

Theory of the thermoelectric power or Seebeck coefficient: The case of phonon scattering for a degenerate free-electron gas

K. Durczewski*

Institute for Low Temperatures and Structure Research, Polish Academy of Sciences, P.O. Box 937, PL-50 950 Wrocław, Poland

M. Ausloos†

S.U.P.R.A.S., Institute of Physics, B 5, University of Liège, Sart Tilman, B-4000 Liège, Belgium

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In order to illustrate the flexibility of the variational solution of the Boltzmann equation for transport coefficients, and in particular for the thermoelectric power of solids, we use a simple model of free electrons and consider their scattering from a spherical Fermi surface by acoustic phonons alone, without any mass enhancement effect or umklapp process. We recall the variational method, pointing out that formal constraints exist; we take two trial functions only, and we calculate the Seebeck effect in such a framework. The low-temperature behavior of this effect is known to be very complicated. Sign reversals occur which cannot be explained by a model based upon free or nearly free electrons. As shown hereby, when the inelasticity of the scattering of quasifree electrons by phonons is taken into account, nontrivial behavior in the intermediate (but still low) temperature range can be found. The Appendixes contain analytical expressions.

I. INTRODUCTION

The theory of the thermoelectric power (TEP) is certainly not yet given in a complete form. The various techniques and/or approximations for describing TEP still receive much attention. In related work,¹ we have discussed two methods based on the Boltzmann equation, i.e., the relaxation-time approximation and the variational method. It was found that they are not easily related to each other from a theoretical point of view. Thus it seems of interest to perform some analytical and numerical calculations on standard models in order to sort out the features of various approximations and to understand the order in which they can be made in order to obtain reliable results, and if possible to recover qualitatively features of experimental data. This of course means that some model system must be defined, and that the number of scattering processes must be limited in order to have a handle on the final results.

One could consider dissipation due to phonons, magnons, impurities, etc. No need to say that in some systems those scatterers must be taken into account. However, such an accumulation of dissipative processes will obscure the main features. It is best to concentrate on a simple metallic system and consider the scattering by phonons only. In so doing one can expect to observe whether such a process gives the overall behavior and whether other events or approximations must be taken into account. It will appear below which effects can or cannot be described within a simple model, e.g., in a free-electron band approximation within a Boltzmann equation.

In fact other approaches,²⁻⁴ through linear-response theory, sometimes including fluctuation effects near critical transitions,⁴ have been used. They have led to

theoretical concepts such as a “mass enhancement effect”⁵ which serves to explain some experimental features. In this formalism electron-electron interactions^{2,3} can be taken into account. However, there is no proof that such a formalism is better suited to describe experimental data nor consequently that the model features which can be used in that formalism are the main ones to be considered for explaining the experimental findings.

Moreover, such a formalism^{2,3} is restricted to either the low-temperature region or the high-temperature range. It has sometimes been concluded that since the behavior at high and low temperature is linear with a finite slope (depending on the charge carrier sign) the whole TEP behavior was smooth, including at intermediate temperature, when phonon drag^{6,7} is neglected.

However, in keeping with the most simple physics scheme, it appears that one should remember that the main effect of the thermal gradient leading to the observation of a related potential difference on a sample is the spreading with distortion of the Fermi sea.⁷ The notion of vertical and horizontal scattering should also be recalled. In the case of the electrical resistivity the Fermi sphere is merely displaced by the electric field, and the scattering is quasielastic (horizontal); hence the scattering can be thought to be somewhat restricted to the Fermi level, so a metallic approximation is valid. This is not the case when a thermal gradient is applied. So-called vertical scattering and hence inelastic scattering take place and a metallic limit from the very beginning of a calculation will not be quite correct. This leads to restrictions of scattering events on the Fermi sheet.

A simple physical picture can show that at finite temperatures the scattering events should be affected by the charge distribution distorted around the Fermi level by

the thermal gradient.⁷ In some sense electron states are emptied and hole states created. Therefore a competitive distribution of charge carriers with different signs occurs and the carriers are intrinsically inelastically scattered. Therefore a change of sign and some fine structure can be expected in the TEP vs T data at intermediate temperature. One should notice that the intermediate temperature range is hardly investigated in a linear-response formalism.

We stress that in the variational approach method^{1,7} the metallic-limit approximation is not necessary from the start, nor is the "equilibriumlike" situation mandatory. Furthermore, if necessary, a nontrivial band structure can even be considered.^{8,9} We also wish to stress that the scattering mechanisms have different features in the case of an applied electric field and in the case of thermal gradient.

Therefore it is still worthwhile to investigate the simplest case: that of free electrons scattered by phonons. The Fermi surface is taken as spherical at zero temperature; there is no consideration of mass enhancement or U processes. Under such a simple model the probability of occupation of electronic states near the Fermi level, depending on the phonon distribution, will be the main cause of TEP features. This expectation has often been underlined in earlier works.¹⁰ In the following (Sec. II) we define the simple model which is used here. In Sec. III we outline the variational method. In Sec. IV we calculate the Seebeck effect in such a framework. We give some conclusions in Sec. V, stressing some differences with respect to previous work and theories, and outlining that theoretical features could be those found in experimental work.

II. MODEL

We shall thus consider electrons in a single band with the spectrum

$$\epsilon = (\hbar^2/2m)\mathbf{k}^2. \quad (2.1)$$

They are to be scattered by acoustic phonons with energy

$$\hbar\omega = \hbar v_s q \quad (2.2)$$

where v_s is the sound velocity with the corresponding value for the Debye frequency ω_D . T_D means the Debye temperature and q_D is the phonon wave vector length cutoff. The phonon system is considered in the continuum medium approximation (see, e.g., Ref. 11). To avoid complications concerning the lattice anisotropy¹² we confine ourselves to a cubic lattice with mass M per unit cell. Phonon drag will be neglected; thus the phonon system will be assumed to be in thermal equilibrium. The electron-phonon interaction will be treated in the deformation-potential approximation.¹³ The equilibrium transition rate for the scattering of electrons will be assumed to be

$$C(\mathbf{k}, \mathbf{k}') = \frac{V}{4\pi^2} \frac{(E_1 q)^2}{M\omega} \beta f(\epsilon) [1 - f(\epsilon')] W_q \delta(\epsilon - \epsilon' - \hbar\omega) \quad (2.3)$$

where ϵ and \mathbf{k} are the electron energy and wave vector before and ϵ' and \mathbf{k}' after the scattering, while E_1 is the q -independent scattering potential, and V stands for the volume of the primitive cell of mass M . $\beta = 1/k_B T$, and $W_q = [\exp(\beta\hbar\omega) - 1]^{-1}$,

$$f(\epsilon) = [1 + \exp\beta(\epsilon - \zeta)]^{-1}$$

with the chemical potential ζ . The above transition rate and the spectrum (2.2) are in fact mean quantities averaged over the directions in a cubic crystal (see Ref. 11). The concentration of electrons or the value of the Fermi energy will determine the temperature dependence of the chemical potential. Let n_e denote the number of electrons with spin up or down in a unit volume. We have

$$n_e = \frac{1}{2\pi^2} \left[\frac{2m}{\hbar} \right]^3 \left[\frac{2}{3} \right] \epsilon_F^{3/2}, \quad (2.4a)$$

$$\frac{2}{3}(\epsilon_F/k_B T)^{3/2} = F_{1/2}(z), \quad z = \zeta/k_B T, \quad (2.4b)$$

where ϵ_F is the Fermi energy and the Fermi-Dirac integral is defined by

$$F_n(z) = \int_0^\infty \frac{dx x^n}{1 + e^{x-z}}. \quad (2.5)$$

The integrals (2.5) are convergent for $n > -1$ (see, e.g., the Appendix in Ref. 14). For $z > 20$ the Sommerfeld asymptotic expressions¹⁵ can be applied $F(z) \simeq z^{n+1}/(n+1)$, which yield simply $\zeta(T) \simeq \epsilon_F$. The final formulas for TEP in this paper are presented under this approximation.

III. THE APPLICATION OF THE ZIMAN VARIATIONAL METHOD TO THE MODEL

A convenient procedure of calculating the transport coefficients on the basis of the Boltzmann equation is the variational method developed by Ziman.^{7,16} The thermoelectric power due to the phonon scattering within the same model has been calculated by us in a restricted approximation.^{11,12,17} Recently, we also discussed the validity of the method and compared its results to the standard relaxation-time approximation.¹ The crux is to calculate the elements of a matrix describing the scattering and the components of two vectors governing the flow of the electric charge and heat: i.e., the P matrix, see Eq. (3.2) below, and trial currents J and U . The matrix and the vectors are expressed in terms of trial functions proposed by Ziman⁷

$$\begin{aligned} \Omega_1(\mathbf{k}) &= \mathbf{k} \cdot \mathbf{a}, \Omega_2(\mathbf{k}) = (\epsilon - \zeta)(\mathbf{k} \cdot \mathbf{a}), \\ \Omega_i(\mathbf{k}) &= (\epsilon - \zeta)^{i-1}(\mathbf{k} \cdot \mathbf{a}), \end{aligned} \quad (3.1)$$

where \mathbf{a} is the unit vector in the direction of the electric field and/or the thermal gradient. We shall use these functions in the present paper but note that for systems containing electrons and holes¹⁸ and/or describing the carriers beyond the free-electron approximation the choice $\Omega_i(\mathbf{k}) = (\epsilon - \zeta)^{i-1}(\mathbf{v} \cdot \mathbf{a})$ with $\mathbf{v} = (\hbar/m)\nabla\epsilon$ is more convenient.

It should also be noted that the assumption (3.1) is

equivalent to looking for the variational solution with an accuracy to the single directional harmonic which for a spherical Fermi surface should suffice (see Sec. 6.1 in Ref. 19 or, e.g., also Refs. 1 and 8). The only approximation within the method consists in truncating the sequence of the functions in (3.1) and considering only the first two of the sequence (3.1), i.e., the second-order scattering matrix P and the two-component (trial) currents J and U . This is the lowest-order approximation which in a proper qualitative way can describe TEP by taking into account both the electrical and thermal currents.⁷ The elements of the scattering matrix are simply expressed by the transition rate for the scattering $C(\mathbf{k}, \mathbf{k}')$ and read

$$P_{ij} = \int d\mathbf{k}' \int d\mathbf{k} C(\mathbf{k}, \mathbf{k}') u_{ij}(\mathbf{k}, \mathbf{k}'), \quad (3.2)$$

$$u_{ij}(\mathbf{k}, \mathbf{k}') = [\Omega_i(\mathbf{k}) - \Omega_i(\mathbf{k}')][\Omega_j(\mathbf{k}) - \Omega_j(\mathbf{k}')].$$

Notice that $P_{ij} = P_{ji}$. The trial currents are defined by

$$J_i = -e \int d\mathbf{k} (-df/d\epsilon) v(\mathbf{k}) \Omega_i(\mathbf{k}), \quad (3.3)$$

$$U_i = \int d\mathbf{k} (-df/d\epsilon)(\epsilon - \xi) v(\mathbf{k}) \Omega_i(\mathbf{k}),$$

where $v(\mathbf{k})$ is the component of the electron velocity along the external field and/or the temperature gradient, and e is the absolute value of the electron charge ($-e$ is the electron charge). In this "second-order approximation" the expression for the Seebeck coefficient is

$$S = (T\Delta)^{-1} [P_{22}J_1U_1 - P_{12}(J_1U_2 + J_2U_1) + P_{11}J_2U_2], \quad (3.4)$$

where

$$\Delta = P_{22}J_1^2 - 2P_{12}J_1J_2 + P_{11}J_2^2. \quad (3.5)$$

The expression for the resistivity in the same approximation is

$$\rho = \Delta^{-1} [P_{11}P_{22} - P_{12}^2] \quad (3.6)$$

which in the metallic limit will be used only for demonstrating that our results for the Seebeck coefficient (TEP) are counterparts of certain standard ones for the electrical resistivity. The trial currents for free electrons to any arbitrary-order approximation are expressed by the Fermi-Dirac integrals. The expressions up to the second order are

$$J_1 = -J_0(k_B T)^{3/2} L_0(z),$$

$$J_2 = -J_0(k_B T)^{5/2} L_1(z), \quad (3.7a)$$

$$U_1 = -J_2/e,$$

$$U_2 = U_0(k_B T)^{7/2} L_2(z),$$

where

$$L_0(z) = \frac{3}{2} F_{1/2}(z),$$

$$L_1(z) = -\frac{3}{2} z F_{7/2}(z) + \frac{5}{2} F_{3/2}(z), \quad (3.7b)$$

$$L_2(z) = \frac{3}{2} z^2 F_{1/2}(z) - 2 \frac{5}{2} z F_{3/2}(z) + \frac{7}{2} F_{5/2}(z),$$

$$U_0 = \frac{V}{6\pi^2} \left[\frac{2m}{\hbar^2} \right]^{5/2}, \quad J_0 = eU_0.$$

The values of U_0 and J_0 are not essential for TEP in our approximation. The lowest-order u_{ij} matrices are

$$u_{11} = (\mathbf{q} \cdot \mathbf{a})^2,$$

$$u_{12} = u_{21} = [(\epsilon - \xi) + (\epsilon' - \epsilon)](\mathbf{q} \cdot \mathbf{a})^2, \quad (3.8)$$

$$u_{22} = [(\epsilon - \xi)^2 + 2(\epsilon' - \epsilon)(\epsilon - \xi)](\mathbf{q} \cdot \mathbf{a})^2$$

$$+ (\epsilon' - \epsilon)^2[(\mathbf{q} \cdot \mathbf{a})^2 + (\mathbf{k} \cdot \mathbf{a})^2],$$

if the terms linear in \mathbf{k} and \mathbf{k}' , which do not contribute to P_{ij} , (3.2), are omitted. We note that in our notation $\epsilon' - \epsilon$ means the electron energy difference before and after the scattering. Therefore in (3.2) there are terms responsible for inelastic scattering processes.¹⁷ The scattering matrix elements P_{11} , P_{12} , and P_{22} for our model assumptions can be represented as double integrals and then computed without any further approximations. To perform it (Appendix A) we represent the integral (3.2) in terms of the electron energies ϵ and ϵ' , the transferred wave vector length $q = |\mathbf{k} - \mathbf{k}'|$, and the angles of the scattering. The integration with respect to one of these energies, e.g., ϵ' , and with respect to the scattering angles can be performed analytically. The energy conservation constraint in $C(\mathbf{k}, \mathbf{k}')$ reduces the wave vector cutoff below the value q_D for sufficiently low energies. This reduced cutoff is sometimes related to the name of Sondheimer²⁰ who first noticed that in systems with low electron concentration the energy conservation constraint provides a cut for the transferred electron momentum and thus also reduces the maximal transferred phonon momentum. Therefore the integral with respect to q has to be performed in the interval $[0, q_{\max}]$,²¹ where the ratio q_{\max}/q_D is

$$\frac{q_{\max}}{q_D} = \begin{cases} \left(\frac{\epsilon}{\epsilon_D} \right)^{1/2} + \frac{\epsilon_s}{k_B T_D} \equiv Q_{\max}(\epsilon), & \epsilon < \epsilon_m \\ 1, & \epsilon \geq \epsilon_m \end{cases} \quad (3.9)$$

where ϵ_m is the value of ϵ at which $Q_{\max}(\epsilon) = 1$. We express q_{\max} in terms of the characteristic energies ϵ_D and ϵ_s introduced by us in our earlier papers. The first one is the electron energy corresponding to $|\mathbf{k}| \equiv k = q_D/2$, and the second one is the electron energy at wave vector $q_s = (2m/\hbar)v_s$. This energy ϵ_D has been introduced by us to discuss the electrical transport for the above model in the relaxation-time approximation;²² the second energy ϵ_s has been found to be a parameter of the expression for TEP in the metallic limit (see Sec. IV) and its value has been found relevant for the behavior of TEP at low temperatures. The parameter ϵ_s has been also used by Ziman⁷ in his studies of semimetals. The two parameters are interrelated, $4\epsilon_s\epsilon_D = (k_B T_D)^2$ and their values for typical metals are presented in Table I.

In order to represent the final expressions for P_{11} , $P_{12} = P_{21}$, and P_{22} we introduce the reduced quantities $x = \beta\epsilon$, $p = \beta\omega = \beta\hbar v_s q$, and $z = \beta\xi(T)$ and as in Ref. 18 define the integrals

TABLE I. Material constants corresponding to values of ϵ_s . A value $T_D = 200$ K is assumed, and a free-electron mass.

ϵ_s (K)	ϵ_D (eV)	ϵ_m (eV)	v_s (m/s)	q_D (nm ⁻¹)
1.5	0.575	0.566	337 0	7.77
3.0	0.287	0.279	476 0	5.49
6.0	0.144	0.135	674 0	3.88
12.0	0.0718	0.0635	953 0	2.75
24.0	0.0359	0.0278	134 00	1.94
48.0	0.0180	0.0104	191 00	1.37

$$G_{km}(z, T) = \int_0^\infty \frac{dx(x-z)^m}{1+e^{x-z}} \times \int_0^{p_{\max}} \frac{dp p^k}{(e^p - 1)[1 + e^{-(x-z+p)}]} \quad (3.10)$$

with the counterparts of (3.9)

$$p_{\max} = \begin{cases} 2(x\epsilon_s\beta)^{1/2} + \beta\epsilon_s, & x < \beta\epsilon_m \\ T_D/T \equiv 1/t, & x \geq \beta\epsilon_m \end{cases} \quad (3.11)$$

The integration over \mathbf{k} and \mathbf{k}' of $C(\mathbf{k}, \mathbf{k}')$ and $u_{ij}(\mathbf{k}, \mathbf{k}')$ defined is performed in Appendix A. It yields

$$\begin{aligned} P_{11} &= P_0 t^5 G_{4,0}(z, T), \\ P_{12} &= P_0 t^5 (k_B T) \{ G_{4,1}(z, T) + G_{5,0}(z, T) \}, \\ P_{22} &= P_0 t^5 (k_B T)^2 \left\{ G_{4,2}(z, T) + 2G_{5,1}(z, T) + G_{6,0}(z, T) \right. \\ &\quad \left. + \frac{\epsilon_s}{k_B T} [G_{4,1}(z, T) + zG_{4,0}(z, T)] \right\}. \end{aligned} \quad (3.12)$$

The value of the constant P_0 is not essential for the TEP considerations and is given in Appendix A. Notice that each term of (3.8a)–(3.8c) is represented by an integral $G_{k,m}$ in (3.12). The only exception is the last term in u_{22} which is represented by the square bracket with the coefficient $\epsilon_s/k_B T$ in P_{22} (see Appendix A).

Consider now the elastic scattering approximation. The approximation is equivalent to considering only the scattering events in which electrons do not change sheets of equal energy, i.e., in our notation $\epsilon' = \epsilon$. This constraint means that (i) the value of p is neglected with respect to $x - z$ in the last exponential of the denominator in (3.10), (ii) $Q_{\max} = (\epsilon/\epsilon_D)^{1/2}$ in (3.9) which is equivalent to putting $p_{\max} = 2(x\epsilon_s\beta)^{1/2}$ for $x < \beta\epsilon_D$ in (3.11), and finally (iii) the first terms of the matrix elements u_{ij} contribute to the final integral as seen from (3.8).

Consequently the scattering matrix elements are expressed by the integrals

$$G_{k_1, m}^{(E)}(z, T) = \int_0^\infty \frac{dx(x-z)^m e^{x-z}}{(1+e^{x-z})^2} \mathcal{D}_k[p_{SD}(x, T)], \quad (3.13)$$

where

$$\mathcal{D}_k(p_{\max}) = \int_0^{p_{\max}} \frac{dp p^k}{e^p - 1} \quad (3.14)$$

is the standard Debye function²³ and

$$p_{SD}(x, T) = \begin{cases} 2(x\epsilon_s\beta)^{1/2} & \text{for } x < \beta\epsilon_D \\ T_D/T & \text{for } x \geq \beta\epsilon_D \end{cases} \quad (3.15)$$

Due to (iii) only the Debye function with index $k=4$ contributes, whence the final expression for the matrix elements reads

$$P_{ij}^{(E)} = P_0 (k_B T)^{i+j-2} t^5 G_{4, i+j-2}^{(E)}(z, T). \quad (3.16)$$

Another common approximation is to assume the Debye cutoff $[T_D/T \text{ in (3.14)}]$ for all electron energies. This can be done if the value of ϵ_D is sufficiently low. As can be expected from the form of the integral (3.12) the criterion is $\epsilon_D \ll \epsilon_F$ which is satisfied for a well degenerate electron gas. Otherwise, when ϵ_D is of the order of ϵ_F there is no clear criterion to test the validity of such an approximation. It we nevertheless take it for granted we obtain

$$G_{k, m}^{(ED)} = \psi_m(z) \mathcal{D}_k(T_D/T), \quad (3.17)$$

where $\psi_m(z)$ is defined in (B6). Such a product can then be inserted into (3.16) in place of $G_{4, i+j-2}^{(E)}$. The resultant matrix elements along with the trial currents (3.7) can be inserted into (3.4). It is then found that the explicit temperature dependence is canceled in the final expression for the Seebeck coefficient. The latter then only depends on T through z in a ratio of combinations of functions $\psi_0, \psi_1, \psi_2, L_0, L_z$, and L_2 . The final formula was compared to the standard expression derived in the relaxation-time approximation in Ref. 1.

The above approximation may have some physical significance for systems with low carrier concentration. For a highly degenerate electron gas which is the main subject here, it can be assumed that $\xi(T) \simeq \epsilon_F$ in the whole temperature interval ($0 < T < 800$ K) usual for transport measurements. In this case, only the electrons with energies from a narrow sheet near ϵ_F contribute to the scattering. It means in terms of the parameter z that one can use asymptotic expressions ($z \rightarrow \infty$) for the trial currents, the scattering matrix elements, and the final transport coefficients. In particular, the asymptotic expression for P_{11} (within the accuracy of a temperature-independent factor) yields then the Bloch-Grüneisen formula for the electrical resistivity. The asymptotic formula for TEP, which will be derived in the next section, is in fact the counterpart of this standard expression.

Some numerical estimation has shown that this asymptotic approximation yields reliable results for an electron gas of moderate effective mass for $\epsilon_F \gtrsim 0.5$ eV.

IV. TEMPERATURE DEPENDENCE OF THE SEEBECK COEFFICIENT IN THE CASE OF A HIGHLY DEGENERATE ELECTRON GAS

In order to find expressions describing the Seebeck coefficient in the case of a highly degenerate electron gas or, in other words, in the metallic-limit case, we shall use

the asymptotic ($z \rightarrow \infty$) forms for the trial currents and the scattering matrix elements. The asymptotic forms of the functions describing the trial functions follow simply from the asymptotic expressions for the Fermi-Dirac integrals (Appendix A41 in Ref. 14; see also Ref. 15). More precise recent consideration^{24,25} confirms them, yielding also

$$\begin{aligned} L_0(z) &\simeq z^{3/2}, \quad L_1(z) \simeq (\pi^2/2)z^{1/2}, \\ L_2(z) &\simeq (\pi^2/3)z^{3/2} \end{aligned} \quad (4.1)$$

for $z \rightarrow \infty$.

The metallic-limit expressions for the quantities describing the scattering due to phonons, such as in the relaxation-time approximation, are usually considered under the assumption of the Debye cutoff. It is obvious from our consideration of the previous section that the assumption of the Debye cutoff in the whole ($0 < \epsilon < \infty$) electron energy range is equivalent to assuming that the energy ϵ_m of (3.9) is sufficiently small ($\epsilon_m \ll \epsilon_F$). The latter requirement is fulfilled as seen in Table I. Thus having taken the Debye cutoff for granted we find metallic-limit expressions for the scattering matrix elements P_{ij} . The mathematical details are described in Appendix B. One can also find there a short description of the mathematical procedures leading to less general metallic-limit expressions for P_{ij} as applied in Refs. 11 and 17.

We stress at the beginning that the mathematical treatment such as in Appendix B is valid only under the assumption of inelastic collisions, i.e., $\epsilon' \neq \epsilon$. The consequences from $\epsilon' = \epsilon$ before taking the metallic limit ($z \rightarrow \infty$) are described in the previous section.

The metallic-limit expressions for the first matrix elements are

$$P_{ij} = P_0(k_B T)^{i+j-2} t^5 \mathcal{P}_{ij}(t), \quad (4.2a)$$

where

$$\begin{aligned} \mathcal{P}_{11}(t) &= \mathcal{F}_5^{(B)}(t), \\ \mathcal{P}_{12}(t)\mathcal{P}_{21}(t) &= \frac{1}{2}\mathcal{F}_6^{(B)}(t), \\ \mathcal{P}_{22}(t) &= \mathcal{F}_7^{(B)}(t) - \mathcal{P}_-(t), \end{aligned} \quad (4.2b)$$

with

$$\mathcal{P}_-(t) = \frac{\epsilon_s}{k_B T} \left[\frac{1}{2}\mathcal{F}_6^{(B)}(t) - \frac{\epsilon_F}{k_B T} \mathcal{P}_{11}(t) \right] \quad (4.2c)$$

and $t = T/T_D$. The generalized ($n = 5, 6, 7$) Bloch-(Grünseisen) functions

$$\mathcal{F}_n^{(B)}(t) = \int_0^{1/t} \frac{dy y^n}{(e^y - 1)(1 - e^{-y})} \quad (4.3)$$

with the material constants T_D , ϵ_s , and ϵ_F are sufficient for the description of the scattering. With the trial currents expressed by (4.1) and the scattering matrix elements by (4.2) the final metallic-limit form of (3.4) can be represented as in Refs. 11 and 17:

$$S = S_0(t) + S_1(t) \frac{k_B T}{\epsilon_F}, \quad (4.4)$$

where

$$\begin{aligned} S_0(t) &= \frac{\pi^2}{3} \left[\frac{k_B}{e} \right] \frac{\mathcal{P}_{12}(t)}{\mathcal{P}_{22}(t)}, \\ S_1(t) &= -\frac{\pi^2}{2} \left[\frac{k_B}{e} \right] \left\{ 1 + \frac{\pi^2}{3} \frac{\mathcal{P}_{11}(t)}{\mathcal{P}_{22}(t)} \right\}. \end{aligned} \quad (4.5)$$

The high- and low-temperature expression for (4.4) can also be represented as in Refs. 11 and 17. They are

$$S_{\text{asym}} = -\pi^2 \left[\frac{k_B}{e} \right] \frac{k_B T}{\epsilon_F} \quad (4.6)$$

for $t \rightarrow \infty$, and

$$S \simeq \left[\frac{k_B}{e} \right] \left\{ -\frac{\pi^2}{2} \frac{k_B T}{\epsilon_F} + \frac{\pi^2}{3} \frac{(k_B T)^2}{\epsilon_F \epsilon_s} \frac{\mathcal{P}_{12}(0)}{\mathcal{P}_{11}(0)} \right\} \quad (4.7)$$

for $t \rightarrow 0$. The linear term in (4.7) exactly corresponds to that found by Klemens.²⁶ $\mathcal{P}_{11}(0)$ and $\mathcal{P}_{12}(0)$ are linear combinations of the Riemann functions $\xi(n-1)$ with $n = 4, 5, 6$. The numerical value of $\mathcal{P}_{12}(0)/\mathcal{P}_{11}(0)$ for the integrals (4.3) representing \mathcal{P}_{ij} in the present paper is 2.943 55. The corresponding value for the approximation of Ref. 11 is 3.434 00. For completeness, we repeat the value 4.492 47 corresponding to the approximation of Ref. 17.

Figure 1(a) illustrates the temperature dependence of S following from (4.4) and (4.5) with the functions $\mathcal{P}_{ij}(t)$ given by (4.2b) and (4.2c). For illustration the results of the approximations used in Refs. 11 and 17 are also marked. The bump of S at moderate temperatures and the small minimum at very low temperatures are confirmed by the present, best approximation. In Fig. 1(b) we present the corresponding temperature dependence of the reduced resistivity and pay attention that the approximation of Ref. 17 should be used with caution since it yields a qualitatively improper dependence of S at moderate temperatures for the electrical resistivity.

In Fig. 2 we show the dependence of S in the representation in which T_D and ϵ_F are kept constant and ϵ_s is treated as a parameter. The corresponding values of other material constants, which change with the magnitude of ϵ_D , are compiled in Table I. Notice that a decrease of ϵ_s at a given value of T_D means an increase of q_D and ϵ_D .

The latter quantity is a measure of the maximal phonon energy gained and lost during the scattering. The bump at moderate temperatures increases with an increase of this energy. It is also obvious from (4.7) that the value of ϵ_D influences the temperature behavior of S . Thus, one can expect that the structure of $S(T)$ at low and moderate temperatures is caused by energy exchange between the energy-dependent electron and phonon systems. To show explicitly this conjecture we shall consider TEP in the elastic scattering approximation.

We shall first pay attention that the formulas (4.2b), (4.2c), and (4.3) are invalid in the elastic scattering limit. This is obvious from the considerations of Appendix B. One can also conclude on the ground of Appendix C in Ref. 18 that the form of \mathcal{P}_{ij} in the approximations used in

Ref. 11 and 17 is invalid in the elastic approximation. In order to consider the elastic approximation in the metallic limit we have to start from (3.13). In the limit $z \rightarrow \infty$ the matrix element $P_{12}^{(E)}$ vanishes since $\psi_m(0)=0$ for $m=1,3,\dots,(2n+1)$ [see (A7)] and with the accuracy to linear terms in $1/z$ we obtain for the Seebeck coefficient in the elastic approximation

$$S^{(E)} = S_{\text{asym}} \quad (4.8)$$

V. CONCLUSIONS

As a conclusion, it is best (i) to observe the differences in content between our previous work in Ref. 17 and the above, and (ii) recall the findings in the three temperature regions of interest, i.e., to put them in the proper perspective.

The differences between Ref. 17 and the above are as follows.

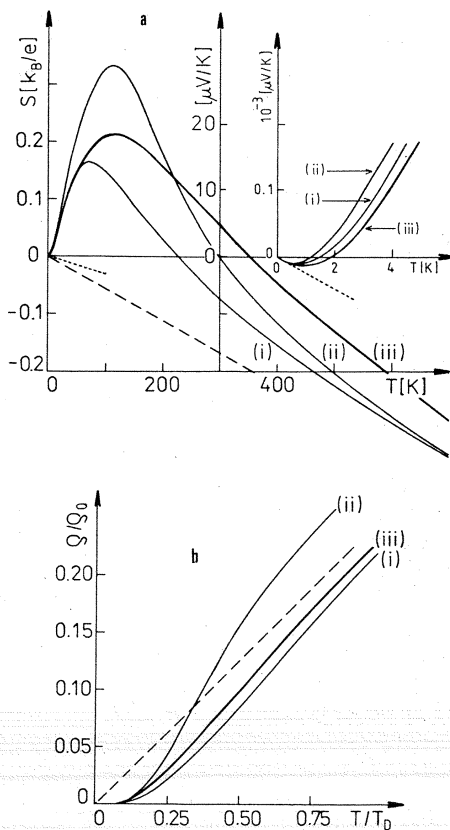


FIG. 1. (a) The metallic-limit dependence $S(T)$ in k_B/e units following from various approximations: (i) from Ref. 11; (ii) from Ref. 17; (iii) from the present work Eq. (4.4) with a Bloch-Grüneisen approximation (see Appendix II). The dashed line is the Mott-Jones asymptotic value (4.6). The dotted line corresponds to the linear term of (4.7). The inset shows the corresponding low-temperature behavior. In all cases $T_D = 200$ K, $\epsilon_F = 1.5$ eV, and the Debye cutoff $q_D = 5.0 \text{ nm}^{-1}$. (b) The temperature dependence of P_{11} (reduced resistivity) in the same approximation as in (a). All three curves approach an asymptotic (dashed) line.

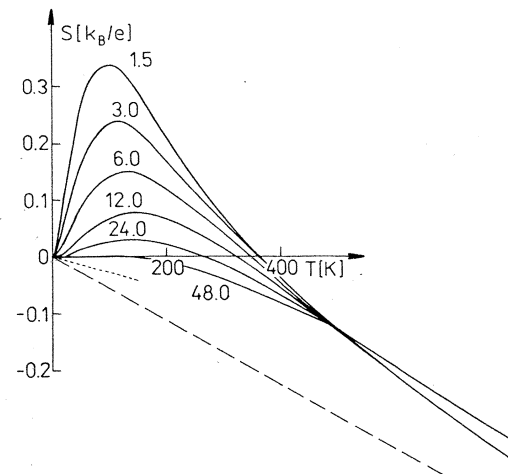


FIG. 2. The temperature dependence of S in a Bloch-Grüneisen approximation for $T_D = 200$ K, $\epsilon_F = 1.5$ eV, and various indicated values of ϵ_s for an order of magnitude corresponding to the free-electron mass and the sound velocity of solids (see Table I). The bump growing with increasing ϵ_D (or decreasing ϵ_s) implies an effect of energy exchange between the electron and phonon systems. Other approximations lead to the indicated curves: Mott-Jones high-temperature limit [Eq. (4.6)] and the low-temperature limit of Eq. (4.7) for any value of the parameter ϵ_s . Notice that TEP is always negative for $\epsilon_s > \text{ca. } 48$ K.

The scattering matrices are here represented by the generalized Bloch-Grüneisen functions, which—as claimed in Appendix B—is a better approximation than both used previously in Ref. 17.

Holes as current carriers are considered in Ref. 17 but are not used here in order to avoid confusion and limit the number of indices in presenting the mathematical treatment.

The main goal of this paper was to present explicitly the mathematical treatment which was not done in Ref. 17.

Furthermore, we show in Appendix A that we explicitly take the inelastic collisions into account while in Sec. III and Appendix B we emphasize that the “metallic limit” should be used very carefully. As a comment to the latest statement we stress that one cannot interchange the “metallic limit” ($z \rightarrow \infty$) with the “elastic limit” ($\epsilon' \rightarrow \epsilon$). This is the reason for presenting z -dependent expressions here for the trial currents (3.7) and the scattering matrices (3.10), expressions which were not presented in Ref. 17.

This being set we can consider the various temperature ranges of interest. At high temperature, the behavior of TEP is given by (4.6) and (4.8). This is a well-known result, generally well accepted, and easily found as a consequence of the often used Mott-Jones formula.^{2,3,10}

At low temperature, i.e., $T \rightarrow 0$, the temperature behavior has long been unclear till Klemens²⁶ corrected Bethe finding²⁷ (a T^3 behavior) and showed on the basis of a Boltzmann equation approach, but without making use of the relaxation-time notion or any variational method, that the low-TEP behavior is linear in T and is

given with the coefficient written in (4.7). Klemens, however, did not have the second term of (4.7). This $(-\pi^2/2)$ coefficient has been recently confirmed by a linear-response-theory approach.³

The next interesting region is the intermediate temperature range, where "intermediate" can nevertheless refer to quite low temperature. Along the variational method approach, invented by Köhler,²⁸ Sondheimer²⁹ derived expressions for the electrical resistivity and thermal conductivity, but failed to find a concise expression for TEP. He had only obtained the following expression:³⁰

$$S = - \left[\frac{\pi^2}{3} \right] \left[\frac{k_B}{e} \right] \left[\frac{k_B T}{\epsilon_F} \right] \times \frac{\mathcal{F}_5^{(B)}(t) + (\epsilon_D t^2 / 2\pi^2 \epsilon_F) [2\pi^2 \mathcal{F}_5^{(B)}(t) + \frac{1}{2} \mathcal{F}_7^{(B)}(t)]}{\mathcal{F}_5^{(B)}(t) + (\epsilon_D t^2 / 2\pi^2 \epsilon_F) [(2\pi^2/3) \mathcal{F}_5^{(B)}(t) + \frac{1}{3} \mathcal{F}_7^{(B)}(t)]} \quad (5.1)$$

within a relaxation-time approximation following the solution of the Boltzmann equation in successive approximations for a relaxation time as investigated by Wilson.³¹ The above expression is written in our notation. A constant (D in the original expression) was found by Marison.³² It can be shown that it is equal to $\epsilon_D/(2\pi^2)$ when the volume of the first Brillouin zone of a simple cubic lattice is assimilated to a sphere. In so doing the coefficient of the low-temperature expression is found to be $(-\pi^2/3)$, as also presented by Wilson.¹⁴ The temperature behavior of such a Sondheimer result is shown in Fig. 3 for three different values of ϵ_D . In this figure it is worth comparing the Mott-Jones expression sometimes extrapolated to low temperature with the Sondheimer result and ours.

"For most metals, the thermoelectric phenomena at

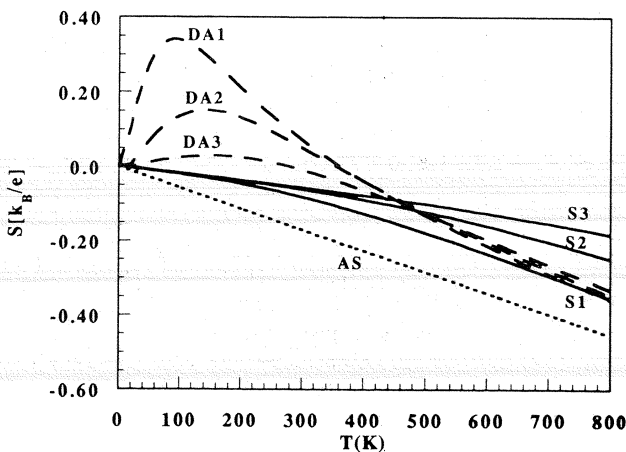


FIG. 3. Thermoelectric power or Seebeck coefficient S in k_B/e units for different approximations: from Sondheimer (Ref. 30) (Si), i.e., Eq. (5.1), from this work (DA i), i.e., Eq. (4.4), and the asymptotic (AS) value Eq. (4.6), with extrapolation to low temperature. The parameter values correspond to Table I for $\epsilon_D = 0.575$ eV (1); 0.144 eV (2); and 0.0359 eV (3); $i = 1, 2, 3$.

low temperatures are very complicated, and sign reversals occur which cannot be explained by a model based upon free or nearly free electrons," writes Wilson.¹⁴ As shown through the above work when the inelasticity of the scattering of quasifree electrons by phonons can be taken into account the intermediate- (but still low) temperature features can be recovered. This is essentially due to the flexibility of the variational method, even when limited to two trial functions of the form (3.1) only. It is as accurate as the methods in the elastic scattering regime. Thus one can believe that the method leads to at least qualitatively correct results in the inelastic cases. The origin of the features at intermediate temperature can thus receive a simple interpretation consistent with the recalled "vertical scattering processes" and the inherent distortion of the carrier distribution function near the Fermi level in a temperature gradient. More elaborate models can thus receive some attention in such a framework.

The interesting point in this work and Ref. 17 is the main source of physical-feature differences with respect to other theories. The source stems in our opinion from the fact that we treat the electron and phonon energy spectra on the same footing while others do not do so. This is probably essential for TEP considerations in which energy dispersion has some subtle influence. In general, in all previous calculations dealing with metals, only the electron energy sheets close to the Fermi energy ϵ_F were considered to be important. Since the greatest energy of the phonon system is considerably less than ϵ_F the phonon energy was usually neglected or was treated as an expansion parameter with respect to ϵ_F . These remarks certainly hold true for, e.g., important theoretical papers recently published and using sophisticated theoretical methods.^{2,3} Moreover, within the standard relaxation-time approximation one usually uses the relaxation time derived strictly for elastic collisions [see, e.g., (3.1.1) in Ref. 1]. That means that one neglects the transfer of phonon energy to and from the conduction-electron systems and destroys the effects found here above for TEP.

In semiconductors the scattering can be considered elastic or velocity randomizing. The scattering effects have thus less influence on the final temperature dependence of TEP than those related to the number of various carriers in particular bands or on discrete levels. We stress that this is not the case in metallic systems.

Our analysis shows that there are quite fine correlations between the electric and heat currents in metallic systems. These correlations seem thus to be responsible for the enhancement of TEP at intermediate temperatures but do vanish when the phonon energy transfer goes to zero. This is seen from our present considerations and was also stressed in Ref. 17.

From a purely phenomenological point of view, it is the matrix element $P_{12} = P_{21}$ which is responsible for these subtle effects. The element describes the lowest-order coupling between the electric and thermal currents and in fact vanishes in case of elastic collisions. Sometimes, that scattering matrix element does not appear in theoretical work, and in our opinion it is the reason why

the structure of TEP in metals has often been erroneously predicted or misunderstood. The matrix element P_{12} , however, appears in the original Ziman considerations (see Chap. 9, paragraph 12, in Ref. 7) but has not been carefully examined by numerical methods. Therefore its role has gone unnoticed.

Finally, in addition to theoretical considerations of the role played by approximations it is of interest to check whether experimental features agree with the theoretical prediction. Of course, it should be realized that we put the emphasis here on analytical work, thus using quite approximate band structure and simplified phonon and interaction models, whence only qualitative results can be discussed. In magnetic rare-earth metallic compounds a flat bump of TEP vs temperature at intermediate temperatures is seen.^{11,12} The effect was, and thus still is, attributed to electron-phonon scattering origin, rather than to electron-impurity or electron-spin scattering as could be at first expected. The bump magnitude has the order of magnitude of the theoretical one. The observed bump in the normal-state TEP of high-temperature superconductors is also of the order of magnitude of that theoretically predicted here.³⁴ This bump in TEP is often attributed to a phonon drag mechanism even though the temperature region might not be right at all. We therefore conclude that experimental findings and our theory have some common features at intermediate temperature.

It seems that one important argument in favor of our remarks and work is the usual existence of a minimum in TEP at very low temperatures (followed by the bump at intermediate ones). This implies a double change of sign of TEP which does not seem to be easily predicted by simple considerations—except if one introduces multi-band considerations. Not arguing that this should be unrealistic, we point out that the origin of these features might arise not only from the change in carrier concentration, but also could pertain to a scattering mechanism by phonons. Such a double-extremum behavior was found in many experimental investigations in metals (see, e.g., Ref. 35) and its origin was debated upon.³⁶ Moreover, the quoted results show that TEP was not linear even at rather high temperatures. This can be explained in our present work, and was already hinted at in a previous paper of our group.³⁷

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APPENDIX A

In order to find the form of the scattering matrix elements (3.2) in which they can be easily computed or represented in terms of the standard integrals we shall first consider P_{11} . As is obvious from (3.2) and (3.8) this matrix element is represented by the double inverse volume integral of the single term of u_{11} . If we neglect effects of the crystal periodicity such as the umklapp scattering we have

$$\epsilon' = \epsilon + \frac{\hbar^2}{2m}(2\mathbf{k} \cdot \mathbf{q} + q^2) \quad (\text{A1})$$

for $\mathbf{k}' = \mathbf{k} + \mathbf{q}$ (we keep here our notation that ϵ and \mathbf{k} are energy and the wave vector before scattering and ϵ' and \mathbf{k}' after the scattering). It is now convenient to perform the integration in P_{11} with respect to \mathbf{k}, \mathbf{q} instead of \mathbf{k}, \mathbf{k}' . The trial function difference is simply $(\mathbf{q} \cdot \mathbf{a})$ and in cubic crystals one can assume $\mathbf{a} = (0, 0, 1)$, $(0, 1, 0)$, or $(1, 0, 0)$ without any loss of generality.

Our task is to perform an analytical integration with respect to angles of the scattering under the constraint of energy and momentum conservation, which is expressed by the δ function in (2.3) and (A1). The task is simplified if we rotate the coordinate frame [with change of components $(k_x, k_y, k_z) \rightarrow (K_x, K_y, K_z)$, $(q_x, q_y, q_z) \rightarrow (Q_x, Q_y, Q_z)$] in such a way that the scalar product $\mathbf{k} \cdot \mathbf{q}$ can be simply written $K_z Q_z$ (or $Q_x K_x$ or $Q_y K_y$) with $K = |\mathbf{k}|$ and $Q_z = q \cos \vartheta$.

The angle ϑ is, of course, between \mathbf{k} and \mathbf{q} but after the rotation also between the transfer wave vector \mathbf{q} and an axis of the new coordinate frame which can be chosen as the polar axis of the spherical coordinates. The three transformation matrices which satisfy our conditions ($\mathbf{k} \cdot \mathbf{q} \rightarrow K_z Q_z$, $K_y Q_y$, or $K_x Q_x$) are given in Ref. 33. An inverse transformation with K_z as the polar axis implies the following change of variables:

$$\begin{aligned} q_x &= - \left[\frac{k_x}{k_\perp} \right] Q_x - \left[\frac{k_x k_z}{k_\perp k} \right] Q_y + \left[\frac{k_x}{k} \right] Q_z, \\ q_y &= + \left[\frac{k_x}{k_\perp} \right] Q_x - \left[\frac{k_y k_z}{k_\perp k} \right] Q_y + \left[\frac{k_y}{k} \right] Q_z, \\ q_z &= \left[\frac{k_\perp}{k} \right] Q_y + \left[\frac{k_y}{k} \right] Q_z. \end{aligned} \quad (\text{A2})$$

The final integration in P_{11} is performed with respect to

$$\int d\mathbf{k} \int d\mathbf{Q} \cdots = \frac{1}{2} \left[\frac{2m}{t^2} \right]^{3/2} \int_0^\infty d\epsilon \epsilon^{1/2} \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \int_0^{q_D} dq q^2 \int_0^\pi d\vartheta \sin\vartheta \int_0^{2\pi} d\varphi \cdots, \quad (\text{A3})$$

where θ and ϕ are polar angles of \mathbf{k} , while ϑ and φ are their counterparts in $\mathbf{Q} = (Q_x, Q_y, Q_z)$. We assume the maximum value of $q \equiv |\mathbf{q}| = |\mathbf{Q}|$ to be equal to q_D as we stated at the beginning of Sec. II.

After inserting (A2) into the expression for P_{11} and integrating with respect to φ, ϕ , and θ we obtain

$$P_{11} = P'_0 \int_0^\infty d\epsilon \epsilon^{1/2} \int_0^{q_D} dq \frac{q^5 W_q}{\omega(q)} \int_0^\pi d\vartheta \sin\vartheta W(\epsilon, \epsilon' - \epsilon) \delta(2k \cos\vartheta + q - q_s), \quad (\text{A4})$$

where P'_0 is a constant, $q_s = (2m/\hbar)v_s$, and

$$W(\epsilon, \epsilon' - \epsilon) = \frac{\beta}{[1 + e^{\beta(\epsilon - \xi)}][1 + e^{-(\epsilon - \xi)} + e^{-\beta(\epsilon' - \epsilon)}]}. \quad (\text{A5})$$

The form of this function follows from the factor $f(\epsilon)[1 - f(\epsilon')]$ in $C(\mathbf{k}, \mathbf{k}')$. It should be noted that W depends, in fact, on q and ϑ due to (A1). Now the final expression for P_D can be easily found if one notices that

$$\int_0^{q_D} dq \int_0^\pi d\vartheta \sin\vartheta F(q, \cos\vartheta) \delta(2k \cos\vartheta + q - q_{0s}) = \int_0^{q_s} dq F(q, w) \{ \Theta_H(2k - q + q_s) + \Theta_H(2k + q - q_s) \}, \quad (\text{A6})$$

where $w = (q_s - q)/2k$. F is an arbitrary function, and Θ_H stands for the Heaviside step function. P_{11} reads

$$P_{11} = P_0 \beta \sum_{i=1}^2 \int_{C_0}^\infty d\epsilon \int_{q_{\min}^{(i)}}^{q_{\max}^{(i)}} \frac{dq q^4}{(e^{\beta\hbar v_s q} - 1)(e^{\beta(\epsilon - \xi)} + 1)[1 + e^{-\beta(\epsilon - \xi) - \beta\hbar v_s q}]}. \quad (\text{A7})$$

The limits of the inner integral are

$$\begin{aligned} q_{\min}^{(1)} &= 0, \quad q_{\max}^{(1)} = \min\{q_D, 2k + q_s\}, \\ q_{\min}^{(2)} &= \begin{cases} q_s - 2k & \text{if } q_s > 2k \\ 0 & \text{if } q_s \leq 2k \end{cases}, \\ q_{\max}^{(2)} &= q_s, \end{aligned} \quad (\text{A8})$$

and

$$P_0 = \left[\frac{VE_1^2}{12M} \right] \left[\frac{2m}{\hbar^2} \right]^4 v_s^{-1}. \quad (\text{A9})$$

The $i=1$ integral in (A7) describes the scattering with $-\pi/2 \leq \vartheta \leq \pi/2$ and yields the leading contribution. The second one with $\pi/2 \leq \vartheta \leq 3\pi/2$ —as our estimations show—can be neglected since its contribution is smaller by a few orders of magnitude. It will not be considered any further. The contribution of both terms of u_{12} and the three first terms of u_{22} in (3.8) can be calculated in exactly the same way; the factors $(\epsilon - \xi)^m$ and $(\epsilon' - \epsilon)^n$ can be easily taken into account. Only the contribution of the factor $(\mathbf{k} \cdot \mathbf{a})(\epsilon' - \epsilon)^2$ under the integrals (3.2) for cubic crystals can be written as $(\mathbf{k}^2/3)(\hbar v_s q)^2 = \epsilon_s \epsilon q^2/3$ with $\epsilon_s = 2mv_s^2$.

In the reduced variables used in (3.12) this term is represented by the integral

$$\frac{\epsilon_s}{k_B T} \int_0^\infty \frac{x dx}{1 + e^{x-z}} \int_0^{p_{\max}} \frac{dp p^4}{(e^p - 1)(1 + e^{-x+z-p})}, \quad (\text{A10})$$

which after letting $x = (x - z) + z$ is finally represented as a sum of two integrals defined by (3.10), i.e., $G_{4,1}(z, T)$ and $G_{4,0}(z, T)$.

APPENDIX B

In our first considerations on TEP by the Ziman variational method¹¹ we calculated high- z P -matrix elements in a standard (but not accurate in the asymptotic regime) method which consisted in (i) assuming a Debye cutoff of

the linear phonon spectrum in the integrals with respect to q for all electron energies [cf. (3.9)] and (ii) taking into account only the first nonvanishing term of the Sommerfeld expansion in the integrals with respect to the electron energy. The assumption (ii) means that P_{11} is calculated only up to terms of zero order in $\epsilon - \xi$, whereas, e.g., in P_{12} there are linear terms coming from the first term of (3.2) and only zero-order terms for the second term of (3.2). This is equivalent to picking up terms of various order in $\epsilon - \xi$ while finally calculating the integrals P_{ij} in the metallic limit ($z \rightarrow \infty$). In order to improve on this inconsistency,¹⁷ we calculated the integrals in the metallic limit up to the second-order terms in $\epsilon - \xi$ in P_{11} , $P_{12} = P_{21}$, and P_{22} . [The second-order term in P_{11} for instance, arises from the expansion of $C(\mathbf{k}, \mathbf{k}')$ in powers of $\epsilon - \xi$.] In so doing, we obtain additional functions which have not been considered in Ref. 11. It occurs, however, that, although the zero-order expansion applied to P_{11} is qualitatively correct for the resistivity [see Fig. 1(b)] the next-order term added in Ref. 17 creates some qualitative discrepancy [see Fig. 1(b) in which the standard Bloch-Grüneisen results are shown]. Note, however, that both the approximations describe TEP qualitatively in the same way. This is obvious from comparison of the results illustrated in figures in Refs. 11 and 17. Those results are compiled in Fig. 1(a).

In the present paper we supplement them with those obtained in the approximation yielding the Bloch-Grüneisen function in case of the resistivity. The approximation consists in (i) and (iii) asymptotic ($z \rightarrow \infty$) estimation of the integrals $G_{k,m}$ without making a Sommerfeld expansion.

Under the assumption (i) we put $p_{\max} = 1/t$ in (3.10) and denote the approximate function $G_{k,m}(z, T)$ by $G_{k,m}^{(D)}(z, T)$. The approximation permits us to change the order of integration and after the substitution $y = x - z$ and some simple algebra, we get

$$G_{k,m}^{(D)}(z, t) = - \int_0^{1/t} \frac{dp p^k}{(e^p - 1)(1 - e^{-p})} g_m(p, z), \quad (\text{B1})$$

where

$$g_m(p, z) = \int_{-z}^{\infty} dy y^m \left[\frac{1}{1+e^{-y}} - \frac{1}{1+e^{-(y+p)}} \right]. \quad (\text{B2})$$

The function $g_0(p, z)$ in the limit $z \rightarrow \infty$ is elementary, i.e., $g_0(p, \infty) = -p$ and therefore we obtain

$$G_{k,0}^{(D)}(\infty, t) = \int_0^{1/t} \frac{dp p^{k+1}}{(e^p - 1)(1 - e^{-p})} \equiv \mathcal{F}_{k+1}^{(B)}(t). \quad (\text{B3})$$

For $m \neq 0$ we can integrate (B2) by parts and find

$$g_m(p, z) = (-1)^{m+1} z^{m+1} \left[\frac{1}{1+e^z} - \frac{1}{1+e^{z-p}} \right] + h_m(p, z), \quad (\text{B4})$$

where

$$h_m(p, z) = \frac{1}{m+1} \left[\int_{-z+p}^{\infty} dy \varphi(y) (y-p)^{m+1} - \int_{-z}^{\infty} dy \varphi(y) y^{m+1} \right], \quad (\text{B5})$$

with $\varphi(y) = e^y / (1 + e^y)^2$.

The above form enables us to represent $h_m(p, z)$ in terms of the functions

$$\psi_m(z) = \int_{-z}^{\infty} dy y^m \varphi(y), \quad (\text{B6})$$

which in the limit $z \rightarrow \infty$ have the values (see, e.g., Appendix A4 in Ref. 14)

$$\psi_0(\infty) = 1, \quad \psi_1(\infty) = 0, \quad \psi_2(\infty) = \pi^2/3, \dots \quad (\text{B7})$$

Since $g_m(p, \infty) = h_m(p, \infty)$ and

$$h_m(p, z) = \frac{1}{m+1} [\psi_{m+1}(z-p) - \psi_{m+1}(z)] + \frac{1}{m+1} \sum_{k=1}^{m+1} \binom{m+1}{k} (-1)^k \psi_{m+1-k}(z-p), \quad (\text{B8})$$

we get for the lowest-order functions

$$\begin{aligned} g_0(p, \infty) &= -p, \\ g_1(p, \infty) &= \frac{1}{2} p^2, \\ g_2(p, \infty) &= -\frac{\pi^2}{3} p - \frac{1}{3} p^3. \end{aligned} \quad (\text{B9})$$

After inserting them into (B1), we get

$$\begin{aligned} G_{k,1}^{(D)}(\infty, t) &= -\frac{1}{2} \mathcal{F}_{k+2}^{(B)}(t), \\ G_{k,2}^{(D)}(\infty, t) &= \left[\frac{\pi^2}{3} \right] \mathcal{F}_{k+1}^{(B)}(t) + \frac{1}{3} \mathcal{F}_{k+3}^{(B)}(t), \end{aligned} \quad (\text{B10})$$

with $\mathcal{F}_k^{(B)}(t)$ defined by (B3). The functions $G_{k,m}^{(D)}(z, t)$ after putting them into (3.2) in place of $G_{k,m}(z, T)$ lead to (4.2) and (4.3).

Note that the starting formula (B1) is such that the value of p is not neglected with respect to $x - z$. In view of (i) in our discussion in Sec. III that means that the inelastic scattering is well taken into account.

*Electronic address: durczew@highscreen.int.pan.wroc.pl

†Electronic address: ausloos@gw.unipic.ulg.ac.be

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