Thermoelectric power in alloys with phase separation (comment to Vaney et al., J. Mater. Chem. C 3, 11090 (2015))

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Vaney et al.[1] have found that the thermopower formula for composites derived in Ref.2 clearly fails to predict the thermopower of the man-made composites $Si_{10}As_{15}Te_{75}$-$Bi_{0.4}Sb_{1.6}Te_3$. Reason for this mistake was the fact that the thermal conductivities, κ_i and κ, occurring in this formula were interpreted as the *total* thermal conductivities. However, only the *electronic* contributions to the thermal conductivities of the phases are to be taken into account. If this is considered, the thermopower formula derived in Ref.2 is a good description for naturaly grown composites. For man-made composites as considered in Ref.1, percolation elements should additonally be included as proposed by Vaney et al.[1]

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In a recently published paper Vaney et al.[1] have tested experimentally the thermopower formula[2]

$$\sum_i \upsilon_i \frac{\kappa_i/\alpha_i - \kappa/\alpha}{\kappa_i/\alpha_i + 2\kappa/\alpha} = 0 \qquad (1)$$

by comparison with man-made composites, $Si_{10}As_{15}Te_{75}$-$Bi_{0.4}Sb_{1.6}Te_3$. (α_i and α are the Seebeck coefficients of the phase i and the composite, respectively. κ_i and κ are the corresponding thermal conductivities. υ_i is the volume fraction of the phase i.) Eq.(1) was derived applying J and J_S, the electrical and entropy flux density, respectively, based on effective medium theory (EMT). Vaney et al. found that Eq.(1) clearly fails to predict the thermopower (Seebeck coefficient).

I agree with this valuation. This failure is caused by the fact that in the original work, Ref.2, κ and κ_i had been interpreted as the *total* thermal conductivities. This is, however, only an approximation for composites with phases for which the electrical condutivities are not too small as studied in Ref.2. For the general case of a composite the correct formula reads

$$\sum_i \upsilon_i \frac{\kappa_{e,i}/\alpha_i - \kappa_e/\alpha}{\kappa_{e,i}/\alpha_i + 2\kappa_e/\alpha} = 0, \qquad (2)$$

where $\kappa_{e,i}$ and κ_e are the *electronic* contribution to κ_i and κ, respectively. The origin for the incorrect formula, Eq.(1), comes from the fact that in J_S [Eq.(1.17.1a) in Ref.3] which was applied in Ref.2 for the derivation of Eq.(1), κ occurs. However, only the *electronic* contribution to κ is to be taken into account. This corresponds with the comment in Ref.3, after formula (1.17.1b) that J and J_S "... apply equally well to one-band or to multiband models, depending on κ (or more accurately, κ') ..."; ($\kappa' \equiv \kappa_e$). Hence, Eq.(1) is to be replaced by the correct formula Eq.(2).

Considering both the Wiedemann-Franz rule and the EMT formula for the electrical conductivity in composites,[4,5]

$$\sum_i \upsilon_i \frac{\sigma_i - \sigma}{\sigma_i + 2\sigma} = 0, \qquad (3)$$

Eq.(2) can be transformed to

$$\sum_i \upsilon_i \frac{\sigma_i/\alpha_i - \sigma/\alpha}{\sigma_i/\alpha_i + 2\sigma/\alpha} \approx 0, \qquad (4)$$

where σ_i and σ are the electrical conductivities of the phase i and the composite, respectively. Eq.(4) agrees with the approximation formula Eq.(54) in Ref.6 derived three years before Eq.(1) applying J and J_Q. (J_Q is the heat current density).

Inserting the σ_i and α_i data (given by Vaney et al.) in Eq.(4), it follows the concentration dependence of α on υ_1 as drawn in Fig.1(a) named Eq.(4). For $\upsilon_1 > 1/3$ the calculated α on υ_1 curve agree with the experimental data. For $\upsilon_1 < 1/3$ the EMT formulae are no longer a good description, because the phase grains in the man-made composites as studied in Ref.1 are arranged randomly (accidentally). Considering this effect, Vaney et al.[1] have introduced the parameters t and A taking into account percolation elements. Considering this proposel, Eq.(4) is to be modified to the generalized form (GEMT)

$$\sum_i \upsilon_i \frac{(\sigma_i/\alpha_i)^{1/t} - (\sigma/\alpha)^{1/t}}{(\sigma_i/\alpha_i)^{1/t} + A\cdot(\sigma/\alpha)^{1/t}} \approx 0, \qquad (5)$$

where A is given by $A = (1-\varphi_c)/\varphi_c$. φ_c is the volume fraction of the phase 1, where the actual percolation threshould is assumed to occur. t represents the asymmetry of the microstructure.[1] Eq.(2) and Eq.(5) replace the equations Eq.(5) and Eq.(6) in Ref.1, respectively.

In Fig.1(b), α versus υ_1 is drawn calculated by Eq.(5) for $t = 2$ and $\varphi_c = 0.16$ (as applied in Fig.7(A) of Ref.1) as well as for $t = 2$ and $\varphi_c = 0.10$. As can be seen in Fig.1(b), for the parameters $t = 2$ and $\varphi_c = 0.10$ there is an excellent agreement with the experimental data.

Both in Ref.1 and in Fig.1, the values for α_i and σ_i were assumed to be independent of υ_i. This is, however,

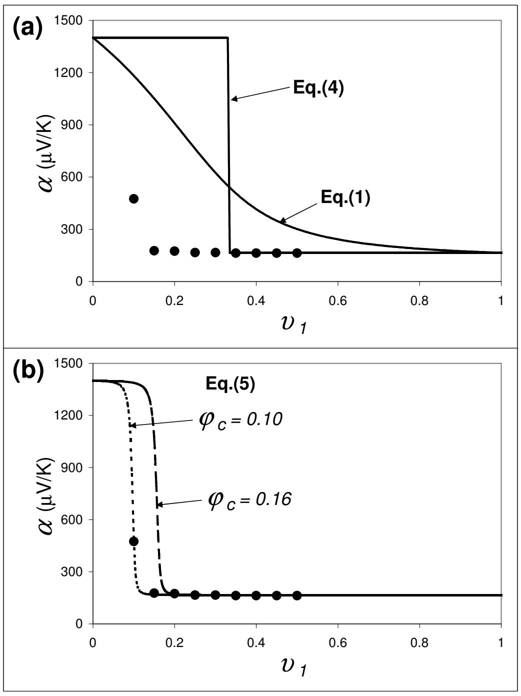

FIG. 1: α versus υ_1, the volume fraction of the crystalline phase, $Bi_{0.4}Sb_{1.6}Te_3$, and comparison with the experimental data (full points, $T = 300K$), **(a)**, calculated by Eq.(1) and Eq.(4), **(b)**, calculated by the GEMT[1] equation, Eq.(5), for $\varphi_c = 0.16$ and $\varphi_c = 0.10$; $t = 2$ for both curves. For the calculations the same values have been applied as given by Vaney et al.[1]: $\sigma_1 = 40\Omega^{-1}\mathrm{cm}^{-1}$ and $\alpha_1 = 165\mu V/K$ for the crystalline phase ($Bi_{0.4}Sb_{1.6}Te_3$), $\sigma_2 = 29.5 \cdot 10^{-6}\Omega^{-1}\mathrm{cm}^{-1}$ and $\alpha_2 = 1400\mu V/K$ for the glassy phase ($Si_{10}As_{15}Te_{75}$).

only an approximation, because the electrochemical potential, μ, in the two phases is generally different, as long as the phases are separated from each other. In the composite, however, μ must be uniform. This is sured by an electron transfer δn between the phases. The temperature dependent part of δn leads to a change of $d\mu/dT$ as described by Eqs.(39),(40) in Ref.6. This provides an additional contribution to the thermopower, $\Delta\alpha = \frac{1}{|e|}\frac{d\mu}{dT}$ (Ref.2, section 3. therein). $|e|$ and T are the elementary charge and the temperature, respectively. For a calculation of $d\mu/dT$, knowledge of the band structure data of the phases is necessary. For the composite considered by Vaney et al.[1], the contribution of $d\mu/dT$ to α is surely small, because α_1 and α_2 have the same sign. However, for composites with different signs of α_1 and α_2, the effect of $d\mu/dT$ can be essentially larger. That is, a really sensitive hardness test of Eq.(4), respectively Eq.(5), would be a composite with $\alpha_1 > 0$ and $\alpha_2 < 0$ or vice versa.

Another specific feature of composites with $\alpha_1 > 0$ and $\alpha_2 < 0$ or vice versa is the fact that a discontinuity (step) in the calculated α vs. υ_i can occur, which is an additional possibility to check experimentally the thermopower formula.

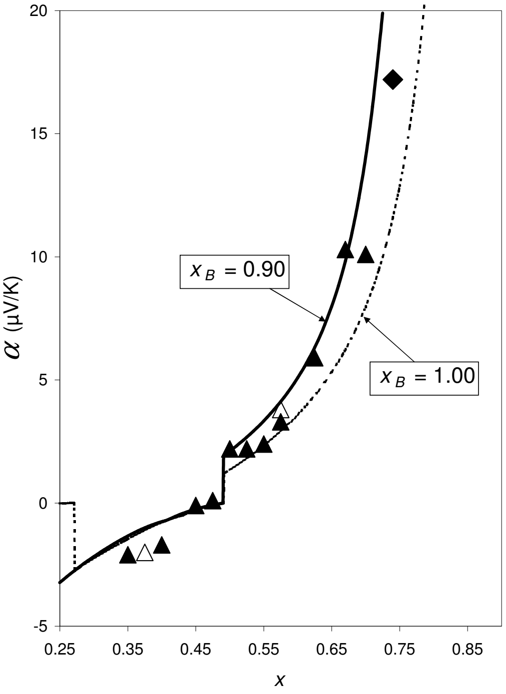

FIG. 2: Thermopower versus x for $a{-}Cr_{1-x}Si_x$ at $T = 300$K calculated by Eq.(4) with $x_A = 0.25$ and $x_B = 0.90$ (bold line) and $x_A = 0.25$ and $x_B = 1.00$ (dotted line) and comparison with experimental data. Details of the calculations and experimental data are described in Ref.6, section IVB therein.

INSERTION-2-start

This discontinuity has its origin in the mathematic structure of the formula

$$\alpha(\pm) = \frac{4 \cdot \kappa_e}{\frac{\kappa_{e,1}}{\alpha_1}(3\upsilon_1 - 1) + \frac{\kappa_{e,2}}{\alpha_2}(3\upsilon_2 - 1) \pm \sqrt{\left(\frac{\kappa_{e,1}}{\alpha_1}(3\upsilon_1 - 1) + \frac{\kappa_{e,2}}{\alpha_2}(3\upsilon_2 - 1)\right)^2 + 8\frac{\kappa_{e,1} \cdot \kappa_{e,2}}{\alpha_1 \cdot \alpha_2}}} \tag{6}$$

following from Eq.(2) for two-phase composites, where $\upsilon_2 = 1 - \upsilon_1$. Eq.(6) has two solutions, $\alpha(-)$ and $\alpha(+)$, which both show a discontinuity (step) at the same concentration, when $\alpha(-)$ and $\alpha(+)$ passes the value "0" coming from negative values crossing to positive values or vice versa. The physics follows only one of them, $\alpha(-)$, as suggested by the results of Ref.6 (compare Fig.4(g) and Fig.4(h) with Fig.5 therein).

As this discontinuity occurs at $\alpha = 0$, this phenomenon opens the possibility to produce reference standards for absolute thermopower $\alpha = 0$ also for temperatures beyond T_c (T_c stands for the transition temperature of any superconductor).

INSERTION-2-end

One example for a composite with different signs of α_1 and α_2 is $a{-}\mathrm{Cr}_{1-x}\mathrm{Si}_x$ consisting of the two amorphous phases[7] $a{-}\mathrm{Cr}_{1-x_A}\mathrm{Si}_{x_A}$ and $a{-}\mathrm{Cr}_{1-x_B}\mathrm{Si}_{x_B}$. (Amorphous phase separation is typical for many amorphous transition-metal–metalloid alloys.[8–12]) In Ref.2 α versus x had been calculated for $a{-}\mathrm{Cr}_{1-x}\mathrm{Si}_x$ applying Eq.(1).

Now, the calculations of Ref.2 we have done once more, but with Eq.(4). The result is shown in Fig.2. Both the discontinuity (step) at $x = 0.49$ and the general trend of the calculated curves agree with the ones in Fig.1 and Fig.2 of Ref.2. This correspondence is to be expected, because for $a{-}\mathrm{Cr}_{1-x}\mathrm{Si}_x$ the difference between $\kappa_{e,i}$ and κ_i is relatively small.

For man-made composites as considered in Ref.1, percolation elements play an essential role (GEMT), because the phase grains are arranged randomly (accidentally). On the contrary, for naturaly grown composites as $a{-}\mathrm{Cr}_{1-x}\mathrm{Si}_x$ thin films, the EMT is rather a good description as justified in Ref.7 (section IVA therein).

INSERTION-1-start

Eq.(4) is a relatively good approximation for Eq.(2) even if the Lorenz numbers of the phases, L_i, defined by

$$L_i = \frac{\kappa_{e,i}}{\sigma_i \cdot T}, \tag{7}$$

(T - temperature) are very different: For a comparison let us assume that $L_1 = 1.6 \cdot 10^{-8}$ (V/K)^2 and $L_2 = 2.44 \cdot 10^{-8}$ (V/K)^2. Substituting $\kappa_{e,i}$ in Eq.(2) by Eq.(7) we get

$$\sum_i \upsilon_i \frac{\sigma_i \cdot L_i/\alpha_i - \kappa_e/\alpha}{\sigma_i \cdot L_i/\alpha_i + 2\kappa_e/\alpha} = 0. \tag{8}$$

κ_e necessary for calculation of α by Eq.(8), can be calculated by[4]

$$\sum_i \upsilon_i \frac{\kappa_{e,i} - \kappa_e}{\kappa_{e,i} + 2\kappa_e} = \sum_i \upsilon_i \frac{\sigma_i \cdot L_i - \kappa_e}{\sigma_i \cdot L_i + 2\kappa_e} = 0. \tag{9}$$

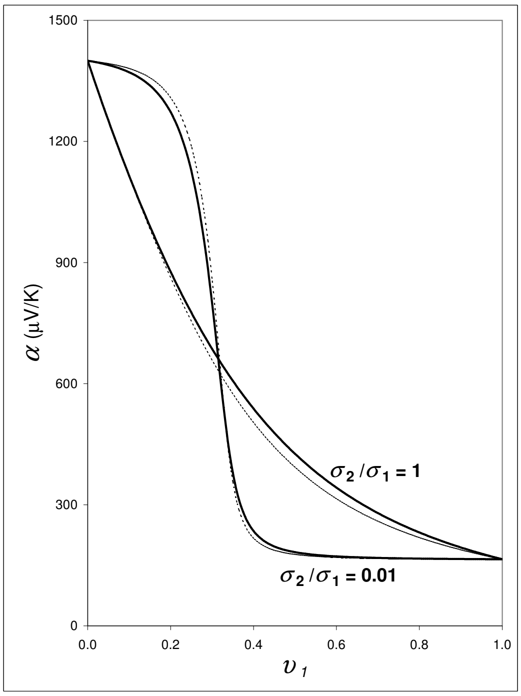

FIG. 3: Comparison of the α versus υ_1 curves calculated by Eq.(2) (bold curves) and the approximation solution Eq.(4) (dotted curves) for different quotients σ_2/σ_1 for the case that $L_1 \neq L_2$ (assumed values: $L_1 = 1.6 \cdot 10^{-8} V^2/K^2$ and $L_2 = 2.44 \cdot 10^{-8} V^2/K^2$. The values for σ_1, α_1 and α_2 are the same as given in Fig.1)

Inserting the σ_i and α_i data and the assumed values for L_i in Eq.(8) and Eq.(9), it follows that the two α versus υ_1 curves calculated by Eq.(8),Eq.(9) on the one hand and Eq.(4),Eq.(3) on the other hand, cannot be distinguished in Fig.1(a); they practically agree. This result seems to be surprising. Reason for this conformity is the fact that $\sigma_1 >> \sigma_2$. The situation is another one, if σ_2 would be of the same order as σ_1. Fig.3 shows the situation for two hypothetical composites with $\sigma_2 = \sigma_1 = 40$ $\Omega^{-1}\mathrm{cm}^{-1}$ and $\sigma_2 = 0.01 \cdot \sigma_1$, where the values of σ_1, α_1 and α_2 are maintained.

INSERTION-1-end

Allthough Eq.(1) has been applied in Ref.13, the conclusions drawn in this paper are unchanged, because only metallic composites were considered with $\kappa_i \approx \kappa_{e,i}$.

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