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# Disordered electronic systems. III. Thermoelectric power in alloys with phase separation

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Applying effective medium theory and the Boltzmann transport equation, a formula is derived for calculation of the Seebeck coefficient $\alpha$ (thermoelectric power) of alloys with phase separation (composite) under especial consideration of the electrochemical potential $\mu$ and its change with temperature $T$, $d\mu/dT$. $d\mu/dT$ is essentially determined by the electronic structure, carrier densities, and electron-electron-interaction in the phases. For *metal-metal* composites and *metal-insulator* composites, $\alpha$ can be calculated approximately by $\Sigma_i \upsilon_i(\sigma_i/\alpha_i - \sigma/\alpha)/(\sigma_i/\alpha_i + 2\sigma/\alpha) \simeq 0$ and $\alpha \simeq \alpha_A$, respectively, where $\sigma$ is the specific electrical conductivity of the composite. $\sigma_i$, $\alpha_i$, and $\upsilon_i$ are the specific electrical conductivity, the Seebeck coefficient, and the volume fraction, respectively, of the phase $i$ ($i=A,B$). Both $\sigma_i$ and $\alpha_i$ depend on concentration caused by the condition of a common electrochemical potential in the composite. The $\alpha$ formulas derived can also be applied to composites with *strong scattering*. $\alpha$ vs $x$ is calculated for $a$-$\mathrm{Cr}_{1-x}\mathrm{Si}_x$ alloys and compared with experimental data.

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## I. INTRODUCTION

The purpose of the present paper is the derivation of an equation for the thermoelectric power (Seebeck coefficient) in alloys with phase separation (composites). In the scientific literature there exist already formulas for the Seebeck coefficient for composites,[1–13] mostly derived applying effective medium theory (EMT), where, however, the electrochemical potential and its change with temperature and concentration have generally not been considered.

The basis for the present paper is the *alternative concept* developed in the first and second parts of the present paper series [called paper I (Ref. 14) and paper II (Ref. 15) in the following]. Essential elements of this *alternative concept* are the conclusions *(i)–(iii)* (summarized in paper II, Sec. I therein) and the alternative interpretation of the *Ioffe-Regel criterion* (described in paper II, Sec. IV B therein). This *alternative concept* includes the fact that the scattering within a phase is elastic and the concepts of Fermi surface and effective mass can be applied to each of the phases, even for the case of *strong scattering*, as long as $\upsilon_i > 1/3$ (spherical phase grains) and

$$k_{F,i}L_i > c^*, \tag{1}$$

with $c^*=1/4$. $L_i$, $k_{F,i}$, and $\upsilon_i$ are the (elastic) mean free path, the wave number at the Fermi surface, and the volume fraction, respectively, of the phase $i$. Under these conditions the relaxation time approximation of the Boltzmann transport equation[16–23] (BTE) can be applied to each of the phases of a composite, where additionally the boundary condition of a common electrochemical potential $\mu$ in the composite is to be taken into account.

Starting with the kinetic transport equations (the BTE's) for a single phase, in Sec. II A the formulas for the *local* electric and heat current densities in the phases will be written down, which are the basis for the EMT equation for $\alpha$ to be derived in Sec. II B.

Under especial consideration of the electrochemical potential $\mu$ and its change with temperature $T$, $d\mu/dT$, in Sec. III this EMT equation will be applied for the calculation of $\alpha(\upsilon_B)$ for important special cases as *metal-metal* composites, *metal-insulator* composites, and *metal-semiconductor* composites. Section IV A is concerned with the contribution of the electron-electron interaction to $d\mu/dT$, and the result will be applied in Sec. IV B for calculation of $\alpha$ vs $x$ for $a$-$\mathrm{Cr}_{1-x}\mathrm{Si}_x$ alloys. In Sec. V the results are summarized.

In Appendix A details of the derivation for the EMT equation for $\alpha$ are considered, and in Appendix B the connection between Eq. (1) and the *metal-insulator transition* in disordered alloys is considered.

## II. TRANSPORT THEORY FOR ALLOYS WITH PHASE SEPARATION

### A. Kinetic transport equations

Before reading Sec. II A it is helpful to read Sec. III A of paper II.

Let us consider a *composite* consisting of the phases $i=A,B$ in a symmetrical fashion regarding the average geometric form of the phase grains and without preferred orientations. Let us assume that each phase $i$ can be characterized by a set of transport coefficients $\sigma_i$, $\alpha_i$, and $\kappa_{e,i}$, which are the specific electrical conductivity, the Seebeck coefficient, and the electronic contribution to the specific thermal conductivity, respectively, in the phase $i$. The corresponding transport coefficients of the *composite*, $\sigma$, $\alpha$, and $\kappa_e$, are to be calculated, if the $\sigma_i$, $\alpha_i$, and $\kappa_{e,i}$ are known. The discussion will be restricted to small and constant electric field $\mathbf{E}$, small temperature gradients, and zero magnetic field.

Applying the kinetic transport equations for electrons in *homogeneous materials*[16–23] to each of the phases separately, the *local* electric current density $J_i$, the *local* heat current density $J_{Q,i}$, and $\sigma_i$, $\alpha_i$, and $\kappa_{e,i}$ can be written

$$J_i = e_i^2 K_{1,i}\mathbf{E}_i + |e|K_{1,i}T\,\mathrm{grad}\frac{\mu_i^0}{T} + |e|K_{2,i}\frac{\mathrm{grad}\,T}{T}, \tag{2}$$

$$J_{Q,i} = -|e| K_{2,i}\mathbf{E}_i - K_{2,i} T \,\mathrm{grad}\frac{\mu_i^0}{T} - K_{3,i}\frac{\mathrm{grad}\, T}{T}, \tag{3}$$

$$\sigma_i = e_i^2 K_{1,i}, \tag{4}$$

$$\alpha_i = \frac{K_{2,i}/K_{1,i} - \mu_i^0}{\mathrm{e}_i T}, \tag{5}$$

$$\kappa_{e,i} = \frac{K_{3,i} - K_{2,i}^2/K_{1,i}}{T}, \tag{6}$$

where $K_{r,i}$ are the transport integrals defined by

$$K_{r,i} = -\frac{4}{3m_i}\int E^r \tau_i \frac{\partial f_i^0(E,T)}{\partial E} N_i(E) dE. \tag{7}$$

$f_i^0(E,T)$ is the Fermi-Dirac distribution function,

$$f_i^0(E,T) = \frac{1}{1 + \dfrac{E - \mu_i^0}{k_B T}}, \tag{8}$$

with $\mu_i^0$, the *chemical potential* in the phase $i$,

$$\mu_i^0 = E_{F,i} - \frac{\pi^2 k_B^2 T^2}{6}\frac{d}{dE}[\ln N_i(E)]_{E=E_{F,i}} = E_{F,i} - \frac{\pi^2 k_B^2 T^2}{12 E_{F,i}} \tag{9}$$

(lowest order in powers of $k_B T / E_{F,i}$). The second equation in Eq. (9) corresponds to nearly free electrons (NFE approximation). $k_B$ is the Boltzmann constant, $T$ the temperature, and $E$ the energy. $|e_i| = |e|$ is the elementary charge, $\mathbf{E}_i$ the electric field, $N_i(E)$ the density of states, $m_i$ the effective mass, $\tau_i$ the relaxation time of the carriers, and $E_{F,i}$ the Fermi energy in the phase $i$.

We introduce the "extended electrochemical potential"[24] $\mu_i$ in the phase $i$ defined by

$$\mu_i = E_{C,i} + \mu_i^0 - |e|\varphi_i, \tag{10}$$

for the case shown in Fig. 1(a). $-\varphi_i$ is the electrostatic potential, $-|e_i|\varphi_i$ the electrostatic potential energy[16,19] in the phase $i$. For the cases shown in Figs. 1(b) and 1(c), Eq. (10) holds also for the phase $A$, whereas for the phase $B$ in Fig. 1(c),

$$\mu_B = E_{V,B} - \mu_B^0 - |e|\varphi_B \tag{11}$$

holds. $E_{C,i}$ and $E_{V,i}$ characterize the band edges of the conduction band and valence band, respectively, in the phase $i$; see Fig. 1.

Equations (2) and (3) are a coupled equation system, i.e., coupled by the additional boundary condition

$$\mu_A = \mu_B = \mu, \tag{12}$$

because in the composite there is a *common extended electrochemical potential* $\mu$ or, shortly, *electrochemical potential* of the composite. The condition (12) can be realized by an electron redistribution between the phases $A$ and $B$, which generally depends on concentration, temperature, and pressure (phase transitions in the phases are not considered).

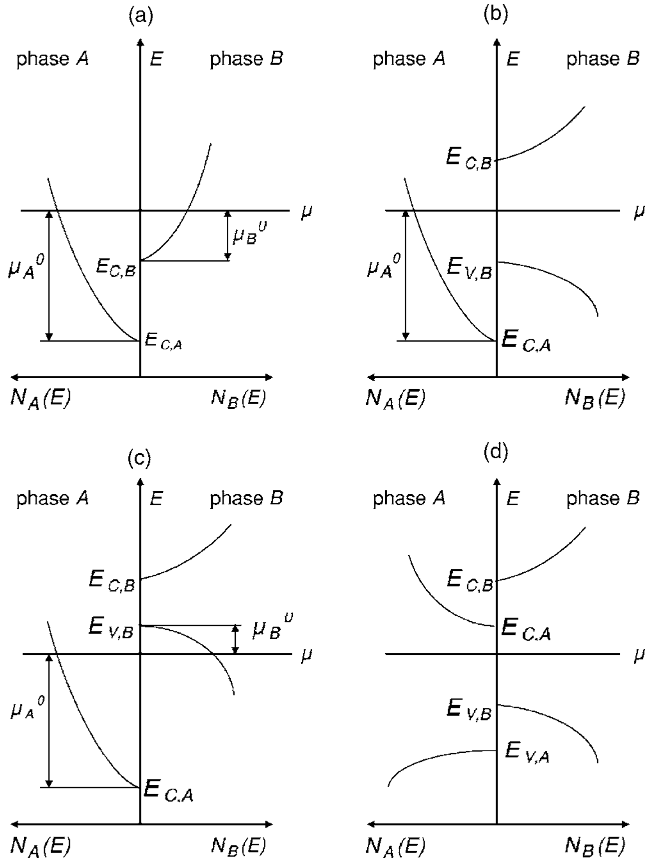

FIG. 1. Schematic band model for *metal-metal* composites (a), *metal-semiconductor* composites (b), (c), and *semiconductor-semiconductor* composites (d): density of states $N_A(E)$ and $N_B(E)$ in dependence on energy $E$ in the two phases $A$ and $B$.

For determination of the transport coefficients of a composite, we need two physical connections (functions), first,

$$\alpha = \alpha(\alpha_i, v_i) \tag{13}$$

and, second,

$$\alpha_i = \alpha_i(v_i), \tag{14}$$

and corresponding functions for the other transport coefficients $[\sigma = \sigma(\sigma_i, v_i), \sigma_i = \sigma_i(v_i), \ldots]$ as well. The first function, Eq. (13), will be derived in Sec. II B and applied in Secs. III B–III D to the special cases of composites shown in Figs. 1(a)–1(c). Additional consideration of Eq. (14) allows the calculation of $\alpha(v_i)$ [or $\alpha(x)$] for real composites as *a*-$\mathrm{Cr}_{1-x}\mathrm{Si}_x$ alloys, which is the subject of Sec. IV. Before deriving the function (13), Eqs. (2) and (3) can be simplified: Replacing $\mathbf{E}_i$ by $\mathbf{E}_i = -\mathrm{grad}\,\varphi_i$ and introducing $\sigma_i$, $\alpha_i$, and $\kappa_{e,i}$, Eqs. (4)–(6), into Eqs. (2) and (3), we get[25]

$$J_i = -\sigma_i \mathrm{grad}\,\varphi_i - \sigma_i\left(\alpha_i - \frac{1}{|e|}\frac{d\mu_i^0}{dT}\right)\mathrm{grad}\, T, \tag{15}$$

$$J_{Q,i} = -\sigma_i\left(\alpha_i T - \frac{\mu_i^0}{|e|}\right)\text{grad }\varphi_i - \left[\kappa_{e,i} + \sigma_i\left(\alpha_i T - \frac{\mu_i^0}{|e|}\right)\left(\alpha_i - \frac{1}{|e|}\frac{d\mu_i^0}{dT}\right)\right]\text{grad }T. \tag{16}$$

Measurement of the thermopower takes place at $J=0$, where $J$ is the *total* electrical current density. As long as the phase $i$ forms an infinite cluster through the whole specimen ($v_i > 1/3$, spherical phase grains), $J_i=0$ can be assumed as well, and it follows, from Eq. (15),

$$\text{grad }T = -\frac{\text{grad }\varphi_i}{\alpha_i - \dfrac{1}{|e|}\dfrac{d\mu_i^0}{dT}} \tag{17}$$

and, introduced in Eq. (16),

$$J_{Q,i} = \mathfrak{Z}_i \text{grad }\varphi_i, \tag{18}$$

with

$$\mathfrak{Z}_i = \frac{\kappa_{e,i}}{\alpha_i - \dfrac{1}{|e|}\dfrac{d\mu_i^0}{dT}}. \tag{19}$$

Equations (17)–(19) are valid also for $v_i \leqslant 1/3$, because, in this case, the other phase serves to show the fact that electric current does not flow through the phase $i$ if the *total* electrical current $J$ is zero—i.e., $J_i=0$ for the complete concentration range $0 \leqslant v_i \leqslant 1$, if $J=0$.

Equation (18) is the transport equation which describes the *local* heat current densities in the phases under the conditions realized at thermopower measurements and is the basis for the derivation of the function (13). Equations (18) and (19) and Eq. (12) suggest the fact that $\alpha$ depends not only on $\alpha_i$ and $v_i$, as stated in Eq. (13), but additionally on $\kappa_{e,i}$, $\mu_i^0$, and $\mu$—i.e., $\alpha = \alpha(\alpha_i, \kappa_{e,i}, \mu_i^0, \mu, v_i)$.

### B. EMT equation for $\alpha$

Before reading Sec. II B it is helpful to read Sec. IV A of paper II.

The strategy underlying the EMT is the following: a single-phase grain of the phase $i$ is considered to be completely embedded in an *effective* medium consisting of the two phases randomly arranged and characterized by the *total* transport coefficients. At the boundary face between this single-phase grain and the surrounding effective medium continuity of the current densities and potentials and their gradients are to be saved, where in our case considered the additional condition $J=J_i=0$ is to be fulfilled.

In analogy to Eqs. (18) and (19) we write, for the electronic contribution to the *total* heat current density $J_Q$ in the specimen,

$$J_Q = \mathfrak{Z} \text{ grad }\varphi, \tag{20}$$

with

$$\mathfrak{Z} = \frac{\kappa_e}{\alpha - \dfrac{1}{|e|}\left\langle \dfrac{d\mu_i^0}{dT}\right\rangle}, \tag{21}$$

where $\kappa_e$, $\alpha$, and $\mathfrak{Z}$ represent the transport parameters of the composite. The angular brackets characterize an average. $\langle d\mu_i^0/dT\rangle$ can be calculated by

$$\left\langle \frac{d\mu_i^0}{dT}\right\rangle = \sum_i v_i \frac{d\mu_i^0}{dT}. \tag{22}$$

Now we follow the basic idea of Webman *et al.*[2] and demand that the *total* heat current density be equal to the average of the *local* heat current density,

$$J_Q = \langle J_{Q,i}\rangle, \tag{23}$$

and the same for the potential

$$\text{grad }\varphi = \langle \text{grad }\varphi_i\rangle. \tag{24}$$

Let us assume a spherical inclusion of the phase $i$ with radius $r_0$, embedded in an uniform medium with the transport parameter $\mathfrak{Z}$ given by Eq. (21) and that for the enclosed phase $i$ the *local* transport equation (18) holds. With Eqs. (18)–(24) we get

$$J_Q = \mathfrak{Z}\langle \text{grad }\varphi_i\rangle = \langle \mathfrak{Z}_i \text{grad }\varphi_i\rangle. \tag{25}$$

The local potential $\varphi_i$ obeys the Laplace equation

$$\Delta\varphi_i = 0, \tag{26}$$

where the boundary conditions

$$\varphi = \varphi_i, \tag{27}$$

$$J_Q^n = J_{Q,i}^n \tag{28}$$

at $r=r_0$ are to be fulfilled, which is equivalent to

$$\mathfrak{Z} \text{ grad}_r \varphi = \mathfrak{Z}_i \text{grad}_r \varphi_i \tag{29}$$

at $r=r_0$. $\text{grad}_r$ is the gradient into the radial direction. $J_{Q,i}^n$ and $J_Q^n$ are the normal components of the heat current density in the sphere $i$ and the surrounding effective medium, respectively. Solving this boundary value problem we get (see Appendix A)

$$\sum_i v_i \frac{\mathfrak{Z}_i - \mathfrak{Z}}{\mathfrak{Z}_i + 2\mathfrak{Z}} = 0, \tag{30}$$

$$\sum_i v_i = 1. \tag{31}$$

In the case of elastic scattering the Wiedemann-Franz rule holds true and $\kappa_{e,i}$ and $\kappa_e$ in $\mathfrak{Z}_\text{i}$ and $\mathfrak{Z}$ can be substituted by $\sigma_i$ and $\sigma$, respectively, leading to

$$\sum_i v_i \frac{\mathfrak{z}_i - \mathfrak{z}}{\mathfrak{z}_i + 2\mathfrak{z}} = 0 \tag{32}$$

with

$$\mathfrak{z}_i = \frac{\sigma_i}{\alpha_i - \frac{1}{|e|}\frac{d\mu_i^0}{dT}}, \tag{33}$$

$$\mathfrak{z} = \frac{\sigma}{\alpha - \frac{1}{|e|}\left\langle \frac{d\mu_i^0}{dT} \right\rangle}, \tag{34}$$

if the phases in the composite are metallic phases or degenerated semiconducting phases. Equation (32), resolved for $\alpha$, provides

$$\alpha(\pm) = \frac{\sigma}{\mathfrak{z}(\pm)} + \frac{1}{|e|}\left\langle \frac{d\mu_i^0}{dT} \right\rangle, \tag{35}$$

$$\mathfrak{z}(\pm) = \frac{1}{4}[\mathfrak{z}_A(3v_A - 1) + \mathfrak{z}_B(3v_B - 1) \pm \sqrt{[\mathfrak{z}_A(3v_A - 1) + \mathfrak{z}_B(3v_B - 1)]^2 + 8\mathfrak{z}_A\mathfrak{z}_B}]. \tag{36}$$

$\alpha(\pm)$ in Eq. (35) stand for the two solutions, $\alpha(+)$ and $\alpha(-)$ corresponding to $\mathfrak{z}(+)$ and $\mathfrak{z}(-)$ in Eq. (36).

Equations (19), (21), (33), and (34) hold also for the case that the carriers are holes corresponding to the phase $B$ in Fig. 1(c). This follows from the fact that $\mu_B^0$ is measured into the negative direction on the energy scale [Eq. (11)], whereas $\mu_A^0$ is measured into the positive direction on the energy scale [Eq. (10)].

With Eq. (32) and the EMT formula for $\sigma$,[26]

$$\sum_i v_i \frac{\sigma_i - \sigma}{\sigma_i + 2\sigma} = 0, \tag{37}$$

we have now the possibility to calculate $\sigma$ and $\alpha$, if $\sigma_i$, $\alpha_i$, and $d\mu_i^0/dT$ are known.

## III. APPLICATION OF EQ. (32)

### A. General considerations

Before reading Sec. III it is helpful to read Sec. IV B of paper II.

Electron redistribution (electron transfer) to the phase with the deeper average potential can lead to the fact that a constituent, which alone (i.e., not yet alloyed with another constituent) would be a *semiconductor*, becomes a *metallic* phase if it is composed with another constituent forming a composite. Such a situation is realized in $a$-$N_{1-x}M_x$ and many[27] $a$-$T_{1-x}M_x$ alloys, Fig. 1(c) (see paper II, Secs. II A, III B, and III C therein). Figure 1(b) represents a situation realized in $S_{1-x}M_x$ alloys and cermets[28–30] (see paper II, Secs. II B and III D therein; $N$ and $T$ stand for a transition metal with completely and incompletely occupied $d$ band, respectively, $M$ for a metalloid element such as Si or Ge, and $S$ for a simple metal such as Al, Ga, In, …). Examples for Fig. 1(a) are alloys between metallic elements with miscibility gap(s) in the phase diagram [$\mathrm{Au}_{1-x}\mathrm{Ni}_x$, $\mathrm{Al}_{1-x}\mathrm{Cu}_x$,… (Ref. 31)]. An example for Fig. 1(d) is $\mathrm{C}_{1-x}\mathrm{Si}_x$ with phases C, CSi, and Si.[31]

We are looking for analytical expressions for $d\mu_i^0/dT$ with $T$ and $n$ as variables,

$$\frac{d\mu_i^0}{dT} = \frac{\partial\mu_i^0}{\partial T} + \frac{\partial\mu_i^0}{\partial n}\frac{dn}{dT}, \tag{38}$$

where $n$ is the electron density in the phase $A$. $dn/dT$ is determined by the boundary condition (12),

$$\frac{d\mu_i}{dT} = \frac{d\mu}{dT} = \frac{\partial\mu_A}{\partial T} + \frac{\partial\mu_A}{\partial n}\frac{dn}{dT} = \frac{\partial\mu_B}{\partial T} + \frac{\partial\mu_B}{\partial n}\frac{dn}{dT}, \tag{39}$$

leading to

$$\frac{dn}{dT} = -\frac{\frac{\partial\mu_A}{\partial T} - \frac{\partial\mu_B}{\partial T}}{\frac{\partial\mu_A}{\partial n} - \frac{\partial\mu_B}{\partial n}}. \tag{40}$$

For calculation of the terms $\partial\mu_i^0/\partial T$ and $\partial\mu_i^0/\partial n$ in Eq. (38) and $\partial\mu_i/\partial T$ and $\partial\mu_i/\partial n$ in Eq. (40), the position of $\mu$ in relation to the band structures in the phases and the band structures themselves must be known. For simplicity, in the following the NFE approximation will be applied in order to discuss the basic connection between structure and electronic transport properties. Additional assumptions are that the positions of the band edges ($E_{C,i}$, $E_{V,i}$; see Fig. 1) are fixed on the energy scale and the electron redistribution to or away from the $d$ band (in alloys containing transition metals) does not change with a changing temperature, corresponding to the assumption of a constant sum of electrons.

Now, we study the special cases of Figs. 1(a)–1(c), where at least one of the phases is *metallic* (or degenerated); those of Fig. 1(d) will be considered in a separate paper.

### B. Special case: Metal-metal composites, Fig. 1(a)

With the assumption of a constant sum of electrons, the electron transfer between the phases can be described by

$$dn = -\zeta_v dn_B, \tag{41}$$

where $n_B$ is the electron density[32] in phase $B$ and

$$\zeta_v = v_B/v_A. \tag{42}$$

Using Eqs. (10) and (41), Eq. (40) can be written as

$$\frac{dn}{dT} = -\frac{\frac{\partial\mu_A^0}{\partial T} - \frac{\partial\mu_B^0}{\partial T}}{\frac{\partial\mu_A^0}{\partial n} + \frac{1}{\zeta_v}\frac{\partial\mu_B^0}{\partial n_B} - 2|e|\frac{\partial\varphi_A}{\partial n}}, \tag{43}$$

where, additionally, $\partial\varphi_i/\partial T=0$ and

$$\frac{1}{\zeta_v}\frac{\partial\varphi_B}{\partial n_B} = \frac{\partial\varphi_A}{\partial n} \tag{44}$$

are applied. $\partial\mu_i^0/\partial T$ and $\partial\mu_i^0/\partial n_i$ can be calculated by

$$\frac{\partial\mu_i^0}{\partial T} = -\frac{\pi^2 k_B^2 T}{6E_{F,i}}, \tag{45}$$

$$\frac{\partial \mu_i^0}{\partial n_i} = \frac{2}{3}\frac{E_{F,i}}{n_i} \tag{46}$$

(NFE approximation) following from Eq. (9) and

$$E_{F,i} = \frac{h^2}{8m_i}\left(\frac{3}{\pi}\right)^{2/3} n_i^{2/3}, \tag{47}$$

with $n_A = n$.[32] $h$ is Planck's constant. Now, $d\mu_i^0/dT$, Eq. (38), can be calculated by Eqs. (43) and (45)–(47) if the term $\partial\varphi_A/\partial n$ can be neglected (the term $\partial\varphi_A/\partial n$ will be considered in Sec. IV A).

$\sigma_i$ and $\alpha_i$ can be calculated by Eqs. (4) and (5) solving the transport integrals, Eq. (7), which provide, for $v_i > 1/3$,

$$K_{1,i} = \frac{16\pi}{3}\frac{m_i L_i}{h^3}\mu_i^0\left[1 + r_i(1+r_i)\frac{\pi^2}{6}\left(\frac{k_B T}{\mu_i^0}\right)^2\right], \tag{48}$$

$$K_{2,i} = \frac{16\pi}{3}\frac{m_i L_i}{h^3}\mu_i^{0^2}\left[1 + (1+r_i)(2+r_i)\frac{\pi^2}{6}\left(\frac{k_B T}{\mu_i^0}\right)^2\right] \tag{49}$$

(lowest order in the powers of $k_B T/\mu_i^0$), where

$$\tau_i = L_i\left(\frac{m_i}{2E}\right)^{1/2} \tag{50}$$

is applied. $r_i$ characterizes the scattering mechanism and represents the energy dependence of $L_i$ according to

$$L_i = L_0 E^{r_i} \tag{51}$$

(near $\mu_i$); i.e., *one* scattering process is assumed to dominate and it can be characterized by the energy dependence given by Eq. (51).[16–19,34]

With Eqs. (48)–(51) and Eqs. (4) and (5) it follows that[35]

$$\sigma_i = 2\left(\frac{\pi}{3}\right)^{1/3}\frac{e^2}{h}L_i n_i^{2/3}, \tag{52}$$

$$\alpha_i = \frac{\pi^2 k_B^2 T(1+r_i)}{3e_i E_{F,i}}. \tag{53}$$

Let us consider a hypothetical metal-metal composite with $n = 10^{23}$ cm$^{-3}$ and $n_B = 10^{22}$ cm$^{-3}$, which provide, at $T = 300$ K, $\sigma_A = 4238\ \Omega^{-1}$ cm$^{-1}$, $\alpha_A = -2.8\ \mu$V/K, $\sigma_B = 913\ \Omega^{-1}$ cm$^{-1}$, and $\alpha_B = -13.0\ \mu$V/K if Eqs. (47), (52), and (53) (Ref. 33) are applied with $L_i \simeq d_i \simeq 0.25$ nm (strong scattering; see paper II, Sec. IV B therein), $m_i/m_0 = 1$, and $r_i = 2$ (Conwell-Weisskopf scattering[16–18]). The $\alpha(v_B)$ curve calculated by Eq. (32) corresponding to Eq. (35) is drawn in Fig. 2 (solid line), where $\sigma$ is calculated by Eq. (37), $\langle d\mu_i^0/dT\rangle$ by Eq. (22), and $d\mu_i^0/dT$ by Eq. (38) [with Eqs. (43) and (45)–(47) and $\partial\varphi_A/\partial n = 0$]. Only the solution $\alpha(-)$ of Eq. (35) is drawn, because it agrees with $\alpha_A$ and $\alpha_B$ for $v_B = 0$ and $v_B = 1$, respectively, whereas $\alpha(+)$ does not. The second $\alpha(v_B)$ curve in Fig. 2 (dotted line) is calculated by

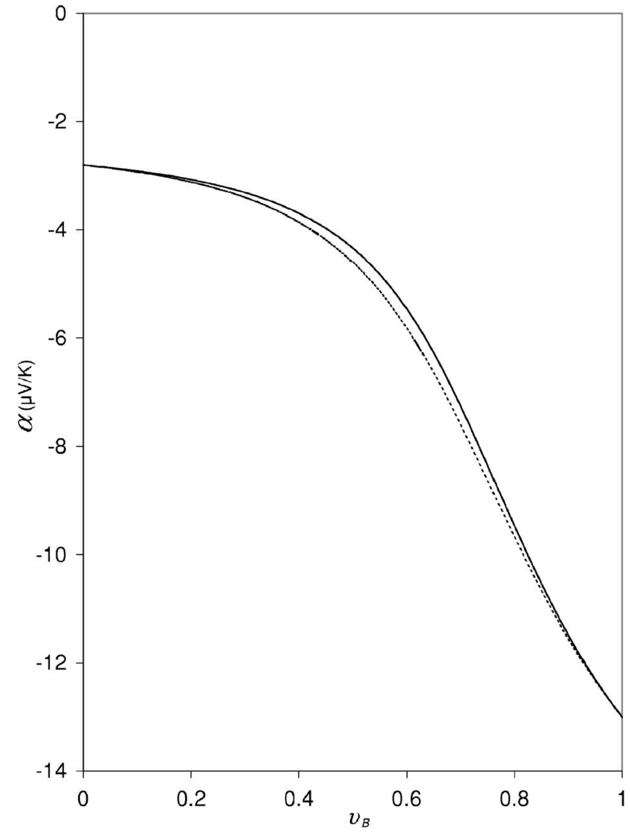

FIG. 2. $\alpha$ vs $v_B$ calculated by Eq. (32) for a hypothetical metal-metal composite with $\alpha_A = -2.8\ \mu$V/K, $\sigma_A = 4238\ \Omega^{-1}$ cm$^{-1}$, $\alpha_B = -13.0\ \mu$V/K, and $\sigma_B = 913\ \Omega^{-1}$ cm$^{-1}$ corresponding to $n = 10^{23}$ cm$^{-3}$ and $n_B = 10^{22}$ cm$^{-3}$ [NFE approximation (Ref. 33) and $\partial\varphi_A/\partial n = 0$, solid line]. The dotted line is calculated by the approximation formula (54).

$$\sum_i v_i \frac{\sigma_i/\alpha_i - \sigma/\alpha}{\sigma_i/\alpha_i + 2\sigma/\alpha} \simeq 0, \tag{54}$$

following from Eq. (32) if $d\mu_i^0/dT = 0$ is set. For metal-metal composites (with $e_A = e_B$), Eq. (54) can be a relatively good approximation for Eq. (32) if the difference between $n$ and $n_B$ is not very large and if the term $\partial\varphi_A/\partial n$ can be neglected.

### C. Special case: Metal-insulator composites, Fig. 1(b)

For metal-insulator mixtures,

$$N_A(\mu) \gg N_B(\mu) \tag{55}$$

holds, where $A$ characterizes the metallic phase. Because of Eq. (55), the change of electron transfer by *temperature* can be neglected—i.e., $\partial n/\partial T \simeq 0$—and Eq. (38) simplifies to

$$\frac{d\mu_A^0}{dT} \simeq \frac{\partial\mu_A^0}{\partial T} \simeq \frac{\partial\mu_A}{\partial T} \simeq \frac{\partial\mu_B}{\partial T} \simeq \frac{d\mu_B}{dT}, \tag{56}$$

and $d\mu_B^0/dT$ in Eq. (22) can be replaced by $d\mu_B/dT$, leading to

$$\left\langle \frac{d\mu_i^0}{dT} \right\rangle \simeq \frac{d\mu_A^0}{dT}. \tag{57}$$

With Eqs. (32)–(34), (56), and (57) and $\sigma_B=0$ it follows that

$$\frac{\alpha - \dfrac{1}{|e|}\dfrac{d\mu_A^0}{dT}}{\alpha_A - \dfrac{1}{|e|}\dfrac{d\mu_A^0}{dT}} \simeq \frac{2\sigma/\sigma_A}{3v_A - 1} \tag{58}$$

and, with Eq. (37),

$$\alpha \simeq \alpha_A. \tag{59}$$

The EMT formulas applied for the derivation of Eq. (59) hold for the symmetrical case, where both the $A$ and $B$ phase form spherical grains. However, in real $S_{1-x}M_x$ alloys and cermets, especially in the metallic range, the phases are not arranged in a symmetrical fashion (*modified physical model*; see paper II, Sec. III D therein). Nevertheless, Eq. (59) is assumed to hold for this asymmetric case as well, because the effect of the different geometric forms of the two phases is the same for Eqs. (32) and (37).

### D. Special case: Metal-semiconductor composites ($\mu$ cutting the valence band below the energy gap), Fig. 1(c)

With Eqs. (10), (40), (41), and (44) for phase $A$ and Eq. (11) for phase $B$, as well as

$$dp = -dn_B, \tag{60}$$

where $p$ is the hole density in the valence band (VB), it follows that

$$\frac{dn}{dT} = -\frac{\dfrac{\partial\mu_A^0}{\partial T} + \dfrac{\partial\mu_B^0}{\partial T}}{\dfrac{\partial\mu_A^0}{\partial n} + \dfrac{1}{\zeta_v}\dfrac{\partial\mu_B^0}{\partial p} - 2|e|\dfrac{\partial\varphi_A}{\partial n}}. \tag{61}$$

As $\mu$ lies in the VB [Fig. 1(c)], the electron system in phase $B$ is to be considered as degenerated and Eqs. (48)–(51) hold for phase $B$ as well, leading to

$$\sigma_B = 2\left(\frac{\pi}{3}\right)^{1/3}\frac{e^2}{h}L_B p^{2/3}, \tag{62}$$

$$\frac{\partial\mu_B^0}{\partial p} = \frac{2}{3}\frac{E_{F,B}}{p}, \tag{63}$$

$$E_{F,B} = \frac{h^2}{8m_B}\left(\frac{3}{\pi}\right)^{2/3} p^{2/3} \tag{64}$$

(NFE approximation), where $\alpha_B$ is given by Eq. (53) with $e_B=|e|$ and $\partial\mu_B^0/\partial T$ by Eq. (45) with $i=B$. The corresponding equations for phase $A$ are given by Eqs. (45)–(47), (52), and (53) with $i=A$. $d\mu_i^0/dT$ can now be calculated by Eqs. (38) and (61) with Eqs. (45)–(47) (phase $A$) and Eqs. (45), (63), and (64) (phase $B$) if the term $\partial\varphi_A/\partial n$ can be neglected and $\langle d\mu_i^0/dT\rangle$ by Eq. (22).

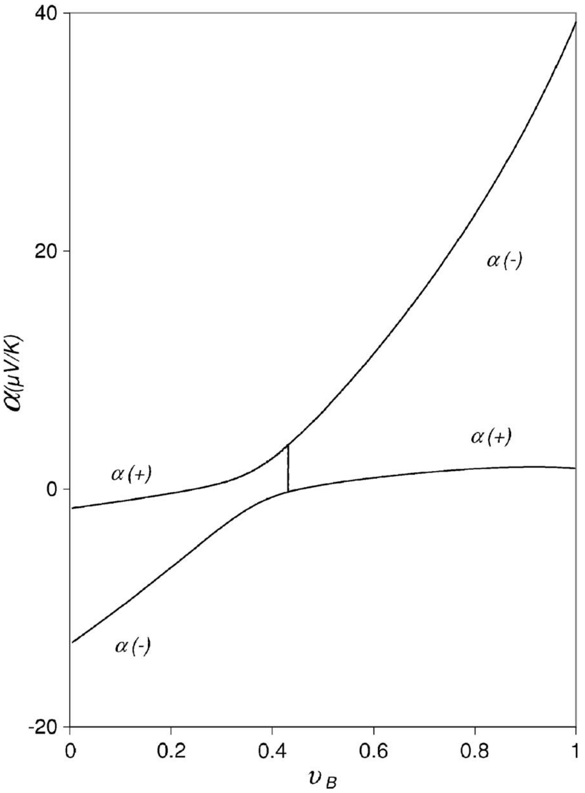

FIG. 3. $\alpha$ vs $v_B$ calculated by Eq. (32) for a hypothetical composite with electrons and holes in phases $A$ and $B$, respectively, where $\alpha_A=-13.0$ $\mu$V/K, $\sigma_A=913$ $\Omega^{-1}$ cm$^{-1}$, $\alpha_B=+1.75$ $\mu$V/K, and $\sigma_B=1357$ $\Omega^{-1}$ cm$^{-1}$ corresponding to $n=10^{22}$ cm$^{-3}$ and $p=2\times10^{22}$ cm$^{-3}$ [NFE approximation (Ref. 33) and $\partial\varphi_A/\partial n=0$].

Let us consider a hypothetical composite with $n=10^{22}$ cm$^{-3}$ and $p=2\times10^{22}$ cm$^{-3}$, which provide, at $T=300$ K, $\sigma_A=913$ $\Omega^{-1}$ cm$^{-1}$, $\alpha_A=-13.0$ $\mu$V/K, $\sigma_B=1357$ $\Omega^{-1}$ cm$^{-1}$, and $\alpha_B=+1.75$ $\mu$V/K, if Eqs. (47), (52), and (53) for phase $A$ and Eqs. (53), (62), and (64) for phase $B$ are applied[33] with $L_i\simeq d_i\simeq0.25$ nm, $m_A/m_0=1$, $m_B/m_0=0.2$, and $r_i=2$. In Fig. 3, $\alpha$ vs $v_B$ is drawn calculated by Eq. (32) corresponding to Eq. (35), where $\sigma$ is calculated by Eq. (37), $\langle d\mu_i^0/dT\rangle$ by Eq. (22), $d\mu_i^0/dT$ by Eq. (38) with Eq. (61) [and Eqs. (45)–(47) for phase $A$, Eqs. (45), (63), and (64) for phase $B$], and $\partial\varphi_A/\partial n=0$. For $v_B\leqslant0.45$, $\alpha(-)$ is a physically reasonable solution, whereas for $v_B\geqslant0.45$, $\alpha(+)$, because $\alpha(-)$ agrees with $\alpha_A$ for $v_B=0$, but not for $v_B=1$, whereas $\alpha(+)$ agrees with $\alpha_B$ for $v_B=1$, but not for $v_B=0$.

In the hypothetical examples, Figs. 2 and 3, the change of $n_i$ with $T$ calculated by Eqs. (43) and (61) is very small and practically does not influence $n_i$, $\sigma_i$, and $\alpha_i$.[33]

## IV. DISCUSSION

### A. Electron-electron interaction

In the *model calculations* of Sec. III, $n_i$ and the transport coefficients $\sigma_i$ and $\alpha_i$ were still considered to be *independent* of concentration. However, in a real composite there is an electron redistribution between the phases, which depends on the concentration. It was one of the results of paper I that in amorphous transition-metal–metalloid alloys this electron redistribution can be described by

$$-dn = \beta_v n d\zeta_v, \tag{65}$$

$$n(\zeta_v) = n(0)\exp(-\beta_v\zeta_v), \tag{66}$$

with $\beta_v$ as a constant for a given composite.[36] $n(0)=n_A(0)$ is the electron density in the $A$ phase at $\zeta_v=0(v_B=0)$. Because of this electron redistribution (electron transfer), $\alpha_i$, $\sigma_i$, and $\kappa_{e,i}$ depend on $v_B$ (or $\zeta_v$) as well.

Electron transfer to the phase with the deeper potential (phase $B$) leads to an increase of the electrostatic potential $\varphi_B$ corresponding to an increase of the electron-electron interaction in the phase $B$. The additional energy contribution $|e|\varphi_B$ could be calculated, on principle, by solution of the Poisson equation,[20,21,37] which, however, does not appear to be promising because of the special boundary conditions: high density of phase boundaries, smallness of the phase grains ($\sim$ nm), and considerable amounts of structure faults and foreign atoms solved in the phases which are considered to be part of a *complex energy balance* realized during solidification of the alloy. And the electron redistribution described by Eq. (66), as well as the microscopical and electronic structure itself, is *part and the result* of this *complex energy balance*.

As argued in paper I, for a given composite, $\beta_v$ is determined by the average potential difference between the phases $A$ and $B$, $\Delta V$, expressed by $\beta_v=\beta_v(\Delta V)$. There is an essential difference between the electron transfer described by Eq. (66) and the electron transfer by change of temperature, $dn/dT$, Eq. (40): While Eq. (66) is the result of a *complex energy balance* as described, $dn/dT$ is determined under conditions where the microscopical and electronic *structure* is given (constant), and we assume that an additional (small) change of the electron distribution (between the phases) due to temperature change leads to a (small) change of $\Delta V$ and, therefore, to a (small) change of $\beta_v$ as well, because $\beta_v=\beta_v(\Delta V)$. With this assumption for the change of $\Delta V$ due to additional (small) electron transfer to the $B$ phase it follows that

$$\frac{\partial(\Delta V)}{\partial n} = -\frac{1}{\zeta_v n(\partial\beta_v/\partial(\Delta V))} \tag{67}$$

if Eq. (66) is used. For the simplest assumption that $\beta_v$ depends linearly on $\Delta V$ corresponding to

$$\beta_v = \frac{1}{c}\Delta V, \tag{68}$$

with $c$=constant, it follows that

$$\frac{\partial(\Delta V)}{\partial n} = -\frac{\Delta V}{\beta_v\zeta_v n} = -\frac{c}{\zeta_v n}. \tag{69}$$

Equation (69) corresponds with the term $|e|\partial\varphi_A/\partial n$ in Eq. (61), and we get

$$|e|\frac{\partial\varphi_A}{\partial n} = \frac{c}{\zeta_v n}. \tag{70}$$

### B. Calculation of $\alpha(x)$ for $a$-Cr$_{1-x}$Si$_x$ alloys

Although the scattering is *strong*, the NFE approximation (especially the formulas of Sec. III) can be applied to $a$-Cr$_{1-x}$Si$_x$ alloys, as long as $v_B$ (or $\zeta_v$) is not too small. Justification is given in paper II (Sec. IV B therein).

For the calculations the same physical parameters are applied as in paper II (Sec. III C therein): $\mathcal{N}_A=7.9\times10^{22}$ cm$^{-3}$, $\mathcal{N}_B=5.0\times10^{22}$ cm$^{-3}$, $d_A=0.250$ nm, $d_B=0.234$ nm, $D_A=1.7$ nm, $\beta_v=0.5$, $x_A=0.25$, $x_B=0.90$, $Z_{\mathrm{Cr}}=0.5$, and $Z_{\mathrm{Si}}=4$, where $\mathcal{N}_i$, $d_i$, $D_i$, and $x_i$ are the atomic densities, the atomic distances, the average diameters of the phase grains, and the Si-atomic concentrations, respectively, in phase $i$. $Z_{\mathrm{Cr}}$ and $Z_{\mathrm{Si}}$ are the valences of Cr and Si, respectively, which are assumed to be independent of concentration. Additionally, $m_A/m_0=1$ and $m_B/m_0=0.2$, $r_i=2$ (Conwell-Weisskopf scattering[16–18]) and $D_B=1$ nm are set.

We calculate the concentration dependence of $n$ by Eq. (66), where $n(0)=10.8\times10^{22}$ cm$^{-3}$ calculated by

$$n(0) = \mathcal{N}_A[(1-x_A)Z_{\mathrm{Cr}} + x_A Z_{\mathrm{Si}}]. \tag{71}$$

In Fig. 4(a), the calculated $n$ is drawn versus $v_B$. For calculation of $p(v_B)$ we apply the *physical model* proposed in paper II (Secs. III B and III C therein), where

$$p = p_0 - n_B(0) - \Delta n - p_{loc}, \tag{72}$$

$$n_B(0) = \mathcal{N}_B[(1-x_B)Z_{\mathrm{Cr}} + x_B Z_{\mathrm{Si}}], \tag{73}$$

$$\Delta n(v_B) = \frac{n(0) - n(v_B)}{\zeta_v}, \tag{74}$$

$$p_0 = 4\mathcal{N}_B x_B\left(1 + \frac{X_{B^*}}{X_B}\right). \tag{75}$$

$X_{B^*}$ is the atomic fraction of the phase boundary face atoms in the $B$ phase. $X_i$ are the *atomic* fractions of the phases connected with the *volume* fractions by

$$\frac{X_B}{X_A} = \frac{\mathcal{N}_B}{\mathcal{N}_A}\frac{v_B}{v_A}. \tag{76}$$

$n(0)[=n_A(0)]$ and $n_B(0)$ are the electron densities in phases $A$ and $B$ at $x=x_A$ and $x=x_B$ corresponding to $v_B=0$ and $v_A=0$, respectively,[32] where $x$ and $v_i$ are connected by

$$x = \frac{x_A\mathcal{N}_A v_A + x_B\mathcal{N}_B v_B}{\mathcal{N}_A v_A + \mathcal{N}_B v_B}, \tag{77}$$

with $v_B=1-v_A$, Eq. (31).

For $p_{loc}$, representing the *loss* of density of states in the VB due to structure defects, $p_{loc}\ll p$ is assumed. Assuming spherical phase grains and $\mathcal{N}_B$ to be uniform in the whole $B$ phase, then

$$X_{B^*}/X_B = v_{B^*}/v_B, \tag{78}$$

with

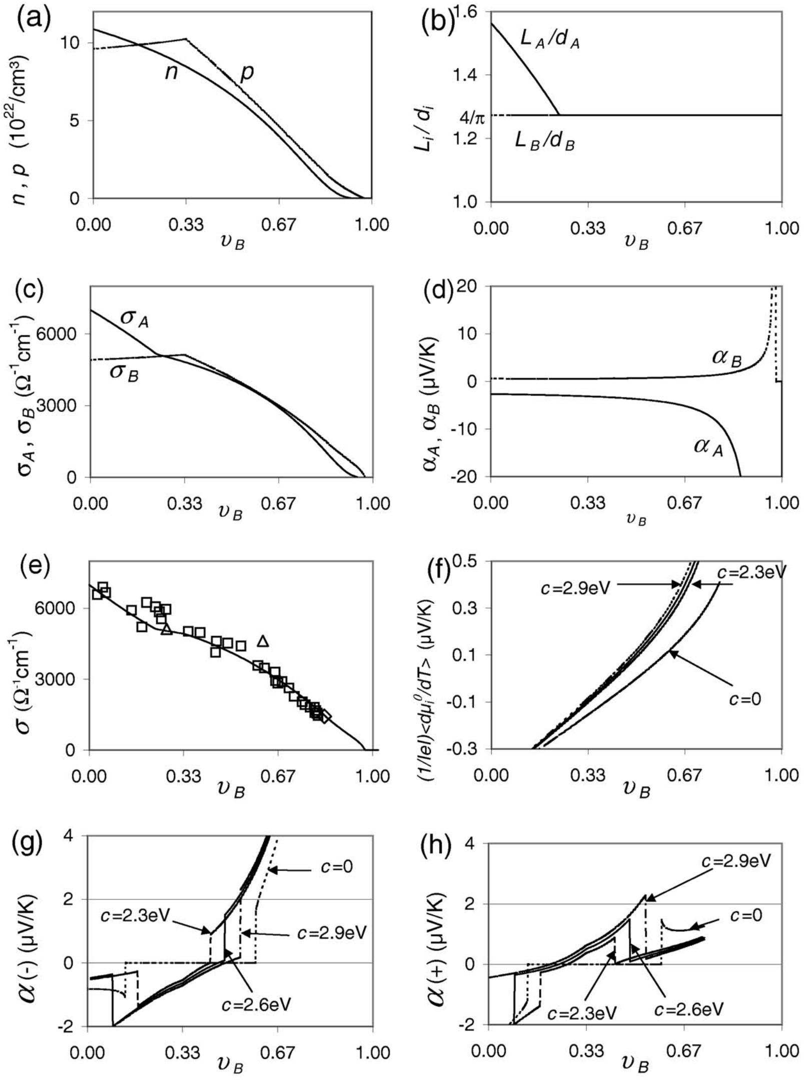

FIG. 4. Calculated electronic parameters for $a$-$\mathrm{Cr}_{1-x}\mathrm{Si}_x$ vs $\upsilon_B$ at 300 K and comparison with experimental data ($\sigma$) taken from Helms *et al.* (Ref. 38) (cosputtered, squares), Weser (Ref. 39) (sputtered, triangles), and Gladun *et al.* (Ref. 40) (sputtered, rhombus). $c$ is a parameter characterizing the electrostatic contribution to $d\mu/dT$, which is varied: $c$=2.3 eV, 2.6 eV (solid line), 2.9 eV and $c$=0 (dotted line).

$$\frac{\upsilon_{B^*}}{\upsilon_B} = \left[1 - \left(1 - \frac{2d_B}{D_B}\right)^3\right] \quad (\upsilon_B < 1/3) \tag{79}$$

and

$$\frac{\upsilon_{B^*}}{\upsilon_B} = \frac{1}{\zeta_\upsilon}\left[\left(1 + \frac{2d_B}{D_A}\right)^3 - 1\right] \quad (\upsilon_B > \upsilon_{B,k}), \tag{80}$$

where $\upsilon_{B,k}$=0.839 calculated by

$$\upsilon_{B,k} = 1 - \frac{1}{3}\left(1 + \frac{2d_B}{D_A}\right)^{-3} \tag{81}$$

(for details see paper II, Sec. II A therein). In the concentration range of $1/3 \leqslant \upsilon_B \leqslant \upsilon_{B,k}$, $X_{B^*}/X_B$ is linearly interpolated (relating to $X_B$). The concentration dependence of $p$ vs $\upsilon_B$ calculated by Eqs. (72)–(81) is drawn in Fig. 4(a) as well.

With $n(0)$ calculated earlier and the experimental value for $\sigma(0)=\sigma(x=0.25)=7000\ \Omega^{-1}\,\mathrm{cm}^{-1}$ (taken from Ref. 38), $L_A(0)$=0.39 nm calculated by

$$L_A(0) = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/3} \frac{h}{e^2} \frac{\sigma(0)}{n(0)^{2/3}} \tag{82}$$

following from Eq. (52). $L_A(\upsilon_B)$, drawn in Fig. 4(b), is calculated by

$$L_A(\upsilon_B) = L_A(0)\left(\frac{n(\upsilon_B)}{n(0)}\right)^{2r_A/3} \quad (\text{for } L_A \geqslant L_{A,min}); \tag{83}$$

otherwise, $L_A = L_{A,min}$, where

$$L_{i,min} = \frac{4}{\pi} d_i \tag{84}$$

(Ref. 16, p. 348). [Equation (83) follows from Eqs. (47), (51), and (52).] For the holes in the $B$ phase $L_B(\upsilon_B)=L_{B,min}$, Eq. (84), is assumed for the complete concentration range.

With the calculated $n(\upsilon_B)$ and $p(\upsilon_B)$, now $\sigma_A(\upsilon_B)$ is calculated by Eq. (52) and $\sigma_B(\upsilon_B)$ by Eq. (62), $\alpha_i(\upsilon_B)$ by Eq. (53) with Eq. (47) (phase $A$) and Eq. (64) (phase $B$), $\sigma$ and $\alpha$ by Eqs. (32) and (37), $d\mu_i^0/dT$ by Eqs. (38) and (61) with Eqs. (45)–(47) (phase $A$) and Eqs. (45), (63), and (64) (phase $B$), $\langle d\mu_i^0/dT\rangle$ by Eq. (22), and $\partial\varphi_A/\partial n$ by Eq. (70), where $c$ is

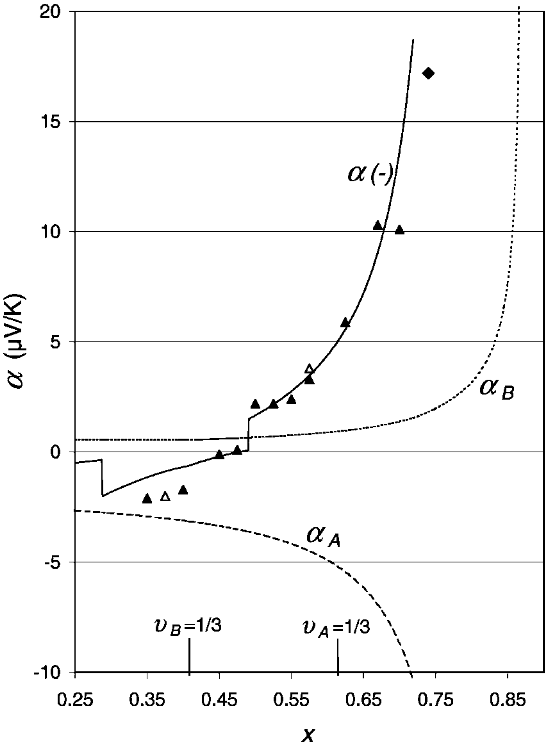

FIG. 5. Calculated thermopower for $a$-Cr$_{1-x}$Si$_x$ corresponding to Figs. 4(d) and 4(g) with $c=2.6$ eV, but redrawn vs $x$, and a comparison with experimental data taken from Gladun *et al.* (Ref. 40) (rhombus), Weser (Ref. 39) (open triangles), and Sonntag (Ref. 41) (solid triangles).

used as a parameter with $c=2.3$, 2.6, and 2.9 eV and $c=0$. $\sigma$, $1/|e|\langle d\mu_i^0/dT\rangle$, $\alpha(+)$, and $\alpha(-)$ [the two solutions of Eq. (35)] are drawn in Figs. 4(e)–4(h). [For $c=0$, Eq. (35) does not have a solution for $0.134<\upsilon_B<0.589$; see Figs. 4(g) and 4(h).] Additionally, in Fig. 4(e), experimental $\sigma$ data of sputtered $a$-Cr$_{1-x}$Si$_x$ thin films are drawn taken from Helms *et al.*,[38] Weser,[39] and Gladun *et al.*,[40] where $\upsilon_B$ is calculated by Eqs. (31) and (77).

The $\alpha(-)$ curve of Fig. 4(g) for $c=2.6$ eV as well as $\alpha_A$ and $\alpha_B$ of Fig. 4(d) is drawn once more in Fig. 5 vs $x$ commonly with experimental data for $\alpha$ taken from Gladun *et al.*,[40] Weser,[39] and Sonntag[41] (sputtered from alloy targets), where Eq. (77) is used. The experimental $\alpha$ data are described relatively well by the theoretical $\alpha(-)$ curve in Fig. 5 (excepting $x\leqslant 0.41$ corresponding to $\upsilon_B\leqslant 1/3$) and even the *sign* change of $\alpha(-)$ at $x=0.48$ (corresponding to $\upsilon_B=0.46$) and the drastic increase of $\alpha(x)$ with increasing $x$. This is especially remarkable, although, for $x>0.49$, $\alpha_B$ remains *essentially smaller* than $\alpha(-)$ itself and $\alpha_A$ is even *negative* in the complete concentration range considered. Above the *sign* change of $\alpha(-)$ there is a discontinuity in the $\alpha(x)$ curve, and the question arises whether or not this discontinuity calculated can be confirmed experimentally by independent authors. This discontinuity calculated does also occur if some of the physical parameters applied are changed within the scope of physically reasonable values.

We consider the relatively good correspondence between the calculated and experimental $\alpha$ and $\sigma$ data, Figs. 5 and 4(e), respectively, as support for the *alternative concept* of papers I and II. Nevertheless, the calculations described are to be considered as temporary example calculations because of the simplifying approximations, where the most problematic one is the assumption that the energies of the band edges do not depend on temperature and that the electron redistribution to other electronic bands (for instance, the $d$ band in alloys containing transition metals) does not change with changing temperature. Moreover, for calculation of $p$, Eqs. (72)–(81), $X_{B^*}/X_B$ is only linearly interpolated between $\upsilon_B=1/3$ and $\upsilon_{B,k}$, where specific features of the boundary faces are not considered and the phase grains are assumed to be spherical. By additional measurement of $R_H$ there would be the possibility to determine $p(x)$ independently. Such additional $R_H$ data also would enable an independent determination of $n(x)$, and Eq. (66) could be checked directly as well as the validity of the physical model applied. In this context, additional precise experimental data of $x_A$, $x_B$, $\mathcal{N}_A$, $\mathcal{N}_B$, $D_A$, $D_B$ vs $x$—e.g., determined according to the examples of Refs. 42–44—would be useful.

Above $\upsilon_B\simeq 0.80$ (corresponding to $x\simeq 0.72$), $\alpha(+)$, $\alpha(-)$, and $(1/|e|)\langle d\mu_i^0/dT\rangle$ are drawn only partially in Figs. 4 and 5 because there are considerable discontinuities and fluctations. Notice that outside of the concentration range $1/3<\upsilon_B<2/3$ (corresponding to the condition $\upsilon_i>1/3$) the assumptions for the calculations become worse. $L_i/d_i(\upsilon_B)$ calculated by Eqs. (82)–(84) as well as the equations for $\sigma_i$, $\alpha_i$, $\partial\mu_i^0/\partial T$, and $\partial\mu_i^0/\partial n_i$ applied, only have a physical content if both $\upsilon_i>1/3$ (spherical phase grains) and $k_{F,i}L_i>c^*$, Eq. (1). The latter condition corresponds to $\sigma_i>\sigma_{min,i}$ (at $T=0$) with

$$\sigma_{min,i}=\frac{c^{*2}}{6}\left(\frac{e^2}{h}\right)\frac{1}{d_i} \tag{85}$$

following from Eq. (B3), if $L_i=L_{i,min}$, Eq. (84), is set (see Appendix B). For the phase $B$ it follows from Eq. (85) with $d_B=0.234$ nm, $\sigma_{min,B}=17\ \Omega^{-1}\,\mathrm{cm}^{-1}$; for phase $A$ such a consideration is not necessary, because the first condition $\upsilon_i>1/3$ is violated for phase $A$, already, before $\sigma_A$ becomes small; see Fig. 4(c). For phase $B$, the condition $\sigma_B>\sigma_{min,B}$ is violated above $\upsilon_B=\upsilon_{B,c}=0.97$ corresponding to $x=x_c=0.87$; this is the concentration of the metal-insulator transition—i.e., $\sigma_B=0$ for $T=0$ (see Sec. III C of paper II). Because of $\sigma_B=0$, $\sigma=0$ (at $T=0$) as well, since $\upsilon_A<1/3$ for $\upsilon_B\geqslant\upsilon_{B,c}$ (see Sec. III A of paper II). Although the consequences described refer especially to the situation at $T=0$, they have basic meaning, because Eqs. (45)–(47), (52), (53), and (62)–(64) applied are constraint basically to the *metallic* regime; for $T>0$, transport contributions due to *activation* processes of carriers are superimposed to the "*metallic* transport." The effect of these *activation* processes on the electronic transport properties (not considered in the present paper) plays a role also for $\upsilon_B<\upsilon_{B,c}$, but it is larger for the larger $\upsilon_B$. For $\upsilon_i<1/3$, *tunnelling* of electrons through the minor phase is to be taken into account.

## V. SUMMARY

Applying EMT and the BTE, a formula is derived for calculation of the Seebeck coefficient of composites,

$$\sum_i v_i \frac{\mathfrak{Z}_i - \mathfrak{Z}}{\mathfrak{Z}_i + 2\mathfrak{Z}} = 0, \tag{86}$$

which can be transformed to

$$\sum_i v_i \frac{\mathfrak{z}_i - \mathfrak{z}}{\mathfrak{z}_i + 2\mathfrak{z}} = 0 \tag{87}$$

if the phases are *metallic* phases or *degenerated* semiconducting phases and if the scattering is elastic. The term $d\mu_i^0/dT$ in $\mathfrak{Z}_i$, $\mathfrak{Z}$, $\mathfrak{z}_i$, and $\mathfrak{z}$, defined by Eqs. (19), (21), (33), and (34), depends also on the electrochemical potential $\mu$ and its change with temperature, $d\mu/dT$. $d\mu/dT$ is essentially determined by the electronic structure, the carrier densities, and electron-electron-interaction in the phases.

Equations (86) and (87) can also be applied to composites with *strong scattering*.

For *metal-metal* composites (with $e_A = e_B$) and *metal-insulator* composites, Eq. (87) can be approximated by

$$\sum_i v_i \frac{\sigma_i/\alpha_i - \sigma/\alpha}{\sigma_i/\alpha_i + 2\sigma/\alpha} \simeq 0 \tag{88}$$

and

$$\alpha \simeq \alpha_A, \tag{89}$$

respectively.

In Sec. III, Eq. (87) is applied for calculation of the concentration dependence $\alpha(v_B)$ for several special cases of composites with the following simplistic assumptions: (a) positions of the *band edges* are fixed on energy scala, (b) sum of electrons in the considered bands is constant, (c) NFE approximation, (d) spheric phase grains, (e) *carrier densities* do not depend on concentration, and (f) neglect of the *electron-electron interaction*.

In Sec. IV the concentration dependence $\alpha(x)$ is calculated for $a$-Cr$_{1-x}$Si$_x$ alloys, where both the concentration dependence of the *carrier densities* and the *electron-electron-interaction* are taken into account; i.e., assumptions (e) and (f) are abolished. The NFE approximation (c) is kept, because it is a relatively good approximation for $a$-$N_{1-x}M_x$ and many[27] $a$-$T_{1-x}M_x$ alloys (for not too small $v_B$) as justified in Sec. IV B of paper II.

The equations for $\sigma_i$, $\alpha_i$, $\partial\mu_i^0/\partial T$, and $\partial\mu_i^0/\partial n_i$, applied for the calculations, only have a physical content if both $v_i > 1/3$ (spherical phase grains) and $k_{F,i}L_i > c^*$, Eq. (1), corresponding to $\sigma_i > \sigma_{min,i}$, Eq. (85) (at $T=0$). If the condition $v_i > 1/3$ is not fulfilled, *tunneling* of the electrons through the minor phase is to be taken into account. If Eq. (1) is not fulfilled, *metallic* conductivity is absent.

## ACKNOWLEDGMENTS

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## APPENDIX A: DERIVATION OF THE EMT EQUATION FOR $\alpha$

Equation (26) has the solution[2]

$$\varphi_i = \varphi_0 + r a_i \cos\vartheta \tag{A1}$$

within the sphere $i$ and

$$\varphi = \varphi_0 + (br + c r_0^3/r^2)\cos\vartheta \tag{A2}$$

within the effective medium. $\vartheta$ is the angle between the direction of $\mathbf{E}$ and the position vector $\mathbf{r}$ with $|\mathbf{r}| = r$. $a_i$, $b$, $c$, and $\varphi_0$ are constants. With

$$\mathrm{grad}_r \varphi_i = a_i \cos\vartheta \tag{A3}$$

following from Eq. (A1), Eq. (25) can be written as

$$\mathfrak{Z}\langle a_i\rangle = \langle a_i \mathfrak{Z}_i\rangle. \tag{A4}$$

With the boundary condition, Eq. (27), it follows that

$$a_i = b + c, \tag{A5}$$

and with Eq. (29) and Eqs. (A1) and (A2) for $r = r_0$,

$$\mathfrak{Z}(b - 2c) = \mathfrak{Z}_i a_i. \tag{A6}$$

Equations (A5) and (A6) resolved for $a_i$ providing

$$a_i = \frac{3b\mathfrak{Z}}{\mathfrak{Z}_i + 2\mathfrak{Z}} \tag{A7}$$

and introduced in Eq. (A4) provide

$$\mathfrak{Z}\left\langle \frac{1}{\mathfrak{Z}_i + 2\mathfrak{Z}} \right\rangle = \left\langle \frac{\mathfrak{Z}_i}{\mathfrak{Z}_i + 2\mathfrak{Z}} \right\rangle \tag{A8}$$

in correspondence with Eq. (30).

## APPENDIX B: MINIMUM METALLIC CONDUCTIVITY

Equation (85) follows from the BTE formula for $\sigma_i$,

$$\sigma_i = \frac{S_{F,i} e^2 L_i}{6\pi^2 h}, \tag{B1}$$

if $S_{F,i}$, the Fermi surface related to the phase $i$, is replaced by

$$S_{F,i} = 4\pi k_{F,i}^2 \tag{B2}$$

(*spherical* Fermi surface, $v_i > 1/3$) and $k_{F,i}$ by $k_{F,i} = c^*/L_i$ [the lower boundary for $k_{F,i}$, Eq. (1)] leading to

$$\sigma_{min,i} = \frac{2c^{*2}}{3\pi}\left(\frac{e^2}{h}\right)\frac{1}{L_i}. \tag{B3}$$

$L_i = L_{i,min}$, Eq. (84), introduced in Eq. (B3), provides Eq. (85). Justification for the assumption of *spherical* Fermi surfaces, Eq. (B2), follows from the fact that, for small $\sigma_i$ [corresponding to small $n$ (or $p$)], $k_{F,i}$ is small and sufficiently distant to the first Brillouin zone boundary in the phase $i$.

Unfortunately, in the original formula for the minimum metallic conductivity derived in Sec. IV C of paper II there is an error: in Eqs. (45) and (47) of paper II "$c^*/6$" is to be replaced by "$2c^{*2}/3\pi$;" i.e., Eqs. (45) and (47) of paper II read in correct form

$$\sigma_{min} = \frac{2c^{*2}}{3\pi}\left(\frac{e^2}{h}\right)\frac{1}{L} \tag{B4}$$

and

$$\sigma_{min} \simeq \frac{2c^{*2}}{3\pi}\left(\frac{e^2}{h}\right)\frac{1}{d} \simeq 20\ \Omega^{-1}\ \mathrm{cm}^{-1}, \tag{B5}$$

respectively. Equation (B5) follows from Eq. (B4) if $L \simeq d \simeq 0.25$ nm is set (see Sec. IV C of paper II).

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[24] In the kinetic theory for *homogeneous* materials the term "$\mu_i^0 - |e_i|\varphi_i$" is generally called electrochemical potential; to avoid confusion, we call $\mu_i$ *extended* electrochemical potential, since the energy of the band edge is added. Note that $\mu_i$ characterize energy levels on the energy scale, whereas $\mu_i^0$ are energies defined by the Fermi-Dirac statistics.

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[32] Different from papers I and II (where $n_A$ and $n_B$ were defined as the electron densities at $\upsilon_A = 1$ and $\upsilon_B = 1$, respectively), in the present paper III both $n_A = n$ and $n_B$ are used for the *concentration-dependent* electron densities in phases $A$ and $B$, respectively, so it is possible to write uniform equations for the different phases.

[33] In the examples considered in Sec. III, $n_i$, $\sigma_i$, and $\alpha_i$ are still assumed to be independent of *concentration* ($\upsilon_B$). Later it will be argued that, in real composites, $n_i$, $\sigma_i$, and $\alpha_i$ depend generally on $\upsilon_B$ because of the condition of a common electrochemical potential in the alloy (see Sec. IV).

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