Diffusion of Excess Carriers in a Many-Valley Band Structure

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By means of simple kinetic-theory considerations, an expression is derived for the diffusion constant $D^{(i)}$ of thermal carriers in the ith valley of a many-valley semiconductor. $D^{(i)}$ is shown to be a tensor, the $\alpha\beta$ component of which is $\langle\tau v_\alpha v_\beta\rangle$, where τ is the relaxation time and v_α the αth component of the velocity. The Einstein relation is shown to hold between $D^{(i)}$ and $\mu^{(i)}$, the mobility tensor for the ith valley. The anisotropy of $D^{(i)}$, which may be quite considerable, should produce observable effects if the intervalley scattering rate is low enough. When the latter condition is not satisfied, effects may still be found in situations where the equivalence of the valleys is destroyed.

FOR a gas of molecules, the diffusion constant D is a scalar quantity that can be defined by the equation,

$$\mathbf{j}=-D\nabla n, \tag{1}$$

where $\mathbf{j}$ is the particle current density that flows due to a concentration gradient ∇n. Simple kinetic theory considerations lead to a relation between D and the properties of the molecules[1]:

$$D=\langle lv\rangle/3=\langle\tau v^2\rangle/3=2\langle\tau\epsilon\rangle/3m, \tag{2}$$

where l is the mean free path, v the speed, ϵ the energy, m the mass, and $\tau=l/v$. The averages indicated are to be taken over the velocity distribution of the particles. Equations (1) and (2) hold also for the diffusion of conduction electrons or holes inside a semiconductor with the simple model of the band structure, provided, of course, injection is small enough that the carriers diffuse independently.[2] The quantity m in (2) must in this case be replaced by m^*, the effective mass, and τ is more accurately the relaxation time. For a semiconductor with a many-valley band structure,[3] however, the equations must be modified; it is the purpose of this paper to show the modification. It will be assumed throughout that τ is a function of ϵ only, i.e., any anisotropy of τ will be neglected. This has been shown by Herring to be a good approximation, for example, for electrons in germanium scattered by lattice vibrations.[3]

For a simple many-valley model the energy of an electron with wave vector $\mathbf{P}$ measured from the valley minimum can be written

$$\epsilon(\mathbf{P})=P_1^2/2m_1^*+P_2^2/2m_2^*+P_3^2/2m_3^*, \tag{3}$$

where m_1^*, m_2^*, and m_3^* are the effective masses and P_1, P_2, and P_3, the components of $\mathbf{P}$ in the three coordinate directions that are principal axes for the constant-energy surfaces of the valley. When the electron density is small enough for Maxwell-Boltzmann statistics to be valid, the thermal equilibrium distribution function for electrons in the ith valley can be written

$$\begin{aligned}f_0^{(i)}&=\exp[-\epsilon_F/kT]\exp[-\epsilon(\mathbf{P}^{(i)})/kT]\\&=n^{(i)}\exp[-\epsilon(\mathbf{P}^{(i)})/kT]/\sum\exp[-\epsilon(\mathbf{P}^{(i)})/kT],\end{aligned} \tag{4}$$

where ϵ_F, the Fermi energy, is to be measured from the conduction band edge, $n^{(i)}$ is the density of carriers in the ith valley, and the summation is to be taken over all $\mathbf{P}^{(i)}$ in a unit volume of material and over both signs of spin. To write $f_0^{(i)}$ in the form at the right of (4) we have made use of the fact that $n^{(i)}=\sum f_0^{(i)}$.

Consider the case of material in a steady state at the temperature T with a concentration gradient $\nabla n^{(i)}$ that is taken to be in the $+x$ direction. It will be assumed that the variation in $n^{(i)}$ is small over a mean free path. The distribution function can then be written

$$f_0^{(i)}(x)=n^{(i)}(x)\exp[-\epsilon(\mathbf{P}^{(i)})/kT]/\sum\exp[-\epsilon(\mathbf{P}^{(i)})/kT]. \tag{5}$$

Because of the concentration gradient, there will be a net current of electrons flowing. To calculate this current it will be assumed, as is customary,[1] that the properties of an electron found at x_0 are characteristic of the x at which its last collision occurred. If $\hat{x}$ denotes a unit vector in the $+x$ direction, on the average the electrons found at x_0 will have had their last collision at $x_0-\hat{x}\cdot\mathbf{v}\tau$ for either direction of motion. The particle current density at x_0 due to electrons in the ith valley is then:

$$\mathbf{j}^{(i)}(x_0)=\sum f_0^{(i)}(x_0-\hat{x}\cdot\mathbf{v}\tau)\mathbf{v}. \tag{6}$$

Since we have assumed that the variation of f is small in the distance l, we can take

$$f_0^{(i)}(x_0-\hat{x}\cdot\mathbf{v}\tau)=f_0^{(i)}(x_0)-\hat{x}\cdot\mathbf{v}\tau(\partial f_0^{(i)}/\partial x)_{x_0}. \tag{7}$$

When (4) and (7) are used in (6), we get

$$\mathbf{j}^{(i)}(x_0)=\sum\exp[-\epsilon(\mathbf{P}^{(i)})/kT]\tau\mathbf{v}\mathbf{v}\cdot\nabla n^{(i)}/\sum\exp[-\epsilon(\mathbf{P}^{(i)})/kT], \tag{8}$$

since in the absence of a concentration gradient $\mathbf{j}^{(i)}(x_0)=0$. By analogy with (1) we can define the coefficient of $\nabla n^{(i)}$ as the diffusion constant $D^{(i)}$ for carriers in the ith valley. It is seen that $D^{(i)}$ is a tensor rather than

[1] See, for example, J. H. Jeans, *Kinetic Theory of Gases* (Cambridge, University Press, New York, 1940).
[2] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, New York, 1950).
[3] C. Herring, Bell System Tech. J. **34**, 237 (1955).

a scalar. The components of $D^{(i)}$ are given by

$$D_{\alpha\beta}^{(i)}=\sum \exp[-\epsilon(\mathbf{P}^{(i)})/kT]\tau v_\alpha v_\beta/\sum \exp[-\epsilon(\mathbf{P}^{(i)})/kT]=\langle\tau v_\alpha v_\beta\rangle, \quad (9)$$

which is the analog of (2) for this case. Since by assumption τ is independent of position on the constant-energy surface, (9) can be simplified by replacing $v_\alpha v_\beta$ by its average over such a surface.

The components of the mobility tensor for the ith valley are given by[3]

$$\mu_{\alpha\beta}^{(i)}=(q/kT)\sum \exp[-\epsilon(\mathbf{P}^{(i)})/kT]\tau v_\alpha v_\beta/\sum \exp[-\epsilon(\mathbf{P}^{(i)})/kT]. \quad (10)$$

Thus

$$D_{\alpha\beta}^{(i)}=\mu_{\alpha\beta}^{(i)}kT/q. \quad (11)$$

This is the Einstein relation for the many-valley model.

It is useful to relate $D^{(i)}$ to the S tensor introduced earlier in the theoretical treatment of magnetoresistance and mobility in a many-valley semiconductor.[4] For the case of spheroidal constant energy surfaces it is seen that

$$D_{\alpha\beta}^{(i)}=\langle\tau\bar{S}_{\alpha\beta}^{(i)}\rangle, \quad (12)$$

where $\bar{S}_{\alpha\beta}^{(i)}$ is given by Eq. (24) of reference 4 with ω taken to be zero. With this it is possible to find $D_{\alpha\beta}^{(i)}$ quickly for any set of axes.

Using (12) and the results of reference 4 we find that in the principal axis system $D_{xx}^{(i)}=D_{yy}^{(i)}=2\langle\tau\epsilon\rangle/3m_t$, while $D_{zz}^{(i)}=2\langle\tau\epsilon\rangle/3m_l$, where m_t and m_l are effective masses for the transverse and longitudinal directions of the ellipsoids. These results can also be obtained from (9) by making use of the fact that the average of $v_\alpha v_\beta$ over a constant-energy ellipsoid is $(2\epsilon/3m_\alpha)\delta_{\alpha\beta}$. When m_l and m_t have quite different values, as is the case in germanium and silicon, the anisotropy of $D^{(i)}$ is quite considerable. To observe this anisotropy one might, at least in principle, do an experiment in which electrons are injected at a point, and their diffusion rate measured by observing the current arriving at a second point within a diffusion length. If the valleys were oriented along the cube axes, for example, with m_l greater than m_t, and the second point displaced along the [100] direction from the first, we would expect to find that electrons from the [010] and [001] valleys would arrive first, together, and those from the [100] valley would arrive later. Such effects have never been observed in germanium or silicon because of the existence of intervalley scattering. In germanium the intervalley scattering rate has been found[5] to be so high down to the lowest temperatures investigated, about 20°K, as to make it unlikely that any effects of the kind described could be seen at all. The intervalley scattering rate might, of course, be smaller in other materials. Even if it is not, however, it should be possible to observe effects of the anisotropy of $D^{(i)}$ if the equivalence of the valleys is destroyed, by a shear or a high electric field, for example. Such measures have, of course, made it possible to observe the anisotropy of the mobility tensor.[3,6]

When intervalley scattering is sufficiently rapid, the diffusion constant for any carrier is the average of $D^{(i)}$ over the valleys. Denoting this average by D, we have

$$D=\sum_{i=1}^{N} D^{(i)}/N=\langle\tau\sum_{i=1}^{N}\bar{S}^{(i)}/N\rangle, \quad (13)$$

where N is the number of equivalent valleys. The average of $\bar{S}^{(i)}$ over the valleys has been evaluated for a cubic crystal.[4] In the absence of magnetic field it is a diagonal tensor with identical elements, so that the average diffusion constant becomes a scalar:

$$D=2\langle\tau\epsilon\rangle/3m^{(I)}, \quad (14)$$

$m^{(I)}$ being the inertial mass,[3] the reciprocal of the average of the reciprocals of the principal masses. It is seen that the Einstein relation holds between D and the average mobility μ. This has been verified experimentally in the Haynes-Shockley experiment.[7]

[4] E. M. Conwell, Phys. Rev. **123**, 454 (1961).

[5] G. Weinreich, T. M. Sanders, Jr., and H. G. White, Phys. Rev. **114**, 33 (1959).

[6] W. Sasaki and M. Shibuya, J. Phys. Soc. Japan **11**, 1202 (1956).

[7] Transistor Teachers Summer School, Phys. Rev. **88**, 1368 (1952).