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Theory of the low-temperature Seebeck coefficient in dilute alloys. II. The empty-core pseudopotential calculation

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The Seebeck coefficient S in dilute alloys at low temperatures is calculated for an impurity scattering potential derived from the empty-core pseudopotential. In the model considered here, free electrons are scattered by a random array of fixed impurities and interact with longitudinal phonons. The electron-phonon correction to S in alkali-alkali alloys is found to be positive if an impurity is heavier than a solvent and negative otherwise. In most other alloys where the valence of the impurity and the solvent is different, the net electron-phonon enhancement of S is found to be numerically close to the usual mass-enhancement ratio, in accord with the results in the case of the screened Coulomb potential.

I. INTRODUCTION

In previous papers[1,2] (which are referred to as I and II) Ono and Taylor calculated the low-temperature Seebeck coefficient S of dilute alloys in a simple model in which free electrons interact with fixed impurities and longitudinal Debye phonons through the Fröhlich Hamiltonian. The screened Coulomb potential in the Thomas-Fermi approximation was used as a model impurity potential. The wave-number dependence of the Fourier-transformed impurity potential yielded an additional contribution to the Seebeck coefficient besides contributions considered before by Hasegawa,[3,4] Lyo,[5-7] and Vilenkin and Taylor.[8-10] The electron-phonon enhancement of S was found to be numerically close to the original suggestion of Opsal, Thaler, and Bass,[11] who obtained the enhancement factor $1+\gamma$ using Mott's formula,[12] where $-\gamma$ is the energy derivative of the electron self-energy correction. The inclusion of the wave-number–dependent impurity potential in the calculation of the thermoelectric coefficients was discussed before by Meyer and Young,[26] Hasegawa,[3,4] and Vilenkin.[13]

For the screened Coulomb potential in the Thomas-Fermi approximation, however, the case where impurities have the same valence as the solvent metal is meaningless, since the effect of the impurity on the potential is only through the valence difference δZ. This can be easily seen from the form of the impurity potential $U_{\mathrm{TF}}(r)$ in the Thomas-Fermi (TF) approximation given by[14]

$$U_{\mathrm{TF}}(r) = -\delta Z e^2 \exp(-qr)/r \,, \tag{1}$$

where q is the Thomas-Fermi wave number defined by Eq. (18) in Sec. III. Furthermore, in this approximation the electron-phonon enhancement of the Seebeck coefficient does not depend on δZ. One attempt to include this effect was performed by Ono and Taylor[15] by using the extension of the Thomas-Fermi approximation to the finite-impurity concentration case due to Friedel.[16] It was found that the enhancement correction was reduced by as much as 50% when δZ is positive and enhanced by as much as 20% when δZ is negative. Again, impurities of the same valence have the same effects on the Seebeck coefficient for this model potential. Therefore a more realistic impurity potential should be considered when one wants to compare theoretical results with experiments.

In the present paper we use the empty-core model of the pseudopotential proposed by Ashcroft[17] to obtain a model impurity potential. Ashcroft and Langreth[18] applied the empty-core pseudopotential to a calculation of the compressibility and the binding energy of simple metals and found good agreement with experimentally measured values not only for the alkalis but also for polyvalent metals. Recently Harrison[19] used this pseudopotential extensively in the discussion of the nearly-free-electron features of simple metals in his new textbook on properties of solids. In a substitutional-impurity case, the Fourier-transformed impurity potential can be expressed by the difference of the pseudopotential form factors[19,20] of the impurity and the solvent metal. Thus we can discuss the above-mentioned situations which were not amenable to treatment in the Thomas-Fermi approximation of the screened Coulomb interaction. We have found the following: (i) In alkali metals when the core radius of the impurity is larger than that of a solvent, the electron-phonon enhancement correction a defined by Eq. (14) in Sec. II is positive, while a is negative otherwise. (ii) In dilute alloys of combinations of impurities and solvent metals with $\delta Z \neq 0$, the enhancement of the Seebeck coefficient is of the order of $1+\gamma$ (a is of the order of unity).

This is in accord with the results of I and II.

In Sec. II we present a short discussion of a method of calculating the Seebeck coefficient S, while the formal empty-core pseudopotential calculation of S is given in Sec. III. Results for specific combinations of solvent metals and impurities are given in Sec. IV and a summary is given in Sec. V.

II. EXPANSION FORMULA OF SEEBECK COEFFICIENT S

In this section we give a brief account of a method of obtaining an expansion formula of the Seebeck coefficient in dilute alloys at low temperatures (for detail, see paper II). We consider a spherically symmetric impurity potential $U(r)$. Then the Fourier transform $U_{\vec{k}\vec{k}'}$ is real and depends only on $|\vec{k}-\vec{k}'|$ and can be written as

$$\begin{aligned} U_{\vec{k}\vec{k}'} &= U(|\vec{k}-\vec{k}'|^2) \\ &= U[2k^2(1-\cos\theta)] = U(4k^2\sin^2\tfrac{1}{2}\theta), \end{aligned} \tag{2}$$

where θ is the angle between $\vec{k}$ and $\vec{k}'$.

The Seebeck coefficient S at low temperature in dilute alloys can be expressed as[1,2]

$$S = (\phi^{(0)} + \phi^{(1)} + \phi^{(2)})/\sigma^{(0)}T. \tag{3}$$

Here $\phi^{(0)}$ is the heat current density per unit electric field[21] in the absence of the electron-phonon interaction, $\phi^{(1)}$ arises from the renormalization of electron energy, velocity, and relaxation time due to electron-phonon interaction, $\phi^{(2)}$ is the contribution from the electron-phonon impurity-vertex correction, and T is the temperature. The electric conductivity $\sigma^{(0)}$ at the Fermi surface is given by

$$\sigma^{(0)} = n_e e^2 \tau^{(0)}/m, \tag{4}$$

where $n_e = k_F^3/3\pi^2$ is the electron density, e is the charge of an electron (negative), and m is the electron mass. The Fermi wave number k_F and the Fermi energy μ are related by $\mu = \hbar^2 k_F^2/2m$. The "bare"-electron relaxation time at the Fermi surface, $\tau^{(0)}$, is given by

$$\tau^{(0)} = \pi\hbar^3/[Nmk_F t^0(\mu)]. \tag{5}$$

Here N is the impurity concentration and

$$t^0(\mu) = \frac{1}{4\pi}\int_{\epsilon_{\vec{k}}=\epsilon_{\vec{k}'}=\mu} d\Omega_{\vec{k}'}|U_{\vec{k}\vec{k}'}|^2(1-\cos\theta_{\vec{k}\vec{k}'}), \tag{6}$$

where $\epsilon_{\vec{k}}$ is the bare-electron energy given by $\hbar^2k^2/2m$. The quantities $\phi^{(0)}$ and $\phi^{(1)}$ are given by

$$\phi^{(0)} = \pi^2(k_BT)^2\sigma^{(0)}(1-\lambda_1)/3e\mu, \tag{7}$$

$$\phi^{(1)} = \gamma\phi^{(0)}(2-\lambda_1)/(1-\lambda_1). \tag{8}$$

Here λ_1 is a parameter specifying the energy dependence of the unperturbed total scattering probability near the Fermi surface and is given by

$$\lambda_1 = \mu t^{0\prime}(\mu)/t^0(\mu), \tag{9}$$

and $-\gamma$ is the energy derivative of the electron self-energy correction due to the electron-phonon interaction:

$$\gamma = 3C^2k_F/8M_i v_s^2 \mu q_m. \tag{10}$$

Here C is the Sommerfeld-Wilson constant (in a free-electron model $C = -2\mu/3$), 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 ion density). In a free-electron model with Debye phonons, γ is simplified to

$$\gamma = \mu(\tfrac{1}{2}Z)^{1/3}/6M_i v_s^2, \tag{11}$$

where Z is the valence of the solvent metal ($Z = n_e/n_i$).

On the other hand, $\phi^{(2)}$ can be expanded as a double sum of the form

$$\phi^{(2)} = \gamma\phi^{(0)}\frac{2+\lambda_1}{1-\lambda_1}\left(-\sum_{n=0}^{\infty} A_n \frac{1}{n+1}\frac{(2n)!!}{(2n+1)!!}\xi^{2n} + \sum_{n=0}^{\infty}\sum_{m=1}^{\infty} A_n \frac{(2m-3)!!}{m!2^m}\frac{1}{n+m+1}\frac{(2n+2m)!!}{(2n+2m+1)!!}\xi^{2n+2m}\right), \tag{12}$$

where the A_n are coefficients of expansion of $|U_{\vec{k}\vec{k}'}|^2$ from the backward-scattering limit in powers of $\cos^2\frac{1}{2}\theta_{\vec{k}\vec{k}'}$ and $\xi^2 = (q_m/2k_F)^2 = (4Z)^{-2/3}$.

Finally the Seebeck coefficient can be written as

$$S = (eL_0T/\mu)(1-\lambda_1)(1+a\gamma) \tag{13}$$

with

$$\begin{aligned} a &= (\phi^{(1)} + \phi^{(2)})/\gamma\phi^{(0)} \\ &= \frac{1}{1-\lambda_1}\left[2-\lambda_1+(2+\lambda_1)\left(-\sum_{n=0}^{\infty} A_n\frac{1}{n+1}\frac{(2n)!!}{(2n+1)!!}\xi^{2n}\right.\right. \\ &\qquad \left.\left.+\sum_{n=0}^{\infty}\sum_{m=1}^{\infty} A_n\frac{(2m-3)!!}{m!2^m}\frac{1}{n+m+1}\frac{(2n+2m)!!}{(2n+2m+1)!!}\xi^{2n+2m}\right)\right], \end{aligned} \tag{14}$$

where L_0 is the Lorenz number $\pi^2 k_B^2/3e^2$, and use is made of Eqs. (7), (8), and (12).

III. EMPTY-CORE PSEUDOPOTENTIAL CALCULATION

In this section we use the empty-core pseudopotential proposed by Ashcroft[17] as a model impurity potential. In a substitutional-impurity case, the scattering potential $U_{\vec{k}\vec{k}'}$ can be written as[19,20]

$$U_{\vec{k}\vec{k}'} = (W^s_{\vec{k}\vec{k}'} - W^i_{\vec{k}\vec{k}'})/n_i \,, \tag{15}$$

where $W^s_{\vec{k}\vec{k}'}$ and $W^i_{\vec{k}\vec{k}'}$ are, respectively, the pseudopotential form factor of the solvent atom and of the impurity and are given by[19]

$$W^s_{\vec{k}\vec{k}'} = -\frac{4\pi Z e^2}{\Omega_0}\,\frac{\cos(|\vec{k}-\vec{k}'|r_c)}{(|\vec{k}-\vec{k}'|^2+q^2)} \tag{16}$$

$$W^i_{\vec{k}\vec{k}'} = -\frac{4\pi Z' e^2}{\Omega_0}\,\frac{\cos(|\vec{k}-\vec{k}'|r_c')}{(|\vec{k}-\vec{k}'|^2+q^2)} \,. \tag{17}$$

Here Z' is the valence of the impurity, r_c (r_c') is the core radius of the solvent (impurity) atom for the empty-core model, and Ω_0 is the atomic volume ($\Omega_0 = n_i^{-1}$). The quantity q is the screening parameter which is given in the Thomas-Fermi approximation by

$$q = (6\pi n_e e^2/\mu)^{1/2} = (4e^2 k_F m/\pi\hbar^2)^{1/2} \,. \tag{18}$$

In the calculation of λ_1 and A_n the magnitudes of $\vec{k}$ and $\vec{k}'$ can be put equal to k_F. Then $U_{\vec{k}\vec{k}'}$ can be written as

$$\begin{aligned} U_{\vec{k}\vec{k}'} &= U(4k_F^2 \sin^2\tfrac{1}{2}\theta) \\ &= -\frac{4\pi e^2 Z r_c^2}{\alpha^2 \sin^2\frac{1}{2}\theta + \beta^2} \\ &\qquad \times \left(\cos(\alpha \sin\tfrac{1}{2}\theta) - \frac{Z'}{Z}\cos(\alpha' \sin\tfrac{1}{2}\theta)\right) , \end{aligned} \tag{19}$$

where α, α', and β are dimensionless parameters defined by

$$\begin{aligned} \alpha &= 2k_F r_c \,, \\ \alpha' &= 2k_F r_c' \,, \\ \beta &= q r_c \,. \end{aligned} \tag{20}$$

Then λ_1 is given by

$$\lambda_1 = \tfrac{1}{2}\delta^2 [\cos\alpha - (Z'/Z)\cos\alpha']^2/F(\alpha) - 2 \,, \tag{21}$$

where

$$\delta = 4k_F^2/(4k_F^2 + q^2) = \alpha^2/(\alpha^2+\beta^2) \,, \tag{22}$$

$$F(\alpha) = \int_0^\alpha dx\, x^3 \frac{[\cos x - (Z'/Z)\cos(\alpha' x/\alpha)]^2}{(x^2+\beta^2)^2} \,. \tag{23}$$

The expansion coefficients A_n are given by

$$\begin{aligned} A_0 &= 1 \,, \\ A_1 &= 2\delta + B_1 \,, \\ A_2 &= 3\delta^2 + 2\delta B_1 + \tfrac{1}{4}C_1 \,, \\ A_3 &= 4\delta^3 + 3\delta^2 B_1 + \tfrac{1}{8}(4\delta+1)C_1 - \tfrac{1}{24}C_2 \,, \\ A_4 &= 5\delta^4 + 4\delta^3 B_1 + \tfrac{1}{64}(48\delta^2 + 16\delta + 5)C_1 \\ &\quad - \tfrac{1}{96}(8\delta+3)C_2 - \tfrac{1}{192}C_3 \,, \\ A_5 &= 6\delta^5 + 5\delta^4 B_1 + \tfrac{1}{128}(128\delta^3 + 48\delta^2 + 20\delta + 7)C_1 \\ &\quad - \tfrac{1}{128}(16\delta^2 + 8\delta + 3)C_2 - \tfrac{1}{192}(2\delta+1)C_3 + \tfrac{1}{1920}C_4 \,, \\ &\ldots \,, \end{aligned} \tag{24}$$

where

$$\begin{aligned} C_1 &= B_1 + B_1^2 - B_2 \,, \\ C_2 &= 3B_1B_2 + B_3 \,, \\ C_3 &= 4B_1B_3 - 3B_2^2 - B_4 \,, \\ C_4 &= 10B_2B_3 + 5B_1B_4 + 2B_5 \,, \\ &\ldots \,, \end{aligned} \tag{25}$$

and

$$\begin{aligned} B_1 &= [\alpha\sin\alpha - (Z'/Z)\alpha'\sin\alpha']/[\cos\alpha - (Z'/Z)\cos\alpha'] \,, \\ B_2 &= [\alpha^2\cos\alpha - (Z'/Z)\alpha'^2\cos\alpha']/[\cos\alpha \\ &\qquad - (Z'/Z)\cos\alpha'] \,, \\ B_3 &= [\alpha^3\sin\alpha - (Z'/Z)\alpha'^3\sin\alpha']/[\cos\alpha \\ &\qquad - (Z'/Z)\cos\alpha'] \,, \\ B_4 &= [\alpha^4\cos\alpha - (Z'/Z)\alpha'^4\cos\alpha']/[\cos\alpha \\ &\qquad - (Z'/Z)\cos\alpha'] \,, \\ B_5 &= [\alpha^5\sin\alpha - (Z'/Z)\alpha'^5\sin\alpha']/[\cos\alpha \\ &\qquad - (Z'/Z)\cos\alpha'] \,, \\ &\ldots \,. \end{aligned} \tag{26}$$

We note that the first term of each coefficient A_n is equal to that of the screened Coulomb potential in the Thomas-Fermi approximation.

The electron-phonon enhancement correction a can now be expressed explicitly in an expansion form as

$$
\begin{aligned}
a=\frac{1}{1-\lambda_1}\{&-2\lambda_1+\tfrac{1}{6}(2+\lambda_1)(1-4\delta-2B_1)\xi^2+\tfrac{1}{45}(2+\lambda_1)[1+8\delta-24\delta^2+4B_1(1-4\delta)-2C_1]\xi^4\\
&+\tfrac{1}{140}(2+\lambda_1)[1+4\delta+24\delta^2-64\delta^3+2B_1(1+8\delta-24\delta^2)-8\delta C_1+\tfrac{2}{3}C_2]\xi^6\\
&+\tfrac{1}{1575}(2+\lambda_1)[5+16\delta+48\delta^2+256\delta^3-640\delta^4+8B_1(1+4\delta+24\delta^2-64\delta^3)\\
&\qquad+2C_1(1-48\delta^2)+\tfrac{4}{3}C_2(1+8\delta)+\tfrac{2}{3}C_3]\xi^8\\
&+\tfrac{1}{4158}(2+\lambda_1)[7+20\delta+48\delta^2+128\delta^3+640\delta^4-1536\delta^5\\
&\qquad+2B_1(5+16\delta+48\delta^2+256\delta^3-640\delta^4)+4C_1(1+2\delta-64\delta^3)\\
&\qquad+\tfrac{2}{3}C_2(1+8\delta+48\delta^2)+\tfrac{2}{3}C_3(1+4\delta)+\tfrac{2}{15}C_4]\xi^{10}+\cdots\}\ .
\end{aligned}
\tag{27}
$$

For 0.2% accuracy, terms of order ξ^{10} are sufficient even for small values of Z.

IV. RESULTS

For an explicit evaluation of a we have to specify solvent metals and impurities. The relevant parameters for metals in a free-electron theory, k_F, r_c, q, and δ, are tabulated in Table I. Values of the core radius for the empty-core model of the pseudopotential r_c are given by Harrison,[19] and values of the Fermi wave number k_F are taken from Ashcroft and Mermin.[22]

First we discuss the case where the valence of the impurities is equal to that of the solvent atom ($Z=Z'$ case), since it was not possible to discuss this case for a screened Coulomb potential in the Thomas-Fermi approximation where the potential $U_{\mathrm{TF}}(r)$ for the substitutional-impurity case was given by Eq. (1):

$$U_{\mathrm{TF}}(r)=-\delta Z e^2\exp(-qr)/r\ ,$$

where δZ is the difference of valence between the impurity and the solvent atom and q is the screening parameter defined by Eq. (18). As discussed in I and II, there was no scattering due to impurity in this model if $\delta Z=0$. This, however, is not the case in real metals, and using the empty-core model of the pseudopotential as a model impurity potential, we can discuss the following cases with $Z=Z'$: (i) alkali metals, (ii) alkaline-earth metals, and (iii) trivalent metals.

(i) Alkali metals. The electron-phonon enhancement correction a of the Seebeck coefficient for the *alkali*-alkali case is given in Table II together with λ_1. From this table we observe the following rules: (a) The enhancement correction a is positive when the core radius of the impurity r_c' is larger than that of the solvent atom r_c (or when the impurity is heavier than the solvent in the alkali case), while a is negative when r_c' is smaller than r_c. (b) The enhancement correction a is very small when r_c' is very close to r_c. The second rule is due to the fact that the impurity potential is very small for $r_c'\simeq r_c$, so that electrons are not scattered very much at the impurity site. We also note that the parameter λ_1, which specifies

TABLE I. Values of Z, k_F, r_c, q, and δ for metals in free-electron model.

Metals	Z	k_F[a] ($10^8\,\mathrm{cm}^{-1}$)	r_c[b] ($10^{-8}\,\mathrm{cm}$)	q ($10^8\,\mathrm{cm}^{-1}$)	δ
Li	1	1.12	0.92	1.642	0.651
Na	1	0.92	0.96	1.488	0.605
K	1	0.75	1.20	1.343	0.555
Rb	1	0.70	1.38	1.298	0.538
Cs	1	0.65	1.55	1.251	0.519
Be	2	1.94	0.58	2.161	0.763
Mg	2	1.36	0.74	1.809	0.693
Ca	2	1.11	0.90	1.634	0.648
Sr	2	1.02	1.14	1.567	0.629
Al	3	1.75	0.61	2.052	0.744
Ga	3	1.66	0.59	1.998	0.734
In	3	1.51	0.63	1.906	0.715

[a] Reference 22.

[b] Reference 19.

TABLE II. Values of γ, λ_1, a, and $1+a\gamma$ for *alkali*-alkali alloys.

Solvent atom	γ	Impurity	λ_1	a	$1+a\gamma$
Na	0.175[a]	Li	0.134	−0.230	0.960
		K	−0.179	0.235	1.041
		Rb	−0.427	0.467	1.082
		Cs	−0.694	0.648	1.113
K	0.173[a]	Li	0.351	−0.816	0.859
		Na	0.325	−0.727	0.874
		Rb	−0.026	0.033	1.006
		Cs	−0.207	0.259	1.045
Rb	0.163[a]	Li	0.348	−0.810	0.868
		Na	0.324	−0.730	0.881
		K	0.159	−0.295	0.952
		Cs	−0.155	0.198	1.032
Cs	0.106[a]	Li	0.370	−0.894	0.905
		Na	0.349	−0.818	0.913
		K	0.204	−0.398	0.958
		Rb	0.071	−0.127	0.987

[a] The value of v_s is taken from Ref. 23.

TABLE III. Values of γ, λ_1, a, and $1+a\gamma$ for *alkaline-earth metal*–alkaline-earth-metal alloys.

Solvent atom	γ	Impurity	λ_1	a	$1+a\gamma$
Be	0.154^a	Mg	−1.298	1.008	1.155
		Ca	−1.781	1.189	1.183
		Sr	−1.837	1.333	1.205
Mg	0.141^a	Be	−0.100	0.157	1.022
		Ca	−0.656	0.689	1.097
		Sr	−1.218	0.978	1.138
Ca	0.145^b	Be	0.118	−0.233	0.966
		Mg	−0.046	0.070	1.010
		Sr	−0.647	0.677	1.098

[a] The values of v_s are taken from Ref. 25.

[b] The value of v_s is taken from Ref. 23.

the energy dependence of the unperturbed total-scattering probability, is very small for $r'_c \simeq r_c$. Thus in this case the Seebeck coefficient S is very close to the free-electron value.

(ii) Alkaline-earth metals. In Table III the electron-phonon enhancement correction a is given together with λ_1. From the table we find that rule (a) found in alkalis applies only for light solvent atoms. For heavier atoms, a is reduced and very small but not necessarily negative for $r'_c \lesssim r_c$.

(iii) Trivalent metals. Table IV is for combinations of Al, Ga, and In. The rules found for alkalis do not seem to apply, and the values of a depend only on the solvent atoms and not very much on the impurity.

In conclusion, for the $Z=Z'$ case the electron-phonon enhancement correction a depends on the core-radius difference of an impurity and a solvent atom. If $r'_c \simeq r_c$, a is reduced very much. Also a is negative if $r'_c < r_c$ in most cases.

For specific evaluation of the correction factor we need values of γ, defined by Eq. (11). With appropriate values of the ionic mass[22] M_i and the longitudinal sound velocity[23-25] v_s, we are able to list the values of γ and the net electron-phonon enhancement of the Seebeck coefficient, $1+a\gamma$, in Tables II–IV.

Next we discuss the case where the valence of the impurity and the solvent atom differs ($Z \neq Z'$). It is found that the electron-phonon enhancement correction a does not depend much on the difference of the core radius and a is of order unity (between 0.8 and 1.3). This is in accord with the result obtained in I and II in the screened Coulomb interaction.

TABLE IV. Values of γ, λ_1, a, and $1+a\gamma$ for *trivalent metal*–trivalent metal alloys.

Solvent atom	γ	Impurity	λ_1	a	$1+a\gamma$
Al	0.204^a	Ga	−0.545	0.637	1.130
		In	−0.640	0.706	1.144
In	0.176^b	Al	−0.215	0.316	1.056
		Ga	−0.182	0.274	1.048

[a] The value of v_s is taken from Ref. 24.

[b] The value of v_s is taken from Ref. 23.

V. SUMMARY

The purpose of this paper has been to extend the calculation of the Seebeck coefficient S in alloys at low temperatures given in I and II to include a more realistic impurity potential than the screened Coulomb potential in the Thomas-Fermi approximation. The empty-core model of the pseudopotential proposed by Ashcroft[17] has been used to obtain a model impurity potential. We have considered a simple model of fixed impurities and longitudinal Debye phonons interacting with free electrons. The main results are summarized as follows. (i) $Z=Z'$ case (Z and Z' are valences of the solvent atom and the impurity, respectively): If the core radius of the impurity r'_c is larger than that of the solvent, r_c, the electron-phonon enhancement correction a, defined by Eq. (14), is positive (enhancement), while a is negative in the opposite case (decrease of S). In alkalis and light alkaline-earth metals, which can be described by a free-electron model, this rule applies. When $r_c \simeq r'_c$, a is substantially reduced because the electrons are not scattered very much by substitutional impurities. (ii) $Z \neq Z'$ case: In dilute alloys in this combination of impurity and solvent, the enhancement of the Seebeck coefficient S due to the electron-phonon interaction is found to be of the order of $1+\gamma$, where $-\gamma$ is the energy derivative of the electron self-energy correction, but differs from one impurity to another. This is in accord with the results of Opsal *et al.*[11]

At this point we compare our results with experiments of Guénault and MacDonald.[27,28] They measured the thermoelectric power (the Seebeck coefficient) S in alkali alloys and found that S of potassium is positive for sodium impurities and negative for rubidium and cesium impurities. From Table II we find that for the KNa case the enhancement correction a is negative and λ_1 is positive and consequently the overall magnitude of S is decreased, although the sign of S does not change. [We note that S in a free-electron model is negative, since e is negative; see Eq. (13).] On the other hand, for KRb and KCs the magnitude of S is increased. This trend is in accord with the experiments. In order to understand the sign change of S due to impurities in alkali alloys[27,28] and tin alloys,[29] we should include the virtual-recoil effects considered by Nielsen and Taylor.[30-33] These phenomena were discussed by Krempasky and Schmid[34] using the formalism of Holstein,[35] but their calculations invoked some assumptions, including that of electron-hole symmetry, that make it inappropriate for comparison with the present work.

Various aspects of the problems 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. For example, the value of γ of Al in a free-electron theory is smaller than that obtained in experiments.[36] This discrepancy may be due to the umklapp process. Also the Fröhlich Hamiltonian considered here does not include any virtual-recoil effects mentioned above. A more complete treatment in which such effects are treated remains a goal to be reached.

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[1] Y. A. Ono and P. L. Taylor, J. Phys. F 10, L129 (1980).
[2] Y. A. Ono and P. L. Taylor, Phys. Rev. B 22, 1109 (1980).
[3] A. Hasegawa, Solid State Commun. 15, 1361 (1974).
[4] A. Hasegawa, J. Phys. F 4, 2164 (1974).
[5] S. K. Lyo, Phys. Rev. Lett. 39, 363 (1977).
[6] S. K. Lyo, in *Thermoelectricity in Metallic Conductors*, edited by F. J. Blatt and P. A. Schroeder (Plenum, New York, 1978), p. 223.
[7] S. K. Lyo, Phys. Rev. B 17, 2545 (1978).
[8] A. Vilenkin and P. L. Taylor, Phys. Rev. B 18, 5280 (1978).
[9] A. Vilenkin and P. L. Taylor, Phys. Rev. Lett. 42, 597 (1979).
[10] A. Vilenkin and P. L. Taylor, Phys. Rev. B 20, 576 (1979).
[11] J. L. Opsal, B. J. Thaler, and J. Bass, Phys. Rev. Lett. 36, 1211 (1976).
[12] N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Clarendon, Oxford, 1936), p. 310.
[13] A. Vilenkin, Phys. Rev. B (in press).
[14] See, for example, J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 1960), Chap. 4.
[15] Y. A. Ono and P. L. Taylor (unpublished).
[16] J. Friedel, Adv. Phys. 3, 446 (1954).
[17] N. W. Ashcroft, Phys. Lett. 23, 48 (1966).
[18] N. W. Ashcroft and D. C. Langreth, Phys. Rev. 155, 682 (1967).
[19] W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980), Chaps. 15 and 16.
[20] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966), Chap. 4.
[21] P. L. Taylor, *A Quantum Approach to the Solid State* (Prentice-Hall, Englewood Cliffs, New Jersey, 1970), p. 276.
[22] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976), Chaps. 1 and 2.
[23] D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1955), Vol. I., p. 367.
[24] C. Kittel, *Introduction to Solid State Physics*, 2nd ed. (Wiley, New York, 1956), p. 100.
[25] *Handbook of Chemistry and Physics*, edited by R. C. Weast, 56th ed. (CRC Press, Cleveland, 1975), E-47.
[26] A. Meyer and W. H. Young, Phys. Rev. 184, 1003 (1969).
[27] A. M. Guénault and D. K. C. MacDonald, Proc. R. Soc. London, Ser. A 264, 41 (1961).
[28] A. M. Guénault and D. K. C. MacDonald, Proc. R. Soc. London, Ser. A 274, 154 (1963).
[29] N. V. Zavaritskii and A. A. Altukhov, Zh. Eksp. Teor. Fiz. 70, 1861 (1976) [Sov. Phys.—JETP 43, 969 (1976)].
[30] P. E. Nielsen and P. L. Taylor, Phys. Rev. Lett. 21, 893 (1968).
[31] P. E. Nielsen and P. L. Taylor, Phys. Rev. Lett. 25, 371 (1970).
[32] P. E. Nielsen and P. L. Taylor, Phys. Rev. B 10, 4061 (1974).
[33] P. E. Nielsen, P. L. Taylor, and F. D. Manchester, Phys. Lett. 32A, 161 (1970).
[34] J. J. Krempasky and A. Schmid, J. Low Temp. Phys. 34, 197 (1979).
[35] T. Holstein, Ann. Phys. (N.Y.) 29, 410 (1964).
[36] N. W. Ashcroft and J. W. Wilkins, Phys. Lett. 14, 285 (1965).