

Effect of temperature-dependent energy-level shifts on a semiconductor's Peltier heat

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The Peltier heat of a charge carrier in a semiconductor is calculated for the situation in which the electronic energy levels are temperature dependent. The temperature dependences of the electronic energy levels, generally observed optically, arise from their dependences on the vibrational energy of the lattice (e.g., as caused by thermal expansion). It has been suggested that these temperature dependences will typically have a major effect on the Peltier heat. The Peltier heat associated with a given energy level is a thermodynamic quantity; it is the product of the temperature and the change of the entropy of the system when a carrier is added in that level. As such, the energy levels cannot be treated as explicitly temperature dependent. The electron-lattice interaction causing the temperature dependence must be expressly considered. It is found that the carrier's interaction with the atomic vibrations lowers its electronic energy. However, the interaction of the carrier with the atomic vibrations also causes an infinitesimal lowering ($\sim 1/N$) of each of the N vibrational frequencies. As a result, there is a finite carrier-induced increase in the average vibrational energy. Above the Debye temperature, this cancels the lowering of the carrier's electronic energy. Thus, the standard Peltier-heat formula, whose derivation generally ignores the temperature dependence of the electronic energy levels, is regained. This explains the apparent success of the standard formula in numerous analyses of electronic transport experiments.

I. INTRODUCTION

The Peltier heat of a charge carrier is a basic electronic transport quantity. It is the heat transported with a charge carrier in isothermal current flow. However, in practice the Peltier heat is usually obtained indirectly by measuring the Seebeck coefficient, S . Here, one measures the emf developed across a material, ΔV , in response to an imposed temperature differential ΔT : $S = \Delta V / \Delta T$. The Seebeck coefficient is then related to the Peltier heat Π by the Kelvin relation $S = \Pi / qT$, where q is the charge of the carrier and T is the temperature.

Since the Peltier heat is an isothermal quantity, it is somewhat easier to understand than its companion transport coefficient, the Seebeck coefficient. In particular, for a quasifree carrier in the k th electronic state the Peltier heat is simply $E_k - \mu$, where E_k is the energy of the k th electronic state and μ is the chemical potential. The measured Peltier heat is the average of this quantity weighted by the contribution of the k th electronic state to the electrical conductivity $\Pi = \langle \sigma_k \Pi_k \rangle / \langle \sigma_k \rangle$. Physically, the Peltier heat associated with a carrier in the k th state is simply the product of the temperature T and the change of the entropy of the electronic system when a charge carrier is added in state k , $\Delta S_k = (E_k - \mu) / T$.

These results are both well known and well established. They are the subjects of discussion in texts on irreversible thermodynamics¹ and solid-state physics.² However, in deriving these results it is always assumed that the electronic energy levels are constants independent of temperature. It is, nonetheless, well known that the electronic energy levels of an electronic charge carrier in a semiconductor shift with temperature.³ These shifts are the result of the electron-lattice interaction and thermal expansion.

Specifically, the k th electronic energy level moves from its value at absolute zero, $E_k(0)$, as the average phonon occupation numbers increase. Namely,

$$E_k = E_k(0) - [\gamma(k) / k_B N] \sum_q \hbar \omega_q N_q . \quad (1)$$

Here, ω_q and N_q are, respectively, the eigenfrequency and population of the q th of N vibrational modes, and $\gamma(k)$ is the coefficient which characterizes the shift of the k th electronic energy levels; k_B is the Boltzmann constant.

It has been suggested⁴ that one can take account of these temperature-dependent shifts of the electronic energy levels by simply replacing E_k in the expression for the Peltier heat by its temperature-dependent value. Then, for example, at high temperatures (above the phonon temperature) where

$$E_k = E_k(0) - \gamma(k)T , \quad (2)$$

the Peltier heat associated with the k th state becomes

$$\Pi_k = E_k(0) - \mu - \gamma(k)T . \quad (3)$$

This is a major effect. Namely, upon performing the average over the partial conductivities associated with each state, k , one finds that

$$\Pi = E_e - \mu + (A - \gamma / k_B) k_B T . \quad (4)$$

Here, E_e is the edge of the band of the semiconductor associated with the transport (conduction band for electrons and valence band for holes). A is a constant which indicates the range of energies, in units of $k_B T$, beyond the edge of the band of conducting states in which conduction takes place. For a wide-band semiconductor A is generally between 1 and 2 and γ / k_B is larger than A . Thus, the

presence of the γ -dependent term of this equation shifts its final term from being an increasing function of temperature to being a decreasing function of temperature. With a "pinned" (temperature-independent) chemical potential, as in many amorphous semiconductors,⁴ it is this term which provides the total temperature dependence of the Peltier heat. Thus, the direction of this temperature dependence is of considerable significance.

In a prior work,⁵ this author has addressed the problem of calculating the Seebeck coefficient when the electron energy levels of the system are temperature dependent, i.e., dependent on the phonon occupation numbers. It is found that the previously mentioned conjecture is incorrect. Rather, for example, in the high-temperature regime, in which the electronic energy levels depend linearly on temperature, the γ -dependent term disappears from the expression for the Peltier heat. This finding reflects the nature of the interaction which provides the temperature dependence of the electronic energy levels. Specifically, while the electronic energy is affected by the phonon occupation, the vibrational frequencies are altered by the presence of the charge carrier. As a result, the interaction not only lowers the energy of the electron, it also raises the thermally averaged energy of the vibrational system. These two effects exactly cancel one another in the Peltier heat. Thus, the γ -dependent term should not appear in Eq. (4).

A similar situation occurs in the case of the Peltier heat of the small polaron. There, the energy which enters into the Peltier heat is also not the electronic energy of the polaron but rather the net change of the energy of the system when a self-trapped electron is added to it.⁶ In particular, while the electronic energy of the charge carrier is reduced as a result of it being self-trapped, the strain energy of the system is increased in forming the self-trapping potential well. However, for the form of electron-lattice interaction which enters into the small-polaron problem these two effects only partially cancel one another.

These findings have been challenged in a paper by Butcher and Friedman.⁷ They, as well as the present author,⁵ attempt to calculate the Seebeck coefficient directly. As such, they must also contend with the effect of a temperature gradient. In particular, they assume that the spatially varying shifts of the electronic energy levels induced by the externally imposed temperature gradient are equivalent to spatially varying energy levels that are internal to the system. In the latter case, the spatial dependence of the electronic energy levels is due to structural variations in the material. Then the explicit dependence of the electronic energy on position gives rise to a so-called "internal force." This internal force is absent in this author's calculation of the Seebeck coefficient. Physically, its absence indicates that an externally maintained gradient of the carrier density generates an emf but an internally sustained space charge does not. Thus, the difference between this author's initial work and that of Butcher and Friedman resides simply in the latter authors' presumption that the energy-level shifts produced by the imposition of a temperature gradient are identical to those arising from structural inhomogeneities.

Since the Peltier heat is an isothermal quantity that is

directly related to the Seebeck coefficient, a way to resolve the issue is to directly calculate the Peltier heat. This is the task of this paper. In Sec. II a general method of computing the Peltier heat is presented. Then, in Sec. III it is applied to the case at hand. Namely, the general procedure is administered with the electron-lattice interaction being given by Eq. (1). The resulting Peltier heat is found to be consistent with that previously obtained by this author from an analysis of the Seebeck coefficient. Finally, Sec. IV contains a summary of the essential physics of the problem.

II. FORMALISM

The Peltier heat is the heat that must be supplied when a charge carrier is isothermally injected into a material.¹ Most generally, this heat is the sum of that associated with placing the carrier in the material and the net energy flow associated with moving the carrier. The first contribution can be calculated from equilibrium thermodynamics. The later contribution depends upon the specific transport process. For example, for itinerant motion this transported energy arises from phonon drag. However, in most commonly studied situations the former contribution dominates. Then the Peltier heat is simply the product of the temperature and the change of the entropy of the material when a carrier is added to it, $T\Delta\bar{S}$:

$$\Pi = T\Delta\bar{S} . \quad (5)$$

It is this situation which is investigated here.

The change of the entropy of the system upon the addition of a carrier can be expressed in terms of the derivative with respect to the temperature of the change of the Helmholtz free energy of the system. In particular, the Peltier heat is then given by

$$\Pi = T\Delta\bar{S} = -T\delta(F_{n+1} - F_n)/\delta T , \quad (6)$$

where F_n is the Helmholtz free energy of the system containing n carriers. With a sufficiently low density, the carriers may be treated as being independent particles. Then, the free energy of a system of n carriers is simply related to the change of the free energy when a solitary carrier is added to an otherwise carrier-free system, $F_1 - F_0$:

$$F_n = n(F_1 - F_0) - k_B T \ln g_n , \quad (7)$$

where g_n is the degeneracy factor associated with n equivalent carriers being in the system. Furthermore, the chemical potential μ is just the change of the free energy of the system when a carrier is added to it:

$$\mu = F_{n+1} - F_n = F_1 - F_0 - k_B T \ln(g_{n+1}/g_n) . \quad (8)$$

Inserting Eq. (7) into Eq. (6) and using Eq. (8) yields an expression for the Peltier heat:

$$\Pi = F_1 - F_0 - T\delta(F_1 - F_0)/\delta T - \mu . \quad (9)$$

This expression is the basis of the subsequent discussion. Note that it reduces to the standard expression when one considers quasifree carriers. Then the Peltier heat associated with the k th electronic state is simply $E_k - \mu$, where E_k is a constant. The Peltier heat of carriers which experience energy levels that change with temperature as a result of an electron-lattice interaction will now be considered.

III. EVALUATION OF PELTIER HEAT

To proceed further we must introduce a specific model of the carrier interactions. Here, we adopt the model presented in Eq. (1). Namely, the temperature dependence of carrier energy levels arises from its interaction with the lattice vibrations. In particular, the change of the system's free energy upon introducing a single electronic carrier is

$$F_1 - F_0 = -k_B T \ln \left[\frac{\sum_k \sum_{\dots, N_q, \dots} \exp[-(E_k + E_L)/k_B T]}{\sum_{\dots, N_q, \dots} \exp(-E_L/k_B T)} \right]. \quad (10)$$

It is useful to define an effective electronic energy, E'_k , by suppressing the k summation in the above equation. Then, the expression for the change of the free energy due to the introduction of a carrier is of the same form as that for a noninteracting carrier. Specifically,

$$F_1 - F_0 = -k_B T \ln \left[\sum_k \exp(-E'_k/k_B T) \right], \quad (11)$$

where

$$E'_k = -k_B T \ln \left[\frac{\sum_{\dots, N_q, \dots} \exp[-(E_k + E_L)/k_B T]}{\sum_{\dots, N_q, \dots} \exp(-E_L/k_B T)} \right]. \quad (12)$$

The Peltier heat of a carrier in the k th electronic state is then

$$\Pi_k = E'_k - T \frac{\partial E'_k}{\partial T} - \mu. \quad (13)$$

The first two terms on the right-hand side of this equation should collectively be viewed as the quasiparticle energy associated with a carrier in the k th state of the coupled electron-lattice system. This is explicitly shown in the following section. Thus, the second term is the difference between the quasiparticle energy and the effective electronic energy. As will be shown subsequently, this difference is the change of the system's vibrational energy resulting from the addition of a charge carrier. In the absence of the electron-lattice interaction the effective electronic energy, E'_k , is simply the energy of the bare carrier, E_k , a constant. Then, the second term of Eq. (13) vanishes and the textbook expression is reobtained.

For the model of Eq. (1) we can explicitly calculate the effective electronic energy which is defined in Eq. (12). In particular, we have

$$E'_k = E_k(0)$$

$$-k_B T \ln \left[\frac{\sum_{\dots, N_q, \dots} \exp \left[-\sum_q N_q \hbar \omega'_q / k_B T \right]}{\sum_{\dots, N_q, \dots} \exp \left[\sum_q N_q \hbar \omega_q / k_B T \right]} \right], \quad (14)$$

where $\omega'_q = \omega_q [1 - \gamma(k)/k_B N]$. Thus, the presence of a charge carrier causes a shift of each of the N vibrational modes by an infinitesimal amount, proportional to $1/N$. Separating the contribution of each of the vibrational modes, and then carrying out the summation over each of the N_q 's, yields

$$E'_k = E_k(0) - k_B T \ln \left[\prod_q \left[\frac{1 - \exp(-\hbar \omega_q / k_B T)}{1 - \exp(-\hbar \omega'_q / k_B T)} \right] \right] \quad (15)$$

$$= E_k(0) - k_B T \sum_q \ln \left[\frac{1 - \exp(-\hbar \omega_q / k_B T)}{1 - \exp(-\hbar \omega'_q / k_B T)} \right]. \quad (16)$$

The smallness of the frequency shifts of the vibrational modes is now exploited in rewriting the argument of the logarithm as

$$1 + [\gamma(k)/k_B N] (\hbar \omega_q / k_B T) / [\exp(\hbar \omega_q / k_B T) - 1].$$

Incorporating this result in Eq. (16) yields

$$E'_k = E_k(0) - [\gamma(k)/k_B N] \sum_q \frac{\hbar \omega_q}{[\exp(\hbar \omega_q / k_B T) - 1]}. \quad (17)$$

At temperatures well in excess of the phonon frequencies the effective electronic energy becomes

$$E'_k = E_k(0) - \gamma(k) T. \quad (18)$$

The average electronic energy of the carrier can also be calculated. This is not generally the same as the effective electronic energy computed above. Nonetheless, as will be evident shortly, in the high-temperature limit these energies are identical to one another. The average electronic energy of a carrier in state k is

$$\langle E_k \rangle = \frac{\sum_{\dots, N_q, \dots} E_k \exp \left[-\sum_q \hbar \omega'_q / k_B T \right]}{\sum_{\dots, N_q, \dots} \exp \left[-\sum_q \hbar \omega'_q / k_B T \right]}, \quad (19)$$

where E_k is given by Eq. (1). This is readily evaluable in exactly the manner that the average energy of a harmonic oscillator is computed in texts. The result is

$$\langle E_k \rangle = E_k(0) - [\gamma(k)/k_B N] \sum_q \frac{\hbar \omega_q}{[\exp(\hbar \omega_q / k_B T) - 1]}, \quad (20)$$

where it is noted that terms of order $1/N$ vanish in the usual infinite- N limit. In the high-temperature limit, $k_B T \gg \hbar\omega_q$ for all q , Eq. (20) becomes

$$\langle E_k \rangle = E_k(0) - \gamma T. \quad (21)$$

Inserting the expression for the effective electronic energy at high temperature, Eq. (18), into the formula for the Peltier heat of a carrier of wave vector k , Eq. (12), a simple expression is obtained:

$$\Pi_k = E_k(0) - \mu. \quad (22)$$

The high-temperature Peltier heat is independent of $\gamma(k)$. This might appear to be a surprising result. In the next section its physical origins will be further elucidated.

IV. DISCUSSION

A major task of this section is to present the physical interpretation of the quasiparticle energy

$$E_k^Q = E'_k - T \frac{\partial E'_k}{\partial T}. \quad (23)$$

In addition, the physical reason why the quasiparticle energy is temperature independent at high temperatures, despite the linear temperature dependence of the average electronic energy, $\langle E_k \rangle$, is explained.

To understand the meaning of the quasiparticle energy, E_k^Q , it is first written in a more transparent form than that of Eq. (23). This is readily accomplished by inserting the definition of the effective electronic energy, E'_k , from Eq. (12) into Eq. (23). The differentiations with respect to temperature are readily carried out to yield

$$E_k^Q = \langle E_k + E_L \rangle - \langle E_L \rangle_0. \quad (24)$$

Here, the first term is the average energy of the system in the presence of a charge carrier; the energy is the sum of the energy of the charge carrier and that of the lattice vibrations E_L . The second term is simply the average vibrational energy in a system devoid of a carrier. Explicitly,

$$\langle E_k + E_L \rangle = \frac{\sum_{\dots, N_q, \dots} (E_k + E_L) \exp[-(E_k + E_L)/k_B T]}{\sum_{\dots, N_q, \dots} \exp[-(E_k + E_L)/k_B T]} \quad (25)$$

and

$$\langle E_L \rangle_0 = \frac{\sum_{\dots, N_q, \dots} (E_L) \exp(-E_L/k_B T)}{\sum_{\dots, N_q, \dots} \exp(-E_L/k_B T)}. \quad (26)$$

Thus, what has been designated as the quasiparticle energy is the change of the energy of the system when a charge carrier is added to it. That is, E_k^Q , is, in fact, the

quasiparticle energy.

To understand why the quasiparticle energy is temperature independent in the high-temperature regime, the averages defined above are evaluated. The energies that enter into these averages are

$$E_k + E_L = E_k(0) + \sum_q \hbar\omega'_q N_q \quad (27)$$

and

$$E_L = \sum_q \hbar\omega_q N_q. \quad (28)$$

With Eqs. (24)–(27) these averages are readily carried out. The results are

$$\langle E_k \rangle = E_k(0) - [\gamma(k)/k_B N] \sum_q \frac{\hbar\omega'_q}{[\exp(\hbar\omega'_q/k_B T) - 1]}, \quad (29)$$

$$\langle E_L \rangle = \sum_q \frac{\hbar\omega_q}{[\exp(\hbar\omega_q/k_B T) - 1]}, \quad (30)$$

and

$$\langle E_L \rangle_0 = \sum_q \frac{\hbar\omega_q}{[\exp(\hbar\omega_q/k_B T) - 1]}. \quad (31)$$

It is important to note the distinctions between the vibrational frequencies with and without the presence of the charge carrier, ω'_q and ω_q , respectively.

In the high-temperature regime the average electronic energy depends linearly on temperature:

$$\langle E_k \rangle = E_k(0) - \gamma(k)T. \quad (32)$$

The average vibrational energy in the system containing the charge carrier is increased relative to that of the carrier-free system. Namely,

$$\langle E_L \rangle = Nk_B T + \gamma(k)T, \quad (33)$$

while

$$\langle E_L \rangle_0 = Nk_B T. \quad (34)$$

The increase of the average vibrational energy of the system upon the addition of a charge carrier results from the carrier-induced reduction of the vibrational frequencies. Each vibrational frequency is reduced by an infinitesimal amount of order $1/N$. This produces an infinitesimal increase in the thermally averaged energy of each vibrational mode. However, the net increase of the average vibrational energy of the totality of the N vibrational modes is finite, equal to $\gamma(k)T$. Thus, although the energy of the carrier falls with temperature, the change in the vibrational energy of the system increases. In the high-temperature regime these effects cancel one another. At lower temperatures the temperature-dependent contributions to both the electronic energy and the shift of the vibrational energy are both much smaller. However, their cancellation is not complete.

The results of this direct calculation of the Peltier heat agree with the prior Seebeck coefficient calculation.⁵ That is, both results satisfy the Kelvin relation

$\Pi_k = qTS_k$, where S_k is the Seebeck coefficient associated with a charge carrier in the k th state. However, the calculation of the Peltier heat is, perhaps, easier to understand. The essential point is that the temperature dependence of the electronic energy levels arises from the electronic charge interaction with the lattice vibrations.³ Including this effect generally requires one to study the coupled electron-lattice system. Then, not only is the charge carrier affected by the lattice vibrations but the lattice vibrations are affected by the charge carrier. In texts,² the temperature dependences of the electronic energy levels are generally ignored. Mott and Davis⁴ appreciated the fact that this temperature dependence might significantly affect the Seebeck coefficient. They suggested that it is sufficient to replace the electronic energy which arises in the textbook (constant-energy-level) formula with its temperature-dependent value. However, it is shown here that at the temperatures of interest, the additional temperature dependence associated with the carrier-induced shift of the vibrational frequencies cancels the electronic energy-level temperature dependence. Thus, the textbook expression is regained. It is presumably this cancellation which accounts for the apparent success of numerous

transport analyses based on the standard textbook expressions.

Finally, it is noted that the present formalism may also be used in calculating the Peltier heat for other interacting systems. For example, the Peltier heat of a small polaron in a magnetic semiconductor has been calculated by this method.⁸ There, instead of the interaction between an itinerant charge carrier and the atomic vibrations, one is concerned with the interaction between a localized carrier and the local magnetic moments of the material.

Note Added in Proof. In a recent article [P. N. Butcher, *Philos. Mag. B* **50**, L5 (1984)], the calculation of Ref. 7 has been repeated. In Butcher's work the electron-lattice interaction is not explicitly considered. Rather, the electronic energy levels are treated as being explicitly temperature dependent. As a result, the contribution to the system's Peltier heat from the carrier-induced change of the vibrational frequencies is missing.

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