

Electron Theory of Metals - Answers to Unsolved Problems/Questions

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Abstract

Why are there simple metals with *positive* thermopower? Why are there metals with a *negative* temperature coefficient of resistivity? What is the reason for the *Mooij correlation* and the *Giant Hall effect*? These are questions that have not yet been answered with the known transport theories (Mizutani, 2001, pp. 474). However, they can be answered by considering the phenomenon of phase separation connected with an electron transfer between the phases. In this paper answers are proposed to these questions mentioned. Answers to other fundamental problems/questions are proposed in the recently published book (Sonntag, 2023).

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1. Introduction

In 1979 the 2nd edition of the famous book "Electronic Processes in Non-Crystalline Materials" by Mott & Davis (1979) was published by Oxford University Press as part of the series Oxford Classic Texts IN THE PHYSICAL SCIENCES. Ten years later, Sonntag (1989) has added a new aspect to this topic, namely that metallic non-crystalline alloys can consist of two different phases that differ in short-range order and bonding properties and that between these phases there is an electron transfer which has an essential effect on the electronic transport. Already in the year 1980 Mangin et al. have discussed such an "amorphous phase separation" for amorphous $\text{Au}_{1-x}\text{Si}_x$ alloys. This "amorphous phase separation" was initially only a hypothesis derived from experimental data on electrical conductivity and Hall coefficients. A few years later, however, this hypothesis was confirmed by Edwards et al. (1991), Lorentz et al. (1994), Regan et al. (1994) and Raap et al. (1995) for a series of amorphous transition-metal-metalloid alloys using high-resolution structural analyses.

On the basis of this confirmed hypothesis, a set of formulas was then developed with which the electronic transport coefficients in phase-separated alloys (short: composites) can be described mathematically. The thermoelectric power (Seebeck coefficient; thermopower for short) in amorphous Cr-Si alloys calculated with these formulas can be regarded as an outstanding result that describes the experimental findings with surprising accuracy (Appendix in Sonntag, 2023).

In this context, previously unsolved physical questions could also be answered, for example what is the reason for the phenomenon of the *Giant Hall effect* in metal-insulator layers? What is the reason for *Mooij's correlation*? What are the reasons for the different structures in sputtered and vapor-deposited thin layers: *amorphous*, *granular* or *fractal* structures depending on the composition of the alloy?

Answers also follows to such questions, which basically have nothing to do with "amorphous phase separation": Why are there simple metals with *positive thermopower*? Why does the electrical conductivity σ of very thin metal layers decrease *exponentially* with decreasing layer thickness? Why does the metal-insulator transition occur at a relatively small Ge concentration in disordered $\text{Al}_{1-x}\text{Ge}_x$ alloys ($x_c \approx 0.44$), but at a relatively high Ge concentration in disordered $\text{Au}_{1-x}\text{Ge}_x$ alloys ($x_c \approx 0.88$)?

And further questions related to the *Ioffe-Regel criterion* could be answered: Is there a finite *minimal metallic conductivity*? Are there mobility edges and how can they be calculated? And why does the metal-insulator transition in *man-made* (artificially produced) metal-insulator compounds occur at much smaller metal concentrations than it follows from classical effective medium theory (EMT)?

In this paper answers are given on the following problems/questions:

Why are there simple metals with *positive thermopower*?

Why are there metals with a *negative* temperature coefficient of resistivity, *TCR*?

What is the reason for *Mooij's correlation*?

What is the reason for the *Giant Hall effect* in metal-insulator layers?

A more detailed representation of this subject including the other open problems/questions mentioned is given and discussed in the recently published book "*The Influence of Phase Separation on Structure and Electronic Transport in Solid-State Physics*" (Sonntag, 2023).

2. The Physical Background

Until 1989 there was a general consensus that

a) the approximation of nearly free electrons (NFE) is not an appropriate method for description of the electrons in strongly scattering systems, especially if the resistivity ρ increases higher than $\approx 100\mu\Omega\text{cm}$. The same point of view has been also consolidated regarding the

b) Boltzmann transport equation (BTE): when the mean free path of the carriers, L , becomes comparable with the average atomic distance, d , the wave number k is no longer a good quantum number for describing the eigenstates, and the BTE cannot be applied (Mott & Davis, 1979; Mott, 1990). However, in 1989, with the appearance of the publication (Sonntag, 1989) this general consensus was questioned. The main finding from this publication was that many of the alloys under consideration are composed of different phases and that these must also be treated separately in the transport equations. In amorphous transition-metal-metalloid alloys there is

(i) *amorphous phase separation* between two different amorphous phases called phase A and phase B , where each phase has its "own" short-range order (SRO),

(ii) the *amorphous phase separation* leads to *band separation* in the conduction band (CB) and valence band (VB) connected with the phases A and B , respectively, and the electrons are freely propagating and the corresponding *wave functions* are extended with respect to connected phase ranges.

(iii) Between the two coexisting phases there is *electron redistribution (electron transfer)* which can be described by

$$n = n_A \cdot \exp\left(-\beta \frac{v_B}{v_A}\right). \quad (1)$$

(n is the electron density in the phase with $n(0) = n_A$. v_A and v_B are the volume fractions of the phases A and B , respectively. β is a constant for a given alloy, which is determined by the average potential difference between the two phases, ΔV .) An electron moving through the alloy is *not restricted to a single phase*, but it can overcome the phase boundaries, provided both the CB and the VB are incompletely occupied. The crucial point is that in the two different phases, this electron is exposed to different local band structures (1) with different densities of states at the Fermi level (2) depending on the local band structure and the distribution of the electrons to the available electronic bands.

In 2009 a formula for the thermopower for composites have been derived (Sonntag, 2009) which received the general final form

$$\sum_{i=A,B,\dots} v_i \frac{\sigma_i/S_i - \sigma/S}{\sigma_i/S_i + 2\sigma/S} = 0 \quad (2)$$

(Sonntag, 2016). S and σ are the thermopower and conductivity of the composite, respectively. For a two phase composite S_A and S_B are the thermopowers, σ_A and σ_B the conductivities of the phases A and B , respectively, and $v_B = 1 - v_A$.

In 2016 a formula for the Hall coefficient for composites has been derived

$$R = \frac{\sigma_A^2 R_A [\sigma_B + \sigma(3v_A - 1)] + \sigma_B^2 R_B [\sigma_A + \sigma(3v_B - 1)]}{\sigma(\sigma_A \sigma_B + 2\sigma^2)} \quad (3)$$

(Sonntag, 2016a). R , R_A and R_B are the Hall coefficients of the composite and the phases A and B , respectively.

A comparison has shown that other previously derived thermopower and Hall coefficient formulas for composites are based on approximations that may produce erroneous results (Sonntag et al., 2019). Therefore, in the following the Equations (2) and (3) are applied for a discussion of the previously mentioned unsolved questions/problems.

3. Answers to the Unsolved Problems in Solid State Physics

3.1 Why Are There Simple Metals with Positive Thermopower?

In the past, there have already been some attempts to physically explain the existence of positive thermopower in metals, for example by peculiarities of the Fermi surface topology and others, Jones (1955), Xu and Verstraete (2014), He et al.

(2019). Further work on this question is cited by Sonntag (2010) (there Ref. numbers 4 and 12-20). However, these cannot explain the positive thermopower in liquid simple metals, for which the Fermi surface can be assumed to be spherical. On the other hand, Equation (2) provides a simple and logical answer:

When one applies Equation (2) to calculate the thermopower of a two-phase composite, where the two phases have different sign, $e_B = -e_A$, one finds that this equation never has real solutions for the *entire* concentration range $\nu_A = 0 \dots 1$ (respective $\nu_B = 1 \dots 0$), if the classical formula for the thermopower of the phase i

$$S_i^0 = \frac{\pi^2 k_B^2 T (1 + r_i)}{3e_i E_{F,i}}, \quad (4)$$

is applied. (k_B is the Boltzmann constant, T is the temperature, $E_{F,i}$ and r_i are the Fermi energy and the *scattering* parameter, respectively, in the phase i . $|e_i|$ is the amount of the elementary charge with $e_i = -|e|$ and $+|e|$ for electrons and holes, respectively.) Reason is the fact, because Equation (4) describes the thermopower of the phase i incomplete. Equation (4) considers only the *scattering* contribution to the thermopower, but not the effect of band edge shift $dE_C/dT \neq 0$ or $dE_V/dT \neq 0$. E_C and E_V characterize the band edge of the conduction band (in the phase A) and the valence band (in the phase B), respectively.

Therefore Sonntag (2010) has introduced an additional term to the thermopower formula which considers the change of the thermopower by band edge shift,

$$\Delta S = \left[\frac{1}{|e|} \frac{d\mu}{dT} \right]_{J=0}^{thermodyn.} \equiv \frac{1}{|e|} \frac{d\mu}{dT} \quad (5)$$

justified in the sections 2.2 & 3.1 in (Sonntag, 2010). Consideration of Equation (5) leads to the extended thermopower

$$S_i = S_i^0 + \Delta S \quad (6)$$

for the phase i of a composite, and

$$S = S^0 + \Delta S \quad (7)$$

for a homogeneous alloy. S^0 agrees with the old (but incomplete) definition of the thermopower, which considers only the scattering of the carriers. S_i^0 is the scattering term of the phase i . In fact, S_i and S in Equation (2), derived via the electrical and entropy flux densities, is consistent with Equation (6) (Sonntag, 2009), and in the final form (Sonntag, 2016).

In order to solve Equation (2), $d\mu/dT$ is to be calculated. For a two phase composite with different signs of the carriers, electrons and holes, $e_B = -e_A$, it follows that

$$\frac{d\mu}{dT} = \frac{\partial E_{C,A}}{\partial T} + \frac{\partial \mu_A^0}{\partial T} - \frac{\frac{\partial \mu_A^0}{\partial T} + \frac{\partial \mu_B^0}{\partial T} + \frac{\partial E_{C,A}}{\partial T} - \frac{\partial E_{V,B}}{\partial T}}{1 + \frac{\nu_A \left(\frac{\partial \mu_B^0}{\partial p} - |e| \frac{\partial \varphi_B}{\partial n} \right)}{\nu_B \left(\frac{\partial \mu_A^0}{\partial n} - |e| \frac{\partial \varphi_A}{\partial n} \right)}}, \quad (8)$$

where the formulas for the electrochemical potentials of the phases,

$$\mu_A = E_{C,A} + \mu_A^0 - |e|\varphi_A, \quad (9)$$

and

$$\mu_B = E_{V,B} - \mu_B^0 - |e|\varphi_B, \quad (10)$$

are considered. μ_i^0 and φ_i are the chemical potential and the electrostatic potential, respectively, in the phase i . p and n_B are the hole density and the total valence electron concentration in the phase B, respectively, where $dn_B = -dp$. (For a derivation of Equation (8) see Equations (25)-(30) in Sonntag, 2010)

Equation (7) corresponds with the original definition of the thermopower,

$$S = \frac{\nabla(\mu/e)}{\nabla T} \quad (11)$$

(∇ is the Nabla operator), which, according to the standard work by Harmann and Honig (1967) (page 47), reduces to

$$S = \frac{d(\mu/e)}{dT} \quad (12)$$

for physically and chemically homogeneous materials. The new one is the fact that the term ΔS encloses additionally band edge shifts as well as the influence of the temperature dependence of the chemical potentials μ_i^0 of the phases i in composites, mediated via Equation (8). ΔS , especially μ_i^0 , is also the reason for the Mooij correlation (details in section 3.2).

For an experimental verification of Equation (7), respective Equation (6), see Sonntag et al. (2011).

Now let us make the transition from the thermopower formula for a composite to a homogeneous alloy by setting $\nu_B = 0$ or $\nu_B = 1$ in Equations (2) and (8). For $\nu_B = 0$ the composite degenerates to a *homogeneous* alloy consisting exclusively of the phase A. On the opposite side, for $\nu_B = 1$ we get a *homogeneous* alloy consisting exclusively of the phase B.

For these two limiting cases the formulas must hold as well. Setting $\nu_B = 0$, it follows that

$$\frac{d\mu}{dT} = \frac{\partial E_{C,A}}{\partial T} + \frac{\partial \mu_A^0}{\partial T} \quad (13)$$

and

$$S(+)=S_A = \frac{\pi^2 k_B^2 T(1+r_A)}{3e_A E_{F,A}} + \frac{1}{|e|} \left(\frac{\partial E_{C,A}}{\partial T} + \frac{\partial \mu_A^0}{\partial T} \right) \quad (14)$$

(section 3.3 in (Sonntag, 2010)).

Analogously it follows for $\nu_B = 1$ that

$$\frac{d\mu}{dT} = \frac{\partial E_{V,B}}{\partial T} - \frac{\partial \mu_B^0}{\partial T}, \quad (15)$$

$$S(+)=S_B = \frac{\pi^2 k_B^2 T(1+r_B)}{3e_B E_{F,B}} + \frac{1}{|e|} \left(\frac{\partial E_{V,B}}{\partial T} - \frac{\partial \mu_B^0}{\partial T} \right). \quad (16)$$

In other words, the classical formula for the thermopower of a homogeneous metal,

$$S^0 = -\frac{\pi^2 k_B^2 T(1+r)}{3|e|E_F}, \quad (17)$$

is incomplete. It must be supplemented by the term ΔS represented by the second term in Equation (14). E_F and r are the Fermi energy and the *scattering* parameter, respectively, in the homogeneous metal.

The second term in Equation (14) can be positiv or negativ. As a trend, *positive* sign of thermopower will be measured, if the conduction band edge shifts to higher values with increasing T and if this effect overcompensates for the influence the scattering term. Thus, for the *crystalline* Cu, Ag, Au, and Li the experimental thermopowers also have positive sign; at 0°C they are +1.7, +1.4, +1.1, and +11.5 $\mu\text{V/K}$, respectively (Schulze, 1967, p. 316).

It is usually to write the thermopower formula as a function of $\sigma(E)$ according to

$$S^0 = \frac{\pi^2 k_B^2 T}{3e} \left(\frac{\partial \ln \sigma(E)}{\partial E} \right)_{E_F} \quad (18)$$

(Barnard, 1972, section 3.2., p. 62; Mott & Davis, 1979, section 2.13, pages 52ff). E is the energy. Considering the additional thermodynamic term in correspondence with Equation (5) and Equation (7), the thermopower formula for a homogeneous material is to be extended according to

$$S = \frac{\pi^2 k_B^2 T}{3e} \left(\frac{\partial \ln \sigma(E)}{\partial E} \right)_{E_F} + \frac{1}{|e|} \frac{d\mu}{dT}. \quad (19)$$

Corresponding relations as Equation (19) hold separately also for each phase of a composite,

$$S_i = \frac{\pi^2 k_B^2 T}{3e_i} \left(\frac{\partial \ln \sigma_i(E)}{\partial E} \right)_{E_{F,i}} + \frac{1}{|e|} \frac{d\mu}{dT}, \quad (20)$$

where the term $\frac{1}{|e|} \frac{d\mu}{dT}$ is characteristic for the composite.

Equation (16) has only theoretic meaning; because as we approach $\nu_B \rightarrow 1$ we obtain a semiconductor if the B phase is Si or Ge because the number of $s^2 p^2$ states in the B phase decreases more and more while the number of sp^3 hybrid states increases more and more (Sonntag, 2023, there section 7.1).

3.2 What Is the Reason for Negative TCR in Metallic Alloys and the Mooij's Correlation?

For a long time it was a large mystery that disordered metallic alloys can have *negative* temperature coefficient of resistivity, *TCR*,

$$TCR = \frac{1}{\rho} \frac{d\rho}{dT}. \quad (21)$$

The negative *TCR* phenomenon is a characteristic feature of a semiconductor with a well-defined energy gap, $\rho = 1/\sigma$. Thus, one may address a naive question as to why a negative *TCR*, though its magnitude is small, appears for many liquid and amorphous alloys, in which the carrier concentration is as high as $10^{22}/\text{cm}^3$ and a well defined Fermi edge exists without any energy gap. (Mizutani, 2001, pp. 474).

In 1973 Mooij found a correlation between ρ and *TCR* (Mooij, 1973). Mooij's correlation says that in disordered metallic alloys the *TCR* change sign from positive to negative as the resistivity ρ increases higher than $\approx 100\mu\Omega\text{cm}$. For $\rho \gg 100\mu\Omega\text{cm}$ the amount of the negative *TCR* increases with increasing ρ .

The Mooij correlation can be interpreted very convincing, if the phase separation in disordered materials is taken into account and when the carriers in the two phases have different signs, electrons (phase *A*) and holes (phase *B*), as typical for disordered alloys between a transition-metal and Si or Ge. For these two phases the Fermi statistics is to be applied separately. In accordancs with Fermi statistics the chemical potentials μ_A^0 and μ_B^0 decrease with increasing temperature,

$$\frac{\partial\mu_i^0}{\partial T} = -\frac{\pi^2 k_B^2 T}{6E_{F,i}}. \quad (22)$$

Because of Equation (9) and (10) μ_A^0 has the same sign as μ_A , but μ_B^0 has the opposite sign as μ_B . Therefore, with increasing temperature, a (small) *back-electron transfer* takes place from the phase with the lower potential (phase *B*) to the one with the higher potential (phase *A*), because in the alloy a common electrochemical potential μ must be maintained. This *back-electron transfer* from the *B* phase to the *A* phase leads to an increase of both n and p with increasing T , corresponding to a negative contribution to the *TCR*, because ρ decreases with increasing n and p . As follows from Equation (22), this effect on *TCR* is the larger the smaller $E_{F,A}$ and $E_{F,B}$ (or the smaller n and p), what correlates with larger ρ . This negative contribution is in competition to the positive contribution to *TCR* due to scattering of the electronic carriers. This means that the negative contribution to *TCR* due to back-electron transfer dominates more and more the positive contribution due to scattering as ρ increases. Precise this property is reflected by the Mooij correlation between ρ and *TCR*.

It should not go unmentioned here that there are also *homogeneous* disordered metallic alloys with a negative *TCR*. A blatant example are (crystalline) $\text{Cr}_{1-x}\text{Al}_x$ alloys, which have extremely high values for ρ and negative *TCR* with maximum values for $x \approx 0.23$, both atypical for metallic alloys (Chakrabarti & Beck, 1971). This phenomenon is discussed in detail in the book (Sonntag, 2023, there section 5.6).

3.3 What Is the Reason for the Giant Hall Effect in Metal-Insulator Composites?

The Giant Hall effect (GHE) means that in thin films of metal-insulator composites (M-I composites) near the metal-insulator transition (M-I transition) the Hall coefficient can be up to 10000 times larger than that in the pure metal (Zhang, Liu, & Pakhomov, 2000; Pakhomov, Yan, & Zhao, 1995; Zhao & Yan, 1997; Wu, Li, & Lin, 2010; Wen et al., 2005; Miao & Xiao, 2004; Pakhomov et al., 1997; Zhang et al., 2001; Liu et al., 2004; Denardin et al., 2004; Denardin et al., 2000). Since M-I composites also consist of two separate phases with phase grains at the nanoscale, it is obvious to ask whether Equation (1) is reflected in the concentration dependence of the Hall coefficient R of M-I composites as well. Indeed, we have found that in the metallic regime of $\text{Cu}_{1-y}(\text{SiO}_2)_y$ and $\text{Ni}_{1-y}(\text{SiO}_2)_y$ thin films, the concentration dependence of R can be approximated by linear relations

$$d \ln |R| = \alpha' \cdot d\eta \quad (23)$$

with constant slope α' . $\eta = y/(1 - y)$, where y is the volume fraction of SiO_2 . This finding is illustrated in Figure 1, where the absolute R values measured by Zhang et al. (2000), Saviddes et al. (1982) and Pakhomov et al. (1995) are drawn versus η . The signs of the R values are negative. For $\text{Ni}_{1-y}(\text{SiO}_2)_y$, Figure 1, the extraordinary R values (taken from Figure 3 in Pakhomov, Yan, & Zhao, 1995) are drawn. For $\text{Cu}_{1-y}(\text{SiO}_2)_y$ and $\text{Ni}_{1-y}(\text{SiO}_2)_y$ it follows from Figure 1 (upper graphics), $\alpha' = 7.9$ and $\alpha' = 10.3$.

Figure 1 (upper graphics) reflects immediately Equation (1) provided that $|R| \propto 1/n$ (nearly free electrons - NFE). For a more precise discussion, we have to separate the contribution of the metallic phase to R , which can be done by Equation (3). For the boundary case " $\sigma_B = 0$ and $\sigma_A \neq 0$ " we get from Equation (3)

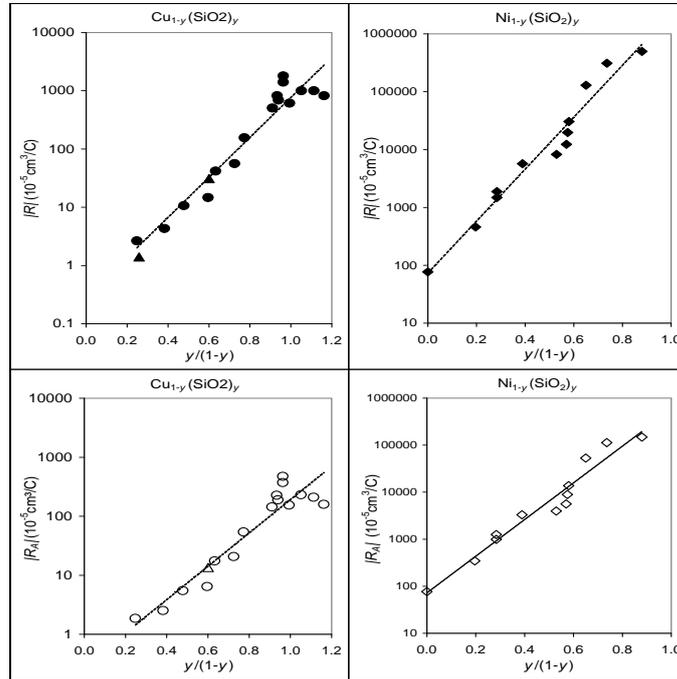


Figure 1: Upper graphics. Experimental Hall coefficient R at 5 K versus $y/(1 - y)$ for $\text{Cu}_{1-y}(\text{SiO}_2)_y$ and $\text{Ni}_{1-y}(\text{SiO}_2)_y$ taken from Zhang et al. (2000) (circles), Savvides et al. (1982)(triangles) and Pakhomov et al. (1995) (diamonds). Lower graphics R_A : calculated by $R_A = R \frac{(3v_A - 1)}{2}$ according to Equation (24), where $v_A = 1 - y$ is set.

$$\frac{1}{R} = \frac{1}{R_A} \frac{(3v_A - 1)}{2}, \tag{24}$$

and for σ ,

$$\sigma = \sigma_A \frac{(3v_A - 1)}{2}, \tag{25}$$

following from

$$\sum_i v_i \frac{\sigma_i - \sigma}{\sigma_i + 2\sigma} = 0, \tag{26}$$

derived by Odelevskii (1951) and Landauer (1952), where σ_A and σ_B mean the conductivities of phase A and phase B, respectively.

For R_A calculated by Equation (24) applied to the R data of Figure 1, we find that they can be approximated by a relation similar to Equation (23),

$$d \ln |R_A| = \beta' \cdot d\eta, \tag{27}$$

where β' is a constant for a given M-I composite: For $\text{Cu}_{1-y}(\text{SiO}_2)_y$ and $\text{Ni}_{1-y}(\text{SiO}_2)_y$ it follows from Figure 1 (lower graphics), $\beta' = 6.5$ and $\beta' = 9.0$, respectively. This finding suggests that the colossal increase of $|R|$ is caused by *one* (!) effect acting in the *complete* metallic regime. Inserting $|R_A| \propto 1/n$ (NFE approximation) in Equation (27) leads to Equation (1), or in differential representation,

$$-dn = \beta \cdot n \cdot d\zeta, \tag{28}$$

where $\beta \approx \beta'$. n is the electron density in the metallic phase and $\zeta = v_B/v_A$. v_B and v_A are the volume fractions of the insulator phase (B) and metallic phase (A), respectively. v_B and v_A are identical with y and $1 - y$, respectively, if the insulating phase consists only of SiO_2 and the metallic phase only of Cu or Ni. In this case, $\beta = \beta'$. If, however, a certain portion of the metalloid atoms is dissolved in the metallic phase and/or a certain portion of the metal atoms is solved in the insulating phase, then β' is only an approximation for β .

Equations (1) and (28) agree with the equations (15a) and (15b), respectively, in the publication by Sonntag (1989) which describe electron transfer between the phases in amorphous transition-metal–metalloid alloys. There the parameter β was interpreted to be a constant for a given composite, which is determined by the average potential difference between the phases, ΔV .¹ Phase B is the phase with the deeper potential. Because of this analogy, Equation (27) suggests the following interpretation of the GHE: The colossal increase of $|R|$ with decreasing metal content is essentially caused by a decrease of n due to electron transfer to the insulator phase (SiO_2) which can be described by Equation (1), respectively Equation (28).

Because the Fermi level lies in the energy gap between the valence band and conduction band of the insulator SiO_2 phase, the transferred electrons occupy surface states on the SiO_2 phase. This is the reason for the *granular* structure: spherical metal grains are embedded in the amorphous SiO_2 phase (see, e.g., Abeles et al. (1975), there Figures 13-16). A minimum energy is realized if, *firstly*, the transferred (pinned) electrons are arranged on *spherical* surfaces and, *secondly*, the insulating phase forms very thin layers around the metal grains providing the largest possible surface to accommodate the large number of transferred electrons. This electron transfer from the metallic phase to the phase boundaries provides the logical explanation for the *granular* structure in M-I composites. Such a granular structure has been found in many M-I films, Abeles et al. (1975), Zhang et al. (2001), Wu et al. (2010), and Denardin et al. (2003). This proposal applies to magnetic M-I composites as well. For *nonmagnetic* M-I composites the parameter C in

$$R_A = -\frac{C}{|e| \cdot n} = \frac{\mu_{H,A}}{\sigma_A} \quad (29)$$

(NFE-approximation) is of the order of *one*, depending slightly on the magnetic field (Kirejew, 1974, p.348). σ_A and $\mu_{H,A}$ are the conductivity and Hall mobility, respectively, of the phase A . For *magnetic* M-I composites Equation (29) holds approximately if " = " is replaced by " \propto " considering the effect of the additional *internal* magnetic field due to the magnetization: An electron sees the effective magnet field $H_w = H + H_i$, where $H_i \gg H$. H is the external field applied to the specimen and H_i is the internal field produced by the quantum mechanical exchange forces (Schulze, 1975, p.341). An electron does not distinguish between H and H_i . It moves according to the Lorentz force determined by H_w and the electrical field E . One can assume that H_w is nearly proportional to H as long as H_i is nearly proportional to the magnetization produced by H . This assumption is supported by the experimental finding by Xiong et al. (1992) that (for not too small fields H), in the granular Co-Ag system, the Hall resistivity ρ_{xy} is linearly proportional to H . If so, the measured R values differ from the calculated R values, Equation (29), only by a factor which is nearly constant. Therefore, we assume that the EMT-formula for R , Equation (3), can be applied to magnetic composites as well.

If the metallic phase of a M-I composite is a *noble metal*, the NFE-approximation is a good one for the metallic phase, above all as the Fermi surface moves away from the Brillouin zone boundary as n decreases. For the metallic phase in Ni- SiO_2 the NFE-approximation is surely also a good one, because Ni has only 0.55 4s valence electrons per Ni atom (Schulze, 1967, p.271).

If the metallic phase of a M-I composite is a *transition-metal*, the electron transfer is expected to be composed of both the d and s electrons. As the d density of states at the Fermi level is essentially larger than the s electron density, the principal share of electrons transferred to the insulating phase, is made up of d electrons, that is, the s electron density in the metallic phase remains relatively large. Because the electronic transport is determined by the s valence electrons in the A phase, the effect of the electron transfer on the electronic transport in the metallic phase is expected to be relatively small, and the increase of R_A due to electron transfer should be essentially smaller as in M-I composites containing a noble metal as metallic phase. For instance, in $\text{Mo}_{1-y}(\text{SnO}_2)_y$ (Wu et al. 2010, there Figure 2), we do not find an exponential change of R_A with increasing $y/(1-y)$: for $0 < y < 0.55$ (i.e. $0 < y/(1-y) < 1.22$), the experimental R values (Wu et al. 2010) of Mo-SnO₂ fluctuate slightly where the average of R_A calculated by Equation (24) remains nearly independent of y . Only approaching the M-I transition ($y > 0.6$), R_A increases drastically.²

Now the question arises: why do we find an exponential dependence of $n(\zeta)$ in $\text{Ni}_{1-y}(\text{SiO}_2)_y$ although Ni is a transition-metal? X-ray emission spectra of amorphous and crystalline $\text{Ni}_{1-y}\text{Si}_y$ and $\text{Pd}_{1-y}\text{Si}_y$ alloys by Tanaka et al. (1985) have shown that there are strong bonds between d orbitals (of Ni and Pd) and Si p orbitals leading to a stronger splitting of the d band into a bonding and antibonding fraction, where the former is lifted, whereas the latter lies below the Fermi level. Analogously, for $\text{Ni}_{1-y}(\text{SiO}_2)_y$ one can also expect strong bonds between Ni d orbitals and Si (and O) p orbitals which leads to a strong reduction or disappearance of the d density of states at the Fermi level. Therefore, we find an

¹The potential difference ΔV is identical with the difference of the electrochemical potentials of the phases, as long as they are not in contact to each other. Only, when a contact is realized, a common electrochemical potential is realized by electron transfer between the phases.

²In $\text{Mo}_{1-y}(\text{SnO}_2)_y$, the carriers are holes (Wu et al. 2010); electron transfer away from the metallic phase can lead to an increase of the hole density p , but also to a decrease of it depending on the position of the Fermi surface in relation to the Brillouin zones.

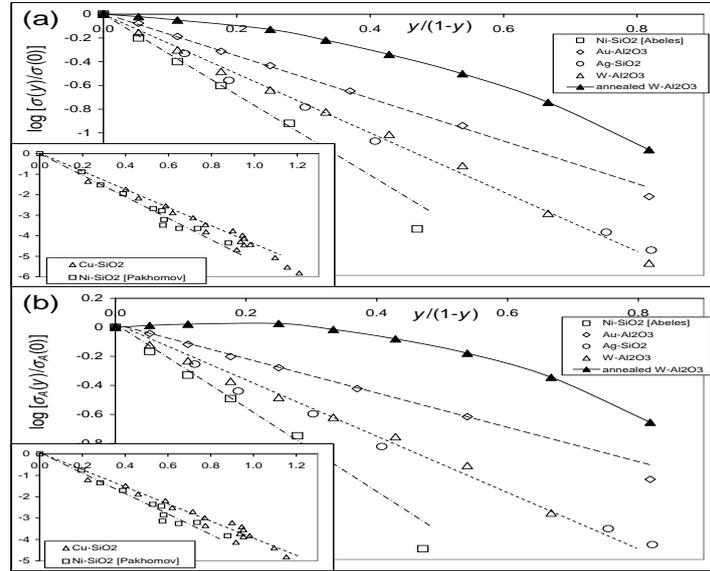


Figure 2: (a) $\log[\sigma(y)/\sigma(0)]$ versus $y/(1-y)$ for $Ni_{1-y}(SiO_2)_y$, $Au_{1-y}(Al_2O_3)_y$, $W_{1-y}(Al_2O_3)_y$ and *annealed* $W_{1-y}(Al_2O_3)_y$ (at 1200^oC in H₂) taken from Abeles et al. (1975)(there Figure 19) and $Ag_{1-y}(SiO_2)_y$, Priestley et al. (1975). (b) $\log[\sigma_A(y)/\sigma_A(0)]$ versus $y/(1-y)$, calculated by Equation (25) and $\nu_A = 1 - y$. Insets in (a) and (b): $Cu_{1-y}(SiO_2)_y$ and $Ni_{1-y}(SiO_2)_y$, taken from Liu et al. (2004) and Pakhomov et al. (1995) , respectively.

experimental increase of $|R_A|$, Figure 1. Moreover, there is strong evidence for the assumption that the metallic phase does not consist of Ni alone, but that there is a certain fraction of Si (and O atoms) dissolved in the metallic phase.

In summary, for M-I composites containing a *noble metal*, we expect an exponential $n(\zeta)$ dependence because the electron transfer is made up entirely of the *s* electron density. For M-I composites containing a *transition-metal*, an exponential $n(\zeta)$ dependence can be expected if the *d* density of states at the Fermi level is strongly reduced, for instance caused by a hybridization of the *d* states with the *p* states of the metalloid.

Comparing granular M-I composites with amorphous transition-metal–metalloid alloys, we state that the exponential increase of *R* and the exponential decrease of σ with *y* (respectively $y/(1-y)$) is essentially caused by the same phenomenon: decrease of the electron density in the metallic phase due to electron transfer to the metalloid or insulator phase. The essential difference between these two material classes is the fact that in the metalloid phase of the amorphous transition-metal–metalloid alloys an *incompletely* occupied *sp* band can exist for accepting the transferred electrons (Sontag 2005, there Section 2.1). In contrast, in the insulator phase of M-I composites only localized states on the surface of it are available for acceptance of the transferred electrons. This difference is also the reason for the different microscopic structures of M-I composites and amorphous transition-metal–metalloid alloys. Another, rather quantitative difference is the fact that the decrease of *n* in M-I composites is essentially larger than in amorphous transition-metal–metalloid alloys, as the average potential difference between the phases, ΔV , is essentially larger.

Our *electron transfer* model is compatible with a series of other experimental findings:

- 1) The GHE occurs both in magnetic M-I composites and non-magnetic ones suggesting a mechanism independent from magnetism, Zhang et al. (2001).
- 2) In M-I composites, σ and σ_A decrease exponentially with decreasing metal content in correspondence with the exponential increase of *R*. For some M-I composites, in Figure 2, $\log[\sigma(y)/\sigma(0)]$ and $\log[\sigma_A(y)/\sigma_A(0)]$ are drawn versus $y/(1-y)$. In the NFE approximation the connection between σ_A and *n* is given by

$$\sigma_A = 2 \left(\frac{\pi}{3} \right)^{1/3} \frac{e^2}{h} L n^{2/3} = |e| \mu_{H,A} n, \tag{30}$$

where $\mu_{H,A}$ is the mobility of the carriers which is assumed to be equal to the Hall mobility. *h* is Plancks constant. *L* is the (elastic) mean free path of the electronic carriers in the (metallic) phase *A*. Because of Equation (30) the exponential concentration dependence of *n*, Equation (1), is also reflected by the concentration dependence of $\sigma_A(y)/\sigma_A(0)$ in Fig.2

if the concentration dependences of L or μ_A can either be neglected or change exponentially with $y/(1-y)$ as well. For $W_{1-y}(Al_2O_3)_y$ we assume that there are strong bonds between W d orbitals and Si (and O) p orbitals, comparable with the situation in $Ni_{1-y}(SiO_2)_y$, discussed earlier.

The only exception in Fig.2, where such an exponential concentration dependence of σ , respectively σ_A , does not occur, is represented by the *annealed* $W_{1-y}(Al_2O_3)_y$ samples where grown crystalline phase grains influence the electronic properties.

3) With increasing y the temperature coefficient of resistivity ρ ($= 1/\sigma$), TCR , decreases and changes sign from positive to negative (Denardin et al. 2003, Zhang et al., 2000, Liu et al., 2004, Pakhomov et al., 1997, Zhao and Yan, 1997, Ren et al., 2007). The reason is an activation of localized electrons to the conduction band of the metallic phase. This conductivity contribution by activation is in competition with the positive contribution to the TCR due to scattering. The activation contribution is the larger the larger the amount of transferred electrons, i.e., the larger y , in correspondence to Equation (1).

In earlier papers it was suggested "that the GHE is a result of the drastic reduction of both the effective electron density and (in case of EHE³) the effective carrier mobility" (Pakhomov et al., 1997) or a drastic reduction of carrier density (Jing et al., 1996). These two suggestions (Jing et al., 1996; Pakhomov et al., 1997) correspond to our physical model described. We emphasise, however, that it is not any *effective* electron density or *carrier* density (electrons or holes), but it is the *real electron* density which is reduced in the M-I composites.

3.4 The Effect of the Grain Size on the GHE

Approaching the M-I transition, the charging energy arising from the positively charged metal ions grows more and more and one could assume that such 'metal' phase cannot exist, because the electrostatic contribution by the positive ions increases more and more as n decreases. However, the growth of the electrostatic energy is not unbounded; decrease of n is accompanied with a decrease of the sizes of the metal grains. For *granular* $Al_{1-y}Ge_y$ films, with increasing y the sizes of the metal grains, D_A , decrease from 10-20 nm (on the metallic-rich side) to sizes < 2 nm beyond the MIT (Rosenbaum et al., 1994, Lereah et al., 1991). This decrease of D_A with decreasing metal content even continues in the dielectric regime, as found for $Ni_{1-y}(SiO_2)_y$, $Pt_{1-y}(SiO_2)_y$ and $Au_{1-y}(Al_2O_3)_y$ thin films (Abeles et al., 1975, there Figure 17), where D_A decreases from 4 nm at $y \approx 0.5$ to 1 nm at $y \approx 0.9$. For co-sputtered granular $Ni_{1-y}(SiO_2)_y$ films, Abeles et al. (1975) found that the average particle size, D_A , decreases with Ni content: $D_A = 14$ nm, 9.4 nm, 5.7 nm, and 3.7 nm for 87, 67, 56 and 37 vol % Ni, respectively (Abeles et al., 1975, there Figure 11).

We suppose that the electron transfer described by Equation (1), respectively Equation (28), holds also beyond the M-I transition. This assumption correlates with the concentration dependence of D_A , which decreases continuously through the M-I transition as cited.

Equation (1), is part and result of a complex energy balance realized during solidification of the alloy, where *the sizes of the phase grains are part of this balance*. Equation (1) holds for situations, where atomic diffusion does practically not play a role because of the high cooling rate during the film deposition process. Because of this suppression of the long-range diffusion, the EMT provides a more realistic description of the electrical properties of disordered alloys with phase separation than any percolation description. This is discussed by Sonntag (2005) (there Section 4.1).

On the other hand, at sufficiently high temperatures, appreciable diffusion can take place leading to additional growth of D_A . With increasing D_A , for instance due to annealing, the electron transfer to the phase boundaries can no longer be expected to follow Equation (1). Otherwise, the growth of the electrostatic energy could be shoreless. Therefore, the GHE decreases or disappears by annealing at sufficiently high temperatures, Liu et al. (2004). This phenomenon is also reflected by the concentration dependences of σ and σ_A which can be essentially smaller than before annealing. One typical example is $W_{1-y}(Al_2O_3)_y$, Figure 2: Before annealing, $\log[\sigma(y)/\sigma(0)]$ is approximately linear in $y/(1-y)$, but after annealing at 1200°C it is not. Reason is the fact that after annealing the metallic phase grains are essentially larger than before, for instance $D_A \approx 20$ nm for $y \approx 0.47$ (Abeles et al. (1975), there Figure 2), whereas $D_A \approx 2$ nm for the *unannealed* samples (Abeles et al., 1975, there Figure 1). Because of the large phase grains in the *annealed* $W_{1-y}(Al_2O_3)_y$ samples, the electron transfer (related to $n(0)$) is essentially smaller than in the unannealed samples. Elsewise, the electrostatic energy would be too large.

This can also explain the experimental finding by Liu et al. (2004) that the maximum of the enhancement of R in $Zn_{1-y}(SiO_2)_y$ is about 60, but 700 in $Cu_{1-y}(SiO_2)_y$: the size of the granules in $Zn_{1-y}(SiO_2)_y$ is much larger ($D_A \approx 20$ nm, Liu et al., 2004, p.608) than in $Cu_{1-y}(SiO_2)_y$, for which $D_A \approx 1$ nm is given as the minimum value (Liu et al., 2004,

³"EHE" is applied in (Pakhomov et al., 1997) for the extraordinary Hall effect in magnetic M-I composites.

p.606). Apparently, in $Zn_{1-y}(SiO_2)_y$, a certain measure of atomic diffusion has been happen during film deposition, so that this balance was shifted to smaller electron transfer, i.e., Equation (1) does no longer apply.

4. Summary

Until the end of the twentieth century, it was generally assumed that in amorphous metallic alloys the atoms are arranged randomly and homogeneously. On this basis a quantitative calculation of the electronic transport coefficients σ , κ^4 , S and R applying classical transport theories met with little success. Moreover, there were a series of open questions/problems, which were unsolved for a long time. Only the realization that many of these amorphous metallic alloys are composites consisting of different amorphous phases led to a breakthrough and progress and provided the basis for solving a number of previously unsolved mysteries of solid state physics. Based on this realization a new theory has been developed with the following key results:

Between the two phases in amorphous alloys and *nano*-scaled composites there is *electron redistribution (electron transfer)* which can be described by $n = n_A \cdot \exp(-\beta \frac{U_B}{U_A})$.

Formulas have been derived for calculation of the thermopower and the Hall coefficient of composites.

Starting with these key results, a number of previously unsolved physical problems/questions have now been answered, for example these, which are subject of this paper:

Why are there simple metals with positive thermopower?

Why are there metals with a negative *TCR*

What is the reason of the Mooij correlation?

What is the reason for the Giant Hall effect?

Answers to a series of other problems/questions are described in the book (Sonntag, 2023), for instance, is there a finite *minimum metallic conductivity* σ_{min} as originally proposed by Mott (1972, 1981).

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

- Abeles, B., Pinch, H. L., & Gittleman, J. I. (1975). Percolation conductivity in $W-Al_2O_3$ granular metal films. *Physical Review Letters*, 35(4), 247. [https://doi.org/10.1016/0029-5493\(75\)90200-9](https://doi.org/10.1016/0029-5493(75)90200-9)
- Abeles, B., Sheng, P., Coutts, M. D., & Arie, Y. (1975). Structural and electrical properties of granular metal films. *Advances in Physics*, 24(3), 407-461. <https://doi.org/10.2307/583027>
- Barnard, R. D. (1972). *Thermoelectricity in Metals and Alloys*. London: Taylor and Francis.
- Chakrabarti, D. J., & Beck, P. A. (1971). Transport properties of Cr-Al solid solutions. *Journal of Physics and Chemistry of Solids*, 32(7), 1609-1615.
- Denardin, J. C., Knobel, M., Zhang, X. X., & Pakhomov, A. B. (2003). Giant Hall effect in superparamagnetic granular films. *Journal of magnetism and magnetic materials*, 262(1), 15-22.
- Denardin, J. C., Pakhomov, A. B., Knobel, M., Liu, H., & Zhang, X. X. (2000). Giant Hall effect in Co-SiO₂ nanocomposites. *Journal of Physics: Condensed Matter*, 12(14), 3397. <https://doi.org/10.1088/0953-8984/12/14/315>
- Edwards, A. M., Fairbanks, M. C., & Newport, R. J. (1991). Structural studies of amorphous Ge-Au alloys. *Philosophical Magazine B*, 63(2), 457-463. <https://doi.org/10.3406/slave.1991.5987>
- He, B., Wang, Y., Arguilla, M. Q., Cultrara, N. D., Scudder, M. R., Goldberger, J. E., ... & Heremans, J. P. (2019). The Fermi surface geometrical origin of axis-dependent conduction polarity in layered materials. *Nature materials*, 18(6), 568-572. <https://doi.org/10.1038/s41563-019-0309-4>
- Harman, T. C., & Honig, J. M. (1967). *Thermoelectric and thermomagnetic effects and applications*. New York, San Francisco, Toronto, London, Sydney: McGraw-Hill Book Company.
- Jing, X. N., Wang, N., Pakhomov, A. B., Fung, K. K., & Yan, X. (1996). Effect of annealing on the giant Hall effect. *Physical Review B*, 53(21), 14032. <https://doi.org/10.1103/PhysRevB.53.14032>
- Jones, H. (1957). The specific heat of metals and alloys at low temperatures. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 240(1222), 321-332. <https://doi.org/10.1088/0370-1298/68/12/413>

⁴ κ is the thermal conductivity

- Kirejew, P. S. (1974). *Physik der Halbleiter*. Berlin: Akademie-Verlag. <https://doi.org/10.3138/ctr.3.013>
- Landauer, R. (1952). The electrical resistance of binary metallic mixtures. *Journal of applied physics*, 23(7), 779-784. <https://doi.org/10.1063/1.1702301>
- Lereah, Y., Deutscher, G., & Grnbaum, E. (1991). Formation of dense branching morphology in the crystallization of Al-Ge amorphous thin films. *Physical Review A*, 44(12), 8316.
- Liu, H., Zheng, R. K., Wen, G. H., & Zhang, X. X. (2004). Giant Hall effect in metal/insulator composite films. *Vacuum*, 73(3-4), 603-610.
- Lorentz, R. D., Bienenstock, A., & Morrison, T. I. (1994). Structural studies of the phase separation of amorphous $\text{Fe}_x\text{Ge}_{100-x}$ alloys. *Physical Review B*, 49(5), 3172.
- Mangin, P., Marchal, G., Mourey, C., & Janot, C. (1980). Physical studies of $\text{Au}_x\text{Si}_{1-x}$ amorphous alloys. *Physical Review B*, 21(8), 3047. [https://doi.org/10.1016/S0040-4039\(00\)77403-X](https://doi.org/10.1016/S0040-4039(00)77403-X)
- Miao, G. X., & Xiao, G. (2004). Giant Hall resistance in Pt-based ferromagnetic alloys. *Applied physics letters*, 85(1), 73-75. <https://doi.org/10.1063/1.1757645>
- Mizutani, U. (2001). *Introduction to the electron theory of metals*. Cambridge university press.
- Mooij, J. H. (1973). Electrical conduction in concentrated disordered transition metal alloys. *physica status solidi (a)*, 17(2), 521-530. <https://doi.org/10.1002/pssa.2210170217>
- Mott, N. (1990). *Metal-insulator transitions*. London, New York, Philadelphia: Taylor and Francis.
- Mott, N. F. (1972). Conduction in non-crystalline systems IX. The minimum metallic conductivity. *Philosophical Magazine*, 26(4), 1015-1026. <https://doi.org/10.1080/14786437208226973>
- Mott, N. F. (1981). The minimum metallic conductivity in three dimensions. *Philosophical Magazine B*, 44(2), 265-284. <https://doi.org/10.1080/01418638108222560>
- Mott, N. F., & Davis, E. A. (1979). *Electronic processes in non-crystalline materials* (2nd ed.). Oxford university press.
- Odelevskii, V. I. (1951). Calculation of the generalized conductivity of heterogeneous systems. *Zh. Tekh. Fiz*, 21(6), 678-685.
- Pakhomov, A. B., Yan, X., & Zhao, B. (1995). Giant Hall effect in percolating ferromagnetic granular metal-insulator films. *Applied physics letters*, 67(23), 3497-3499.
- Pakhomov, A. B., Yan, X., Wang, N., Jing, X. N., Zhao, B., Fung, K. K., ... & Wong, S. K. (1997). On the origin of the giant Hall effect in magnetic granular metals. *Physica A: Statistical Mechanics and its Applications*, 241(1-2), 344-349.
- Priestley, E. B., Abeles, B., & Cohen, R. W. (1975). Surface plasmons in granular Ag-SiO₂ films. *Physical Review B*, 12(6), 2121.
- Regan, M. J., Rice, M., van Raap, M. B. F., & Bienenstock, A. (1994). Anisotropic phase separation through the metal-insulator transition in amorphous alloys. *Physical review letters*, 73(8), 1118. <https://doi.org/10.1103/PhysRevLett.73.1118>
- Ren, S. L., You, B., Du, J., Bai, X. J., Zhang, J., Zhang, W., ... & Zhang, X. X. (2007). *Physica B400*, 185.
- Rosenbaum, R. L., Slutzky, M., Mobius, A., & McLachlan, D. S. (1994). Various methods for determining the critical metallic volume fraction ϕ_c at the metal-insulator transition. *Journal of Physics: Condensed Matter*, 6(39), 7977. <https://doi.org/10.1088/0953-8984/6/39/018>
- Savvides, N., McAlister, S. P., Hurd, C. M., & Shiozaki, I. (1982). Localization in the metallic regime of granular Cu-SiO₂ films. *Solid State Communications*, 42(2), 143-145. [https://doi.org/10.1016/0038-1098\(82\)90370-2](https://doi.org/10.1016/0038-1098(82)90370-2)
- Schulze, G. E. R. (1967). *Metallphysik Akademie-Verlag*. Berlin: Akademie-Verlag.
- Sonntag, J. (1989). Disordered electronic systems: concentration dependence of the dc conductivity in amorphous transition-metal-metalloid alloys (metallic regime). *Physical Review B*, 40(6), 3661. <https://doi.org/10.1103/PhysRevB.40.3661>
- Sonntag, J. (2005). Disordered electronic systems. II. Phase separation and the metal-insulator transition in metal-metalloid alloys. *Physical Review B*, 71(11), 115114. <https://doi.org/10.1103/PhysRevB.71.115114>

- Sonntag, J. (2009). Thermoelectric power in alloys with phase separation (composites). *Journal of Physics: Condensed Matter*, 21(17), 175703. <https://doi.org/10.1088/0953-8984/21/17/175703>
- Sonntag, J. (2010). The effect of the band edges on the Seebeck coefficient. *Journal of Physics: Condensed Matter*, 22(23), 235501. <https://doi.org/10.1088/0953-8984/22/23/235501>
- Sonntag, J. (2016). Comment on Effective medium theory based modeling of the thermoelectric properties of composites: comparison between predictions and experiments in the glass-crystal composite system $\text{Si}_{10}\text{As}_{15}\text{Te}_{75}-\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ by J.-B. Vaney et al., *J. Mater. Chem. C*, 2015, 3, 11090. *Journal of Materials Chemistry C*, 4(46), 10973-10976.
- Sonntag, J. (2016a). The Origin of the Giant Hall Effect in Metal-Insulator Composites. *Open Journal of Composite Materials*, 2016, 6, 78. <http://dx.doi.org/10.4236/ojcm.2016.63008>
- Sonntag, J. (2023). *The Influence of Phase Separation on Structure and Electronic Transport in Solid-State Physics*. Cambridge: Cambridge Scholars Publishing. <https://www.cambridgescholars.com/product/978-1-4438-5723-9>
- Sonntag, J., Ziolkowski, P., Savan, A., Kieschnick, M., & Ludwig, A. (2011). High-throughput characterization of the Seebeck coefficient of $a-(\text{Cr}_{1-x}\text{Si}_x)_{1-y}\text{O}_y$ thin film materials libraries as verification of the extended thermopower formula. *Journal of Physics: Condensed Matter*, 23(26), 265501. <https://doi.org/10.1088/0953-8984/23/26/265501>
- Sonntag, J., Lenoir, B., & Ziolkowski, P. (2019). Electronic Transport in Alloys with Phase Separation (Composites). *Open Journal of Composite Materials*, 9, 21. <https://doi.org/10.1016/B978-0-12-819957-2.00002-X>
- Tanaka, K., Saito, T., Suzuki, K., & Hasegawa, R. (1985). Role of atomic bonding for compound and glass formation in Ni-Si, Pd-Si, and Ni-B systems. *Physical Review B*, 32(10), 6853. <https://doi.org/10.1103/PhysRevB.32.6853>
- van Raap, M. F., Regan, M. J., & Bienenstock, A. (1995). Evidence of phase separation in amorphous $\text{Fe}_x\text{Si}_{1-x}$ films. *Journal of non-crystalline solids*, 191(1-2), 155-163. [https://doi.org/10.1016/0022-3093\(95\)00286-3](https://doi.org/10.1016/0022-3093(95)00286-3)
- Wu, Y. N., Li, Z. Q., & Lin, J. J. (2010). Giant Hall effect in nonmagnetic Mo/SnO_2 granular films. *Physical Review B*, 82(9), 092202.
- Wen, J. F., Wang, J. F., Zou, W. Q., Zhang, F. M. & Du, Y. W. (2005). Investigation on the giant Hall effect of $(\text{Fe}_x\text{Sn}_{100-x})_{1-y}(\text{SiO}_2)_y$ granular films. *Journal of alloys and compounds*, 393(1-2), 77-80. <https://doi.org/10.1016/j.jallcom.2004.10.02>
- Xu, B., & Verstraete, M. J. (2014). First principles explanation of the positive seebeck coefficient of lithium. *Physical review letters*, 112(19), 196603.
- Xiong, P., Xiao, G., Wang, J. Q., Xiao, J. Q., Jiang, J. S., & Chien, C. L. (1992). Extraordinary Hall effect and giant magnetoresistance in the granular Co-Ag system. *Physical review letters*, 69(22), 3220. <https://doi.org/10.1103/PhysRevLett.69.3220>
- Zhang, X. X., Wan, C., Liu, H., Li, Z. Q., Sheng, P., & Lin, J. J. (2001). Giant Hall effect in nonmagnetic granular metal films. *Physical Review Letters*, 86(24), 5562. <https://doi.org/10.1103/PhysRevLett.86.5562>
- Zhang, X. X., Liu, H., & Pakhomov, A. B. (2000). Observation of giant Hall effect in non-magnetic cermets. *Physica B: Condensed Matter*, 279(1-3), 81-83.
- Zhao, B., & Yan, X. (1997). Giant Hall effect in granular Fe-SiO₂ film. *Journal of applied physics*, 81(8), 4290-4292. <https://doi.org/10.1063/1.364804> }

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