

Resistance of Monovalent Metals<sup>1</sup>E. L. PETERSON AND L. W. NORDHEIM  
*Purdue University, Lafayette, Indiana*

(Received November 19, 1936)

With the detailed knowledge available at present of the nature of the metallic state, an attempt has been made to estimate quantitatively the resistivity of the monovalent metals. It is shown that the older conception of a "deformable" potential gives for Na a resistivity about 9 times too high. In our new formulation the resistivity is simply due to the fact that in a distorted crystal the proper solutions are not of the type of progressive waves, but linear combinations of these. The transition probabilities can be worked out under the assumptions that the charge distribution of the conduction electrons almost compensates the electrostatic potential due to the shift of

the ions from their equilibrium positions and that in the undistorted crystal the periodic factor  $u_k$  in the wave functions  $u_k \exp(2\pi i \mathbf{k} \cdot \mathbf{R})$  does not depend sensibly on the wave number  $\mathbf{k}$ . In this case only the average electronic density and not the exact form of the wave functions and potentials is found to be relevant. The result can be expressed by an interaction constant  $C$ , which measures the average scattering effectiveness of the elastic waves. The computation gives  $C/E_0=0.84$ , where  $E_0$  is the Fermi energy. The empirical values are for Na 0.77, K 0.81, Cu 1.12, Ag 1.21, Au 1.19.

## §1. THE MODEL

THE present theory of metals explains the normal resistance by the interaction of the heat motion of the lattice ions and the conduction electrons. By describing the heat motion by the Debye concept of elastic waves, it has been found under rather general assumptions that the mechanism of interaction which produces the resistance consists of Bragg reflections of the electronic waves from the elastic longitudinal waves, the transverse waves being ineffective. Though this picture is certainly correct in its essence, a satisfactory theoretical computation of the resistivity has not yet been given even for the simplest metals. It is the purpose of this paper to attempt such a computation for monovalent metals.

The main problem in such a computation is to achieve an unambiguous description of the mode of interaction of electronic and elastic waves. In the nearest previous approach to a definite theory, Bethe,<sup>2</sup> following the ideas of Bloch,<sup>3</sup> has used the hypothesis of a "deformable potential." In an undistorted crystal the electrons are subject to a perfectly periodic potential  $V(\mathbf{R})$ ,  $\mathbf{R}$  being the coordinate vector. The heat oscillations

cause a shift of the points of the crystal which we will represent by  $\delta\mathbf{R}$ . By "deformable potential" it is meant that the potential at the point  $\mathbf{R}+\delta\mathbf{R}$  in the distorted crystal is the same as that at the point  $\mathbf{R}$  when the crystal is not deformed. Starting from this assumption and taking the change in the potential due to the distortion as a perturbation acting on the electronic wave functions of the undistorted crystal, S.B. obtained a simple expression for the resistivity,<sup>4</sup> in which only one "interaction constant" was left undetermined. This constant was expressed as an integral requiring only the unperturbed wave functions (compare (22)). Wigner and Seitz<sup>5</sup> have since determined the wave functions for Na and we have used them to evaluate the constant. The value obtained when substituted in the S.B. formula gives a resistivity about nine times that observed.

That the assumptions made in this theory should lead to a very high value for the resistivity is quite understandable. The wave functions and the potentials are both large and vary rapidly near the centers of the ions. A displacement of the ions would, according to the Bloch hypothesis, cause a shift of the large part of the potential against the large part of the wave functions, and would produce an asymmetry in the potential near the center of the ion. Neither effect actually

<sup>1</sup> Presented at the Washington meeting of the American Physical Society, May, 1936. Submitted as a thesis to the Faculty of Purdue University by E. L. Peterson.

<sup>2</sup> A. Sommerfeld and H. Bethe, *Handbuch der Physik*, Vol. 24, second edition (Berlin, 1933). Quoted henceforth as S.B.

<sup>3</sup> F. Bloch, *Zeits. f. Physik* **52**, 525 (1928).

<sup>4</sup> S.B., p. 523 (36, 11).

<sup>5</sup> E. Wigner and F. Seitz, *Phys. Rev.* **43**, 804 (1933); **46**, 509 (1934). Henceforth quoted as W.S.

occurs. The inner part of the wave function will remain in the same position relative to the ion and the inner part of the potential cannot be much changed by the small shifts of the ions against one another. It is therefore clear that the Bethe-Bloch formulation overestimates the interaction and therefore the resistivity. The entire method of describing the effect of the elastic waves as a perturbation of the wave functions of an undistorted crystal is hardly adequate, because the displacements due to heat motion, while small compared to the normal distance between ions, are not small compared to the dimensions of the region where the potential and wave functions are large. Therefore, though the wave functions and the potential in a distorted crystal will be quite similar to those in the undistorted crystal it is not possible to represent them by a Taylor development in terms of the undisturbed functions.

The consideration that the large part of the wave functions should follow closely the motion of the ions suggests a procedure better suited to the actual physical situation. Due to the relatively slow motion of the massive ions it will probably be a fair approximation to assume that the electronic wave functions follow them adiabatically. Such an adiabatically deformed wave function will be a much better starting point for calculating transition probabilities than the wave functions of an undistorted crystal.

The wave functions in an undistorted crystal are of the well-known Bloch type

$$\psi_k = u_k \cdot \exp(2\pi i(\mathbf{k} \cdot \mathbf{R})), \quad (1)$$

where  $u_k$  has all the periodicities of the lattice and  $\mathbf{k}$  is the propagation vector. Since the exponential factor does not affect the electronic charge density, Wigner and Seitz first determined the function  $u_0$  for an electron at rest by the self-consistent field method. The functions belonging to moving electrons, ( $\mathbf{k} \neq 0$ ), were then treated by a perturbation calculation. It was found that the  $u_k$  were practically independent of  $\mathbf{k}$ , i.e., that the wave functions of the higher states were given in good approximation by multiplying the function  $u_0$  by the proper exponential factor. This seems to hold very well for Na and fairly

well for the other monovalent metals<sup>6</sup> with the exception of Li, Rb, Cs. If the crystal is distorted the function  $u_0$  will go over into a new function  $U_0$  which would again have to be found by the self-consistent field method and which is, in principle, unique.

As  $u_0 \exp(2\pi i\mathbf{k} \cdot \mathbf{R})$  represents well the wave functions in the undistorted crystal, it is suggestive to approximate the wave functions in the general case by  $U_0 \exp(2\pi i\mathbf{k} \cdot \mathbf{R})$ . It is then found that one such function alone does not give a sufficient approximation but that a better one can be found by a superposition of such waves. This only expresses but the well-known fact that, in presence of a perturbation, not the progressive exponential waves but standing sine and cosine waves would be the proper solutions. The same fact can also be expressed in this way that in a description by progressive waves one will have transitions from one state to the other.

The transition probabilities can be worked out by a straightforward scheme<sup>7</sup> which is slightly more general than the usual one. The matrix element in question can then be transformed into an expression which contains only one Fourier component of the electronic density  $U_0^2$  in the distorted crystal and does not contain the potential. A complete solution would thus require the determination of the function  $U_0$  perhaps by a method similar to the W.S. method for the undistorted crystal. This seems to be an extremely complicated problem. But for the value of our matrix element only the deviation from the practically constant density in the crystal at rest is relevant. The general features of this density can be obtained directly. In a monovalent metal the electrons are easily movable. Therefore no differences of electric potential can exist over distances greater than atomic ones, that is, the electronic fluid will have a very high dielectric susceptibility. Since the volume of the elementary cells and therefore the distribution of positive electricity will be changed by an elastic wave,

<sup>6</sup> For a general survey of metallic eigenfunctions compare J. C. Slater, *Rev. Mod. Phys.* **6**, 209 (1934). Wave functions for Li have been calculated by F. Seitz, *Phys. Rev.* **47**, 400 (1935), for Cu by H. M. Krutter, *Phys. Rev.* **48**, 665 (1935) and K. Fuchs, *Proc. Roy. Soc.* **A151**, 585 (1935).

<sup>7</sup> It is to be noted that we use a perturbation calculation only to go over from the states  $k=0$  to those with  $k \neq 0$ , and not for obtaining the eigenfunctions in the distorted crystal from the eigenfunctions in the undistorted one.

there will be an additional electronic density which in the average will compensate the former. This average density alone determines the magnitude of the interaction integral and can be obtained easily. The statement that the charge distribution of the conduction electrons will be such that it will destroy a potential due to the displacement of the ions is clearly the correct formulation of the deformable potential hypothesis.

With the above picture the resistivity can be obtained by a very simple calculation the results of which fit the experimental data remarkably well. The resistance of Na and K is given quantitatively if one uses the new values for the Debye temperature for these substances as given by Fuchs.<sup>8</sup> For Cu, Ag, Au one obtains somewhat too low values for the resistivity which is probably due to the fact that the principal assumption that the  $u_k$  are independent of  $\mathbf{k}$  for the *undisturbed* crystal is not so nearly fulfilled.

In our theory, the factor which determines the resistance is essentially the change of volume of the elementary cells due to the elastic displacement. From this follows that in our case only the longitudinal waves are effective. It follows further that also for molten metals only the compression waves will contribute to resistivity and not other types of disorder which may be present. We obtain thus a justification for Mott's<sup>9</sup> treatment of the liquid metals. The argument for this may be put more directly. In the case of a displacement which does not change the volume of the elementary cells, a practically self-consistent set of proper functions of the progressive wave type can be constructed.

In §2 we collect the formulae of the general theory of conductivity which are necessary for our purpose and we evaluate the Bloch-Bethe interaction constant. §3 contains our new theory and our final results. In §4 we have attempted a more detailed discussion of the function  $U_0$  by a more direct method. In the appendix we give a

generalization of the scheme for calculating transition probabilities so as to include functions which are not strictly orthogonal.

## §2. GENERAL FORMULAE OF CONDUCTIVITY, BLOCH-BETHE THEORY

We will need certain formulae of the general theory. The wave functions of the electrons are of the form (1). For monovalent metals the energy as a function of the propagation vector  $\mathbf{k}$  is practically spherically symmetric. It is closely approximated by

$$E_k = (\hbar^2 k^2) / 2m. \quad (2)$$

The group velocity has the form

$$v_x = \frac{1}{\hbar} \frac{\partial E_k}{\partial k_x} = \frac{\hbar k_x}{m}. \quad (3)$$

The resistivity<sup>10</sup> for temperatures well above the Debye temperature  $\theta$  may be written in the well-known Drude-Lorentz-Sommerfeld form

$$\sigma = \frac{Ne}{\hbar k_0} \left( \frac{1}{\hbar} \frac{dE}{dk} \right)_0 \cdot \tau \Big|_{k=k_0} = \frac{Ne^2}{m} \cdot \tau_0, \quad (4)$$

in which  $N$  is the number of conduction electrons per unit volume and where the subscript  $_0$  means that the quantities have to be taken at the top of the zero Fermi distribution.  $1/\tau$  is the probability that an electron will have its state changed by a "collision" in unit time. If there exists an elementary probability  $V_{kk'}$  for the transition  $k \rightarrow k'$ , we have

$$1/\tau = 2\pi \int V_{kk'} k'^2 (dk'/dE') (1 - (k'/k) \cos \vartheta) \times \sin \vartheta d\vartheta dE', \quad (5)$$

$\vartheta$  being the angle between  $k$  and  $k'$ .

Following the concepts of the general theory of resistivity, we assume that such transitions are caused by the interaction of electronic and lattice ion motion. The Debye theory describes the ion motion as a superposition of independent elastic waves, whose wave number we may represent by  $\mathbf{f}$ . The displacement of a point  $\mathbf{R}$  in the lattice due to such a superposition of elastic

<sup>8</sup> K. Fuchs, Proc. Roy. Soc. **A153**, 622 (1936).

<sup>9</sup> N. F. Mott, Proc. Roy. Soc. **A146**, 465 (1934) has shown that the change in resistivity at the melting point can be fully accounted for by the change in the Debye temperature  $\theta$  which may be deduced from other physical properties. He also gives the interpretation that in the liquid state only longitudinal waves contribute.

<sup>10</sup> L. Nordheim, Helv. Phys. Acta **7** (supplementum II), 3 (1934).

waves will be

$$\delta\mathbf{R} = \sum_f \delta\mathbf{R}_f, \quad (6)$$

$$\delta\mathbf{R}_f = \mathbf{n}_{fj} [a_{fj} \exp(2\pi i(\mathbf{f} \cdot \mathbf{R})) + a_{fj}^* \exp(-2\pi i(\mathbf{f} \cdot \mathbf{R}))]$$

$a_{fj}$  is the wave amplitude and  $\mathbf{n}_{fj}$  is a unit vector giving the direction of displacement, being parallel to  $\mathbf{f}$  for longitudinal waves and perpendicular to  $\mathbf{f}$  for transverse waves. The wave number  $\mathbf{f}$  takes all integral values up to the maximum given by

$$hf_m = h(3N/4\pi)^{1/3} = h\nu_m/c = k\theta/c. \quad (7)$$

where  $N$  is the number of ions per unit volume which for monovalent metals is equal to the number of electrons per unit volume,  $\nu_m$  the maximum frequency corresponding to the maximum wave number  $f_m$ ,  $c$  is the velocity of sound, and  $\theta$  is the Debye temperature. The wave amplitudes  $a_{fj}$  have to be quantized:

$$\left. \begin{array}{l} a_{fj}^* \\ a_{fj} \end{array} \right\} = \left( \frac{h}{8\pi^2 d \nu_j} \right)^{1/2} \begin{cases} N_j^{1/2} \text{ for the transition} \\ N_j \rightarrow N_j - 1 \text{ (absorption);} \\ (N_j + 1)^{1/2} \text{ for the transition} \\ N_j \rightarrow N_j + 1 \text{ (emission).} \end{cases} \quad (8)$$

$N_j$  is the quantum number of an oscillator and  $d$  the density of the material. For high temperatures ( $T > \theta$ ) the average number of quanta per oscillator is

$$N_j \approx N_j \pm 1 = kT/h\nu_j \quad (9)$$

$$\text{and } |2\pi f a_j|^2 = \frac{kT}{2d} \frac{f^2}{\nu_j^2} = \frac{kT}{2dc^2}. \quad (10)$$

It will be seen later that in our theory, as in the Bloch-Bethe theory, the possible scattering processes will consist of Bragg reflections of the electronic waves from the elastic waves with the emission or absorption of a sound quantum, i.e., an oscillator  $\mathbf{f}$  may suffer a transition for which the interference condition,

$$\mathbf{k}' - \mathbf{k} = \pm \mathbf{f}, \quad (11)$$

is satisfied. The transition probability will be of the general form

$$V_{ss'} = |G_{ss'}|^2 \frac{\partial}{\partial t} \frac{4 \sin^2(\pi/\hbar)(E_{s'} - E_s)t}{(E_s - E_{s'})^2}, \quad (12)$$

where  $s$  denotes a state of the total system, electron plus oscillators, the time factor leading to the factor  $4\pi/\hbar$  after integration over the energies in the well-known way.

The interference condition (11) restricts the direction in which an oscillator can scatter an electron. For this reason  $f$  can be introduced as variable instead of  $\theta$  by the relation,

$$f^2 = k^2 + k'^2 - 2kk' \cos \vartheta. \quad (13)$$

If one introduces this in (5) and carries out the integration over the energies, neglecting the small difference between  $E_k$  and  $E_{k'}$ , one obtains,

$$\frac{1}{\tau} = \frac{4\pi^3}{h} \frac{1}{h^2} \frac{1}{dE/dk} \cdot 2 \int_0^{f_m} |G_{kk'}|^2 f^3 df, \quad (14)$$

the factor 2 arising from the fact that an oscillator can scatter an electron in the process of emission as well as of absorption of a sound quantum, the matrix elements being essentially the same for both processes.

Since the matrix elements are approximately linear in the oscillator amplitudes, it is convenient to define new elements which will be practically independent of them by

$$G_{kk'} = 2\pi i |f| a_f F_{kk'}(k). \quad (15)$$

$F_{kk'}$  will thus be independent of temperature. If we insert (7), (9), (10), (12), (14), (15) in (4) we have the final formula

$$\sigma = \frac{n_0 e^2}{h^3} \frac{16M}{9\pi} k_0 \left| \frac{dE}{dk} \right|_0 \frac{(k\theta)^2}{T} \frac{1}{\overline{F^2}} \quad (16)$$

$$\text{with } \overline{F^2} = \frac{4}{f_m^4} \int_0^{f_m} F_{kk'}^2 f^3 df. \quad (17)$$

$n_0$  is the number of electrons per atom, and  $M$  is the mass of an atom. For  $E$  we take the approximate expression (2) and we have

$$\left. \frac{dE}{dk} \right|_{k=k_0} = \frac{h^2 k_0}{m} \quad \text{with } k_0 = \left( \frac{3N}{8\pi} \right)^{1/3}. \quad (18)$$

In (16) everything except the "interaction constant"  $F$  is known.

If one uses the Bloch-Bethe hypothesis,  $G_{kk'}$  will be the matrix element of the "deformable potential." Up to linear terms in the oscillator amplitudes, we have

$$\delta V = V_0(\mathbf{R} + \delta\mathbf{R}) - V_0(\mathbf{R}) = \delta\mathbf{R} \cdot \text{grad } V_0, \quad (19)$$

where  $V_0$  is the potential in the undistorted lattice. The matrix elements will be

$$G_{kk'} = \int \psi_{k'}^* \delta\mathbf{R} \cdot \text{grad } V_0 \psi_k dv. \quad (20)$$

By using (6) and the periodicity properties of  $V_0$  and  $\psi_k$  it is easily shown that only longitudinal waves give nonvanishing matrix elements and they do so only if (11) is fulfilled. The expression reduces to

$$G_{kk'} = a_f \int u_k^*(\mathbf{f}/|f|) \cdot \text{grad } V_0 u_k dv, \quad (21)$$

which is to be integrated over only one elementary cell. The function  $u_k$  is normalized in one cell. By partial integration and use of the Schrödinger equation (21) reduces to<sup>11</sup>

$$G_{kk'} = 2\pi i a_f F, \quad (22)$$

$$F = \frac{2}{3} C = \frac{2}{3} (h^2/8\pi^2 m) \int |\text{grad } u_0|^2 dv.$$

In this expression the fact that  $u_k$  and  $u_{k'}$  are practically identical has been used. The interaction constant  $F$ , according to this hypothesis, is independent of the wave number.

If (22) is inserted in (16)  $\sigma$  becomes identical with Bethe's expression<sup>12</sup> except for the differences of notation. There we find  $2\pi\mathbf{k}$  replaced by  $\mathbf{K}$ ,  $h$  replaced by  $2\pi\hbar$  and  $\bar{F}^2$  replaced by  $(4/9)C^2$ .

We have used the function  $u_0$  calculated by W. S.<sup>1, 13</sup> to find the theoretical value by numerical integration of the expression (22) for  $C$ . The value obtained was 7.6 eV or about 2 to 3 times the empirical value. (Compare the table at the end of §3.) Since the resistivity is proportional to  $C^2$ , the theoretical value is 5 to 9 times the observed value.<sup>14</sup>

<sup>11</sup> Compare S.B., pp. 512–513.

<sup>12</sup> Compare S.B., p. 523 (36, 11).

<sup>13</sup> We are indebted to Dr. F. Seitz for kindly furnishing us a tabulation of  $u_0$  for Na.

<sup>14</sup> In an earlier paper one of the authors (L. Nordheim, Ann. d. Physik 9, 607 (1931)) has discussed as an alternative to the Bethe-Bloch hypothesis that of a "rigid ion." Here the ionic potential is thought to be shifted rigidly as a whole by the elastic displacement and again the difference to the unshifted potential is taken as a "perturbation." This would give, as can be shown easily, a smaller resistance

### §3. NEW CALCULATION OF RESISTIVITY

We assume that in an undistorted crystal the wave functions are of the type (1) with  $u_k$  independent of the wave number, which is equivalent with the assumption that the energies have the form (2). We consider now a crystal deformed by heat oscillations of the type (6). In this case we have to work with a Hamiltonian for the electron,

$$H = -(\hbar^2/8\pi^2 m)\Delta + V(\mathbf{R}, a_f) + \Sigma H_f \\ = H_{e1} + \Sigma H_f, \quad (23)$$

where  $\Sigma H_f$  is the Hamiltonian of the oscillators, and  $H_{e1}$  represents the kinetic and potential energies of the electron.  $V$ , we may suppose, has been determined by the Hartree method and contains the oscillator amplitudes as parameters. It is to be noticed that we do not separate  $V$  into a part  $V_0$  and a perturbation term according to the usual procedure. The potential  $V$  is real since we have taken  $\delta\mathbf{R}$  as real. Of the several solutions of the Schrödinger equation

$$H_{e1}U = -(\hbar^2/8\pi^2 m)\Delta U + VU = EU \quad (24)$$

there will be one,  $U_0$ , which will go over into  $u_0$  as the oscillator amplitudes vanish. This function must be real since it must be nondegenerate if  $u_0$  is nondegenerate and it must satisfy the same boundary condition (periodicity with respect to a cube of 1 cm in length) as  $u_0$ . The proper value  $E_0$  for the distorted crystal will be practically the same as for the undistorted crystal. A development of  $E_0$  in terms of the amplitudes  $a_f$  must start with quadratic terms since a change in the sign of the amplitudes could not change the energy.

For the calculation of the conductivity we must have in addition to  $U_0$  the higher functions  $\psi_k$  corresponding to  $k \neq 0$ . As we have assumed that  $u_k$  is practically independent of  $k$  we will try the following combination for  $\psi_k$ .

$$\psi_k = U_0 \exp 2\pi i(\mathbf{k} \cdot \mathbf{R}). \quad (25)$$

than the "deformable ion" and would agree better with experiment. Also the rigid ion probably represents more closely the actual physical situation as the effective potential is now known to be nearly that of the ion (without much contribution from the conduction electrons) which certainly will not be deformed to any appreciable extent. We have, however, not taken up the discussion from this point of view since the same inconsistency, a shift of the rapidly varying parts of the potential and the wave functions against each other, would appear also in this case.

The functions (25) are not true characteristic functions of the Hamiltonian in contrast to the case of the undistorted crystal, but they have certain properties which show that they must be closely related to them.

I. Since  $U_0$  is real they give the same current as the corresponding functions of the undistorted crystal

$$\frac{\hbar}{4\pi im} \int (\psi_k^* \text{grad } \psi_k - \psi_k \text{ grad } \psi_k^*) dv = \frac{\hbar k}{m}. \quad (26)$$

This ensures that the  $\psi_k$  (25) are suitable for the treatment of conductivity.

II. The average value of the energy is different from  $E_0$  by the same amount as for an undistorted crystal

$$\int \psi_k^* H_{e1} \psi_k dv = E_k = E_0 + \hbar^2 k^2 / 2m. \quad (27)$$

We have for  $H_{e1} \psi_k$  the expression,

$$\begin{aligned} H_{e1} \psi_k &= \left[ -\frac{\hbar^2}{8\pi^2 m} \Delta + V \right] U_0 \exp(2\pi i(\mathbf{k} \cdot \mathbf{R})) \\ &= \exp(2\pi i(\mathbf{k} \cdot \mathbf{R})) \left[ -\frac{\hbar^2}{8\pi^2 m} \Delta U_0 + V U_0 \right. \\ &\quad \left. + \frac{\hbar^2 k^2}{2m} U_0 - \frac{i\hbar^2}{2\pi m} \mathbf{k} \cdot \text{grad } U_0 \right] \\ &= \exp(2\pi i(\mathbf{k} \cdot \mathbf{R})) \left[ E_k - \frac{i\hbar^2}{2\pi m} \mathbf{k} \cdot \text{grad } U_0 \right]. \end{aligned} \quad (28)$$

In the integral (27) the term

$$\int U_0 \mathbf{k} \cdot \text{grad } U_0 dv = \frac{1}{2} \int \mathbf{k} \cdot \text{grad } U_0^2 dv \quad (29)$$

vanishes, as it can be transformed into a surface integral, and  $U_0$  takes the same value at two opposite boundaries of the crystal. (27) ensures that there will not be any appreciable second order terms if we take (25) as the starting point of a perturbation consideration.

The functions (25) have the same average energy and current as the proper functions of the normal lattice and become identical with them if the oscillator amplitudes become vanishingly small. They have, furthermore, the same charge distribution  $U_0^2$  as those corresponding to an electron at rest, so that the latter alone

would enter into the determination of the self-consistent field. The effect of the distortion can therefore be adequately described by considering the secular perturbations between the functions (25) or, which amounts to the same thing, by transitions between those states, as we shall show. The functions are different from the functions usually used only in that they are not strictly orthogonal to each other. This requires, as is shown in an appendix, that the matrix elements must be corrected for the non-orthogonality. The matrix elements  $H_{kk'}$  have to be replaced by

$$G_{k'k} = H_{k'k} - E_k d_{k'k} = \int \psi_{k'}^* (H - E_k) \psi_k dv, \quad (30)$$

where  $E_k$  is the average energy of the state  $k$  and  $d_{k'k}$  the nonorthogonality integral. The expression  $G_{k'k}$  can be introduced directly in (14) to (17) to obtain the conductivity. (It is understood that the integration over the oscillator functions has already been carried out. Since  $H$  contains the amplitudes  $a_f$  the oscillator matrix elements for the transitions considered have to be inserted.) From (25), (28), (30), one finds

$$G_{k'k} = -\frac{i\hbar^2}{4\pi m} \int \exp(2\pi i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}) \cdot \mathbf{k} \cdot \text{grad } U_0^2 dv,$$

and integration by parts yields

$$G_{k'k} = \frac{\mathbf{k} \cdot (\mathbf{k} - \mathbf{k}') \hbar^2}{2m} \int \exp(2\pi i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}) \cdot U_0^2 \cdot dv. \quad (31)$$

It will be shown that to a reasonable approximation  $G_{k'k}$  vanishes unless the interference condition,  $\mathbf{k}' - \mathbf{k} = \pm \mathbf{f}$ , is satisfied. Conservation of energy requires that  $k$  and  $k'$  are practically identical and if we neglect the small difference,  $\mathbf{k} \cdot (\mathbf{k} - \mathbf{k}')$  can easily be expressed in terms of  $f$ ,

$$\mathbf{k} \cdot (\mathbf{k} - \mathbf{k}') = |k| |f| \cos \vartheta = f^2 / 2.$$

With this (31) becomes

$$G_{k'k} = -(f^2 \hbar^2 / 4m) \cdot K_{k'k} \quad (32)$$

with  $K_{k'k}$  defined by

$$K_{k'k} = \int \exp(2\pi i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}) \cdot U_0^2 dv. \quad (33)$$

The only formal difference between our theory

and the Bloch-Bethe theory is therefore that their matrix elements have to be replaced by the new ones (33). The essential point here is that  $U_0$  is supposed to be the actual self-consistent wave function for an electron at rest in a crystal distorted by an elastic wave with wave number  $\mathbf{f} = \mathbf{k} - \mathbf{k}'$  and contains the amplitudes  $a_f$  as does (22). The integration is over the whole crystal.

$U_0^2$  represents the electronic density in the crystal; (33) is therefore one Fourier component of this density, and one belonging to a comparatively long wave-length. Therefore, the value of this integral will be determined chiefly by the variation of the total charge from cell to cell and deformations of the distribution inside the single cells will not be important. This total charge of the cell will be such, that it compensates, to a high degree of accuracy, the positive charge of the ion since otherwise electrostatic potential differences over large distances would be produced. This will hold at least as long as  $(1/|\mathbf{k} - \mathbf{k}'|)$  is large compared to the atomic distance. In this case it does not matter for the value of  $K_{kk'}$  how the charge is distributed over the individual cell.  $K_{kk'}$  will therefore be given to a fair approximation by a smooth function  $U_0^2$  which just compensates the change in volume.

The volume  $v$  of a space element changed by the distortion  $\delta\mathbf{R}$  (compare (6)) is given by

$$v = v_0(1 + \text{div } \delta\mathbf{R}). \quad (34)$$

The density which compensates the change of volume expressed by the second term is therefore,

$$\rho = (\rho_0/1 + \text{div } \delta\mathbf{R}) \cong \rho_0(1 - \text{div } \delta\mathbf{R}). \quad (35)$$

If  $U_0$  is normalized in unit volume, one obtains for the interaction integral (32)

$$\begin{aligned} G_{kk'} &= \frac{\mathbf{k} \cdot (\mathbf{k}' - \mathbf{k})}{2m} h^2 \int \exp(2\pi i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}) \\ &\quad \times (1 - \text{div } \delta\mathbf{R}) dv \\ &= -\frac{\mathbf{k} \cdot (\mathbf{k}' - \mathbf{k})}{2m} h^2 \int \exp(2\pi i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}) \\ &\quad \times \text{div } \delta\mathbf{R} dv, \end{aligned} \quad (36)$$

since the integral over the undistorted part vanishes.

$\text{div } \delta\mathbf{R}$  is different from zero only for longitudinal waves ( $\mathbf{n}_{fj} \parallel \mathbf{f}$ ) and therefore

$$\begin{aligned} \text{div } \delta\mathbf{R}_j &= 2\pi i f a_f \exp(2\pi i(\mathbf{f} \cdot \mathbf{R})) \\ &\quad + \text{conj. complex.} \end{aligned} \quad (37)$$

(33) is different from zero only if the interference condition,

$$\mathbf{k}' - \mathbf{k} = \pm \mathbf{f},$$

is satisfied for a certain oscillator. The emission of a sound quantum ( $-$  sign) involves only the amplitude  $a_f$ , the absorption ( $+$  sign) only  $a_f^*$ . In both cases we get the same absolute value for  $G_{kk'}$ . With (37) we get for emission

$$\begin{aligned} G_{kk'} &= \frac{h^2 f^2}{4m} \cdot 2\pi i f \cdot a_f = 2\pi i f a_f \cdot F; \\ F &= h^2 f^2 / 4m, \end{aligned} \quad (38)$$

and this has to be inserted in (17) and (16) to obtain the conductivity.

In the Bethe-Bloch theory  $F$  was to be replaced by  $\frac{2}{3}C$  (compare (22)). In distinction to their interaction constant  $C$ , our  $F$  still contains the wave number of the elastic waves. With (38) and (17) we obtain

$$\bar{F}^2 = \left(\frac{h^2}{2m}\right)^2 \cdot \frac{1}{f_m^4} \int_0^{f_m} f^7 df = \frac{1}{8} \left(\frac{h^2 f_m^2}{2m}\right)^2. \quad (39)$$

From (7) and (18) we get  $f_m = k_0 \cdot 2^{\frac{1}{2}}$  and therefore instead of the Bethe  $C$

$$C_{\text{calc}} \rightarrow \frac{3}{2} (\bar{F}^2)^{\frac{1}{2}} = \frac{3 \cdot 2^{\frac{3}{2}} k_0^2 h^2}{2 \cdot 2^{\frac{3}{2}} 2m} = 0.84 E_0, \quad (40)$$

where  $E_0$  is the Fermi zero point energy.

The comparison with experiment has been made in the same way as in S.B.,<sup>15</sup> that is from the empirical conductivity and Debye temperature a value  $C_{\text{obs}}$  has been determined and compared to the value (40). Table I gives the relevant data for those metals for which one can expect that our assumptions are sufficiently fulfilled. There is rather an uncertainty in the Debye temperatures for the alkalis. The higher values for  $\theta$  are those used by S.B. The lower ones are those given by Fuchs<sup>8</sup> in a recent paper which are probably better. The best values will probably be slightly higher than his lowest values (perhaps  $\sim 170^\circ$  for Na and  $\sim 110^\circ$  for K), as he extrapolates to  $T=0$  whilst for the conductivity the values of  $\theta$  for room temperature are relevant.

<sup>15</sup> Reference 2, page 524.

TABLE I. Calculated and observed values of  $C$  and pertinent data for Na, K, Cu, Ag, Au.

Element	Na	K	Cu	Ag	Au
Atomic weight	23	39	63.6	108	197
Conductivity $\times 10^4$ (in $\Omega^{-1} \text{ cm}^{-1}$ ) at $0^\circ\text{C}$	22.6	15.3	64	67	68
Debye temperature $\theta$	202-150	126-100	315	215	175
Zero point energy $E_0$ (in ev)	3.16	2.06	7.10	5.52	5.56
Radius of $s$ sphere $\times 10^8$ (in cm)	2.11	2.56	1.41	1.59	1.59
$C_{\text{obs}}$ (ev)	3.28-2.44	2.35-1.66	7.9	6.7	6.6
$C_{\text{calc}}$ (ev)	2.66	1.81	5.91	4.68	4.68

$C_{\text{obs}}$  is directly proportional to  $\theta$  (compare (16)). We have given therefore in the table the limits for  $C_{\text{obs}}$  corresponding to the values of  $\theta$  quoted.

We see an almost perfect agreement of our  $C$  with the  $C_{\text{obs}}$  obtained with Fuchs' values for  $\theta$ . By comparing this with the value of 7.6 ev as obtained from Bloch-Bethe theory for Na we see the improvement compared to the older theory. The calculated values for the noble metals come out too low, i.e., the observed resistivities are higher than those calculated. This is most probably due to the circumstance that our principal assumption that in the undistorted crystal the functions  $u_k$  are independent of  $k$ , holds less well.

Because the theory uses the Debye model for heat motion and the Hartree approximations for the electrons, both of which are certainly none too good, the excellent agreement for the alkalis is not really significant. In our calculation the effect of the shorter wave-lengths (near  $f_m$ ) is probably overestimated since in this case the compensation of the ionic charges might not be so complete. On the other hand, the effect of the long wave vibrations (small  $f$ ) is probably underestimated. Our matrix element is proportional to  $f^2$  and therefore becomes very small for small  $f$ . Other effects neglected in our approximation may be important in this range, though for the average they do not matter much.

The matrix elements for small  $f$  will be most important at low temperatures, since then they alone are thermally excited. A substitution of our

expression (38) for the matrix element in the Bloch formula for the conductivity at low temperatures would lead to proportionality to  $T^9$  instead of the usually assumed  $T^5$  law. We do not consider this as a serious objection against our theory. As mentioned above any neglects will be much more serious for small  $T$ . It will probably not be justified to take  $U_{k_0}$  for the Fermi energy as equal  $U_0$ , and the distinction between the two should introduce a term similar to the Bethe-Bloch theory, though much smaller. We have not investigated the resistance at low temperatures more closely in this paper because the whole theory for this case is still not in order. The new W.S. results on the eigenvalue distribution in monovalent metals exclude the possibility of the *Umklapp-Prozesse* of Peierls and therefore the mechanism of producing equilibrium between thermal and electronic motion is uncertain.

#### §4. WAVE FUNCTIONS IN THE DISTORTED CRYSTAL

We discuss in this section the properties of the wave functions which we have used, and the problems which an accurate treatment of a distorted crystal by the self-consistent field method would involve. This leads to another approximation for the calculation of the integral (33) which gives practically the same results as those given in the last section.

To obtain the self-consistent field and wave function in a crystal Wigner and Seitz divide the crystal into elementary polyhedrons constructed by passing planes perpendicularly through the midpoints of lines joining the neighboring atoms with each other. If the potential and wave function are found for a single polyhedron they can be found for the entire crystal from the periodicity properties. It has been found that the self-consistent field in any polyhedron is given in good approximation by that due to the ion in the polyhedron and that the boundary condition for  $u_0$ , vanishing derivative normal to the faces of the cell, can be replaced by the requirement that the derivative normal to the surface of a sphere<sup>16</sup>

<sup>16</sup> We use the following notation:  $\mathbf{R}$  is the coordinate vector in the crystal. The equilibrium position of the  $n$ th ion is denoted by  $\mathbf{R}_n^0$ . A shift in the position of an ion is denoted by  $\delta\mathbf{R}_n$  so that  $\mathbf{R}_n = \mathbf{R}_n^0 + \delta\mathbf{R}_n$ . The coordinate vector taken from the center of an ion to a position in the cell is denoted by  $\mathbf{r}$  so that in the  $n$ th cell we have  $\mathbf{R} = \mathbf{R}_n + \mathbf{r}$ .



("s sphere") of equal volume shall vanish.<sup>17</sup> That this substitution involves only a very small error is insured by the extreme flatness of the wave function in the outer parts of the polyhedron.

If one inserts the form (1) for the higher functions in the Schrödinger equation one obtains

$$\Delta u_k + 4\pi i \mathbf{k} \cdot \text{grad } u_k + (8\pi^2 m / h^2)(E_k - h^2 k^2 / 2m - V)u_k = 0. \quad (41)$$

This is different from the equation for  $u_0$  by the shift in the energy,  $h^2 k^2 / 2m$  and the term  $4\pi i \mathbf{k} \cdot \text{grad } u_k$ . If the term  $4\pi i \mathbf{k} \cdot \text{grad } u_k$  is treated as a perturbation term one finds that the first order change of energy vanishes. Wigner and Seitz have computed for the Na ion the second-order term also and have found it to be very small, due to the flatness of  $u_0$ . It is for this reason that the higher functions are fairly well approximated by multiplying  $u_0$  by the term  $\exp 2\pi i \mathbf{k} \cdot \mathbf{R}$ .

We have now to consider the distorted crystal. The first difference from the normal case is that the ions and their contribution to the potential will be shifted to new places.

While the ionic potential alone gives approximately the complete self-consistent field in an undistorted crystal a distortion will give rise to other terms, one due to imperfect compensation of negative and positive charge and another due to deformation of the electron charge distribution. If such terms did not appear one could take the wave functions simply as the Wigner-Seitz functions around each ion. They would join smoothly even in a distorted crystal due to the flatness in the outer portions of the cell.

If the distortion were such that no change in volume of the cell were produced the only new potential would be a weak electrostatic action of one cell upon neighboring cells. This would be caused by the distortion of the cells from almost perfect spheres to ellipsoids. If this small term is neglected one would obtain a solution for any wave number  $\mathbf{k}$  by taking the solution which behaves like  $\exp(2\pi i \mathbf{k} \cdot \mathbf{r})$  in the cell and multiplying it by a factor  $\exp(2\pi i \mathbf{k} \cdot \mathbf{R}_n)$  in the  $n$ th cell. This function would be practically continuous over the whole crystal since it would approach  $\exp(2\pi i \mathbf{k} \cdot \mathbf{R})$  between the ions and it

<sup>17</sup> The potential and charge distribution are then spherically symmetric and a cell does not contribute to the potential outside its boundaries.

would be a solution of the Schrödinger equation. To this approximation there would therefore be no transitions between different states and thus no contribution to resistivity. The fact that the molten monovalent metals show no additional resistivity which can be attributed to the disorder of the liquid state can be taken as an empirical justification of the above argument.

If, however, we consider displacements which cause a change in the volume of the elementary cell the situation is quite different. If we took for  $U_0$  simply the Wigner-Seitz function around each ion they would still join smoothly. They would, however, give a nonuniform electron charge distribution. Cells which were reduced in volume would be positively charged while those increased in volume would be negative. Such an effect would cause a strong electrostatic disturbance. However, since the electrons in the metals considered behave nearly like free electrons, as we have pointed out above, this effect will be almost perfectly compensated by redistribution of the negative charge.

It would be desirable to justify this assumption rigorously by setting up and solving the self-consistent field problem including the electrostatic forces mentioned. We have not been able to do so thus far, but as these forces must be small because of the compensation mentioned, the main part of the potential will still be given by the ionic potential. It must be possible, therefore, to construct a fairly close approximation to the function  $U_0$  by a proper combination of W.S. solutions. We have made such a calculation and we reproduce it here not because we believe that it is a better approximation than that used in the previous section, but more to show that the final result does not depend sensibly on the exact form of  $U_0$ . Furthermore one can see by this method that the irregularity of the wave function near the centers of the ions is of no importance for our problem.

The simplest approximation one can make is to take the spherically symmetric W.S. function around each ion and to multiply it by a factor that will give the proper negative charge in each cell. This function is given in the  $n$ th cell by

$$U_0 = (1/\sqrt{v_0})(1 + 2\pi f y_n)u_0, \quad (42)$$

where  $v_0$  is the volume of the undistorted W.S.

sphere and  $2\pi f y_n$  is  $-\frac{1}{2} \text{div } \delta \mathbf{R}$  taken at the center of the ion in its actual place in the crystal. This means, of course, an approximation of the true continuous function by a step-like function which otherwise has all the required properties. To better the fit at the boundaries one could try to introduce other solutions of different symmetry, but we have not found a systematic way of doing this.

With  $U_0$  given by the function (42) the integral (33) can be evaluated by integrating over each cell separately and then summing over all cells. In this evaluation the change of the amplitude of  $\exp(2\pi i \mathbf{f} \cdot \mathbf{r})$  within the cells contributes to the integral. We have found by numerical calculation that neglecting the variation of  $u_0$  in the cell introduces an error of only about 1 percent, since the rapidly varying part is small compared to the wave-length of the elastic wave. The integrals over the cell can be divided into two parts, one over the undistorted cell, and another over the change in volume, and all integrations carried out by elementary methods.

As a result of this calculation one obtains finally

$$F_{kk'} = (i\hbar^2 r_s / 4m v_0) \times [4 \sin x / x - 4 \cos x - x \sin x] \quad (43)$$

with  $x = 2\pi f r_s$ , and where  $r_s$  and  $v_0$  are radius and volume, respectively, of the undistorted W.S. spheres. This  $F_{kk'}$  is the equivalent of (38). Since it contains  $f$  only in the combination  $f r_s$ , which is dimensionless, the integration (17) to obtain  $\bar{F}^2$  is the same for all monovalent metals with the upper limit  $x_m = 2\pi f_m r_s = 2\pi(3/4\pi)^{3/2}$ . The only dependence of (45) on the particular metal considered is contained in the factor  $r_s/v_0 \sim 1/r_s^2$  which is the same as that of the zero point energy as shown in the previous section. The final result can also be given the same form as in §3.

$$C = (3/2)(\bar{F}^2)^{1/2} = 1.04 E_0. \quad (44)$$

We obtain thus a somewhat higher value than by the previous calculation. (Compare (40).) The difference is of course due to the different assumptions about the distribution of negative charge and it shows roughly the uncertainty which is involved in our theory at the present stage.

#### APPENDIX

##### TRANSITION PROBABILITIES FOR NONORTHOGONAL WAVE FUNCTIONS

Our functions  $\psi_k$  (25) are not strictly orthogonal as one sees from the discussion of the matrix element (33) which represents directly the nonorthogonality integral. This is small as long as  $\text{div } \delta \mathbf{R} \ll 1$  which is fulfilled in our case. The calculation of transition probabilities can then be carried out in close analogy to the treatment of secular perturbations with nonorthogonal functions.

We consider the total system of an electron and the lattice oscillators. The full wave equation

$$H\psi = -(h/2\pi i)(\partial\psi/\partial t) \quad (45)$$

may be solved approximately by a set of functions  $\psi_s$  with the matrix elements and nonorthogonality integrals

$$E_s = \int \psi_s^* H \psi_s; \quad H_{ss'} = \int \psi_s^* H \psi_{s'}; \quad d_{ss'} = \int \psi_s^* \psi_{s'}. \quad (46)$$

The  $\psi_s$  are in our case the functions (25) multiplied by the corresponding oscillator functions. We try to solve (45) by the linear combination

$$\psi = \sum_s c_s(t) \psi_s \exp(-2\pi i/h) E_s t. \quad (47)$$

Substituted in (45) this gives

$$\begin{aligned} \sum_s c_s \exp(-2\pi i/h) E_s t (H\psi_s - E_s \psi_s) \\ = -(h/2\pi i) \sum_s \dot{c}_s \exp(-2\pi i/h) E_s t \psi_s. \end{aligned}$$

Multiplication by a particular function  $\psi_{s_1}$  and integration yields

$$\begin{aligned} -(h/2\pi i) \dot{c}_{s_1} \\ = \sum' c_s \exp(-2\pi i/h)(E_s - E_{s_1})t (H_{s_0 s_1} - E_{s_0} d_{s_0 s_1}) \\ + (h/2\pi i) \sum' \dot{c}_s \exp(-2\pi i/h)(E_s - E_{s_1})t d_{s s_1}. \end{aligned}$$

Introducing the initial conditions;  $c_{s_0} = 1$ ,  $c_{s_i} = 0$ , if  $i \neq 0$ , we obtain for small  $t$

$$\begin{aligned} -(h/2\pi i) \dot{c}_{s_1} = \exp(-2\pi i/h)(E_{s_0} - E_{s_1})t (H_{s_0 s_1} - E_{s_0} d_{s_0 s_1}) \\ + (h/2\pi i) \sum' \dot{c}_s \exp(-2\pi i/h)(E_s - E_{s_1})t d_{s s_1}. \end{aligned}$$

Here the terms in  $\sum'$  (over all the states excluding  $s_1$ ) contain the factor  $d_{s s_1}$  and can therefore be regarded as small compared to the derivative on the left side. Therefore the value for  $\dot{c}_{s_1}$  as obtained by neglecting this correction term can be introduced in this term itself, giving

$$\begin{aligned} -(h/2\pi i) \dot{c}_{s_1} = \exp(-2\pi i/h)(E_{s_0} - E_{s_1})t \{ [H_{s_0 s_1} \\ - E_{s_0} d_{s_0 s_1}] - \sum_s [H_{s_0 s} - E_{s_0} d_{s_0 s}] d_{s s_1} \}. \quad (48) \end{aligned}$$

This has now the same form as the usual perturbation equations. The second term on the right side being small compared to the first one we obtain by the usual method

$$V_{s_0 s_1} = |H_{s_0 s_1} - E_{s_0} d_{s_0 s_1}|^2 \frac{\partial}{\partial t} \left[ \frac{4 \sin^2(\pi/h)(E_{s_0} - E_{s_1})t}{(E_{s_0} - E_{s_1})^2} \right], \quad (49)$$

as used in §3.