transmission through thick BaO-deposits (Table II) may indicate the presence of thin regions, formed in the process of oxidation of thick Ba-films. That these regions are not bare is evidenced by the shift of the Ag-peak.

The distribution of energy losses appears to offer a new, sensitive tool for the study of surfaces and surface layers. If the substance of the film has a distribution curve reasonably different from that of the backing material, layers only a few atoms thick can be detected. This test appears to be somewhat more sensitive, and less likely to alter the conditions studied, than present electron diffraction methods employing high voltages.[19] In the case of Ca, the metal can be detected in a thickness decidedly <1 on a backing of the oxide. This is now being used to study the surfaces of thermionic emitters made from CaO and BaO. For the detection of small amounts of foreign material on a surface this method is probably never as sensitive as thermionic measurements, but in favorable cases it has one great advantage compared with these: it not only detects, it identifies.

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[19] The diffraction beams obtained with single crystals at low bombarding voltages appear to be even more sensitive than the energy loss distribution to a small coverage of foreign material on the surface: Farnsworth, Phys. Rev. **49**, 605 (1936).

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Theory of Inelastic Scattering of Electrons from Solids

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The general properties of the single electron wave functions for a crystal are discussed, and an expression derived for the probability of excitation by electron bombardment as a function of the two electronic levels involved in the transition. When the excitation energy is small compared with the energy of the bombarding electron, the relative transitions probabilities approach those for excitation by radiation. A detailed calculation has been carried out for the case of solid copper, for which the energy levels are now known from other work. Approximate wave functions—of the atomic type for the lower state, free-electron-like for the upper state—were used to evaluate the transition integrals. The calculated distribution curve for the inelastically scattered electrons is in fair agreement with the experimental curve in the region of small energy losses: the rapid rise from small values and the following two maxima exhibited by the experimental curve are all reproduced in their proper positions. The departures for higher losses are attributed to the fact that the free-electron-like wave functions used are not a proper approximation to the actual functions in this region.

THE problem of inelastic scattering of electrons in matter, early discussed for relatively fast electrons by Thomson[1] and others as a problem of atomic scattering, was treated very completely by Bohr[2] on the basis of classical electron theory. More recently, quantum theory has been applied particularly to the scattering by free atoms. Fröhlich[3] has given a wave-mechanical treatment of the inelastic scattering from metals, using a special Bloch-Sommerfeld model for the metal. He was able to deduce from this the characteristic features exhibited by the distribution of the low energy secondary electrons. In the present paper we consider the transition probabilities for electronic excitation on the basis of the general electron theory of solids. In experiments on inelastic collisions, the target is usually bombarded by a nearly parallel, homogeneous beam of electrons and the energy distribution is measured for those electrons which are scattered into a small solid angle about a definite fixed direction with respect to the target and the incident beam. Tests with polycrystalline targets have shown the energy distribution to be essentially independent of both this latter direction and of the angle of incidence. For this reason we have calculated the total probability of all

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[1] J. J. Thomson, *Conduction of Electricity through Gases*, 343 (1903).

[2] N. Bohr, Phil. Mag. **25**, 10 (1913); **30**, 581 (1915).

[3] H. Fröhlich, Ann. d. Physik **13**, 229 (1932).

transitions with a given energy loss and arbitrary direction of the scattered electron, assuming an isotropic distribution in direction of the primary particles. It seems likely that the isotropic distribution of primary and scattered electrons here involved is actually nearly established inside the target as a result of the frequent processes of elastic scattering by the massive ions in the lattice.

While most experimental work in this field, for technical reasons, has been done on metallic conductors, the theory applies to solids in general. The present discussion divides into three main parts. In the first the wave functions and their properties are reviewed; in the second the general expressions for the transition probabilities are developed. In the third part approximate calculations are carried out for the case of copper, for which the energy levels are now known and approximate wave functions available, and the results are compared with experimental data.

1.

We wish to consider a collision in which a fast and a slow electron collide, the fast one losing a little energy and the slow one gaining it. The unperturbed problem is that in which each electron moves through a periodic potential field, representing the crystal, unaffected by the particular motions of other electrons. Each electron in this approximation is represented by a modulated periodic function of the type well known in the theory of metallic lattices:

$$\psi_{ak_0}(\mathbf{r}) = \exp\,[i\mathbf{k}_0\cdot\mathbf{r}]u_{ak_0}(\mathbf{r}), \qquad (1)$$

u_{ak_0} having the periodicity of the potential field. We shall often use the equivalent Fourier resolution:

$$\psi_{ak_0}(\mathbf{r}) = \sum_p a(\mathbf{k}_0+\mathbf{K}_p)\exp\,[i(\mathbf{k}_0+\mathbf{K}_p)\cdot\mathbf{r}]. \qquad (1\text{a})$$

The stationary states are divided into a number of bands, and the index a represents a particular band. The vector $\mathbf{k}_0$ is different for the various states within a band. To satisfy Bloch's condition of periodicity,[4] the vectors $\mathbf{K}_p$ must form a discrete set, constituting what is called the reciprocal lattice in the $\mathbf{k}$-space. This reciprocal lattice is determined by the crystal structure, and is face-centered cubic for a body-centered cubic crystal, and *vice versa*. We can conveniently set up polyhedral cells in the $\mathbf{k}$-space, one surrounding each point of the reciprocal lattice, and of such a shape that they fill the $\mathbf{k}$-space completely without overlapping. We may imagine $a(\mathbf{k}_0+\mathbf{K}_p)=a(\mathbf{k})$ as a single-valued function of the continuous variable $\mathbf{k}$ in the $\mathbf{k}$-space; then the Fourier coefficients of a particular state $\mathbf{k}_0$ of the band a will be the values of a at the appropriate points $\mathbf{k}$ of the various cells, points reached from $\mathbf{k}_0$ by the translations $\mathbf{K}_p$. It can be shown that the square of the magnitude of one of these a's is proportional to the probability that the electron in question have a momentum $(h/2\pi)\mathbf{k}=(h/2\pi)(\mathbf{k}_0+\mathbf{K}_p)$, when in the state $(a, \mathbf{k}_0)$. For this reason the a's are sometimes called momentum eigenfunctions. It is evident that ψ_{ak_0} is a periodic function of $\mathbf{k}_0$; for if $\mathbf{k}_0$ is increased by one of the vectors of the reciprocal lattice, say $\mathbf{K}_q$, the whole lattice of points $\mathbf{k}_0+\mathbf{K}_p$ will be shifted back into itself. The same Fourier coefficients must then be chosen, leading to the same function as before, since by arranging the states according to bands we have made ψ a single-valued function of $\mathbf{k}_0$ within each band. At the same time the energy of this state will return to its initial value, so that the energy within a band may be regarded as a periodic function of the continuous variable $\mathbf{k}_0$ (or $\mathbf{k}$). Often, on account of this periodicity, it is convenient to restrict $\mathbf{k}_0$ to the central polyhedron of $\mathbf{k}$ space, but this is not always desirable.

If in particular the state a represents a free electron, its wave function is a plane wave, a constant times $\exp\,[i\mathbf{k}_1\cdot\mathbf{r}]$ (where $\mathbf{k}_1$ need not be in the central polyhedron in $\mathbf{k}$ space), so that only one a is different from zero. The energy of the free electron is $p^2/2m$, where p is its momentum. If we express energy in Rydberg units, distances in atomic units, this becomes simply k_1^2, where k_1 is proportional to the momentum. For the sake of uniformity, it is often convenient to represent the state of a free electron by a function in $\mathbf{k}$ space, and to make this single-valued one must break up the free electron states arbitrarily into bands. We could do this by deciding to group together all those states for which $\mathbf{k}_1$ was in a particular polyhedron in $\mathbf{k}$ space. For this particular band, $a(\mathbf{k}_0+\mathbf{K}_p)$,

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[4] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

regarded as a function $a(\mathbf{k})$ of the continuous variable $\mathbf{k}=\mathbf{k}_0+\mathbf{K}_p$, would be zero outside this polyhedron, constant within it. The energy, within the polyhedron, would be given by k_1^2, and by the periodicity property this would be repeated in every other polyhedron. This particular assignment, however, is not very reasonable when there is a small periodic perturbative potential. In this case, the wave function and energy will be slightly perturbed, and it can be shown that the periodic energy function which we have just discussed would be distorted by the introduction of certain planes of discontinuity, across which the energy would change discontinuously. Brillouin has shown[5] that it is much better to take unperturbed functions by setting up certain zones in $\mathbf{k}$ space. Such a zone is formed from parts of many polyhedrons, all having about the same energy and $|\mathbf{k}_1|$ value, but spread more or less uniformly about the surface of a sphere. These parts of polyhedrons are so chosen that they could be fitted together, by pure translations $\mathbf{K}_q$, to form a single polyhedron. We now assume a single energy band of the free electron to be one in which $a(\mathbf{k})$ is constant within one Brillouin zone, zero outside it. The energy within the Brillouin zone is given by k_1^2, and outside the zone it is a periodic function of $\mathbf{k}$, coming back to the same value at corresponding points of each polyhedral cell. The Brillouin zone is chosen in such a way that this determines the energy at each point of $\mathbf{k}$ space uniquely. The energy, however, is a rather complicated function of $\mathbf{k}$ within an individual polyhedron. The polyhedron, as we have said, can be divided into parts which could be displaced by $\mathbf{K}_q$ to form the zone, and within each of these parts the energy is represented by $|\mathbf{k}+\mathbf{K}_q|^2$, a parabolic function of $\mathbf{k}$; but this function changes from one part of the polyhedron to another, since the proper translation vector $\mathbf{K}_q$ is different for different parts. Because of this, the slope or gradient of the energy as a function of $\mathbf{k}$ changes discontinuously from one part of the polyhedron to another, though the function itself is continuous. This is because the direction of the vector $\mathbf{k}_1$ for the free electron, but not its magnitude or k_1^2, changes discontinuously with $\mathbf{k}$ in going from one part to another. When small perturbations appear, however, the discontinuous changes of slope are rounded off, and the energy function is a smooth one. It is this property that leads one to say that the Brillouin zone is the correct zone to use for describing the free electrons. The resulting type of function is the sort actually found in the wave functions of fast electrons in real lattices.

We shall have occasion to consider the orthogonality and normalization of our wave functions. The vector $\mathbf{k}$ as a matter of fact cannot take on arbitrary values in the $\mathbf{k}$ space, but only a discrete set lying on a sublattice much more closely spaced than the reciprocal lattice, such that the number of points within a single polyhedron of the latter equals the number of atoms in the crystal. Each state is capable of holding two electrons, one of each spin, so that each band can accommodate two electrons for every atom of the crystal. This sublattice has the property that, if $\mathbf{k}$ and $\mathbf{k}'$ are any two points of it, $\int \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]d\tau=0$, if the integration is carried over the whole crystal, unless $\mathbf{k}=\mathbf{k}'$, in which case the integral of course is V_0, the volume of the crystal. Now consider two wave functions, ψ_{ak_0} and $\psi_{bk_0'}$. The normalization and orthogonality conditions demand that

$$\int \sum_p \sum_q a^*(\mathbf{k}_0+\mathbf{K}_p)b(\mathbf{k}_0'+\mathbf{K}_q) \times \exp[-i(\mathbf{k}_0+\mathbf{K}_p-\mathbf{k}_0'-\mathbf{K}_q)\cdot\mathbf{r}]d\tau = \begin{matrix} 1, \text{ if } a=b,\ \mathbf{k}_0=\mathbf{k}_0' \\ 0, \text{ otherwise.} \end{matrix}$$

If $\mathbf{k}_0 \neq \mathbf{k}_0'$, the property of the sublattice mentioned above immediately shows that the integral is zero, so that the only remaining case is that in which $\mathbf{k}_0=\mathbf{k}_0'$. This yields the conditions

$$\sum_p a^*(\mathbf{k}_0+\mathbf{K}_p)b(\mathbf{k}_0+\mathbf{K}_p) = \begin{matrix} 0 \text{ if } a\neq b \\ 1/V_0 \text{ if } a=b. \end{matrix} \qquad (2)$$

For a plane wave, when only one a is different from zero, we at once see that the wave function is $V_0^{-\frac{1}{2}} \exp[i\mathbf{k}_1\cdot\mathbf{r}]$.

2.

Returning now to our problem, we assume the fast electron both before and after collision to

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[5] L. Brillouin, *Quantenstatistik* (1931).

be moving fast enough so that it can be represented by a plane wave. If it has values $\mathbf{K}$ and $\mathbf{K}'$ before and after collision, its wave functions will be $V_0^{-\frac{1}{2}} \exp[i\mathbf{K}\cdot\mathbf{r}]$ and $V_0^{-\frac{1}{2}} \exp[i\mathbf{K}'\cdot\mathbf{r}]$. It is immaterial whether these happen to belong to the same Brillouin band or not. We assume the slow electron to have wave functions ψ_{ak_0} and $\psi_{a'k_0'}$ before and after collision, described by the Fourier components $a(\mathbf{k}_0+\mathbf{K}_p)$, $a'(\mathbf{k}_0'+\mathbf{K}_q)$, respectively. Let the total energy of the two electrons before collision be W, afterwards W', where $W=W'$ if conservation of energy holds. The unperturbed wave function of the two electrons together will be the product of the separate functions. Thus before collision, the function, including its time variation, is

$$e^{-2\pi iWt/h}\frac{1}{V_0^{\frac{1}{2}}}\exp[i\mathbf{K}\cdot\mathbf{r}_2]\psi_{a,\,k_0}(\mathbf{r}_1), \tag{3}$$

where $\mathbf{r}_1$ is the coordinate of the slow electron, $\mathbf{r}_2$ that of the fast one. We treat the collision by the perturbation method of variation of constants. At time $t=0$ we assume that the Coulomb interaction $e^2/|\mathbf{r}_2-\mathbf{r}_1|$ commences to act. The solution of the time-dependent Schrödinger equation can then be expanded as a sum of terms

$$\sum_{a'k_0'K'} c(a'\mathbf{k}_0'\mathbf{K}'t)e^{-2\pi iW't/h}$$
$$\times\frac{1}{V_0^{\frac{1}{2}}}\exp[i\mathbf{K}'\cdot\mathbf{r}_2]\psi_{a'k_0'}(\mathbf{r}_1). \tag{4}$$

If we assume that at $t=0$ the only one of the coefficients c different from zero is the one multiplying the function (3), and that this is unity, perturbation theory leads to the value

$$c(a'\mathbf{k}_0'\mathbf{K}'t)=w^{-1}(1-e^{2\pi iwt/h})I, \tag{5}$$

where $w=W'-W$, the difference in energy between the final and initial states, and

$$I=\frac{1}{V_0}\int\int\frac{e^2}{|\mathbf{r}_2-\mathbf{r}_1|}\exp[i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}_2]$$
$$\times\psi_{ak_0}(\mathbf{r}_1)\psi^*_{a'k_0'}(\mathbf{r}_1)d\tau_1 d\tau_2. \tag{6}$$

The square of the modulus of $c(a'\mathbf{k}_0'\mathbf{K}'t)$ measures the probability of finding the system in the state $(a'\mathbf{k}_0'\mathbf{K}')$ at time t; for large values of t this will have appreciable values only near $w=0$, representing conservation of energy. $(\partial/\partial t)|c|^2$ measures the transition probability.

Let us consider first the interaction integral (6). Following Bethe,[6] we perform the integration first over the coordinates of the fast particle. Letting $\mathbf{\Delta K}=\mathbf{K}-\mathbf{K}'$, $\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1$ and $\mathbf{\Delta K}\cdot\mathbf{r}=\Delta Kr\cos\theta$, we have

$$\int\frac{\exp[i\mathbf{\Delta K}\cdot\mathbf{r}_2]}{|\mathbf{r}_2-\mathbf{r}_1|}d\tau_2=\exp[i\mathbf{\Delta K}\cdot\mathbf{r}_1]$$
$$\times\int_0^\infty\int_0^\pi r^{-1}e^{i\Delta Kr\cos\theta}2\pi r^2\sin\theta d\theta dr$$
$$=\exp[i\mathbf{\Delta K}\cdot\mathbf{r}_1]\cdot\frac{4\pi}{\Delta K}\int_0^\infty\sin(\Delta Kr)dr.$$

The last integral does not converge. To avoid this difficulty, Bethe averages over a small range in ΔK, and after integration makes this range approach zero. Another method is to replace the exact Coulomb potential $1/r$ by $e^{-\alpha r}/r$, perform the integration, and then let $\alpha\rightarrow 0$. Both methods give for the integral the value $1/\Delta K$. Hence

$$I=\frac{4\pi e^2}{(\Delta K)^2V_0}\int\psi_{ak_0}(\mathbf{r}_1)\exp[i\mathbf{\Delta K}\cdot\mathbf{r}_1]\psi^*_{a'k_0'}(\mathbf{r}_1)d\tau_1$$
$$=\frac{4\pi e^2}{(\Delta K)^2V_0}\sum_{p,q}a(\mathbf{k}_0+\mathbf{K}_p)a'^*(\mathbf{k}_0'+\mathbf{K}_q)$$
$$\times\int\exp[i(\mathbf{k}_0+\mathbf{K}_p-\mathbf{k}_0'-\mathbf{K}_q+\mathbf{\Delta K})\cdot\mathbf{r}_1]d\tau_1. \tag{7}$$

As mentioned above, the integral is zero unless $\mathbf{k}_0+\mathbf{K}_p-\mathbf{k}_0'-\mathbf{K}_q+\mathbf{\Delta K}=0$, or $\mathbf{k}_0'+\mathbf{K}_q-(\mathbf{k}_0+\mathbf{K}_p)=\mathbf{\Delta K}$, in which case it is V_0. If this condition is satisfied, we have

$$I=\frac{4\pi e^2}{(\Delta K)^2}\sum_p a(\mathbf{k}_0'+\mathbf{K}_p-\mathbf{\Delta K})a'^*(\mathbf{k}_0'+\mathbf{K}_p) \tag{8}$$

or

$$I=\frac{4\pi e^2}{(\Delta K)^2}\frac{1}{V_0}\int_{V_0}\psi_{ak_0}(\mathbf{r}_1)\exp[i\mathbf{\Delta K}\cdot\mathbf{r}_1]$$
$$\times\psi^*_{a'k_0'}(\mathbf{r}_1)d\tau_1=\frac{4\pi e^2}{(\Delta K)^2}\cdot\frac{1}{v_0}\int_{v_0}\psi_{ak_0}(\mathbf{r})$$
$$\times\exp[i\mathbf{\Delta K}\cdot\mathbf{r}]\psi^*_{a'k_0'}(\mathbf{r})d\tau, \tag{8a}$$

where v_0 is the volume of one lattice cell of the

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[6] H. Bethe, Ann. d. Physik 5, 325 (1930).

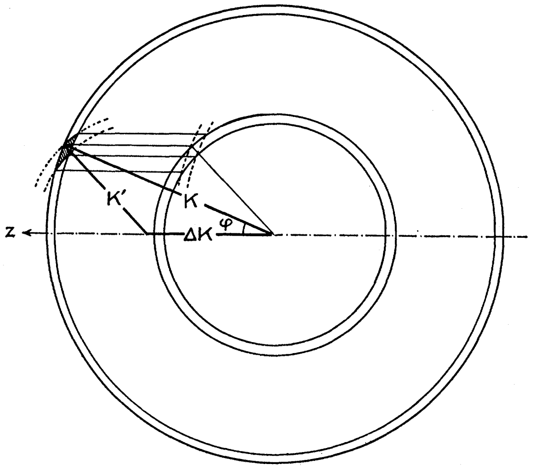

FIG. 1. Illustrating the possible transitions in the K space of the fast electron.

crystal and the last integration is over such a cell. The last step depends on the space periodicity of the wave functions (1). In (8) the quantity I, whose square determines the transition probability, is written as a sum of terms, of which each one represents a transition of the fast electron from momentum $\mathbf{K}$ to a value $\mathbf{K}-\mathbf{\Delta K}$, and an equal and opposite transition of the slow electron to momentum $\mathbf{k}'=\mathbf{k}_0'+\mathbf{K}_p$ from a value $\mathbf{k}'-\mathbf{\Delta K}$. This term has in the numerator the product of the amplitudes of the probabilities of finding the slow electron initially with momentum $\mathbf{k}'-\mathbf{\Delta K}$, when in the state $(a, \mathbf{k}_0'-\mathbf{\Delta K})$, finally with momentum $\mathbf{k}'$, when in the state $(a', \mathbf{k}_0')$, and in the denominator the square of the momentum change ΔK.

We are now ready to return to expression (5), giving the rate of transition from the initial to the final state. We really are not considering a single transition, however, but all possible transitions for which the fast electron originally has approximately a definite energy, but arbitrary direction, and the bound electron changes from state $(a\,\mathbf{k}_0)$ to state $(a'\mathbf{k}_0')$, gaining an amount of energy ϵ; we wish to compute $(\partial/\partial t)\sum|c|^2$ for all these transitions. Let Fig. 1 represent a plane section through $\mathbf{k}$ space (the reciprocal lattice and the sublattice are not shown) parallel to the vector $\mathbf{\Delta K}$, the z axis lying along the direction of $\mathbf{\Delta K}$. The points $\mathbf{K}$ where the incident electrons have nonvanishing Fourier components are assumed to lie in a spherical shell of thickness δK and radius K. This shell will not in general be entirely in one Brillouin zone, but will include parts of several zones. It contains a stationary state for each point of the sublattice, so that it is populated to a uniform density ρ. These incident electrons all have approximately the same energy K^2. A second shell, inside the first, includes all vectors $\mathbf{K}'$ for such states that the net energy increase of the system is between w and $w+dw$. Thus $K'^2+\epsilon=K^2+w$, and the thickness of the shell is $dw/2K'$. From the figure it will be seen that the number of primary electron states which can give rise to transitions in the range dw is $dn=\rho dv$, where dv is the volume generated by the small shaded area upon rotation around the z axis. Each of these states gives rise to one single transition. With the notations of Fig. 1,

$$dv=2\pi K\sin\varphi\delta KKd\varphi=\pi K\delta Kd(-2K\cos\varphi)$$

and from the triangle

$$K^2+\Delta K^2-2\Delta KK\cos\varphi=K'^2$$

so that

$$d(-2K\cos\varphi)=(1/\Delta K)d(K'^2)=(1/\Delta K)dw$$

and
$$dn=\rho\pi K\delta K(1/\Delta K)dw. \tag{9}$$

The probability of all the specified transitions with a given ΔK is then

$$\frac{\partial}{\partial t}\left\{I^2\int_{-\infty}^{\infty}\left|\frac{1-e^{2\pi iwt/h}}{w}\right|^2\frac{\rho\pi K\delta Kdw}{\Delta K}\right\}$$
$$=\frac{\partial}{dt}\left\{I^2\frac{\rho\pi K\delta K}{\Delta K}\frac{\pi^2 t}{h}\right\}=\frac{A}{\Delta K^5}J^2(\mathbf{k}_0', \mathbf{\Delta K}), \tag{10}$$

where $A=16\pi^5e^4\rho K\delta K/h$ and

$$J(\mathbf{k}_0', \mathbf{\Delta K})=\frac{1}{V_0}\int_{V_0}\psi_{ak_0}(\mathbf{r})\exp\left[i\mathbf{\Delta K}\cdot\mathbf{r}\right]\times\psi^*_{a'k_0'}(\mathbf{r})d\tau \tag{11}$$

or

$$J(\mathbf{k}_0', \mathbf{\Delta K})=\sum_p a(\mathbf{k}_0'+\mathbf{K}_p-\mathbf{\Delta K})a'^*(\mathbf{k}_0'+\mathbf{K}_p). \tag{11a}$$

This holds provided this type of transition is possible at all. From Fig. 1 it can be seen that transitions are possible only if

$$2K-\epsilon/2K>\Delta K>\epsilon/2K=\Delta K_m. \tag{12}$$

In the experiments on inelastic scattering from solids, the lower limit ΔK_m in (12) is usually quite small compared with the spacing of the reciprocal lattice. For small values of ΔK the exponential factor in (11) can be expanded and higher terms than the second neglected, giving

$$J(\mathbf{k}_0', \mathbf{\Delta K}) = \frac{1}{V_0}\int_{V_0} \psi_{ak_0}(\mathbf{r})\psi^*_{a'k_0'}(\mathbf{r})\{1+i\mathbf{\Delta K}\cdot\mathbf{r}\}d\tau$$

$$= \frac{1}{V_0}\int_{V_0} \psi_{ak_0}(\mathbf{r})\psi^*_{a'k_0'}(\mathbf{r})d\tau + \frac{i}{V_0}\mathbf{\Delta K}\cdot\mathbf{L}$$

$$= \frac{i}{V_0}\Delta K L \cos(\Delta K, L), \qquad (13)$$

the first term vanishing on account of orthogonality. Here

$$\mathbf{L} = \int_{V_0} \psi_{ak_0}(\mathbf{r})\mathbf{r}\psi^*_{a'k_0'}(\mathbf{r})d\tau, \qquad (14)$$

the linear moment for this pair of states.

Given the upper state $(a', \mathbf{k}_0')$ there will be a number of lower states a from which transitions to this state can take place with a change of momentum of magnitude between ΔK and $\Delta K + d\Delta K$ and direction (of $\mathbf{\Delta K}$) within the solid angle element $d\omega$. This number is proportional to $\Delta K^2 d\Delta K d\omega$; each transition has a probability (10). The total probability of transition to the state $(a', \mathbf{k}_0')$ will therefore be proportional to

$$\int\int \frac{J^2(\mathbf{k}_0', \mathbf{\Delta K})}{\Delta K^3} d(\Delta K)d\omega, \qquad (15)$$

the limits of integration being determined by the condition (12).

It turns out that, when small values of $\epsilon/2K$ are possible, the greater part of all transitions to the state $(a', \mathbf{k}_0')$ comes from those terms in the probability sum (15) for which ΔK is very near its minimum value ΔK_m. In that region we can use the expression (13) for J. We should therefore obtain a fairly good approximation to the actual distribution of small energy losses of the scattered primary electrons, by allowing each $\mathbf{k}_0'$ of an unoccupied state to receive transitions only from the occupied lower state with $\mathbf{k}_0 = \mathbf{k}_0'$, assigning to each such transition a probability proportional to

$$\int_0^{4\pi}\int_{\Delta K_m}^{\infty} \frac{L^2 \cos^2(\Delta K, L)}{\Delta K} d(\Delta K)d\omega$$

$$= \tfrac{1}{3}\overline{L^2}\cdot \ln(2K/\epsilon) \qquad (16)$$

or proportional to $\overline{L^2}$ for very high K where $\epsilon =$ the energy difference between the two states. This approximation must be restricted to the region of small energy losses. When ϵ is large, the approximation would introduce a considerable error, except for very fast primary electrons, because ΔK_m would not be small. The effect in the region of small losses is essentially to make the peaks and valleys in the calculated energy distribution appear sharper than they should be, because of the sharp selection rule by which we have replaced the distribution of transition probabilities in the sum (15). For high K and small energy losses, where the selection is quite strong, the transition probabilities for electronic excitation become practically proportional to those for optical absorption, both being determined by the square of the moment L.

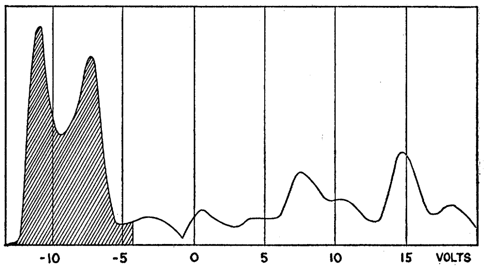

FIG. 2. Distribution in energy of the higher electronic levels in solid copper.

3.

We shall apply the method outlined in the preceding section to the calculation of the energy losses on scattering from solid copper. The transitions involved in this case are from the partly occupied band deriving from the $3d$ of the free atom to the unoccupied states above it, of which the nearest ones correspond to the atomic $4s$. Fig. 2 shows the distribution in energy of the electronic states for solid copper;[7] the shaded area represents the part normally

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[7] From an extension of the work by H. Krutter, Phys. Rev. **48**, 664 (1935); see also J. C. Slater, Phys. Rev. **49**, 537 (1936).

occupied by electrons. Since the energy levels are known for the different states of all the bands in question, the energy required for each particular "vertical" transition, $\mathbf{k}_0=\mathbf{k}_0'$, can be found. To calculate L from (14), however, and hence the weight $\overline{L^2}$ to be attached to each such transition, we have to find approximate wave functions for the lower and upper states involved.

The lower states a constitute a band of essentially bound electrons. If the solid is imagined as formed by bringing the free atoms together, the overlapping of neighboring atomic $3d$ functions will therefore be small for this band and Bloch's approximation to the wave functions can be used. From the general properties of the Bloch function it can readily be shown that its introduction to represent the lower state in (11) and (14) results in replacing ψ_{ak_0} in these equations by $(V_0/v_0)^{\frac{1}{2}}\psi_a$, where ψ_a is the corresponding atomic wave function, in this case $3d$. Thus for a given $\mathbf{k}_0'$, L is independent of ΔK, and $\overline{L^2}=L^2$. The integral over the finite volume V_0 of the entire crystal can then be replaced by an integral over all space, since the atomic function $\psi_a(\mathbf{r})$ has appreciable values only in a very small region of $\mathbf{r}$.

Actually the $3d$ band is 5-fold, as is the atomic d state, and accommodates 10 electrons per atom like the atomic state. This multiplicity arises from the five possible m values, 2, 1, 0, -1, -2 for a d state; in general, however, a single member of the band does not correspond to one particular m, but to a linear combination of all five. We shall only need the average L for all five components. To a good approximation the wave function for the mth component state of the $3d$ in copper may be written[8] as the product of a radial function $R(r)$ and the tesseral harmonic $T_l^m(\varphi, \theta)$ in the polar angles of $\mathbf{r}$ for $l=2$, each normalized to unity for the entire range of the variables:

$$\psi_a=R(r)\cdot\left\{\frac{(l-|m|)!}{(l+|m|)!}\right\}^{\frac{1}{2}} e^{im\varphi}P_l^{|m|}(\cos\theta) \quad (17)$$

with

$$R(r)=r^2(75.8e^{-6.29r}+4.236e^{-2.65r}+0.1185e^{-1.15r}). \quad (18)$$

The unoccupied upper states behave much like states of free electrons, at least those immediately above the $3d$ band, which may be said to derive from the atomic $4s$. One might therefore try to represent such a state by a free electron wave function $V_0^{-\frac{1}{2}}\exp[i\mathbf{k}_1\cdot\mathbf{r}]$, where k_1 could be determined by the condition that k_1^2 should equal the energy of the state in question, measured from a suitable zero, fixed by the location (in energy) of the lowest $4s$ level. This choice of function, however, does not satisfy the condition of orthogonality, and therefore makes (13) invalid; for the same reason it does not make J vanish for $\Delta K=0$, as the proper function should according to (11). To represent the upper state $(a', \mathbf{k}_0')$ one would therefore have to set up a function ψ_{k_1}, which is orthogonal to the atomic function ψ_a and yet which resembles the plane wave $V_0^{-\frac{1}{2}}\exp[i\mathbf{k}_1\cdot\mathbf{r}]$. Such a function can be found by using the expansion for a plane wave in a series of spherical harmonics, corresponding to s, p, d, f, $\cdots$ components, and by assuming that the function ψ_{k_1} equals the plane wave, without the d spherical harmonic:

$$\psi_{k_1}(r)=\frac{1}{V_0^{\frac{1}{2}}}\left(\frac{2\pi}{k_1r}\right)^{\frac{1}{2}}\sum_{\substack{l=0\\ l\neq 2}}^{\infty}(l+\tfrac{1}{2})i^lJ_{l+\frac{1}{2}}(k_1r)\times P_l(\cos\theta). \quad (19)$$

Here r, θ are spherical polar (zonal) coordinates, the polar axis being the direction of $\mathbf{k}_1$. Since the other harmonics are orthogonal to the atomic d function (17), this removes the difficulty of nonorthogonality. As far as the calculation of L is concerned, it really makes no difference whether we use the simple plane wave or the expression (19), since the contribution of the omitted d term to the moment is zero. Of course (19) is not quite correctly normalized for a crystal of finite size, because of the omission of the d term; we have ignored this. The resulting function resembles a plane wave in the region where the atomic function is appreciable, but is distorted particularly for fairly small values of r where the d spherical harmonic is relatively large. This is the type of behavior actually shown by the wave function for one of the higher states in the metal in the neighborhood of the lattice points. In $\mathbf{k}$ space the simple plane wave has a single component for its Fourier resolution at $\mathbf{k}=\mathbf{k}_1$.

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[8] J. C. Slater, Phys. Rev. **42**, 33 (1932).

Actually, with the d term missing, the Fourier resolution of (19) will still have a large component at the point $\mathbf{k}_1$, but in addition there will be fairly small components at all possible points $\mathbf{k}_1+\mathbf{K}_q$ in $\mathbf{k}$ space. This in general is true of the correct wave functions of electrons in crystals, since they are never exactly plane waves. Of course our approximation is not very good. The correct function can be represented as a sum of s, p, d, $\cdots$ components, which are not very well approximated by the Bessel's functions, and the coefficients multiplying them are not well given by the coefficients in the plane wave expansion. Nevertheless, the general features are fairly well given by our assumption, in particular the way in which the wave-length of the oscillations of the function changes with energy, and this is the determining feature in the variation of $\overline{L^2}$ for different upper states, which is the fundamental thing we shall get from our calculations. In the approximation adopted here the atomic d state is degenerate, the five m values all corresponding to the same energy. We are therefore free to choose any orientation of the coordinate system in (17); we shall take a polar axis that coincides with the axis used in (19), the direction of $\mathbf{k}_1$. With this choice, the vector $\mathbf{L}$ is most conveniently determined from the matrix elements of $r\cos\theta$, $r\sin\theta e^{i\varphi}$, $r\sin\theta e^{-i\varphi}$, representing the three components of the vector $\mathbf{r}$, rather than x, y, z. The only terms in (19) which contribute anything to the moment are the p and f terms for $l=1$, 3, according to the same selection rules which apply for atoms. Furthermore, only the functions (17) for $m=\pm 1$, 0 contribute anything, again in agreement with the selection rule for atomic transitions. For a case $m=0$, the only component of $\mathbf{L}$ different from zero is that of $r\cos\theta$; for $m=1$, that of $r\sin\theta e^{i\varphi}$, and for $m=-1$, $r\sin\theta e^{-i\varphi}$. The components have the following values:

$m=0$,

$$L_{r\cos\theta}=V_0^{-\frac{1}{2}}((4\pi i/5)M_p+(6\pi i/5)M_f),$$

$m=\pm 1$,

$$L_{r\sin\theta e^{\pm i\varphi}}=V_0^{-\frac{1}{2}}(2\pi i\sqrt{6/5})(M_p+M_f), \qquad (20)$$

where

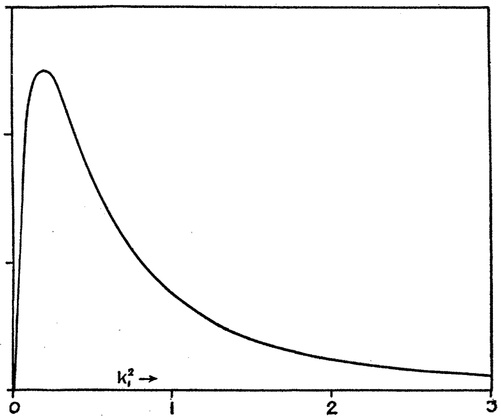

FIG. 3. The average square moment $\overline{L^2}$ as a function of the energy k_1^2 for the upper state.

$$M_p=\int_0^\infty r^3R(r)\left(\frac{2\pi}{k_1r}\right)^{\frac{1}{2}}J_{3/2}(k_1r)dr$$
$$=k_1\left\{0.0933\frac{1-0.01516k_1^2}{(1+0.0253k_1^2)^5}+2.218\right.$$
$$\left.\times\frac{1-0.0856k_1^2}{(1+0.1425k_1^2)^5}+21.35\frac{1-0.4545k_1^2}{(1+0.757k_1^2)^5}\right\}$$

and (21)

$$M_f=\int_0^\infty r^3R(r)\left(\frac{2\pi}{k_1r}\right)^{\frac{1}{2}}J_{7/2}(k_1r)dr$$
$$=k_1^3\left\{\frac{0.00378}{(1+0.0253k_1^2)^5}+\frac{0.5050}{(1+0.1425k_1^2)^5}\right.$$
$$\left.+\frac{25.85}{(1+0.757k_1^2)^5}\right\}.$$

To obtain $\overline{L^2}$ we square the L value for each m, add and divide by 5, since all five m values occur with the same weight in the band of d functions. The result is that

$$\overline{L^2}=\text{Const.}\,(M_p{}^2+\tfrac{3}{4}M_pM_f+(21/16)M_f{}^2). \qquad (22)$$

In Fig. 3, $\overline{L^2}$ is shown as a function of the energy k_1^2 of the upper state.

To construct the energy loss curve to be expected on this theory, we now proceed as follows. The energy range in question is divided into elements of the same size, $\Delta\epsilon$—in this case $\Delta\epsilon=0.01$ atomic unit. The transition probability $\overline{L^2}$ is evaluated for each one of a series of upper states, picked with a uniform spacing as regards $\mathbf{k}_0'$. The energy involved in the corresponding

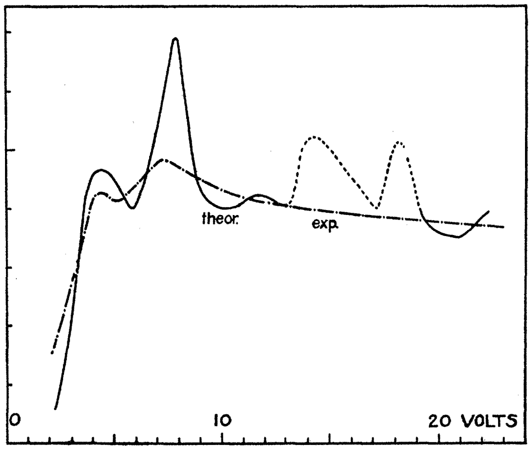

FIG. 4. Comparison of calculated and experimental distribution curves for the energy losses in solid copper.

vertical transition is determined from the tabulated energy levels for the different bands, and the $\overline{L^2}$ value listed in the column for the corresponding element $\Delta\epsilon$. The distribution curve for the energy losses is obtained by adding the $\overline{L^2}$ contributions in each such column. The result is shown in Fig. 4 together with the experimental curve,[9] which is given for comparison. The agreement in general is not unsatisfactory. Both curves start with low values for zero energy loss. In the theoretical case this arises from the small number of possible transitions with small energy losses. The curves then rise rapidly, each one coming to a peak at about 7 volts, preceded by a subsidiary peak at about 4.3 volts. At higher voltages both curves fall off. The agreement here, however, is less satisfactory, since the experimental curve falls off smoothly, while the theoretical one shows marked further peaks. In regard to these differences one may make the following comments. Our calculation of the number of transitions for a given energy difference has been based on actual calculations of energy levels, and should be fairly reliable. It takes account of the distribution of density within the band of *d* electrons and of the deviation of the excited electrons from free electrons. It is this part of the calculations in which the peaks are introduced. Those at 4.7 and 7 volts arise in a rather fundamental way: the band of *d* electrons shows specially large concentration of states at its two extreme energies, about 3 volts apart, and it is roughly these two concentrations which result in the two peaks. The two maxima at 14 and 18 volts also arise from these two concentrations, but here combined with peculiarities in the excited electron bands, about which there is much more uncertainty, on the basis of independent evidence. These peculiarities are connected with an especial concentration of excited *d* components in the stationary states for these bands. But in calculating the transition probability $\overline{L^2}$ we have represented the upper state by a free electron function without the *d* component. If, as it happens in this region, a large part of the correct wave function is actually *d*, our method must give too big values for $\overline{L^2}$, since *d*–*d* transitions should not occur. One thus infers that the proper transition probability to be used in this case should be small, which would tend to counteract the high concentration of transitions, thus reducing the violence of the fluctuations in this range. No such feature is present with the peaks at 4.7 and 7 volts. Of course our approximation to consider the transitions as vertical becomes increasingly poor for higher energy losses. Apart from this, one must bear in mind that there is no direct way of distinguishing between the effects produced by single and multiple impacts in the experimental curves. A fast electron may have two or more inelastic impacts before escaping from the metal. Since it tends to lose only a few volts on one impact, it would then emerge with something like double the energy loss in a single collision, tending to raise the number escaping with a moderate energy loss. Since the experimental distribution curves show very few electrons for quite small energy losses, however, it is fairly certain that the first two peaks represent single inelastic impacts.

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[9] E. Rudberg, Phys. Rev., preceding paper.