Disordered electronic systems: Concentration dependence of the dc conductivity in amorphous transition-metal–metalloid alloys (metallic regime)

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In the metallic regime of several a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys, the concentration dependence of the electrical resistivity ρ can be approximated by $d\ln\rho = \alpha^* d\xi$, where α^* is constant for a given alloy and $\xi = x/(1-x)$. N and T stand for a transition metal with completely and incompletely occupied d bands, respectively, and M stands for a metalloid element. If, in the alloy, phase separation is realized, there is electron redistribution between the two phases A and B. For a-$N_{1-x}M_x$ alloys this can be described by $-dn = \beta n d\zeta$ with $\zeta = X_B/X_A$, where n is the electron density in the conduction band (CB) formed by the A phase. X_A and X_B are the fractions of the A and B phases having the average concentrations x_A and x_B, respectively. β depends on the average potential difference between the A and B phases. B is the phase with the deeper average potential. Part of the electrons in the B phase occupies the valence band (VB) formed by the B phase. Another part occupies trap states (as far as available below E_F), leading to electron localization. The electron redistribution leads to long-range electron-density fluctuations expressed by $\delta n = (1+\zeta^{-1})(n_0-n)$; n_0 is the total s and p valence-electron concentration. Under certain conditions both CB and VB can contribute to the electronic transport. $-dn = \beta n \, d\zeta$ is expected to apply also to a-$T_{1-x}M_x$ alloys, where the electron redistribution can enclose part of the d electrons as well. Positive Hall coefficients are expected, when both the VB has "hole" conductivity, and this contribution dominates compared with those of the CB. Activation of electrons from the B to the A phase with increasing temperature can lead to a negative temperature coefficient of ρ.

I. INTRODUCTION

For more than 20 years, enormous efforts have been made to understand the electronic transport in disordered electronic systems. While essential aspects of the transport behavior in the semiconducting regime are well understood,[1] there are still many open questions with respect to both the metallic regime (e.g., Mooij's correlation,[2] resistivity saturation,[3] occurrence of the positive Hall coefficient)[4] and the metal-semiconductor transition (MST); the scaling theory of localization[5] predicts a continuous MST in three dimensions, whereas a reinterpretation of conductivity data by Möbius[6] suggests the MST to be discontinuous at temperature $T=0$ in agreement with the original prediction by Mott.[7] When ρ lies in the high-resistivity regime ($\gtrsim 150 \ \mu\Omega$ cm), the nearly-free-electron (NFE) approximation is generally considered to fail more and more as ρ increases and other concepts are applied for discussion of the transport properties. Such a basis concept is Anderson's localization model[8] and its scaling theory[5] including electron-electron interaction[9] applied to amorphous transition-metal–metalloid (a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$) alloys[10] as well. In the high-resistivity regime, the electrons are considered to be diffusive corresponding to a behavior which cannot be described in the framework of the Boltzmann transport theory.

In spite of this generally accepted opinion, in this paper we present an alternative and independent discussion of the transport properties in a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys based on the Boltzmann transport equation (BTE).

Although the systems under consideration belong to the class of strong scattering systems, a surprisingly consistent description of transport behavior is obtained. The decisive consequence of this description is the fact that the carriers in the considered disordered systems are, after all, to be considered as freely propagating. This surprising result will be generalized in a planned following paper including the MST due to disorder.

In Sec. II A known resistivity data of a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys are analyzed and a universal relation between resistivity and composition is found. Applying this universal relation in Sec. II B a two-band model describing the electronic transport in a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys is proposed. Under consideration of conductivity and Hall-effect data in Sec. II C the contributions of the two bands to the dc conductivity σ are separated for the example a-$(AgCu)_{1-x}Ge_x$. In Sec. III it will be shown that the two-band situation in a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys is caused by the coexistence of different amorphous phases having different short-range order (SRO) known as amorphous phase separation. In Sec. IV, results and discussions are summarized.

II. ELECTRONIC TRANSPORT IN a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ ALLOYS

A. Concentration dependence of the electrical resistivity

N and T stand for a transition metal with completely and incompletely occupied d bands, respectively, and M

for a metalloid element. We have found that—for not too small x—in the metallic regime of several a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys, the concentration dependence of ρ can be approximated by linear relations with a slope given by

$$\frac{d\ln\rho}{d\xi}=\alpha^*, \tag{1}$$

where $\xi=x/(1-x)$ and α^* is constant for a given alloy. This finding will be illustrated in the following applying known resistivity data. The used systems do not provide a complete survey. Only such systems are enclosed where the concentration range of our disposal is not too small. As long as x is not too small, in many cases in the metallic regime the temperature dependence of ρ in the amorphous state may be neglected in comparison to the concentration dependence.[11-18] Therefore, room-temperature (RT) data have also been used. The difference of the corresponding residual resistivities can, however, no longer be neglected, when x approaches the MST.[11-18] The characteristic parameters α^* and ρ_0, according to $\rho=\rho_0\exp(\alpha^*\xi)$, are estimated for some a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys (Figs. 1–5) and are listed in Table I. In Fig. 1 the $\log_{10}\rho$ versus ξ plot is shown for a-$Au_{1-x}Si_x$ films applying data from Morigaki[11] (2 K), Nishida et al.[12] (4 K), and Mangin et al.[19] (77 K). Equation (1) is a very good approximation for $\xi<2$. With increasing x the data scatter more and more in the $\log_{10}\rho$ versus ξ plot, since at large ξ small errors in the analysis of concentration lead to large errors in ξ. The data published in Ref. 20 are not drawn, since the concentration range is too small or part of the samples are ordered or partially crystalline as pointed out by the authors; the deviations of these data points from the straight line in Fig. 1 are partially considerable.

The $\log_{10}\rho$ versus ξ plot for a-$Cu_{1-x}Ge_x$ films applying residual resistivities from Stritzker and Wühl[21] are shown in Fig. 1 as well. Equation (1) is a relatively good approximation for $\xi>0$. The $\log_{10}\rho$ versus ξ plot for the residual resistivities of a-$Au_{1-x}Ge_x$ films published by Stritzker and Wühl[21] and Dodson et al.[13] (1.5 K) is drawn in Fig. 2(a). With the exception of small ξ Eq. (1) is a gross approximation for a relatively large concentration range. At $\xi=11.5$ the samples are semiconducting (J_3 and J_4) or just metallic (J_1 and J_2) as reflected by the σ versus T curves in Ref. 13.
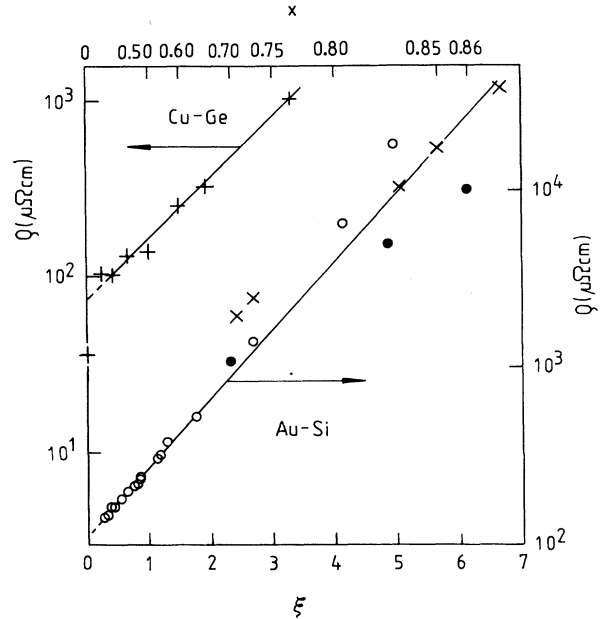

FIG. 1. Dependence of the specific electrical resistivity ρ on $\xi=x/(1-x)$ for a-$Au_{1-x}Si_x$ and a-$Cu_{1-x}Ge_x$. For Au-Si the data are taken from Mangin et al. (Ref. 19, Figs. 7 and 9), $\bigcirc$ (77 K); Morigaki (Ref. 11), $\bullet$ (2 K); and Nishida et al. (Ref. 12), $\times$ (4 K). The data for Cu-Si are taken from Stritzker and Wühl (Ref. 21), $+$ ($\simeq$0 K).

The $\log_{10}\rho$ versus ξ plot of RT resistivities for a-$(Ag_{0.5}Cu_{0.5})_{1-x}Ge_x$ films (Mizutani and Yoshida[22]) is drawn in Fig. 2(a) as well. This system will be investigated later in more detail.

In Fig. 3 the $\log_{10}\rho$ versus ξ plot of a-$Cr_{1-x}Si_x$ films is shown. The points below $\xi<3$ are RT resistivities from Helms et al.,[16] while for $\xi\gtrsim3$ both RT and 4-K values from Möbius et al.[14] are applied indicating that the temperature effect is considerable only for large ξ approaching the MST (the MST lies according to Ref. 14 immediately at sample no. 3). Similar to data point no. 1 the temperature coefficient of resistivity (TCR) curves shown in Refs. 16 and 17 suggest a sufficiently small temperature dependence of ρ for $0.3<\xi\lesssim2.5$ as well. Without the RT data above $\xi\simeq3$, Eq. (1) is a very good approximation.

TABLE I. Estimate of ρ_0, α^*, and β according to $\rho=\rho_0\exp(\alpha^*\xi)$ and $-dn=\beta n\,d\zeta$ for some a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys where $\xi=x/(1-x)$ and $\zeta=X_B/X_A$. n is the ED in the CB; X_A and X_B are the volume (or atomic) fractions of the amorphous phases A and B which are neighbors in the approximate crystalline diagram of state. The determined β value corresponds to the concentration range $x>\hat{x}$. $\hat{x}$ is the composition of the "metallic" phase in the considered a-$N_{1-x}M_x$ or a-$T_{1-x}M_x$ alloy.

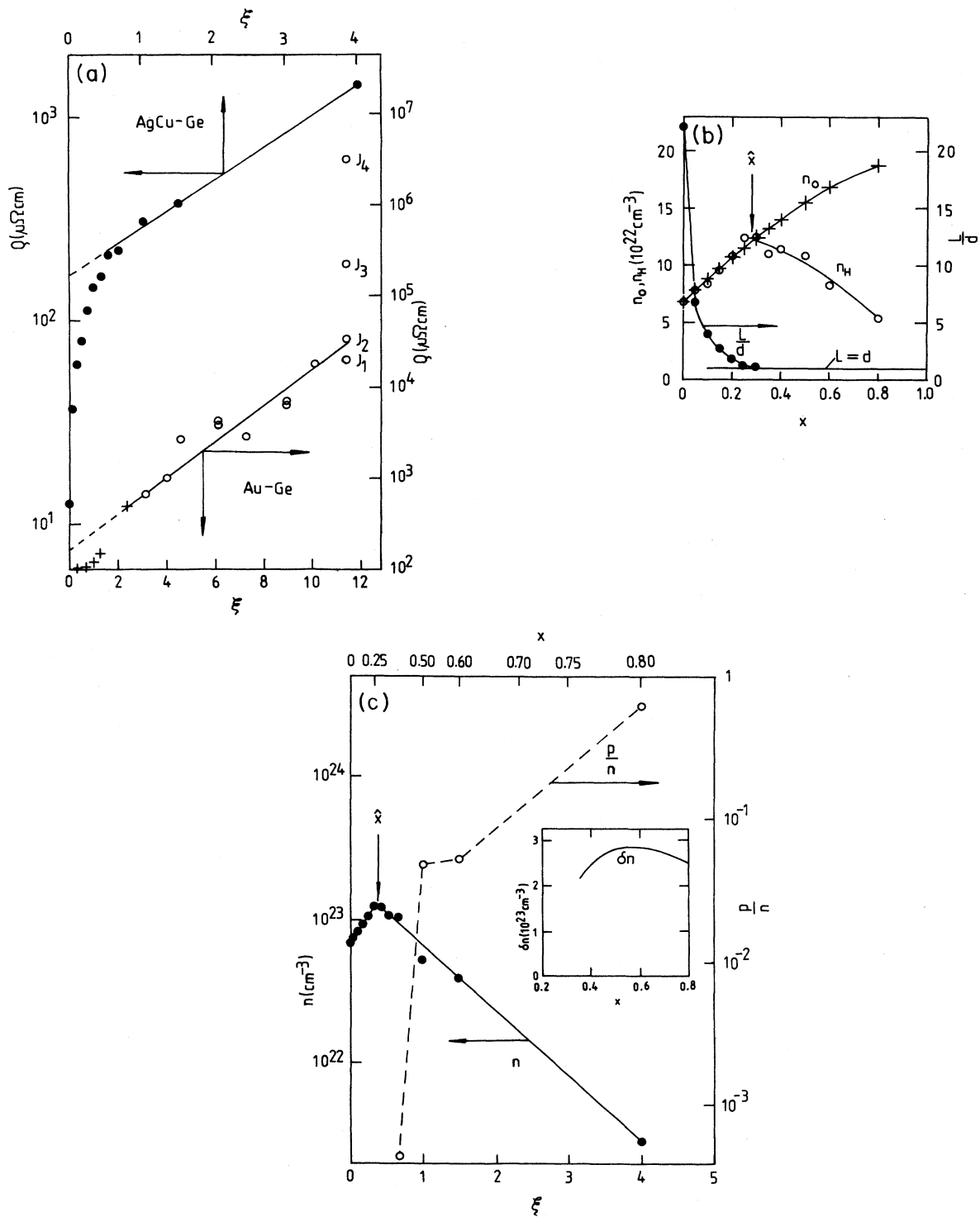| Alloy	Au-Si	Cu-Ge	Au-Ge	AgCu-Ge	Cr-Si	Mo-Si	Fe-B	Fe-Si	$Cr_{1-y}Si_y$-O		
Fig.	1	1	2(a)	2(a)	3	3	4	4		5	
y									0.74	0.68	0.55
ρ_0 ($\mu\Omega$ cm)	112	74	167	170	122	107	115	240	670	550	240
α^*	0.90	0.79	0.45	0.53	0.65	0.84	0.51	1.0	3.6	3.8	4.4
$\hat{x}$				0.28					0	0	0
β				1.42							

FIG. 2. (a) As Fig. 1, but for a-$Au_{1-x}Ge_x$ and a-$(Ag_{0.5}Cu_{0.5})_{1-x}Ge_x$. For Au-Ge the data are taken from Stritzker and Wühl (Ref. 21), + ($\simeq 0$ K), and Dodson *et al.* (Ref. 13), O (1.5 K), and for AgCu-Ge from Mizutani and Yoshida (Ref. 22), ● (RT). The samples J_3 and J_4 are semiconducting, whereas J_1 and J_2 are just metallic as reflected by the $\sigma(T)$ curves in Fig. 2 of Ref. 13. (b) Concentration dependence of L/d (●) and comparison of n_0 (+), the total valence-electron concentration, with n_H calculated by $n_H = (eR_H)^{-1}$ (O) for a-$(Ag_{0.5}Cu_{0.5})_{1-x}Ge_x$ applying experimental data from Ref. 22. R_H is the measured Hall coefficient; L and d are the electronic mean free path and the average atomic distance, respectively. (c) n (●) and p/n (O) for a-$(Ag_{0.5}Cu_{0.5})_{1-x}Ge_x$ calculated applying experimental data from Ref. 22 (see. Sec. II C). The inset shows the concentration dependence of the long-range electron density fluctuations expressed by δn [see Sec. III, Eq. (18)].
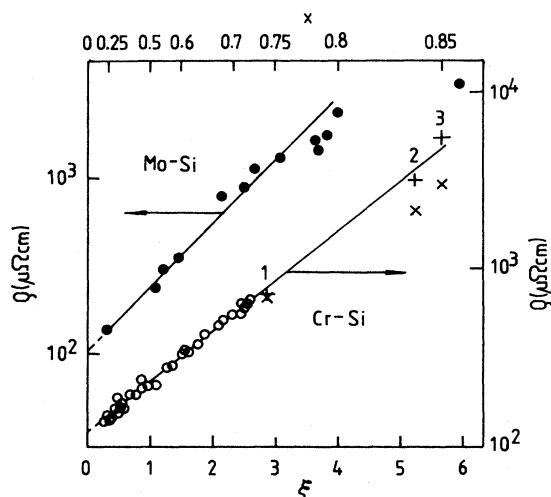
FIG. 3. As Fig. 1, but for a-$Cr_{1-x}Si_x$ and a-$Mo_{1-x}Si_x$. For Cr-Si the data are taken from Helms *et al.* (Ref. 16), ○ (RT), and Möbius *et al.* (Ref. 14), × (RT), + (4 K); nos. 1–3 agree with those in Fig. 1 of Ref. 14; after Ref. 14 the MST lies immediately at sample no. 3. The data for Mo-Si (●) are RT values taken from Beddies *et al.* (Ref. 18).

The $\log_{10}\rho$ versus ξ plot of RT values of a-$Mo_{1-x}Si_x$ films published by Beddies *et al.*[18] is shown in Fig. 3 as well. For $\xi \lesssim 3$, Eq. (1) is a relatively good approximation. Unfortunately we do not know low-temperature data above $\xi = 3$.

In Fig. 4 the $\log_{10}\rho$ versus ξ plot of RT resistivities for
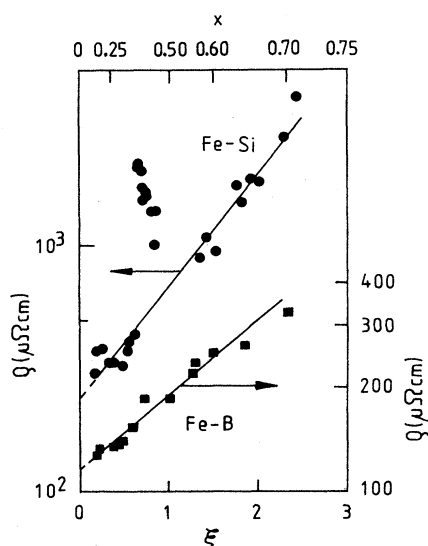

FIG. 4. As Fig. 1, but for a-$Fe_{1-x}B_x$ and a-$Fe_{1-x}Si_x$. For Fe-B (■) the data are RT values taken from Stobiecki and Hoffmann (Ref. 23), those for Fe-Si (●) are RT values taken from Luciński and Baszyński (Ref. 24). After Ref. 24 the considerable deviations from a solid curve at $0.6 < \xi < 1$ are due to the ordered η-Fe_5Si_3 phase.
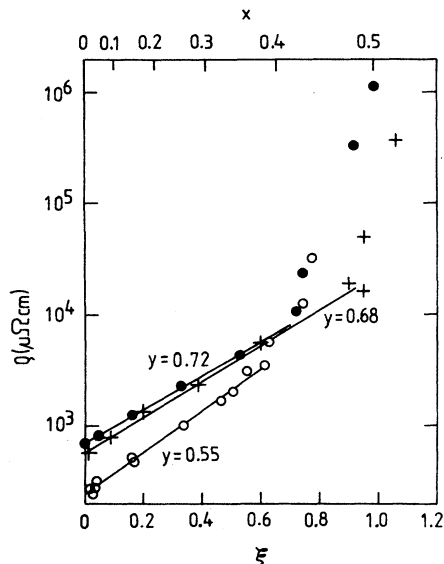

FIG. 5. As Fig. 1, but for a-$(Cr_{1-y}Si_y)_{1-x}O_x$ films with $y = 0.72$ (●), $y = 0.68$ (+), $y = 0.55$ (○). y was given by the used Cr-Si target (the target used for the series "$y = 0.55$" contained additionally 2 at. % wolfram). The beginning of the systematic deviations from the straight line at large ξ indicates the MST. The slopes α^* increase with decreasing Si:Cr quotient [i.e., with $y/(1-y)$] suggesting the fact that the larger the average potential difference between the metallic component and the metalloid one the stronger the increase of ρ by alloying. This suggested connection between potential difference and ρ increase is also supported by the finding that the N-M and T-M alloys with M=Si, Ge, or B have essentially smaller α^* values, see Figs. 1–4 and Table I.

$Fe_{1-x}B_x$ films published by Stobiecki and Hoffmann[23] is shown. Equation (1) is a relatively good approximation below $\xi = 2$. The $\log_{10}\rho$ versus ξ plot of RT data for $Fe_{1-x}Si_x$ films published by Luciński and Baszyński[24] is shown in Fig. 4 as well. Above $\xi = 0.6$ a rapid increase of ρ occurs which is attributed by the authors to the appearance of the ordered η-Fe_5Si_3 phase. Without these ordered samples the data can be well approximated by Eq. (1).

Figure 5 shows $\log_{10}\rho$ versus ξ plots of RT data of a-$(Cr_{1-y}Si_y)_{1-x}O_x$ films[25] with y =const. The films were deposited by reactive dc sputtering of CrSi targets in oxygen-argon mixtures where the oxygen partial pressure has been varied. The methods of deposition and chemical analysis were the same as described by Gladun *et al.*[15] Figure 5 shows, for every series with y =const, the data can be approximated very well by Eq. (1) in the metallic regime; breaking off of these straight lines already occurs at relatively small ξ and indicates the MST. It is noteworthy that the MST is already reflected by the RT data and that the description by Eq. (1) includes $\xi = 0$ as well. With the increasing Si:Cr quotient [i.e., increasing $y/(1-y)$] the slope α^* with respect to oxygen addition decreases suggesting the fact that the larger the average potential difference between the "metallic" com-

ponent (CrSi) and the metalloid one (O) the stronger the ρ increase by alloying. This suggested connection between potential difference and ρ increase is also supported by the finding that the alloys with silicon, germanium, or boron have essentially smaller α^* values (see Figs. 1–4 and Table I).

Summarizing Figs. 1–5 we state, for most of the considered a-(N,T)-M alloys, Eq. (1) is a good approximation in the metallic regime; essential deviations are due to ordered structures or the MST.

B. Concentration dependence of the electron density in the conduction band

The experimental finding of Eq. (1) suggests a simple interpretation, if the NFE approximation can be applied. For this interpretation we make two assumptions.

(1) For not-too-small metalloid contents, the elastic mean free path (MFP) of the conduction electrons L is approximately equal to the mean atomic distance d.

(2) Above a critical concentration $\hat{x}$ the conduction band splits into two separated bands,[26] called conduction band (CB) and valence band (VB) in the following.

Assumption (1) comes from the fact that, in strong scattering disordered systems, L is of the order of d, but cannot be smaller than d. Confidence for assumption (2) comes from Hall-coefficient measurements (R_H) of a-$(AgCu)_{1-x}Ge_x$ alloys by Mizutani and Yoshida.[22] They have shown that below $x \simeq 0.3$ there is a relatively good agreement between the measured R_H and the free-electron values

$$R_H^0 = (en_0)^{-1} , \tag{2}$$

i.e., occurrence of a separated band [assumption (2)] containing part of the valence electrons seems to be suggestive only above $x \simeq 0.3$. e is the elementary charge and n_0 is the total s and p valence-electron concentration. In Fig. 2(b) the electron density (ED) calculated by $n_H = (eR_H)^{-1}$ is compared with n_0 applying experimental data from Ref. 22: While for $x \lesssim 0.3$, $n_H \simeq n_0$, for $x > 0.3$ the difference $n_0 - n_H$ increases rapidly with x. Because of the good agreement between n_H and n_0 for $0 \le x < 0.3$, the NFE approximation is actually a good approximation in this concentration range. Since the difference $n_0 - n_H$ arises suddenly and so rapidly above $x \simeq 0.3$, this divergence is suggested not to be caused by a sudden breaking off of the NFE approximation, but that is only still a fraction of all the valence electrons which occupy the CB.[27] In the NFE approximation the BTE can be expressed as

$$\sigma = \left[\frac{\pi}{3} \right]^{1/3} \frac{2e^2L}{h} n^{2/3} , \tag{3}$$

where $h = 2\pi\hbar$ is Planck's constant. Since $n_H \simeq n_0$ for $x \lesssim 0.3$ in a-$(AgCu)_{1-x}Ge_x$, n can be replaced by n_0 (or n_H) in this concentration range and L can be calculated applying Eq. (3) and the ρ data from Fig. 2(a), where $\sigma = \rho^{-1}$. The resulting L/d dependence on x is drawn in Fig. 2(b). L/d decreases rapidly with increasing x and approaches the limit value 1 at $x \simeq 0.3$. This result is an additional argument supporting assumption (1).

As shown in Fig. 2(b), the comparison between $n_H(x)$ and $n_0(x)$ provides the value for $\hat{x}$. For a-AgCu-Ge it follows that $\hat{x} = 0.28 \pm 0.05$. Assuming the VB does not contribute to σ,[28] with Eqs. (1) and (3) and assumptions (1) and (2), it follows for the ED in the CB for $x \ge \hat{x}$ the simple relation

$$-dn = \beta^* n \, d\xi \tag{4}$$

with

$$\beta^* = \tfrac{3}{2}\alpha^* = \text{const} . \tag{5}$$

Equation (4) is a relation for determination of the ED in the CB and is valid only for $x \ge \hat{x}$ [assumption (2)]. Setting $\hat{x}$ as the lower integration limit, by integration of Eq. (4) we get

$$\ln\left[\frac{n}{\hat{n}}\right] = -\beta^*(\xi - \hat{\xi}) = -\beta^* \frac{x - \hat{x}}{(1-\hat{x})(1-x)} \tag{6}$$

with $\hat{\xi} = \hat{x}/(1-\hat{x})$ and the ED can be expressed by

$$n(x) = \hat{n} \exp\left[-\beta \frac{x - \hat{x}}{1-x}\right] \tag{7}$$

for $x \ge \hat{x}$, and

$$\beta = \frac{\beta^*}{1-\hat{x}} = \text{const} \tag{5'}$$

for a given a-N-M alloy. For $x = \hat{x}$, $n = n_0$ since σ does not jump in the complete metallic regime; the same is to be assumed for n. That is why $\hat{n}$ in Eq. (7) is identical to n_0 at $x = \hat{x}$. For an a-$N_{1-x}M_x$ alloy n_0 is given by

$$n_0 = \mathcal{N}((1-x)Z_N + xZ_M) \tag{8}$$

and can be determined by density measurements. Z_N and Z_M are the valences of the N component and the M component, respectively, and $\mathcal{N} = \mathcal{N}(x)$ is the average atomic density in dependence on x. In agreement with Eqs. (7) and (3) in an a-$N_{1-x}M_x$ alloy, the increase of ρ with x is essentially due to decrease of n, if $x > \hat{x}$. In the concentration range $x < \hat{x}$ the increase of ρ is determined by the decrease of L, since the electron scattering increases with the added deep potentials of the M atoms [compare L/d versus x for a-$(AgCu)_{1-x}Ge_x$ in Fig. 2(b)].

For a-$T_{1-x}M_x$ alloys, the situation is more complicated: n_0 is not given by Eq. (8), generally. Because of a strong interaction between Td and Mp states[29–33,34] redistribution of valence electrons between the CB and the d band caused by modification and displacement of the d band against the CB cannot be excluded. Additionally, the effect of the d band on the transport is not known and for small x it is generally not clear which part the s-d hybridization takes. On the other hand, because of the strong hybridization between Td and Mp states[29–33,34] the s-d hybridization is reduced or canceled[29–33] and for not-too-small x the NFE approximation is assumed to be applicable for a-$T_{1-x}M_x$ alloys as well. This assumption is also supported by the fact that Eq. (1) is found in both a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys,

i.e., the physical interpretation of this experimental finding is expected to be similar in both kinds of alloys.

In a-$(Cr_{1-y}Si_y)_{1-x}O_x$ alloys $L/d \simeq 1$ is realized in the *complete* concentration range *considered* (i.e., $x \geq 0$, ($y \geq 0.55$). This conclusion is suggested by the finding that even in a-$(AgCu)_{1-x}Ge_x$ $L/d \simeq 1$. is realized for $x > 0.3$. That is why, in the complete metallic regime, the $\log_{10}\rho$ versus ξ plots in Fig. 5 reflect—according to Eq. (3)—the concentration dependence of the ED alone. Moreover, since in the complete metallic regime Eq. (1) is a very good description for these a-T-M alloys, the NFE approximation is suggested to be actually a good description and we find $\hat{x} \simeq 0$ for the regarded a-CrSi-O alloys. For confirmation of this suggestion, Hall-effect measurements should be supplemented.

C. The effect of the valence band on the electronic transport

According to Eq. (4) and assumption (2) above $\hat{x}$ the loss of ED in the CB, $-dn$, is expected to lead to an increase of the ED in the VB, n_V. In other words, n_V depends essentially on n. On the other hand, the total number of states in the VB per unit volume, D_V, is determined by the band structure and, therefore, one could conjecture that not all the electronic states available in the VB are occupied. If this conjecture is true, the VB could have a nonzero density of holes given by $p = D_V - n_V$ and contribute to σ as well. If so, then the CB and VB overlap each other. Although such band overlap accompanied with incompletely occupied bands[35] is hard to believe, let us calculate $n(\xi)$ and $p(\xi)$ for a-$(AgCu)_{1-x}Ge_x$ alloys applying the σ and R_H data published by Mizutani and Yoshida.[22] Later (Sec. III) we shall discuss which importance this calculation has for the physics of a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys. If for the holes in the VB the same assumptions are made as for the electrons, i.e., NFE approximation and MFP $\simeq d$, then their contribution to σ can be separated by measuring of both σ and R_H applying the known formulas for a two-band situation

$$R_H = -\frac{p - nb^2}{e(p + nb)^2} , \quad (9)$$

$$\sigma = \sigma_C + \sigma_V = \left[\frac{\pi}{3}\right]^{1/3} \frac{2e^2 d}{h}(n^{2/3} + p^{2/3}) , \quad (10)$$

where n and p are the densities of the electrons and holes in the CB and VB, respectively. σ_C and σ_V are the corresponding contributions to the conductivity. b is the quotient of the electron and hole mobility and depends in the applied approximation only on the ratio p/n, i.e.,

$$b = \left[\frac{p}{n}\right]^{1/3} . \quad (11)$$

Combining Eqs. (9)–(11) b is obtained as

$$b = \frac{1 \pm (2c - c^2)^{1/2}}{1 - c} \quad (12)$$

with

$$c = \frac{3h^3 R_H^2 \sigma^3}{8\pi e^4 d^3} . \quad (13)$$

The positive sign in Eq. (12) refers to the case where $R_H > 0$, that is $b > 1$, in other words, the hole contribution would be dominant in this case, while the negative sign refers to $R_H < 0$, i.e., the electron contribution dominates and $b < 1$. With Eqs. (10)–(13) and the σ and R_H data from Ref. 22, n and p are calculated and the resulting plots $\log_{10}n$ versus ξ and $\log_{10}(p/n)$ versus ξ are drawn in Fig. 2(c). The formulas (9)–(13) only have solutions for $x \geq 0.40$. For $x < 0.40$, $p \simeq 0$ and $n \simeq n_H = (eR_H)^{-1}$ can be set, since $n \gg p$, as the tendency of the concentration dependence of p/n above $x = 0.40$ shows, see Fig. 2(c).

Figure 2(c) shows that n dominates in comparison to p for all the concentrations inspected and can be described above $\hat{x}$ by Eq. (7) with $\hat{x} = 0.28 \pm 0.05$, $\hat{n} = (1.3 \pm 0.2) \times 10^{23}$ cm^{-3}, and $\beta = 1.42$. This value for β is larger than those calculated by Eqs. (5) and (5') with $\alpha^* = 0.53$ estimated from the $\log_{10}\rho$ versus ξ plot in Fig. 2(a) where the effect of the VB has been neglected, i.e., Eqs. (5) and (5') represent only an approximation which is worse the larger the conductivity contribution by the VB. The same is true for the approximation (1).

III. DISCUSSION

There is increasing experimental evidence for the fact that amorphous alloys cannot be regarded as a random arrangement of the atoms, but contain microscopical ranges which may differ with respect to SRO. This fact, well known for nonmetallic oxide glasses,[36] has also been found in many other types of amorphous systems, both semiconducting and metallic.[37] Mangin et al.[19] describes the structure and electrical properties of a-$Au_{1-x}Si_x$ films in the framework of a model, where two different amorphous phases, the a-μ phase and the a-Si phase, coexist. In the free-energy diagram for Au-Si (Fig. 6) taken from Ref. 19 the energy minima of these two amorphous phases lie near the minima of the corresponding crystalline phases c-μ and c-Si ($x \simeq 0.25$ and $x \simeq 1$). Let us adopt this amorphous phase separation model. In the spirit of this model the alloy is to be considered as heterogeneous. The concentration term in Eq. (7) looks like the well-known lever rule for determination of the volume ratio of two phases with the concentrations $x = \hat{x}$ and $x = 1$ and we can write

$$\frac{x - \hat{x}}{1 - x} = \frac{X_{a\text{-Si}}}{X_{a\text{-}\mu}} ,$$

where $X_{a\text{-Si}}$ and $X_{a\text{-}\mu}$ denote the volume (or atomic) fractions of the phases a-Si and a-μ (Fig. 6) and Eq. (7) can be written as

$$\frac{n}{\hat{n}} = \exp\left[-\beta \frac{X_{a\text{-Si}}}{X_{a\text{-}\mu}}\right] . \quad (14)$$

$\hat{n}$ is the ED of the phase a-μ for $x = \hat{x}$. If Eq. (14) reflects a general regularity of a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys,
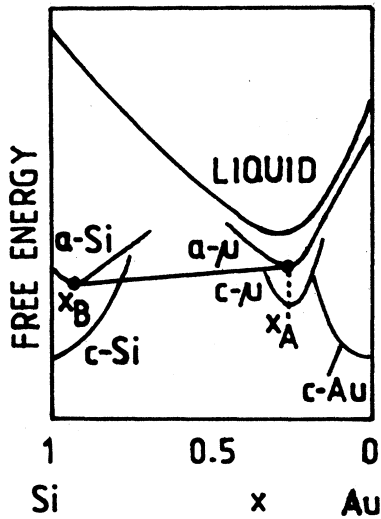
FIG. 6. Hypothetical free-energy diagram for $Au_{1-x}Si_x$ taken from Mangin et al. (Ref. 19) with the following change: the curves for the two amorphous phases a-μ and a-Si are not connected, since the SRO are different. Additionally, the tangent construction for determination x_A and x_B, the compositions of the two amorphous phases $A(\hat{=}a-\mu)$ and $B(\hat{=}a$-Si), is drawn.

then Eq. (14) can be generalized in such a way that

$$\frac{n}{n_A} = \exp(-\beta\zeta) \qquad (15a)$$

or

$$-dn = \beta n \, d\zeta \qquad (15b)$$

describes the ED in the CB with

$$\zeta = \frac{X_B}{X_A} = \frac{x - x_A}{x_B - x} ; \qquad (16)$$

X_A and X_B are the volume (or atomic) (Ref. 38) fractions of the amorphous phases A and B corresponding to the phases which are neighbors in the approximate crystalline diagram of state. x_A and x_B are the average compositions of the phases A and B in the alloy. n_A is the ED of an alloy with $x = x_A$ (i.e., $X_B = 0$). We interpret Eqs. (15) in such a way that they describe a partial electron redistribution from the A phase to the B phase. Since n in Eqs. (15) is the ED in the CB, this interpretation suggests the fact that the CB is accompanied with the A phase, whereas the VB is accompanied with the B phase. In other words, there are two electron systems in the alloy, one in the A phase and another one in the B phase. The average potential in the a-Si phase is deeper than in the a-μ phase and, therefore, such an electron redistribution from the a-μ phase to the a-Si phase is reasonable. In the generalized Eqs. (15) B is, therefore, to be considered as the phase with the deeper average potential and the larger the average potential difference (ΔV) between the phases A and B the larger the fraction of electrons to be redistributed for a given ζ according to Eqs.

(15). Therefore, β in Eqs. (15) depends essentially on $\overline{\Delta V}$ and indirectly on the potential difference of the different atomic sorts in the two phases A and B. Because of the electron redistribution from A to B it follows that

$$n < n_A < n_0 < n_r \qquad (17)$$

if the two-phase regime is realized; n_r is the ED in the B phase.

Let us consider an a-$N_{1-x}M_x$ alloy with M=Si or Ge. Since there is a strong similarity between the phase diagrams of different N-M systems,[39] the free-energy diagram for Au-Si in Fig. 6 can be applied as a model for other N-M systems as well and in the concentration range $x > \hat{x}$ the two phases A and B can generally be attributed to the concentration $x \simeq \hat{x}$ and $x \simeq 1$, i.e., $x_A \simeq \hat{x}$ and $x_B \simeq 1$. In the two amorphous phases A and B, different band structures are realized superimposed by a finite density of defect states. For $x = 1$ the M atoms have sp^3 configuration.[40] If with decreasing x there is an increasing fraction of M atoms with an electron configuration s^2p^2,[41] then the VB might be assumed to be formed essentially by Mp states. If so, then n_V can be essentially smaller than n_r. With decreasing x the fraction of the phase A increases at the expense of the phase B until at $x = x_A$ the phase A exists alone. In the case $x = x_A$ and $x = x_B$ the ED in the alloy is given by $n = n_A = n_0$ and $n_r = n_0$, respectively. If $x_A < x < x_B$, the valence electrons are shared between the phases A and B. This sharing is not proportional to the volume fractions of the two phases, but there are—with the inequality (17)—long-range electron density fluctuations (LEDF) correlated with the concentration fluctuations due to the coexistence of the two different phases. A measure for these LEDF is

$$\delta n = n_r - n = (1 + \zeta^{-1})(n_0 - n) \qquad (18)$$

with n from Eq. (15a).[42] In the inset of Fig. 2(c) $\delta n (x)$ is shown for a-$(AgCu)_{1-x}Ge_x$ calculated applying $n_0(x)$ and $n(x) = 1.3 \exp[-1.42(x - 0.28)(1 - x)^{-1}] \times 10^{23}$ cm^{-3} drawn in Figs. 2(b) and 2(c), respectively. As long as the VB is incompletely occupied, the electron redistribution from A to B according to Eqs. (15) leads to increased occupation of the VB at the expense of the CB. Besides the VB the defect states below E_F in the B phase are to be occupied as well leading to electron localization.[43]

With Eqs. (15) and the given discussion, assumptions (1) and (2) of Sec. II B and Eqs. (4) and (7) are to be considered special cases and we conjecture that Eqs. (15) reflect a general property of disordered phase-separated systems. If so, then assumptions (1) and (2) and Eqs. (4) and (7) are to be replaced in the general case by the assumption of band separation caused by phase separation connected with electron redistribution described by Eqs. (15). Thus, in the general case, the electronic transport in a phase-separated system is determined by both the band structure of the different phases and their occupation described by Eqs. (15). Consequently, in the concentration range $0 < x < \hat{x}$ the a-$(AgCu)_{1-x}Ge_x$ alloys are expected to consist of two phases as well with $x_A \simeq 0$ and $x_B \simeq \hat{x}$ (see Fig. 6). On the other hand, it could be possible that

with decreasing x below $\hat{x}$ the B phase is, after all, realized alone containing structure defects in the amorphous structure which can be assumed to play a role similar to that of a vacancy in a crystalline phase.[44,45] Such a situation is to be expected when formation of the amorphous A phase with $x_A \simeq 0$ is energetically highly unfavored. Because of $n_H \simeq n_0$ for $0 < x < 0.3$ [Fig. 2(b)] in a-$(AgCu)_{1-x}Ge_x$ one could assume that actually a one-phase situation is realized. However, this assumption is difficult to be examined applying the available σ and R_H data alone, since the difference between a one-phase interpretation and a two-phase one is not very large, if both assumed phases have "electron" conductivity.

In T-M systems the situation is—because of the incompletely occupied d band—expected to be more complicated than in N-M systems. Moreover, in T-M systems there are generally more stable phases[39] than in N-M systems. For example, for the system $Cr_{1-x}Si_x$ the phases Cr, Cr_3Si, Cr_5Si_3, $CrSi$, $CrSi_2$ and Si are known.[46] Nevertheless, electron redistribution between different phases is also expected in a-$T_{1-x}M_x$ alloys if phase separation is realized. On the other hand, the question of which amorphous phases in a given a-$T_{1-x}M_x$ alloy are actually realized does not depend alone on the crystalline diagram of states, but also on the preparation conditions and on the question of whether or not there are corresponding amorphous phases to the known crystalline phases. If the top of the d band lies above E_F (at least in one of the two phases), the ED's in formulas (14)–(18) should enclose the d electrons as well. The electron density ratio of the d electrons to the other valence electrons to be redistributed to the B phase is expected to depend on the corresponding density of states (DOS) at E_F. Since Eqs. (15) describe the concentration range between two phases, deviations from the straight lines in $\log_{10}\rho$ versus ξ and kinks in the $\log_{10}n$ versus x plots could be expected at the concentrations where amorphous phases are realized. However, the available experimental data are not yet sufficient for such a discussion and additional investigations are necessary which should enclose both structural studies [e.g., extended x-ray-absorption fine structure (EXAFS)] and combined σ and R_H measurements in dependence on x at low temperatures accompanied with precise density and concentration measurements (after the model of Ref. 22).

Now let us consider the example a-$(Cr_{1-y}Si_y)_{1-x}O_x$. The finding that the α^* values[47] are essentially larger than for a-$Cr_{1-x}Si_x$ (see Table I) can be understood in terms of Eqs. (15) if the added oxygen atoms with their very deep potentials are essentially only incorporated in a "semiconducting" phase[48] with nearly defined composition, whereas the "metallic" phase[48] remains nearly oxygen free. Such a situation is actually found in a-$(Cr_{0.45}Si_{0.55})_{1-x}O_x$ films (Nguyen Van Den et al.[49]): From ir absorption measurements at 11 different samples with $x = 0.25$–0.53 it follows that, independent of x, a dielectric oxide phase is formed with the same structural unit and that with increasing x the volume part of this dielectric oxide increases (Ref. 49, p. 168). This finding is also consistent with the finding $\hat{x} \simeq 0$ (see Sec. II B), i.e.,

the "metallic" phase is actually nearly oxygen-free.

According to the applied amorphous phase separation model, the CB exists only in ranges of the A phase, while the VB exists only in ranges of the B phase. However, formulas (3), (9), and (10) are derived under the assumption that the carriers are movable in the total volume and the question arises whether n and p calculated in Sec. II C are the true or some "effective" carrier densities: There is an argument that n and p are to be interpreted as true carrier densities: At the phase interfaces A/B, the wave functions of the electrons in the CB fall off exponentially with distance since they do not overlap with wave functions belonging to atoms of the B ranges, i.e., the electrons in the CB are freely propagating and the corresponding wave functions are extended only with respect to connected A ranges. Consequently, the number of (quasifree) electrons in the CB, n_q, is to be related to the (quantum) phase volume by

$$\frac{4\pi}{3}(\hbar k_F)^3 X_A V = \frac{n_q}{2}h^3 . \tag{19}$$

V is the total volume, k_F is the Fermi wave number. Putting Eq. (19) into the BTE and replacing the area of the (spherical) Fermi surface by $4\pi k_F^2$, we get for the contribution by the CB

$$\sigma_C = \left[\frac{\pi}{3}\right]^{1/3} \frac{2e^2 L}{h} \left[\frac{n_q}{X_A V}\right]^{2/3} ,$$

and by comparison with Eq. (3) it follows that

$$n = \frac{n_q}{X_A V} \tag{20}$$

corresponding to a true ED in the A phase. For the carriers in the VB of a-$N_{1-x}M_x$ alloys the situation is analogous. Nevertheless, it is not completely clear whether or not the used formulas, especially Eq. (9), are only a gross approximation for the regarded situation and additional investigations are necessary.

Since the electrons in the CB are restricted to the A phase, the CB can only contribute to σ if the A phase forms an infinite cluster. For the example a-$Au_{1-x}Ge_x$ the MST lies at a relatively large metalloid content $[\xi \simeq 11.5 \hat{=} x \simeq 0.92$, see Fig. 2(a)] where an infinite cluster of the A phase seems to not be possible if a random mixture of A and B ranges is assumed.[50] However, since the A phase does not consist of Au atoms alone, but contains also a considerable portion of Ge atoms ($\hat{x}$), the relative portion of the B Phase at the MST is significantly lower than 0.92. In other words, ξ is not a suitable measure to characterize the MST, but ζ characterizing the phase ratio. In this sense, it is no longer surprising that in the a-CrSi-O alloys the MST occurs at relatively small ξ (Fig. 5), since after Ref. 49 the oxidation degree of the Si components in the oxid phase is essentially smaller than in SiO_2. A necessary condition that the VB can contribute to σ is the fact that the B phase forms an infinite cluster. In this sense, it is not surprising that for the example a-$(AgCu)_{1-x}Ge_x$ in the concentration range $\hat{x} < x < 0.40$, Eqs. (9)–(13) did not provide finite hole

densities (Sec. II C). On the other hand, a conductivity contribution by the VB is only possible, if the VB is incompletely occupied. Such a situation was found in a-$(AgCu)_{1-x}Ge_x$ for $x \geq 0.40$ (Sec. II C).

The question arises whether the proposed model describes also the electronic structure and transport of other kinds of heterogeneous systems such as disordered crystalline alloys, transition-metal-free alloys, granular metals,[51] liquid alloys showing phase separation, or such alloys which are solely composed of metallic elements.

On the basis of the proposed physical model some puzzling problems in the subject of disordered electronic systems[2-4] can be discussed, e.g., the occurrence of the positive Hall coefficient is expected when the contribution of the holes in the incompletely occupied VB dominates in comparison to those of the CB. "Activation" of electrons from the B to the A phase with increasing temperature can lead to negative TCR—in competition with "positive scattering contributions." Negative TCR caused by such "activation"[52] is expected to be correlated with the thermopower regarding sign and amount. These mentioned aspects are intended to be discussed in detail in a following paper.

As suggested above, reason for the electron redistribution from A to B expressed by Eqs. (15) is the fact that the average potential in the B phase is deeper than in the A phase. The energy gain possible by such an electron redistribution might be assumed to be balanced by the resulting (long-range) Coulomb interaction between the A and B ranges which are charged by this electron redistribution. However, such an exponential dependence in Eq. (15a) is hard to understand. Obviously, this energy balance is more complex. For example, Eq. (15b) might be expression for the fact that as a result of this electron sharing between the A and B ranges an optimized screening of the cores against one another results, minimizing the energy, or that the average largeness of the phase ranges is affected by Eqs. (15) as well. Additional theoretical investigations for understanding Eqs. (15) are necessary.

IV. SUMMARY

We have found that—for not too small x—in the metallic regime of several a-$N_{1-x}M_x$ and a-$T_{1-x}M_x$ alloys the concentration dependence of the electrical resistivity ρ can be approximated by $d \ln\rho = \alpha^* d\xi$ (1), where $\xi = x/(1-x)$ and $\alpha^* = $ const for a given alloy. Applying this finding a physical model is developed characterized by the two basic assumptions.

(1) For not too small x the MFP of the conduction electrons is approximately equal to the mean atomic distance.

(2) Above a critical concentration $\hat{x}$ the conduction band splits in two bands called conduction band (CB) and valence band (VB).

Applying these assumptions and Eq. (1) a reinterpretation of known experimental data results that for $x \geq \hat{x}$ the electron density (ED) in the CB can be described by $-dn = \beta^* n \, d\xi$ (4). Under consideration of known conductivity and Hall-effect data, it is found for a-$(AgCu)_{1-x}Ge_x$ alloys that there is actually a concentra-

tion $\hat{x}$ above which two bands coexist and that for sufficiently large x the VB is incompletely occupied, i.e., between CB and VB there is no energy gap.

The physical model characterized by assumptions (1) and (2) is to be considered as a special case which is replaced in the general case by the assumption of band separation caused by phase separation in two amorphous phases with different SRO. If in an a-$N_{1-x}M_x$ alloy phase separation is realized, there is electron redistribution between the two phases described by the generalized equation (15b) $-dn = \beta n \, d\zeta$ with $\zeta = X_B/X_A$. X_A and X_B are the volume (or atomic) fractions of the two coexisting phases A and B having the average concentrations x_A and x_B, respectively. B is the phase with the deeper average potential. The CB and VB belong to the different phases, i.e., the electrons in the CB are constrained in ranges of the A phase, n, and the electrons in the VB are constrained in ranges of the B phase, n_V. While in the metallic regime, the ED in the CB, n, is identical with the ED in the A phase, the ED in the VB (n_V) is only part of all the electrons in the B phase (with the ED n_r): another part of n_r occupies trap states in the B phase (as far as available below E_F) leading to electron localization; n_V can be essentially smaller than n_r.

Since $n < n_A < n_0 < n_r$ for $x_A < x < x_B$, there are long-range electron-density fluctuations (LEDF) correlated with the concentration fluctuations caused by phase separation. A measure for the LEDF is $\delta n = n_r - n = (1 + \zeta^{-1})(n_0 - n)$. Equation (15b) is the result of an energy balance, where β depends essentially on the average potential difference between the phases A and B, $\overline{\Delta V}$, and indirectly on the potential difference of the different atomic sorts in the two phases. The larger $\overline{\Delta V}$ the larger β in Eq. (15b). The described physical model is also assumed to apply to a-$T_{1-x}M_x$ alloys, on principle, if phase separation is realized. In this case, occupation of the d band is expected to be changed by this electron redistribution as well, as far as incompletely occupied. If the two phases form infinite clusters and if CB and VB are incompletely occupied, both CB and VB can contribute to the electronic transport and the contribution of the VB can be described as a shunt resistor in parallel to the CB. Positive Hall coefficients are expected, when the contribution of the holes in the incompletely occupied VB dominate compared with those of the CB. Activation of electrons from the B to the A phase with increasing temperature can lead to negative TCR which is expected to be correlated with the thermopower regarding sign and amount.

The results of this paper support the valuation by Mazurin: "I am sure that the scientific community have lost interest to metastable phase separation too early."[53]

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surements by Tanaka *et al.* (Ref. 29) result in a considerable fraction of Mp states separated from Ms states (see also Refs. 32, 33, and quotations in Ref. 29).

[42]The term "measure" for LEDF is used, since the formulas applied in Sec. II refer to homogeneous materials and it is not yet clear whether n is the true or some "effective" ED in the A phase. This problem will be considered later [Eqs. (19) and (20)].

[43]This localization is due to occupation of trap states in the B ranges; it is not a disorder effect in Anderson's sense (Refs. 5 and 8).

[44]Johnson and Williams (Ref. 45) suggest for several melt-quenched a-$T_{1-x}M_x$ alloys with $T=$Mo,W,Ru,..., and $M=$Si,B,..., "that an ideal amorphous phase forms at a specific composition" corresponding to our $\hat{x}$ "and that this phase has a well-defined atomic short-range order" (Ref. 45, p. 1640). Thus, an amorphous one-phase structure with $x<\hat{x}$ can be interpreted as "a nonstochiometric metallic glass containing a deficiency of metalloid atoms" accomodating "this deficiency through a structure characterized by excess volume in the same manner that nonstoichiometry in many intermetallic compounds is accomodated by vacancy formation" (Ref. 45, p. 1647).

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[51]In a separate paper the proposed model will be applied to granular metals and (transition-metal-free) metal-metalloid mixtures.

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