On Electro- and Thermomigration and Thermoelectric Transport Coefficients in Metals

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The system of coupled Boltzmann transport equations for electrons, phonons and impurities in metals is set up and solved with special interest for the effect of the cross-coupling terms. General expressions for the effective charge in electromigration and heat of transport in thermomigration are given. The cross-coupling terms in the transport equations lead to a number of corrections in the thermoelectric transport coefficients. Noteworthy is the result that the resistance by impurities depends now on the temperature. The investigation is restricted to high temperatures, isotropic dependence of the energies of electrons and phonons on wave number vector, and to normal scattering processes of phonons.

1. Introduction

Electro- and thermotransport of impurity atoms in metals is mainly caused by impact of electrons [1, 2] and of phonons [3]. To treat the problem in a general way, we consider the system as a gas mixture of impurity atoms, electrons and phonons [3]. The transport problem is formulated within the framework of conventional Boltzmann theory. If $f(\boldsymbol{k}, \boldsymbol{r})$, $g(\boldsymbol{q}, \boldsymbol{r})$ and $s(\boldsymbol{p}, \boldsymbol{r})$ are respectively the distribution functions for electrons, phonons and impurity atoms the transport equations are given by

$$\left.\frac{\partial f(\boldsymbol{k}, \boldsymbol{r}, t)}{\partial t}\right|_{\text{FIELD}} = \left.\frac{\partial f}{\partial t}\right|_{\text{COLL}} = F^{\text{ee}}(f, f) + F^{\text{ep}}(f, g) + F^{\text{ei}}(f, s)\,, \tag{1.1}$$

$$\left.\frac{\partial g(\boldsymbol{q}, \boldsymbol{r}, t)}{\partial t}\right|_{\text{FIELD}} = \left.\frac{\partial g}{\partial t}\right|_{\text{COLL}} = F^{\text{pe}}(g, f) + F^{\text{pp}}(g, g) + F^{\text{pi}}(g, s)\,, \tag{1.2}$$

$$\left.\frac{\partial s(\boldsymbol{p}, \boldsymbol{r}, t)}{\partial t}\right|_{\text{FIELD}} = \left.\frac{\partial s}{\partial t}\right|_{\text{COLL}} = F^{\text{ie}}(s, f) + F^{\text{ip}}(s, g) + F^{\text{ii}}(s, s)\,. \tag{1.3}$$

The left hand sides of these equations are the field terms and the right hand sides the scattering terms. These are functionals of the variables indicated.

The transport equations (1.1) to (1.3) are usually solved with the assumption that phonons and impurity atoms can be considered to be in equilibrium. Without this assumption the solution of the transport equation leads not only to the desired coefficients of electro- and thermotransport but also — as a byproduct — to generalized expressions for the dc thermoelectric transport coefficients of metals. This is the aim of this paper. As one of the results of the generalized transport coefficients we find that the electrical resistivity which is due to the impurity atoms depends on the temperature. More precisely, the distribution function $g(\boldsymbol{q}, \boldsymbol{r})$, appearing in (1.1) for the conduction electrons depends via (1.2) and (1.3) on the distribution function $s(\boldsymbol{p}, \boldsymbol{r})$ of the impurities. This induces indirectly temperature dependent terms for the resistivity by impurities.

General expressions for electro- and thermomigration [4, 5, 6, 7] and dc thermoelectric coefficients [8, 9] are obtained.

In this paper we consider only the situation at high temperatures. The case of low temperatures will be treated in a separate publication [10].

The present paper is arranged as follows. In Chapter 2 the interactions and the collision integrals are described. The solution of the transport equations is essentially straightforward but tedious. The main points of it are indicated in Chapter 3 without going into too much details. Finally the results of the calculations are given and discussed in Chapter 4. Moreover in order not to burden the formulae too much the utmost tolerable simplifications are made (only one conduction band, spherical Fermi surface, only one phonon mode and so on).

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2. Interactions and Collision Integrals

Only one-phonon transitions are taken into account for the interactions of the phonons with electrons [11, 12] and with impurities [13], furthermore only normal processes. This may turn out to be a serious restriction. The electron-impurity interaction is described by hard-sphere-scattering. The collision terms in (1.1) to (1.3) are then

$$F^{\mathrm{ep}}(f,g)=\frac{\Omega}{(2\pi)^3\hbar}\iiint_{\boldsymbol{q}}|M^{\mathrm{pe}}_{\boldsymbol{k},\boldsymbol{q}}|^2(\delta(\varepsilon^{\mathrm{e}}_{\boldsymbol{k}-\boldsymbol{q}}-\varepsilon^{\mathrm{e}}_{\boldsymbol{k}}+\hbar\omega_{\boldsymbol{q}})\{f_{\boldsymbol{k}-\boldsymbol{q}}(1-f_{\boldsymbol{k}})g_{\boldsymbol{q}}-f_{\boldsymbol{k}}(1-f_{\boldsymbol{k}-\boldsymbol{q}})(1+g_{\boldsymbol{q}})\}$$
$$+\delta(\varepsilon^{\mathrm{e}}_{\boldsymbol{k}+\boldsymbol{q}}-\varepsilon^{\mathrm{e}}_{\boldsymbol{k}}-\hbar\omega_{\boldsymbol{q}})\{f_{\boldsymbol{k}+\boldsymbol{q}}(1-f_{\boldsymbol{k}})(1+g_{\boldsymbol{q}})-f_{\boldsymbol{k}}(1-f_{\boldsymbol{k}+\boldsymbol{q}})g_{\boldsymbol{q}}\})\,\mathrm{d}^3q\,, \tag{2.1}$$

$$F^{\mathrm{ei}}(f,s)=\frac{\hbar}{4m}\iiiint_{\boldsymbol{p}\,\boldsymbol{e}}\sigma_{\mathrm{ei}}\left|\boldsymbol{e}\cdot\left(\boldsymbol{k}-\frac{m}{M}\boldsymbol{p}\right)\right|\{s'f'(1-f)-sf(1-f')\}\,\mathrm{d}^2e\,\mathrm{d}^3p\,, \tag{2.2}$$

$$F^{\mathrm{pe}}(g,f)=\frac{\Omega}{2(2\pi)^3\hbar}\iiint_{\boldsymbol{k}}|M^{\mathrm{pe}}_{\boldsymbol{k},\boldsymbol{q}}|^2(\delta(\varepsilon^{\mathrm{e}}_{\boldsymbol{k}-\boldsymbol{q}}-\varepsilon^{\mathrm{e}}_{\boldsymbol{k}}+\hbar\omega_{\boldsymbol{q}})\{f_{\boldsymbol{k}}(1-f_{\boldsymbol{k}-\boldsymbol{q}})(1+g_{\boldsymbol{q}})-f_{\boldsymbol{k}-\boldsymbol{q}}(1-f_{\boldsymbol{k}})g_{\boldsymbol{q}}\}$$
$$+\delta(\varepsilon^{\mathrm{e}}_{\boldsymbol{k}+\boldsymbol{q}}-\varepsilon^{\mathrm{e}}_{\boldsymbol{k}}-\hbar\omega_{\boldsymbol{q}})\{f_{\boldsymbol{k}+\boldsymbol{q}}(1-f_{\boldsymbol{k}})(1+g_{\boldsymbol{q}})-f_{\boldsymbol{k}}(1-f_{\boldsymbol{k}+\boldsymbol{q}})g_{\boldsymbol{q}}\})\,\mathrm{d}^3k\,, \tag{3.1}$$

$$F^{\mathrm{pi}}(g,s)=\frac{\Omega}{2(2\pi)^3\hbar}\iiint_{\boldsymbol{p}}|M^{\mathrm{pi}}_{\boldsymbol{p},\boldsymbol{q}}|^2(\delta(\varepsilon^{\mathrm{i}}_{\boldsymbol{p}-\boldsymbol{q}}-\varepsilon^{\mathrm{i}}_{\boldsymbol{p}}+\hbar\omega_{\boldsymbol{q}})\{s_{\boldsymbol{p}-\boldsymbol{q}}g_{\boldsymbol{q}}-s_{\boldsymbol{p}}(1+g_{\boldsymbol{q}})\}+\delta(\varepsilon^{\mathrm{i}}_{\boldsymbol{p}+\boldsymbol{q}}-\varepsilon^{\mathrm{i}}_{\boldsymbol{p}}+\hbar\omega_{\boldsymbol{q}})$$
$$\cdot\{s_{\boldsymbol{p}+\boldsymbol{q}}(1+g_{\boldsymbol{q}})-s_{\boldsymbol{p}}g_{\boldsymbol{q}}\})\,\mathrm{d}^3p\,, \tag{3.2}$$

$$F^{\mathrm{ie}}(s,f)=\frac{\hbar}{2(2\pi)^3m}\iiiint_{\boldsymbol{k}\,\boldsymbol{e}}\sigma_{\mathrm{ei}}\left|\boldsymbol{e}\left(\boldsymbol{k}-\frac{m}{M}\boldsymbol{p}\right)\right|\{s'f'(1-f)-sf(1-f')\}\,\mathrm{d}^2e\,\mathrm{d}^3k\,, \tag{4.1}$$

$$F^{\mathrm{ip}}(s,g)=\frac{\Omega}{(2\pi)^3\hbar}\iiint_{\boldsymbol{k}}|M^{\mathrm{pi}}_{\boldsymbol{p},\boldsymbol{q}}|^2(\delta(\varepsilon^{\mathrm{i}}_{\boldsymbol{p}-\boldsymbol{q}}-\varepsilon^{\mathrm{i}}_{\boldsymbol{p}}+\hbar\omega_{\boldsymbol{q}})\{s_{\boldsymbol{p}-\boldsymbol{q}}g_{\boldsymbol{q}}-s_{\boldsymbol{q}}(1+g_{\boldsymbol{q}})\}+\delta(\varepsilon^{\mathrm{i}}_{\boldsymbol{p}+\boldsymbol{q}}-\varepsilon^{\mathrm{i}}_{\boldsymbol{p}}-\hbar\omega_{\boldsymbol{q}})$$
$$\cdot\{s_{\boldsymbol{p}+\boldsymbol{q}}(1+g_{\boldsymbol{q}})-s_{\boldsymbol{p}}g_{\boldsymbol{q}}\})\,\mathrm{d}^3q\,. \tag{4.2}$$

Ω Volume of a unit cell, m effective mass of the electrons, M mass of an impurity atom, σ_{ei} scattering cross section for electron-impurity scattering, $\omega_{\boldsymbol{q}}$ frequency of a phonon with wave number $\boldsymbol{q}$, $\varepsilon^{\mathrm{e}}_{\boldsymbol{k}}$ energy of an electron with wave number $\boldsymbol{k}$, $\varepsilon^{\mathrm{i}}_{\boldsymbol{p}}$ energy of an impurity with wave number $\boldsymbol{p}$, $\hbar$ Planck's constant, k_{B} Boltzmann's constant, T temperature, n_{i} number density of impurity atoms, n_{h} number density of host lattice atoms.

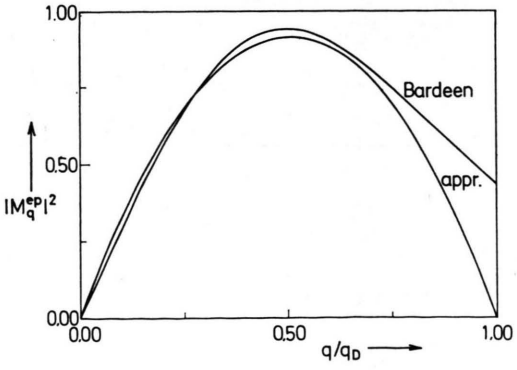

Fig. 1. Bardeen's matrix element and it's approximation (5) in dependence on the wave number q/q_{D}.

The primed distribution functions are the distribution functions after the collision.

For the electron-phonon interaction Bardeen's matrix-element is used, but the quite complicated q-dependence of this matrix-element is replaced simply by (see Figure 1).

$$|M^{\mathrm{pe}}_{\boldsymbol{k},\boldsymbol{q}}|^2=|M^{\mathrm{pe}}_{\boldsymbol{q}}|^2=D\frac{q}{q_{\mathrm{D}}}\left(1-\frac{q}{q_{\mathrm{D}}}\right),$$
$$D=\frac{2\hbar\varepsilon_{\mathrm{F}}^2q_{\mathrm{D}}}{9M'c_1n_{\mathrm{e}}\Omega}\,; \tag{5}$$

q_{D} Debye wave number, ε_{F} Fermi energy, M' mass of a host atom, c_1 velocity of sound, n_{e} number density of the electrons.

For the phonon-impurity coupling we choose the matrix-element according to Maradudin [13]:

$$|M^{\mathrm{pi}}_{\boldsymbol{p},\boldsymbol{q}}|^2=|M^{\mathrm{pi}}_{\boldsymbol{q}}|^2=P\frac{q^4}{q_{\mathrm{D}}^4}N^{-1}(\beta,q) \tag{6}$$
$$P=4\pi\frac{\Omega\hbar^4q_{\mathrm{D}}^7}{M^2}\beta^2,$$
$$N(\beta,q)=\left(1+3\beta\frac{q^2}{q_{\mathrm{D}}^2}\right)^2+\frac{9\pi^2q^6}{4q_{\mathrm{D}}^6}\beta^2,$$
$$\beta=\frac{M-M'}{M'}.$$

(In (6) only the mass difference is taken into account, for contributions of changes in force and lattice constants see [15].)

The self-interactions of the impurity atoms can of course be neglected and at high temperatures only the self-interaction of the phonons is needed. This is represented by a relaxation process with relaxation time τ_p.

3. Solution of the Transport equations

The transport equations are treated in the usual manner. The collision integrals are identically zero for the equilibrium distributions of the particles. The driving forces — electrical field E_x and temperature gradient dT/dx — are supposed to be in x-direction. The distribution functions are expanded up to first order, that is:

$$f(\boldsymbol{k}) = f_0(k) - k_x \frac{\partial f_0}{\partial \varepsilon_k^e} \Gamma\left(k; E_x, \frac{dT}{dx}\right), \tag{7.1}$$

$$g(\boldsymbol{q}) = g_0(q) + q_x \Psi\left(q; E_x, \frac{dT}{dx}\right), \tag{7.2}$$

$$s(\boldsymbol{p}) = s_0(p)\left(1 + p_x \Lambda\left(p; E_x, \frac{dT}{dx}\right)\right) \tag{7.3}$$

and the right hand side of equations (1.1) to (1.3) is linearized in the deviations of the distribution functions from equilibrium. The equilibrium distribution functions are known (Fermi, Bose and Maxwell-Boltzmann).

It is assumed that equilibrium is locally established. Then within linear response theory the field terms in the transport equations depend only on the local equilibrium distribution functions. The field terms can be expressed in a well known manner by the driving forces E_x and dT/dx.

All these manipulations transform the transport equations into an inhomogeneous, linear system of integral equations. The inhomogeneous term is given by the driving forces

$$\frac{D}{Dt} f = k_x \frac{\hbar}{m} \frac{\partial f_0}{\partial \varepsilon_k^e} \cdot \left\{ e E_x - \frac{1}{T} \frac{dT}{dx} \left(T \frac{d\varepsilon_F}{dT} + \varepsilon_k^e - \varepsilon_F \right) \right\}, \tag{8.1}$$

$$\frac{D}{Dt} g = q_x \frac{h c_1^2}{k_B T} \cdot \frac{\exp(\hbar \omega_q / k_B T)}{(\exp(\hbar \omega_q / k_B T) - 1)^2} \frac{1}{T} \frac{dT}{dx}, \tag{8.2}$$

$$\frac{D}{Dt} s = p_x s_0 \frac{\hbar}{M k_B T} \cdot \left\{ Z e E_x + \frac{1}{T} \frac{dT}{dx} \cdot \left((\varepsilon_p^i - V_0)\, \theta(\varepsilon_p^i - V_0) - \frac{5}{2} k_B T \right) \right\}. \tag{8.3}$$

In (8.3) V_0 is the maximum height of the lattice potential of the impurity atoms and $\theta(x)$ the unit step function. This takes care of the fact, that only impurity atoms with $\varepsilon_p^i > V_0$ can contribute to impurity migration.

In (1.1) and (1.3) the collision terms F^{ee} and F^{ii} are — as already mentioned — neglected. The remaining terms can be written as integrals:

$$F^{ep} = S_{12}^p[\Psi] + S_{12}^e[\Gamma], \tag{9.1}$$

$$F^{ei} = S_{13}^i[\Lambda] + S_{13}^e[\Gamma], \tag{9.2}$$

$$F^{pe} = S_{21}^e[\Gamma] + S_{21}^p[\Psi], \tag{10.1}$$

$$F^{pp} = S_{22}^p[\Psi], \tag{10.2}$$

$$F^{pi} = S_{23}^i[\Lambda] + S_{23}^p[\Psi], \tag{10.3}$$

$$F^{ie} = S_{31}^e[\Gamma] + S_{31}^i[\Lambda], \tag{11.1}$$

$$F^{ip} = S_{32}^p[\Psi] + S_{32}^i[\Lambda]. \tag{11.2}$$

These integrals can be calculated straightforward but are of some length, so we do not reproduce them here. The indices on the right-hand side are selfexplanatory.

If we go back to Bloch's assumption (phonon gas in equilibrium) and no impurity migration, then all integrals can be ignored except $S_{12}^e[\Gamma]$ and $S_{13}^e[\Gamma]$. For electron- and thermomigration the expressions $S_{31}^e[\Gamma]$ and $S_{32}^p[\Psi]$ describe "electron wind" and "phonon wind" respectively. Since impurity migration is naturally very slow, all terms depending on Λ are negligible. The most important new feature is, that the deviation Ψ of phonons from equilibrium is determined not solely by electron-phonon interaction, $S_{21}^p[\Psi]$, but by phonon-impurity interaction, $S_{23}^p[\Psi]$ as well.

Turning to the collision integrals in detail, the rather well known procedure of solution can be pursued. That is the energy-transfer in the collision processes can be taken to be small, which leads to relaxation time solutions. The system of transport equations reduces to a system of algebraic equations for the deviations Γ, Ψ and Λ coupled by integrals over these deviations. The solution of this system

leads to integral equations with degenerate kernels, which can be solved analytically. The calculations are lengthy and we give only the results in the next section.

4. Results and Discussion

The quantities J_n and $K_{n/2}$ are given in the appendix.

(*A*) *Electrical resistivity* ϱ

constitutive equation: $j_e = (1/\varrho)\, E_x$

$$\varrho = \{\varrho_{ph}(1 - 20 J_3) + \varrho_i(1 - \delta\varrho_i')\} \cdot \{1 - \delta\varrho_i\}^{-1},$$

$$\varrho_{ph} = \frac{3\pi\Omega D k_B T m^{1/2}}{20\, 2^{3/2}\hbar c_1 \varepsilon_F^{3/2} e^2} \frac{n_x}{n_e},$$

$$\varrho_i = \frac{\pi \sigma_{ei} n_i}{2^{3/2} e^2 n_e} \sqrt{m \varepsilon_F}, \tag{12}$$

$$\delta\varrho_i' = \frac{J_1}{3\pi^{7/2} I_1}\left(K_2 + 12\pi^3 K_{1/2} + K_0 \frac{Z_{eff}^{ph}}{Z_{eff}^{el}} + 12\pi^3 K_{3/2} \frac{Z_{eff}^{el}}{Z_{eff}^{ph}}\right),$$

$$\delta\varrho_i = \frac{4 J_1 n_i}{\sqrt{\pi} I_1 n_e} K_2 \frac{Z_{eff}^{el}}{Z_{eff}^{ph}} (1 + F K_{3/2}/K_2),$$

$$F = \frac{1}{12\pi^3} \frac{Z_{eff}^{ph}}{Z_{eff}^{el}}.$$

(*B*) *Thermopower* S

constitutive equation:

$$j_e = \frac{1}{\varrho}\left(S - \frac{d\varepsilon_F}{|e|\, dT}\right) \frac{1}{T} \frac{dT}{dx},$$

$$S = -S_0 \left\{1 - \frac{1}{3} \frac{2\varrho_i + \left.\frac{d\varrho_i}{d\varepsilon}\right|_{\varepsilon=1}}{\varrho} + (S_1(1 + \delta S_1) + S_2)/(1 - \delta\varrho_i)\right\},$$

$$S_0 = \frac{\pi^2 k_B^2 T}{|e|\, \varepsilon_F},$$

$$S_1 = \frac{2}{\pi^2} J_2 \frac{\varepsilon_F}{k_B T} \frac{n_x}{n_e}, \tag{13}$$

$$\delta S_1 = \frac{1}{5\pi^{5/2}} K_{1/2} \frac{\varrho_i}{\varrho_{ph}} (1 + F K_0/K_{1/2}),$$

$$S_2 = \frac{4 J_1 n_i \varepsilon_F}{\pi^{5/2} I_1 n_e k_B T} K_2 \frac{Z_{eff}^{el}}{Z_{eff}^{ph}} \frac{5}{2} \cdot (1 + F K_{3/2}/K_2),$$

$$\frac{n_x}{n_e} = \begin{cases} \text{ratio of number density of atoms to} \\ \text{electrons if } < 4,\ 4 \text{ (for semi metals).} \end{cases}$$

(*C*) *Heat conductivity* λ

constitutive equation:

$$w_x = -\lambda (dT/d_x) \quad \text{and} \quad j_e = 0,$$

electronic part:

$$\lambda_{el} = \frac{\pi^2 k_B^2}{3 e^2} \frac{T}{\varrho} (1 - L_1 - L_2 - L_3),$$

$$L_1 = 20 J_3 \frac{\varrho_{ph}}{\varrho_{ph} + \varrho_i},$$

$$L_2 = 3 \frac{|e|\, S T}{\varepsilon_F}, \tag{14}$$

$$L_3 = \left(\frac{Z|e|S}{k_B} - \frac{5}{2}\right) \frac{8 J_1 n_i Z_{eff}^{el} k_B T}{\sqrt{\pi} I_1 n_e Z_{eff}^{ph} \varepsilon_F} K_2 + \frac{4 J_5 K_{1/2} n_x \varrho_i k_B T}{5\sqrt{\pi} n_e \varrho_{ph} \varepsilon_F};$$

lattice part:

$$\lambda_1 = \frac{\pi^2 k_B^2}{3 e^2} \frac{T}{\varrho} (L_4 + L_5)$$

$$L_4 = \frac{J_6 n_x^2 \varrho}{15\pi^3 n_e^2 \varrho_{ph}}, \tag{15}$$

$$L_5 = \frac{K_0 J_5^2 n_i n_x^2 \varrho_i}{900\pi^{13/2} J_1 n_e^3 \varrho_{ph}} Z_{eff}^{ph}$$

(*D*) *Lorenz-number* L

constitutive equation: $L = \lambda\varrho/T$, (16)

$$L = \frac{\pi^2 k_B^2}{3 e^2} (1 - L_1 - L_2 - L_3 + L_4 + L_5).$$

(*E*) *Electromigration*

constitutive equation:

$$j_i = n_i D_u Z_{eff} e E_x / k_B T,$$

$$Z_{eff} = Z_{eff}^{el} + \bar{Z}_{eff}^{ph} (1 - E_1 K_0)^{-1} - Z(1 + \delta Z),$$

$$Z_{eff}^{el} = \frac{n_e \varrho_i}{n_i \varrho},$$

$$\bar{Z}_{eff}^{ph} = Z_{eff}^{ph} (k_B T/Q)^{3/2}, \tag{17}$$

$$Z_{\mathrm{eff}}^{\mathrm{ph}} = \frac{3\pi\Omega M^{3/2} c_1 P n_{\mathrm{h}} J_1}{2^{3/2}(k_{\mathrm{B}}T)^{3/2}\hbar e^2 n_{\mathrm{e}} \varrho},$$

$$\delta Z = \frac{J_1 n_{\mathrm{i}} K_2}{3\pi^{7/2} I_1 n_{\mathrm{e}}(1 - E_1 K_0)} \cdot (Z_{\mathrm{eff}}^{\mathrm{el}} + Z_{\mathrm{eff}}^{\mathrm{ph}}(1 - E_1 K_0)^{-1}),$$

$$E_1 = \frac{1}{60\pi^{9/2}} \frac{J_4}{I_1 J_1} \frac{\varrho_{\mathrm{i}} Z_{\mathrm{eff}}^{\mathrm{ph}}}{\varrho_{\mathrm{ph}} Z_{\mathrm{eff}}^{\mathrm{el}}};$$

Q activation energy for impurity migration, D_{u} total diffusion constant ($D_{\mathrm{u}} = D_0 \exp(-Q/k_{\mathrm{B}}T)$, e charge of an electron, Z excess valence of an impurity atom.

(*F*) *Thermomigration*

constitutive equation:

$$j_{\mathrm{i}} = -(n_{\mathrm{i}} D_{\mathrm{u}} Q_{\mathrm{heat}}/k_{\mathrm{B}}T)(1/T)(\mathrm{d}T/\mathrm{d}x)$$

and for closed circuits $j_{\mathrm{e}} = 0$,

$$Q_{\mathrm{heat}} = Q_{\mathrm{tp}} + Q_{\mathrm{ph}} + Q_{\mathrm{va}} + Q_{\mathrm{ent}},$$

$$Q_{\mathrm{tp}} = Z|e|\,T\left(S - \frac{\mathrm{d}\varepsilon_{\mathrm{F}}}{|e|\,\mathrm{d}T}\right), \tag{18}$$

$$Q_{\mathrm{ph}} = \frac{J_5 I_1 \varrho}{10 J_1 \varrho_{\mathrm{ph}}} Z_{\mathrm{eff}}^{\mathrm{ph}} k_{\mathrm{B}} T,$$

$$Q_{\mathrm{va}} = Q - V_0,$$

$$Q_{\mathrm{ent}} = -\tfrac{5}{2} k_{\mathrm{B}} T(1 + \delta Z).$$

The parts ϱ_{ph} and ϱ_{i} of the electrical resistivity are the well-known contributions from phonons and impurities, the factor $1 - 20\,J_3$ is due to phonon-drag. New are the terms $\delta\varrho_{\mathrm{i}}'$ and $\delta\varrho_{\mathrm{i}}$. Both are small, $\delta\varrho_{\mathrm{i}}'$ being still smaller than $\delta\varrho_{\mathrm{i}}$. The latter one is observable in metallic alloys [14].

For the thermopower S the first terms in curly brackets in (13) are the Nordheim-Gorter terms, S_1 is due to phonon-drag (already knowns), modified in our case by δS_1 and $\delta\varrho_{\mathrm{i}}$ due to impurities. S_2 is a new contribution due simultaneously to impurities, electrons and phonons. A detailed comparison with experimental results, however, is not advisible, since we used isotropic distributions for electrons and phonons, and neglected umklapp processes. It is well known [9], that these assumptions are insufficient to treat thermopower. The additional term $\tilde{S}$, caused by the cross-coupling terms in the transport equations, is

$$\tilde{S} = S_0 S_1 \delta S_1 + S_0 S_1 \delta\varrho_{\mathrm{i}} + S_0 S_2 = n_{\mathrm{i}}\left(\frac{a}{T} + b\,T^{3/2} + c\frac{T^{3/2}}{\varrho}\right) \tag{19}$$

with constants a, b, c.

For the heat conductivity the terms L_2, L_3, L_4 and L_5 seem to be rather small and there may be a chance for observation only for the phonon-drag contribution L_1, which is of the order of 0.1. It should be noted, that for noble metals ϱ_{i} might at high temperatures be of the order of ϱ_{ph}.

In electromigration the electron wind contribution $Z_{\mathrm{eff}}^{\mathrm{el}}$ and the phonon wind contribution $Z_{\mathrm{eff}}^{\mathrm{ph}}$ can be of the same order and have been described earlier [3]. In contrast to [3] we have used Maradudin's [13] matrix element for phonon-impurity scattering instead of Callaway's [15], which leads to better agreement with empirical values.

New features are a factor $(1 - E_1 K_0)^{-1}$ at $Z_{\mathrm{eff}}^{\mathrm{ph}}$, which is very close to unity and an additional term $Z\,\delta Z$. It is seen from (17) that this can also be thought of as a factor to $Z_{\mathrm{eff}}^{\mathrm{el}} + Z_{\mathrm{eff}}^{\mathrm{ph}}$, deviating only a little from unity. But it should be noted, that this factor introduces a different dependence of Z_{eff} on Z.

For a unique determination of $Z_{\mathrm{eff}}^{\mathrm{el}}$ and $Z_{\mathrm{eff}}^{\mathrm{ph}}$ it is necessary to know certain other transport coefficients, for example ϱ_{i}. Both contributions are inversely proportional to ϱ. A difficulty consists in the fact that the microscopic quantity P (phonon-impurity-interaction) cannot easily be connected to measurable macroscopic properties. Consistency in the determination of P can be checked in the small contribution of $(1 - \delta\varrho_{\mathrm{i}})^{-1}$ to the electrical resistivity, in $\tilde{S}$ to the thermopower, in L_5 to heat conductivity (which is very small) and above all in Q_{ph} of thermomigration.

In thermomigration the vacancy contribution Q_{va} is as given in [2] and [16, 17]. The term Q_{tp} has been predicted by Huntington [2], but contrary to our result with Z_{eff} instead of Z. This should be the case for closed circuits. Gerl [18] uses the specific thermopower instead of S.

The phononwind contribution Q_{ph} has been mentioned by Huntington [2], but not explicitly given. The last term Q_{ent} is due to the enthalpy of the impurities.

Finally we would like to stress that it is desirable to establish and check relations between all of the transport coefficient for a system, including electro- and thermomigration.

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Appendix

The quantities J_n and $K_{n/2}$ are defined by:

$$K_{n/2} = K_{n/2}(c) = \int_0^\infty \frac{x^{n/2}\exp(-x)}{c\,x^{3/2}+1}\,\mathrm{d}x\,, \qquad C = \frac{J_1 Z_{\mathrm{eff}}^{\mathrm{el}}}{I_1 Z_{\mathrm{eff}}^{\mathrm{ph}}}\,. \tag{20}$$

$$I_1 = I_1(\beta) = \int_0^1 \frac{u^6}{N(\beta,u)}\,\mathrm{d}u\,,$$

$$J_1 = J_1(\beta, b_1, b_2) = \int_0^1 \frac{u^6-u^7}{N[1-u+b_1+b_2(u/N)]}\,\mathrm{d}u\,,$$

$$J_2 = J_2(b_1, b_2) = \int_0^1 \frac{u^2-u^3}{[1-u+b_1+b_2(u/N)]}\,\mathrm{d}u\,,$$

$$J_3 = J_3(b_1, b_2) = \int_0^1 \frac{u^3-2u^4+u^5}{[1-u+b_1+b_2(u/N)]}\,\mathrm{d}u\,,$$

$$J_4 = J_4(\beta, b_1, b_2) = \int_0^1 \frac{u^9}{N^2[1-u+b_1+b_2(u/N)]}\,\mathrm{d}u\,,$$

$$J_5 = J_5(\beta, b_1, b_2) = \int_0^1 \frac{u^5}{N[1-u+b_1+b_2(u/N)]}\,\mathrm{d}u\,,$$

$$J_6 = J_6(b_1, b_2) = \int_0^1 \frac{u}{[1-u+b_1+b_2(u/N)]}\,\mathrm{d}u\,, \tag{21}$$

$$u = q/q_{\mathrm{D}}\,,$$

$$b_1 = \frac{2\pi\hbar^4 k_{\mathrm{B}} T}{\Omega m^2 c_{\mathrm{e}} D \tau_{\mathrm{pr}}}\,,$$

$$\tau_{\mathrm{p}}^{-1} = \tau_{\mathrm{pr}}^{-1} k_{\mathrm{B}} T\, u\,,$$

$$b_2 = \frac{n_{\mathrm{i}} M^{1/2} P \hbar^3}{(2\pi)^{3/2}(k_{\mathrm{B}} T)^{3/2} m^2 D}\,.$$

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