

purifications, the  $\text{Sc}(\text{OH})_3$  was dissolved in dilute HCl. Finally the solution was neutralized and the scandium precipitated as oxalate.

The filtrate from the first precipitation of  $\text{Sc}(\text{OH})_3$  was purified by adding traces of inactive  $\text{ScCl}_3$  and precipitating the scandium as hydroxide with  $\text{NH}_4\text{OH}$ .  $\text{Sc}(\text{OH})_3$  was removed three times in this manner, and it was assumed that the solution was thus freed of active scandium. Calcium was then extracted as follows: The solution was heated on a water bath and the calcium precipitated as oxalate by adding ammonium oxalate in excess. The calcium oxalate was filtered off and after washing was redissolved in HCl. Inactive NaCl and KCl were added to the solution which was then neutralized. The calcium was reprecipitated as oxalate, filtered and washed. It was assumed to be free of Sc, Na and K.

The residual solution was heated and oxalate removed by adding inactive calcium chloride in excess. The insoluble calcium oxalate was removed and the solution thus purified

of calcium. Excess calcium was then carefully removed by adding small amounts of ammonium oxalate and filtering. After four such treatments, it was assumed that the solution was free of calcium.

After removing the calcium, the filtrate was evaporated to dryness to drive off  $\text{NH}_3$  and the residue was dissolved in water. From this potassium was precipitated as perchlorate by the addition of perchloric acid and ethyl alcohol.

The residual solution was finally acidified with concentrated  $\text{HNO}_3$  and the perchloric and nitric acids distilled off. The small residue containing the sodium was dissolved in water and evaporated to dryness.

It was found that the scandium and potassium precipitates were completely inactive as determined with a thin-walled counter. Most of the activity was found in the calcium oxalate which was observed to emit the soft electrons of  $\text{Ca}^{46}$  and  $\gamma$ -rays, but some activity remained in the sodium residue and could not be separated from it.

## Acceleration of Electrons in a Crystal Lattice

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The motion of an electron in a periodic potential field, and accelerated by a uniform field, can be obtained by treating the time-dependent Schroedinger equation. The result shows that the wave vector increases linearly with the time within the bounds of a single Brillouin zone. At the boundaries of the zones transitions to other zones may take place if the accelerating field is large enough.

THE motion of an electron in a periodic potential field has been studied extensively in connection with the theory of solid bodies. The energy characteristic functions are known to have the form

$$\psi_{\mathbf{k}}(\mathbf{r}, t) = u_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \exp[-iE_{\mathbf{k}}t/\hbar], \quad (1)$$

where  $\mathbf{k}$  is called the wave vector, and the function  $u_{\mathbf{k}}(\mathbf{r})$  is periodic in  $\mathbf{r}$  with the period of the potential energy. When no boundary conditions are imposed,  $\mathbf{k}$  can take on any value, and, except along certain surfaces which are boundaries of the Brillouin zones,  $u_{\mathbf{k}}$  and  $E_{\mathbf{k}}$  are continuous functions of  $\mathbf{k}$ . It is frequently convenient to use, instead of  $\mathbf{k}$ , the reduced wave vector. This differs from  $\mathbf{k}$  by a vector of the reciprocal lattice, and lies in the first Brillouin zone.

The motion of the electrons when a uniform

electric field is superimposed on the periodic field has presented a little difficulty, because of the fact that the potential of such a field becomes infinite, and the position of its zero value has no physical significance. If boundaries are put on the field there appear boundary effects that are believed to be of no significance in treating the behavior of electrons in crystals. If such boundaries are not used, the integrals involved diverge. Bloch<sup>1</sup> originally handled the problem by constructing a wave packet out of functions of the form (1). The motion of such a packet led to the conclusion that the wave vector  $\mathbf{k}$  changes at a uniform rate under the influence of an external field, but the method of proof was such as to be valid only when  $\mathbf{k}$  was far from the edge of a Brillouin zone. No indication was given of the

<sup>1</sup> F. Bloch, *Zeits. f. Physik* **52**, 555 (1928).

behavior at the zone boundary. This question was considered later by Jones and Zener<sup>2</sup> and by Zener.<sup>3</sup> Zener showed that with a sufficiently large field some electrons will jump from one band of energy levels to the next, and he evaluated the probability of such a transition. Although Zener's work leads to a correct understanding of the process, it may be worth while to consider a more direct method of derivation.

The result of the wave packet treatment suggests the study of the function

$$\psi(\mathbf{r}, t) = u_{\mathbf{k}+\lambda t}(\mathbf{r}) \exp [i(\mathbf{k}+\lambda t) \cdot \mathbf{r}] \times \exp \left[ -\frac{i}{\hbar} \int^t E_{\mathbf{k}+\lambda \tau} d\tau \right], \quad (2)$$

with  $\lambda = e\mathbf{e}/\hbar$ . This function satisfies the Schrodinger equation,

$$-\left(\hbar^2/2m\right)\nabla^2\psi + \{V(\mathbf{r}) - e\mathbf{e} \cdot \mathbf{r}\}\psi = -\left(\hbar/i\right)\partial\psi/\partial t, \quad (3)$$

except for the quantity

$$-\left(\hbar/i\right)\{\lambda \cdot \mathbf{grad}_{\mathbf{k}} u_{\mathbf{k}+\lambda t}\} \exp [i(\mathbf{k}+\lambda t) \cdot \mathbf{r}] \times \exp \left[ -\frac{i}{\hbar} \int^t E_{\mathbf{k}+\lambda \tau} d\tau \right]. \quad (4)$$

The remainder is zero in case  $\lambda=0$ , when no field is present, and also in case  $\mathbf{grad}_{\mathbf{k}} u_{\mathbf{k}}=0$ , the free electron case. In the case of free electrons Eq. (2) reduces to the solution given by Darwin.<sup>4</sup> It is to be emphasized that there is no question of attempting to define energy characteristic states, but rather of solving the whole Schrodinger equation for the time dependence of the wave functions.

In case neither  $\lambda$  nor  $\mathbf{grad}_{\mathbf{k}} u_{\mathbf{k}}$  is zero, but their product is very small, the function (2) will be an

approximate solution of the differential equation. For small values of the electric field it will be a good solution for a general periodic potential, except when  $\mathbf{k}+\lambda t$  approaches the edge of a zone. Here, even though  $\lambda$  is small,  $\mathbf{grad}_{\mathbf{k}} u_{\mathbf{k}}$  is large or undefined, so that other considerations must be invoked. Qualitatively one can see that the whole function  $\psi$  will be identical with the function corresponding to a point on the opposite side of the zone, so that the electron may be said to suffer a Bragg reflection. The end of the vector  $\mathbf{k}+\lambda t$  then starts again to move across the Brillouin zone in the direction of the field. A very weak field ( $\lambda \rightarrow 0$ ) will not cause an electron to jump from one zone to another, but will only cause the energy and the wave vector to move among the possible values in a single zone. This is a case to which the adiabatic principle of Ehrenfest is applicable.

To treat the above case more precisely, and to include the case in which  $\lambda$  is not vanishingly small, the remainder (4) must be taken into account. A general solution can be written as the infinite sum

$$\psi = \sum_{\mathbf{n}} a_{\mathbf{n}}(t) u_{\mathbf{k}+2\pi\mathbf{n}+\lambda t}(\mathbf{r}) \exp [i(\mathbf{k}+2\pi\mathbf{n}+\lambda t) \cdot \mathbf{r}] \times \exp \left[ -\frac{i}{\hbar} \int^t E_{\mathbf{k}+2\pi\mathbf{n}+\lambda \tau} d\tau \right], \quad (5)$$

where the  $\mathbf{n}$  are the vectors of the reciprocal lattice associated with the periodic potential energy. That such an expansion is adequate is due to the fact that for any value of  $\mathbf{k}+\lambda t$ , the functions  $u_{\mathbf{k}+2\pi\mathbf{n}+\lambda t}(\mathbf{r}) \exp [i(\mathbf{k}+2\pi\mathbf{n}+\lambda t) \cdot \mathbf{r}]$  form a complete orthogonal set. This solution is of the form usual in the method of variation of constants, and the problem is to determine the time variation of the coefficients. Substitution of (5) in (2) leads to the set of equations

$$da_{\mathbf{n}}/dt = -\sum_{\mathbf{s}} a_{\mathbf{s}} \left\{ \int u_{\mathbf{k}+2\pi\mathbf{n}+\lambda t}^* \lambda \cdot \mathbf{grad}_{\mathbf{k}} u_{\mathbf{k}+2\pi\mathbf{s}+\lambda t} \exp [2\pi i(\mathbf{s}-\mathbf{n}) \cdot \mathbf{r}] \right\} \times \exp \left[ -\frac{i}{\hbar} \int^t (E_{\mathbf{k}+2\pi\mathbf{s}+\lambda \tau} - E_{\mathbf{k}+2\pi\mathbf{n}+\lambda \tau}) d\tau \right]. \quad (5a)$$

Since both  $\mathbf{s}$  and  $\mathbf{n}$  are vectors of the reciprocal

<sup>2</sup> H. Jones and C. Zener, Proc. Roy. Soc. **144**, 101 (1934).

<sup>3</sup> C. Zener, Proc. Roy. Soc. **145**, 523 (1934).

<sup>4</sup> C. G. Darwin, Proc. Roy. Soc. **154**, 61 (1936).

lattice, the integral over the volume has the periodicity of the potential energy, and need be taken only over one cell, if the normalization is based on a single cell. From the differential

equation for  $u_k$  it follows that

$$\int u_{k+2\pi n+\lambda t}^* \boldsymbol{\lambda} \cdot \mathbf{grad}_k u_{k+2\pi s+\lambda t} \exp [2\pi i(\mathbf{s}-\mathbf{n}) \cdot \mathbf{r}] dv$$

$$= (i\hbar^2/m) \left\{ \int u_{k+2\pi n+\lambda t}^* \boldsymbol{\lambda} \cdot \mathbf{grad}_r u_{k+2\pi s+\lambda t} \exp [2\pi i(\mathbf{s}-\mathbf{n}) \cdot \mathbf{r}] dv \right\} / (E_{k+2\pi n+\lambda t} - E_{k+2\pi s+\lambda t}),$$

whence

$$\frac{da_n}{dt} = (\hbar^2/im) \sum_{s \neq n} \left\{ \left[ \int u_{k+2\pi n+\lambda t}^* \boldsymbol{\lambda} \cdot \mathbf{grad}_r u_{k+2\pi s+\lambda t} \exp [2\pi i(\mathbf{s}-\mathbf{n}) \cdot \mathbf{r}] dv \right] / (E_{k+2\pi n+\lambda t} - E_{k+2\pi s+\lambda t}) \right\} a_s$$

$$\times \exp \left[ (i/\hbar) \int' (E_{k+2\pi n+\lambda \tau} - E_{k+2\pi s+\lambda \tau}) d\tau \right]. \quad (6)$$

In the case of overlapping bands of energy values,  $(E_{k+2\pi n+\lambda t} - E_{k+2\pi s+\lambda t})$  may become zero. In this case transitions between different bands will take place for any value of  $\lambda$ . However, even in case the energy bands do not overlap, and  $(E_{k+2\pi n+\lambda t} - E_{k+2\pi s+\lambda t})$  does not become zero, a transition from one band to the next can occur if  $\lambda$  is sufficiently large.

An idea of the magnitude of the probability of transition from one Brillouin zone to another can be obtained by considering the case of almost free electrons in one dimension. In this case the wave vector has only one component, and the values between  $-\pi/d$  and  $+\pi/d$  constitute the first zone.  $d$  is the period of the potential energy. Consider an electron whose wave vector is in the neighborhood of  $+\pi/d$ . The only other state to which there is an appreciable probability of transition is that one whose wave vector is in the

neighborhood of  $\pi/d - 2\pi/d = -\pi/d$ . If it is assumed that at the time  $t=0$  the coefficient  $a_0=1$ , and  $a_{-1}=0$ , the coefficient  $a_{-1}$  will increase in accordance with Eq. (6). If the probability of transition is small enough so that  $a_0$  does not diminish appreciably in the time necessary for  $(k+\lambda t)$  to pass the point  $\pi/d$ , the total probability of transition for the passage over this zone boundary turns out to be

$$P = 4\pi^2 e^{-\alpha} / (1 + e^{-\alpha})^2,$$

where  $\alpha = mV_0^2 d / e\epsilon\hbar^2$ , and  $2V_0$  is the discontinuity in the energy. This is very similar to the result of Zener. It is vanishingly small for large values of  $\alpha$  but increases rapidly as  $\alpha$  decreases toward one. This rapid increase suggests the application to the breakdown of insulating crystals which was pointed out by Zener.