Nature of the thermopower in bipolar semiconductors

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(Received 17 February 1994; revised manuscript received 13 October 1994)

The thermo-emf in bipolar semiconductors is calculated. It is shown that it is necessary to take into account the nonequilibrium distribution of electron and hole concentrations (Fermi quasilevels of the electrons and holes). We find that electron and hole electric conductivities of contacts of semiconductor samples with connecting wires make a substantial contribution to thermo-emf.

INTRODUCTION

In calculating thermo-emf and explaining its nature, it is common to consider at first the unipolar case.[1] The physical transparency of this phenomenon and the clearness of calculation lead to the following paradoxical results: in the case of a bipolar medium the situation seems to be equally obvious, and so the same calculation scheme is used.[1] The aim of this paper is to show that the situation changes in bipolar media in principle, from the point of view of both the physics of the proceeding processes and the methods of thermo-emf calculations.

Let us begin with the unipolar situation. Dating back to the paper of Thomson[2] in 1856 the theory of the origin of the thermo-emf in this case has found its most precise description in the publications of Seeger and Kaydanov and Nuramski.[3] It is necessary to connect the electric circuit (Fig. 1) for determining the thermo-emf in the case of the absence of electric current (broken circuit). A semiconductor sample whose thickness is $2a$ $(-a \leq x \leq a)$ contacts with a heater with temperature T_1 on the surface $x = -a$ and with a cooler with temperature T_2 on the surface $x = +a$. The connecting wires are made of the same material (metal) and are hooked up to the terminals of a measuring compensating circuit which allows us to measure the difference of voltage φ_b and φ_c in the absence of an electric current. Leads of connecting wires have equal temperatures [for example, $T^* = (T_1 + T_2)/2$] at points b and c. As follows from Ohm's law, for a closed

electric circuit $V = j(R + r)$ (V is the emf of the power source, r is the source's resistance, R is the resistance of the external load, and j is the density of the electric current). If $R \to \infty$ (broken circuit), then the density of electric current $j \to 0$ and $V = jR = \varphi_c - \varphi_b$.[4]

Since the electron's chemical potentials $\mu_n(x)$ are equal in the points b and c, then

$$\varphi_c - \varphi_b = (\tilde{\mu}_n^b - \tilde{\mu}_n^c)/e, \tag{1}$$

where $\tilde{\mu}_n(x) = \mu_n(x) - e\varphi(x)$ is an electrochemical potential. At the same time,

$$\tilde{\mu}_n^b - \tilde{\mu}_n^c = \int_c^b \frac{d\tilde{\mu}_n(x)}{dx}\,dx. \tag{2}$$

As is well known, the expression for the density of the electric current is of the form[1]

$$\mathbf{j}_n = \sigma_n(x)\left(\nabla\frac{\tilde{\mu}_n(x)}{e} - \alpha_n(x)\nabla T\right), \tag{3}$$

where $\sigma_n(x)$ is the electric conductivity and $\alpha_n(x)$ is the thermoelectric power. In the absence of an electric current $d\tilde{\mu}_n(x)/dx = e\,\alpha_n(x)dT/dx$. Let us emphasize that this correlation is correct all over the circuit, where $\sigma_n(x) \neq 0$, e.g., outside the region $[b, c]$, where $\sigma_n(x) \to 0$ (this condition provides $\mathbf{j}_n = \mathbf{0}$ everywhere in the circuit). Therefore the expression (2) can be rewritten in the form

$$\tilde{\mu}_n^b - \tilde{\mu}_n^c = \int_c^b e\,\alpha_n(x)\frac{dT}{dx}\,dx$$
$$= \int_{T^*}^{T_2} e\,\alpha_M\,dT + \int_{T_2}^{T_1} e\,\alpha_n\,dT + \int_{T_1}^{T^*} e\,\alpha_M\,dT,$$

where α_n and α_M are the values of $\alpha_n(x)$ in the semiconductor and in the connecting wires. Finally we have for the difference $\varphi_c - \varphi_b$, which coincides with the thermo-emf V of the broken circuit,
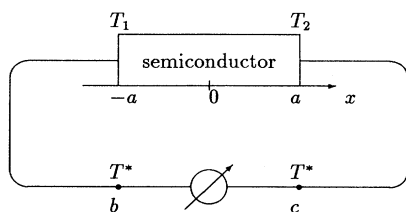

FIG. 1. The electric circuit for measuring of thermo-emf.

$$V = \varphi_c - \varphi_b = (\alpha_n - \alpha_M)(T_1 - T_2). \tag{4}$$

To simplify the calculations we have assumed that $T_1 - T_2 \ll T^*$ which does not restrict the generality. Since usually $|\alpha_M| \ll |\alpha_n|$, then

$$V = \alpha_n(T_1 - T_2). \tag{5}$$

The last expression coincides formally with $\int_{-a}^{+a} \nabla[\varphi - (\mu_n/e)]\, dx$.

Thus the general scheme of calculating the thermo-emf comes to the following for a unipolar broken circuit. The gradient of the electrochemical potential $\nabla\tilde{\mu}_n(x)$ is obtained by setting expression (3) equal to zero. Then integration of $\nabla\tilde{\mu}_n(x)$ in the anticlockwise direction (together with multiplying by e^{-1}) gives the value of the thermo-emf. It is important to emphasize that, as above, the extreme points of the circuit (b and c) would have the same temperatures.

It follows from (2), in a unipolar medium, that even if the condition of quasineutrality is not fulfilled and nonequilibrium electrons (this notion will be defined more exactly below) arise, the gradient of concentration of these carriers n does not give a contribution to the thermo-emf [the summand $(\partial\mu_n/\partial n)\nabla n$ disappears from the expression for V]. This argument confirms the following idea of Ioffe:[5] the potential difference created by the bulk concentration's gradient is compensated by the contact potential difference ("diffusion voltages") on the boundaries $+a$ and $-a$.

Let us note in conclusion that the obviousness of the above scheme is lost when thermo-electric current flows in a closed circuit [$j_n \neq 0$, see Eq. (13)].

I. BIPOLAR SEMICONDUCTORS: TRADITIONAL APPROACH

The systems of equations for electrons and holes are analogous to (3):[1,6]

$$\mathbf{j}_n = \sigma_n(x)\left[+\nabla\frac{\tilde{\mu}_n(x)}{e} - \alpha_n(x)\nabla T\right],$$

$$\mathbf{j}_p = \sigma_p(x)\left[-\nabla\frac{\tilde{\mu}_p(x)}{e} - \alpha_p(x)\nabla T\right]. \tag{6}$$

Here $\mathbf{j}_p$ is the density of the hole electric current, $\sigma_p(x)$ and $\alpha_p(x)$ are the electric conductivity and thermoelectric power of the holes [$\alpha_n(x)$ and $\alpha_p(x)$ have opposite signs],

$$\tilde{\mu}_p = -\varepsilon_g - \tilde{\mu}_n = \mu_p + e\varphi \tag{7}$$

is the hole electrochemical potential,[1] and ε_g is the band gap. It is important to emphasize that in expressions (6) $\nabla\mu = (\partial\mu/\partial T)\nabla T$ usually. The full current $\mathbf{j}$ is equal to

$$\mathbf{j} = \mathbf{j}_n + \mathbf{j}_p = 0, \tag{8}$$

if a bipolar semiconductor is represented as in Fig. 1.

It is easy to obtain $\nabla[\tilde{\mu}_n(x)/e]$ from (8) taking into

account (6) and knowing that $\nabla\tilde{\mu}_p = -\nabla\tilde{\mu}_n$ [see (7)],

$$\nabla\left[\frac{\tilde{\mu}_n(x)}{e}\right] = \frac{1}{\sigma(x)}[\sigma_n(x)\alpha_n(x) + \sigma_p(x)\alpha_p(x)]\nabla T,$$

$$\sigma(x) = \sigma_n(x) + \sigma_p(x).$$

Then we find the thermo-emf V (it is assumed that $\alpha_{n,p} \gg \alpha_M$ and $T_1 - T_2 \ll T^*$ as above):

$$V = \int_c^b \nabla\left[\frac{\tilde{\mu}_n(x)}{e}\right]dx = \frac{1}{\sigma}(\sigma_n\alpha_n + \sigma_p\alpha_p)(T_1 - T_2). \tag{9}$$

This expression, especially the method of the calculation, causes serious objections. Really, the electron concentration and hole concentration should be lower in the heating lead in the stationary state due to thermodiffusion if bulk and surface recombinations are absent. In contrast, these concentrations should increase in the cooling lead. On the one hand, this causes the appearance of appreciable diffusion currents[7] in expression (6) [$\nabla\mu_n = (\partial\mu_n/\partial n)\nabla n$]. On the other hand, it leads to a violation of relation (7). Two Fermi quasilevels $\tilde{\mu}_n$ and $\tilde{\mu}_p$ arise instead of a single level of the electrochemical potential, and as a result $|\nabla\tilde{\mu}_n| \neq |\nabla\tilde{\mu}_p|$. In this case the procedure described in the beginning of this section becomes incorrect, because the single common "gradient of electrochemical potential" of electrons and holes is absent. Moreover, if bulk and surface recombinations are absent then both partial currents $\mathbf{j}_n$ and $\mathbf{j}_p$ should be equal to zero, not only the full current $\mathbf{j}$ ($\mathbf{j}_n + \mathbf{j}_p = 0$). As a result we have two equations ($\mathbf{j}_n = 0$, $\mathbf{j}_p = 0$) for both thermoelectric fields $\nabla(\tilde{\mu}_n/e)$ and $\nabla(\tilde{\mu}_p/e)$ instead of one equation (8). One more problem arises when bulk and surface recombinations take place: the correct determination of electron and hole equilibrium concentrations.[7]

Finally, the question remains how to obtain the thermo-emf in this case, and which physical phenomena determine its value. The answer to the first of these questions has been given,[4] where the general scheme was proposed for calculation of an emf of any nature. It follows from this paper that[7]

$$V = \oint\left(\frac{\sigma_n}{e\sigma}\frac{d\tilde{\mu}_n}{dx} - \frac{\sigma_p}{e\sigma}\frac{d\tilde{\mu}_p}{dx}\right)dl$$

$$- \oint\left(\frac{\sigma_n\alpha_n}{\sigma} + \frac{\sigma_p\alpha_p}{\sigma}\right)\frac{dT}{dx}dl, \tag{10}$$

where integration is carried out clockwise. Let us note that expression (10) is always correct (for a broken circuit just as in the case of a flowing thermoelectric current). The second item in (10) coincides with the expression (9). The first item in (10) vanishes (it is equal to zero identically in the unipolar case) and expression (10) turns into (9) if electrons and holes have a single, common electrochemical potential level. Correlation (7) does not hold if electrons and holes flow from the hot lead to the cool one and electron and hole Fermi quasilevels appear. In this situation the first item in (10) differs from zero and the

gradients of concentrations and corresponding diffusion currents contribute to the thermo-emf.

II. THERMOELECTRIC PHENOMENA IN BIPOLAR MEDIA

Let us go on to the description of an approach to exploration of the thermo-emf, which does not involve either the contradictions or the incorrectness pointed out above. Note that some aspects of this approach have previously been expounded.[7,8]

Let us restrict ourselves to the first case

$$T(x) = T^* - \frac{\Delta T}{2a} x, \tag{11}$$

for simplicity. Here T_1 is the heater temperature at the point $x = -a$, T_2 is the condenser temperature at the point $x = +a$, $T^* = (T_1 + T_2)/2$, and $\Delta T = T_1 - T_2$.

The condition when the temperature field of the quasiparticles (electrons, holes, and phonons) is common and is a linear function of coordinates has been obtained earlier.[6] Let us assume that

$$\Delta T \ll T^*. \tag{12}$$

Let an arbitrary semiconductor be defined by the function $\mu_n^0(T^*)$ which is found from the condition of electroneutrality.[1] Then μ_n^0 becomes a function of the coordinate $\mu_n^0\big(T(x)\big)$ in the temperature field (11), and

$$\mu_n^0(x) = \mu_n^0(T^*) + \delta\mu_n^0(x), \quad \delta\mu_n^0(x) = -\frac{\partial \mu_n^0(T^*)}{\partial T^*} \Delta T \frac{x}{2a},$$

$$\left| \delta\mu_n^0 \right| \ll \left| \mu_n^0(T^*) \right|. \tag{13}$$

Function (13) gives, uniquely, the concentration distribution in the sample:

$$n_0(x) = n_0(T^*) + \delta n_0(x),$$

$$n_0(T^*) = \gamma_n(T^*) \exp\left[\frac{\mu_n^0(T^*)}{T^*} \right],$$

$$\delta n_0(x) = n_0(T^*) \left[\left(\frac{\mu_n^0(T^*)}{T^*} - \frac{3}{2} \right) \frac{\Delta T}{T^*} \frac{x}{2a} + \frac{\delta\mu_n^0}{T^*} \right]. \tag{14}$$

Here $\gamma_n(T) \propto T^{3/2}$ is the density of states at the bottom of the conduction band.

If we introduce (here it was assumed that the energy gap ε_g is independent of temperature)

$$\mu_p^0(T^*) = -\varepsilon_g - \mu_n^0(T^*),$$

then we can write

$$\mu_p^0(x) = \mu_p^0(T^*) + \delta\mu_p^0(x), \qquad \delta\mu_p^0 = -\delta\mu_n^0, \tag{15}$$

analogously to (13). Then the hole concentration is

$$p_0(x) = p_0(T^*) + \delta p_0(x),$$

$$p_0(T^*) = \gamma_p(T^*) \exp\left[\frac{\mu_p^0(T^*)}{T^*} \right],$$

$$\delta p_0(x) = p_0(T^*) \left[\left(\frac{\mu_p^0(T^*)}{T^*} - \frac{3}{2} \right) \frac{\Delta T}{T^*} \frac{x}{2a} + \frac{\delta\mu_p^0}{T^*} \right], \tag{16}$$

where $\gamma_p(T) \propto T^{3/2}$ is the density of states at the top of the valence band.

Let us note that condition (12) is not sufficient for the correctness of formulas (14) and (16) in contrast to (13) and (15). The additional conditions

$$|\delta\mu_{n,p}^0| \ll T^*, \qquad \frac{\Delta T}{T^*} \ll \frac{T^*}{\max[|\mu_n^0|, |\mu_p^0|]}$$

are necessary.

It is important to emphasize that $n_0(x)$ and $p_0(x)$ are not "equilibrium" concentrations (see the Appendix). Inverted commas are used here because it is impossible to use the term "equilibrium," strictly speaking, in the presence of a temperature field (11).

The situation becomes nonequilibrated in the authentic sense (see the Appendix) when the gradient of electrochemical potential becomes nonzero because of taking into account the terms $\alpha_n \nabla T$ and $\alpha_p \nabla T$. Let us examine this situation, assuming that bulk and surface recombinations are absent, and under the condition of a broken circuit (as in Sec. I).

In this case the stationary distributions of concentrations

$$n(x) = n_1(x) + \delta n, \qquad p(x) = p_1(x) + \delta p$$

and electric potential

$$\varphi(x) = \delta\varphi_1(x) + \delta\varphi$$

are described by the system of equations $\mathbf{j}_n = 0$, $\mathbf{j}_p = 0$, and

$$\frac{d^2(\delta\varphi)}{dx^2} = 4\pi e(\delta n - \delta p)$$

[expressions for $n_1(x)$, $p_1(x)$, and $\delta\varphi_1(x)$ are contained in (A3) and (A7)].

Let us note [see (6)] that the quantities $[\mu_n^{(1)}\ (\mu_p^{(1)})$ are the "equilibrium" electron (hole) chemical potentials; see (A3) and (A7)]

$$\mu_n = \mu_n^{(1)} + \delta\mu_n, \qquad \mu_p = \mu_p^{(1)} + \delta\mu_p,$$

$$\delta n = \frac{n_0(T^*)}{T^*} \delta\mu_n, \qquad \delta p = \frac{p_0(T^*)}{T^*} \delta\mu_p,$$

which are contained in the expressions for $\mathbf{j}_n$ and $\mathbf{j}_p$ are not already connected by expression (15), e.g., they are compatible with Fermi quasilevels. As for quantities α_n and α_p, depending on μ_n and μ_p respectively,[1] they are determined by the quantities $\mu_n^0(T^*)$ and $\mu_p^0(T^*)$, since we carry out all calculations up to the members of order $(\Delta T/T^*)$. Thus δn_0, δp_0, δn_1, δp_1, and $\delta\varphi_1$ ($\delta\mu_n^0$, $\delta\mu_p^0$, $\delta\mu_n^{(1)}$, $\delta\mu_p^{(1)}$, and $\delta\varphi_1$) are not incorporated into the system of equations for finding δn, δp, and $\delta\varphi$ (or $\delta\mu_n$, $\delta\mu_p$, and $\delta\varphi$). As a result, the determining of unknown quantities needs no calculations presented by formulas (13)–(16) and (A1)–(A7). We shall recall, however, that these calculations are necessary if we have to take into account recombination. Conditions (A5) and $\varphi|_{x=0} = 0$

are used for determining integration constants.

Then

$$\delta\varphi = A_1(e^{\lambda x} - 1) + A_2(e^{-\lambda x} - 1) + \alpha\Delta T\frac{x}{2a},$$

$$\delta\mu_n = +e\,\delta\varphi + e\,\alpha_n T(x) + e\,C_1,$$

$$\delta\mu_p = -e\,\delta\varphi - e\,\alpha_p T(x) + e\,C_2. \tag{17}$$

Here

$$\alpha = \frac{\alpha_n n_0(T^*) + \alpha_p p_0(T^*)}{n_0(T^*) + p_0(T^*)}.$$

Constants $A_{1,2}$ and $C_{1,2}$ [see (17)] are connected by correlations

$$\frac{n_0(T^*)C_1 - p_0(T^*)C_2}{n_0(T^*) + p_0(T^*)} = A_1 + A_2 - \alpha T^*,$$

$$\xi_p C_2 - \xi_n C_1 = (\alpha_p\xi_p + \alpha_n\xi_n)T_2 + (\xi_n + \xi_p)\varphi_c$$

[for definitions of ξ_n and ξ_p, see (A4)].

For determining all the constants presented in (17), it is necessary to give conditions $\delta\varphi|_{x=\pm a}$ and $\delta\mu_n$ (or $\delta\mu_p$) at $x = 0$, for example.[9]

Let [see (A5)]

$$\delta\varphi|_{x=\pm a} = \varphi_{c,b}, \qquad \delta\mu_n(0) = \delta\mu_p(0) = 0.$$

Then expressions (17) turn into

$$\delta\varphi = \frac{\Delta T}{2}\left[\alpha\frac{x}{a} - \left(\alpha + \frac{\alpha_n\xi_n + \alpha_p\xi_p}{\xi_n + \xi_p}\right)\frac{\sinh\lambda x}{\sinh\lambda a}\right],$$

$$\delta\mu_n = +e\,\delta\varphi - e\,\alpha_n\Delta T\frac{x}{2a},$$

$$\delta\mu_p = -e\,\delta\varphi + e\,\alpha_p\Delta T\frac{x}{2a}. \tag{18}$$

As follows from formulas (17) and (18), $\delta\mu_n \neq -\delta\mu_p$, e.g., two Fermi quasilevels really appear.

If we use the condition of quasineutrality $\lambda a \gg 1$, then

$$\delta\varphi = \alpha\Delta T\frac{x}{2a},$$

$$\delta\mu_n = e\,\frac{p_0(T^*)}{n_0(T^*) + p_0(T^*)}(\alpha_p - \alpha_n)\Delta T\frac{x}{2a},$$

$$\delta\mu_p = e\,\frac{n_0(T^*)}{n_0(T^*) + p_0(T^*)}(\alpha_p - \alpha_n)\Delta T\frac{x}{2a},$$

$$\delta n = \delta p = e\,\frac{n_0(T^*)p_0(T^*)}{n_0(T^*) + p_0(T^*)}(\alpha_p - \alpha_n)\frac{\Delta T}{T^*}\frac{x}{2a}. \tag{19}$$

Thus there are two Fermi quasilevels even in the quasineutrality approximation and the condition of quasineutrality reduces to the equality $\delta n = \delta p$ [compare with (A7)].

When the semiconductor is unipolar [for example, $n_0(T^*) \gg p_0(T^*)$] $\delta n = \delta p \ll p_0(T^*) \ll n_0(T^*)$, and $\delta\mu_n = 0$, e.g., the redistribution of concentration and Fermi level change do not take place. This is in accordance with the results of the Introduction.

To conclude, let us note that expressions (19) could be derived from the equations $\mathbf{j}_n = \mathbf{0}$ and $\mathbf{j}_p = \mathbf{0}$ only without using the Poisson equation, assuming at once that the relation $\delta n = \delta p$ takes place when $\lambda a \gg 1$.

III. THERMO-EMF OF BIPOLAR SEMICONDUCTOR

As was noted above, the thermo-emf is described by the expression (10) in a bipolar medium, and it is important to emphasize that this expression does not contain the electric potential $\varphi(x)$. The latter is quite natural if we wish to use the correct determination of the thermo-emf, which is formed by forces of nonelectric origin, but not to use the artificial scheme which was presented in the first section.

Let us assume that a semiconductor sample is placed in the interval $-a \leq x \leq +a$. It is connected with an instrument by metal wires with chemical potential μ_M which does not depend on temperature. Let the thermoelectric power α_M be equal to zero $(\alpha_M \ll \alpha_n, \alpha_p)$. We assume that $\mu_n(T^*) = \mu_M$ for simplicity.

As was noted, the first integral in expression (10) tends to zero when electrons and holes have a single level of chemical potential $(\delta\mu_n = -\delta\mu_p)$. So we have

$$V = \oint \left(\frac{\sigma_n}{e\,\sigma}\frac{d}{dx}\delta\mu_n - \frac{\sigma_p}{e\,\sigma}\frac{d}{dx}\delta\mu_p\right)dl$$

$$- \oint \left(\frac{\sigma_n\alpha_n}{\sigma} + \frac{\sigma_p\alpha_p}{\sigma}\right)\frac{dT}{dx}dl.$$

Taking into account that $\delta\mu_n$ and $\delta\mu_p \propto \Delta T$ [and so σ_n and σ_p depend on $n_0(T^*)$ and $p_0(T^*)$], we get

$$V = \frac{1}{e\sigma(T^*)}\left[\sigma_n(T^*)\int_{-a}^{+a} d(\delta\mu_n) - \sigma_p(T^*)\int_{-a}^{+a} d(\delta\mu_p)\right] + \frac{\xi_n}{e\,\xi}[\delta\mu_n(-a) - \delta\mu_n(+a)] - \frac{\xi_p}{e\,\xi}[\delta\mu_p(-a) - \delta\mu_p(+a)]$$

$$- \frac{1}{\sigma(T^*)}[\sigma_n(T^*)\alpha_n + \sigma_p(T^*)\alpha_p](T_2 - T_1),$$

$$\xi = \xi_n + \xi_p. \tag{20}$$

The second and third terms in the expression (20) correspond to the contributions of the jumps of μ_n and μ_p on the surfaces $x = \pm a$ to the first integral (10). The analogous contribution of the second integral is ab-sent, since in our problem temperature is continuous at $x = \pm a$ [compare with (A5)]. Two additional terms $[(\xi_n\alpha_n^s/\xi) + (\xi_p\alpha_p^s/\xi)]\Delta T_\pm$ appear in expressions (A5) and (20) if the thermoconductivity of planes $x = \pm a$

is a finite quantity, and thus the temperature has discontinuities $\Delta T_{\pm}$.[6] The index "s" serves to show the relation to the planes $x = \pm a$.

We find from expressions (20) and (17):

$$V = \frac{\xi_n \alpha_n + \xi_p \alpha_p}{\xi} \Delta T. \tag{21}$$

For example, the Fermi quasilevel contribution to the thermo-emf compensates completely the conventional thermo-emf expression (9). The nonzero thermo-emf is caused only by Fermi quasilevel breaks in the contacts of the semiconductor sample with connecting wires. Let us emphasize once again that the last assertion is true with any form of boundary conditions on planes $x = \pm a$.

CONCLUSION

Thus the thermo-emf V is determined by thermoelectric powers $\alpha_{n,p}$ and surface characteristics $\xi_{n,p}$. Comparing formula (21) with formula (9) we see that taking into account Fermi quasilevels in the thermo-emf changes its value substantially. So if $\alpha_n \sigma_n(T^*) + \alpha_p \sigma_p(T^*) = 0$ then expression (9) becomes zero but the value V obtained from (21) does not equal zero. In the general case expressions (9) and (21) may have different signs.

Returning to the unipolar case ($\xi_n \gg \xi_p$) we come to the expression (5) as was noted above. Let us notice only that the condition $\xi_p \gg \xi_n$ does not follow from the condition $p_0(T^*) \gg n_0(T^*)$ in a hole semiconductor. The problem is that the ratio of the electron mobility to the hole mobility can become very large in some semiconductors [for example, it is more than 80 in InSb (Ref. 5)], and the transition from expression (21) to (5) does not always take place.

It is clear that use of expression (21) can essentially change the calculated value of the efficiency of a thermoconverter. We would like to finish with one comment. It is impossible to say anything about the order of magnitude of V in typical experimental situations, because nobody knows the value of ξ.

ACKNOWLEDGMENTS

APPENDIX

The chemical potential $\mu_n^0\big(T(x)\big)$ [see (13)] corresponding to concentrations $n_0(x)$ and $p_0(x)$ is heterogeneous in space. So diffusion currents will arise in the process of the establishment of "thermodynamic equilibrium," which leads to redistribution of concentrations, the appearance of bulk charge layers, and an internal thermoelectric field characterized by the electric potential

$\delta \varphi_1(x)$. Here the situation is analogous to the process of establishing thermodynamic equilibrium in heterogeneously doped semiconductors.[1] The following distributions of the electric potential $\delta \varphi_1(x)$, concentrations, and chemical potentials:

$$n_1(x) = n_0(x) + \delta n_1(x), \qquad p_1(x) = p_0(x) + \delta p_1(x),$$

$$\mu_n^{(1)}(x) = \mu_n^0(x) + \delta \mu_n^{(1)}(x),$$

$$\mu_p^{(1)}(x) = \mu_p^0(x) + \delta \mu_p^{(1)}(x),$$

correspond to "equilibrium" when the electrochemical potential is constant:

$$\mu_n^{(1)}(x) - e\,\delta\varphi_1(x) = -\varepsilon_g - \mu_p^{(1)}(x) - e\,\delta\varphi_1(x) = \text{const.} \tag{A1}$$

The functions $\delta n_1(x)$ and $\delta p_1(x)$ are connected with $\delta \mu_n^{(1)}$ and $\delta \mu_p^{(1)}$ [see (14) and (16)] naturally by the formulas

$$\delta n_1 = n_0(T^*)\frac{\delta\mu_n^{(1)}}{T^*}, \qquad \delta p_1 = p_0(T^*)\frac{\delta\mu_p^{(1)}}{T^*},$$

$$\delta\mu_p^{(1)} = -\delta\mu_n^{(1)}. \tag{A2}$$

Thus there are two unknown independent functions. It is necessary to use the Poisson equation to determine them, besides Eq. (A1),

$$\frac{d^2(\delta\varphi_1)}{dx^2} = 4\pi e(\delta n_1 - \delta p_1). \tag{A3}$$

It is easy to formulate boundary conditions for Eqs. (A1) and (A3) if we introduce electron and hole electric conductances per unit area of the contacts of the semiconductor sample with connecting wires (ξ_n and ξ_p, respectively). If the thickness of the junction δ is negligible compared to the thickness $2a$ of the bulk semiconductor and σ_n^s (σ_p^s) is the junction conductivity of electrons (holes), we have (σ_n^s and σ_p^s are supposed to depend on δ)[6]

$$\xi_n = \lim_{\delta \to 0} \frac{\sigma_n^s}{\delta} \text{ and } \xi_p = \lim_{\delta \to 0} \frac{\sigma_p^s}{\delta}. \tag{A4}$$

We choose the origin of $\varphi(x)$ at the point $x = 0$ $[\varphi(x)|_{x=0} = 0]$.

Then the condition of continuity of electric current in contacts in the broken circuit [considering that $\alpha_n = \alpha_p = 0$ in the connecting wires and μ_M does not depend on temperature (metal)] is reduced to[6]

$$\frac{1}{e}\xi_p\delta\tilde{\mu}_p - \frac{1}{e}\xi_n\delta\tilde{\mu}_n\bigg|_{x=\pm a} = (\xi_n + \xi_p)\varphi_{c,b}. \tag{A5}$$

Condition (A5) in the "thermodynamic equilibrium state" turns into

$$\delta\mu_n^0 + \delta\mu_n^{(1)} - e\,\delta\varphi_1\bigg|_{x=\pm a} = 0,$$

since $\varphi_c = \varphi_b = 0$ and $\delta\mu_p = -\delta\mu_n$.

As a result, for $\delta\varphi_1$, $\delta\mu_n^{(1)}$ ($\delta\mu_p^{(1)} = -\delta\mu_n^{(1)}$) and δn_1 $[n_0(T^*)\,\delta p_1 = -p_0(T^*)\,\delta n_1]$ we find

$$\delta\varphi_1 = \frac{1}{e}\delta\mu_n^{(0)}(x) + 2\,C\,\sinh\lambda x,$$

$$\delta\mu_n^{(1)} = 2\,C\,e\,\sinh\lambda x, \qquad (A6)$$

$$\delta n_1 = 2\,C\,e\frac{n_0(T^*)}{T^*}\,\sinh\lambda x.$$

Here

$$\lambda^{-1} = \left\{ \frac{T^*}{4\pi e^2\,[n_0(T^*) + p_0(T^*)]} \right\}^{1/2}$$

is the Debye radius.

It is necessary to formulate boundary conditions either on $\delta\varphi_1$ or on $\delta\mu_n^{(1)}$ for determining the constant C. It is natural to assume that $\delta\varphi_1|_{x=\pm a} = 0$. Then

$$C = \frac{\partial\mu_n^0(T^*)}{\partial T^*}\frac{\Delta T}{2\,e}\frac{1}{2\,\sinh\lambda a}.$$

If the condition of quasineutrality holds, e.g., $\lambda a \gg 1$, as usual, takes place, then

$$\delta\varphi_1 = -\frac{d\mu_n^0(T^*)}{dT^*}\frac{\Delta T}{e}\frac{x}{2a},$$

$$\delta n_1 = \delta p_1 = \delta\mu_n^{(1)} = \delta\mu_p^{(1)} = 0. \qquad (A7)$$

At first sight it seems that Eq. (A3) implies the condition $\delta n_1 = \delta p_1$ only. But we see from (A7) that the condition of quasineutrality reduces to the stronger requirement $\delta n_1 = \delta p_1 = 0$ in a bipolar medium as in a unipolar semiconductor during the process of establishing "equilibrium."

It is clear that functions $n_1(x)$ and $p_1(x)$ have to be named the "equilibrium" concentrations of the carriers because

$$\frac{d}{dx}\left[\mu_n^{(1)}(x) - e\,\delta\varphi_1(x)\right] = 0,$$

$$\frac{d}{dx}\left[\mu_p^{(1)}(x) + e\,\delta\varphi_1(x)\right] = 0.$$

These functions must participate exactly as "equilibrium" concentrations in the expressions for the bulk and surface recombinations.

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[9] It is important to emphasize (see Sec. III) that constants $C_{1,2}$ and $A_{1,2}$ are displaced out from the answer under calculation of the thermo-emf, e.g., the value of the thermo-emf does not depend on the concrete form of the boundary conditions for $\delta\varphi(x)$ and $\delta\mu_{n,p}(x)$.