Coexistence of metallic and activation conductivities in metallic glasses

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It is found that the temperature dependence of the electrical conductivity of metallic glasses can be approximated by an equation with the general form $\sigma(T) = \sigma_0 + A \exp(-B/T^n)$. (1) High accuracy and mathematical stability of the description are achieved with $n = 1/2$.

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We studied a specimen of the amorphous alloy $Zr_{75}Rh_{25}$ with dimensions $6.5 \times 2.14 \times 0.037$ mm in the temperature range 4.2–298 K. For the measurements of electrical resistance, we used a four-contact scheme with clamped iridium point-contacts. Special measures allowed us to measure the resistance with a relative error not exceeding $1 \times 10^{-3}\%$ and with the temperature remaining constant at any point in the region to within ± 0.01 K during the course of the measurement.

The data obtained by us are shown in Fig. 1 by the open circles. It is evident that in nearly the entire temperature range studied, a negative temperature coefficient of resistance (TCR) is observed in the amorphous alloy $Zr_{75}Rh_{25}$. The drop in the electrical resistance in the low-temperature range is related to the onset of superconducting condensation.[1]

It is well known that for this set of experimental points, with a certain number of adjustable parameters, the accuracy of the description can be quite high for an entire

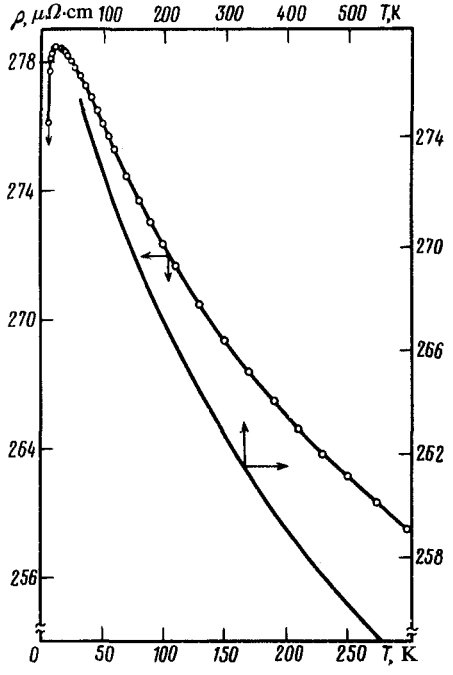

FIG. 1. Temperature dependences of the electrical resistivity of amorphous alloys $Zr_{75}Rh_{25}$ (O) and $Be_{40}Ti_{50}Zr_{10}$ (—).[3]

series of physically possible regression equations. For this reason, in order to distinguish them, we used a special procedure for processing the data with the help of a computer, involving a search for mathematically stable solutions, i.e., solutions such that the regression coefficients are independent of the number of points chosen in the interval of description to within the statistical spread. The analysis was repeated for values of the coefficient $n = 1/4$, $1/2$, and 1, according to presently existing models.[2]

The magnitudes and behavior of the coefficients in Eq. (1) σ_0, A, and B, as well as the linear correlation coefficient r and the mean-square error s as a function of the number of points processed in the temperature range 12–298 K are shown in Fig. 2 in the form of histograms (as the number of points is increased, the temperature range widens into the low-temperature range).

It is evident that in spite of the possibility of obtaining a satisfactory approximation for any $n = 1/4$, $n = 1/2$, and $n = 1$ (the maximum error in this case constitutes 0.15%), a stable description is obtained only with $n = 1/2$ in the temperature range 35–298 K. The maximum error in this case is 4×10^{-3}% and approaches the experimental error. The variation in the coefficients with a small number of points, on the left side of the histogram 2b, is due to the regular statistical spread.

The data on the temperature dependence $\rho(T)$ in the metallic glass $Be_{40}Ti_{50}Zr_{10}$, available in the literature, were also analyzed in an analogous manner.[3] This dependence is shown in Fig. 1 by the solid line. The best description was achieved in the

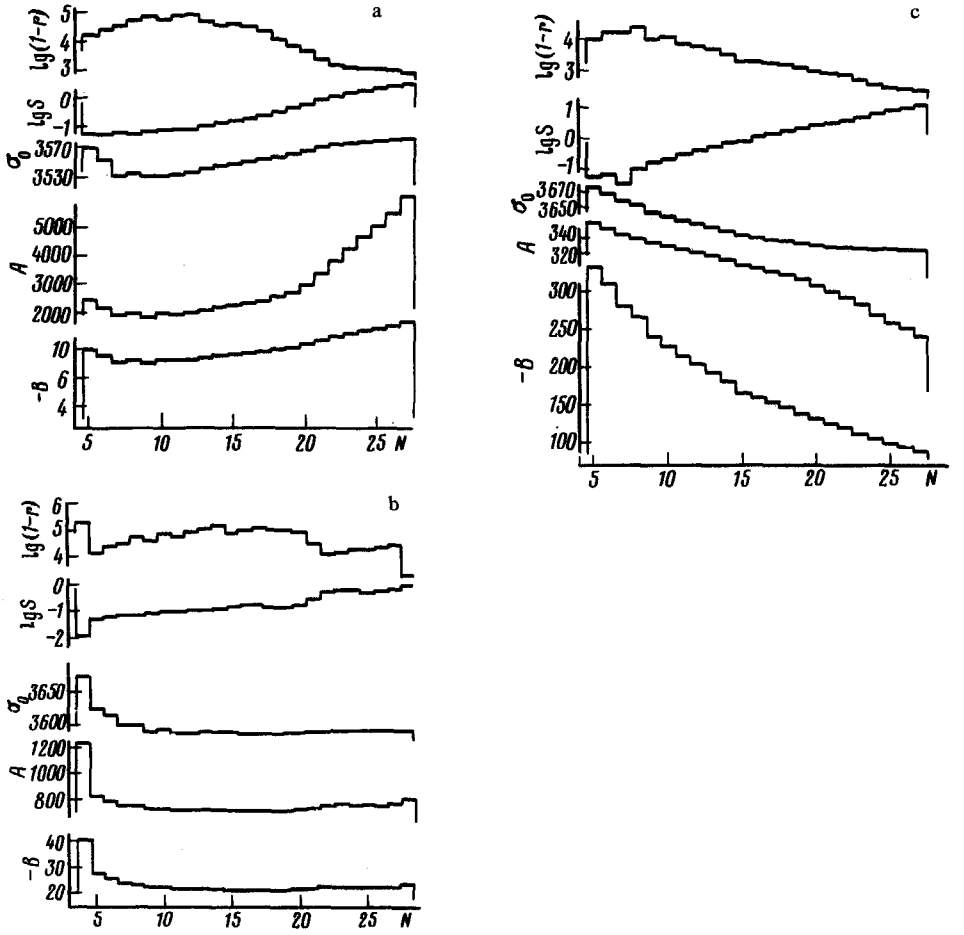

FIG. 2. Variations of the coefficients σ_0, A, and B in expression (1), of the correlation coefficient r, and of the mean-square deviation s as a function of the number of experimental points included in the optimization for the following cases: a) $n = 1/4$, b) $n = 1/2$, c) $n = 1$.

range 50–550 K also with $n = 1/2$. It also was mathematically stable in the interval described. Both dependences are shown in Fig. 3 in coordinates $\ln(\sigma - \sigma_0)$ versus $T^{-1/2}$.

A characteristic feature of expression (1) is the coexistence, in the form of a sum, of a temperature independent metallic contribution σ_0 and an activation-type contribution. Qualitatively, the suitability of sums for the description of experimental dependences $\rho(T)$, which have negative TCR, was observed previously in compounds with variable valence SnB_6,[4] in disordered crystalline titanium alloys,[5] and in metallic granular films.[6] It has now been observed in metallic glasses. In addition, a systematic quantitative analysis has been performed, here probably for the first time, on determining the index n, and the expression

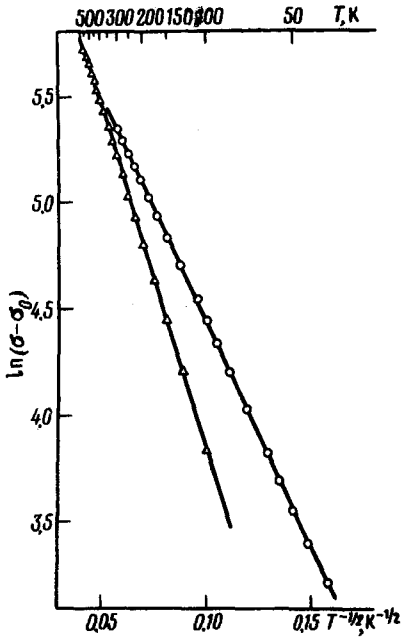

FIG. 3. The dependence $\ln(\sigma - \sigma_0)$ as a function of $T^{-1/2}$. The lines correspond to the calculation using expression (2). O are the measured values for $Zr_{75}Rh_{25}$; Δ refer to the experimental curve for $Be_{40}Ti_{50}Zr_{10}$.[3]

$$\sigma(T) = \sigma_0 + A \exp(-B/T^{1/2}) \tag{2}$$

can be viewed as an empirical law for the temperature dependence of the electrical conductivity of metallic glasses.

There is now a simple explanation for the fact that $n \neq 1$ and that $n = 1/2$. This could indicate that hopping conductivity occurs with variable hopping length. In addition, inclusion of correlation effects changes Mott's $T^{1/4}$ law[2] to the Éfros-Shklovskiĭ $T^{1/2}$ law.[7] However, the single-electron homogeneous models of disordered systems do not explain the coexistence of conductivities.

On the other hand, there is a simple way to explain the co-existence of conductivities. Such a coexistence in the form

$$\sigma(T) = \sigma(0) + aT \exp(-\Delta/T) \tag{3}$$

was predicted by Abrikosov[8] for the excitonic phase of a reduced metal, arising in semimetals in the presence of several groups of carriers (several energy minima in the conduction band). The fundamental possibility of partial dielectrification of carriers for isotropic substances with high carrier density, to which metallic glasses apparently belong, was discussed by Keldysh and Kopaev (see, for example, Ref. 9).

A compromise could be facilitated by the following circumstance. It has not been ruled out that metallic glasses are spatially inhomogeneous systems. The sum of conductivities and the $T^{1/2}$ law that we observed in these materials were observed pre-

viously by McLean *et al.*[6] in an intermediate state of metal-insulator granular systems. With all of the apparent diversity of metallic glasses and granular metals, there are indications that these materials belong to a single class: they are particularly nonequilibrium materials. Evidence for their morphological generality will be discussed in greater detail in a subsequent paper.

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