

Formulation and measurement of the thermo-emf in unipolar semiconductors

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It is shown that a correct definition of the thermo-emf is possible only for a closed electric circuit. In this case, the concept of a thermoelectric field is devoid of any physical meaning. It is noted that for thermoelectric systems, it makes sense to speak either of a thermo-emf or of a voltage drop.

Generally, the approach to investigating the thermo-emf in a unipolar medium is based on the electric current expression accounting for the temperature gradient, i.e.,

$$j = -\sigma[\nabla\varphi + (1/e)\nabla\mu + \alpha\nabla T], \tag{1}$$

where σ is the electric conductivity; φ and μ are the electrical and the chemical potentials, respectively; α is the differential thermo-emf; T is temperature and e is the electron charge.

Assuming that the electric circuit is open ($j=0$), the thermoelectric field can be determined from (1) to be

$$E = -\nabla\varphi = (1/e)\nabla\mu + \alpha\nabla T. \tag{2}$$

Since $\nabla\mu = (d\mu/dT)\nabla T$ in a homogeneous material, Eq. (2) can be rewritten as

$$E = \left[\frac{1}{e} \frac{d\mu}{dT} + \alpha \right] \nabla T. \tag{3}$$

In this connection, immediately the definition of the thermo-emf coefficient is subject to further scrutiny: should it be α or $\alpha + (1/e)d\mu/dT$?

To introduce the thermo-emf, it seems natural to write

$$\varepsilon = \int E \cdot dl. \tag{4}$$

However, it was pointed out in Refs. 1 and 2 that because of the temperature-dependent contact-potential difference at the semiconductor-metal boundary, the thermo-emf should be determined from

$$\varepsilon = \int E^* \cdot dl, \tag{5}$$

with $E^* = -\nabla[\varphi + (1/e)\mu]$, rather than from Eq. (4). Therefore, it might seem natural to define the thermoelectric field as

$$E^* = \alpha\nabla T \tag{6}$$

instead of Eq. (3).

However, it is easy to understand that such an approach cannot be correct either. A correct description of an emf of any kind should proceed, according to the general definition, from³

$$\begin{aligned} \varepsilon = jR &= \oint \frac{j \cdot dl}{\sigma} \\ &= - \oint \{ \nabla[\varphi + (1/e)\mu] + \alpha\nabla T \} \cdot dl, \end{aligned} \tag{7}$$

where R is the total resistance of the closed electric circuit including the semiconductor thermoelement, metal-connecting wires, and the load resistance, and dl is the displacement vector.

In this connection we emphasize two important points. First, it is necessary to consider a closed electric circuit for correctly determining the thermo-emf (then the open circuit is just the limiting case of the general situation, in which the load resistance R_L tends to infinity). Second, the very connection of a meter to measure the thermo-emf violates the initial assumption of $j=0$. Since $\oint \nabla[\varphi + (1/e)\mu] \cdot dl = 0$, we have

$$\varepsilon = - \oint \alpha \nabla T \cdot dl. \tag{8}$$

If we compare Eq. (8) with (5), then we might be led to believe that definition (6) is correct. Meanwhile, it should be remembered that differential relations do not necessarily follow from integral relations. Besides, the integral relation (8) has been derived under the assumption $j \neq 0$.

It should also be noted that the electric (as well as the electrochemical) potential has dropped out of the definition of the thermo-emf. Therefore, the coincidence of Eqs. (5) and (8) should be regarded as completely fortuitous (this becomes especially obvious when the thermo-emf is considered in a bipolar medium).^{4,5}

As follows from the above consideration, the concept of a thermoelectric field as defined either by Eq. (2) or (3) is devoid of any physical meaning. For thermoelectric systems, it makes sense to speak either of a thermo-emf or of a voltage drop u .

As was mentioned in Ref. 3, the voltage drop can be defined correctly only in the case of a closed electric circuit involving a section with an equilibrium electron density and equilibrium constant temperature. If the thermoelement is connected to a load meeting these conditions, then

$$u = jR_L. \tag{9}$$

Let the load resistance be a metal specimen with a negligible thermo-emf coefficient. Then we find, from (8),

$$\varepsilon = \alpha(T_1 - T_2). \tag{10}$$

To obtain (10), we have assumed for simplicity that the thermoelement is in isothermal contact with the heater (at temperature T_1) and the condenser (at temperature

T_2), i.e., the temperature is continuous across the semiconductor-metal boundaries. Otherwise, Eq. (10) would involve terms due to the surface thermo-emf and Peltier's effect (for further detail, see Ref. 6). As a result, the thermo-emf ε would depend on the external load R_L .

We note that

$$R = a/\sigma_t + b/\sigma_L + 2/\sigma_s = R_0 + R_L, \quad (11)$$

where σ_t , σ_L , and σ_s are the electric conductivities of the thermoelement, external metal load, and surface contacts, respectively; a and b are lengths of the thermoelement and the metal section of the electric circuit; $R_0 = a/\sigma_t + 2/\sigma_s$ is the thermoelement resistance; and $R_L = b/\sigma_L$. The cross section of the circuit is assumed to be constant and taken to be unity everywhere.

Combining (7), (10), and (11), we obtain an expression for the thermoelectric current density for a closed circuit:

$$j = \alpha(T_1 - T_2)/(R_0 + R_L). \quad (12)$$

Now we are in a position to express the voltage drop u as

$$u = \alpha(T_1 - T_2)R_L/(R_0 + R_L). \quad (13)$$

Equations (12) and (13) specify parametrically the voltage-current characteristics of the thermoelement.

Eliminating R_L from (12) and (13), we finally arrive at

$$j = [\alpha(T_1 - T_2) - u]/R_0. \quad (14)$$

As is obvious from (14), in the "open circuit" region (i.e., $R_L \rightarrow \infty$ and $j \rightarrow 0$) $u = \alpha(T_1 - T_2)$, i.e., the voltage drop coincides with the thermo-emf value (10). On the contrary, in the short-circuit limit ($R_L \rightarrow 0$ and $u \rightarrow 0$), we have $j = \alpha(T_1 - T_2)/R_0$.

In conclusion, we note the analogy between the V - A characteristics of the thermoelement and the photocell,⁷ which is characteristic of electric circuits with a non-equilibrium element generating the emf.

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