The Influence of Phase Separation on Structure and Electronic Transport in Solid-State Physics

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By

Joachim Sonntag

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This book is dedicated to my parents
Irmgard Sonntag
Willy Sonntag

$$dn = -\beta \cdot n \cdot d\left(\frac{v_B}{v_A}\right)$$

Differential representation of the most important formula in this book: Equation (1). It determines both structure and electronic transport in amorphous alloys and *nano*-scaled composites.

CONTENTS

PREFACE

Each epoch has its dominant scientific themes. Since 1900, there have been three major epochs in physics that have particularly shaped scientific research:

1) Quantum Theory and Theory of Relativity (1900 - ca. 1950),
2) Disordered Electronic Systems (1950 - 2000),
3) Nanotechnology (since about 2000).

While the first half of the 20th century was dominated by quantum theory, beginning in 1900 with Planck's groundbreaking ray theory and culminating in the 1920s and 1930s, the dominant scientific theme in the second half of the 20th century was electronic processes in disordered electronic systems, on which tens of thousands of articles have appeared in scientific journals. Towards the end of the 20th century, this area of research gradually faded into the background. One reason for this was that the most important questions and problems on this subject (Mooij correlation, metal-insulator transition, etc.) could not really be answered or could only be answered with additional assumptions. Another reason was new breakthrough discoveries (e.g., high temperature superconductors, quantum Hall effect, graphene tubes, and fullerenes).

A major milestone in the field of disordered electronic systems was the famous book “Electronic Processes in Non-Crystalline Materials” by Mott & Davis, published by Oxford University Press in 1970 as part of the Oxford Classic Texts series IN THE PHYSICAL SCIENCES and 1979 the second edition [1]. Ten years later, a publication [2] appeared that added a new aspect to this topic, namely that amorphous transition-metal–metalloid alloys 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. [3] have discussed such an “amorphous phase separation” for amorphous $Au_{1-x}Si_x$ 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 for a series of

amorphous transition-metal–metalloid alloys using high-resolution structural analyses. [4-7]

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 thermopower (Seebeck coefficient) in amorphous Cr-Si alloys calculated with these formulas can be regarded as an outstanding result that describes the experimental findings with surprising accuracy. [8, 9]

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? Why does the metal-insulator transition occur at a relatively small Ge concentration ($\simeq 0.44$) in Al-Ge alloys, but at a relatively high Ge concentration ($\simeq 0.88$) in Au-Ge alloys?

Answers also followed 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?

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)?

The metal-insulator transition (M-I transition) in disordered electronic systems is one of the most challenging problems in condensed matter science. The fundamental question is whether the electrical conductivity at the transition disappears discontinuously or smoothly at the transition (Edwards et al. [10]). This is immediately connected with the question of whether there exists a minimum metallic conductivity σ_{min} as originally proposed by Mott [11,12]. After several decades of intensive studies, there is general consensus that the M-I transition is continuous and that there is no σ_{min} in agreement with the predictions of the scaling theory of localization [1, 13–21], where the potential disorder plays the most

important role (Anderson localization) [22, 23]. For metal-metalloid alloys this view seems to be in good agreement with experimental results [24–26]. This view applies to homogeneous alloys. It can, however, also be extended to each individual phase in a phase-separated alloy. However, there is one key difference. As a result of electron transfer, the total number of electrons is not evenly distributed between the two phases.

To make matters worse, also hole conduction is possible in one of the phases, depending on both the structure and the amount of electron transfer. If you think this through, you have to ask yourself anew whether there is a minimum metallic conductivity or not. N. F. Mott's original thesis that there is a minimum metallic conductivity, but which he retracted under the influence of Anderson's 1958 paper [22], is now supported by the new arguments presented in this book. And time will tell if the revival of Mott's original hypothesis will last.

Finally, I would like to thank my former teachers during my studies at the Technical University of Dresden, Professors A. Recknagel, G.E.R. Schulze, G. Wenzel and G. Heber. Through them I learned to work scientifically and to question scientific "certainties". My thanks also go to Professor Dr.-Ing. A. Ludwig from the Institute for Materials Science at the Ruhr University Bochum and his colleagues A. Savan, Dr. M. Kieschnick and Dr. S. Thienhaus as well as Dr. P. Ziolkowski from the Institute for Materials Research in Cologne for the exciting collaboration that led to the experimental confirmation of the additional term to the thermopower, equation (96). My thanks also go to the Professors H. Keiter and J. Stolze (Faculty of Physics at the University of Dortmund) for reading the manuscripts to the subjects of this book. I thank also my former employer and managing director of HL-Planartechnik GmbH, Mr. J. Herrnsdorf, who has supported my work on this book for many years. And finally I would like to thank my former colleagues at the IFW Dresden (formerly the Zentralinstitut für Festkörperphysik und Materialforschung), my group leader Dr. Wich and Dr.-Ing. G. Weise supporting my early experimental works to the systems Cr-Al and Cr-Si as well as D. Kraut, Dr. W. Hinüber, H. Waydbrink, J. Trost, Ms. C. Hornauf, Ms. U. Rauschenbach, Dr. K.-H. Mueller, Dr. Hemschik, Dr. A. Möbius, Dr. H Vinzelberg, Dr. J. Schumann, Dr. R. Voigtmann, Dr. J. Edelmann, Dr. L. Illgen, Dr. G. Zies, Dr. S. Roth and many others.

Dortmund
Januar 2023 J. S.

I

INTRODUCTION

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 as, e.g., metal-metalloid alloys. 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 [1, 15].

However, with the appearance of a publication from 1989 [2] this general consensus was questioned and shaken by new findings. 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. The essential conclusions were especially related to amorphous transition-metal--metalloid alloys. For large ranges of concentration in the metallic regime of 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

$$n(\zeta) = n_A \exp(-\beta\zeta), \tag{1}$$

where $\zeta = \upsilon_B/\upsilon_A$ is the quotient of the volume fractions υ_B and υ_A of the two coexisting phases. $n(\zeta)$ is the electron density in the phase A with $n_A = n(0)$. Phase A is the phase with the larger potential. 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.

The conclusion (i) amorphous phase separation is now confirmed experimentally for a series of amorphous transition-metal--metalloid alloys: Edwards et al. [28] reported on measurements of rf reactive co-sputtered *a*-$Ni_{1-x}Si_x$:H using Raman spectroscopy, IR absorption and extended x-ray absorption fine structure (EXAFS) that for $x > 0.7$ there is indication for close-packed Si:Ni clusters beside an *a*-Si matrix and they speculated that the system contains two amorphous phases: one being semiconducting and the other being semi-metallic. For *a*-$Au_{1-x}Ge_x$ ($x > 0.63$) Edwards et al. [4] concluded from EXAFS that regions of an Ge-Au alloy are embedded in amorphous Ge host network. From small-angle x-ray scattering (SAXS) and x-ray-absorption near-edge spectroscopy (XANES) experiments at co-sputtered a-$Fe_{1-x}Ge_x$ films with $0.28 < x < 0.63$ Lorentz et al. [5] concluded phase separation into two phases likely to be *a*-$FeGe_2$ and *a*-Fe_3Ge. Applying anomalous small-angle x-ray scattering (ASAXS), Regan et al. [6] found in co-sputtered *a*-$W_{1-x}Ge_x$, *a*-$Fe_{1-x}Ge_x$, *a*-$Fe_{1-x}Si_x$, and *a*-$Mo_{1-x}Ge_x$ films phase separated regions of the order of 1 nm in the growth plane and 1.5-2.0 nm in the growth direction. They could show that their measurements are in agreement with the assumption of two coexisting amorphous phases, *a*-Ge or *a*-Si, on the one side and a metallic phase with $FeGe_2$, $FeSi_2$, or $MoGe_3$ compositions for the last three systems, respectively, on the other side. Raap et al. [7] found amorphous phase separation in co-sputtered *a*-$Fe_{1-x}Si_x$ films into regions of *a*-Si and an intermetallic close in composition to *a*-$FeSi_2$ with ~0.6 nm in the film plane and ~1 nm in size in the growth direction using ASAXS.

Support for the conclusion (ii) comes from measurements of the electronic specific heat coefficient γ of *a*-$Mo_{1-x}Ge_x$ (Yoshizumi et al.[29,30]), *a*-$Au_{1-x}Si_x$ (Fischer and Löhneysen [31]), *a*-$V_{1-x}Si_x$ (Mizutani et al. [32]), and *a*-$Ti_{1-x}Si_x$ (Rogatchev et al. [33]): γ does not go to zero at the M-I transition, but varies smoothly across the M-I transition.

Support for the conclusion (ii) comes also from the result by Abkemeier et al. [34, 35] who found by an analysis of conductivity data in *a*-Ni-Si:H on the insulating side that a consistent interpretation is obtained, if it is assumed that the wave functions of the electrons contributing to conduction are extended through clusters of metal atoms and only localized by longer-range disorder, where the metal atoms are assumed to be Ni.

The conclusion (iii) is not yet confirmed or supported by independent authors. However, as will be shown later, there is a series of experimental findings supporting this conclusion indirectly. On the basis of these conclusions (i) - (iii), a number of previously unsolved problems can be solved. On the one hand, this concerns the question of whether there is a minimum metallic conductivity or whether the metal-insulator transition is continuous or discontinuous. On the other hand, this also applies to questions/problems that, at first glance, have nothing to do with disorder or phase separation. Here is a brief overview of these unresolved questions/issues:

1) Why are there simple metals with positive thermopower, although according to classical theory the thermopower of simple metals should always be negative? (section IV B, short Sec. IV B)
2) What is the reason for the phenomenon of the Giant Hall effect in metal insulator layers? (Sec. V D)
3) Why does the metal-insulator transition in man-made (artificially produced) composites appear at much smaller metal concentrations than follows from classical effective medium theory (EMT)? (Secs. III G and III H)
4) Why can amorphous metal layers exist at all, although the crystalline state is the more stable? (Sec. V C)
5) Is there a finite minimum metallic conductivity? (Sec. II D)
6) What is the secret to good adhesion of thin metal films to insulator substrates? (Sec. V G)
7) Why does the electrical conductivity σ of a thin metal layer decrease exponentially with decreasing layer thickness? (Proximity effect; Sec. V G)

8) What is the reason for Mooij's correlation? (Sec. V F)
9) What are the reasons for the different structures in sputtered, respective evaporated, thin films: amorphous, granular or fractal structures depending on the composition of the film alloys? (Sec. VIII)
10) Why does the metal-insulator transition occur at a relatively small Ge concentration in disordered $Al_{1-x}Ge_x$ alloys ($x_c \simeq 0.44$), but at a relatively high Ge concentration in disordered $Au_{1-x}Ge_x$ alloys ($x_c \simeq 0.88$)? (Sec. VIII)

Applying known valence band spectra a *microscopical model* has been developed for describing the electronic structure and electronic transport in metal-metalloid alloys which takes into account in particular

1. the internal surfaces (phase boundaries),
2. the average compositions of the two phases, and
3. electron redistribution (electron transfer) between the phases.

Based on this microscopical model, the effect of both the local band structure and the electron distribution between the phases on the electronic conductivity σ is studied applying effective medium theory (EMT) and the Boltzmann transport equation (BTE). Formulas for the concentration dependence of the thermopower (Seebeck coefficient) and Hall coefficient are derived as well as for the electron-electron interaction in alloys with phase separation (composites). It will be shown that the classical thermopower formula is incomplete. It is proposed to supplement this with an additional "thermodynamic" term. $\sigma(x)$ closed to the M-I transition is calculated and compared with experimental results published in the literature.

In Sec. II the central equation (1) (short Eq. (1)) will be derived and a quantitative form of the Ioffe-Regel criterion applying Heisenberg's uncertainty principle which provide formulas for the minimum metallic conductivity and for the mobility edges.

In Sec. III the transport equations for the electrical and thermal conductivity in composites are derived, supplemented by new formulas for the Hall coefficient and the thermopower. It will be shown, that the thermopower formulas applied earlier are incomplete. This is founded theoretically and experimentally. An additional term is proposed, the socalled thermodynamic term, which also explains why there are simple metals in nature with positive thermopower. A bridge is built from the

Effective Medium Theory (EMT) to the classical Percolation Theory through special consideration of incomplete packing densities in artificially generated composites, but also in naturally thin films produced by co-sputtering or co-evaporation. (More to this point in Sec. VI.)

In Sec. IV, a new thermopower formula is derived for homogeneous materials, a special case of the thermopower formula derived in Section III for the limit cases $\upsilon_i = 0$. Using this thermopower formula, band edge shifts are calculated for simple metals and liquid metals.

Sec. V deals with nanocomposites under special consideration of island formations for small υ_i. It will be shown that Mooij's correlation is a consequence of phase separation and that the Giant Hall effect (GHE) in granular metals is a consequence of Eq. (1). A formula for consideration of the electron-electron interaction will be proposed. What is the secret for good adhesion of thin layers and why there are amorphous metal layers at all is discussed. It is shown that discontinuities in the concentration dependence of the thermopower can occur and how they can be used to characterize the microstructure in alloys with phase separation.

In Sec. VI, a problem associated with the co-sputtering or co-evaporation process is addressed, namely that the layers produced on these ways can have other physical properties than single coatings with only one alloy target. It is hypothesized that the structure of the forming layer is not only determined by the diffusivity of the atoms and whether there is a relative minimum in the Gibbs' free energy. The structure realized depends also on the fact whether it is compatible with the demand that continuity of the entropy and energy flux densities and their gradients is saved during the solidification process, a consequence of the Gibbs equation and its conditions of validity.

Sec. VII is dedicated to the atomic structure, short range order, bonding, and band structure in naturally grown metal-metalloid alloys. These considerations form the basis for quantitative calculations of the electronic transport properties of phase-separated alloys. The practical application of that is shown in the Appendix, an example calculation for the thermopower and conductivity in a-$Cr_{1-x}Si_x$ alloys. In Sec. VIII the influence of equation (1) on structure formation and the metal-insulator transition is considered. For some metal-metalloid alloys the concentration dependence of the conductivity σ near to the metal-insulator transition is calculated for $T \approx 0$ and compared with experimental data.

II

THEORY OF ELECTRONS IN A NON-CRYSTALLINE MEDIUM

A. Introduction

As in the monograph by Mott & Davis, [1] the Ioffe-Regel criterion also plays a central role in the present book. Starting with a derivation of the central electron transfer formula Eq. (1), it follows a quantitative consideration of the Ioffe-Regel criterium leading to a lower limit for the wave number at the Fermi surface, k_F, where metallic conductivity is still possible. Based on this lower limit a minimum metallic conductivity and mobility edges separating extended states in a conduction band or valence band from localized states can be defined.

B. Derivation of the electron transfer formula for Nanocomposites

The derivation of the formula Eq. (1) was obvious after it had been recognized that numerous amorphous alloys such as *a*-$Au_{1-x}Si_x$, *a*-$Cr_{1-x}Si_x$, *a*-$Cu_{1-x}Ge_x$, *a*-$Au_{1-x}Ge_x$, *a*-$Mo_{1-x}Si_x$, *a*-$Fe_{1-x}Si_x$, *a*-$Fe_{1-x}B_x$ showed a simple relationship between the electrical resistance ρ and the concentration ratio $x/(1-x)$:[2]

$$\lg \rho \propto \frac{x}{1-x}. \tag{2}$$

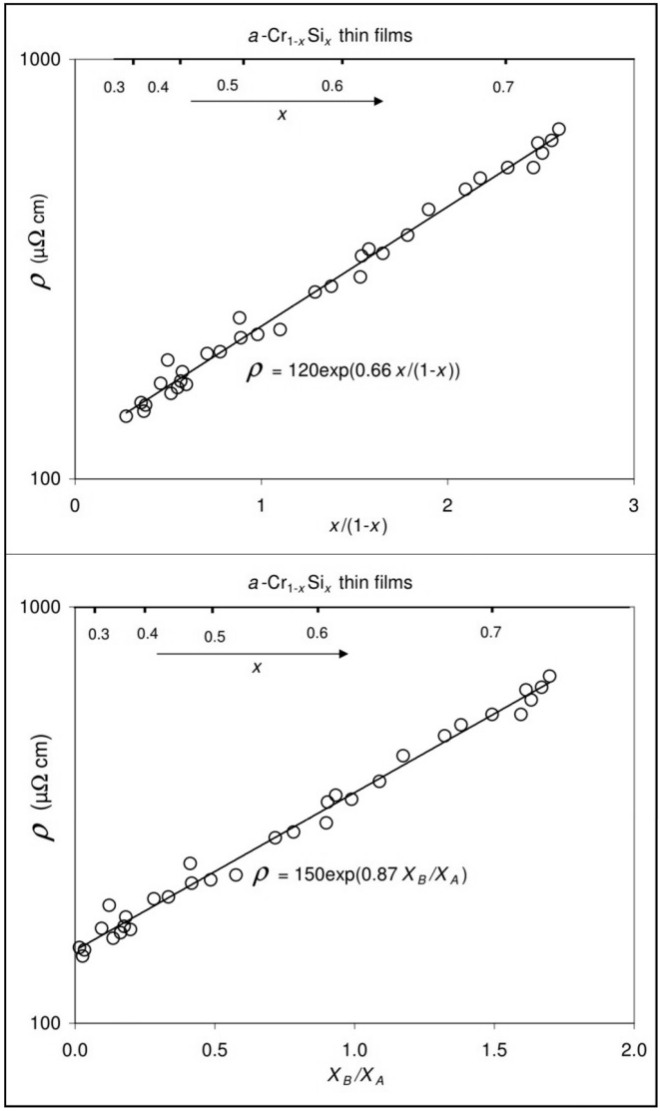

FIG. 1: Experimental data ρ versus $x/(1 - x)$ (upper diagram) and ρ versus X_B/X_A (lower diagram) in logarithmic representation for a-$Cr_{1-x}Si_x$ thin films at $T = 300$K taken from Helms et al. [36]. X_B/X_A is calculated by Eq. (4) with $x_A = 0.25$ and $x_B = 1.00$. X_B and X_A are the atomic fractions of the amorphous phases a-Cr_3Si (= phase A) and a-Si (= phase B).

The upper diagram in Fig.1 shows an example of the concentration dependence of ρ of a-$Cr_{1-x}Si_x$ thin films as a function for $x/(1-x)$. Eq. (2) suggests a simple relationship to the concentration dependence of the electron density n in these alloys according to the transport equation for the conductivity (BTE)

$$\sigma = \frac{1}{\rho} = 2\left(\frac{\pi}{3}\right)^{\frac{1}{3}} \frac{e^2}{h} L n^{\frac{2}{3}}. \tag{3}$$

(NFE-approximation, h is Planck's constant and e the elementary charge.)

In order to recognize this, one simply had to admit that the electron scattering in these amorphous alloys is very strong, which is why the mean free path L of the electrons is already at its lower physical limit, the mean atomic distance d was reached, $L \approx d$. This immediately led to the assumption that $\lg n \propto -x/(1-x)$, which would mean a strong, exponential decrease in electron density with increasing metalloid content in the alloy. The question was, where did the electrons go? The answer was: these amorphous alloys were not homogeneous alloys, but were composed of different (amorphous) phases, in one phase the electron density n determines the resistance, while the other, the second phase, the loss of electrons took over. This part of the "disappeared" electrons could no longer or only to a very small extent participate in the transport of electricity. Thus the picture of the two-phase nature of these amorphous alloys, whose phases we call A and B, was born. The logical conclusion was now the formula Eq. (1), where the electron density is assigned to the phase A, while the phase B is the one in which the redistributed electrons were absorbed. In other words, with these amorphous alloys we were dealing with two-phase alloys, so-called composites, or more appropriately with "nanocomposites", since, as it turned out later, the phases are present as microscopic grains with an expansion of ≈ 1 - 2 nm.

The two phases in a-$Cr_{1-x}Si_x$ thin films can be characterized by a-$Cr_{1-xA}Si_{xA}$ and a-$Cr_{1-xB}Si_{xB}$, where x_A and x_B are the silicon concentrations in the two phases A and B. By comparison with the phase diagrams of the corresponding crystalline alloys, x_A and x_B are suggested to be $x_A \approx 0.25$ and $x_B \approx 1$, i.e. a-Cr_3Si (= phase A) and a-Si (= phase B). In the concentration range $0 \leq x < 0.25$, the films are assumed to be one-phase. This assumption was confirmed by Hall coefficient measurements for the related system a-$(Au_{0.5}Cu_{0.5})_{1-x}Ge_x$. (see Fig. 2 (b) in [2] based on experimental Hall coefficient data taken from [37]). The transition from a

concentration dependence represented by Eq. (2) to ζ as given in Eq. (1) follows from the well-known lever rule for two-phase alloys,

$$\zeta = \frac{X_B}{X_A} = \frac{x - x_A}{x_B - x}. \tag{4}$$

As can be seen in Fig.1 (lower diagram), ρ follows an exponential dependence on X_B/X_A. And considering the empirical fact that generally $X_B/X_A \approx \upsilon_B/\upsilon_A$ it follows Eq. (1) if the effect of σ_B can be neglected.

But now two further questions arose: 1) Why do these transferred electrons in the phase B not or hardly contribute to the conductivity? 2) If so, why can the phase *A* determine the resistance, respective conductivity, almost alone, when the total conductivity of a composite is composed of the contributions of both phases, according to

$$\sum_i \upsilon_i \frac{\sigma_i - \sigma}{\sigma_i + 2\sigma} = 0 \tag{5}$$

($i = A, B$), where σ_A and σ_B mean the conductivities of phase *A* and phase B. (Details on the formula Eq. (5) in Sec. III A).

If the phase *B* does not contribute to the current transport, then lg σ should not be proportional to $x/(1 - x)$, but rather deviate from such a dependency, the more so the volume fraction of phase *B*, υ_B, is greater. This aspect remained unclear for a long time. A solution was only found in 2006, in [8]. The special feature of these amorphous transition-metal–metalloid alloys in the two-phase range is that both phases in the metallic range are to be regarded as metallic phases or as degenerate semiconductors, and that phase *B* usually has hole conductivity in contrast to phase *A*, which has electron conductivity. Using the example *a*-$Cr_{1-x}Si_x$ thin films it could be shown that the phase *B* also contributes to the conductivity and that this decreases as *x* increases, however not exponentially, as in the phase *A*, but only in a tendency. But this tendency to decrease was sufficient within the scope of the measurement accuracy that this linear concentration dependency "lg σ vs. $x/(1-x)$", respective "lg ρ vs. $x/(1-x)$", was retained even with larger *x*. The exponential dependence dominated the concentration dependence of σ even with larger *x*.

The validity of formula Eq. (1) is also confirmed for metal-insulator nanocomposites, although the insulator phase (= phase *B*) does not contribute to σ. In the metal-insulator composite materials, however, the β values are very large due to the very large potential difference between the two phases, so that σ, respective ρ, is dominated by phase *A*. Details see Sec. V D, Fig. 10.

C. Ioffe-Regel criterion quantitative

The Ioffe-Regel criterion states that values of *L* with $kL < 1$ are impossible. Based on this plausible statement, it was the general consensus that NFE approximation and the Boltzmann transport equation (BTE) cannot be applied (the points a) and b) in Sec. I). This consensus is appropriate for homogeneous alloys.

We will now show that considering phase separation in disordered metallic alloys can lead to an alternative view to this consensus. We give two arguments, a theoretical argument and an experimental example.

Historically seen, the view b) cited above was concluded from the fact that in metals[38]

$$k_F \simeq \frac{\pi}{d} \tag{6}$$

is a lower limit for extended states, where k_F is the wave number at the Fermi surface. Inserting Eq. (6) and measured σ data of any metal-metalloid alloy on the metallic side, but close to the M-I transition, in the BTE,

$$\sigma = \frac{S_F \mathrm{e}^2 L}{6\pi^2 h}, \tag{7}$$

and assuming a spherical Fermi surface $S_F = 4\pi k_F^2$, then it follows $L < d$, which is physically not possible, because the average free path cannot be smaller than the average distance of the scattering centres. However, considering phase separation, with decreasing fraction of the “metallic” phase (in the two-phase range), Eq. (6) is no longer valid and Eq. (7) is to be applied to the two phases separately, where each phase has its “own” Fermi surface, if $\upsilon_A > 1/3$ or $\upsilon_B > 1/3$ (Sec. V B). And the carrier densities

in the two phases are essentially different from a situation corresponding to Eq. (6).

Since the electron density in the metallic phase decreases with increasing x (or with increasing ζ), k_F in the phase A decreases as well according to

$$k_F = (3\pi^2 n)^{\frac{1}{3}} \tag{8}$$

(spherical Fermi surface and NFE approximation). For the hole density p in the phase B, the situation is analoguous, because p decreases with increasing x as well (see Secs. VII and VIII). This leads to the fact that application of the BTE in NFE approximation and $\sigma(x)$-data for any metallic alloy remains compatible with the condition "$L \geq d$" even near the M-I transition.

Experimental example: Mizutani and Yoshida [37] have shown for a-$(AgCu)_{1-x}Ge_x$ alloys that for $x < 0.3$ there is a good agreement between the measured Hall coefficient data, R, and the free-electron values

$$R_0 = (en_0)^{-1} \tag{9}$$

derived from the BTE in NFE-approximation, where n_0 is the total valence electron density in the alloy (Eq. (8) in [2]). This agreement between R and R_0 gives the justification for application of the BTE in NFE-approximation to the conductivity for $x < 0.3$ as well. Applying Eq. (3) to the measured σ-data [37] of a-$(AgCu)_{1-x}Ge_x$ for $x < 0.3$, where $\sigma_A = \sigma$ (one-phase-range), it follows that $L \simeq d$ for $0.2 < x < 0.3$ (see [2], Sec. II B and Fig. 2 (b) in it). In other words, in the concentration range $0 < x < 0.3$ the BTE in NFE-approximation provides a good description for the Hall coefficient, although $L \simeq d$ is already reached. This is in contradiction to the view that k_F is no longer a good quantum number, since L is comparable with d.

With these two arguments, and in agreement with the points (i)-(iii) stated in Sec.I, we propose an alternative interpretation: L cannot be smaller than d; therefore in disordered electronic systems, d is the lower limit for L, and k can be considered as a good quantum number for describing the eigenstates, as long as

$$kL > c^*, \tag{10}$$

where c^* is of the order of 1 (Ioffe-Regel criterion). The decisive difference to the point of view b) cited above (page 1) is the fact that (independent of the degree of disorder represented by the mean free path L) the electronic states can be extended for connected ranges of the same phase, and the concept of a Fermi surface is after all applicable, as long as Eq. (10) is fulfilled, even for $L \simeq d$. Considering the experimental example a-$(AgCu)_{1-x}Ge_x$, the abrupt splitting between n_0 and $n_H = (eR)^{-1}$ at $x \simeq 0.3$ is a consequence of the beginning phase separation for $x > 0.3$, because only still part of the total electron density is available in the phase A due to the electron redistribution to the second phase [Eq. (1)]. On the other hand, in granular metal-metalloid alloys (Sec. V) on the metallic side the Fermi level lies in ranges of trap states in the phase B, however in ranges of extended states in the phase A.

For consideration of the electronic transport processes in a phase at $T = 0$ we concentrate our attention to k_F,

$$k_F > \frac{c^*}{L}. \tag{11}$$

For the case, when scattering is strong, L can approach d, but cannot be smaller than d, and with Eq. (11) it follows a lower limit, where k_F still can be applied for description of the wave functions of the carriers at the Fermi surface, given by

$$k_F \gtrsim \frac{c^*}{d}, \tag{12}$$

if $L \simeq d$ is realized. k_F in Eqs. (11), (12) is limited to continuous range of atoms with overlapping wave functions. Outside of this range the wave functions decrease exponentially. Now let us consider the question of whether and under which conditions the BTE and NFE-approximation can be applied for disordered alloys with phase separation. The decrease of n with increasing x or ζ [Eq. (1)] leads also to decrease of the Fermi energy, E_F, in the phase A, and the corresponding Fermi surface approaches a spherical form also in crystalline alloys, the smaller n, approaching a NFE behaviour, since the Fermi surface for the phase A is sufficiently distant to the first Brillouin zone boundary, when n is sufficiently small. The situation in the phase B is similar regarding the hole density p for sufficiently large v_B, where p is small (see Secs. VII and VIII). This is especially so near to the M-I transition, provided Eq. (11) is still fulfilled.

D. Minimum metallic conductivity

Because of Eq. (11) - in connection with Eq. (8) - there exists a lower limit for n, below it extended electronic states cannot be exist. Regarding Eq. (11), in the literature different values for c^* are given ranging from $1/2\pi$ until π which differ by a factor 20 corresponding to a factor of 4 orders of magnitude for n according to Eq. (8). For the Ioffe-Regel criterion $kL \simeq \pi$ [38] or $kL \simeq 1/2\pi$ [39] or $kL \simeq 1$ [1] is given or proposed. And because of this large span for n the question of the lowest possibly limit of $k_F L$ becomes importantly. From Heisenberg's uncertainty principle it follows $c^* = 1/4$. This can be shown as following: Let us consider the propagation of an electron with the energy E_F in a disordered homogeneous system characterized by a spherical Fermi surface and a single parabolic band with

$$E_F = \frac{\hbar^2 k_F^2}{2m} \tag{13}$$

($\hbar = h/2\pi$). Under influence of an electric field a single electron at E_F is accelerated between two successive scattering events covering the path L. The amount of its momentum before and after an elastic scattering event is given by $|p| = (2mE_F)^{1/2}$ and it follows that the amount of the momentum change during scattering, $|\delta p|$, cannot be larger than $2(2mE_F)^{1/2}$. In accordance with Heisenberg's uncertainty principle the uncertainties of locality, $<\Delta x>$, and momentum, $<\Delta p>$, of the electron are determined by [40]

$$<\Delta x><\Delta p> \geq \frac{\hbar}{2}. \tag{14}$$

The momentum uncertainty cannot be larger than $|\delta p|$, otherwise the momentum change by scattering would not be defined, i.e.

$$<\Delta p> \leq |\delta p| \leq 2(2\mathrm{m}E_F)^{1/2} \tag{15}$$

must be fulfilled. The locality uncertainty, $<\Delta x>$, cannot be larger than L, otherwise L would not have a physical sense and with Eqs. (14), (15) it follows $2L(2m\,E_F)^{1/2} > \hbar/2$ and with Eq. (13)

$$k_F L \geq 1/4, \tag{16}$$

i.e., c^* = 1/4 and it follows the lowest possibly limit where extended electronic states still can exist. When n decreases below n_{crit} given by

$$n_{crit} = \frac{1}{3\pi^2} \left(\frac{c^*}{L} \right)^3, \tag{17}$$

corresponding to a minimum metallic conductivity

$$\sigma_{min} = \frac{2c^{*2}}{3\pi} \left(\frac{e^2}{h} \right) \frac{1}{L}, \tag{18}$$

latest then localization in the metallic phase of a disordered alloy must occur. Eqs. (17), (18) result from Eq. (3) and Eqs. (8), (11). This limit, σ_{min}, applies to each of the two phases separately. Therefore, in a two-phase alloy (composite), the lower limit can even be fall below the value given by Eq. (18), if the second phase is non-metallic and if the (metallic) phase i forms an infinite (coherent) cluster in the composite. As long as in the composite the phase grains of the phase i are uniformly (even) distributed, the lower limit where an infinite (coherent) cluster still exists, is given by υ_i = 1/3. For strong scattering characterized by $L \simeq d \simeq 0.25$ nm it follows from Eqs. (17), (18)

$$n_{crit} \simeq 3 \cdot 10^{19} cm^{-3} \tag{19}$$

and

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

Kireyev [41] gives $L = 4d/\pi$ as the lowest possible limit for the mean free path. This relation he has derived using the general theory of quantum transitions to determine the effective cross section of the scattering of electrons and holes by impurity ions in semiconductors. Although the difference compared with "$L = d$" as the lowest limit is small, let's use this relation. Then we get for the minimum metallic conductivity for strong scattering

$$\sigma_{min} = \frac{c^{*2}}{6} \left(\frac{e^2}{h} \right) \frac{1}{d} = \frac{1}{96} \left(\frac{e^2}{h} \right) \frac{1}{d} \simeq 20\Omega^{-1} cm^{-1}. \tag{21}$$

For a nearly completely filled band the same equations, Eqs. (10), (12), (18), (20), hold, where L has the meaning of the mean free path of the holes at the Fermi energy of the nearly completely filled band, and for the critical hole density it follows

$$p_{crit} = \frac{1}{3\pi^2} \left(\frac{c^*}{L} \right)^3, \tag{22}$$

which for strong scattering, i.e. $L \simeq d \simeq 0.25$nm, again leads to

$$p_{crit} \simeq 3 \cdot 10^{19} cm^{-3}. \tag{23}$$

The first equation of Eq. (20) looks like the original relation for a minimum metallic conductivity derived by Mott ([1], p.30)

$$\sigma_{min} \simeq 0.026 \left(\frac{e^2}{\hbar} \right) \frac{1}{d} \tag{24}$$

derived using the concept of disorder by random potentials. Mott's relation, Eq. (24), leads to $\sigma_{min} \simeq 200\ \Omega^{-1}\text{cm}^{-1}$ if $d = 0.3$ nm is set, i.e. about one order of amount greater than get by Eq. (20).

The difference consists in the fact that for the derivation of the Eqs. (17), (18), (22) random atomic potentials within a single phase are not assumed. In other words, we cannot see any reason for the assumption that in one of the two phases of an alloy with phase separation there would be essential potential fluctuations growing with increasing v_B from $v_B = 0$ to larger values until $v_{B,c}$ (the B phase fraction at the M-I transition) or beyond it. The disorder effect on the electronic transport properties can be characterized alone by the "ordering parameter" L, and, if $L \simeq d$ is already realized, σ at $T = 0$ decreases (with increasing v_B) not by further increasing "disorder", but by decrease of n (according to Eq. (1)) or p.

The conclusion of a minimum metallic conductivity σ_{min} seems to be in contradiction to the conclusion by Okuma et al. [26] and Hertel et al. [25], that the M-I transition in a-$Cr_{1-x}Si_x$ and a-$Nb_{1-x}Si_x$ occurs continuously and that for $T \rightarrow 0$, essentially smaller σ were measured than $20\ \Omega^{-1}\text{cm}^{-1}$. This finding is, however, not really in contradiction considering the fact that the samples are produced by co-evaporation [26] and co-sputterring [25, 26] from two locally separated sources, one with the element Cr or Nb and the

other with the element Si, and in the samples a concentration gradient is to be expected. If there is a concentration gradient perpendicularly to the direction of the measuring current for measurement of σ, then a continuous M-I transition with increasing (average) x can be pretended, because the sample occurs to be metallic as long as there is still a narrow metallic current path through the sample. A concentration gradient is connected with a gradient of ζ and leads, therefore, also to a gradient of p (according to the equations of Secs. VIII B, VIII D). Immediately at the M-I transition locally limited metallic ranges ($p > p_{crit}$, $\sigma > 0$ at $T = 0$) and locally limited insulating ranges ($p < p_{crit}$, $\sigma = 0$ at $T = 0$) can coexist leading to an average $\sigma < \sigma_{min}$ at $T = 0$, i.e., the M-I transition can be smeared out across a concentration range and the resulting conductivity at $T = 0$ can be smaller than given by Eq. (18) or Eq. (20) caused by the "dilution" of the metallic fraction within a phase. As long as there is still a connected cluster of metallic ranges (of the same phase) through the whole sample, this sample shows metallic conductivity ($\sigma > 0$ at $T = 0$). Moreover, we have to take into account that L can be larger than d (for instance in crystalline alloys) corresponding to a smaller σ_{min} according to Eq. (18) compared with Eq. (20).

Möbius et al. concluded from phenomenological considerations of conductivity data of a-$Ni_{1-x}Si_x$ [42] and a-$Cr_{1-x}Si_x$ [43–47] that the M-I transition is very likely discontinuous at $T = 0$. This conclusion corresponds with our result of a minimum metallic conductivity in a metallic phase. More details see Sec. VIII.

E. Mobility edges

For a nearly empty parabolic band in NFE approximation, the density of states is given by $N(E) = 4m\,k/h^2$, and - replacing k by Eq. (10) - it follows for the density of states at the mobility edge, E_C,

$$N(E_C) = \frac{4c^* m}{h^2 L}, \tag{25}$$

and for the energy at the mobility edge, E_C,

$$E_C = E_A + \frac{(c^* \hbar / L)^2}{2m}. \tag{26}$$

m is the effective electron mass, E_A characterizes the bottom of the band.

For a nearly filled parabolic band in NFE approximation it follows for the density of states at the mobility edge, E_V,

$$N(E_V) = \frac{4c^* m}{h^2 L}, \tag{27}$$

and for the energy at the mobility edge, E_V,

$$E_V = E_B - \frac{(c^* \hbar / L)^2}{2m}, \tag{28}$$

where m and L have the meaning of an effective mass and mean free path of the holes at the Fermi energy of the nearly filled band. E_B characterizes the top of the band. For the case of strong scattering, in Eqs. (25)-(28), L is to be replaced by d (or L by $4d/\pi$ [41]). For any (non-parabolic) band, the Eq. (26) and Eq. (28) have no longer a physical meaning in this context and we apply the terms E_C and E_V only to characterize the points on the energy scale, where *N(E)* crosses a mobility edge defined by the Eqs. (25) and (27). In other words, Eq. (25) and Eq. (27) can be applied to define mobility edges also for any (non-parabolic) band, provided effective masses can be defined according to

$$\frac{1}{m} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \tag{29}$$

with a defined *E(k)*-dependence for $kL > c^*$.

III

ELECTRONIC TRANSPORT IN ALLOYS WITH PHASE SEPARATION (COMPOSITES)

A. Electrical conductivity

Let us consider a two phase-composite consisting of the phases $i = A, B$ in a symmetrical fashion regarding the average geometric form of the phase grains and without preferred orientations. Let us assume that each phase can be characterized by a set of transport coefficients σ_i, $\kappa_{e,i}$, S_i and R_i for the phase i, which are the electrical conductivity, electronic contribution to the thermal conductivity, Seebeck coefficient and the Hall coefficient, respectively, in the phase i. The corresponding transport coefficients of the composite, σ, κ_e, S and R are to be calculated, if the σ_i, $\kappa_{e,i}$, S_i and R_i are known. The discussion will be restricted to small temperature gradients, small and constant electric and magnetic fields, **E** and **H**, respectively.

Applying effective medium theory (EMT), let us derive the relation between σ_i and σ, the electrical conductivities in the phases i and the composite, respectively. The strategy underlying the EMT is the following: a single phase grain of the phase i is considered to be completely embedded in an effective medium consisting of the two phases randomly arranged and characterized by the total transport coefficients. At the boundary face between this single phase grain and the surrounding effective medium continuity of the current densities and potentials and their gradients are to be saved.

The local electric current density J_i can be written as

$$\mathrm{J}_i = \sigma_i \mathbf{E}_\mathrm{i} = -\sigma_i \mathrm{grad}\varphi_i. \tag{30}$$

In analogy to Eq. (30) we write for the electric current density J in the specimen