERG, M. S., 1958 a, *Phys. Rev.*, **110**, 772 ; 1958 b, *Ibid.*, **110**, 1467 ; 1958 c, *Ibid.*, **111**, 425.

4.6. *Size Effects*

AZBEL', M. YA., 1958, *J. Phys. Chem. Solids*, **7**, 105.
BABISKIN, J., and SIEBENMANN, P. G., 1957, *Phys. Rev.*, **107**, 1249.
SONDHEIMER, E. H., 1950, *Phys. Rev.*, **80**, 401 ; *1952, *Advanc. Phys.* (*Phil. Mag.*, Suppl.), **1**, 1.

§ 5. APPLICATIONS

ABELES, B., and MEIBOOM, S., 1956, *Phys. Rev.*, **101**, 544.
HEINE, V., 1956 b, *Proc. Phys. Soc.* A, **59**, 513.
*MCCLURE, J. W., 1958, *Phys. Rev.*, **112**, 715.
PIPPARD, A. B., 1957 a, *Phil. Trans. Roy. Soc.* A, **250**, 325.
SHOENBERG, D., 1957, *Progress in Low Temperature Physics* (ed. C. J. Gorter) (Amsterdam : North-Holland), **2**, 226 ; 1959, *Nature, Lond.*, **183**, 171.
*SOULE, D. E., 1958 b, *Phys. Rev.*, **112**, 708.

Note added in Proof.

Since the article was written a very significant advance has been made by Shoenberg (1960), who has continued his examination of the de Haas–van Alphen effect in copper, silver and gold to the point where the general forms of the Fermi surface have become clear. The variety of oscillatory periods and their angular dependence leave little doubt that there is contact with the zone boundary around the (111) position in all three, of the type shown in figure 48. The area of contact is greatest in copper and least in silver. It appears that the contact region in copper is about 12% greater in diameter than was suggested by the anomalous skin effect, but this is probably not a serious discrepancy since the latter is not sensitive to small variations in this region. There are other discrepancies in detail which are still unresolved, and will remain so until a more extensive body of de Haas–van Alphen data has been collected and a thorough analysis made of all alternative interpretations. Recent measurements of the anomalous skin effect in silver by

V. M. Morton reveal a variation of resistance which is similar to that of copper but over a smaller range ; this agrees with Shoenberg's suggestion of a smaller contact area, but it must be admitted that in the absence of his evidence for contact one would have been reluctant to infer it from the skin effect data. Nevertheless, however unwilling one may be to accept the idea that the same independent-particle model can be made to fit all the facts exactly, it is surely very unlikely that one set of facts will require contact and another set not. Clearly a good deal of examination of alternative models will be needed here also, and it will be particularly important to try to estimate the range of shapes which are consistent with the skin effect data.

Cyclotron resonance has been observed in copper by Langenberg and Moore (1959) ; the results are not sufficiently detailed yet to allow a clear interpretation, but it is interesting to note that the cyclotron frequency shows singularities at certain orientations of the magnetic field which may be associated with a change in character of the dominant orbits according as the sections of the Fermi surface enclose electron or hole orbits. This behaviour indicates that studies of cyclotron resonance may yield topological information about the connectivity of the Fermi surface, quite apart from the quantitative information about the Fermi velocity which is discussed in the text. The qualitative problem, of finding what sort of surface the Fermi surface is, has in fact been rather neglected in the article, and this recent work serves as a reminder of the fundamental importance of determining whether and where zone boundary contacts occur.

But perhaps the most serious error in the article is one both of fact and of emphasis. It has been pointed out by Lifshitz and Peschanskii (1958) that open orbits are not confined to magnetic field orientations which lie in planes normal to the high symmetry axes discussed on p. 203. If **H** is oriented in such a way (say rather close to (100) or (110) or (111)) that some plane sections normal to **H** define electron orbits and some hole orbits, then there must be an intermediate set of sections which define open orbits. These latter are not regularly periodic trajectories of the type shown in figure 14, but are formed of a succession of different partial revolutions of the Fermi surface at different levels, such as will allow the general trend of the trajectory in reciprocal space to be linear but not parallel to a symmetry axis. This analysis crystallizes the meaning of Chambers' (1956 b) ' quasi-ergodic ' orbits, and shows them often to be genuinely open. For a Fermi surface such as that of copper open orbits are by no means a rarity, though they are confined to orientations of **H** which lie within cones centred on the axes of high symmetry. It is therefore possible to make a start at interpreting Gaidukov's (1959) most valuable observations on the transverse magneto-resistance of the noble metals, which fails to saturate when **H** lies within just such cones as these. Indeed Priestley (1960) has shown that the details of the observations of saturation and non-saturation in gold are almost quantitatively explained on the basis of Shoenberg's estimate of the size of the contact regions in the (111) directions. As a result of this Russian work it appears for the first time as if a complete account of the high-field magneto-resistance may be given along quasi-classical lines (or of course the more sophisticated approaches mentioned in the text). This in itself is a conclusion of great importance, for, if justified, it removes what appeared to be a serious impediment to the understanding of transport phenomena in metals. In addition, the essential simplicity of the topological argument of

Lifshitz and Peschanskii opens the door for the systematic use of magneto-resistance for determining the connectivity of the Fermi surface—a most attractive development in view of the elementary character of the experimental techniques involved.

Further experimental work by Gavenda and Morse (1959) on magneto-acoustic oscillations in copper has revealed a long-period oscillation which may be interpreted as an orbit around the contact region on the zone-boundary, the estimated size agreeing well with Shoenberg's estimate. In view of the discussion on p. 203 it should not be a surprise to find that a detailed analysis of the effect in metals of arbitrary Fermi surface shows how the attenuation and its oscillations, particularly for longitudinal waves, are dominated by any regions which are especially sensitive to deformation, as one might expect the contact regions to be. It seems likely, in fact, that the apparently anomalous periodicity of the oscillations in figure 43 are to be explained in this way ; they do not arise from a central orbit, but from a rather squarer orbit (or a rosette-like hole orbit of the sort found by Shoenberg) which passes near four contact regions. The dimensions of such an orbit are consistent with the observed periodicity.

Our conclusion at the moment, then, is that there is every reason for optimism. Unless something unexpected happens the electronic structure of the noble metals should be fairly exactly known within a very few years, and the hoped-for test of the basic assumptions should then be possible. Moreover, it seems that there is a good chance that the independent-particle model will prove a close approximation to the truth.

GAIDUKOV, YU. P., 1959, *J. Exper. Theor. Phys.*, **37**, 1281.
GAVENDA, J. D., and MORSE, R. W., 1959, *Bull. Amer. Phys. Soc.*, **4**, 463.
LANGENBERG, D. N., and MOORE, T. W., 1959, *Phys. Rev. Lett.*, **3**, 328.
LIFSHITZ, I. M., and PESCHANSKII, V. G., 1958, *J. Exper. Theor. Phys.*, **35**, 1251.
PRIESTLEY, M. G., 1960, *Phil. Mag.*, in the press.
SHOENBERG, D., 1960, *Phil. Mag.*, in the press.