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Abstract
The classical thermopower formulae generally applied for the calculation of the Seebeck coefficient S are argued to be incomplete. S can be separated into two different contributions, a scattering term, S^0, and a thermodynamic term, ΔS, representing the additional change of the electrochemical potential μ with temperature T caused by 'non-scattering' effects, for instance, the band edge shift with T. On the basis of this separation into S^0 and ΔS, it is shown that shifts of the band edges with T lead to an additional contribution to the classical thermopower formulae. This separation provides the basis for an interpretation of *positive* thermopowers measured for many metals. *Positive* thermopower is expected if the energy of the conduction band edge increases with T and if this effect overcompensates for the influence of the energy dependent conductivity, $\sigma(E)$. Using experimental thermopower data, the band edge shifts are determined for a series of liquid normal metals.

1. Introduction

The thermopower is a transport coefficient which can provide essential insight into the electronic structure of a material as well as information about which electronic scattering mechanisms are active. Unfortunately, it is often very difficult to interpret the experimental thermopower data even for the simplest metals. Even for such simple one-electron metals as Cu, Ag, Au, and Li the theory of nearly free electrons (NFE approximation) predicts a *negative* sign of the thermopower, while experimentally one finds a *positive* sign both in the *solid* state [3, 4] and in the *liquid* state [5–7]. This finding is unexpected, especially for the *liquid* state insofar as by melting of a metal the periodicity of long-range order of the atomic arrangement is lost, and therefore, the transport coefficients can be expected to approach a free-electron behavior. This expectation is supported by the fact that the experimentally determined Hall coefficients, R_{exp}, are equal to the values predicted by the NFE approximation [8, 9], $R_0 = -1/(|e|n)$, where n is the electron density and $|e|$ is the elementary charge. Such a discrepancy is also found in other (liquid) metals as demonstrated in table 1. Except for the rightmost column, this table is a collection of data taken from Busch and Güntherodt [1] (table 1 and table 4 therein) and Künzi and Güntherodt [2] (table 2 therein): while the

experimentally determined Hall coefficients, R_{exp}, of almost all liquid normal metals[1] are equal to R_0, the experimentally determined thermopowers, S_{exp}, generally differ from the theoretical ones calculated in the framework of the NFE approximation [3, 4, 10],

$$\alpha_0 = -\frac{\pi^2 k_B^2 T}{3|e|E_F}. \tag{1}$$

k_B is the Boltzmann constant, E_F the Fermi energy and T the temperature.

Following [1], the deviation of the experimental thermopower data from the theoretical one calculated by using equation (1) is expressed by the thermoelectric parameter,

$$X_{exp} = \frac{S_{exp}}{\alpha_0}. \tag{2}$$

A widespread description of the thermopower in disordered metals is the Ziman theory [11] in connection with the Mott formula,

$$\alpha = \alpha_0 E_F \left[\frac{1}{\sigma} \frac{\partial \sigma(E)}{\partial E} \right]_{E_F}, \tag{3}$$

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[1] 'Normal metals' or 'sp metals'; the term 'normal metals' is used in honor of G Busch and H-J Güntherodt who used this term in their pioneer work on liquid metals and alloys.

Table 1. Experimental thermopowers, S_{exp}, and Hall coefficients, R_{exp}, compared with calculated NFE values, α_0 and R_0, respectively, taken from [1, 2]. (S_{exp} was measured at the melting temperature T_m, R_{exp} at T_m and higher.) The band edge shifts, dE_C/dT, are calculated by using equation (41) with $r = 0$ and $z = 3/2$.

Metal	Z	S_{exp} $(\mu V\,K^{-1})$	S_{exp}/α_0 $(=X_{exp})$	R_{exp}/R_0	dE_C/dT $(10^{-6}\,eV\,K^{-1})$
Cu	1	17.7	−3.4	1.00	25.5
Ag	1	11.0	−1.8	1.02; 0.97	20.0
Au	1	5.6; 4.8	−0.9; −0.8	1.00	14.4
Li	1	21.7	−9.0	0.98	25.3
Na	1	−7.9	2.6	0.98; 1.00	−3.3
K	1	−14.0	3.3	1.00	−7.6
Rb	1	−6.3	1.4	1.00	0.5
Cs	1	6.4	−1.3	1.00 ± 0.03; 1.00	13.8
Mg	2	1.5			
Zn	2	0.1	−0.1	1.00; 1.01	1.6
Cd	2	0.5	−0.2	0.96; 0.98; 1.04; 0.99	4.3
Hg	2	−3.5	4.1	0.98; 0.96; 1.22; 1.04; 0.99; 1.00; 1.20; 1.00; 1.00; 1.00; 1.07	−2.2
Al	3	−2.3; −2.1	1.1; 1.0	1.00	0.9
Ga	3	−0.4	0.6	0.96; 0.99; 0.97; 1.00; 1.04; 1.00; 1.02	0.6
In	3	−1.0	0.8	0.98; 0.80; 1.04; 0.93; 0.95; 1.00; 0.94; 0.92	0.9
Tl	3	−0.5	0.3	0.76	2.0
Ge	4	0	0	1.00	
Sn	4	−0.5	0.4	0.98; 1.07; 1.00; 1.00; 1.00; 1.00; 1.00	1.4
Pb	4	−3.4	2.1	0.38; 0.88; 0.73; 0.88	−1.0
Sb	5	0	0	1.14; 1.07	
Bi	5	−0.7	0.6	0.95; 0.60; 0.69; 0.68; 0.96	

where $\sigma(E)$ is the energy dependent conductivity. According to equation (3) the key to the *sign* of the thermopower apparently is the energy derivative of $\sigma(E)$. In general, $\sigma(E)$ is expected to increase with increasing energy of the electrons, so as a general rule negative thermopowers are to be expected ([4], p 63), because $\alpha_0 < 0$, equation (1). On the other hand, if one can show that the more energetic an electron is, the more it is scattered (i.e. $\sigma(E)$ decreases with increasing energy), then the positive sign of α can be understood. Until the 1960s, such a situation was thought to be unphysical. However, because positive thermopowers do exist in Cu, Ag, Au, and Li, this thought was called into question: by construction of special atomic model potentials (pseudopotentials; [4], pp 195–196) and applying the extended Ziman formula for the energy dependent specific electrical resistivity $\rho(E)$ $(=1/\sigma(E))$ and considering (experimental) structure factors, it was possible to calculate $\sigma(E)$ with the property $\partial\sigma(E)/\partial E < 0$ at E_F. The thermopowers calculated from these $\rho(E)$ correspond relatively well to the experimental thermopowers of a series of metals [12–20], while calculations by Geertsma *et al* [21] provided negative thermopowers for liquid Li and Cs, in contrast to the positive sign measured. It is clear that the calculated thermopowers depend essentially on the choice made for the pseudopotential.

All the efforts spent on an interpretation of the positive thermopowers of metals were concentrated on the *energy* dependence of the scattering process of the electrons. In the present paper we shall attract attention to another possible cause for positive thermopowers of metals: the *temperature dependence* of the band edge E_C. The classical thermopower formula for homogeneous metals is [3, 4, 10, 22]

$$S = \frac{\pi^2 k_B^2 T(1+r)}{3eE_F},\qquad(4)$$

where $e = -|e|$ and $+|e|$ for electron and hole conductivity, respectively. r characterizes the scattering mechanism and represents the energy dependence of the mean free path L according to $L \propto E^r$.

In the present paper it will be argued that equation (4) is to be extended by an additional term, $\frac{1}{|e|}\frac{dE_C}{dT}$.

In section 2.1 it will be shown that the classical thermopower formula, equation (4), leads to contradictions if formally applied to the phases of a composite (alloy with phase separation). As a possible cause for these contradictions, in section 2.2 the neglect of scattering independent effects on the electrochemical potential μ will be identified. These scattering independent contributions to S will be taken into account by an additional term $\Delta S = \frac{1}{|e|}\frac{d\mu}{dT}$ proposed in section 3.1. By application of this modified thermopower formula to composites, in section 3.2 it will be shown that the basic problem (pointed out in section 2.1) can be solved. In section 3.3 an analytical expression for $d\mu/dT$ in composites will be derived, where the influence of the band

edges is included. In section 4 the thermopower formula for homogeneous metals will be derived as limiting cases of a two-phase composite, and it will be applied for a calculation of band edge shifts in liquid normal metals. The results of sections 3 and 4 will be discussed in section 5 and summarized in section 6. In the appendix the effect of the electrostatic potential on the thermopower in a-Cr$_{1-x}$Si$_x$ alloys will be discussed.

2. The problem: incompleteness of equation (4)

2.1. Breakdown of equation (4)

In the following we shall show that the thermopower formula equation (4) is *incomplete*, because it leads to contradictions if applied to the phases of a *composite*. The thermopower formula for composites is [23]

$$\sum_i \upsilon_i \frac{\kappa_i/S_i - \kappa/S}{\kappa_i/S_i + 2\kappa/S} = 0. \tag{5}$$

S and κ are the Seebeck coefficient and specific thermal conductivity of the composite, κ_i, S_i, and υ_i are the corresponding parameters and the volume fraction of the phase i (A, B, . . .). S versus υ_i can be calculated by using equation (5) if S_i, κ_i and κ are known. S_i and κ_i are to be calculated with the same formulae as for homogeneous materials, which for metallic phases are

$$S_i = \frac{\pi^2 k_B^2 T (1 + r_i)}{3e_i E_{F,i}}, \tag{6}$$

$$\kappa_i \approx \kappa_{e,i} = \frac{16\pi^3}{9} \frac{m_i L_i E_{F,i}}{h^3} k_B^2 T, \tag{7}$$

where h is Planck's constant. $E_{F,i}$ is the Fermi energy in the phase i. $e_i = -|e|$ and $+|e|$ for electrons and holes, respectively. κ is to be calculated by using [24]

$$\sum_i \upsilon_i \frac{\kappa_i - \kappa}{\kappa_i + 2\kappa} = 0. \tag{8}$$

Equation (6) corresponds to equation (4) applied for the phase i. Analogously to the homogeneous materials case, r_i characterizes the energy dependence of the mean free path L_i in the phase i according to $L_i \propto E^{r_i}$. The approximation in equation (7) is certainly a good one for metallic phases if the carrier densities are not too small and if the phases form macroscopic clusters ([23], section 5.2. therein).

Let us consider a two-phase composite where the phase A has electron conductivity with n as the electron density, whereas the phase B has hole conductivity with the hole density p (characterized by figure 1(c) in [25]). Equation (5) has two solutions, $S(+)$ and $S(-)$:

$$S = S(\pm) = \frac{4\kappa}{\Re \pm \sqrt{\Re^2 + 8(\kappa_A/S_A)(\kappa_B/S_B)}} \tag{9}$$

with $\Re = (3\upsilon_A - 1)\kappa_A/S_A + (3\upsilon_B - 1)\kappa_B/S_B$ and $\upsilon_A + \upsilon_B = 1$. If the scattering properties and the carrier densities
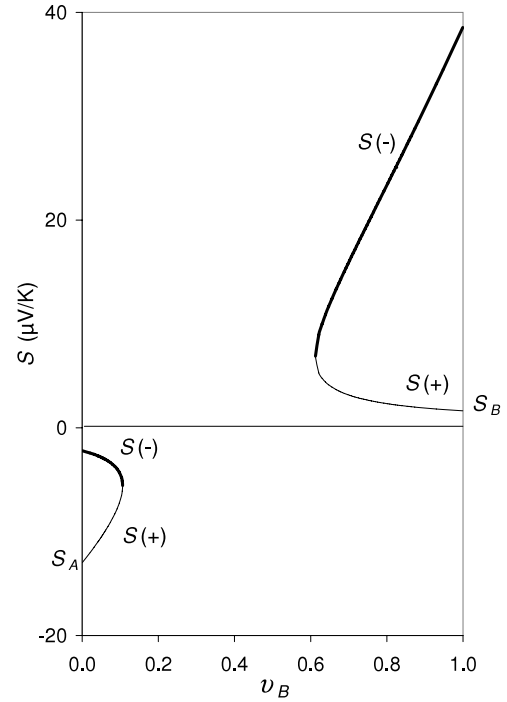

Figure 1. $S(-)$ (bold line) and $S(+)$ (fine line) versus υ_B calculated by using equation (9) with $\kappa_A = 8.5$, $\kappa_B = 12.7$, $S_A = -13.0$, and $S_B = +1.7$ (in units of mW cm^{-1} K^{-1} and μV K^{-1}, respectively). For $\upsilon_B = 0.11 \ldots 0.61$, equation (9) has no real solutions.

in the phases do not change with the composition, the S_i, equation (6), and κ_i, equation (7), are constant for a given temperature T. However, for constant S_i and κ_i, one can easily show that equation (9) never has real solutions for the *entire* concentration range if the S_A and S_B have different sign, no matter which fixed numbers are chosen for the S_i and κ_i. This result is dubious, because equation (5) in fact holds generally, when for the phases i their own transport coefficients, S_i and κ_i, are inserted, independently of the signs of the carriers in the different phases of the composite ([23], section 5.1. therein). In figure 1 an example calculation is shown for a hypothetical composite with $S_A = -13.0 \ \mu$V K^{-1}, $S_B = +1.7 \ \mu$V K^{-1}, $\kappa_A = 8.5$ mW cm^{-1} K^{-1}, and $\kappa_B = 12.7$ mW cm^{-1} K^{-1}.[2] As can be seen in figure 1, for $\upsilon_B = 0.11 \ldots 0.61$, equation (9) does not have real solutions, because the square root in equation (9) becomes imaginary. The situation is not essentially changed if the changes of n and p due to electron transfer between the phases maintaining $\mu_A = \mu_B = \mu$ are taken into account by equations (6), (7) and

$$E_{F,A} = \frac{h^2}{8m_A} \left(\frac{3}{\pi}\right)^{2/3} n^{2/3}, \tag{10}$$

$$E_{F,B} = \frac{h^2}{8m_B} \left(\frac{3}{\pi}\right)^{2/3} p^{2/3}, \tag{11}$$

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[2] S_i and κ_i correspond to $n = 10^{22}$ cm^{-3} and $p = 2 \times 10^{22}$ cm^{-3} if calculated by using equations (6), (7), (10), (11) with $m_A = m_0$, $m_B = 0.2 \times m_0$, $r_i = 2$, and $L_i = 4/\pi \times d_i$, where d_i are the interatomic distances in the phases, $d_A = 0.25$ nm and $d_B = 0.234$ nm. m_0 is the electron mass.

because this electron transfer (expressed by dn/dT, equation (26)) is relatively small, so the changes of S_i and κ_i are only marginal. μ_A and μ_B are the electrochemical potentials in phase A and phase B, respectively.

In conclusion of this section we state: the problem that for $e_A = -e_B$, equation (9) (or equation (5)) does not have real solutions over the entire concentration range is a basic problem. This finding suggests that the theoretical formulae equations (4) and (5) are not compatible with each other, that is, either equation (4) is *incomplete* or equation (5) is *incomplete*. With the argumentation given in [23] (sections 1 and 5.1 therein) we believe that equation (5) is actually correct; the same formula, equation (5), would also be obtained if the energy-flux density J_E was applied for the derivation (instead of the entropy-flux density J_S as is done in [23]). Because these two flux densities, J_S and J_E, are of fundamental importance for the electronic transport in homogeneous and heterogeneous materials ([10], p 28 therein), we suppose that the incompatibility of equations (4) and (5) is caused by equation (4).

2.2. Cause for the breakdown of equation (4)

Equation (4) reflects the incomplete *equalization* of the electrochemical potential μ at the ends of a sample if they have different temperatures, T_1 and T_2. This *equalization* is incomplete, because a balance is realized between acceleration and scattering of the electronic carriers: acceleration in an electric field (due to potential differences) counterbalanced by deceleration due to scattering (at phonons and structure faults). In consequence of this counterbalance there remains a *residual difference* in μ, $\Delta\mu$. This $\Delta\mu$ divided by the temperature difference $\Delta T = T_2 - T_1$ is what is measured in a measurement of the Seebeck coefficient S_{exp}, i.e.,

$$S_{exp} = \frac{1}{|e|}\frac{\Delta\mu}{\Delta T}, \tag{12}$$

in correspondence with the definition of the (differential) Seebeck coefficient [4, 10],

$$S = \left[\frac{grad\,\mu}{|e|grad\,T}\right]_{J=0}, \tag{13}$$

which for *homogeneous* materials reduces to ([10], p 47)

$$S = \left[\frac{1}{|e|}\frac{d\mu}{dT}\right]_{J=0}. \tag{14}$$

Only in superconductors does the *residual difference* in μ disappear, $\Delta\mu = 0$, because scattering does not happen, i.e., the effect of deceleration by scattering disappears completely. That is why $S = 0$ for superconductors, in spite of the displacement of the electrical charges.

Now let us consider a simple one-band metal, where the band edge E_C depends on temperature, i.e., $dE_C/dT \neq 0$. The Boltzmann transport equation (BTE) provides for the Seebeck coefficient the formula equation (4) replacing equation (14) in the NFE approximation. Aside from T, in equation (4) there are only two *variables*, the Fermi energy E_F and the scattering

parameter r, i.e., any influence of the amount of dE_C/dT is not contained therein. Because dE_C/dT is generally very small, it is reasonable to assume that both E_F and r are practically independent of the value of dE_C/dT, i.e., equation (4) provides the same value for S irrespective of the value of dE_C/dT. This result is suspect, because μ increases with E_C according to

$$\mu = E_C + \mu_C^0 - |e|\varphi, \tag{15}$$

where φ and μ_C^0 are the electrostatic potential and the chemical potential, respectively. While the deceleration effect due to scattering is not changed, the acceleration effect due to the potential difference increases with increasing difference of the electrochemical potential between the ends of the sample. Therefore, the total *residual difference* $\Delta\mu$ between the ends of the sample is also expected to be larger if $dE_C/dT > 0$ compared with $dE_C/dT = 0$. This can be expressed by

$$\Delta\mu = (\Delta\mu)_0 + \delta(\Delta\mu), \tag{16}$$

where $(\Delta\mu)_0$ represents the *residual difference* in μ for $dE_C/dT = 0$; $\delta(\Delta\mu)$ represents the additional contribution to $\Delta\mu$ if $dE_C/dT > 0$ (or $dE_C/dT < 0$). Thus, different values for S are expected for $dE_C/dT = 0$ compared with $dE_C/dT \neq 0$. This exception is, however, not reflected by equation (4). This argumentation holds, in principle, also for the more general BTE formula,

$$S = \frac{K_2/K_1 - \mu_C^0}{eT}, \tag{17}$$

where the K_s are the transport integrals. Also in this formula, S only depends on μ_C^0 and the scattering properties of the carriers, and not on dE_C/dT.

3. The proposal for a solution of the problem

3.1. The extension of the thermopower formula

The dilemma described in the previous sections can be solved by the introduction of an additional term taking into account additional influences on the *residual difference* of μ. One example of such an influence is the band edge shift, $dE_C/dT \neq 0$, considered in section 2.2, already. Another example is the change of the carrier densities in the phases of a composite (considered in section 3.3) or due to interband transfer of electrons in (homogeneous) transition metals if the band edge shifts of the s and d bands are different. We define, in correspondence with equation (16) and in analogy with the relation between equation (12) and equation (14), the extended thermopower formula

$$S' = S^0 + \Delta S, \tag{18}$$

already introduced in [23] (equation (17) therein) for the (homogeneous) phases i in a composite. S^0 and ΔS correspond to $(\Delta\mu)_0$ and $\delta(\Delta\mu)$, respectively, in equation (16). Considering the different origins of S^0 and ΔS, we denote them as the scattering term,

$$S^0 = \left[\frac{1}{|e|}\frac{d\mu}{dT}\right]_{J=0}^{scatt}, \tag{19}$$

and the thermodynamic term,

$$\Delta S = \left[\frac{1}{|e|} \frac{d\mu}{dT} \right]^{\text{thermodyn}}_{J=0} \equiv \frac{1}{|e|} \frac{d\mu}{dT}, \qquad (20)$$

respectively. S^0, equation (19), corresponds with equation (4) (for the case of NFE-approximation) and with equation (17) (for the more general case). ΔS, equation (20), representing the non-scattering influences, is to be determined separately; this will be the subject of the following considerations.

3.2. Application of the extended thermopower formula, equation (18), to composites

Now we shall show that the basic problem described in section 2.1 can be solved by the extended thermopower formula, equation (18), i.e., S_i, equation (6), is replaced by S_i' defined by

$$S_i' = S_i^0 + \frac{1}{|e|} \frac{d\mu}{dT} \qquad (21)$$

with

$$S_i^0 = \frac{\pi^2 k_B^2 T (1 + r_i)}{3 e_i E_{F,i}}, \qquad (22)$$

and equations (5) and (9) are replaced by

$$\sum_i v_i \frac{\kappa_i / S_i' - \kappa / S'}{\kappa_i / S_i' + 2\kappa / S'} = 0 \qquad (23)$$

and

$$S' = S'(\pm) = \frac{4\kappa}{\mathfrak{R}' \pm \sqrt{\mathfrak{R}'^2 + 8(\kappa_A / S_A')(\kappa_B / S_B')}}, \qquad (24)$$

where $\mathfrak{R}' = (3v_A - 1)\kappa_A / S_A' + (3v_B - 1)\kappa_B / S_B'$.

Equation (24) has solutions for the *entire* concentration range $0 \leqslant v_B \leqslant 1$, as shown in figure 2. For the calculation of $d\mu/dT$, equations (39), (61) of [25] are applied, where the contributions of the electrostatic potential to $d\mu/dT$ were still neglected, i.e., $\partial \varphi_i / \partial n_i = 0$ was set.

The result that equation (5) only has solutions in the entire concentration range if the S_i and S are replaced by S_i' and S', respectively, supports the fact that the extended thermopower formula, equation (18), can be an adequate description. Furthermore, this result suggests that in real composites the thermopowers of the *phases* can generally not be assumed to be independent of the concentration. In other words, *constant* values for S_i would not be consistent with the rules of thermodynamics which was the basis for the derivation of the thermopower formula, equation (5) ([23], sections 2. and 5.1 therein).

3.3. The influence of the band edges on the Seebeck coefficient of composites

Until now fixed band edges have been assumed. As is known, for many semiconductors, the energy gap, $\Delta E = E_C - E_V$, depends on temperature T [3, 22, 26], where E_C and E_V characterize the band edges of the conduction band (CB) and valence band (VB), respectively, i.e., at least $dE_C/dT \neq 0$ or
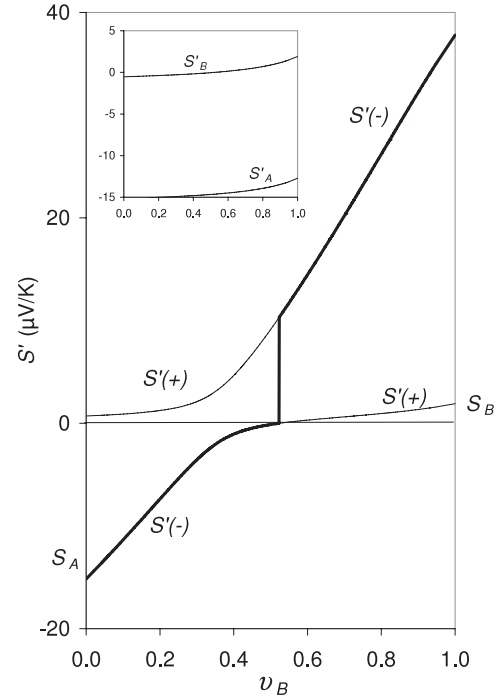

Figure 2. $S'(-)$ and $S'(+)$ versus v_B calculated by using equation (24) for $T = 300$ K, where the term $d\mu/dT$ is calculated from the condition $d\mu_A/dT = d\mu_B/dT$ with $\partial E_{C,A}/\partial T = \partial E_{V,B}/\partial T = \partial \varphi_i/\partial n_i = 0$. Equation (24) has real solutions for the entire concentration range. In the inset the Seebeck coefficients of the phases i calculated by using equation (21) are drawn versus v_B.

$dE_V/dT \neq 0$. Analogously, also for metals the band edge can depend on T which influences the term $d\mu/dT$, and via equation (21) also the Seebeck coefficient. In a (metallic) composite, $d\mu/dT$ can be expressed by

$$\frac{d\mu}{dT} = \frac{d\mu_i}{dT} = \frac{\partial \mu_i}{\partial T} + \frac{\partial \mu_i}{\partial n} \frac{dn}{dT}, \qquad (25)$$

which for a two-phase composite leads to

$$\frac{dn}{dT} = - \frac{\frac{\partial \mu_A}{\partial T} - \frac{\partial \mu_B}{\partial T}}{\frac{\partial \mu_A}{\partial n} + \frac{v_A}{v_B} \frac{\partial \mu_B}{\partial n_B}}, \qquad (26)$$

if the total number of electrons is assumed to be constant, i.e., $v_A dn + v_B dn_B = 0$. For a *metallic* composite specified in section 2.1, equation (26) leads to

$$\frac{dn}{dT} = - \frac{\frac{\partial \mu_A^0}{\partial T} + \frac{\partial \mu_B^0}{\partial T} + \frac{\partial E_{C,A}}{\partial T} - \frac{\partial E_{V,B}}{\partial T}}{\frac{\partial \mu_A^0}{\partial n} - |e| \frac{\partial \varphi_A}{\partial n} + \frac{v_A}{v_B} \left(\frac{\partial \mu_B^0}{\partial p} - |e| \frac{\partial \varphi_B}{\partial n_B} \right)}, \qquad (27)$$

where $dp = -dn_B$ is used and

$$\mu_A = E_{C,A} + \mu_A^0 - |e| \varphi_A, \qquad (28)$$

$$\mu_B = E_{V,B} - \mu_B^0 - |e| \varphi_B. \qquad (29)$$

φ_i, μ_i^0, and n_i are the electrostatic potential, the chemical potential, and the electron density, respectively, for the phase i
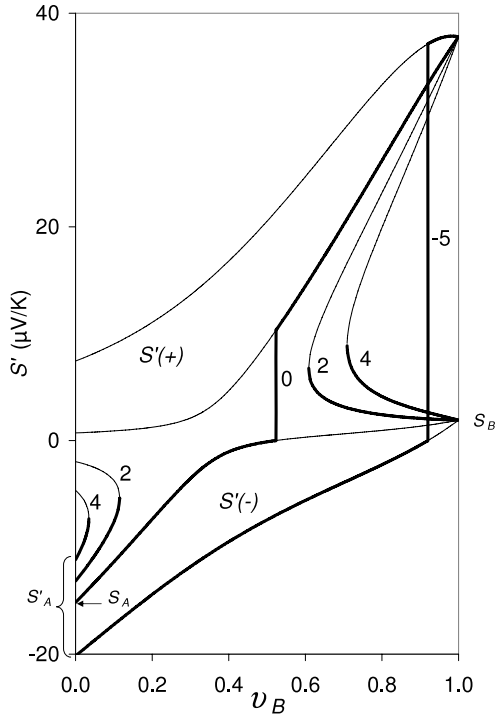
Figure 3. Same as figure 2, but for $\partial E_{\mathrm{C,A}}/\partial T = -5, 0, 2,$ and 4×10^{-6} eV K^{-1}, while $\partial E_{\mathrm{V,B}}/\partial T = 0$ and $\partial \varphi_i/\partial n_i = 0$. The discontinuity in the curves shifts to lower υ_{B} as $\partial E_{\mathrm{C,A}}/\partial T$ increases. For $\partial E_{\mathrm{C,A}}/\partial T > 0.28 \times 10^{-6}$ eV K^{-1}, equation (24) does not have real solutions for the entire concentration range.

Figure 4. Same as figure 2, but for $\partial E_{\mathrm{V,B}}/\partial T = -1.5, 0,$ and 2×10^{-6} eV K^{-1}), while $\partial E_{\mathrm{C,A}}/\partial T = 0$ and $\partial \varphi_i/\partial n_i = 0$. The discontinuity in the curves shifts to lower υ_{B} as $\partial E_{\mathrm{V,B}}/\partial T$ increases. For $\partial E_{\mathrm{V,B}}/\partial T > 1.9 \times 10^{-6}$ eV K^{-1}, equation (24) does not have real solutions for the entire concentration range.
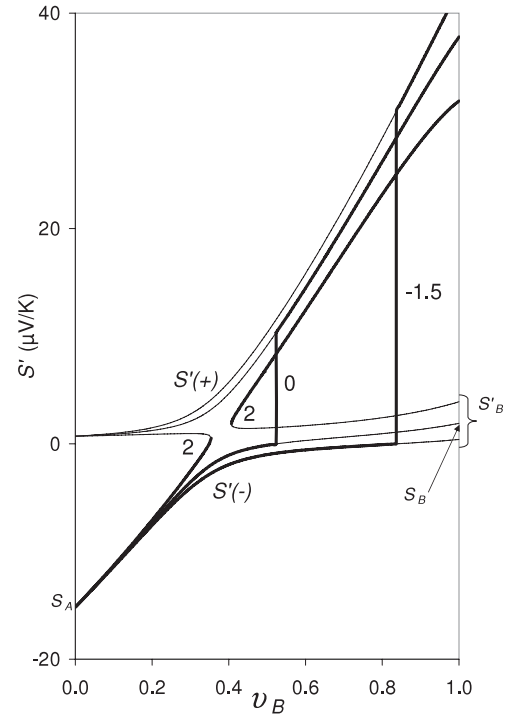
($n_{\mathrm{A}} \equiv n$). $E_{\mathrm{C,A}}$ and $E_{\mathrm{V,B}}$ are the band edges of the CB and VB for the phases A and B, respectively.

Inserting equations (27) and (28) in equation (25) leads to

$$\frac{\mathrm{d}\mu}{\mathrm{d}T} = \frac{\partial E_{\mathrm{C,A}}}{\partial T} + \frac{\partial \mu_{\mathrm{A}}^0}{\partial T} - \frac{\frac{\partial \mu_{\mathrm{A}}^0}{\partial T} + \frac{\partial \mu_{\mathrm{B}}^0}{\partial T} + \frac{\partial E_{\mathrm{C,A}}}{\partial T} - \frac{\partial E_{\mathrm{V,B}}}{\partial T}}{1 + \frac{\upsilon_{\mathrm{A}}\left(\frac{\partial \mu_{\mathrm{B}}^0}{\partial p} - |e|\frac{\partial \varphi_{\mathrm{B}}}{\partial n_{\mathrm{B}}}\right)}{\upsilon_{\mathrm{B}}\left(\frac{\partial \mu_{\mathrm{A}}^0}{\partial n} - |e|\frac{\partial \varphi_{\mathrm{A}}}{\partial n}\right)}}. \quad (30)$$

In equations (27) and (30), $\partial \varphi_i/\partial T = 0$, $\partial E_{\mathrm{C,A}}/\partial n = 0$, and $\partial E_{\mathrm{V,B}}/\partial p = 0$ are assumed. The first assumption corresponds to the fact that the electrostatic potential does not depend on T; the second and third ones are equivalent to the assumption that $E_{\mathrm{C,A}}$ and $E_{\mathrm{V,B}}$ do not depend on the occupation of the CB and VB.

Now, $\mathrm{d}\mu/\mathrm{d}T$ can be calculated by using equation (30) for different band edge shifts, $\partial E_{\mathrm{C,A}}/\partial T$ and $\partial E_{\mathrm{V,B}}/\partial T$, if

$$\frac{\partial \mu_i^0}{\partial T} = -\frac{\pi^2 k_{\mathrm{B}}^2 T}{6 E_{\mathrm{F},i}}, \quad (31)$$

$$\frac{\partial \mu_{\mathrm{A}}^0}{\partial n} = \frac{2 E_{\mathrm{F,A}}}{3n}, \quad (32)$$

$$\frac{\partial \mu_{\mathrm{B}}^0}{\partial p} = \frac{2 E_{\mathrm{F,B}}}{3p} \quad (33)$$

(following from the Fermi–Dirac statistics) are taken into account. With this $\mathrm{d}\mu/\mathrm{d}T$, S_i' and $S'(\pm)$ can be calculated by using equations (21) and (24), respectively.

In figure 3 the effect of $\partial E_{\mathrm{C,A}}/\partial T$ on the solution of equation (24) is shown. For this variation both $\partial E_{\mathrm{V,B}}/\partial T = 0$ and $\partial \varphi_i/\partial n_i = 0$ were set. Equation (24) has solutions for the entire concentration range as long as $\partial E_{\mathrm{C,A}}/\partial T < 0.28 \times 10^{-6}$ eV K^{-1}. As long as this condition is fulfilled, the discontinuities in the $S'(-)$ and $S'(+)$ curves are shifted to lower υ_{B} as $\partial E_{\mathrm{C,A}}/\partial T$ increases. Simultaneously, the amount of the discontinuity (the distance between the upper and lower kinks) decreases, until it disappears completely at a critical value of υ_{B} and a gap occurs for the real solutions $S'(\pm)$ if $\partial E_{\mathrm{C,A}}/\partial T > 0.28 \times 10^{-6}$ eV K^{-1}.

A variation of $\partial E_{\mathrm{V,B}}/\partial T$ has a similar influence. In figure 4 the influence of $\partial E_{\mathrm{V,B}}/\partial T$ on the solution of equation (24) is shown, where $\partial E_{\mathrm{C,A}}/\partial T = 0$ and $\partial \varphi_i/\partial n_i = 0$ were set. Equation (24) has solutions for the entire concentration range as long as $\partial E_{\mathrm{V,B}}/\partial T < 1.9 \times 10^{-6}$ eV K^{-1}.

The reason for the fact that for $\partial E_{\mathrm{C,A}}/\partial T > 0.28 \times 10^{-6}$ eV K^{-1} (resp., $\partial E_{\mathrm{V,B}}/\partial T > 1.9 \times 10^{-6}$ eV K^{-1}), there are υ_{B} ranges where equation (24) does not have real solutions is the neglect of the electrostatic potentials. Its effect on the discontinuity acts contrarily to those of $\partial E_{\mathrm{C,A}}/\partial T$ (resp., $\partial E_{\mathrm{V,B}}/\partial T$), i.e., taking into account the terms $\partial \varphi_i/\partial n_i$ in equation (30), the discontinuity in the $S'(\pm)$ curves is expected to be shifted into the direction of larger υ_{B}. (The phase B is the one with the deeper average potential.) In the appendix the effect of the electrostatic potential on the discontinuity will be considered for a-Cr$_{1-x}$Si$_x$ alloys.

4. The Seebeck coefficient for homogeneous metals

In the limit $\upsilon_B = 0$, the composite degenerates to a *homogeneous* alloy consisting exclusively of the phase A. On the opposite side, for $\upsilon_B = 1$ we get a *homogeneous* alloy consisting exclusively of the phase B. For these two limiting cases the formulae must hold as well. Setting $\upsilon_B = 0$, it follows from equation (30) that

$$\frac{\mathrm{d}\mu}{\mathrm{d}T} = \frac{\partial E_{C,A}}{\partial T} + \frac{\partial \mu_A^0}{\partial T}, \tag{34}$$

and taking into account equations (21), (22), (24) and equation (8),

$$S'(+) = S'_A = \frac{\pi^2 k_B^2 T(1+r_A)}{3e_A E_{F,A}} + \frac{1}{|e|}\left(\frac{\partial E_{C,A}}{\partial T} + \frac{\partial \mu_A^0}{\partial T}\right). \tag{35}$$

Analogously it follows for $\upsilon_B = 1$ that

$$\frac{\mathrm{d}\mu}{\mathrm{d}T} = \frac{\partial E_{V,B}}{\partial T} - \frac{\partial \mu_B^0}{\partial T}, \tag{36}$$

$$S'(+) = S'_B = \frac{\pi^2 k_B^2 T(1+r_B)}{3e_B E_{F,B}} + \frac{1}{|e|}\left(\frac{\partial E_{V,B}}{\partial T} - \frac{\partial \mu_B^0}{\partial T}\right). \tag{37}$$

Inserting equation (31) in equations (35), (37) we get

$$S' = -\frac{\pi^2 k_B^2 T(z+r)}{3|e|E_F} + \frac{1}{|e|}\frac{\mathrm{d}E_C}{\mathrm{d}T}, \tag{38}$$

$$S' = \frac{\pi^2 k_B^2 T(z+r)}{3|e|E_F} + \frac{1}{|e|}\frac{\mathrm{d}E_V}{\mathrm{d}T}, \tag{39}$$

with $z = 3/2$, where the index i is omitted and $\partial E_{C,A}/\partial T$ and $\partial E_{V,B}/\partial T$ are replaced by $\mathrm{d}E_C/\mathrm{d}T$ and $\mathrm{d}E_V/\mathrm{d}T$, respectively, because a homogeneous metal consists of only one phase. Each of the two limiting cases, equations (38) and (39), represents a homogeneous metal with *electron* conductivity and *hole* conductivity, respectively, and constant carrier density, i.e., interband transfer of electrons (depending on the temperature), is not considered.

The term '$\partial \mu_i^0/\partial T$' reflects the lowering of the chemical potential with T described by the Fermi–Dirac statistics. In equations (34)–(39) it is assumed that equation (22) (resp., equation (4)) exclusively represents the *scattering* part of S. It is, however, not completely clear whether equation (22) (resp., equation (4)) indirectly contains this term '$\partial \mu_i^0/\partial T$' already. If so, then in equations (35), (37)–(39) the term '$\partial \mu_i^0/\partial T$' (resp., '$-\frac{\pi^2 k_B^2 T}{6E_{F,i}}$') is to be deleted, and the value for z is to be replaced by $z = 1$.

Inserting equation (1) into equation (38), it follows that

$$S' = \alpha_0 (z+r) + \frac{1}{|e|}\frac{\mathrm{d}E_C}{\mathrm{d}T}. \tag{40}$$

Equation (40) is to be compared with the experimental data, S_{exp}, listed in table 1. $\mathrm{d}E_C/\mathrm{d}T$ can be calculated by using

$$\frac{\mathrm{d}E_C}{\mathrm{d}T} = |e|S_{exp}\left(1 - \frac{z+r}{X_{exp}}\right) \tag{41}$$

following from equations (40) and (2), where $S' = S_{exp}$ is set. In table 1, $\mathrm{d}E_C/\mathrm{d}T$ calculated by using equation (41) for $r = 0$ and $z = 3/2$ are listed. For the liquid metals $r = 0$ applies rather than $r = 2$ because at high temperatures scattering due to acoustic phonons is the dominant scattering mechanism [10, 22]. If $z = 1$ is set, then the numbers for $\mathrm{d}E_C/\mathrm{d}T$ turn out to be smaller; the differences from $z = 3/2$ are, however, not very large. As can be seen in table 1, there is a general tendency: the larger the valence, Z, the smaller $\mathrm{d}E_C/\mathrm{d}T$.

5. Discussion

For normal metals $\sigma(E)$ can be written as

$$\sigma(E) = e^2 \frac{4}{3m} E\tau(E)N(E), \tag{42}$$

following from the BTE for a spherical Fermi surface. $N(E)$ is the density of states, m the effective mass, and τ the relaxation time of the carriers. Replacing $\tau(E)$ and $N(E)$ by the corresponding NFE formulae, $\sigma(E)$ can be written as

$$\sigma(E) = C E^{r+1}, \tag{43}$$

where r characterizes the scattering properties according to $L \propto E^r$, while C is an energy independent factor containing e, h and m. Inserting equation (43) into equation (3), we get

$$\alpha = -\frac{\pi^2 k_B^2 T(1+r)}{3|e|E_F}. \tag{44}$$

Equation (44) agrees with the first term in equation (38) if $z = 1$ is set. It represents the influence of the energy dependent conductivity, $\sigma(E)$, on the thermopower, whereas the second term in equation (38) represents the effect of the temperature dependent band edge. Therefore, we can say that for normal metals a *positive* sign of thermopower will be measured if $\mathrm{d}E_C/\mathrm{d}T > 0$ and if this effect overcompensates for the influence of $\sigma(E)$ represented by the first term in equation (38). This conclusion holds exactly if $z = 1$. If $z = 3/2$, this fact is to be considered as a tendency. It holds also for the general case as long as the energy dependence of $\sigma(E)$ can be written as $\sigma(E) \propto E^\xi$, where ξ is a number.

As mentioned in section 4, it is not yet completely clear whether $z = 3/2$ or $z = 1$. We believe that for metals $z = 3/2$ is correct. However, the final answer depends on the question of whether or not equation (44) or equation (3) contains exclusively the *scattering* contribution (corresponding to S^0 introduced in section 3.1, equations (18)–(20)). This question is a matter of future studies.

The results of section 2–4 can be applied, in principle, also to crystalline metals: as a trend, a *positive* sign of thermopower will be measured for crystalline metals as well if the conduction band edge shifts to higher values with increasing T and if this effect overcompensates for the influence of $\sigma(E)$. Thus, for the *crystalline* Cu, Ag, Au, and Li the experimental thermopowers also have positive sign;

at $0\,^\circ$C they are $+1.7$, $+1.4$, $+1.1$, and $+11.5$ μV K^{-1}, respectively ([27], p 316). Even the signs for most of the other liquid metals listed in the table 1 agree with those of the corresponding crystalline metals [27].

A possible objection against this conclusion referring to crystalline metals may be that the positive sign could also be caused by the non-spherical Fermi surfaces realized in the crystalline noble metals which have prominent necks in the [111] directions touching the Brillouin zone boundaries. However, this objection cannot explain the large positive thermopower in Li which has a nearly spherical Fermi surface ([4], p 144; for a general discussion of the related problems see [4], pp 191–196).

On the other hand, in the temperature ranges $T < 19$ K and 130 K $< T < 250$ K, S_{exp} for Li depends roughly *linearly* on T ([4], pp 171–173). This finding suggests that an interpretation of its positive sign via the property $\partial\sigma(E)/\partial E < 0$, equation (3), may be rather likely, because $\alpha_0 \propto T$, equation (1). However, recent calculations by Geertsma *et al* [21], based on the diffraction model [11] together with the pseudopotential concept (mentioned in section 1), provided a negative thermopower for liquid Li which does not support such an interpretation. An answer to this open question could be obtained, perhaps, by an experimental determination of the band edge shift with temperature, applying photoemission measurements, which can nowadays resolve a shift in energy as small as what is estimated to occur for Li (as well as for Cu, Ag, Au, and Cs; see the column '$\mathrm{d}E_{\mathrm{C}}/\mathrm{d}T$' in table 1).

For transition metals, interband transfer of electrons (as mentioned in section 3.1) can affect the carrier density n and the Hall coefficient R_{H}. Actually, a considerable temperature change of R_{H} has been measured for a series of amorphous transition metal alloys (see [28], figure 27 therein). Until now, this temperature dependence of R_{H} has been interpreted as being caused by electron–electron interaction effects ([28], pp 316–317).

The results of section 3 can also be assigned to semiconductors, i.e., equation (18) can be applied, on principle, where S^0 stands for the known thermopower formulae for semiconductors due to scattering ([10], pp 133–142). In these formulae, changes of the chemical potential in reference to the band edges are included, already, but not yet the contribution due to band edge *shifts*. These band edge *shifts* provide an additional contribution to $\mathrm{d}\mu/\mathrm{d}T$, in correspondence with the discussion of sections 2.2 and 3.1.

In the formulae for *homogeneous* metals, equations (38), (39), the band edge shifts occur, but not the electrostatic potentials. This result corresponds to the discussion in section 2.2. In contrast to that, for the two-phase range of a *composite* ($0 < \upsilon_{\mathrm{B}} < 1$) both the band edge shifts *and* the electrostatic potentials occur (via $\mathrm{d}\mu/\mathrm{d}T$, equation (30)). In phase B, φ_{A} acts as an external electrostatic field, while in phase A, φ_{B} acts as an external electrostatic field. This is an important difference from homogeneous metals: the electrostatic potential affects the thermopower of a *composite*, but does not affect it in a *homogeneous* metal. This difference is also expected between composites with semiconducting phases and homogeneous semiconductors.

Equations (38)–(40) are not in contradiction to the fact that the absolute thermopower for a superconductor disappears. Because the specific electrical resistivity ρ is zero, scattering of the electrons does not happen; therefore, the *residual difference* in μ between the ends of the sample, $\Delta\mu$, disappears completely, i.e., grad $\mu = 0$ (in correspondence with the considerations in section 2.2). Note that a change of μ (by an increase of T) is completely counterbalanced by the fact that a transient current flows (without resistance) through the sample, until the steady-state condition grad $\mu = 0$ is reached, irrespective of whether or not $\mathrm{d}E_{\mathrm{C}}/\mathrm{d}T = 0$. The resulting concentration gradient of charges does not lead to a non-zero thermopower, because in a thermopower measurement only differences of the electrochemical potential between the two ends of the sample are detected, which is zero due to the complete counterbalance just mentioned.

6. Summary

The Seebeck coefficient can be described as a sum of a scattering term, S^0, and a thermodynamic term, ΔS. It is shown that the classical thermopower formula, equation (4), is *incomplete*, because it leads to contradictions if applied to the phases of a *composite*. By the derivation of an analytic expression for $\mathrm{d}\mu/\mathrm{d}T$ in a (metallic) composite and by consideration of the two limiting cases where the composite degenerates to homogeneous alloys, it is found that the temperature dependence of the band edges leads to an additional contribution to the Seebeck coefficient. This result applies for semiconductors as well. For a liquid or amorphous normal metal a *positive* sign of thermopower will be measured if $\mathrm{d}E_{\mathrm{C}}/\mathrm{d}T > 0$ and if this effect overcompensates for the influence of $\sigma(E)$. This conclusion holds also for crystalline metals as a trend. Applying experimental thermopower data, band edge shifts are determined for a series of liquid normal metals.

While the electrostatic potentials affect the thermopower of a *composite*, for a *homogeneous* material the electrostatic potential does not affect the thermopower.

Acknowledgment

Appendix. The effect of the electrostatic potential

In the following the effect of the electrostatic potentials φ_i on the dependence of $S'(\pm)$, equation (23), versus υ_{B} will be discussed for a-Cr$_{1-x}$Si$_x$ alloys. We shall show that consideration of $\partial\varphi_i/\partial n_i$ in equation (30) leads to a shifting of the discontinuity in the direction of larger values of υ_{B}, where the phase B is the phase with the deeper average potential in the composite. This shifting is demonstrated in figure A.1. For calculation of $\partial\varphi_{\mathrm{A}}/\partial n$ the relation

$$|e|\frac{\partial\varphi_{\mathrm{A}}}{\partial n} = \frac{\upsilon_{\mathrm{A}}}{\upsilon_{\mathrm{B}}}\frac{c}{n} \qquad (45)$$
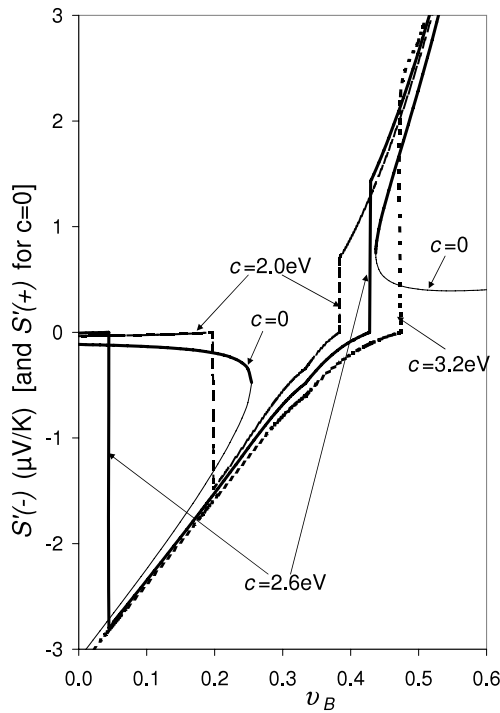
Figure A.1. Effect of the electrostatic parameter c on the $S'(-)$ versus υ_B curve (bold lines) for a-Cr$_{1-x}$Si$_x$ at $T = 300$ K calculated by using equations (23), (30) with equation (45). With increasing value of c, the discontinuity shifts to larger υ_B. (For $c = 0$, additionally $S'(+)$ (fine line) is drawn.)
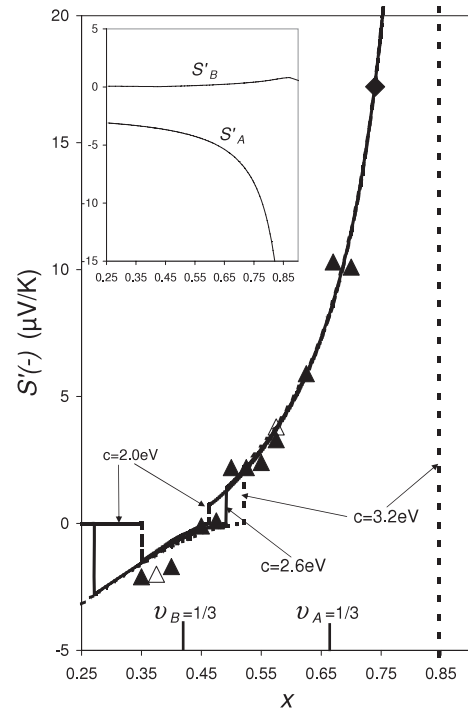

Figure A.2. Same as figure A.1, but for $S'(-)$ versus x. The discontinuity in $S'(-)$ occurs at the same x as for the experimental data if $c = 2.6$ eV is set. The specification of the experimental data is given in figure 1 of [23]. In the inset the Seebeck coefficients of the phases i calculated by using equation (21) are drawn versus x.

derived in [25] (section IVA therein) was applied, where c is a parameter which is to be determined. For the calculations the same physical parameters are applied as are specified in [23] and [25] (sections 4 therein), where $\partial E_{C,A}/\partial T = \partial E_{V,B}/\partial T = 0$ was set, and for calculation of $\partial \varphi_B/\partial n_B$,

$$\frac{1}{\upsilon_B}\frac{\partial \varphi_B}{\partial n_B} = \frac{1}{\upsilon_A}\frac{\partial \varphi_A}{\partial n} \qquad (46)$$

was applied, i.e., the formula for the calculation of $d\mu/dT$, equation (30), reduces to that of [25] (equation (61) in connection with equation (39) therein). As can be seen in figure A.1, with increasing value chosen for the electrostatic parameter c, the discontinuity in $S'(\pm)$ shifts to larger υ_B. For $c < 1.5$ eV, equation (23) no longer has solutions for the entire concentration range; for $c = 0$, equation (23) has no solution for $0.27 < \upsilon_B < 0.43$ (corresponding to $0.39 < x < 0.50$). Figure A.2 shows the curves of figure A.1, but drawn versus x.

The value of c is determined by the condition that the discontinuity in the $S'(\pm)$ curves agrees with those of the experimental data, S_{exp}, occurring at $x = 0.49$ (corresponding to $\upsilon_B = 0.43$). This agreement was found for $c = 2.6$ eV.

For all the curves in figures A.1 and A.2, the same values for $\kappa_{ne,i}$ and x_i are applied: $x_A = 0.25$, $x_B = 1.00$, $\kappa_{ne,A} = 6$ mW cm^{-1} K^{-1}, $\kappa_{ne,B} = 26$ mW cm^{-1} K^{-1}, in agreement with the corresponding $S(-)$ curve in figure 2 of [23] (the fine line curve therein). ($\kappa_{ne,i}$ and x_i are the non-electronic contributions to κ_i and the Si concentration in atomic per cent, respectively, in the phase i). While the amount of the

discontinuity (the distance between the upper and lower kink) depends on the choice of the $\kappa_{ne,i}$, the concentration where this discontinuity occurs is independent of the $\kappa_{ne,i}$.

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