CONCLUSIONS

Measurements of lifetime in plastically deformed p-type germanium yield an electron capture radius of $3.4\times10^{-8}(300/T)^3$ cm. The room-temperature lifetime is given by

$$\tau=0.7\times N_d^{-1}. \quad (5)$$

This suggests that the lifetime in high-purity p-type crystals may be limited by the dislocations introduced in the crystal-growing. Measurements on n-type germanium indicate that, at room temperature,

$$\tau=2.5N_d^{-1}. \quad (6)$$

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Definition of Energy Bands in the Presence of an External Force Field

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It is shown that for an electron moving in a periodic potential perturbed by a weak electric field the "physical energy bands" differ from the energy bands in the absence of the perturbing field. By means of a wave-packet treatment it is shown that for very weak fields the modified bands are those suggested earlier by Wannier and by Adams and Argyres. In stronger fields, no such treatment can be given, and the functions defined by Wannier for that case do not represent "physical energy bands" in the same sense.

INTRODUCTION

IT is well known that the energy levels of an electron in a perfectly periodic potential group themselves into "bands," which are sometimes separated by "forbidden bands." The modern theory of solids predicts that an electron in one of these energy bands, when perturbed by certain kinds of weak perturbing field, accelerates under the perturbing force in somewhat the same manner as would a free particle of rather peculiar inertial properties. It is an outstanding success of the modern theory of solids that it can account quantitatively for many otherwise puzzling phenomena by recourse to the expected properties of these "effective free electrons."

The theory of electronic transport properties in metals and semiconductors assumes that the chief effect of a very weak and slowly varying perturbing field is to accelerate the effective electron about in its allowed energy band. This assumption is used in both semiclassical treatments of electronic motion and quantum-mechanical treatments of the electronic energy levels in a perturbed periodic potential, and with considerable success.

In order to understand the ordinary "effective electron" treatment of the effect of perturbing fields it is necessary to answer a perplexing question of a fundamental nature, *viz.*, what is the status of the energy-band concept in the presence of an external perturbation that destroys the crystalline periodicity. As far as this writer is aware, there has nowhere been given a systematic discussion of how this question is to be answered in principle. However, various authors, when addressing themselves to specific problems,[1–3] have assumed an answer to the question sufficient for their immediate purposes.

Recently Wannier[4] and Adams and Argyres[5] have discussed this problem of definition of the bands in the presence of an external field. They have given definitions of field-dependent Bloch functions which seem to have some of the properties that we might expect for the energy states in the presence of the field. However, their discussions are not complete in that they do not show in what way the functions they construct correspond to a *physical definition* of the "energy bands in the presence of the field."

In the first section we will show that the case of a weak electric field, the field-dependent Bloch functions defined by Wannier and by Adams and Argyres correspond to the physical energy states of an electron accelerating slowly in the electric field. The method of attack is to find the motion of a narrow wave packet, initially in a single energy band, as an electric field is slowly turned on. We find that the wave packet always behaves as though it consisted of a packet of functions from a single energy band of the field-dependent sort. Our results show that the motion of such a packet takes place without any transitions between bands only if

[1] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1936).
[2] E. N. Adams, Phys. Rev. **89**, 633 (1953).
[3] R. Karplus and J. M. Luttinger, Phys. Rev. **95**, 1154 (1954).
[4] G. H. Wannier, Phys. Rev. **100**, 1227 (1955); **101**, 1835 (1956).
[5] E. N. Adams and P. N. Argyres, Phys. Rev. **102**, 605 (1956).

the force field is sufficiently weak as to satisfy an adiabatic condition.

In the second section we discuss the situation with regard to other perturbations. We conclude that it is possible to construct "energy bands in the presence of the field" for other perturbations, in particular that of a magnetic field. However, we believe that Wannier's construction is incorrect for that problem.

I. MOTION OF A WAVE PACKET IN A WEAK ELECTRIC FIELD

We shall study the motion of a wave packet in the presence of a weak electric field. For simplicity we consider a hypothetical one-dimensional material of lattice spacing a, and in it an energy band of width E_B. We expand the wave function ψ of interest in the wave functions ψ_{nk} of the unperturbed lattice. Thus

$$\psi=(a/2\pi)^{\frac{1}{2}}\int dk\sum_n \varphi_n(k)\psi_{nk}. \tag{1.1}$$

The crystal momentum representation of the perturbed Schrödinger problem takes the form[6]

$$\left[E_n(k)-iF\frac{\partial}{\partial k}-i\frac{\partial}{\partial t}\right]\varphi_n-\sum_{n'}F(t)X_{nn'}(k)\varphi_{n'}=0. \tag{1.2}$$

In (1.2) the field $F(t)$ is allowed to depend on time.

In the presence of a field F, the energy bands are tilted as shown in Fig. 1. Every electron energy thus occurs in each energy band. The energy level E in the nth band (of width E_{nB}) will be associated with a wave function spread over a certain space interval of width (E_{nB}/F).

We shall define the physical energy band in terms of the motion of an electron wave packet satisfying these conditions.

(1) The packet has a momentum spread small compared to the Brillouin zone width $\hbar/a$.

(2) The packet has a well-defined energy with an energy spread small compared to the band width E_{nB}.

(3) The packet has a space spread small compared to the width of the region (E_{nB}/F), and its mean position is such that its mean energy lies within the nth energy band.

We shall show that such a packet can be constructed. We wish to find out just what wave functions should be used to construct it.

We shall study the time development of a packet, initially in the nth band, as the field is slowly raised to its final value F. The requirement of slowness merely means that the time required to turn the field on is long compared to that associated with any of the interband frequencies. Our treatment shall also assume that F is weak, i.e., that $FX_{nn'}$ is small compared to any of the interband energies.

[6] E. N. Adams, J. Chem. Phys. **21**, 2013 (1953).

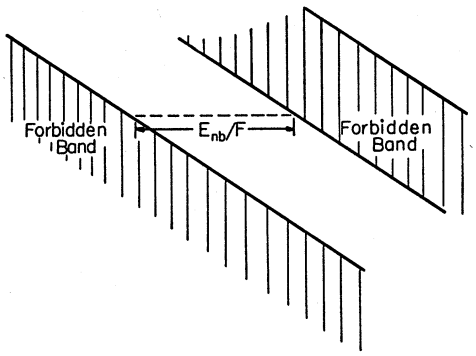

FIG. 1. Energy bands in presence of electric field.

It is convenient in some of what follows to set $\hbar=1$ and measure energies in frequency units. We begin by transforming the Hamiltonian with two unitary transformations. The first transformation is

$$u_1\equiv\exp\left(\int dtF\frac{\partial}{\partial k}\right). \tag{1.3}$$

Then

$$u_1Hu_1^{\dagger}=E\left(k+\int Fdt\right)-FX\left(k+\int Fdt\right)=i\frac{\partial}{\partial t}. \tag{1.4}$$

Next we transform with the unitary operator u_2:

$$u_2=\exp\left[i\int_0^t dt'E\left(k+\int Fdt'\right)\right]. \tag{1.5}$$

Writing ω_n for $(E_n/\hbar)$, we have

$$[u_2u_1Hu_1^{\dagger}u_2^{\dagger}]_{n'n}=-\exp\left[i\int_0^t dt'\omega_{n'n}\left(k+\int Fdt'\right)\right]\times F(t)X_{n'n}\left(k+\int Fdt\right). \tag{1.6}$$

Equation (1.6) gives the Hamiltonian in an "interaction representation" with the $-FX$ perturbation as interaction. We shall use (1.6) to study the growth of the component $\xi_{n'}$ of the wave function. The quantity $\xi_{n'}$ belongs to some other band than the original and is small if F is small. It will be a good approximation to assume that ξ_n is constant in time, therefore, provided we work always to the first order in F. Integrating (1.6) in time, we obtain

$$\xi_{n'}=i\int_0^T dt\exp\left[i\int_0^t dt'\omega_{n'n}\left(k+\int Fdt'\right)\right]\times F(t)X_{n'n}\left(k+\int Fdt\right)\xi_n(k). \tag{1.7}$$

We shall evaluate the integral (1.7) by breaking it up into integrals over the individual cycles of the

exponential factor. If the field is sufficiently weak, the functions $F(t)$, $\omega_{n'n}(k+\int Fdt)$, and $X_{n'n}(k+\int Fdt)$ will remain almost constant during one cycle of the exponential factor, and the time derivative of each will be effectively constant. We can then perform the integration over the single cycle by the following device. Define

$$\phi(t)\equiv\int_0^t dt'\omega_{n'n}\left(k+\int Fdt'\right). \tag{1.8}$$

The integral to be evaluated is therefore given by

$$\int_\phi^{\phi+2\pi} d\phi e^{i\phi}[FX_{n'n}/\omega_{n'n}]. \tag{1.9}$$

In the integrand, $t'\equiv t'(\phi)$. Integrating (1.9) by parts, we get

$$e^{i\phi}\left[\left(\frac{FX_{n'n}}{i\omega_{n'n}}\right)-\frac{d}{d\phi}\left(\frac{FX_{n'n}}{i\omega_{n'n}}\right)\right]_\phi^{\phi+2\pi}. \tag{1.10}$$

When we put in the limits the last term gives zero, and the first gives

$$e^{i\phi(t)}\left[\frac{F(t')X_{n'n}\left(k+\int Fdt'\right)}{i\omega_{n'n}\left(k+\int Fdt'\right)}\right]_t^{t+\tau}, \tag{1.11}$$

with τ the period of the cycle. Summing over all of the cycles and putting the result back into the Eq. (1.7), we obtain

$$\xi_{n'}(T)=\exp\left[i\int_0^T\omega_{n'n}\left(k+\int Fdt\right)dt\right]\times\left[\frac{FX_{n'n}\left(k+\int FdT\right)}{\omega_{n'n}\left(k+\int FdT\right)}\right]\xi_n(k). \tag{1.12}$$

It remains to write the solution function in the original crystal momentum representation. Using the inverses of the transformations u_1 and u_2, we find

$$\begin{aligned}\phi_n(k,T)&=\exp\left[-i\int_0^T dt\omega_n\left(k+\int Fdt\times\int FdT\right)\right]\xi_n\left(k-\int FdT\right),\\ \phi_{n'}(k,T)&=\exp\left[-i\int_0^T dt\omega_n\left(k+\int Fdt-\int FdT\right)\right][FX_{n'n}(k)/\omega_{n'n}(k)]\times\xi_n\left(k-\int FdT\right).\end{aligned} \tag{1.13}$$

It is to be noted that the time dependence of the wave function $\phi_{n'}(k,T)$ is characteristic of the nth band.

We shall examine the motion of an initially well-defined packet as described at the beginning of the section. If the packet is made up initially of wave functions belonging to the nth band, then the condition that its energy and momentum both be well-defined is satisfied if the spread δp of the packet satisfies

$$\delta p\ll(\hbar/a). \tag{1.14}$$

The width δx of the packet can be taken to be of the order of $\hbar/\delta p$, so the condition that the packet lie in the proper space interval requires that

$$(\hbar/\delta p)\ll(E_{nB}/F). \tag{1.15}$$

Combining (1.14) and (1.15), we obtain the conditions on the width of the packet to be

$$(F/\omega_{nB})\ll\delta p\ll(\hbar/a). \tag{1.16}$$

These conditions are not very restrictive and can easily be satisfied simultaneously by taking F sufficiently weak.

The wave function for the packet may now be written down for an arbitrary time after the field has been turned on. It is

$$\psi(t)=\int dk\exp\left[-i\int_0^t dt'\omega_n\left(k+\int Fdt-\int FdT\right)\right]\times[\psi_{nk}+\textstyle\sum_{n'}\psi_{n'k}(FX_{n'n}(k)/\hbar\omega_{n'n}(k))]\times\xi_n\left(k-\int Fdt\right). \tag{1.17}$$

We shall define

$$\psi_{nk}{}^{(F)}\equiv\psi_{nk}+\textstyle\sum_{n'}\psi_{n'k}[FX_{n'n}(k)/\hbar\omega_{n'n}(k)]. \tag{1.18}$$

Equation (1.17) shows that even after a long time, $\psi(t)$ consists of a packet of functions $\psi_{nk}{}^{(F)}$ belonging to a single "band." The envelope $\xi_n(k-\int Fdt)$ of the packet is exactly the same as the envelope $\xi_n(k)$ of the original packet except that it is displaced in momentum space by the integrated momentum transfer $\int Fdt$. This displacement corresponds, of course, to the classical acceleration of the packet under the force field. The time-dependent exponential factor describes the time advance of phase that would be expected for a particle in the original nth field-free band averaged over the momentum states that the particle has occupied. The structure of this factor is entirely analogous to that for the wave function of a free electron accelerating in a force field F, if the kinetic energy of the electron is taken to be $E_n(p)$.

Equation (1.17) shows that in the presence of the weak force field F, the electron accelerates as though it were "a free particle" accelerating in a momentum space exactly like that of the original energy band. In the adiabatic approximation the packet remains com-

pletely within the original band. However, in the presence of the field F, the function space of the nth band is spanned by the functions $\psi_{nk}^{(F)}$ rather than by the functions ψ_{nk}.

It is perhaps worth while to remark that there is an ambiguity in determining the potential arising from a homogeneous electric field that is slowly switched on. In our treatment we have assumed that our packet is situated near the zero of the electric potential. Otherwise there would be an additional time dependence of the phase arising from the potential energy in the electric field.

II. ENERGY BANDS IN THE PRESENCE OF THE FIELD

We have seen that in a weak electric field the energy bands are modified by the field, so that the basic eigenfunctions of the nth band are the $\psi_{nk}^{(F)}$ rather than the ψ_{nk}. These field-dependent functions are the functions recently studied by Adams and Argyres[5] and conjectured by them to be the basic eigenfunctions for the "nth band in the presence of the field."

The results of Adams and Argyres were given only to the first order in F. However, Wannier had earlier considered a more general definition of the Bloch-like functions in the presence of the field in which he proposed to modify the bands to all orders in the field. We shall denote Wannier's modified functions as $\psi_{nk}^{(W)}$. They were required to diagonalize the partial Hamiltonian

$$H_1^{(F)}=E-FX. \tag{2.1}$$

Wannier originally believed[4] that the $\psi_{nk}^{(W)}$ so defined would have the property that in the presence of the electric field they would correspond to electron acceleration within the individual bands just as the $\psi_{nk}^{(F)}$ above. However, it can be shown that the $\psi_{nk}^{(W)}$ do not merely accelerate except in the adiabatic approximation, which holds only for sufficiently small F. Furthermore, Wannier's modified Bloch functions satisfy the wrong equation if quantities of order F^2 or higher must be considered.† Thus Wannier's $\psi_{nk}^{(W)}$ represent the correct energy bands only in the weak-field approximation for which they are the same as the $\psi_{nk}^{(F)}$. In fact, this is the only case of interest, since whenever the adiabatic approximation is invalid, transitions between bands will occur of the sort envisaged by Zener as possibly accounting for dielectric breakdown.

Wannier has also considered the construction of functions that correspond to electron acceleration without interband transitions in the presence of a magnetic field.[4] He proposed that the desired functions are those that diagonalize the Hamiltonian

$$H^{(H)}=(1/2m)[\mathbf{P}-(e/2c)\mathbf{X}\times\mathbf{H}]^2+U. \tag{2.2}$$

† See appendix.

We do not find the functions that diagonalize (2.2) to have the desired property, even in the adiabatic limit. We shall not here construct the functions that would really be of interest, although they can be constructed by means of the unitary transformations which have been given in connection with studies of magnetic susceptibility.[1,2,7] The trouble with Wannier's prescription (2.2) is that it does not account for the fact that in the magnetic Hamiltonian there are terms bilinear in $i(\partial/\partial k)$ and P and terms bilinear in $i(\partial/\partial k)$ and X. These terms make the problem more difficult and less vulnerable to a straightforward formal treatment such as has been made above. In addition, the "force" is not clearly defined in the magnetic problem.

The best approach to the physical energy bands in the presence of a magnetic field is to examine the energy-level structure. For very weak magnetic fields the energy levels are grouped into bands that coincide with the field-independent bands as $H\rightarrow 0$. Then it is natural to define the physical energy bands as those bands for which the energy eigenfunctions are linear combinations of wave functions of different wave numbers but a single band index. These bands are the ones reached by the progressive "decoupling of bands," as carried out first by Wilson. These are just the bands that it has been necessary to construct in studying the magnetic susceptibility of solids.[1,2,7] A superposition of these states can be shown to satisfy an analog of the "acceleration" equation.[6]

The problem of defining the energy bands arises in a number of problems involving weak perturbations, such as problems having to do with the presence of impurity atoms, acoustic distortion, etc. Whether it is important to consider such questions as we have been concerned with here depends on the extent to which one must calculate from first principles. It can be asserted that *in general* it will be necessary to consider such questions in order to deduce from first principles the "effective perturbation potential" acting on a carrier that is thought of as moving always in a single band.

APPENDIX

Wannier's functions diagonalize the partial Hamiltonian

$$H_W=E(p)-FX(p). \tag{A.1}$$

Let $O(F,p)$ be an operator that diagonalizes H_W in the bands, and let $E_W(p)$ be the diagonalized form. Then

$$OHO^+=E_W(p)-F_x-i\hbar FO\frac{\partial O^+}{\partial p}. \tag{A.2}$$

The matrix $O(\partial O^+/\partial p)$ is not diagonal in bands. Its diagonal matrix elements are easily shown to be of order F^2, as stated in the text.

[7] W. Kohn and T. Kjeldaas, Phys. Rev. **105**, 806 (1957).