Generation of an emf in Semiconductors with Nonequilibrium Current Carrier Concentrations

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LIST OF SYMBOLS

b	ratio of electron to hole mobility
c	velocity of light
D_k	diffusion constants ($=\mathrm{k}T\mu_k/e$)
ζ'	Fermi level for thermal equilibrium (Fig. 3)
ζ_k'	chemical potentials of the assembly of electrons in conduction ($k=1$) or valence band ($k=2$) (Fig. 3)
ζ_k	chemical potentials of the assemblies of electrons and holes (Fig. 3)
$\Delta\zeta_k=\zeta_k-\zeta_{k0}$	change in chemical potential with illumination
e	absolute value of electron charge
E	electron energy
E_G	energy gap
ϵ_k	kinetic energy of an electron or a hole (Fig. 3)
$F=-\mathrm{grad}\varphi$	electric field
φ	potential of the electric field
g_f	number of electron-hole pairs produced in a unit volume per unit time
h	Planck's constant
I	electric current density
I_k	density of the electric current transferred by electrons or holes
I_{qk}	density of heat current transferred by electrons or holes
k	Boltzmann constant
k	index
$L_k=(D_k\tau)^{\frac{1}{2}}$	diffusion length of electrons or holes
m	free electron mass
m_k	effective mass of an electron or of a hole
μ_k	electron or hole mobility
$n_k=n_{k0}+\Delta n$	concentration of electrons in the conduction band or of holes in the valence band
Δn	concentration of electrons (=concentration of holes) added to the equilibrium concentrations
n_i	electron concentration in an intrinsic semiconductor in the dark
N_D, N_A	concentrations of donors and acceptors
$N=N_D-N_A$	
$\omega(E)$, $\omega_k(\epsilon_k)$	number of permitted quantum states per unit energy interval per unit volume of the crystal
$Q_k^{*\prime}$	mean heat energy transferred by an electron or a hole
Q_k^*	mean kinetic energy transferred by an electron or a hole
ρ	electric resistivity
σ	electric conductivity
σ_k	electric conductivity of electrons or holes
$t_k=\sigma_k/\sigma$	transfer numbers
T	absolute temperature (ΔT temperature interval)
τ	mean lifetime of an electron-hole pair
U	voltage or emf
x	distance
Index:	0 denotes thermal-equilibrium state $k=1$ refers to electrons in the conduction band $k=2$ refers to holes in the valence band i means intrinsic semiconductor

1. INTRODUCTION

THE problem of direct transformation of solar or nuclear energy into electrical energy by means of the photovoltaic effect in semiconductors has aroused new interest recently owing to new kinds of photocells which promise important practical applications. In the present survey, we discuss fundamental ideas dealing with the physical aspects of the generation of a photovoltage in a semiconductor which is always related to the presence of nonequilibrium current carrier concentrations. These can be created not only by absorption of radiation but in other ways as well. We deal with the more general question, under what conditions nonequilibrium current carrier concentrations give rise to an emf.

1.1 Historical Remarks

The photovoltaic effect was first observed by Adams and Day in 1876 in selenium.[1] Later, much attention was devoted to photovoltaic effects in cuprous oxide

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(Cu_2O). Coblenz[2] and Dember[3] observed the generation of an emf between the illuminated and nonilluminated parts of some semiconducting crystals, in particular Cu_2O. This effect was then studied by A. F. Joffe and his collaborators experimentally and theoretically. In 1927, Grondahl[4] and later Lange[5] observed the generation of an emf at the contact between Cu_2O and Cu, the so-called barrier-layer photovoltaic effect, the essential features of which were explained by Schottky and his collaborators.[6] An account of the literature of this older work is given in a review by Grondahl[7] and in the books by Joffe,[8] Boutry,[9] and Lange.[10]

This work made clear that the photovoltaic effect is not caused by the pressure of photons on the electrons as was originally supposed by some workers, but it is closely related to the diffusion of the current carriers. This point of view was particularly stressed by Frenkel.[11] Of great importance for explanation of the photovoltaic effect was a paper by Landau and Lifshitz[12] and another by Davydov[13] in which it was shown that it can be caused by the excess concentration of minority current carriers.

In 1939, Mott[14] dealt with the question of how the nonequilibrium concentration of minority carriers produces an emf in a barrier-layer photocell.

In addition to Se and Cu_2O the photovoltaic effect was observed in many other semiconductors. The Ag_2S (Bernatzkii and Heikman[15]) and Tl_2S (Kolomietz[16]) photocells were constructed in 1937. Of fundamental importance was the discovery of the photovoltaic effect in a *p-n* junction situated within a semiconductor crystal. The first observation was made by Ohl[17,18] in crystals of silicon; later observations were reported by Simpson, Soole, Sosnowski, and Starkiewicz[19–21] in PbS, by Benzer[22] and by Becker and Fan[23] in Ge. In recent years this effect was observed in semiconducting compounds, e.g., InSb,[24–27] GaAs,[28,29] InAs,[30] InP,[31] AlSb,[32] and CdS.[33,34]

Practical applications were found first for the selenium and cuprous oxide photocells which are used as light intensity indicators or meters.[35] The *p-n* junction silicon photocells attain a high efficiency for the conversion of solar energy into electrical energy[36,37] and are an essential part of a nuclear battery.[37,38]

The theory of the foregoing effects was elaborated in considerable detail by a number of workers (Lashkarev *et al.*,[39,40] Lehovec,[41] Fan,[42] Gubanov,[43] and Moss[44]).

In all these effects the generation of a stationary emf is related either to the presence of a rectifying potential barrier at a contact or in the bulk of the semiconductor (barrier-layer photoeffects) or to the presence of a nonrectifying semiconductor-metal contact (Dember-effect). However, a photovoltage can be produced even in the bulk of a semiconductor.[45,46] This recently observed effect is taken as the point of departure for consideration here as it permits the essential features of the photovoltaic effect to be shown in a particularly simple and general manner.

This paper is chiefly devoted to photovoltaic effects. However, in the last part we deal with the generation of an emf in cases when nonequilibrium carrier concentration is produced by other means than by absorption of radiation.

1.2 Formulation of the Problem

Let us consider the simple semiconductor circuit shown in Fig. 1. The circuit is interrupted at the points

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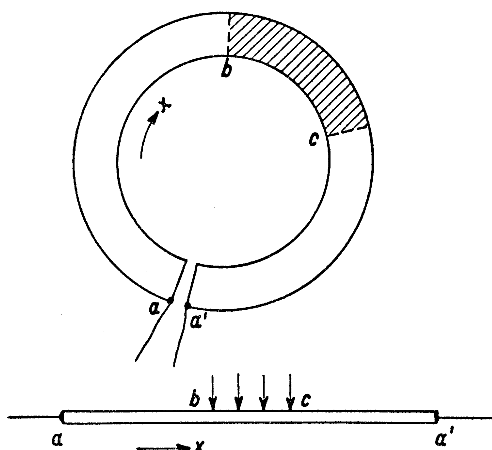

FIG. 1. Semiconductor circuit. Part b, c is illuminated.

a and a' where the leads for measuring the emf by the potentiometric method are connected. In part b, c there is a nonequilibrium current carrier concentration produced, e.g., by illumination. The contacts a and a' are sufficiently distant from the illuminated part so that in their neighborhood the nonequilibrium concentrations of current carriers are zero.

The question is what emf is measured between the contacts a and a' in the stationary case? A necessary condition for generation of an emf is some asymmetry of the circuit. What is the nature of this asymmetry?

Effects at the contacts semiconductor-metal, which we shall not consider in the present paper, are eliminated in the circuit shown in Fig. 1. The boundary effects here take place in the neighborhood of the points b and c situated within the semiconductor of known parameters instead at the contacts of a semiconductor with a metal, the properties of which have not yet been thoroughly investigated. The leads are connected at the points a and a' of identical chemical composition, at the same temperature, situated in the same magnetic field, etc. We thus respect a theorem[47,48] by Gibbs that electrical potential difference is uniquely defined only between two bodies of the same chemical composition and at the same temperature. This circumstance is important since from the history of the photovoltaic effect it is well known that some investigators did not respect it, and thus obtained erroneous results in the case of extrinsic semiconductors, in which illumination produces current carriers of the same type as those present in the dark. Landau and Lifshitz pointed out[12] that the voltage generated within the semiconductor in this case is compensated by the change of the contact potential if the current carrier energy distribution is governed by the Maxwell-Boltzmann statistics.[49]

We simplify the problem by the following assumptions. (α) We deal with semiconductors of the same type as germanium, that is, with large current carrier mobilities, of comparatively high electrical conductivity, practically without traps. Almost all of the whole crystal is therefore practically electrically neutral. The neutrality condition cannot hold exactly since the internal electric field in the crystal can be produced only by the presence of electric charges; the meaning of the neutrality condition is given in Sec. 2.5. It is, of course, possible that considerable space charge densities are located in regions of abrupt inhomogeneities (e.g., near the surface or at a p-n junction). Nevertheless, most of of the volume of the crystal is nearly electrically neutral and keeps its neutrality even if illuminated. This is not the case, for example, in ionic crystals in which space charges often accompany photoelectric effects. The assumptions mentioned are well satisfied in semiconductors with prevailing covalent binding, such as Ge, Si, $A^{III}B^{V}$ and other intermetallic semiconducting compounds.

(β) For the sake of simplicity we assume the geometry to be linear. This means that the thickness of the sample is small compared with the reciprocal value of the absorption constant or with the diffusion length of the carriers so the concentrations are practically constant over the whole cross section of the sample.

1.3 Generation of Nonequilibrium Current Carrier Concentration

In a semiconductor nonequilibrium concentrations n_1 and n_2 of electrons and holes can exist differing from the concentrations, which correspond to the thermal equilibrium n_{10}, n_{20}, by amounts $\Delta n_1 = n_1 - n_{10}$ and

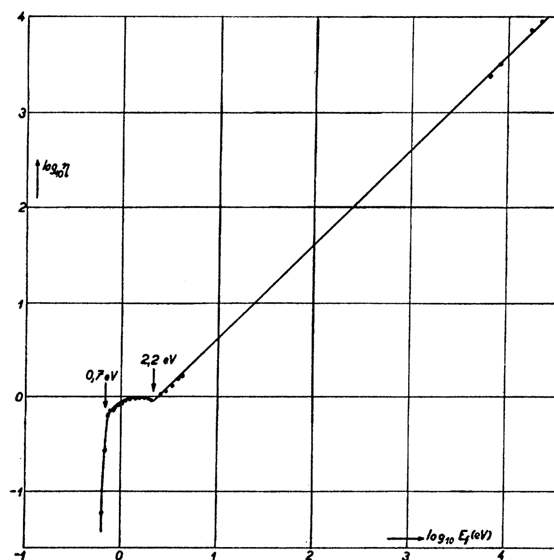

FIG. 2. Dependence of quantum efficiency η of the inner photoelectric effect[50,51] in germanium on the photon energy E_f.

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$\Delta n_2 = n_2 - n_{20}$. If there are no traps in the semiconductor and the condition of electrical neutrality is fulfilled [this is the case if assumption (α) holds] one has practically $\Delta n_1 = \Delta n_2 = \Delta n$. The value of nonequilibrium concentrations is determined by two processes: the rate of generation of excess current carriers, and their rate of recombination.

An important way of generating added carriers is by absorption of radiation. If $n_f dv$ photons or particles are absorbed in a volume dv per second from which each produces η electron-hole pairs with a mean lifetime τ, an excess concentration Δn is created given by $\Delta n = \eta n_f \tau = g_f \tau$, neglecting the diffusion of carriers from or into the volume considered.

The particularly important number η is denoted as the quantum efficiency of the inner photoelectric effect. Its dependence[50,51] on the photon energy E_f was measured in germanium (Fig. 2). A photon is able to produce an electron-hole pair only in case its energy E_f exceeds some minimum energy which corresponds to the infrared absorption limit of the semiconductor. In semiconductors satisfying assumptions (α) and [(ϵ) (see Sec. 3.1)] it is given (at least approximately) by the value of the energy gap E_G. In the neighborhood of the absorption limit towards shorter wavelengths ($E_f > E_G$), we have in germanium $\eta \approx 1$ until we reach an energy $\epsilon' = 2.2$ ev. For $E_f > \epsilon'$ the quantum efficiency is proportional to E_f; the energy needed to produce an electron-hole pair is constant and equal to $\epsilon = 2.5$ ev. In this energy range the kinetic energy of electrons released by the absorption of a high-energy photon is used for generation of additional electrons and holes. The energy $\epsilon - E_G$ is probably transferred to the lattice vibrations. The energy ϵ has been measured[52] with high-energy radiation in some other semiconductors.

Another way of producing nonequilibrium concentrations is diffusion of current carriers from regions of higher concentrations into regions of lower concentrations. The regions of higher concentrations are, e.g., irradiated regions, regions with a higher impurity content, or at a higher temperature.

2. BASIC EQUATIONS

We start from the well-known equations generally used for description of electronic effects in semiconductors: the equations for the current densities, the continuity equation and the Poisson equation. In writing the current density equations we use notation familiar[53] in the thermodynamics of irreversible processes. This helps to show the analogy between generation of an emf in semiconductors and general laws governing energy transformations, e.g., in a galvanic cell. In deriving the equations for current densities it is usual to start from an equation such as Boltzmann's equation for the stationary state and to consider, in final formulas, certain expressions as phenomenological constants which are to be determined experimentally.

Fig. 3. Notation of energies: I conduction band, II valence band, and III energy gap.

We take here a somewhat different point of view. We regard the equations of current densities as purely phenomenological equations which are valid generally, without any assumptions about the zone structure of the semiconductor or the electron scattering mechanism. Of course, their generality is understood in the same sense as the generality of the equations of the thermodynamics of irreversible processes, that is, as a first approximation of more exact kinetic equations which can be developed into approximations of higher orders (compare Sec. 3 of DeGroot[53]).

2.1 Current Density Equation

These can be written in the form (DeGroot,[53] Sec. 52):

$$I_k = \frac{1}{e}\sigma_k\left(-e\,\mathrm{grad}\varphi + T\,\mathrm{grad}\left(\frac{\zeta_k'}{T}\right) + Q_k^{*\prime}\frac{1}{T}\,\mathrm{grad}T\right). \quad (1)$$

The index $k=1$ refers here to electrons in the conduction band, $k=2$ to electrons in the valence band. The energy levels are shown in Fig. 3. This holds for stationary states provided two assumptions are valid: the current carriers undergo many collisions in time intervals which are considered in the theory and further that the change in the electrostatic energy of an electron over a distance equal in order of magnitude to the mean free path of an electron is small compared with the mean thermal energy. The first assumption excludes electric fields of very high frequencies, which are not considered here owing to restriction to stationary states, and further requires that the mean lifetime of an electron-hole pair is sufficiently longer than the relaxation time. The second assumption excludes very high electric fields such as are present, e.g., in a p-n junction. Inside such localized potential barriers the energy distribution of current carriers is substantially different from the dis-

[50] S. Koc, Czechosl. J. Phys. 7, 91 (1957).
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tribution which corresponds to the temperature of the lattice T, and other ways are necessary to calculate the current densities (Sec. 5).

Equation (1) expresses the fact that, on the assumptions just mentioned, the current densities are proportional to the gradients of the electric potential φ, of the chemical potentials ζ_k' and of the temperature T. There is theoretical and experimental evidence[54,55] that if regions of localized potential barriers are excluded even excess current carriers created by photon absorption practically have the energy distribution corresponding to T. This is owing to the fact that interaction of carriers with the lattice is so strong that after their liberation by light they lose[56] their excess energy very quickly (say within 10^{-11} sec). It is thus possible to define the chemical potentials of the assembly of electrons in the conduction and the valence band and other quantities for the case that current carrier concentrations do not correspond to thermal equilibrium.

2.2 Chemical Potentials of the Assemblies of Electrons and Holes

From the Fermi-Dirac statistics the following relation holds between the concentration of electrons in the conduction band n_1 and their chemical potential ζ_1',

$$n_1=\int_{E_1}^{\infty}\frac{\omega(E)dE}{1+e^{(E-\zeta_1')/kT}}. \tag{2}$$

Similarly, for the concentration of holes in the valence band,

$$n_2=\int_{-\infty}^{E_2}\omega(E)\left(1-\frac{1}{1+e^{(E-\zeta_2')/kT}}\right)dE. \tag{3}$$

Here $\omega(E)dE$ denotes the number of permitted energy states of an electron in the interval E, $E+dE$. For the case that the assembly of electrons in the conduction band is in thermal equilibrium with the assembly of electrons in the valence band,

$$\zeta_1'=\zeta_2', \tag{4}$$

and the Fermi level is defined. If this is not the case chemical potentials of both assemblies are different; they were introduced by Shockley[57–59] into the theory of semiconductors and denoted as "quasi-Fermi levels."

It is sometimes advantageous to introduce the following notation (Fig. 3):

in the conduction band: $E=E_1+\epsilon_1,\quad \zeta_1'=E_1+\zeta_1,$

in the valence band: $E=E_2-\epsilon_2,\quad \zeta_2'=E_2-\zeta_2.$

[54] A. B. Giordano *et al.*, Phys. Rev. **88**, 1368 (1952).
[55] S. M. Ryvkin, Zhur. Tech. Fiz. **24**, 2136 (1954).
[56] B. I. Davydov, Zhur. Eksptl. i. Teort. Fiz. **7**, 1069 (1937); *ibid.* 2212 (1937).
[57] W. Shockley, Bell System Tech. J. **28**, 435 (1949).
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[59] Shockley, Sparks, and Teal, Phys. Rev. **83**, 151 (1951).

Equations (2) and (3) then take the simple form

$$n_k=\int_0^{\infty}\frac{\omega_k(\epsilon_k)d\epsilon_k}{1+e^{(\epsilon_k-\zeta_k)/kT}}. \tag{5}$$

The quantities ζ_k will be referred to as chemical potentials of the assembly of electrons (ζ_1) and of the assembly of holes (ζ_2). Using them the thermal equilibrium condition (4) is written

$$\zeta_{10}+\zeta_{20}=-E_G. \tag{6}$$

The density of energy states $\omega_k(\epsilon_k)$ depends on the Brillouin-zone structure. In the simple case of spherical energy surfaces we have

$$\omega_k(\epsilon_k)=4\pi\left(\frac{2m_{dk}}{h^2}\right)^{\frac{3}{2}}\epsilon_k^{\frac{1}{2}}, \tag{7}$$

where $m_{dk}=m_k$ and m_k is the effective mass of an electron ($k=1$) or of a hole ($k=2$). In the case of elliptical energy surfaces where the effective masses are different in the three fundamental directions m_k', m_k'', m_k''', (7) holds with $m_{dk}=(m_k'm_k''m_k''')^{\frac{1}{3}}$. If each surface of constant energy is a set of N_s similar ellipsoids centered on the cubic axes of the Brillouin zone (which is probably the case for the conduction band of germanium with $N_s=4$ or 8) one has $m_{dk}=(N_s^2m_k'm_k''m_k''')^{\frac{1}{3}}$.

Determination of chemical potentials is especially simple for the case that classical statistics hold, that is, if $-\zeta_k/kT\gg1$. Then

$$n_k=e^{\zeta_k/kT}\int_0^{\infty}\omega_k(\epsilon_k)e^{-\epsilon_k/kT}d\epsilon_k=A_k(T)e^{\zeta_k/kT}, \tag{8}$$

where the partition function $A_k(T)$, for the case that the effective mass concept can be used, has the form

$$A_k(T)=2\left(\frac{2\pi m_{dk}kT}{h^2}\right)^{\frac{3}{2}}. \tag{9}$$

Introducing the chemical potentials ζ_k instead of ζ_k' into Eq. (1) and supposing that E_1, E_2 do not depend on x (which can be justified particularly in the case that E_G is independent of x), we obtain

$$I_1=\frac{\sigma_1}{e}\left(-e\,\mathrm{grad}\varphi+T\,\mathrm{grad}\left(\frac{\zeta_1}{T}\right)+Q_1^*\frac{1}{T}\,\mathrm{grad}T\right)$$
$$=\frac{\sigma_1}{e}\left(-e\,\mathrm{grad}\varphi+\mathrm{grad}\zeta_1+S_1^*\,\mathrm{grad}T\right), \tag{10}$$

$$I_2=\frac{\sigma_2}{e}\left(-e\,\mathrm{grad}\varphi-T\,\mathrm{grad}\left(\frac{\zeta_2}{T}\right)-Q_2^*\frac{1}{T}\,\mathrm{grad}T\right)$$
$$=\frac{\sigma_2}{e}\left(-e\,\mathrm{grad}\varphi-\mathrm{grad}\zeta_2-S_2^*\,\mathrm{grad}T\right). \tag{11}$$

The new factors are related to the old ones as follows:

$$Q_1^* = Q_1^{*\prime} - E_1, \tag{12}$$

$$Q_2^* = E_2 - Q_2^{*\prime}, \tag{13}$$

$$S_k^* = (1/T)(Q_k^* - \zeta_k). \tag{14}$$

2.3 Quantities of Transfer $Q_k^{*\prime}$, Q_k^*, S_k^*

The physical significance of the transfer quantities $Q_k^{*\prime}$ is best seen if, together with Eq. (1), we consider the equation for the heat current density transported by electrons in the conduction or valence band, which according to the Onsager principle,[60] can be written

$$I_{qk} = -\frac{1}{e^2}\sigma_k \left\{ Q_k^{*\prime}\left[-e \operatorname{grad}\varphi + T \operatorname{grad}\left(\frac{\zeta_k'}{T}\right)\right] + P_k^{*\prime}\frac{1}{T}\operatorname{grad}T \right\} \tag{15}$$

($P_k^{*\prime}$ are constants). If $\operatorname{grad}T = 0$, we have

$$Q_k^{*\prime} = I_{qk}/I_k/(-e). \tag{16}$$

$Q_k^{*\prime}$ is the heat current density in the conduction ($k=1$) or the valence ($k=2$) band which corresponds to unit current density of electrons (one electron per 1 cm² per sec) for the case that $\operatorname{grad}T=0$. We call $Q_k^{*\prime}$ the heat transfer due to electrons in the conduction or valence band.

These quantities are determined by kinetic considerations. We speak here explicitly about the conduction band. The heat transfer $Q_1^{*\prime}$ is composed of two parts, the electronic part $Q_{1e}^{*\prime}$ and the phonon-drag part $Q_{1p}^{*\prime}$. The electronic part $Q_{1e}^{*\prime}$ can be determined as follows. For the electric current density we have for the case of spherical zone structure (supposing the validity of some assumptions[61] about electron scattering probabilities)

$$I_1 = -\frac{16\pi m_{d1} e^2}{3h^3}\int_0^\infty l_1(\epsilon_1)\epsilon_1 \frac{\partial f_0}{\partial \epsilon_1} d\epsilon_1, \tag{17}$$

where $l_1(\epsilon_1)$ is the mean free path of electrons and f_0 is the Fermi distribution function

$$f_0 = \frac{1}{1+e^{(\epsilon_1 - \zeta_1)/kT}}. \tag{18}$$

Every electron which takes part in the transport of the electric current I_1 transfers an energy $E = E_1 + \epsilon_1$; therefore for I_{q1e}, we obtain

$$I_{q1e} = \frac{16\pi m_{d1} e}{3h^3}\int_0^\infty l_1(\epsilon_1)\epsilon_1(E_1+\epsilon_1)\frac{\partial f_0}{\partial \epsilon_1}d\epsilon_1 = -\frac{1}{e}(E_1 + Q_{1e}^*)I_1, \tag{19}$$

where Q_{1e}^* is the mean kinetic electron energy of transfer given by the following relation (with $k=1$):

$$Q_{ke}^* = \frac{\int_0^\infty l_k(\epsilon_k)\epsilon_k^2(\partial f_0/\partial \epsilon_k)d\epsilon_k}{\int_0^\infty l_k(\epsilon_k)\epsilon_k(\partial f_0/\partial \epsilon_k)d\epsilon_k}. \tag{20}$$

The same expression is valid for holes (with $k=2$). As was pointed out by Price,[62] Eq. (20) is correct only when the energy change on scattering is small compared with kT. If classical statistics are valid and energy zones are spherical, one has

for thermal scattering $l = \text{const}$, $Q_{ke}^* = 2kT$, (21)

for ionized impurities scattering $l \sim \epsilon^2$, $Q_{ke}^* = 4kT$. (22)

The intermediate cases are treated by Anselm and Klachkin.[63]

The heat transfer $Q_{1p}^{*\prime} = Q_{1p}^* + E_1$ is caused by drag of low-frequency phonons on the electrons in the conduction band. This effect was first discussed by Gurevich[64] and later by Klemens[65]; it was experimentally discovered by Frederikse[66] and Geballe[67] on measuring the thermoelectric power of germanium at low temperatures. The theory of the effect was given by Frederikse[68] and by Herring.[69]

The value of Q_{ke}^* at room temperature is about 0.05–0.1 ev. The value of Q_{kp}^* can attain hundredths of electron volts at room temperature but increases considerably with decreasing temperature; in p-type silicon values as high as 18 ev have been observed.[70]

The quantities S_k^* are the entropies transferred by an electron or a hole.

2.4 Continuity Equation

When assumption (α) (Sec. 1.2) holds, the continuity equations for the current of electrons and holes can be written for the stationary case ($\partial n_k/\partial t = 0$) as follows:

$$\operatorname{div}I_1 = -\operatorname{div}I_2 = eR - eg_f. \tag{23}$$

[60] Compare deGroot,[53] Chap. 1. A discussion of its application to semiconductors is given by P. J. Price [Phys. Rev. **104**, 1223 (1956)]. I am indebted to Dr. Price for sending me his manuscript prior to its publication.

[61] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936).

[62] P. J. Price (private communication).

[63] A. I. Anselm and V. I. Klachkin, Zhur. Exptl. i Teort. Fiz. **22**, 297 (1952).

[64] L. Gurevich, J. Phys. U.S.S.R. **9**, 477 (1945); *ibid.* **10**, 67 (1946).

[65] P. G. Klemens, Australian J. Phys. **7**, 520 (1954).

[66] H. P. R. Frederikse, Phys. Rev. **91**, 491 (1953).

[67] T. H. Geballe, Phys. Rev. **92**, 857 (1953).

[68] H. P. R. Frederikse, Phys. Rev. **92**, 248 (1953).

[69] C. Herring, Phys. Rev. **92**, 857 (1953); *ibid.* **96**, 1163 (1954).

[70] T. H. Geballe and G. W. Hull, Phys. Rev. **98**, 940 (1955).

Here R denotes the recombination function (the number of excess electrons and holes recombining in 1 cm^3 per sec). In the most simple case[71] of linear recombination, valid for small concentration of excess current carriers, $\Delta n \ll n_{10}$ or n_{20} and $R=\Delta n/\tau$.

2.5 Poisson Equation

The Poisson equation has the following form:

$$\operatorname{div} F=(e/K)(n_2-n_1+N_D{}^+-N_A{}^-)=(e/K)\delta n. \qquad (24)$$

Here $N_D{}^+$, $N_A{}^-$ are concentrations of ionized donors and acceptors; $e\delta n$ is the space-charge density, K the dielectric constant. We introduce now the following assumption (γ), which holds approximately for semiconductors of the type defined by assumption (α) and for not too low temperatures. (γ) The donors and acceptors are fully ionized whether carrier concentrations correspond to thermal equilibrium or not. We then have $N_D{}^+=N_D-N_A$ in n-type semiconductors, $N_A{}^-=N_A-N_D$ in p-type semiconductors.

Assumption (γ) means a great simplification but can be used only for certain kinds of semiconductors, certain kinds of impurities and in a certain temperature range. For the space-charge density $e\delta n$ we consider two limiting cases.

(a) *Electrical Neutrality*

Small disturbances of electrical neutrality give rise to strong electric fields so that strong forces are always present which tend to restore neutrality. Of course, it is not possible to have complete electrical neutrality because electric fields producing the emf have to be present. But if these fields are feeble, and their variation along the sample is continuous, δn is quite neglegible compared with n_1 and n_2. For instance, an electric field having a gradient 100 v/cm corresponds in germanium ($K_{\text{rel}}=16$) to a quite negligible concentration $\delta n=K/e \operatorname{grad} F=7.5\cdot 10^8$ cm^{-3}. It is possible then in every point in the semiconductor (with the exception of localized potential barriers) to put into the equation for current densities and into the continuity equation the condition of electrical neutrality

$$n_1-n_{10}=n_2-n_{20}=\Delta n. \qquad (25)$$

(b) *Strong Space Charge*

Strong space-charge density is present in regions of large changes of some semiconductor parameters, e.g., near the surface, in a p-n junction, etc. There are strong electric fields inside such regions and Eq. (1) is not valid there (Sec. 5). Under the conditions existing in a p-n junction discussed by Shockley[57] the space-charge density of current carriers can be neglected and the Poisson equation is reduced to the simple form

$$\operatorname{div} F=(e/K)(N_D-N_A). \qquad (26)$$

[71] W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).

From this equation, the potential distribution φ in a p-n junction can be determined (Sec. 5.1).

3. GENERATION OF AN emf

Let us return to the case illustrated in Fig. 1. We now discuss the theoretical expression for the emf generated in the circuit on the assumption that in the whole circuit the current carriers are in thermal equilibrium with the lattice; Eqs. (1), (23), and (25) are then valid at every point. Such a condition is realized for the case that the gradients of the parameters of the semiconductor (e.g., such as the impurity concentration) in the sample are small. In Sec. 5 we consider the case that inside the illuminated parts b and c there is a localized p-n junction in which Eq. (1) does not hold. It turns out that essential conclusions reached by consideration of the quasi-equilibrium case can be extended to the other case.

In the one-dimensional geometry [assumption (β)], we get from (1) for the electric field $F=-\operatorname{grad}\varphi$,

$$F=\frac{I}{\sigma}-\frac{1}{e}t_1T\frac{d}{dx}\left(\frac{\zeta_1'}{T}\right)-\frac{1}{e}t_2T\frac{d}{dx}\left(\frac{\zeta_2'}{T}\right) -\frac{1}{e}t_1Q_1{}^{*\prime}\frac{1}{T}\frac{dT}{dx}-\frac{1}{e}t_2Q_2{}^{*\prime}\frac{1}{T}\frac{dT}{dx}, \qquad (27)$$

on introducing the transfer numbers $t_k=\sigma_k/\sigma$.

To obtain the expression for the emf which can be measured between the contacts a and a' we must put $I=0$ and integrate (27) along the whole circuit of Fig. 1, obtaining

$$U=\oint F dx=U_b+U_t, \qquad (28)$$

$$U_b=-\frac{1}{e}\oint T\sum_{k=1,2} t_k d\left(\frac{\zeta_k'}{T}\right), \qquad (29)$$

$$U_t=-\frac{1}{e}\oint \frac{1}{T}\sum_{k=1,2} t_kQ_k{}^{*\prime}dT. \qquad (30)$$

The sign of U is chosen so that $U>0$ if the contact a is positive.

These expressions are simplified for the case that $dE_G/dx=0$. From (29) and (30), we get

$$U_b=-\frac{1}{e}\oint (t_1d\zeta_1-t_2d\zeta_2) =-\frac{1}{e}\oint (t_1d\Delta\zeta_1-t_2d\Delta\zeta_2), \qquad (31)$$

$$U_t=-\frac{1}{e}\oint (t_1S_1{}^*-t_2S_2{}^*)dT, \qquad (32)$$

in which $\Delta\zeta_k=\zeta_k-\zeta_{k0}$.

3.1 Conditions for Generation of an emf

Conditions for generation of an emf can be obtained by discussion of the integrals (29) to (32).

Case (a) $dE_G/dx=0$, $dT/dx=0$

In this case $U_t=0$. From (31) we see that $U_b=0$ if there are no nonequilibrium carrier concentrations so that $\Delta\zeta_k=0$. Similarly, $U_b=0$ for the case that the semiconductor in the dark is homogeneous so that $d\zeta_{10}=-d\zeta_{20}$ and $b=\mu_1/\mu_2=\text{const}$, because then t_k and $\Delta\zeta_k$ are functions of Δn only and integration over the closed circuit in (31) gives zero. Further, the integral (31) is always equal to zero if we have only one kind of current carriers, that is if $t_1=1$, $t_2=0$ or $t_1=0$, $t_2=1$.

The condition for generation of an emf is the simultaneous presence of nonequilibrium carrier concentration and of an inhomogeneity as the integral (31) differs from zero only if t_k and $\Delta\zeta_k$ vary along the sample so that they cannot be expressed as a single-valued function of one variable. Consequently, the presence of two independent factors determining t_k and $\Delta\zeta_k$ is necessary.

The most important inhomogeneity is the variation of the concentration of donors or acceptors along the sample (Sec. 4). Another possibility is the variation of the ratio of the current carrier mobilities $b=\mu_1/\mu_2$* or of the effective masses of current carriers along the sample. The effects are usually very small. A further possibility is the variation of magnetic field intensity along the sample. In this case, (Sec. 6.1), generation of an emf is due to the dependence of the chemical potentials ζ_k on the magnetic field. On the other hand, the variation of recombination center concentrations along an otherwise homogeneous sample (which influence only the mean lifetime of current carriers) cannot give rise to an emf as it causes the variation only of Δn, equivalent to a nonhomogeneous illumination of a homogeneous sample.

Case (b) $dE_G/dx=0$, $dT/dx\neq 0$

For the case that a temperature gradient is present in the sample an emf is generated even if no nonequilibrium current carriers are present; (32) gives then the usual thermoelectric voltage. In calculating the absolute thermoelectric power of a semiconductor it is expedient to imagine a circuit composed of the semiconductor and of an electrical conductor in which it is possible to put $S^*=0$ (Fig. 4). The integration in (32)

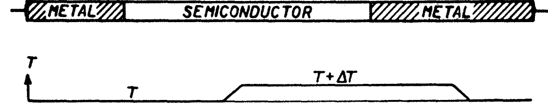

FIG. 4. Measurement of the thermoelectric power.

is easily carried out if $\Delta T\ll T$, and we get[72] the well-known formula for the thermoelectric power:

$$u=\frac{U_t}{\Delta T}=-\frac{1}{e}(t_{10}S_{10}^*-t_{20}S_{20}^*)$$
$$=\frac{k}{e}\left(t_{10}\frac{\zeta_{10}-Q_1^*}{kT}-t_{20}\frac{\zeta_{20}-Q_2^*}{kT}\right). \tag{33}$$

Presence of nonequilibrium carrier concentrations causes a change in thermoelectric voltage in the circuit. This we call a photothermoelectric effect (Sec. 6.2).

Case (c) $dE_G/dx\neq 0$

If E_G cannot be considered as constant in the sample an emf can be generated which is easily calculated from (29). If the sample is assumed to be otherwise homogeneous we get [if $\Delta\sigma=\Delta\sigma_s=\text{const}$ inside the part b, c, $\Delta\sigma=0$ outside, (Sec. 3.2, assumption (ζ))]:

$$U_b=-\frac{1}{e}\Delta t_1(E_{Gc}-E_{Gb}), \tag{34}$$

where $\Delta t_1=t_1-t_{10}$ and E_{Gc}, E_{Gb} are the values of the energy gap at the points c and b. This emf plays a role in the thermal photovoltaic effect owing to the dependence of E_G on the temperature (Sec. 6.2). It would also be of importance in a photovoltaic effect suggested by Price[63] where the inhomogeneity of the semiconductor is caused by strain.

Equations (29) to (32) hold for semiconductors even if assumptions (α) and (γ) are not valid. However, in performing the actual calculations in the following sections we have limited our considerations by the assumptions (α), (β), and (γ) and also the following two: (δ) The ratio of the electron-hole mobilities $b=\mu_1/\mu_2$ is constant throughout the sample. (ϵ) For the assemblies of electrons and holes classical statistics hold; that is, n_k is assumed to be always small compared with $A_k(T)$ even in the illuminated part of the semiconductor.

3.2 Distribution of Current Carrier Concentrations

From (29) to (32) one can calculate the emf generated in the circuit of Fig. 1, provided that the concentrations of current carriers are known in every point of the semiconductor from which ζ_k and t_k can easily be calcu-

* For example, if in an otherwise homogeneous semiconductor (n_{k0} are constant throughout the sample) the values of b at the points b and c are b_b and b_c the integral (31) gives for the emf:

$$U=U_b=\frac{k}{e}\left[\frac{b_c-1}{b_c+1}\frac{\Delta\sigma_{sc}}{\sigma_{0c}}-\frac{b_b-1}{b_b+1}\frac{\Delta\sigma_{sb}}{\sigma_{0b}}\right],$$

where σ_{0c}, σ_{0b} are dark conductivities at the points c and b; $\Delta\sigma_{sc}$, $\Delta\sigma_{sb}$ are excess conductivities at the points c and b due to the presence of nonequilibrium carrier concentration. In deriving the above equation the assumption was made $\Delta n=0$ outside the part b, c and $\Delta n=\Delta n_s=\text{const}$ inside the part b, c (Sec. 3.2 assumption ζ).

[72] J. Tauc, Phys. Rev. 95, 1394 (1954).

lated. For the determination of n_k one has 4 equations (1), (23), and (25) with 4 unknowns: $I_1=-I_2$, φ, n_1, n_2. It is necessary to introduce n_k into (1) instead of ζ_k using (8). One obtains

$$I_1=\sigma_1 F+eD_1\frac{dn_1}{dx}+\frac{\sigma_1}{e}Q_1^{**}\frac{1}{T}\frac{dT}{dx}, \tag{35}$$

$$I_2=\sigma_2 F-eD_2\frac{dn_2}{dx}-\frac{\sigma_2}{e}Q_2^{**}\frac{1}{T}\frac{dT}{dx}, \tag{36}$$

where

$$Q_k^{**}=Q_k^{*}-\langle\epsilon_k\rangle_{\text{Av}} \tag{37}$$

are the excess of the mean transfer kinetic energies Q_k^* over the mean kinetic energies

$$\langle\epsilon_k\rangle_{\text{Av}}=\frac{\int_0^\infty \omega_k(\epsilon_k)\epsilon_k e^{-\epsilon_k/\mathrm{k}T}d\epsilon_k}{\int_0^\infty \omega_k(\epsilon_k)e^{-\epsilon_k/\mathrm{k}T}d\epsilon_k}; \tag{38}$$

for spherical energy surfaces $\langle\epsilon_k\rangle_{\text{Av}}=\frac{3}{2}\mathrm{k}T$.

In some cases it will be sufficient to consider a schematical distribution of Δn for which $\Delta n=0$ outside the illuminated part b, c and $\Delta n=\Delta n_s=$const inside this part. We call this assumption (ζ). It is approximately justified in case the illuminated part b, c is large compared with the diffusion length of excess current carriers and variation of the parameters of the semiconductor over a diffusion length is negligible; variation of τ and μ_k along the sample is neglected.

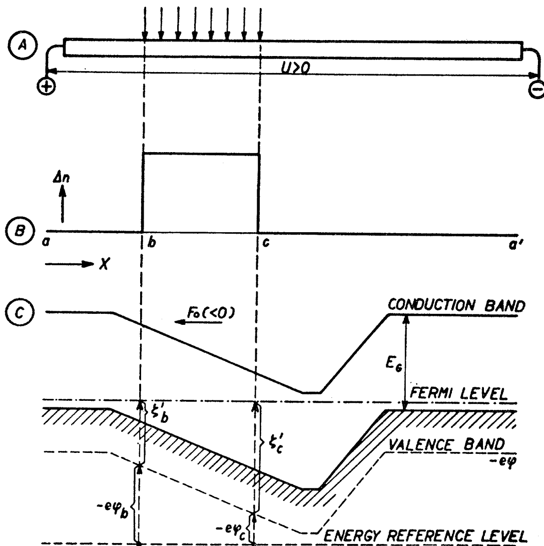

FIG. 5. Bulk photovoltaic effect: A the illuminated sample, B distribution of Δn, C energy levels in the dark.

4. BULK PHOTOVOLTAIC EFFECT

From the point of view of photovoltaic effects, the most important case of inhomogeneity of a semiconductor is an inhomogeneity in distribution of active impurity concentrations. We consider two limiting cases. In the first case the impurity concentration change occurs over a distance long compared with the diffusion length of current carriers; in the second case the change is abrupt. In the first case current carriers are in thermal equilibrium with the lattice; we use the word "bulk" to denote this type of photovoltaic effect. An example of the second case (barrier-layer photovoltaic effect) is the photovoltaic effect in a p-n junction (Sec. 5).

4.1 Basic Equations for the Bulk Photovoltaic Effect

Let us calculate the emf generated between the contacts a and a' in Fig. 1 for the case that in the semiconductor the active impurity concentrations are variable. Denoting the difference between the concentrations of donors and acceptors by $N=N_D-N_A$ we have $dN/dx\neq 0$ at least at some places between b and c. Such a bulk photocell is shown in Fig. 5.

The bulk photo emf is given by the integral (31); we shall perform the integration on assumptions (α), (β), (γ), (δ), and (ϵ). We substitute for $\Delta\zeta_k=\zeta_k-\zeta_{k0}$ from (8) and use the mass-action law

$$n_{10}n_{20}=n_i^2=\text{const}. \tag{39}$$

The emf $U=U_b$ can be expressed as a sum:

$$U=U_c+U_d, \tag{40}$$

where

$$U_c=\frac{\mathrm{k}T}{e}\oint\frac{\mu_1+\mu_2}{\mu_1 n_1+\mu_2 n_2}\frac{\Delta n}{n_{10}}\frac{dn_{10}}{dx}dx, \tag{41}$$

$$U_d=-\frac{\mathrm{k}T}{e}\oint\frac{\mu_1-\mu_2}{\mu_1 n_1+\mu_2 n_2}\frac{d\Delta n}{dx}dx. \tag{42}$$

If U_c is to be different from zero it is necessary that at least at some places between b and c $dn_{10}/n_{10}dx =1/\mathrm{k}T\cdot d\zeta_{10}/dx\neq 0$. This part U_c of the emf is caused by variation of the chemical potential of the assemblies of electrons and holes in the dark along the sample; we denote U_c as a "chemical" emf. The other part of the emf U_d corresponds to the diffusion voltage generated by the gradients of Δn in case electron and hole mobilities are different $\mu_1\neq\mu_2$. We denote U_d as a "diffusion" emf. These notations are analogous to the terminology used in the theory of galvanic cells.

An expression for U is obtained on the assumption of small illumination that is, if everywhere $\Delta\sigma\ll\sigma_0$. For an n-type semiconductor ($n_{10}=N$, $N\gg n_i$), we get

$$U=-\frac{\mathrm{k}T}{e}\frac{2}{1+b}\oint\Delta\sigma\frac{d\rho_0}{dx}dx. \tag{43}$$

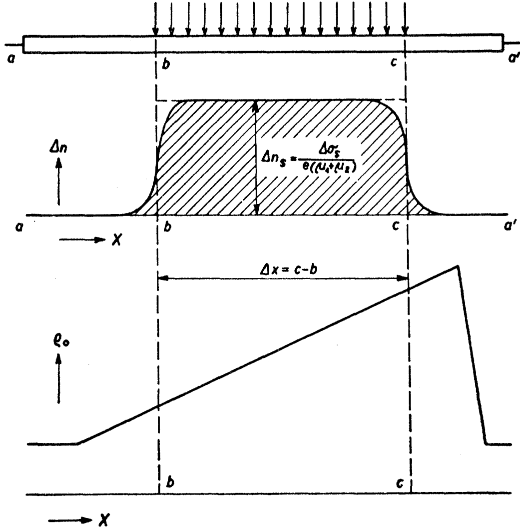

FIG. 6. Example of plot of $\Delta\sigma$ and ρ_0 for calculating the approximation for weak illumination.

An analogous expression for a p-type semiconductor ($n_{20}=-N, -N\gg n_i$) is obtained by changing the sign and putting $1/b$ instead of b. If in the illuminated part $d\rho_0/dx$ is constant then U is proportional to the shaded area as in Fig. 6.

To obtain an idea of the order of magnitude of a bulk emf under small illumination, let us consider a typical numerical example which can be easily realized with germanium: $b=2{,}1$; $\rho_{0c}-\rho_{0b}=15-5=10\ \Omega$ cm, $\sigma_{0,\,\mathrm{av}}\approx 0{,}1\ \Omega^{-1}\,\mathrm{cm}^{-1}$; $\Delta\sigma_s/\sigma_{0,\,\mathrm{av}}=0{,}1$, $\Delta\sigma_s=10^{-2}\,\Omega^{-1}\,\mathrm{cm}^{-1}$; $T=300°\mathrm{K}$. From (43), we obtain $U=0.026\cdot 0.65\cdot 10\cdot 10^{-2}=1.7$ mv.

An equation for U which holds for arbitrary intensity of illumination (compatible of course with our assumptions) can be deduced if for the distribution of Δn assumption (ζ) (Sec. 3.2) is approximately valid. Equation (41) can be then written

$$U_c=\frac{kT}{e}\Delta\sigma_s\int_b^c\frac{d\sigma_{10}}{\sigma_{10}^2+\sigma_{10}\Delta\sigma_s+\sigma_{i1}\sigma_{i2}},\tag{44}$$

where $\sigma_{ik}=e\mu_k n_i$.

Writing $\mathfrak{D}=4\sigma_{i1}\sigma_{i2}-\Delta\sigma_s^2$, the result can be written:
(a) $\mathfrak{D}>0$, it is $\Delta\sigma_s<2(\sigma_{i1}\sigma_{i2})^{\frac{1}{2}}$ (very small illumination)

$$U_c=\frac{kT}{e}\Delta\sigma_s\frac{2}{\sqrt{\mathfrak{D}}}\times\mathrm{arctg}\frac{2(\sigma_{10c}-\sigma_{10b})\sqrt{\mathfrak{D}}}{\mathfrak{D}+(2\sigma_{10c}+\Delta\sigma_s)(2\sigma_{10b}+\Delta\sigma_s)}.\tag{45a}$$

(b) $\mathfrak{D}<0$, it is $\Delta\sigma_s>2(\sigma_{i1}\sigma_{i2})^{\frac{1}{2}}$

$$U_c=-\frac{kT}{e}\Delta\sigma_s\frac{1}{\sqrt{-\mathfrak{D}}}\left(\ln\frac{2\sigma_{10c}+\Delta\sigma_s+\sqrt{-\mathfrak{D}}}{2\sigma_{10c}+\Delta\sigma_s-\sqrt{-\mathfrak{D}}}-\ln\frac{2\sigma_{10b}+\Delta\sigma_s+\sqrt{-\mathfrak{D}}}{2\sigma_{10b}+\Delta\sigma_s-\sqrt{-\mathfrak{D}}}\right).\tag{45b}$$

These expressions are simpler for an extrinsic semiconductor. For an n-type semiconductor we get from (45b) for arbitrary intensity of illumination

$$U_c=-\frac{kT}{e}\ln\frac{1+\Delta\sigma_s/\sigma_{0c}}{1+\Delta\sigma_s/\sigma_{0b}}.\tag{46}$$

Equation (42), giving the part U_d of the emf, can be written

$$U_d=-\frac{kT}{e}\frac{\mu_1-\mu_2}{\mu_1+\mu_2}\oint\frac{d\Delta\sigma}{\sigma_0+\Delta\sigma}.\tag{47}$$

Assuming the distribution (ζ) of Δn one has $d\Delta\sigma\neq 0$ only in the neighborhood of the points $x=b$, c; one easily obtains:

$$U_d=\frac{kT}{e}\frac{\mu_1-\mu_2}{\mu_1+\mu_2}\ln\frac{1+\Delta\sigma_s/\sigma_{0c}}{1+\Delta\sigma_s/\sigma_{0b}}.\tag{48}$$

This holds for a semiconductor of arbitrary type of conductivity.

For the total emf U in a n-type semiconductor, we obtain

$$U=-\frac{kT}{e}\frac{2}{1+b}\ln\frac{1+\Delta\sigma_s/\sigma_{0c}}{1+\Delta\sigma_s/\sigma_{0b}}.\tag{49}$$

The dependence of U on $\Delta\sigma_s$ is illustrated in Fig. 7 for several values of σ_{0c}/σ_{0b}. For very strong illumination $\Delta\sigma_s\gg\sigma_{0c}$ and $\Delta\sigma_s\gg\sigma_{0b}$ the emf approaches a saturation value given by

$$U_{\max}=-\frac{kT}{e}\frac{2}{1+b}\ln\frac{\sigma_{0b}}{\sigma_{0c}}.\tag{50}$$

In the above example $U_{\max}$ is equal to $0.026\cdot 0.65\cdot\ln 3=18.5$ mv.

4.2 Discussion

Let us consider the physical meaning of the "chemical" and "diffusion" parts of U. The generation of U_c

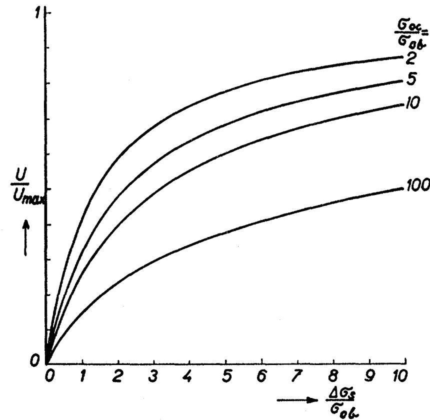

FIG. 7. Dependence of the relative photovoltage from (49) $U/U_{\max}$ on the intensity of illumination characterized by the ratio $\Delta\sigma/\sigma_{0b}$ for different σ_{0c}/σ_{0b}.

is conditioned by the difference in chemical potentials of electrons and holes in the dark at the boundary points of the illuminated part (in other words, by the difference of the Fermi levels relative to the boundaries of energy bands). We see this from (41) which for very strong illumination ($\Delta n_s \gg n_{10}, n_{20}$) on the validity of assumption (ζ) gives

$$U_{c\max} = \frac{1}{e}\int_b^c \frac{d\zeta_{10}}{dx}dx = (\zeta_c' - \zeta_b')/e. \quad (51)$$

We can make the following detailed picture of the process. In Fig. 5, between the points b and c there exists in the dark a certain potential difference $(\zeta_b' - \zeta_c')/e$ because, in thermal equilibrium the electrochemical potential $\zeta' - e\varphi$ is everywhere constant. At every point between b and c there is an electric field F_0. The potential difference between the points b and c is compensated by a potential difference of opposite sign so between the points a and a' the potential difference is zero in the dark. If the condition that the two ends of the semiconductor have the same properties is not fulfilled at least a part of the compensating voltage is situated at the contacts.

If in the part b, c excess current carriers are generated by illumination, the electric field F_0 sets them in motion. When the contacts a and a' are not connected an electric charge is created which causes such a change in the intensity of the field F_0 that the current is annulled. In our case, (Fig. 5) the contact a is charged positively, the contact a' negatively (with our sign convention $U > 0$).

The field intensity in the part b, c decreases by illumination from the dark value $|F_0|$ to the value $|F| = |F_0 - \Delta F$ with $\Delta F > 0$. At every point in part b, c the electric current density produced by the electric field $\sigma_0 F_0$ compensates that produced by diffusion. If, now, the current carrier concentration is increased by illumination by an amount Δn, the electric conductivity increases to a value $\sigma > \sigma_0$ but the diffusion current remains the same, because inside the part b, c in accordance with assumption (ζ) $d\Delta n/dx = 0$. From the equality of both currents we get $|F| < |F_0|$.

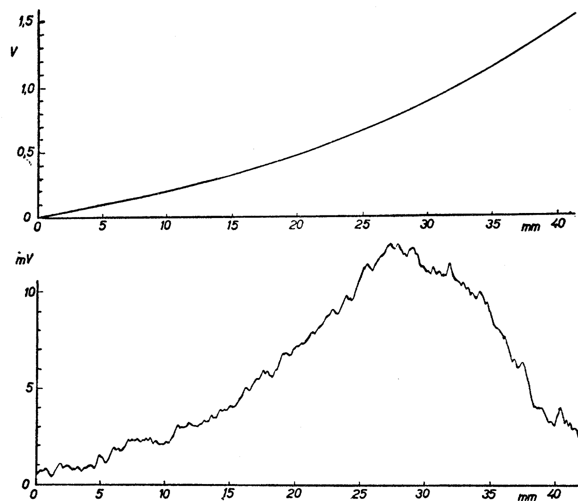

FIG. 8. Example of Trousil's measurement of the bulk photovoltage.

The part ΔF of the electric field is not compensated in the circuit and its integral over x gives the voltage U_c. If the illumination is increased the field intensity $|F|$ decreases. The maximum value that ΔF can attain with very strong illumination is $|F_0|$. In this case the electric field in the part b, c is zero and the potential difference between b and c vanishes. There remains in the circuit the potential difference between c and b which we measure as the maximum emf, $U_{c\max} = -(\zeta_b' - \zeta_c')/e$.

With very strong illumination there exists a close analogy between our photocell and a galvanic cell; in both cases the chemical part of the emf corresponds to the transfer of an electron from the point with a chemical potential ζ_c' to a point with a chemical potential ζ_b'. With weak illumination there is a difference between a photocell and a galvanic cell as the emf of a photocell is a function of the illumination. This is due to the fact that in the photocell the emf is generated only by nonequilibrium current carriers while the conductance of the photocell is determined by all current carriers. When the concentration of excess carriers is very much larger than the concentration of dark carriers the situation is similar to that in a galvanic cell where all current carriers contribute to the generation of the emf. One has a similar case in the photocell proposed by Kramer[73] and later improved by Ohmart.[74] This photocell is constructed of two metal plates of different work functions with a gas between them. The gas is ionized by absorption of radiation. It was shown by experiment that the emf is determined by the contact potential of the metals and is independent of illumination intensity which changes only the internal resistance. Other examples are the photocells described by Nadjakov and Andreitchin[75] which consist of two different metal plates separated by sulfur or other insulator. As the internal resistance is very high, the emf attains its saturation value at low illumination. These examples correspond well with the general point of view on the generation of a "chemical" emf explained in this section.

The other part is the diffusion emf U_d. An electric field arises in those parts of the semiconductor where $d\Delta n/dx \neq 0$ for the case that the electron and hole mobilities are not equal. The direction and intensity of this field are such as to accelerate the motion of current carriers with lower mobility and to slow down the motion of current carriers with larger mobility in order

[73] J. B. Kramer, Electrician 93, 497 (1924).
[74] P. E. Ohmart, J. Appl. Phys. 22, 1504 (1951).
[75] G. Nadjakov and R. Andreitchin, Compt. rend. acad. bulgare sci. 5, 9 (1952); *ibid.*, 7, 13 (1954); Izvest. Ban, Ser. Fiz. 2, 293 (1951).

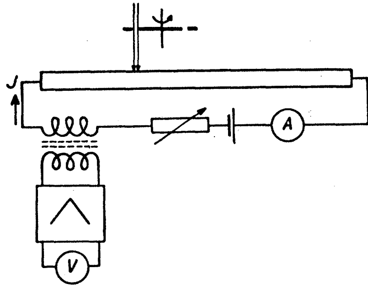

FIG. 9. Compensation method for measuring the bulk photovoltage.

to make the resultant electric current zero. It is usual to denote this kind of electric field as a "Dember field." The voltages generated in the vicinity of both points b, and c [where $d\Delta n/dx \neq 0$ according to assumption (ζ)] are mutually compensated in a homogeneous semiconductor. This is not the case if at the points b, and c the conductivities are not the same [see Eq. (48)] and the resultant emf U_d is measured between a, and a'. This emf is analogous to the diffusion emf generated in a galvanic element between two electrolytes. Just as with galvanic cells it is possible to design semiconductor photocells in which $|U_d|$ is small compared with $|U_c|$.

4.3 Comparison with Experiment and Applications

The first experimental investigation[45,76] of the theory of the bulk photovoltaic effect was carried out by Trousil[46] on long samples cut from germanium single crystals drawn from the melt. An example of Trousil's measurement is given in Fig. 8. In the upper figure there is shown the voltage V measured along the sample in the dark with a current flowing through it; the resistivity $\rho_0 \sim dV/dx$. The lower figure shows the emf generated by a spot of light moved along the sample and measured with a recording galvanometer. Qualitative agreement with the theory is apparent, e.g., the maximum of the emf is situated at the point of the highest value of d^2V/dx^2. From the emf curve small inhomogeneities in the distribution of the concentrations of impurities can be detected even if they are too small to be observable by measurement of conductivity along the sample.

Frank [77] used this effect to work out a highly sensitive compensation method for the determination of inhomogeneities of semiconductor single crystals. His experimental arrangement is shown schematically in Fig. 9; here the bulk emf is compensated by the photoconductive signal $J\delta R$, where δR is the change of the circuit resistance by illumination. If the current density J/Q (Q is the cross section of the sample) is so chosen that the voltmeter has zero deviation then for an n-type semiconductor

[76] J. Tauc, Czechosl. J. Phys. **5**, 300 (1955).
[77] H. Frank, Czechosl. J. Phys. **6**, 433 (1956).

$$\frac{d\sigma_0}{dx}=\frac{e}{kT}\frac{2}{b+1}\frac{J}{Q}. \tag{52}$$

Using this method Frank made a quantitative comparison of the theory[45] of the bulk photovoltaic effect and obtained good agreement. Recently Lashkarev and Romanov[78] have published a paper on the bulk photovoltaic effect investigated with a very narrow light spot.

5. BARRIER-LAYER PHOTOVOLTAIC EFFECT

5.1 Basic Equation of a p-n Junction Photovoltaic Cell

Between a p-type and an n-type semiconductor there is, in the dark, a potential barrier of height $\varphi_{b0}=|\zeta_P'-\zeta_N'|$. This barrier can be made very thin and the electric field within it can attain such high values that the change in potential energy over a distance of the same order of magnitude as the mean free path is comparable with the mean thermal energy of an electron or greater. Then (1) is no longer valid; inside such a barrier some quantities such as chemical potentials lose their meaning. However, it is easy to describe another limiting case when the thermal energy of an electron is negligible compared with the energy the electron acquires over the mean free path. It is then usual to speak of the so-called "diode" theory to stress the fact that, in analogy with the situation met with in vacuum tubes, the electron motion is determined primarily by electric fields and influenced little by electron-ion or electron-electron collisions. Of course, this theory holds only in a limited space, in a p-n junction or in its immediate neighborhood. In other regions (1) is valid. It is thus possible to use (1) and respect the regions where the electron motion is described by the diode theory by convenient boundary conditions.

Let us consider the photocell shown in Fig. 10. The contacts here are again connected to the semiconductor of the same properties. The left p-n junction is illuminated. The illumination extends on both sides of the junction over distances which are large compared with carrier diffusion lengths. The p- and n-type semiconductors are assumed to be homogeneous (n_{k0}=const). The potential distribution is drawn in the lower figure.

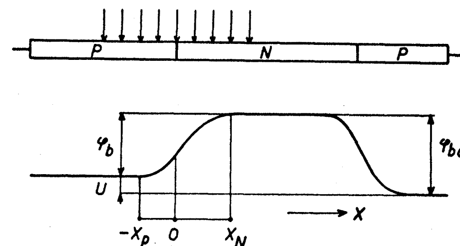

FIG. 10. p-n junction photocell. For the calculation the cross section of the semiconductor is assumed to be unity.

[78] V. E. Lashkarev and V. A. Romanov, Trudy Inst. fiz. Akad. Nauk USSR, Kiev **7**, 50 (1956).

The diode theory holds between $-x_P$, x_N. Calculation of φ_{b0} and x_P, x_N can be based[57,58] on (26). The barrier thicknesses x_P+x_N are assumed to be small compared with the diffusion lengths of carriers so recombination inside the barrier can be neglected. In regions outside the barrier we assume that $n_{2N} \ll n_{1N}$, $n_{1P} \ll n_{2P}$ (not very great illumination). Then the electric fields are small and the current densities are determined by diffusion. If assumptions (α), (β), (γ), (δ), and (ϵ) are valid we get from (35) and (36) for current densities

$$I_k = \pm kT\mu_k \frac{dn_k}{dx} \quad \begin{matrix} + \text{ for } k=1, \\ - \text{ for } k=2. \end{matrix} \tag{53}$$

We consider holes in the n-type material. Substituting from (53) into (23) we get the following equation for $\Delta n = n_k - n_{k0}$:

$$\frac{d^2\Delta n}{dx^2} - \frac{\Delta n}{L_{2N}^2} = -\frac{g_f\tau}{L_{2N}^2}. \tag{54}$$

For boundary conditions we take

$$x=\infty, \quad \Delta n = 0, \tag{55}$$

$$x = x_N, \quad n_{2N} = n_{2P} e^{-e\varphi_b/kT}, \tag{56}$$

where φ_b is the barrier height. The boundary condition (56) expresses the ratio of the concentrations of holes on the two sides of the barrier by the Boltzmann factor as required by classical statistics. We have assumed further that the hole concentration at the point $-x_P$ is so great that its diminution by the diffusion of holes into the n-type material is negligible; we thus have at the point $-x_P$, $n_{2P} = n_{2P0}$.

It is easy to find the solution Δn of (54) with boundary conditions (55) and (56). Putting this solution into (53) we get for the current density

$$I_2 = \frac{kT\mu_2}{L_{2N}} (n_{2P0} e^{-e\varphi_b/kT} - n_{2N0} - \tau g_f) e^{-x - x_N/L_{2N}}. \tag{57}$$

In the dark, for the barrier height φ_{b0}, from (56)

$$n_{2N0} = n_{2P0} e^{-e\varphi_{b0}/kT}. \tag{58}$$

Using φ_{b0} we obtain for the current density at the point x_N:

$$I_{2N} = \frac{kT\mu_2}{L_{2N}} n_{2N0} (e^{-e(\varphi_b - \varphi_{b0})/kT} - 1) - \frac{kT\mu_2}{L_{2N}} g_f\tau. \tag{59}$$

For electron current density in the p-type material at the point $-x_P$ we get an analogous expression. As the electron and hole currents do not diminish by recombination inside the barrier the total current density is $I = I_{1N} + I_{2N} = I_{1P} + I_{2P} = I_{2N} + I_{1P}$.

The barrier height in the dark φ_{b0} is compensated in the circuit (Fig. 10) so for measurable voltage we have $U = -(\varphi_b - \varphi_{b0})$. Thus, we obtain the basic equation for the photocell considered

$$I + I_f = I_s(e^{eU/kT} - 1). \tag{60}$$

I_s is the saturation current density of the photocell in the dark, i.e., I for $I_f = 0$ and $-U \gg kT/e$:

$$I_s = kT\left(\frac{\mu_1 n_{1P0}}{L_{1P}} + \frac{\mu_2 n_{2N0}}{L_{2N}}\right). \tag{61}$$

$-I_f$ is the short circuit current density of the photocell

$$I_f = eg_f(L_{1P} + L_{2N}). \tag{62}$$

I_f is the number of excess electron-hole pairs per cm² reaching the region of the potential barrier by diffusion per sec.

The derivation of formula (60) is analogous to that used by Shockley[57] in his theory of p-n junction rectifiers. Expression (60) reduces to Shockley's equation (4.22) for $I_f = 0$. For other constructions of p-n junction photocells several formulas are given in the literature.[79,80]

The emf which follows from (60) with $I = 0$ is

$$U_c = \frac{kT}{e} \ln\left(1 + \frac{I_f}{I_s}\right). \tag{63}$$

An expression of this form was deduced by Fan[81] and experimentally verified by Becker and Fan.[23] It follows from assumptions on which (63) was derived that U_c cannot exceed the height of the barrier in the dark φ_{b0} and must saturate at very high illumination when (63) is no longer valid. When U_c approaches φ_{b0}, the diode theory ceases to hold as the electric field in the barrier is diminished; we then have a transition to the bulk photovoltaic effect—a problem which has not yet been studied.

We have denoted the emf expressed by (63) as U_c because it actually corresponds to the difference in the chemical potentials and may therefore be denoted as a "chemical" emf. Calculation of the diffusion emf U_d is the same as given in Sec. 4. Under the conditions assumed in the present section and at small illumination we get approximately

$$U_d = \frac{kT}{e} \frac{b-1}{b+1} (\rho_{0P} - \rho_{0N}) \Delta\sigma_s. \tag{64}$$

The p-n junction is usually constructed so that p- and n-type materials have high conductivities so that $\Delta\sigma_s/\sigma_{0P} \ll 1$, $\Delta\sigma_s/\sigma_{0N} \ll 1$ and $|U_d|$ is usually negligible compared with U_c.

5.2 Comparison of the Barrier-Layer and the Bulk Photovoltaic Effects

The bulk and the barrier-layer photovoltaic effects are two limiting cases of one and the same physical phenomenon; in both cases the emf is generated by an

[79] J. Tauc, Českosl. čas. fys. 4, 158 (1954).
[80] R. L. Cummerow, Phys. Rev. 95, 16 (1954).
[81] H. Y. Fan, Phys. Rev. 75, 1631 (1949).

internal electric field and only the details of the process are different. The first case approaches the thermal equilibrium state, the other is radically different from it. If we denote the time an electron spends in the active space of the photocell τ_u, then for a barrier layer photocell $\tau_u \ll \tau$, for a bulk photocell $\tau_u \gg \tau$.

The emf U_c with very strong illumination attains in both cases the same saturation value $(\zeta_c' - \zeta_b')/e$. The maximum value this expression can have in a given semiconductor is approximately the value E_G/e. This is true for the case that at the point b the material is highly doped with p-type impurities and at the point c with n-type impurities. Even if the maximum emf is the same for both effects the short circuit current of a barrier layer photocell is usually much higher for the appropriate geometry of illumination than that of a bulk photocell. Consequently, the barrier layer photocell transforms radiation energy into electrical energy with a higher efficiency than a bulk photocell. Indeed, in the former case all electrons and holes created in the active space of the photocell take part in the generation of the short circuit current while in the latter case the short circuit current is diminished by recombination. We shall make a rough quantitative comparison of both cases.

Let us consider a p-n junction photocell of unit cross section which is transversely illuminated with a narrow light spot so that all incident photons are absorbed in the potential barrier space. With quantum efficiency equal to unity these N_f photons per second give rise to a short circuit current $|I_{sc}^{\text{barrier}}| = eN_f$. Let the same number N_f photons/sec be absorbed in a bulk photocell of unit cross section; the illumination takes place over a distance $c-b=\Delta x$. The added carrier concentration is $\Delta n_s = g_f\tau = N_f\tau/\Delta x$ and the short circuit current $|I_{sc}^{\text{bulk}}| = |U|/R$, where U is the bulk photo emf (Sec. 4.1) and R the resistance of the illuminated photocell. For strong illumination ($\Delta n_s \gg n_{10}$ and n_{20}), we obtain for the ratio of both short circuit currents

$$|I_{sc}^{\text{bulk}}| / |I_{sc}^{\text{barrier}}| = \tau/\tau', \qquad (65)$$

where $\tau' = \Delta x/(\mu_1+\mu_2)F'$, $F' = U/\Delta x$. Putting typical values for germanium into this formula ($\mu_1+\mu_2 = 1700 + 3600 = 5300$ cm²/vs, $U_{\max} \approx 0.6$ v, $\tau = 10^{-4}$ sec) and choosing $\Delta x = 2$ cm ($\gg L_1, L_2$) we get $\tau' = 10^{-3}$ sec and $|I_{sc}^{\text{bulk}}| = 0, 1 |I_{sc}^{\text{barrier}}|$.

However, the bulk photocell can be more advantageous from the point of view of efficiency than a barrier layer photocell for the case that the radiation cannot be concentrated in the barrier layer. This can be the case for high energy radiation which is little absorbed in the semiconductor and cannot be concentrated by optical means. Let us consider a case that the barrier layer photocell is irradiated over distances large compared with L_{1P}, L_{2N} on both sides of the barrier. This case was treated in Sec. 5.1; from (62) we obtain $|I_{sc}^{\text{barrier}}| = I_f = e(L_{1P}+L_{2N})g_f$. Then we have

$$\frac{|I_{sc}^{\text{bulk}}|}{|I_{sc}^{\text{barrier}}|} = \frac{\tau}{\tau'} \frac{\Delta x}{L_{1P}+L_{2N}}. \qquad (66)$$

In the numerical example considered, $L_{1P} = 9.6 \cdot 10^{-2}$ cm, $L_{2N} = 6.6 \cdot 10^{-2}$ cm, $|I_{sc}^{\text{bulk}}| = 1.25 |I_{sc}^{\text{barrier}}|$.

We shall add some general remarks concerning the energy conversion efficiency by a photocell. From the point of view of thermodynamics there is no reason for this efficiency not to approach 100%. Of course this is possible only for a photocell so constructed that $|U_{\max}| = E_G/e$ and illuminated by monochromatic radiation of wavelength hc/E_G. With a radiation of shorter wavelength the efficiency is always smaller; with a high energy radiation (Sec. 1.3) the maximum efficiency can be only E_G/ϵ. An ideal photocell should have an infinite dark resistance [see (63)]; it is desirable to have I_s very small so that $|I| \approx I_f$ even if $U \neq 0$ and zero resistance at illumination for the internal losses to be small.

5.3 Classification of Simple Photovoltaic Effects

As a consequence of the preceding considerations, we can divide photovoltaic effects into barrier layer and bulk effects. We can further distinguish between effects at the contacts or inside a semiconductor crystal.

It is necessary to consider how the well-known Dember effect can be put into this classification. The Dember effect is the generation of an emf in a homogeneous semiconductor without any barrier layers. We consider here, as everywhere in the present paper, only the stationary case and exclude therefore the Dember effect observed with interrupted illumination.[82–86] The inhomogeneity of the circuit necessary from our point of view for the generation of a stationary emf is realized here by the fact that a part of the circuit d, d' is of semiconductor, the other part $(a,d; d',a')$ of metal as shown in Fig. 11. The nonrectifying semiconductor-metal contact is essential for the stationary Dember effect. Table I contains the proposed classification of simple photovoltaic effects.

In the present paper we do not consider generation of an emf at semiconductor-metal contacts. This is more difficult to discuss in detail owing to the more complicated structure of these contacts that is not yet quite understood.

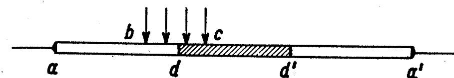

FIG. 11. Dember effect.

[82] L. Bergmann, Physik. Z. **33**, 209 (1932).
[83] L. Bergmann, Z. Physik **100**, 50 (1936).
[84] S. M. Ryvkin, Zhur. Tech. Fiz. **18**, 1521 (1948); **19**, 286 (1949).
[85] K. B. Tolpyvo, Izvest. Akad. Nauk, Ser. Fiz. **16**, 46 (1952).
[86] Moss, Pincherle, and Woodward, Proc. Phys. Soc. (London) **B66**, 743 (1953).

TABLE I. Classification of simple photovoltaic effects.

Photovoltaic effects	Barrier layer	Nonbarrier layer
Noncontact	In p-n junction photocells	Bulk photovoltaic effect
Contact	In barrier-layer photocells (such as cuprous oxide photocells) In point contact photocells	One contact illuminated: Dember effect Both contacts illuminated: Effects observed by Nadjakov and Andreitchin

6. SOME MORE COMPLICATED PHOTOVOLTAIC EFFECTS

An essential condition for the generation of an emf in a semiconductor, following the preceding considerations, is a chemical potential difference between the boundaries of the illuminated part b, c. In cases dealt with in Sec. 4 and 5 this difference was realized by a donor or acceptor concentration gradient. In this section we discuss two other examples of this rule when the chemical potential difference is realized by a magnetic field or a temperature gradient.

6.1 Photoelectromagnetic Effect in a Nonhomogeneous Magnetic Field[87]

Landau[88] was the first to show that the chemical potential of an assembly of free electrons depends on the intensity of the magnetic field. Therefore, if the magnetic field H situated in a plane perpendicular to the axis of the sample at the point b differs from that at the point c an emf is generated between the contacts a, and a'. Using Landau's expression for the thermodynamic potential of the assembly of free electrons we obtain from (31) for the case shown in Fig. 12 the following equation for U_c (with validity of assumptions (α), (β), (γ), (δ), (ϵ), and (ζ) and for $|H|\ll \mathrm{k}Tm_k/\beta m$):

$$U_c=-\frac{\mathrm{k}T}{e}\Delta t_1\left\{1-\frac{1}{6}\left[\left(\frac{m}{m_1}\right)^2+\left(\frac{m}{m_2}\right)^2\right]\right\}\times\frac{\beta^2(H_c^2-H_b^2)}{\mathrm{k}^2T^2}. \quad (67)$$

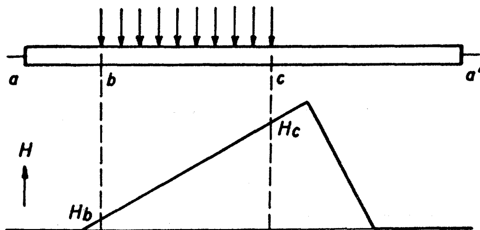

FIG. 12. Photoelectromagnetic effect in a nonhomogeneous magnetic field.

[87] J. Tauc, Czechosl. J. Phys. **6**, 421 (1956).
[88] L. Landau, Z. Physik **64**, 629 (1930).

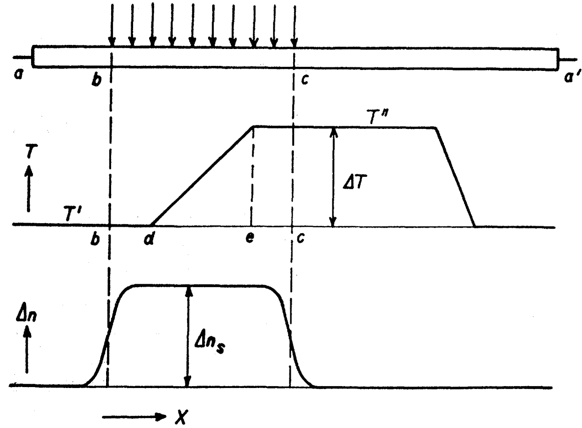

FIG. 13. Scheme of the photothermoelectric effect.

We have assumed spherical energy surfaces in the Brillouin zone and used the effective mass concept for electrons and holes. β denotes the Bohr magneton, $\Delta t_1=t_1-t_{10}$.

This emf differs from that observed by Kikoin and Noskov[89] and others,[90,91] in a homogeneous magnetic field. In the case of Kikoin and Noskov's photoelectromagnetic effect the emf is generated perpendicularly to the magnetic field and to the direction of illumination. It differs also with regard to dependence on magnetic field, which for small fields is linear for the Kikoin-Noskov effect and quadratic for U_c as given by (67). If the direction of the magnetic field is parallel to the direction of illumination the Kikoin-Noskov emf should be theoretically zero but the emf U_c given by (67) is not.

The experimental determination of this emf should be interesting as it could give us some information on effective masses just as cyclotron resonance or magnetic susceptibility measurement. In some materials, such as InSb, U_c is expected to attain measurable values. But this emf is masked by a much stronger emf generated at the boundaries of the illuminated part in a nonhomogeneous magnetic field which acts on the diffusion currents of electrons and holes. With assumptions (α) to (ζ), for small illumination $\Delta\sigma_s/\sigma_0\ll 1$, small induction B of the magnetic field ($B\mu_2\ll 1$) and an n-type semiconductor we obtain for this emf the approximate expression

$$U_e=\frac{\mathrm{k}T}{e}\frac{\Delta\sigma_s}{\sigma_0}\mu_2^2(B_c^2-B_b^2). \quad (68)$$

This emf was actually found experimentally[87] in InSb.

[89] J. K. Kikoin and M. M. Noskov, Physik. Z. Sowjetunion **5**, 586 (1934).
[90] P. Aigrain and H. Bulliard, Compt. rend. **236**, 595 and 672 (1953).
[91] H. Bulliard, Ann. phys. **15**, 52 (1954).

6.2 Photothermoelectric Effect

Another way[92] of realizing the chemical potential difference is by putting the points b, c at different temperatures T', T''. The principle of measurement of this effect is given in Fig. 13. The normal thermoelectric voltage is not generated in the circuit as the points a, and a' are at the same temperature. An experimental arrangement is illustrated in Fig. 14. A thin semiconductor sample is in good thermal contact with two isolated metal blocks and is illuminated with interrupted light. If the temperature of the blocks is different a signal can be measured by means of an alternating current amplifier and a valve voltmeter; the normal thermoelectric voltage is thus eliminated in this experimental arrangement.

The expression for the emf originally given[92] was generalized by Van der Pauw and Polder[93] who took into account the temperature dependence of E_G and b. Their expression is readily deduced from (29) and (30)

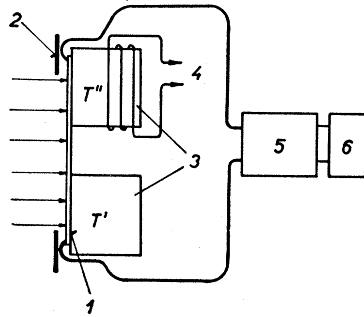

FIG. 14. Experimental arrangement for observing the photothermoelectric effect. 1. The illuminated sample. 2. Diaphragms screening the contacts. 3. Anodized aluminium blocks. 4. Heating of the upper block. 5 and 6. Narrow band amplifier with valve voltmeter.

with the usual assumptions (α), (β), (γ), (ϵ), and (ζ) and $\Delta T = T'' - T' \ll T'$, $\Delta\sigma_s/\sigma_b \ll 1$:

$$U_{PTE} = \frac{\mathrm{k}\Delta T}{e}\left\{\frac{b-1}{b+1} + \frac{b}{b+1}\frac{N}{bn_{10}+n_{20}} \times\left[\frac{Q_1^{**}+Q_2^{**}}{\mathrm{k}T} + \frac{1}{\mathrm{k}}\frac{dE_G}{dT}\right] - \frac{1}{b+1}\frac{T(n_{10}+n_{20})}{bn_{10}+n_{20}}\frac{db}{dT}\right\}\frac{\Delta\sigma_s}{\sigma_0}. \quad (69)$$

From the measurement of this emf the sum $Q_1^{**}+Q_2^{**} = Q_1^*+Q_2^* - \langle\epsilon_1\rangle_{\mathrm{Av}} - \langle\epsilon_2\rangle_{\mathrm{Av}}$ can be determined. Under favorable circumstances the determination of this sum may give certain information on the carrier scattering mechanism (definitions of Q_k^* and $\langle\epsilon_2\rangle_{\mathrm{Av}}$ in Secs. 2.3 and 3.2).

7. OTHER CASES OF GENERATION OF AN emf

Photoelectric generation of nonequilibrium current carrier concentration is not essential for the production of an emf in semiconductors. A nonequilibrium carrier

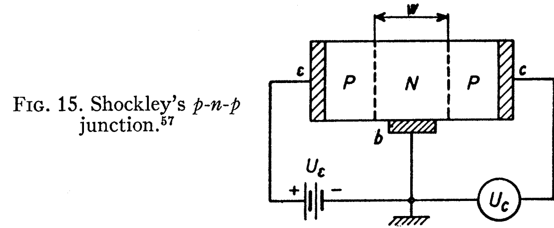

FIG. 15. Shockley's p-n-p junction.[57]

concentration can be generated by other means as well. We shall now deal briefly with some examples. Their theory can be developed from the same basic ideas as in the preceding cases, only the geometry and consequently carrier concentration distribution is usually more complicated.

A very important method for the production of excess carrier concentration is current injection which forms the basis for the functioning of the transistor. Bardeen considers[94] how holes injected by a point contact emitter into n-type germanium produce an emf at another point contact (collector) situated in the neighborhood of the first. His theory is shown to be in agreement with experiments performed by Pearson. Shockley[57] deals with a basically similar case, with the difference that the emitter and the collector are formed by a p-n junction. The arrangement Shockley considers is illustrated in Fig. 15. For U_c he deduces the following expression (on the assumption that $U_\epsilon > \mathrm{k}T/e$):

$$U_c = U_\epsilon - \frac{\mathrm{k}T}{e}\ln\cosh\frac{2w}{L_{2N}}. \quad (70)$$

L_{2N} is the hole diffusion length in n-type material, U_ϵ is the emitter voltage.

An emf may also be generated[95,96] in the case that nonequilibrium carrier concentration is produced in sharp temperature gradients. For a temperature drop concentrated within a distance shorter than the carrier diffusion length a nonequilibrium concentration is produced which is positive ($\Delta n > 0$) in regions of lower temperature and negative ($\Delta n < 0$) in regions of higher temperature. For instance, for an n-type semiconductor for the case that the temperature drop is concentrated

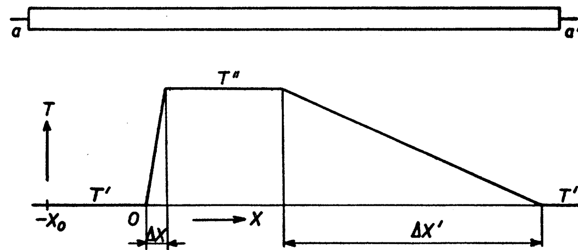

FIG. 16. Principle of measuring the Benedicks effect.

[92] J. Tauc, Czechosl. J. Phys. 5, 528 (1955).
[93] L. J. van der Pauw and D. Polder, J. Electronics 2, 239 (1956).
[94] J. Bardeen, Bell System Tech. J. 29, 469 (1950).
[95] J. Tauc, Czechosl. J. Phys. 3, 282 (1953).
[96] J. Tauc, Czechosl. J. Phys. 6, 108 (1956).

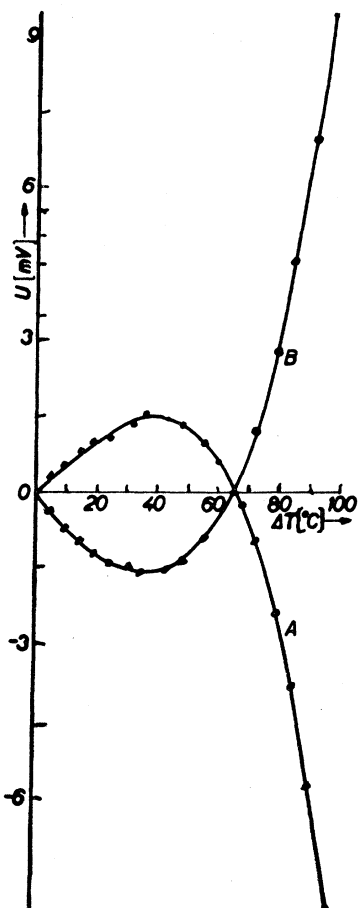

FIG. 17. Trousil's measurement of the Benedicks effect in germanium. The curves A and B correspond to both directions of the temperature drop.

within a distance shorter than the hole diffusion length one obtains (assuming $|\Delta n| \ll bn_{10}$):

$$\Delta U = \frac{\mathrm{k}\Delta T}{e}\left[\frac{Q_1^* + Q_2^*}{\mathrm{k}T} + (b-1)\right]\frac{n_{20}(T'') - n_{20}(T')}{2bn_{10}}. \quad (71)$$

We have denoted this emf as ΔU to emphasize that it adds to the normal thermoelectric voltage and causes its dependence on the temperature gradient—the so-called Benedicks effect. In the circuit shown schematically in Fig. 16 both the ends a, a' are at the same temperature and the normal thermoelectric voltage is zero. In the semiconductor two temperature drops of opposing sign are present, the right one occurring over a distance much longer than the diffusion length (so that here $\Delta U = 0$), the left one at a distance shorter than the diffusion length. Under these conditions the emf measured between a, a' is ΔU. This experiment[95] was realized by Trousil.[97] The result is shown in Fig. 17. As the sample was not quite homogeneous a small ordinary thermoelectric voltage was also generated. However, owing to strong temperature dependence of n_{20} in (71), ΔU rapidly increases with temperature difference and is much greater than the ordinary thermoelectric voltage at higher temperatures T''. This effect is much more easily measurable than the Benedicks effect in metals[98,99] as it is much greater.

If a potential barrier is situated in the neighborhood of a sharp temperature gradient, e.g., at the point $-x_0$ in Fig. 16 an emf is generated in close analogy with the experiments described.[94,57] These effects were actually observed when measuring the thermoelectric voltage in germanium for the case that a sharp metal point was used as one contact. Under suitable conditions one then gets a qualitatively similar temperature dependence[100] of the thermoelectric voltage as in Fig. 17. It is probable that in this way it is possible to explain[101] some observations by Granville and Hogarth[102] concerning an anomalous temperature dependence of the thermoelectric voltage measured with a metal point contact on polished surfaces of Ge or PbS crystals.

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