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A GENERAL DERIVATION OF THE SEEBECK EFFECT
FORMULA

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A GENERAL DERIVATION OF THE SEEBECK EFFECT FORMULA

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ABSTRACT

The Seebeck Effect formula appropriate for a semiconductor with one species of carrier is derived from a general kinetic theory point of view in which the details of the carrier scattering processes are not considered.

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In that it is probably true that any significant improvement in thermoelectric devices will involve much more than a slight modification of existing schemes, it is useful to review the physical basis of the thermoelectric (Seebeck) effect. In particular, a fundamental appreciation of the nature of the phenomena invoked in the Seebeck Effect may suggest useful alterations in the present method of power generation. Thus, I shall present a derivation of the usual Seebeck Effect formula which is unencumbered by mathematical detail and which appears to me to describe the physical essence of the Seebeck Effect. It should be pointed out at the onset that this derivation is completely equivalent to a solution of the linearized Boltzman equation for an electron gas in which the effect of the interactions of the electrons with each other, with the lattice, and with impurities is taken account of simply by the introduction of a finite mean-free-path, ℓ ; this oversimplified procedure is, in fact, the standard one.

To begin, let us write down a general expression for the particle current density J_p (that is, the electric current density divided by the charge of the carriers) for a situation in which only one type of charge carrier--electrons, say--is mobile. In the regime in which the electric field strength, the carrier density gradient, and the thermal gradient are all sufficiently small so as to permit utilization of the so-called linear-response theory (the situation that is usually treated), one has

$$J_p = -n \left(\frac{qD}{kT} \right) \frac{dV}{dx} - D \frac{dn}{dx} - n \frac{dD}{dx} , \quad (1)$$

where the gradients have been taken to be in the x-direction and q is the charge of the carrier (electrons have $q = -|e|$), $-dV/dx$ is the electric

field, n is the carrier density, D is the diffusion constant, qD/kT is (according to the Einstein relation) simply the carrier mobility, k is the Boltzman constant, and T is the absolute temperature. The particle-diffusion constant is defined by

$$D = \langle v\ell \rangle \quad , \quad (2)$$

where v and ℓ are respectively the particle's velocity and mean-free-path and the average symbol denotes a thermodynamic average over the states of the carrier.

In the Seebeck effect measurement one is concerned with the situation in which no current is permitted to flow through the sample, i.e., $J_p = 0$. The voltage drop across the material is then found from Eq. (1) to be given by

$$\Delta V = - \frac{kT}{q} \left[\ell n \left(1 + \frac{\Delta n}{n} \right) + \ell n \left(1 + \frac{\Delta D}{D} \right) \right] \quad , \quad (3)$$

where Δn and ΔD are the carrier-density and diffusion-constant changes across the material. Restricting our attention to small density-gradient changes and small diffusion-constant changes, $\Delta n/n \ll 1$, $\Delta D/D \ll 1$, we have

$$\Delta V = - \frac{kT}{q} \left[\frac{\Delta n}{n} + \frac{\Delta D}{D} \right] \quad . \quad (4)$$

If the diffusion-constant change is solely associated with a temperature gradient,

$$\Delta D = \frac{\partial D}{\partial T} \Delta T, \quad (5)$$

where

$$\frac{\partial D}{\partial T} = \frac{\langle vE \rangle - D\langle E \rangle}{kT^2}, \quad (6)$$

and E is the energy of the charge carrier. Introducing A , the so-called "heat of transport" (measured in units of kT), defined by the relation:

$$A = \frac{\langle vE \rangle}{\langle v \rangle (kT)} = \frac{\langle vE \rangle}{D(kT)}, \quad (7)$$

we have

$$\frac{1}{D} \frac{\partial D}{\partial T} = \frac{A}{T} - \frac{\langle E \rangle}{kT^2}. \quad (8)$$

The voltage developed across the sample in this situation is found from Eqs. (4), (5), (8) to be

$$\Delta V = - \frac{kT}{q} \left[\frac{\Delta n}{n} + \frac{\Delta T}{T} \left(A - \frac{\langle E \rangle}{kT} \right) \right]. \quad (9)$$

Thus, the voltage across the sample is the sum of two terms both of which possess a statistical nature: one characterizes the desire of a collection of identical particles to "even out" their density gradient and the other reflects their tendency to "remove" the carrier's kinetic-energy gradient that is associated with the temperature gradient. Furthermore, if one

produces the carrier-density gradient solely as a result of the temperature gradient,

$$\frac{\Delta n}{n} = \frac{1}{n} \frac{dn}{dT} \Delta T \quad , \quad (10)$$

one has

$$\Delta V = - \frac{kT}{q} \left[\frac{1}{n} \frac{dn}{dT} + \frac{A}{T} - \frac{\langle E \rangle}{kT^2} \right] \Delta T \quad , \quad (11)$$

which, when evaluated for electrons in a conduction band, yields

$$\Delta V = - \left(\frac{k}{q} \right) \left[\frac{(E_c - \mu_c)}{kT} + A \right] \Delta T - \left(\frac{1}{q} \right) \Delta \mu_c \quad , \quad (12)$$

where $\Delta \mu_c \equiv \frac{\partial \mu_c}{\partial T} \Delta T$, E_c is the energy of the bottom of the conduction band and μ_c is the chemical potential.

When a thermoelectric source is connected in a circuit, the net chemical-potential difference between the two leads to the voltmeter vanishes. Hence the emf ascribed to a single element in the thermoelectric circuit is $-[\Delta V + (1/q)\Delta \mu_c]$. Thus, one obtains the standard semiconductor formula for the thermoelectric power, $S = \text{emf}/\Delta T$:

$$S = \left(\frac{k}{q} \right) \left[\frac{(E_c - \mu_c)}{kT} + A \right] \quad . \quad (13)$$

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