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Nontrivial behavior of the thermoelectric power: Electron-electron versus electron-phonon scattering

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The thermoelectric power nontrivial temperature behavior observed in metals and other structures can be due either to electron-electron or electron-phonon scattering as long as approximations do not drastically hide the behavior. The case of electron-electron scattering was treated by Hildebrand *et al.* [Phys. Rev. B **56**, R4317 (1997)]. The case of the electron-phonon scattering is reconsidered here in the framework of the variational method, but also in the relaxation-time approximation. Physical approximations, e.g., on the degeneracy of the the charge carriers, on elastic or inelastic scattering contributions, and on standard cutoffs, are discussed. Dimensionality effects of the phonon and/or electron spectrum are stressed in view of comparing systems for which the electrical resistivity is known. Asymptotic expressions are compared. It is also shown that a direct correspondence between final formulas within different formalisms is hardly available.

I. INTRODUCTION

In a recent paper, Hildebrand *et al.*[1] took into account the effect of electronic correlations in their numerical studies of the thermoelectric power (TEP) of weakly correlated Fermi-liquid metallic systems. Readers of that paper may have the impression that the characteristic smooth but nonlinear shape of the temperature dependence of the Seebeck coefficient (S) as a function of temperature is simply or mainly due to the effect of electronic correlations. Indeed, some emphasis is placed on such statements, as if the authors discovered the reason for a nonconventional nonlinear temperature behavior of TEP originating from correlation effects.

In this paper we would like to point out that the nonlinear temperature dependence of S is also expected even for a free-electron gas subjected to conventional scattering, e.g., by phonons at low and intermediate temperatures[2,3]—independently of the existence or of the phonon drag hypothesis[4–6] or the ''mass enhancement'' mechanism.[7–9] Therefore, we propose considering as strong arguments that the effect found in Ref. 1 may have its origin not in electron correlations only but may result from the fact that TEP was precisely computed, and basic features in $S(T)$ are independent of assumed models about the electron scattering.

Our research was stimulated by the fact that recent papers claimed that the nontrivial behavior of the high-temperature superconductor thermoelectric power, or rather the Seebeck coeficient S, as a function of temperature T, cannot be interpreted in terms of Fermi-liquid theory with a conventional electron-phonon interaction; in particular, see e.g., Ref. 10. Much discussion is due to the fact that different formalisms are used, e.g., kinetic,[11,4,12,13] linear-response theory,[14–16] and the variational method,[13,4,2,3,13] but in our opinion the disagreements arise from a different level of approximations when performing the theoretical calculation rather than from formalisms. While using the Mott(-Jones) formula[11] on which this discussion is usually based, one is in fact limited to elastic scattering, though an effort has been made to generalize it.[15,16] The energy transfer between a conduction electron and a quasiparticle (like a phonon) can be considered only as a correction[16] to the result obtained on the grounds of the Mott(-Jones) formula.

Surely, for electron-phonon scattering the TEP temperature dependence becomes linear as predicted in the approximate Mott (-Jones) formula; however, it only occurs well above the Debye temperature, where the effects of the energy transfer between the electrons and phonons are not effective. This change in behavior and its simple origin have not seemed so obvious since they were discussed only recently.[2,3] One may ask whether the results of Refs. 2 and 3 can be simply applied to a description of alkali and noble metals. This task is, however, still beyond the reach of purely analytical theories like in Refs. 2 and 3. As indicated by considerations[5,6] in the 1960s and 1970s, the magnitudes of the Fourier components of the pseudopotential in the cases of alkali metals and noble metals, as well as details of Fermi surface topology and the Fermi surface contacts with the Brillouin-zone boundaries, play the most essential role in reaching an agreement between the sign of S and the Hall coefficient at high temperatures. Purely numerical methods have to be used to describe these effects. The overall behavior of $S(T)$ resulting from measurements[17,6] of alkali metals (except Li) is in agreement with the numerical analysis of final formulas of Refs. 2 and 3, though there is a disagreement on the temperature at which the maximum occurs.

In Refs. 2 and 3 it was found that standard approximations obscure the overall behavior and the simple phonon scattering's drastic influence. This is why TEP calculations have to be made with special caution. In Ref. 1 precise numerical calculations of TEP were made. However, the calculations showed that the basic feature of TEP in a correlated electron gas, i.e., the maximum at a temperature of the order of 100 K, is the same as that of the free-electron gas.[2,3] A

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common feature of the results presented in Ref. 1 and Refs. 2 and 3 is the existence of a maximum in $S(T)$ at temperatures of the same order of magnitude, even with no phonon drag-like effect taken into account. The differences are in the TEP saturation behavior. The results of Ref. 1 clearly indicate that $S(T)$ saturates to a constant value at high temperature. This is attributed to the finite bandwidth, as in Heikes formula,[18–20] and does not result from a free-electron gas model as in Refs. 2, 3, and 13. One could argue that the similarity in behavior need not be discussed, because one compares the results for a two-dimensional (2D) correlated electron gas[1] to those for a 3D free-electron gas.[2,3]

Thus in the present paper we give results for the in-plane $S(T)$ of the 2D electron gas and also the scattered 2D phonons. According to the investigations reported in Ref. 21, the dispersion of the phonon spectra along the c axis of the high-temperature superconductors considered in Ref. 1, namely, $YBa_2Cu_3O_{7-\delta}$ (YBCO) and $La_{2-x}Sr_xCuO_4$ (LSCO), is very small and can be omitted. We neglect this dispersion, and calculate the TEP of 2D electron gas scattered by 2D phonons. In Sec. III we compare the numerical results to those of 3D electron gas scattered by 3D phonons,[3] and those of 2D weakly correlated gas.[1] In Sec. IV the correspondence between the Ziman variational method used in Sec. III and the relaxation time approximation is made in order to show: (i) that at high temperatures both methods yield the same results; and (ii) how inelastic phonon scattering is accounted for by the variational method, and why a direct correspondence between the results of both methods cannot be found.

II. MODEL

We consider electrons in a single 2D band in a 3D space with the spectrum

$$\varepsilon(\mathbf{k})=\frac{\hbar^2}{2m}\mathbf{k}^2, \quad \mathbf{k}=(k_x,k_y), \quad k=\sqrt{k_x^2+k_y^2} \tag{1}$$

which are scattered by 2D acoustic phonons in a 3D space with the energy

$$\hbar\omega_q=\hbar v_s q, \quad \mathbf{q}=(q_x,q_y), \quad q=\sqrt{q_x^2+q_y^2}, \tag{2}$$

where v_s is the sound velocity. The maximum phonon frequency is the Debye frequency $\hbar\omega_D=\hbar v_s q_D$, which is related to the Debye temperature through the relation $\hbar\omega_D=\hbar v_s k_B T$. The phonon system will be considered in the continuum medium approximation (see, e.g., Ref. 22), which is consistent with treating the electron-phonon interaction in the deformation potential approximation (see, e.g., Ref. 23).

Such a model will be adequate in a first approximation to describe the phonon-limited electron transport in highly anisotropic tetragonal and hexagonal systems composed of conducting layers, when the electric field or temperature gradient is applied in the plane of the layers. The model is too simple to describe quantitatively and in detail the behavior of $S(T)$ in the systems which will be mentioned below. Real, relevant electron bands and phonon modes have to be finally considered by numerical methods. In most cases, however, considerations of such bands and modes can be reduced in the first approximation to the assumptions (1) and (2) and, therefore, a correspondence should be expected between our final results and those of numerical considerations based on more sophisticated models.

We confine ourselves to considering the diffusion thermoelectric power. This means that we neglect the phonon drag; thus the phonon system will be assumed to be in thermal equilibrium. This means we shall assume that the ''in-plane'' temperature gradient will not affect the phonon system which will be described by the distribution

$$N_q=\frac{1}{\exp[\beta\hbar\omega_q]-1}, \tag{3}$$

where $\beta=1/k_BT$. The transition rate for the scattering of electrons will be assumed in the same simple form as in Ref. 3. Details can be found in Ref. 22 and Appendix A. Thus we assume

$$C(\mathbf{k},\mathbf{k}')=\frac{2\pi}{\hbar}|D(\mathbf{q})|^2\beta f(\varepsilon)[1-f(\varepsilon')]N_q\delta(\varepsilon-\varepsilon'+\hbar\omega_q), \tag{4}$$

where ε and $\mathbf{k}$ are the electron energy and wave vector before scattering, and ε' and $\mathbf{k}'$ those after scattering. The standard q-independent scattering (imaginary) potential

$$D(\mathbf{q})=-\mathrm{i}\left[\frac{\hbar}{2\mathcal{M}\omega_q}\right]^{1/2}E_1(\mathbf{e}\cdot\mathbf{q}) \tag{5}$$

will be used in the following considerations. E_1 stands for the interaction constant and $\mathbf{e}$ for the phonon polarization vector, and $\mathcal{M}$ is the mass of the unit cell. The function

$$f(\varepsilon)=\frac{1}{1+\exp[\beta(\varepsilon-\zeta)]}, \tag{6}$$

with the chemical potential ζ, describes the equilibrium electron energy distribution.

The δ function in Eq. (4) is responsible for the energy conservation. As concerns the momentum conservation, we shall assume that $\mathbf{k}$ and $\mathbf{k}'$ are in the same Brillouin zone, which means that we shall neglect the umklapp processes.

While calculating the elements of the scattering matrix in Sec. III, we shall also assume that

$$(\mathbf{e}\cdot\mathbf{q})^2=q^2. \tag{7}$$

which is a consequence of an averaging procedure within the phonon system[24] (see Appendix A).

In view of these assumptions, the model can be applied as a first approach to the phonon-limited transport in materials composed of conducting layers. Let us mention first the in-plane transport in high-temperature superconductors, in particular materials such as $La_{1-x}Sr_xCuO_4$, in which there is no contribution from the CuO chains but only from the CuO_2 layers. Our model can also be applied to describe electronic transport in quasi-two-dimensional electronic systems such as heterostructures or metal-oxide-semiconductor structures. In this case the electron motion is separable in the plane of free motion of the electrons and the direction perpendicular to this plane due to the action of an external potential produced in these layered systems. Our model corresponds to considering only the lowest electron subband.[25] The thermoelectric power of heterostructures was recently measured on a wide temperature scale,[26] and the results of the present paper may be useful in their interpretation. On the other hand, the theoretical ideas used in theories of the electron transport in quasi-two-dimensional electronic systems were used to describe the transport in high-temperature superconductors,[27] and the authors claimed that such a theory, including at least two subbands, may account for their behavior ''atypical of a conventional Fermi liquid.'' For similar physical reasons a model[28] such as that above was used to describe intercalation compounds of graphite[29] before the high-temperature superconductors were found and quasi-two-dimensional electronic systems were widely manufactured.

The first theory of the electronic transport in two-dimensional systems should probably be attributed to the authors of Ref. 30, who studied the influence of the Fermi-surface geometry on the electrical conductivity of metals. In order to examine neck parts of the Fermi surface, they assumed the surface to be of cylindrical symmetry without excluding the electron momentum change along the cylindrical axis.

III. THEORETICAL METHOD

To calculate the TEP we shall use the variational Ziman formalism[13,31,2,3] within the Boltzmann equation approach, which enables to account well for the momentum and energy transfer between a conduction electron and a phonon during the scattering. The notion of relaxation time is not introduced within the variational Ziman formalism.[13] The scattering is described by means of a matrix whose order depends on the number of trial functions. The minimum set consists of two functions[13,31] describing, respectively, the microscopic electric and thermal currents

$$\Omega_i(\mathbf{k})=(\mathbf{v}\cdot\mathbf{a})(\varepsilon-\zeta)^{i-1}, \tag{8}$$

where $i=1$ and 2, and $\mathbf{a}$ denotes the direction of the temperature gradient applied ''in plane'' and $\mathbf{v}=\nabla\varepsilon/\hbar$ is the in-plane electron velocity.

In this approximation the thermoelectric power is expressed by means of the scattering matrix elements

$$\begin{gathered} P_{ij}=\int d\mathbf{k}\int d\mathbf{k}' C(\mathbf{k},\mathbf{k}')u_{ij}(\mathbf{k},\mathbf{k}'), \\ u_{ij}(\mathbf{k},\mathbf{k}')=[\Omega_i(\mathbf{k})-\Omega_i(\mathbf{k}')][\Omega_j(\mathbf{k})-\Omega_j(\mathbf{k}')], \end{gathered} \tag{9}$$

and the trial currents

$$\begin{gathered} J_i=-e\int d\mathbf{k}\left(-\frac{df}{d\varepsilon}\right)\Omega_i(\mathbf{k}), \\ U_i=\int d\mathbf{k}\left(-\frac{df}{d\varepsilon}\right)(\varepsilon-\zeta)\Omega_i(\mathbf{k}), \end{gathered} \tag{10}$$

where $-e$ $(e>0)$ is the electron charge. The integration over the electron wave vectors is three dimensional, with a trivial integration in the z direction (see Appendix B) under the constraint $\mathbf{q}=\mathbf{k}'-\mathbf{k}$, i.e., the transferred wave vector during the scattering is the phonon wave vector.

The relevant expression for the thermoelectric power is

$$S=\frac{1}{T}\,\frac{P_{22}J_1U_1-P_{12}(J_1U_2+J_2U_1)+P_{11}J_2U_2}{P_{22}J_1^2-2P_{12}J_1J_2+P_{11}J_2^2}, \tag{11}$$

where the symmetry $P_{12}=P_{21}$ was taken into account. For the two-dimensional parabolic band, [Eq. (1)], the trial currents are expressed in terms of Fermi-Dirac integrals

$$F_n(z)=\int_0^\infty dx\,\frac{x^n}{1+\exp[x-z]}, \quad z=\frac{\zeta(T)}{k_BT} \tag{12}$$

by the combinations

$$\begin{gathered} L_0(z)=F_0(z), \\ L_1(z)=2F_1(z)-zF_0(z), \\ L_2(z)=3F_2(z)-4zF_1(z)+z^2F_0(z), \end{gathered} \tag{13}$$

and read

$$\begin{gathered} J_1=-J_0(k_BT)L_0(z), \quad J_2=-J_0(k_BT)^2L_1(z), \\ U_1=-J_2/e, \quad U_2=U_0(k_BT)^3L_2(z), \end{gathered} \tag{14}$$

where J_0 and U_0 are interrelated $(J_0=eU_0)$ constants.

To calculate the scattering matrix elements for our model, we represent the functions $u_{ij}(\mathbf{k},\mathbf{k}')$ under integrals (9) in the following way

$$\begin{gathered} u_{11}=(\mathbf{q}\cdot\mathbf{a})^2, \\ u_{12}=u_{21}=[(\varepsilon-\zeta)+(\varepsilon'-\varepsilon)](\mathbf{q}\cdot\mathbf{a})^2, \\ u_{22}=[(\varepsilon-\zeta)^2+2(\varepsilon'-\varepsilon)(\varepsilon-\zeta)](\mathbf{q}\cdot\mathbf{a})^2 \\ +(\varepsilon'-\varepsilon)^2[(\mathbf{q}\cdot\mathbf{a})^2+(\mathbf{k}\cdot\mathbf{a})^2]. \end{gathered} \tag{15}$$

While writing the above expressions, we neglected terms linear in $\mathbf{k}$ and $\mathbf{k}'$, which do not contribute to the integrals. After performing integration with respect to the angles of the scattering and taking exactly into account the energy conservation constraint (see Appendix B) the elements of the scattering matrix can be expressed in terms of the integrals

$$\begin{aligned} H_{kl}(z,T)=&\int_0^\infty dx\,\frac{(x-z)^l}{1+e^{x-z}}\int_{p_{min}}^{p_{max}}dp \\ &\times\frac{p^k}{\sqrt{4\beta\varepsilon_s x-(p-\beta\varepsilon_s)^2}(e^p-1)(1+e^{-(x-z+p)})}, \end{aligned} \tag{16}$$

where k and l are integers, $\varepsilon_s=2mv_s^2$, and the (reduced) minimal and maximal electron momentum p, namely, p_{min} and p_{max}, depend in general on the (reduced) electron energy x. This dependence is exactly the same as in the 3D case, and is presented in Appendix B.

The final expessions for the scattering matrix elements are

$$\begin{gathered} P_{11}=P_0t^3H_{30}(z,t), \\ P_{12}=P_{21}=P_0t^3(k_BT)\{H_{31}(z,t)+H_{40}(z,T)\}, \end{gathered} \tag{17}$$

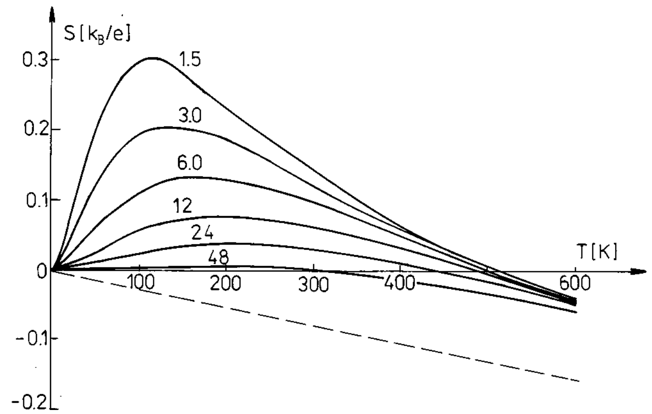

FIG. 1. Temperature dependence of S resulting from formulas in the text for the 2D system for typical values of parameters $T_D = 200$ K and $\varepsilon_F = 1.5$ eV, and values ε_s (in K) as indicated (see Table I).

$$P_{22} = P_0 t^3 (k_B T)^2 \left\{ H_{32}(z,t) + 2H_{41}(z,t) + H_{50}(z,t) + \frac{\varepsilon_s}{k_B T}[H_{31}(z,t) + zH_{30}(z,t)] \right\},$$

where $t = T/T_D$, and P_0 is a constant. They are counterparts of formula (3.12) of Ref. 3; their complicated form is caused by the fact that the energy transfer between the electron and phonon system is taken into account.

As a first approximation we consider that the electron gas is sufficiently degenerate such that $\zeta(T) = \varepsilon_F$ and $z = \beta\zeta(T) \to \infty$ can be taken in the end. Then the model system is one that describes a typical metal to which the standard Sommerfeld expansion or the degenerate (metallic) limit is applied. (see, e.g., Refs. 12 and 13). The final results of Ref. 1 were also obtained in this approximation.

If the Fermi energy is sufficiently large, a Debye momentum cutoff can be assumed, i.e., $p_{max} = 1/t = T_D/T$ and $p_{min} = 0$. Then the asymptopic analysis of the integrals $H_{kl}(z,T)$ can be made exactly in the same way as in Appendix B of Ref. 3 for the integrals $G_{km}(z,T)$. The final asymptotic (at $z \to \infty$) expressions for the scattering matrix elements are

$$P_{ij}(\infty, T) = P_0 (k_B T)^{i+j-2} t^4 \mathcal{P}_{ij}(t), \quad t = T/T_{\mathrm{D}}, \tag{18}$$

where

$$\mathcal{P}_{11}(t) = \mathcal{F}_4(a,b;t),$$

$$\mathcal{P}_{12}(t) = (1/2)\mathcal{F}_5(a,b;t), \tag{19}$$

$$\mathcal{P}_{22}(t,T) = (\pi^2/3)\mathcal{F}_4 + (1/3)\mathcal{F}_6 - (b/2t)\mathcal{F}_5 + (a/2t)^2 \mathcal{F}_4,$$

with the integrals $\mathcal{F}_n(a,b:t)$ defined

$$\mathcal{F}_n(a,b;t) = \int_0^{1/t} \frac{dx}{\sqrt{a^2 - (xt-b)^2}} \frac{x^n}{(e^x - 1)(1 - e^{-x})}, \tag{20}$$

The parameters are

$$a = 2(\varepsilon_F \varepsilon_s)^{1/2}/k_B T_D, \quad b = \varepsilon_s / k_B T_D. \tag{21}$$

TABLE I. The values of the parameters relevant to Figs. 1 and 2 for the free-electron effective mass and the Fermi energy $\varepsilon_F = 1.5$ eV. The ratios of the Debye phonon wave-vector cutoff to the caliper of the Fermi surface are presented in the last column.

No.	ε_s (K)	a	b	$q_D/2k_F$
(i)	1.50	1.62	0.0075	0.619
(ii)	3.00	2.84	0.0150	0.427
(iii)	6.00	3.23	0.0300	0.309
(iv)	12.0	4.57	0.0600	0.219
(v)	24.0	6.46	0.1200	0.154
(vi)	48.0	9.14	0.0240	0.109

They have to satisfy the conditions $a > b$ and $a + b > 1$ for the positiveness of the expression under the square root in integral (20) in the whole interval $0 < x < 1/t$. If these conditions are not satisfied, one cannot assume the Debye cutoff and the degenerate limit (see Appendix B).

By applying these expressions and the asymptotic ones for the trial currents with

$$L_0(z) \approx z, \quad L_1(z) \approx \frac{\pi^2}{3}, \quad L_2(z) \approx \frac{\pi^2}{3} z, \tag{22}$$

we obtain

$$S = S_0(t) + (t/c) S_1(t), \tag{23}$$

where $c = \varepsilon_F / k_B T_D$ and

$$S_0(t) = \frac{\pi^2}{3} \frac{k_B}{e} \frac{\mathcal{P}_{12}(t)}{\mathcal{P}_{22}(t)},$$
$$S_1(t) = -\frac{\pi^2}{3} \frac{k_B}{e} \left\{ 1 + \frac{\pi^3}{3} \frac{\mathcal{P}_{11}(t)}{\mathcal{P}_{22}(t)} \right\}. \tag{24}$$

One can show that $S_0(t \to \infty) = 0$ and $S_1(t \to \infty) = -2\pi^2/3$. Therefore, the high-temperature-describing approximation of Eq. (23) is

$$S \cong -\frac{2\pi^2}{3} \frac{k_B}{e} \frac{k_B T}{\varepsilon_F}. \tag{25}$$

The temperature dependence of S resulting from the above formulas for the 2D system is shown in Fig. 1 for the values of ε_s of Table I and for typical values of ε_F and T_D. The temperature interval in which the TEP is positive is wider for 2D systems. Notice that the carriers are assumed to be electrons not holes for both 3D and 2D systems. The positiveness of $S(T)$ in certain temperature intervals is a consequence of the fact that the first term in Eq. (23), $S_0(T)$, is positive and overwhelms the negative contribution of the second term. The term $S_0(T)$, being expressed in terms of the matrix elements $\mathcal{P}_{12}(t) = \mathcal{P}_{21}(t)$, describes the corrrelations of the electric and thermal currents, just as in the linear-response theory.[14] It is effective only if an inelastic contribution to the scattering is taken into account.[3] As seen from the figures, the influence of this term is more pronounced in the 2D case than in the 3D case (compare Figs. 1 and 2). The

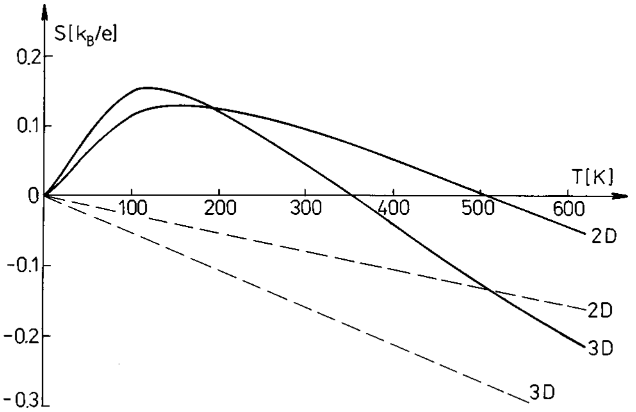

FIG. 2. Temperature dependence of S for 2D systems [curve corresponding to $v_s=6$ K. (iii) of Table I] of Fig. 1 and for 3D systems with the same values of the parameters $V_s=6$ K, $\epsilon_F=1.5$ eV, and $T_D=200$ K.

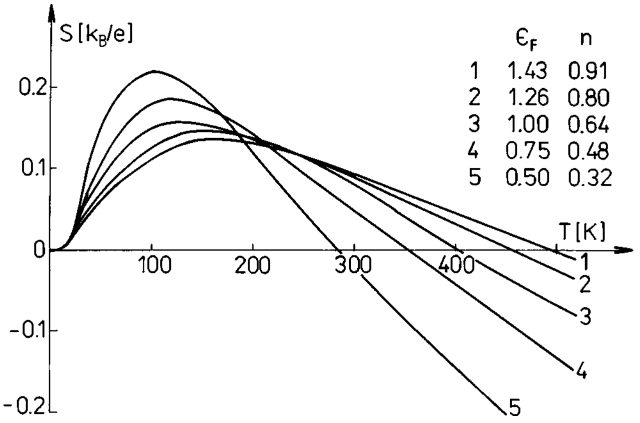

FIG. 3. Temperature dependence of S for 2D systems, with different values of the electron concentration n (or ε_F in eV) as indicated; $\varepsilon_s=6$ K and $T_D=200$ K. The uppermost two curves correspond to those of Fig. 3 in Ref. 1.

agreement between our calculation and the asymptotic values [Eq. (7)] will occur only at very high temperature.

The behavior of $S(T)$ as illustrated is qualitatively the same as that for the underdoped LSCO system of Fig. 1 examined in Ref. 1, and thus for systems with a sufficiently large number of carriers as well. In both cases the maximum in $S(T)$ is a consequence of the fact that the TEP is very sensitive to the excitation of electronic states close to the Fermi surface, as well known from the TEP definition, and to the fact that there is an asymmetry in the scattering rate from unoccupied states (holes) and occupied states (electrons) at and near the Fermi surface. It is well known that the high-temperature behavior of S, as in Eq. (25), is the characteristic one for systems with a positive charge-carrier mass. On the other hand, a positive slope in the asymptotic behavior is obtained for $m<0$ in the above case with a parabolic spectrum. Less obvious is the fact that $S_0(t)$ is positive both for $m>0$ and $m<0$. Consequently $S(T)$ is strictly positive for all T when $m<0$, both in two and three dimensions, and thus the behavior of $S(T)$ in two dimensions for $m<0$ (not considered in this paper) resembles the behavior for hole conduction in the 3D case (Fig. 1 in Ref. 2). In the case attributed to LSCO in Ref. 1, the behavior of S indicates that the free-electron mass is positive. This can be checked by an expansion of the tight-binding electron spectrum considered by Hildebrand *et al.*[1] Furthermore a relationship can be found between the electron concentration n per unit-cell volume, the Fermi energy ε_F, and the tight-binding energy bandwidth Δ.

For a tetragonal lattice, $\varepsilon_F=2\pi n\Delta$. For comparison to Ref. 1, let the parameter $n\approx 1-x$, where x is like the number of holes per site. The dependence of $S(T)$ is given in Fig. 3 for various values of n (between 0.32 and 0.91) and $T_D=200$ K and $\varepsilon_s=6$ K. These correspond to free-electron Fermi energies ranging between 0.50 and 1.43 eV. It is interesting to compare the dependences shown in Fig. 3 with those shown in Fig. 1 of Ref. 1 for different values of x. The temperature dependence of S for all values of ϵ_F (n) are qualitatively the same as that for the highest value of n (or the lowest value of $x=1-$n) in Fig. 1 of Ref. 1. Also the magnitude of S is of the same order as that of Ref. 1. However, the absolute values of the slope of $S(T)$ at high temperatures decrease with an increase of ϵ_F or n in our case while the opposite trend is seen in Fig. 1 of Ref. 1. Furthermore, the maximum values S of Fig. 3 decrease with an increase of n contrary to Ref. 1. These discrepancies can be attributed to the fact that a finite band is considered in Ref. 1 contrary to our free electron approximation. The only qualitative difference is the slope of $S(T)$ at high temperatures, the absolute value of which decreases with increase of ε_F (and n), while the opposite trend is seen in Fig. 1 of Ref. 1. It is known that for a band of finite width the magnitude of S at high temperatures approaches a finite value.[18–20] Such a slope saturation is observed in high-temperature superconductors, in which the conduction-band-width can be narrower than k_BT. The opposite tendency—an increase of the absolute magnitude of the slope with increase of ε_F—is a known feature of the free-electron-gas approximation.[11]

IV. CORRESPONDENCE TO RELAXATION-TIME APPROXIMATION

The question arises if and how the above results correspond to those obtained in the relaxation-time approximation and those resulting from the Mott (-Jones) formula, i.e., in case of a degenerate electron gas $[z=\zeta(T)/k_BT\to\infty]$. For this purpose we have to recall the standard textbook formula[11,13,12]

$$S=-\frac{K_1}{eTK_0}, \tag{26}$$

where

$$K_m=\int d\varepsilon\left(-\frac{df}{d\varepsilon}\right)(\varepsilon-\zeta)^m\tau(\varepsilon)W(\varepsilon), \tag{27}$$

with $m=0$, 1, and 2; the relaxation time is $\tau(\varepsilon)$, and

$$W(\varepsilon)=W_0\int\left(\frac{dS_\varepsilon}{|\nabla\varepsilon|}\right)[v_x^2+v_y^2+v_z^2], \tag{28}$$

where $W_0=1/2$ or 1/3 for 2D or 3D cases, respectively, and with $v_z=0$ in the first case.

In the degenerate limit (with $\zeta = \varepsilon_F$) the above expression for S yields the Mott (-Jones) formula

$$S = -\frac{\pi}{3e} k_B^2 T \frac{1}{\sigma_F} \left(\frac{d\sigma(\varepsilon)}{d\varepsilon} \right)_{\varepsilon=\varepsilon_F}, \tag{29}$$

where

$$\sigma(\varepsilon) = e^2 \tau(\varepsilon) W(\varepsilon) \tag{30}$$

is the electrical conductivity of energy ε.

In this standard formulation of the theory only elastic scattering can be accounted for, and the relaxation time is simply given by

$$\frac{1}{\tau(\varepsilon)} = \int d\mathbf{k}' C(\mathbf{k},\mathbf{k}') \left(-\frac{df}{d\varepsilon} \right) (1 - \cos \theta_{\mathbf{k},\mathbf{k}'}), \tag{31}$$

where $\theta_{\mathbf{k},\mathbf{k}'}$ is the scattering angle, from which, for the parabolic (electron $m > 0$) band, we obtain

$$\tau(\varepsilon) = \tau_0(T)(\varepsilon/k_B T)^{r-1/2}, \tag{32}$$

with the exponent r describing the type of the scattering. The values of r are not negative, and do not exceed the value 4 for known scattering processes. As seen from Eq. (29), the function $\tau_0(T)$ is not essential for TEP considerations. The electron energy dependence of the function $W(\varepsilon)$ is also a power law $W = W_0 \varepsilon^s$ with $s = 1$ in the 3D case and $s = 1/2$ in the 2D case. The temperature dependence of $S(T)$, resulting from Eqs. (26) and (32), is

$$S = -\frac{k_B}{e} \left[\frac{(r+s+1) F_{r+s}(z)}{(r+s) F_{r+s-1}(z)} - z \right], \tag{33}$$

with the temperature dependence of $\zeta(T)$ in $z = \zeta(T)/k_B T$ to be found for a particular model. This is the standard expression used in the physics of degenerate semiconductors,[32] semimetals,[33] metals of low Fermi energy,[34] and quasi-two-dimensional electronic systems.[35,36,26] In the latter systems other scattering source than the phononic source are usually dominant. The exponent describing the acoustic scattering mentioned in Ref. 26 (equal to $r = 0$ in our notation) is usually used to interpret experimental data in systems in which the Fermi energy is so low that scattering angles $\theta_{\mathbf{k},\mathbf{k}'}$ as large as π are allowed. In the language used in Appendix A of Ref. 37, this means that the ''Sondheimer energy interval'' instead of the ''Debye energy interval'' is effective in this case. In the Ziman variational formalism, this corresponds to calculating integral (16) with $p_{\max} = 2(x\varepsilon_s\beta)^{1/2}$ (see Appendix B).

In the degenerate limit the above formula is simply

$$S = -\frac{\pi^2}{3} \frac{k_B}{e} (r+s) \frac{k_B T}{\varepsilon_F}. \tag{34}$$

Since the exponent r takes on the values $r = 3/2$ (the 2D case) and $r = 2$ (the 3D case) for acoustic-phonon scattering, the asymptotic high-temperature dependence of S resulting from the Ziman variational formalism (25) corresponds to the linear dependence following from the relaxation-time approximation. The same concerns the 3D case considered in Refs. 2 and 3.

It is worth mentioning here that by applying the variational Ziman formalism, result (33) cannot be obtained. This seems obvious from form (17) of the expression for the scattering matrices. In the elastic approximation only the first terms of Eq. (15) contribute to P_{12}, P_{22}, and Eq. (9). The counterparts of integrals (16) describing this contribution in this case are

$$H_{kl}^{elast}(z,T) = \int_0^\infty dx \frac{(x-z)^l e^{x-z}}{(1+e^{x-z})^2} \int_0^{p_{max}} dp \times \frac{p^k}{\sqrt{4\beta\varepsilon_s x - p^2}(e^p - 1)}, \tag{35}$$

where $p_{max} = 2(x\varepsilon\beta)^{1/2}$ is the case of the Sondheimer cutoff (corresponding to the energy conservation without the Debye constraint), and $p_{max} = 1/t$ in the case of the Debye cutoff. The form of the above integral follows from neglecting the phonon energy term in the δ function of Eq. (4).

Expression (33) is expected to be obtained from considering a scattering matrix of infinite order in the elastic approximation and an infinite sequence of the trial functions (8) in the expression

$$S = \frac{1}{T} \frac{\sum_{i,j=1} J_i Q_{ij} U_j}{\sum_{i,j=1} J_i Q_{ij} J_j}, \tag{36}$$

where

$$Q_{ij} = (P^{-1})_{ij}. \tag{37}$$

V. CONCLUDING REMARKS

The behavior of the TEP as a function of temperature for metallic systems seems to have certain general features independent of the nature of the scattering. These main features consist of (i) some maximum at intermediate temperature, and (ii) a quasilinear dependence at high temperature (including nearly constant values for systems of narrow bands). Moreover the minimum seen at very low temperatures, and found mainly for simple electron-phonon scattering systems,[6,2,3] arises as a manifestation of the fact that the electrons (not holes) are the current carriers.

A comparison of TEP for 2D (in-plane TEP) and 3D systems indicates that these general features of TEP are the same for dimensionally different systems. Details of the band structure, the Brillouin-zone filling (doping), the source, and the type of scattering as well as the spectrum of the scatterers should, of course, introduce corrections to the ''exact'' temperature dependence of TEP. They should still be studied by reliable theoretical methods without any drastic approximation. Studies of truly 2D (metallic) systems seem particularly useful for this purpose. As concerns their application to particular materials, it is worth mentioning here that the description of a cuprate superconductor in terms of a parabolic band dispersion and accoustic phonons is known to be inadequate, and the theory presented here should rather be applied to more conventional metals. Indeed the nonlinear temperature dependence of S is also expected even for the free-electron gas. Nevertheless the behavior of $S(T)$ in high-temperature superconductors has a simple character. There seems to be no need for complicating the situation with many bands,[38] polaron contributions,[10] and the like, when there are still theoretical questions as to their proper accounting. The investigation of Ref. 1 and that of the present paper indicate how terms describing the scattering contribute to TEP at intermediate and low temperatures. For their description a better theory than the relaxation-time approximation is required, since the latter is capable of properly describing only electronic properties of a material.

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APPENDIX A

The transition rate describing the scattering of electrons by acoustic phonons in tetragonal and hexagonal crystals can be expressed (see, e.g., Ref. 24) by mean spectra and polarizations with respect to directions in crystals. A Fermi golden rule expression such as Eq. (4) for tetragonal and hexagonal crystals in this approximation reads

$$C(\mathbf{k},\mathbf{k}')=C_0\beta f(\varepsilon)[1-f(\varepsilon')]\left[\frac{q_\perp^2}{\omega_{q\perp}}N_{q\perp}\delta(\varepsilon-\varepsilon'+\hbar\omega_{q\perp})+\frac{q_z^2}{\omega_{q,z}}N_{q,z}\delta(\varepsilon-\varepsilon'+\hbar\omega_{qz})\right], \tag{A1}$$

where the phonon wave vector $\mathbf{q}=\mathbf{k}'-\mathbf{k}$ is equal to the transferred electron wave vector in the scattering; the corresponding electron energies before and after the scattering are $\varepsilon(\mathbf{k})=\varepsilon$ and $\varepsilon(\mathbf{k}')=\varepsilon'$, respectively.

C_0 is a constant, $q_\perp=\sqrt{q_x^2+q_y^2}$, $\omega_{q\perp}$ and ω_{qz} are the mean phonon spectra with the polarization perpendicular and parallel to the c axis (the z axis of the coordinatation frame), and $N_{q\perp}$ and N_{qz} are the corresponding Bose distributions. It is seen that the second term in the above mean transition rate does not contribute if the electrons are confined to move in layers perpendicular to the z axis. Thus we obtain Eq. (4) with $q_\perp\equiv q$, $\omega_{q\perp}\equiv\omega$, and $N_{q\perp}\equiv N_q$.

APPENDIX B

While considering thermoelectric power in the 3D case by the variatonal method,[3] we showed that the contribution to P_{11} is determined by the double integral

$$P_{11}=P_{3D}\int_0^\infty d(\beta\varepsilon)f(\varepsilon)\int_{q_{min}}^{q_{max}}dq\,q^4B(q,\varepsilon), \tag{B1}$$

where

$$B(p,\varepsilon)=(e^{\beta p}-1)^{-1}(1+e^{-\beta(\varepsilon-\zeta+p)})^{-1}. \tag{B2}$$

The wavelength limits in integral (B1) are $q_{max}=\min(q_D,2k+q_s)$, $q_{min}=0$ if $q_s\leqslant 2k$, and $q_{min}=q_s-2k$ if $q_s>2k$, with q_D—the Debye cutoff phonon wave number $2k$—the caliper of the electron equienergy surface, and $q_s=2mv_s^2/\hbar$. In the limit of the degenerate gas (metallic limit), which we applied in Ref. 3, one can assume $q_{max}=q_D$ and change the order of integration. This was the approximation of the final formulas of Ref. 3. The same appproximation is used in the final formulas of the present paper.

The considerations leading to P_{11} were performed in Ref. 3 under strict energy and momentum conservation. For this purpose we rotated the coordination frame in the inverse space, which enabled us to integrate analytically appropriate expressions with respect to the angles in spherical coordinates.

For the systems of the layered structure discussed in the present paper the meaning of the integrals in Eqs. (9) and (10) is

$$\int d\mathbf{k}\cdots=\frac{2}{(2\pi)^3}\int_{-b_c}^{b_c}dk_z\int dk_x dk_y\cdots \equiv\frac{4b_c}{(2\pi)^3}\int\left(\frac{dS_\varepsilon}{|\nabla\varepsilon|}\right)\cdots, \tag{B3}$$

where the maximum wave number in the c (or z) direction is $b_c=\pi/d_c$, and d_c is the unit-cell length in that direction. Similar considerations to those in the 3D case with spherical electron equienergy surfaces can be repeated, but for the integration in spherical coordinates. We only mention that to this end we first change the variables from $\mathbf{k}$ and $\mathbf{k}'$ to $\mathbf{k}$ and $\mathbf{q}=\mathbf{k}'-\mathbf{k}$, and we rotate the coordination frame about the z axis through the angle $\varphi=\arctan(k_y/k_x)$, such that the y component of $\mathbf{k}$ vanishes in the coordinates: $\mathbf{k}=(K_x,0,K_z)$. In the same way we obtain the components of the transferred wave vector $Q_x=q_x\cos\varphi+q_y\sin\varphi$, $Q_y=q_x\cos\varphi+q_y\sin\varphi$, and $Q_z=q_z$ and introduce the cylindrical coordinates to integrate analytically with respect to the scattering angle $\cos\theta_{\mathbf{k},\mathbf{k}'}=\mathbf{kq}/(kq)$. In so doing we obtain

$$P_{11}=P_{2D}\int_0^\infty d(\beta\varepsilon)f(\varepsilon)\int_{q_{min}}^{q_{max}}dq\frac{q^3B(q,\varepsilon)}{\sqrt{4k^2-(q-q_s)^2}}, \tag{B4}$$

where $q_s=(2m/\hbar)v_s$, and v_s is the sound velocity. After adding the factors $(\varepsilon-\zeta)^l$ and transforming the above integral to dimensionless variables, one obtains the integrals H_{kl}, [Eq. (16)], in which $p_{max}=\min(2\sqrt{\varepsilon_s\beta x}+\varepsilon_s\beta,1/t)$, and $p_{min}=\beta\varepsilon_s-2\sqrt{\varepsilon_s\beta x}$ if $\beta\varepsilon_s>2\sqrt{\varepsilon_s\beta x}$, and $p_{min}=0$ in the opposite case.

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