Theory of thermoelectric effects in dilute alloys

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The low-temperature thermoelectric coefficient is calculated for a model of fixed impurities, Debye phonons, and free electrons using an expansion in the inverse powers of valence Z. It is shown that the cancellation of the electron-phonon corrections to the thermopower found in the previous papers of this series for the case of isotropic scattering on impurities does not occur in the general case. The convergence of the large-valence expansion is shown to be fast even for small values of $Z \gtrsim 1$. The first term of the expansion gives a simple approximate formula for the thermopower. For a class of model impurity potentials, the accuracy of this formula is found to be of order 5%.

I. INTRODUCTION AND SUMMARY

In previous papers of this series[1-3] the low-temperature thermoelectric coefficient was calculated in a simple model of free electrons interacting with fixed impurities and longitudinal Debye phonons through the Fröhlich Hamiltonian. The scattering on impurities was assumed to be weak and isotropic (s-wave scattering). An unexpected result of that calculation was a considerable cancellation between various electron-phonon corrections to the thermopower. It was shown that these corrections cancel completely in the limit of large-valence Z. An obvious question arising from this result is whether there is some deep physical reason for the cancellation or is it purely coincidental. In the latter case one would expect the cancellation to disappear in a more realistic model. The purpose of the present paper is to extend the treatment of Refs. 1–3 to the case of arbitrary (nonisotropic) scattering on impurities. All other assumptions remain the same.

The electron-phonon corrections to the thermopower can be written as a sum $\phi^{(1)} + \phi^{(2)}$, where $\phi^{(1)}$ is the contribution due to the renormalization of the electron energy, velocity, and mean free time and $\phi^{(2)}$ is the contribution of the electron-phonon vertex correction. The generalization for arbitrary impurity potentials is straightforward in the case of $\phi^{(1)}$, while $\phi^{(2)}$ is given by an integral which cannot be evaluated for the general form of the impurity potential. This difficulty is resolved by observing that in the limit of large valence, $Z \gg 1$, the vertex correction is nonzero only for almost backward scattering, i.e., for $\vec{k}' \approx -\vec{k}$. Expanding the impurity potential $U_{\vec{k}-\vec{k}'}$ in powers of $|\vec{k}+\vec{k}'|^2$ near $\vec{k}' = -\vec{k}$ and performing the integrations, one obtains an expansion of the thermopower ϕ in powers of $(4Z)^{-2/3}$. The first term in this expansion is

$$\phi = [1 + 2\gamma\lambda_1(\lambda_1 - 1)^{-1}]\phi^{(0)}\,, \tag{1}$$

where $-\gamma$ is the energy derivative of the electron self-energy, λ_1 is given by Eqs. (16) and (17) below, and $\phi^{(0)}$ is the thermopower without electron-phonon corrections. For isotropic scattering, when $U_{\vec{k}\vec{k}'} = \text{const}$, $\lambda_1 = 0$ and $\phi = \phi^{(0)}$. However, it is clear from Eq. (1) that in the general case the electron-phonon corrections to the thermopower do not cancel, and thus the cancellation obtained in Refs. 2 and 3 was coincidental.

The asymptotic behavior of ϕ at $Z \to \infty$ would be of little interest, were it not related to the calculation of the thermopower for physically interesting values of Z. The main result of the present paper is to show that such a relation does exist. The convergence of the large-valence expansion is shown to be fast even for small $Z \gtrsim 1$. For a class of model potentials, the first term of the expansion (1) already gives good accuracy ($\sim 5\%$) even for a monovalent metal. If this property of the large-valence expansion is not affected by anisotropies of electron and phonon dispersion relations, umklapp scattering, and other real metal features, then such an expansion can be a useful tool in the calculation of the thermopower for a more realistic model of metals.

II. CALCULATION OF $\phi^{(1)}$

According to Refs. 1–3, the low-temperature thermopower of a dilute alloy can be written as

$$\phi = \phi^{(0)} + \phi^{(1)} + \phi^{(2)}\,, \tag{2}$$

where $\phi^{(1)}$ arises from the renormalization of the electron energy, velocity, and mean free time, and $\phi^{(2)}$ is the contribution due to the electron-phonon vertex correction. We have

$$\phi^{(0)} + \phi^{(1)} = \frac{\pi^2 T^2}{3e} \frac{\partial \sigma^*(\epsilon)}{\partial \epsilon}\bigg|_{\epsilon=\mu}\,, \tag{3}$$

where μ is the Fermi energy,

$$\sigma^*(\epsilon) = \frac{e^2}{12\pi^3} \int_{E_k=\epsilon} dS_k v^*(\epsilon)\tau^*(\epsilon)\,, \tag{4}$$

$$E_k(\epsilon) = \epsilon_k + M_k(\epsilon)\,, \tag{5}$$

where $\epsilon_k = k^2/2m$, $M_k(\epsilon)$ is the electron-phonon energy correction $\vec{v}^*(\epsilon)$ is the renormalized electron velocity,

$$\vec{v}^*(\epsilon) = \left.\frac{\vec{v}_k + \vec{\nabla}_k M_k(\epsilon)}{1 - M_k'(\epsilon)}\right|_{E_k=\epsilon}, \tag{6}$$

and $\tau^*(\epsilon)$ is the renormalized electron mean free time,

$$\tau^*(\epsilon) = \tau(\epsilon)[1 - M_k'(\epsilon)]_{E_k=\epsilon}. \tag{7}$$

Here

$$\tau^{-1}(\epsilon) = \left.\frac{Nk^2 t(\epsilon)}{\pi[k/m + \partial M_k(\epsilon)/\partial k]}\right|_{E_k=\epsilon}, \tag{8}$$

$$t(\epsilon) = \frac{1}{4\pi}\int_{E_k=E_{k'}=\epsilon} |U_{kk'}|^2(1-\cos\theta_{kk'})d\Omega_{k'}, \tag{9}$$

and N is the impurity concentration. It is assumed that the scattering on impurities is weak, so that the T matrix $T_{kk'}$ is approximately equal to $U_{kk'}$,

$$T_{kk'} \approx U_{kk'} \equiv U_{k-k'}, \tag{10}$$

where

$$U_{k-k'} = \int U(\vec{x}) e^{-i(\vec{k}-\vec{k}')\cdot\vec{x}} d^3x, \tag{11}$$

$U(\vec{x})$ is the impurity potential. If $U(\vec{x})$ is spherically symmetric, then

$$U_{kk'} = 4\pi|\vec{k}-\vec{k}'|^{-1}\int_0^\infty U(r)\sin(|\vec{k}-\vec{k}'|r) r\,dr. \tag{12}$$

Note that in this case $U_{kk'}$ is real and depends only on $|\vec{k}-\vec{k}'|$. We shall assume below that $U(\vec{x})$ is spherically symmetric.

Since $M_k(\mu) = 0$ and

$$\left.\frac{\partial\epsilon_k}{\partial E_k}\right|_{E_k=\mu} = 1+\gamma, \tag{13}$$

where

$$\gamma \equiv -M_k'(\mu), \tag{14}$$

we can write for $\epsilon \approx \mu$:

$$t(\epsilon) = t^{(0)}(\mu)[1 + \lambda_1(1+\gamma)(\epsilon-\mu)/\mu]. \tag{15}$$

Here

$$\lambda_1 \equiv \mu t^{(0)\prime}(\mu)/t^{(0)}(\mu) \tag{16}$$

and $t^{(0)}(\epsilon)$ is $t(\epsilon)$ without electron-phonon corrections:

$$t^{(0)}(\epsilon) = \frac{1}{4\pi}\int_{\epsilon_k=\epsilon_{k'}=\epsilon} |U_{kk'}|^2(1-\cos\theta_{kk'})d\Omega_{k'}. \tag{17}$$

Using the results of Sec. V in Ref. 1, we can now write

$$\sigma^*(\epsilon) = \sigma^{(0)}\{1 + [1 + 2\gamma - \lambda_1(1+\gamma)](\epsilon-\mu)/\mu\}, \tag{18}$$

where

$$\sigma^{(0)} = n_e e^2 \tau^{(0)}/m \tag{19}$$

is the dc conductivity and

$$\tau^{(0)} = \pi[Nm k_F t^{(0)}(\mu)]^{-1} \tag{20}$$

is the "bare" electron mean free time.

From Eqs. (3) and (18) we find

$$\phi^{(0)} + \phi^{(1)} = \frac{\pi^2 T^2 \sigma^{(0)}}{3e\mu}[1 + 2\gamma - \lambda_1(1+\gamma)]. \tag{21}$$

$\phi^{(0)}$ is obtained by setting $\gamma = 0$ in Eq. (21):

$$\phi^{(0)} = \frac{\pi^2 T^2 \sigma^{(0)}}{3e\mu}(1-\lambda_1) \tag{22}$$

and thus

$$\phi^{(1)} = (2-\lambda_1)(1-\lambda_1)^{-1}\gamma\phi^{(0)}. \tag{23}$$

III. CALCULATION OF $\phi^{(2)}$ FOR $Z \gg 1$

According to Ref. 3,

$$\phi^{(2)} = -\frac{N\tau^{(0)}\mu\phi^{(0)}}{2\pi^2(1-\lambda_1)}\int\frac{dS_{k'}}{v_{k'}}(1-\cos\theta_{kk'})U_{kk'}\hat{T}'_{kk'}(\mu), \tag{24}$$

where $\hat{T}'_{kk'}(\mu)$ is the energy derivative of the electron-phonon vertex correction[3-5]:

$$\hat{T}'_{kk'}(\mu) = \frac{C^2 U_{kk'}}{4\pi^3 M_i v_s^2 n_i v_F}\,\mathrm{P}\int\frac{dS_{k''}}{\epsilon_{k''+k'-k}-\mu}. \tag{25}$$

Here P stands for principal value, v_s is the sound velocity, M_i and n_i are the ion mass and concentration, respectively, C is the Sommerfeld-Wilson interaction constant and the integration is taken over the sphere $\epsilon_{k''} = \mu$ in the region $|\vec{k}''-\vec{k}| < q_m$.

The integral (24) for $\phi^{(2)}$ with $\hat{T}'_{kk'}(\mu)$ given by (25) cannot be evaluated for the general form of $U_{kk'}$. However, a considerable simplification can be achieved in the case of large valence, $Z = 2(k_F/q_m)^3 \gg 1$. It can be shown that in this case, $\hat{T}'_{kk'}(\mu)$ is nonzero only for $\vec{k}'$ very close to $-\vec{k}$: $|\vec{k}+\vec{k}'| < q_m$. To prove this statement, let us write the integral of Eq. (25) in the form

$$I = m(\sin\psi_0)^{-1}\int_0^{\psi_m} d\psi \times \mathrm{P}\int_0^{2\pi} d\phi(\tan\tfrac{1}{2}\psi\tan\tfrac{1}{2}\psi_0 + \cos\phi)^{-1}, \tag{26}$$

where $\psi = \theta_{kk''}$, $\psi_0 = \theta_{kk'}$ and

$$\psi_m = \arccos(1 - q_m^2/2k_F^2). \tag{27}$$

The ϕ integration is elementary; the result is nonzero only if $\cos\psi_0/2 < \sin\psi/2$, and thus I is nonzero only if $\cos\psi_0/2 < \sin\psi_m/2 = (4Z)^{-1/3}$ or $\sin\frac{1}{2}(\pi-\psi_0) < (4Z)^{-1/3}$. We see that $\hat{T}'_{kk'}(\mu)$ is nonzero only near $\psi_0 = \pi$ in the limit $Z \to \infty$.

Assuming that $U_{kk'}$ does not change considerably

for $\delta k' \sim q_m$ we can replace $|U_{kk'}|^2$ by $|U_{k,-k}|^2$ in the integral for $\phi^{(2)}$. This gives

$$\phi^{(2)} = \phi^{(0)} \alpha\gamma (Z/2)^{2/3} (1-\lambda_1)^{-1} |U_{k,-k}|^2 / t^{(0)}(\mu) , \tag{28}$$

where $t^{(0)}(\mu)$ is given by Eq. (17) and α is the integral (16) of Ref. 3. In the limit of large Z, $\alpha = -2(Z/2)^{-2/3}$ and

$$\phi^{(2)} = -2\gamma\lambda_2 (1-\lambda_1)^{-1} \phi^{(0)} , \tag{29}$$

where

$$\lambda_2 \equiv |U_{k,-k}|^2 / t^{(0)}(\mu) . \tag{30}$$

It can be shown[6] that λ_1 and λ_2 are related by

$$\lambda_2 = 1 + \lambda_1/2 . \tag{31}$$

Combining Eqs. (23), (29), and (31) we get

$$\phi^{(1)} + \phi^{(2)} = 2\gamma\lambda_1 (\lambda_1 - 1)^{-1} \phi^{(0)} . \tag{32}$$

We see that the cancellation of the electron-phonon corrections to the thermopower occurs only if $\lambda_1 = 0$; i.e., when $t^{(0)\prime}(\mu) = 0$. Thus, the cancellation found in Refs. 2 and 3 for isotropic scattering was coincidental.

IV. LARGE-VALENCE EXPANSION

Instead of replacing $|U_{kk'}|^2$ by $|U_{k,-k}|^2$, one could expand $|U_{kk'}|^2$ in powers of $|\vec{k}+\vec{k}'|^2$. Substituting this expansion in Eq. (24) and evaluating the integrals, one would get an expansion of the thermopower in powers of $q_m^2/k_F^2 \sim Z^{-2/3}$. The result of the preceding section, Eq. (32), would then correspond to the lowest-order approximation. In this section we shall calculate the next few terms in the expansion of ϕ.

According to Eq. (12), $U_{kk'}$ is a function of $|\vec{k}-\vec{k}'|$ and we can write

$$|U_{kk'}|^2 \equiv F(\tfrac{1}{2}|\vec{k}-\vec{k}'|^2) . \tag{33}$$

For $|\vec{k}| = |\vec{k}'| = k_F$, $\frac{1}{2}|\vec{k}-\vec{k}'|^2 = k_F^2(1-x)$, where $x = \cos\theta_{kk'}$. Expanding F in powers of $k_F^2(1+x)$ we get

$$|U_{kk'}|^2 = F(2k^2 - k^2(1+x)) = F(2k^2) \sum_{n=0}^{\infty} A_n 2^{-n} (1+x)^n , \tag{34}$$

where

$$A_n = \frac{(-2k^2)^n}{n!} \frac{F^{(n)}(2k^2)}{F(2k^2)} . \tag{35}$$

Note that $2k_F^2(1+x) = |\vec{k}+\vec{k}'|^2$, and thus the expansion (34) is indeed in powers of $|\vec{k}+\vec{k}'|^2$.

Substituting Eqs. (25) and (34) in Eq. (24) we get

$$\phi^{(2)} = \frac{1}{2}\left(\frac{Z}{2}\right)^{2/3} \gamma(2+\lambda_1)(1-\lambda_1)^{-1} \phi^{(0)} \sum_{n=0}^{\infty} A_n \alpha_n , \tag{36}$$

where

$$\alpha_n = \pi^{-1} 2^{-n} \int_0^{\pi} d\psi_0 \int_0^{\psi_m} d\psi \int_0^{2\pi} d\varphi \, \frac{\sin\psi \sin\psi_0 (1-\cos\psi_0)(1+\cos\psi_0)^n}{\cos\psi + \cos\psi_0 - \cos\psi\cos\psi_0 - \sin\psi\sin\psi_0\cos\varphi - 1} . \tag{37}$$

Introduction of new variables $x = \sin\psi/2$, $y = \sin\psi_0/2$, and $z = (x^2+y^2-1)^{1/2}$ brings this integral to the form

$$\alpha_n = -16 \int_0^{\xi} dx \int_0^{x} (x^2 - z^2)^n (1 - x^2 + z^2)^{1/2} dz , \tag{38}$$

where $\xi = \sin\psi_m/2 = (4Z)^{-1/3}$. An expansion of α_n in powers of ξ^2 can now be obtained by expanding $(1-x^2+z^2)^{1/2}$ in powers of (x^2-z^2) and performing the integrations over x. This gives

$$\alpha_n = -8\left(\frac{f_n}{n+1}\xi^{2n+2} - \frac{f_{n+1}}{2(n+2)}\xi^{2n+4} - \frac{f_{n+2}}{8(n+3)}\xi^{2n+6} - \cdots\right) , \tag{39}$$

where

$$f_n = \int_0^1 (1-t^2)^n dt . \tag{40}$$

From these equations we find

$$\begin{aligned} \alpha_0 &= -8\xi^2 + \tfrac{4}{3}\xi^4 + \tfrac{8}{45}\xi^6 + \cdots , \\ \alpha_1 &= -\tfrac{8}{3}\xi^4 + \tfrac{32}{45}\xi^6 + \cdots , \\ \alpha_2 &= -\tfrac{64}{45}\xi^6 + \cdots , \\ &\cdots . \end{aligned} \tag{41}$$

An extension to greater n and to higher powers of ξ^2 can be easily obtained.

The coefficients A_n in Eq. (36) depend on the specific form of the potential $U_{kk'}$. For example, if the impurity potential $U(r)$ is proportional to $r^{-\beta}$ with[7] $1 \leq \beta < 3$, then $U_{kk'} \sim |\vec{k}-\vec{k}'|^{-\sigma}$ with $\sigma = 3-\beta$ and

$$A_n = (n!)^{-1} \sigma(\sigma+1)\cdots(\sigma+n-1) . \tag{42}$$

Using Eqs. (16), (23), (36), (41), and (42) we find

$$\phi^{(1)} + \phi^{(2)} = \gamma\phi^{(0)} (1+\sigma)^{-1} \times [2\sigma - \tfrac{1}{6}(2-\sigma)(2\sigma-1)\xi^2 - \tfrac{1}{45}(2-\sigma)(4\sigma^2-1)\xi^4 + \cdots] . \tag{43}$$

It is interesting to note that the convergence of this series is fast even for small values of Z. If β is not too close to 3, say, $\beta < 2.5$, then, even for a monovalent metal ($Z = 1$), keeping only the first term in the expansion (43) would give an error of no more than 4%. If β is close to 3, then σ is small and the second term can be important. But the first two terms together give a good accuracy for all acceptable values of β.

These results indicate that the large-valence expansion can be used to calculate the thermopower for all values of $Z \gtrsim 1$ and for a wide class of impurity potentials. It should be stressed, however, that in this paper we considered only a simple model of free electrons and Debye phonons. Extension of the results to a more realistic model of metal would be of great interest.

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[6]Representing $|U_{kk'}|^2$ as $F(k^2(1-x))$ with $\epsilon_k = \epsilon_{k'} = \mu$ and $x = \cos\theta_{kk'}$, we can write $t^{(0)\prime}(\mu) = m\int_{-1}^{1} F'(k^2(1-x)) \times (1-x)^2\,dx$. Integrating by parts we obtain Eq. (32).
[7]This requirement for β if necessary for the convergence of the integral (12).