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Effective Seebeck coefficient for semiconductors

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A distinction between two common definitions of Seebeck coefficient is clarified. The effective Seebeck coefficient, which describes the effective electric field induced by a temperature gradient, is found to be a constant for a homogeneous doped semiconductor regardless of its doping.

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I. INTRODUCTION

The Seebeck effect, Peltier effect, and Thomson effect were discovered more than 100 years ago. The theory of these phenomena has been established.[1,2] Based on these effects, solid state refrigerators have been developed.[3] There is a subtlety in the definition of the Seebeck coefficient. This subtleness lies in the inequivalent definition of two related concepts, which we call the phenomenological Seebeck coefficient S and the theoretical Seebeck coefficient $\bar{S}$. This subtlety needs to be understood in order to get the right coefficient for the transfer of heat in a solid state refrigerator.

The Seebeck effect is the generation of a voltage V in an open circuit, which is shown in Fig 1. The circuit is made up of two different materials. The junctions, which are the interfaces between two different materials, are kept at different temperatures T_1, T_2. The phenomenological Seebeck coefficient S is defined as

$$S = \frac{V}{T_1 - T_2} \tag{1}$$

This definition is found in standard textbooks.[1] The junctions do not contribute to the voltage. The voltage difference is due to the difference of the electrochemical potential of the two materials. At a particular temperature, the entire junction has the same electrochemical potential, so there is no voltage difference across the ends of a junction. Based on this argument, we can define the phenomenological Seebeck coefficient as a property of a particular material without reference to any other materials or junctions. In this way, the phenomenological Seebeck coefficient is also define by Eq. (1) with T_1, T_2 the temperatures at the two ends of the material and V the voltage generated. The two definitions above are equivalent.

There is another popular definition of the Seebeck coefficient,[2–6] which is defined as the coefficient for the effective electric field (E) generated by a temperature gradient,

$$\bar{S} = \frac{E}{\vec{\nabla}_r T}. \tag{2}$$

This definition is preferred by theorists. We call it the theoretical Seebeck coefficient. But this is not equivalent to the phenomenal one. The difference is that the electric field $E = -\vec{\nabla}\phi$ is related to the scalar potential ϕ which is not the same as the voltage V. To find the relationship between the theoretical Seebeck coefficient and phenomenological one forms the motivation for this paper. It is shown in Sec. II that the theoretical Seebeck coefficient is the effective Seebeck coefficient defined in a previous paper.[7] This coefficient is a universal constant for homogeneously doped semiconductors. This implies that, for homogeneously doped semiconductors, the electric field induced by a temperature gradient is a constant independent of material or doping.

II. SEEBECK COEFFICIENT

We start from the Boltzmann equation. In steady phenomena, we neglect the time dependence of the distribution function, and have the following equations:

$$0 = \vec{\nabla}_r f \cdot \mathbf{v} + \frac{1}{\hbar}\vec{\nabla}_k f \cdot (e\vec{E} + e\mathbf{v} \times \vec{B}) + \left(\frac{\partial f}{\partial t}\right)_s \tag{3}$$

$$\approx \vec{\nabla}_r f^{(0)} \cdot \mathbf{v} + \frac{1}{\hbar}\vec{\nabla}_k f^{(0)} \cdot (e\vec{E} + e\mathbf{v} \times \vec{B}) + \left(\frac{\partial f}{\partial t}\right)_s, \tag{4}$$

$$f^{(0)} = \begin{cases} \dfrac{1}{e^{\beta(r)(\epsilon-\mu)}+1} = \dfrac{1}{e^{\beta(r)\xi}+1} \\ \text{for Fermi distribution,} \\ e^{-\beta(r)\xi} \\ \text{for Boltzmann distribution,} \end{cases} \tag{5}$$

$$\vec{\nabla}_r f^{(0)} = \left(\vec{\nabla}_r \mu(r) + \frac{\xi}{T}\vec{\nabla}_r T\right)\left(-\frac{df^{(0)}}{d\xi}\right), \tag{6}$$

$$\vec{\nabla}_k f^{(0)} = \hbar \mathbf{v}_{\mathbf{k}} \frac{df^{(0)}}{d\xi}, \tag{7}$$

where e is the particle charge, which has a negative value for electrons and μ is the chemical potential. Most of the equa-

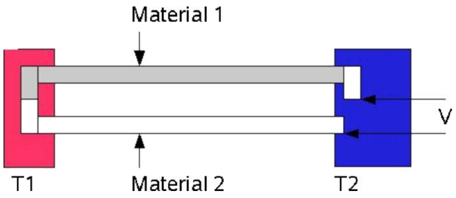

FIG. 1. (Color online) Setup for Seebeck effect.

tions are the same for Fermi and Boltzmann distributions. Concentrating on the zero-magnetic-field case, we regroup these equations in the following way:

$$0 = \mathbf{v}_{\mathbf{k}} \cdot \left(- e\vec{E} + \vec{\nabla}_r \mu(r) + \frac{\xi}{T}\vec{\nabla}_r T \right)\left(- \frac{df^{(0)}}{d\xi} \right) + \left(\frac{\partial f}{\partial t} \right)_s \tag{8}$$

$$= \mathbf{v}_{\mathbf{k}} \cdot \left(\vec{\nabla}_r \bar{\mu}(r) + \frac{\xi}{T}\vec{\nabla}_r T \right)\left(- \frac{df^{(0)}}{d\xi} \right) + \left(\frac{\partial f}{\partial t} \right)_s, \tag{9}$$

$$\bar{\mu} = \mu + e\phi, \tag{10}$$

where $\bar{\mu}$ is the electrochemical potential. Applying the relaxation time approximation,

$$\left(\frac{\partial f}{\partial t} \right)_s = \frac{f - f^{(0)}}{\tau_t(k)} = \frac{\delta f}{\tau_t(k)}. \tag{11}$$

We arrived at equations for the electric current, heat current, and energy current:

$$\mathbf{J} = 2e \int \frac{d^3k}{(2\pi)^3} \mathbf{v}_{\mathbf{k}} \delta f(k) \tag{12}$$

$$= - \sigma[\vec{\nabla}_r(\bar{\mu}/e) + b\vec{\nabla}_r T], \tag{13}$$

$$\sigma = 2e^2 \int \frac{d^3k}{(2\pi)^3} \tau_t(k) \mathbf{v}_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \left(- \frac{df^{(0)}}{d\xi} \right), \tag{14}$$

$$b = \frac{2e}{\sigma} \int \frac{d^3k}{(2\pi)^3} \tau_t(k) \mathbf{v}_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \frac{\xi}{T}\left(- \frac{df^{(0)}}{d\xi} \right), \tag{15}$$

$$\mathbf{J}_Q = 2 \int \frac{d^3k}{(2\pi)^3} \mathbf{v}_{\mathbf{k}} \delta f(k) \xi \tag{16}$$

$$= \frac{\sigma b T}{e} \vec{\nabla}_r \bar{\mu} - 2 \int \frac{d^3k}{(2\pi)^3} \tau_t(k) \mathbf{v}_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \frac{\xi^2}{T}\left(- \frac{df^{(0)}}{d\xi} \right) \vec{\nabla}_r T \tag{17}$$

$$= \frac{\sigma b T}{e} \vec{\nabla}_r \bar{\mu} - K' \vec{\nabla}_r T, \tag{18}$$

$$\mathbf{J}_E = 2 \int \frac{d^3k}{(2\pi)^3} \mathbf{v}_{\mathbf{k}} \delta f(k) (\epsilon + e\phi) \tag{19}$$

$$= \mathbf{J}_Q + \bar{\mu}\mathbf{J}. \tag{20}$$

The driving forces for the current are the potential gradient, the temperature gradient, and the charge density gradient. The current is dependent on these three forces:

$$\mathbf{J} = - \sigma \vec{\nabla}_r \phi - \frac{\sigma}{e}\left(\frac{\partial \mu}{\partial n} \right)_T \vec{\nabla}_r n - \frac{\sigma}{e}\left(\frac{\partial \mu}{\partial T} \right)_n \vec{\nabla}_r T - \sigma b \vec{\nabla}_r T \tag{21}$$

$$= - \sigma \vec{\nabla}_r \phi - \sigma \bar{S} \vec{\nabla}_r T - \frac{\sigma}{e}\left(\frac{\partial \mu}{\partial n} \right)_T \vec{\nabla}_r n, \tag{22}$$

$$\bar{S} = b + \frac{1}{e}\left(\frac{\partial \mu}{\partial T} \right)_n. \tag{23}$$

It is obvious from Eq. (22) that σ is the electrical conductivity and $\bar{S}$ is the theoretical Seebeck coefficient defined in Sec. I. $\bar{S}$ is also the effective Seebeck coefficient defined in Mahan's paper,[7] which takes account of all the effects of temperature gradient. The voltage across a conductor is equal to $\Delta\bar{\mu}/e$, not $\int \vec{E}\, d\vec{l}$. An example is the *p*-*n* junction. When the applied voltage across the junction is zero, then $\int \vec{E}\, d\vec{l}$ is obviously nonzero due to the electric field. The voltmeter measures the difference of electrochemical potential. Setting $\mathbf{J} = \mathbf{0}$ in Eq. (13), we find $V = \Delta\bar{\mu}/e = b\Delta T$. Compared with the definition in Eq. (1), it is obvious that b is the phenomenological Seebeck coefficient S. The theoretical Seebeck coefficient is a description of the effective electric field generated by a temperature gradient. While the phenomenological Seebeck coefficient is a description of voltage generated by a temperature gradient. They are not identical and not proportional to each other. Equation (23) is the relation between these two Seebeck coefficients.

We apply the above equations to a homogeneously doped semiconductor using Maxwell-Boltzmann statistics. We also assume the following dependence of the relaxation time:

$$\tau_t(k) \propto \epsilon(k)^r. \tag{24}$$

We have

$$\mathbf{J} = - \frac{ne\bar{\tau}_t}{m} \vec{\nabla}_r \bar{\mu} - \frac{k_B e \bar{\tau}_t n}{m}\left(\frac{5}{2} + r - \mu\beta \right) \vec{\nabla}_r T, \tag{25}$$

$$\bar{\tau}_t = \frac{\beta^{5/2}}{\Gamma(5/2)} \int_0^\infty d\epsilon\, \epsilon^{3/2} e^{-\beta\epsilon} \tau_t(k), \tag{26}$$

$$S = \frac{k_B}{e}\left(\frac{5}{2} + r - \mu\beta \right) \tag{27}$$

$$= \frac{k_B}{e}\left(\frac{5}{2} + r - \ln \frac{n}{N_c} \right), \tag{28}$$

$$N_c = 2\left(\frac{m k_B T}{2\hbar^2 \pi} \right)^{3/2}, \tag{29}$$

$$\bar{S} = S + \frac{1}{e}\left(\frac{\partial \mu}{\partial T} \right)_n = \frac{k_B}{e}(1 + r). \tag{30}$$

The phenomenological Seebeck coefficient (S) is the one actually measured in Eq. (1). The measurement of the Seebeck coefficient follows the phenomenological definition.[1] The phenomenological Seebeck coefficient decreases linearly with $\ln n$, which agrees with experimental results.[3]

The surprising result is that $\bar{S}$ is an universal constant. For a given temperature gradient, the electric field induced inside a homogeneously doped semiconductor is the same for different materials. This makes sense because for a closed loop made by semiconductors, the current is solely driven by temperature gradient. The loop integral of the electric field should be zero. This conclusion is valid even for inhomogeneously doped semiconductors. People are interested in inhomogeneous doping to increase the efficiency of refrigerators,[8] and $\bar{S}$ may be a useful term in such discussions. $\bar{S}$ is a useful term for the calculation of the electric field inside a material, which is required to find the modification of the carrier density through Poisson's equation. An example of the use of this term is given by Mahan,[7] who finds the modification of charge carrier density due to the presence of current. But the modification is small, which means we can use the same carrier density without current for coefficient calculation.

A few remarks are necessary about solid state refrigerators. A solid state refrigerator is made of two thermal reservoirs with a thermoelectric material sandwiched between them. If we just concentrate on the thermoelectric material, we can use Eqs. (13)–(20) to work out the heat flow from the cold reservoir. An equation derived from Eqs. (13) and (20) is

$$\mathbf{J}_Q = ST\mathbf{J} - K\vec{\nabla}_r T. \tag{31}$$

We emphasize that S is the phenomenological Seebeck coefficient and K is the thermal conductivity. So we can use direct experimental values of the Seebeck coefficients for efficiency calculations. The other details are worked out in Mahan's review paper.[3]

III. CONCLUSION

We have discussed the two expressions for the Seebeck coefficient, which we call the phenomenological and theoretical Seebeck coefficients. They are not equivalent. The phenomenological Seebeck coefficient is the one usually measured, and also enters the figure of merit $Z=\sigma S^2/K$. The previous results and the standards set for refrigerator materials are not changed. The effective Seebeck coefficient is also an interesting and useful term. In homogeneous semiconductors, the effective Seebeck coefficient is a universal constant, which implies that the electric field induced by a temperature gradient is independent of doping.

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