

Theory of the low-temperature Seebeck coefficient in dilute alloys

Y. A. Ono and P. L. Taylor

Department of Physics, Case Institute of Technology, Case Western Reserve University, Cleveland, Ohio 44106

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The Seebeck coefficient in dilute alloys at low temperatures is investigated in a simple model in which free electrons are scattered by a random array of fixed impurities and interact with longitudinal Debye phonons through a Fröhlich Hamiltonian. As has been shown by Vilenkin, the wave-number dependence of the Fourier-transformed impurity potential removes the near cancellation of several contributions due to the electron-phonon renormalizations discussed by Vilenkin and Taylor. The net electron-phonon enhancement of the Seebeck coefficient is found to be close to the usual mass-enhancement ratio in the case of a screened Coulomb potential.

I. INTRODUCTION

The low-temperature Seebeck coefficient S of dilute alloys has been shown by various authors to contain a number of significant terms due to electron-phonon interactions. In recent years the flow of new suggested contributions into the literature has been fast and furious, with each new development tending to negate its predecessors. Thus Opsal, Thaler, and Bass¹ suggested that previous workers² were in error in supposing S not to be modified by those interactions and argued from Mott's formula³ that in the impurity-scattering regime S should be enhanced by a factor $1 + \gamma$, the usual mass-enhancement correction. Following this, Lyo^{4,5} calculated microscopically some many-body effects of the electron-phonon interaction on the electron-diffusion thermopower (Seebeck coefficient) and found S to be enhanced not only by the mass renormalization but also by the electron-phonon modification of the quasiparticle velocity. In a model of weak s -wave scatterers the correction factor was predicted to be $1 + \frac{3}{2}\gamma$. Vilenkin and Taylor⁶ then found some additional corrections in the diagrammatic expansion of the heat-current operator, and showed that for the case of weak impurity scattering the renormalization of the electron energy, velocity, and relaxation time causes an enhancement of the unperturbed Seebeck coefficient by a factor of $1 + 2\gamma$. Their calculation was performed in a simple model where free electrons interact with fixed impurities and longitudinal Debye phonons through a Fröhlich Hamiltonian at low temperatures, thus avoiding the need to consider the virtual recoil⁷ of the impurities.

On the other hand, Hasegawa^{8,9} had previously observed that the electron-phonon renormalization of the impurity-scattering vertex should give an important contribution to thermoelectric coefficients. Vilenkin and Taylor^{10,11} showed that the

transport equations involving vertex and other electron-phonon corrections reduce to the Boltzmann equation at low temperatures, and in the case of weak s -wave scattering they found near-cancellation of electron-phonon corrections to the Seebeck coefficient. Recently, Vilenkin¹² modified the treatment of Vilenkin and Taylor to include arbitrary impurity potentials and found that the above-mentioned cancellation does not occur in the general case. He also proposed an expansion formula for the thermopower.

With the present paper the wheel has turned almost full circle, in that for a more realistic scattering potential the electron-phonon enhancement of S is found to be numerically close to the original suggestion of Opsal *et al.* We calculate the Seebeck coefficient following the argument of Vilenkin and Taylor¹¹ and of Vilenkin¹² in a model in which the wave-number dependence of the Fourier-transformed impurity potential yields additional contributions to the Seebeck coefficient.

As was indicated above, there are two classes of contribution to the electron-phonon enhancement of the Seebeck coefficient: One is due to the renormalization of the electron energy, velocity, and relaxation time, and the other is from the electron-phonon renormalization of the impurity-scattering vertex. The inclusion of the r -dependent impurity potential in the first case is straightforward, while the second correction needs careful treatment. In the Debye model, integrations over phonon wave numbers are limited to the Debye sphere, and this has the effect of weighting heavily the importance of large-angle impurity scattering, especially in the case of large valence. By expanding the impurity potential about the backward scattering angle, we obtain an expression for the vertex contribution. Applying these formulas to impurity potentials of the type considered by Vilenkin,¹² namely, $U(r) \propto r^{-\beta}$ ($1 \leq \beta < 3$), and to a screened Coulomb potential in the Thomas-Fermi

approximation, we find the electron-phonon enhancement of S to be of the order of $1 + \gamma$.

In Sec. II we present a method of calculating the Seebeck coefficient, while an application of the formula to impurity potentials is discussed in Sec. III. A summary is given in Sec. IV.

II. FORMAL CALCULATION OF SEEBECK COEFFICIENT S

In this section we obtain an expression for the Seebeck coefficient at low temperatures in dilute alloys for a spherically symmetric impurity potential $U(r)$ within the model described in the preceding section. Then the Fourier transform $U_{\vec{k}\vec{k}'}$ is real and depends only on $|\vec{k} - \vec{k}'|$:

$$\begin{aligned} U_{\vec{k}\vec{k}'} &= \int U(r) e^{-i(\vec{k} - \vec{k}') \cdot \vec{r}} d\vec{r} \\ &= 4\pi |\vec{k} - \vec{k}'|^{-1} \int_0^\infty U(r) \sin(|\vec{k} - \vec{k}'| r) r dr. \end{aligned} \quad (1)$$

In the following, $U_{\vec{k}\vec{k}'}$ is written as

$$U_{\vec{k}\vec{k}'} = U(|\vec{k} - \vec{k}'|) = U(2k^2(1 - \cos\theta)), \quad (2)$$

where $\cos\theta = \cos\theta_{\vec{k}\vec{k}'}$.

The Seebeck coefficient S can be written in terms of the thermoelectric coefficient ϕ as¹³

$$S = \phi / \sigma^*(\mu) T. \quad (3)$$

Under the restricted circumstances of the model, the Mott relation applies at low temperatures, and one may write

$$\phi = \frac{\pi^2 k_B^2 T^2}{3e} \left. \frac{\partial \sigma^*(\epsilon)}{\partial \epsilon} \right|_{\epsilon=\mu}, \quad (4)$$

where e , k_B , and T are, respectively, electronic charge (negative), Boltzmann's constant, and temperature. The chemical potential μ is given by $\mu = \hbar^2 k_F^2 / 2m$, where k_F is the Fermi wave number ($k_F^3 = 3\pi^2 n_e$, n_e being the electron density) and m is the electron mass. The conductivity $\sigma^*(\epsilon)$ is given by⁶

$$\sigma^*(\epsilon) = \frac{e^2}{12\pi^3 \hbar} \int_{E_{\vec{k}} = \epsilon} dS_{\vec{k}} v_{\vec{k}}^*(\epsilon) \tau_{\vec{k}}^*(\epsilon), \quad (5)$$

where $E_{\vec{k}}$ is the renormalized quasiparticle energy given in terms of the bare-electron energy $\epsilon_{\vec{k}}$ ($= \hbar^2 k^2 / 2m$) by

$$E_{\vec{k}}(\epsilon) = \epsilon_{\vec{k}} + M_{\vec{k}}(\epsilon). \quad (6)$$

Here $M_{\vec{k}}(\epsilon)$ is the real part of the electronic self-energy arising from the virtual one-phonon process and $v_{\vec{k}}^*$ is the renormalized electron velocity given by

$$v_{\vec{k}}^* = [\vec{v}_{\vec{k}} + (1/\hbar) \vec{\nabla}_{\vec{k}} M_{\vec{k}}(\epsilon)] / [1 - M_{\vec{k}}'(\epsilon)] |_{E_{\vec{k}} = \epsilon}, \quad (7)$$

where $\vec{v}_{\vec{k}} = (1/\hbar) \vec{\nabla}_{\vec{k}} \epsilon_{\vec{k}}$ is the bare-electron velocity

and the prime signifies a derivative with respect to the argument. On the other hand, $\tau_{\vec{k}}^*(\epsilon)$ is the renormalized electron relaxation time defined as

$$\tau_{\vec{k}}^*(\epsilon) = \tau_{\vec{k}}(\epsilon) [1 - M_{\vec{k}}'(\epsilon)] |_{E_{\vec{k}} = \epsilon}, \quad (8)$$

where

$$\frac{1}{\tau_{\vec{k}}(\epsilon)} = \frac{N}{\pi \hbar} \frac{k^2 t_{\vec{k}}(\epsilon)}{[\hbar^2 k/m + \partial M_{\vec{k}}(\epsilon)/\partial k]} \Big|_{E_{\vec{k}} = \epsilon}. \quad (9)$$

Here N is the impurity concentration and $t_{\vec{k}}(\epsilon)$ is given by

$$t_{\vec{k}}(\epsilon) = t_{\vec{k}}^I(\epsilon) + 2t_{\vec{k}}^{II}(\epsilon), \quad (10)$$

$$t_{\vec{k}}^I(\epsilon) = \frac{1}{4\pi} \int_{E_{\vec{k}} = E_{\vec{k}'} = \epsilon} d\Omega_{\vec{k}'} |U_{\vec{k}\vec{k}'}|^2 (1 - \cos\theta_{\vec{k}\vec{k}'}), \quad (11)$$

$$t_{\vec{k}}^{II}(\epsilon) = \frac{1}{4\pi} \int_{E_{\vec{k}} = E_{\vec{k}'} = \epsilon} d\Omega_{\vec{k}'} U_{\vec{k}\vec{k}'}^* \hat{T}_{\vec{k}\vec{k}'}(\epsilon) (1 - \cos\theta_{\vec{k}\vec{k}'}), \quad (12)$$

where we have assumed that the scattering is sufficiently weak so that the impurity T matrix can be replaced by $U_{\vec{k}\vec{k}'}$. $\hat{T}_{\vec{k}\vec{k}'}(\epsilon)$ represents impurity vertex correction due to the electron-phonon interaction. Since the second term in Eq. (10) gives a higher-order contribution, $\tau_{\vec{k}}(\epsilon)$ can be given approximately as

$$\begin{aligned} \tau_{\vec{k}}(\epsilon) &= \frac{\pi \hbar^3}{Nm k_F t_{\vec{k}}^I(\epsilon)} \left(1 - \frac{\epsilon - \mu}{2\mu} \right) \\ &\quad - \frac{2\pi \hbar^3}{Nm k_F [t_{\vec{k}}^I(\epsilon)]^2} t_{\vec{k}}^{II}(\epsilon), \end{aligned} \quad (13)$$

where we have also expanded k near k_F , where k satisfies the energy delta function $\delta(\epsilon - E_{\vec{k}}(\epsilon))$:

$$k = k_F [1 + (\epsilon - \mu)(1 + \gamma)/2\mu], \quad (14)$$

where $-\gamma$ is the energy derivative of the electron-phonon self-energy¹⁴ given by

$$\gamma = -M_{\vec{k}}'(\epsilon) = 3C^2 k_F / 8M_i v_s^2 \mu q_m. \quad (15)$$

Here C is the Sommerfeld-Wilson constant (in a free-electron model $C = -\frac{2}{3}\mu$), while M_i is the ion mass, v_s the longitudinal sound velocity, and q_m the Debye radius ($q_m^3 = 6\pi^2 n_i$, n_i being the ion concentration).

We write $\phi = \phi^{(0)} + \phi^{(1)} + \phi^{(2)}$, where $\phi^{(0)} + \phi^{(1)}$ is given by the first term of Eq. (13) and $\phi^{(2)}$ comes from the second term of Eq. (13). Here $\phi^{(0)}$ represents the thermoelectric coefficient without electron-phonon interaction, $\phi^{(1)}$ arises from the renormalization of the electron energy, velocity and the relaxation time, and $\phi^{(2)}$ is the contribution from the electron-phonon renormalization of the impurity-scattering vertex.

First we discuss the first two terms, $\phi^{(0)} + \phi^{(1)}$. In the calculation of the Seebeck coefficient the off-shell energy dependence near the Fermi sur-

face is very important. Therefore, we expand $t_{\mathbf{k}}^{\frac{1}{2}}(\epsilon)$ near $\epsilon = \mu$ and find

$$t_{\mathbf{k}}^{\frac{1}{2}}(\epsilon) = t^0(\mu) [1 + \lambda_1(1 + \gamma)(\epsilon - \mu)/\mu], \quad (16)$$

where λ_1 is a new parameter specifying the energy dependence of the unperturbed total scattering probability, and is given by

$$\lambda_1 = \mu t^{\prime 0}(\mu)/t^0(\mu). \quad (17)$$

Here we have defined $t^0(\mu) \equiv t_{\mathbf{k}}^0(\epsilon = \mu)$ and $t_{\mathbf{k}}^0(\epsilon)$ is equal to $t_{\mathbf{k}}^{\frac{1}{2}}(\epsilon)$ without electron-phonon interaction,

$$t_{\mathbf{k}}^0(\epsilon) = \frac{1}{4\pi} \int_{\epsilon_{\mathbf{k}} = \epsilon_{\mathbf{k}''} = \epsilon} d\Omega_{\mathbf{k}} |U_{\mathbf{k}\mathbf{k}''}|^2 (1 - \cos\theta_{\mathbf{k}\mathbf{k}''}). \quad (18)$$

Combining Eqs. (4), (5), (7), (8), (13), and (16) we find

$$\phi^{(0)} + \phi^{(1)} = \frac{\pi^2 k_B^2 T^2 \sigma^{(0)}}{3e\mu} [1 + 2\gamma - \lambda_1(1 + \gamma)], \quad (19)$$

where $\sigma^{(0)}$ is the dc conductivity given by

$$\sigma^{(0)} = n_e e^2 \tau^{(0)} / m, \quad (20)$$

and

$$\tau^{(0)} = \pi \hbar^3 / [N m k_F t^0(\mu)] \quad (21)$$

is the "bare"-electron relaxation time. At the Fermi surface, $\sigma^*(\epsilon)$ reduces to $\sigma^{(0)}$, and thus the Seebeck coefficient defined by Eq. (3) can be written as

$$S = \phi / \sigma^{(0)} T. \quad (22)$$

In the case of an isotropic s -wave scattering potential, we have $\lambda_1 = 0$ and Eq. (19) reduces to Eq. (86) of Ref. 7 with $\phi^{(0)} = \pi^2 k_B^2 T^2 \sigma^{(0)} / 3e\mu$. In a general potential $\phi^{(0)}$ is obtained by setting $\gamma = 0$ in Eq. (19):

$$\phi^{(0)} = \frac{\pi^2 k_B^2 T^2 \sigma^{(0)}}{3e\mu} (1 - \lambda_1). \quad (23)$$

Then $\phi^{(1)}$ can be expressed in terms of $\phi^{(0)}$ as

$$\phi^{(1)} = \gamma \phi^{(0)} (2 - \lambda_1) / (1 - \lambda_1). \quad (24)$$

Next we consider the term $\phi^{(2)}$. Since this gives a correction of order γ , we can approximate $\phi^{(2)}$ as

$$\begin{aligned} \phi^{(2)} = & -\frac{N\tau^{(0)}\mu\phi^{(0)}k_F m}{2\pi^2(1-\lambda_1)} \\ & \times \int d\Omega_{\mathbf{k}} U_{\mathbf{k}\mathbf{k}''}^* \hat{T}'_{\mathbf{k}\mathbf{k}''}(\mu) (1 - \cos\theta_{\mathbf{k}\mathbf{k}''}), \end{aligned} \quad (25)$$

where we have taken the term giving the largest contribution.¹¹ Use has been made of Eqs. (4), (5), (7), (8), (12), and (13). Here $\hat{T}'_{\mathbf{k}\mathbf{k}''}$ is the energy derivative of the impurity-scattering vertex due to

electron-phonon interaction at the Fermi surface¹¹:

$$\begin{aligned} \hat{T}'_{\mathbf{k}\mathbf{k}''}(\mu) = & -4U_{\mathbf{k}\mathbf{k}''} \sum_{\mathbf{k}'''} |V_{\mathbf{k}\mathbf{k}'''}|^2 \omega_{\mathbf{k}\mathbf{k}'''}^{-1} \delta(\epsilon_{\mathbf{k}'''} - \mu) \\ & \times (\epsilon_{\mathbf{k}'''} - \epsilon_{\mathbf{k}''} + \epsilon_{\mathbf{k}})^{-1}, \end{aligned} \quad (26)$$

where $\omega_{\mathbf{k}\mathbf{k}''} = v_s |\mathbf{k} - \mathbf{k}''|$ and $V_{\mathbf{k}\mathbf{k}''}$ is the electron-phonon coupling constant, given by $V_{\mathbf{k}\mathbf{k}''} = C |\mathbf{k} - \mathbf{k}''| / (2n_i M_i \omega_{\mathbf{k}\mathbf{k}''})^{1/2}$. The summation in Eq. (26) is taken over the region $|\mathbf{k} - \mathbf{k}''| \leq q_m$.

From Eqs. (25) and (26), $\phi^{(2)}$ takes the form

$$\phi^{(2)} = \gamma \phi^{(0)} (\frac{1}{2} Z)^2 \bar{\alpha} / (1 - \lambda_1), \quad (27)$$

with

$$\begin{aligned} \bar{\alpha} = & -\frac{1}{\pi t^0(\mu)} \int_0^\pi d\theta |U(2k_F^2(1 - \cos\theta))|^2 (1 - \cos\theta) \\ & \times \int_0^{\theta_m} d\theta' \int_0^{2\pi} d\phi' \frac{1}{\tan\frac{1}{2}\theta \tan\frac{1}{2}\theta' + \cos\phi'}, \end{aligned} \quad (28)$$

where Z is the valence of the solvent defined by $Z = n_e/n_i$. The angle θ' is $\theta_{\mathbf{k}\mathbf{k}''}$ and ϕ' is the azimuthal angle of \mathbf{k}'' around \mathbf{k} . The upper limit of the θ' integration θ_m comes from the restriction of phonon wave number in the Debye model and is given by

$$\sin\frac{1}{2}\theta_m = q_m / 2k_F = (4Z)^{-1/3} \equiv \xi. \quad (29)$$

Performing the ϕ' integration of Eq. (28), we obtain

$$\begin{aligned} \bar{\alpha} = & -\frac{2}{t^0(\mu)} \int_0^{\theta_m} d\theta' \int_{\pi-\theta'}^\pi d\theta |U(2k_F^2(1 - \cos\theta))|^2 \\ & \times \frac{(1 - \cos\theta) \cos\frac{1}{2}\theta \cos\frac{1}{2}\theta'}{(\sin^2\frac{1}{2}\theta + \sin^2\frac{1}{2}\theta' - 1)^{1/2}}. \end{aligned} \quad (30)$$

The integrals in Eq. (30) cannot be evaluated unless the impurity potential is specified. However, the restriction on the integral with θ_m defined by Eq. (29) leads to the conclusion that large-angle scattering forms the dominant contributor to $\bar{\alpha}$. Therefore, an expansion of impurity potential $|U_{\mathbf{k}\mathbf{k}''}|^2$ from the backward scattering limit in terms of $(1 + \cos\theta)/2$ is appropriate:

$$\begin{aligned} |U(2k_F^2(1 - \cos\theta))|^2 = & |U(4k_F^2)|^2 \\ & \times \sum_{n=0}^{\infty} A_n [(1 + \cos\theta)/2]^n, \end{aligned} \quad (31)$$

where

$$A_n = \frac{(-4k_F^2)^n \partial^n |U(4k_F^2)|^2}{n! (4k_F^2)^n} |U(4k_F^2)|^{-2}. \quad (32)$$

Substituting Eq. (31) into Eq. (30), we find

$$\bar{\alpha} = \lambda_2 \sum_{n=0}^{\infty} A_n \alpha_n, \quad (33)$$

where

$$\lambda_2 = |U(4k_F^2)|^2 / t^0(\mu), \quad (34)$$

$$\alpha_n = -\frac{1}{2^{n-1}} \int_0^{\theta_m} d\theta' \times \int_{\pi-\theta}^{\pi} d\theta \frac{(1-\cos\theta)(1+\cos\theta)^n \cos\frac{1}{2}\theta \cos\frac{1}{2}\theta'}{(\sin^2\frac{1}{2}\theta + \sin^2\frac{1}{2}\theta' - 1)^{1/2}}. \quad (35)$$

It is easily shown that λ_2 is related to λ_1 as¹²

$$\lambda_2 = 1 + \frac{1}{2}\lambda_1. \quad (36)$$

By using Eqs. (27), (33), and (36), $\phi^{(2)}$ can be expressed as

$$\phi^{(2)} = \gamma \phi^{(0)} \frac{2+\lambda_1}{1-\lambda_1} \frac{1}{8\xi^2} \sum_{n=0}^{\infty} A_n \alpha_n. \quad (37)$$

Since ξ^2 , defined by Eq. (29), is a small parameter for normal values of the valence Z , we expand α_n in terms of ξ^2 and find $\phi^{(2)}$ in a double-sum form given by

$$\phi^{(2)} = \gamma \phi^{(0)} \frac{2+\lambda_1}{1-\lambda_1} \left(-\sum_{n=0}^{\infty} A_n \frac{1}{n+1} \frac{(2n)!!}{(2n+1)!!} \xi^{2n} + \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} A_n \frac{(2m-3)!!}{m! 2^m} \frac{1}{n+m+1} \frac{(2n+2m)!!}{(2n+2m+1)!!} \xi^{2n+2m} \right). \quad (38)$$

Finally, the Seebeck coefficient can be written as

$$S = (eL_0 T / \mu)(1 - \lambda_1)(1 + a\gamma), \quad (39)$$

$$a = (\phi^{(1)} + \phi^{(2)}) / \gamma \phi^{(0)} = \frac{1}{1-\lambda_1} \left[(2-\lambda_1) + (2+\lambda_1) \left(-\sum_{n=0}^{\infty} A_n \frac{1}{n+1} \frac{(2n)!!}{(2n+1)!!} \xi^{2n} + \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} A_n \frac{(2m-3)!!}{m! 2^m} \frac{1}{n+m+1} \frac{(2n+2m)!!}{(2n+2m+1)!!} \xi^{2n+2m} \right) \right], \quad (40)$$

where L_0 is the Lorenz ratio, $\pi^2 k_B^2 / 3e^2$, and use is made of Eqs. (22), (23), (24), and (38).

III. IMPURITY POTENTIALS

In this section we apply the formula to some model impurity potentials: (i) $U(r) = Br^{-\beta}$ ($1 \leq \beta < 3$) and (ii) $U(r) = -Z'e^2 \exp(-qr)/r$, the screened Coulomb potential in the Thomas-Fermi approximation. While the first potential does not represent any particular physical model of the effective potential of a solute ion, it is of interest in that the range of the potential is continuously variable while the expansion formula remains of tractable form. On the other hand, the second potential includes the screening effect in a more realistic form.

(i) $U(r) = Br^{-\beta}$ ($1 \leq \beta < 3$). The Fourier transform of this potential is given by

$$U_{\vec{k}\vec{k}'} = B' |\vec{k} - \vec{k}'|^{-\sigma}, \quad (41)$$

where

$$B' = -2\pi^2 B / \Gamma(\beta - 1) \cos(\frac{1}{2}\pi\beta), \quad (42)$$

$$\sigma = 3 - \beta \quad (0 < \sigma \leq 2). \quad (43)$$

The constants λ_1 and A_n are given by

$$\lambda_1 = -\sigma, \quad (44)$$

$$A_n = \frac{C_n}{\sigma + n - 1} = (1/n!) \sigma(\sigma+1)(\sigma+2) \cdots (\sigma+n-1). \quad (45)$$

Then the parameter a defined by Eq. (40) is expressed explicitly in terms of σ and ξ^2 as

$$a = \frac{1}{1+\sigma} \left[2\sigma + \frac{1}{6}(2-\sigma)(1-2\sigma)\xi^2 + \frac{1}{45}(2-\sigma)(1-2\sigma)(1+2\sigma)\xi^4 + \frac{1}{420}(2-\sigma)(1-2\sigma)(1+2\sigma)(3+2\sigma)\xi^6 + \frac{1}{4725}(2-\sigma)(1-2\sigma)(1+2\sigma)(3+2\sigma)(5+2\sigma)\xi^8 + \cdots \right]. \quad (46)$$

The first three terms of Eq. (46) were also obtained by Vilenkin.¹² We note that the convergence of this series is very fast even for small values of Z . In fact, for the particular cases of $\beta = \frac{5}{2}$ and $\beta = 1$, all terms beyond the first vanish because of the presence of the factor $(2-\sigma)(1-2\sigma)$ in all the higher terms, and the correction is independent of Z . For the bare Coulomb interaction, the contribution of $\phi^{(2)}$ to a from the renor-

malization of the impurity vertex completely vanishes for any value of Z .

The β dependence of the parameter a is shown in Fig. 1 for physically interesting values of Z ; $Z = 1, 2$, and 3 . From the graph we observe that for a wide range of β , except near 3 , the electron-phonon enhancement of the Seebeck coefficient is of the order of $1 + \gamma$.

(ii) *The screened Coulomb interaction in the*

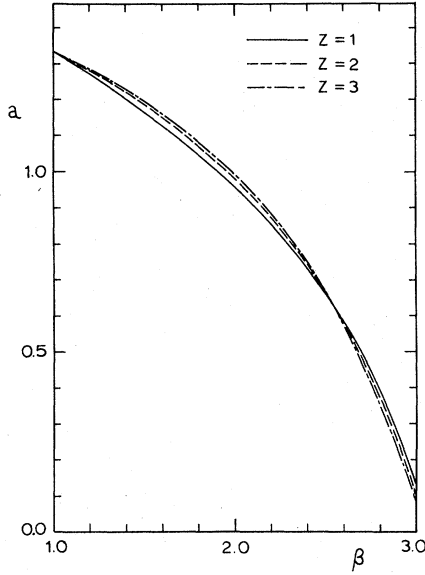


FIG. 1. β dependence of a in the $U(r) \propto r^{-\beta}$ potential for $Z=1, 2$, and 3 .

$$a = \frac{1}{1 - \lambda_1} \left[-2\lambda_1 + \frac{1}{6}(2 + \lambda_1)(1 - 4\delta)\xi^2 + \frac{1}{45}(2 + \lambda_1)(1 + 8\delta - 24\delta^2)\xi^4 + \frac{1}{140}(2 + \lambda_1)(1 + 4\delta + 24\delta^2 - 64\delta^3)\xi^6 + \frac{1}{1575}(2 + \lambda_1)(5 + 16\delta + 48\delta^2 + 256\delta^3 - 640\delta^4)\xi^8 + \dots \right]. \quad (53)$$

In the limit that $q_T \rightarrow 0$, so that $\lambda_1 \rightarrow -2$, the potential reduces to pure Coulomb form, and as previously shown there is no contribution from the vertex correction to the Seebeck coefficient.

For an explicit evaluation of Eq. (53) the val-

TABLE I. Values of Z , k_F , q_T , δ , λ_1 , and a .

Metal	Z	k_F (10^8 cm^{-1})	q_T (10^8 cm^{-1})	δ	λ_1	a
Li	1	1.12	1.64	0.651	-0.945	0.906
Na	1	0.92	1.49	0.604	-0.868	0.866
K	1	0.75	1.34	0.556	-0.792	0.825
Rb	1	0.70	1.30	0.537	-0.762	0.808
Cs	1	0.65	1.25	0.520	-0.736	0.793
Be	2	1.94	2.16	0.763	-1.140	1.027
Mg	2	1.36	1.82	0.691	-1.012	0.966
Ca	2	1.11	1.63	0.650	-0.943	0.931
Sr	2	1.02	1.56	0.631	-0.912	0.915
Ba	2	0.98	1.53	0.621	-0.896	0.906
Zn	2	1.58	1.94	0.726	-1.074	0.996
Cd	2	1.40	1.83	0.701	-1.029	0.974
Hg	2	1.37	1.81	0.696	-1.021	0.971
Al	3	1.75	2.05	0.745	-1.106	1.021
Ga	3	1.66	2.00	0.734	-1.087	1.012
In	3	1.51	1.90	0.716	-1.056	0.998
Sn	4	1.64	1.98	0.733	-1.085	1.017
Pb	4	1.58	1.94	0.726	-1.073	1.011

Thomas-Fermi Approximation. The potential in real space can be written as

$$U(r) = -Z'e^2 \exp(-q_T r)/r, \quad (47)$$

where Z' is the nuclear charge of an interstitial impurity or the difference of valency of a substitutional impurity with the solvent and q_T is the Thomas-Fermi wave number defined by

$$q_T^2 = 6\pi m_e e^2 / \mu. \quad (48)$$

The Fourier-transformed potential is given by

$$U_{\vec{k}\vec{k}'} = -4\pi Z'e^2 / (|\vec{k} - \vec{k}'|^2 + q_T^2). \quad (49)$$

Then λ_1 and A_n can be computed as

$$\lambda_1 = -[\delta^2 + 2\delta + 2 \ln(1 - \delta)] / [\delta + \ln(1 - \delta)], \quad (50)$$

$$A_n = (n + 1)\delta^n, \quad (51)$$

where δ is a dimensionless parameter

$$\delta = 4k_F^2 / (4k_F^2 + q_T^2). \quad (52)$$

The parameter a can be expressed explicitly in an expansion form as

ues of δ for specific metals are required. With k_F , μ , and n_e taking on their free-electron values,¹⁵ one finds the electron-phonon enhancement correction a shown in Table I. From this we observe that the electron-phonon enhancement of the Seebeck coefficient is of the order of $1 + \gamma$ for

TABLE II. Values of v_s , γ , and $a\gamma$ for metals in the free-electron model.

Metals	v_s (10^5 cm/s)	γ	$a\gamma$
Na	3.2 ^a	0.175	0.152
K	2.0 ^a	0.173	0.143
Rb	1.3 ^a	0.163	0.132
Cs	1.2 ^a	0.106	0.0840
Be	12.9 ^c	0.154	0.158
Mg	5.77 ^c	0.141	0.136
Ca	3.6 ^a	0.145	0.135
Ba	2.0 ^a	0.106	0.0960
Zn	4.17 ^b	0.134	0.133
Cd	2.78 ^b	0.138	0.134
Al	6.26 ^b	0.204	0.208
In	2.8 ^a	0.176	0.175
Sn	3.32 ^b	0.158	0.160
Pb	2.16 ^b	0.198	0.200

^a Reference 16.

^b Reference 17.

^c Reference 18.

all the metals quoted, as a does not differ from unity by much more than ten percent.

For specific evaluation of the correction factor we need to calculate γ given by Eq. (15). In a free-electron model with Debye phonons, γ is simplified as

$$\gamma = \mu \left(\frac{1}{2}Z\right)^{1/3} / 6M_i v_s^2. \quad (54)$$

With appropriate values of the ionic mass (Ref. 15) M_i and the longitudinal sound velocity (Refs. 16–18) v_s , we are able to list the values of γ and the electron-phonon correction to the Seebeck coefficient $a\gamma$ in Table II.

IV. SUMMARY

The purpose of this paper has been to calculate the Seebeck coefficient S in alloys at low temperatures. We have considered a simple model of fixed impurities and longitudinal Debye phonons interacting with free electrons. The impurity potential is assumed to be weak but its spatial dependence is retained explicitly, and this introduces some additional contributions to the Seebeck coefficient, as has been shown by Vilenkin.¹² The near cancellation of the electron-phonon corrections to S obtained by Vilenkin and Taylor^{10,11} in the limit of short range of the potential does not

occur. The enhancement of S due to the electron-phonon interaction is found to be of the order of $1 + \gamma$ in the case of the screened Coulomb potential in the Thomas-Fermi approximation, where $-\gamma$ is the energy derivative of the electron self-energy correction. In contrast with the results of some previous calculations the electron-phonon corrections cannot be expressed solely in terms of γ and depend on other parameters.

Many aspects of the problem of thermoelectricity in alloys have been omitted from this discussion. These include the effects of Umklapp scattering and anisotropies of electron and phonon dispersion relations. Also, the Fröhlich Hamiltonian considered here does not include any terms of second order in the ionic displacement in the electron-phonon scattering and thus does not include the expected corrections due to processes involving virtual recoil.⁷ A more complete treatment in which such effects are treated, and in which *ab initio* pseudopotentials are used, remains a goal to be reached.

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