Low-temperature anomalies in the resistance of metallic glasses

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An expression has been derived for the temperature dependence of the resistance of metallic glasses of the metal-metalloid type at low temperatures. The inhomogeneity over the volume has been taken into account. The results are compared with experimental data.

The resistance of several amorphous metal alloys (metallic glasses) exhibits an anomalous behavior. Specifically, at low temperatures (usually, $T \lesssim 20$ K) the resistance R increases with decreasing temperature, and the derivative $|dR/dT|$ also increases as $T \to 0$. Several aspects of this phenomenon, primarily its insensitivity to the presence of a magnetic order in the amorphous alloys and to the imposition of an external magnetic field, cannot be explained by the existing models. Furthermore, as was pointed out in §10 of the review in Ref. 1, the mechanism responsible for these anomalies remains an open question. We should also mention that the existing theories, which predict the appearance of an anomalous term $\Delta R(T)$ in the total resistance and which give a qualitative explanation of the low-temperature resistance anomalies, describe the experimental data only in a narrow temperature interval, as was demonstrated in Ref. 2. It has been pointed out repeatedly that the experimental data can be described best by a function $\sigma(T) = \sigma_0 + \Delta\sigma(T)$, where σ_0 is the metallic conductivity of the disordered alloy, which depends only weakly on the temperature, and $\Delta\sigma(T)$ is a thermally activated component.[2,3] Despite the high accuracy which has been achieved in the description of the experimental results by these sums, the mechanism

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responsible for the coexistence of metallic and activated conductivities remains an unresolved question.

In the present letter we offer a model which links the anomalies in $R(T)$ with structural features of the metallic glasses. The following circumstances underlie this model: First, studies of the structure of the amorphous alloys by small-angle neutron scattering[4,5] reveal the existence of small regions (clusters) in which the components of the alloy deviate from their average concentrations over the volume. In other words, a substantial volume nonuniformity of metallic glasses was observed experimentally for the first time. Second, the low-temperature anomalies of metallic glasses are observed for the most part in metal-metalloid systems and not in metal-metal alloys. It might be suggested that clusters containing an excess of the metalloid become insulating at $T=0$, and the measurement current does not flow through them. This would explain the observed increase in R with decreasing temperature, which is described by a thermally activated component and which is not affected by an external magnetic field or the appearance of a magnetic order in the alloy. We should point out that it is necessary to distinguish this phenomenon, which is observed at low temperatures, from the negative temperature coefficient of the resistance which is observed over a broad temperature range and which is associated with a temperature dependence of a structure factor (the Ziman model). In the Ziman model, the derivative dR/dT may be either positive or negative, but in the limit $T\to 0$ the magnitude $|dR/dT|$ also vanishes.[6] When summed with the anomalous low-temperature term ΔR the Ziman term leads to the familiar minimum or inflection point on the $R(T)$ curve.

Let us consider a binary alloy $A_{1-\bar{x}}B_{\bar{x}}$ where A is a metal and B a metalloid. The nonuniformity over the volume can be described by means of a distribution $p(x)$ of the quantity x around the mean value for the given alloy, $\bar{x}$. Since the alloy becomes a semiconductor with increasing concentration of the metalloid, i.e., as $x\to 100$ at. % (a situation of this sort is real in specifically a glass, in which an alloy can exist in a single "phase" of the glass over a very wide concentration range), a nonvanishing probability for the appearance of regions with an activated conductivity arises in metallic glasses. For these regions the relation $\eta=\mu-E_g<0$ (Fig. 1), where μ is the chemical poten-

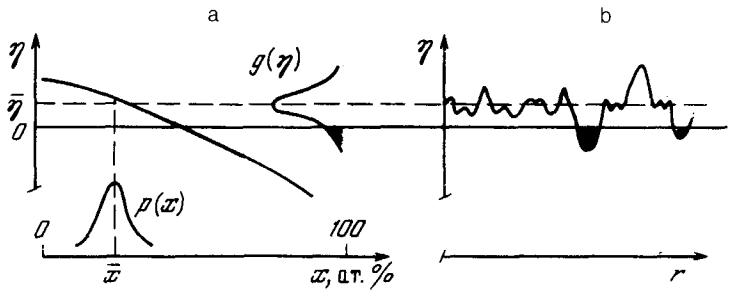

FIG. 1. The quantity $\eta=\mu-E_g$ (μ is the chemical potential, and E_g is the bottom of the conduction band) versus (a) the concentration of the components in $A_{1-x}B_x$ alloys and (b) the coordinate along the sample, r. The hatched regions correspond to regions with an activated conductivity.

tial, and E_g the bottom of the conduction band. A transition from a glassy metallic phase to a glassy semiconducting phase has been observed in $Pd_{1-x}Si_x$ alloys studied by the method of photoelectron spectroscopy, at $x \approx 90$ at. %. The electron state density at the Fermi level, which is proportional to the discontinuity in the photoelectron intensity at $E = E_F$, decreases smoothly with increasing x (§9 in Ref. 1). This result is evidence that the quantity $\eta = \eta(x)$ is a smooth function of the concentration in amorphous alloys. Consequently, under the assumption of a normal distribution $p(x) \propto \exp[-(x-\bar{x}/\beta)^2]$, we also have a functional dependence $g(\eta) = 1/\delta\sqrt{\pi}\exp[-(\eta-\bar{\eta})^2/\delta^2]$, for the probability for the quantity η, where $\bar{\eta}$ is the mean value of η for the given alloy, which is determined by $\bar{x}$, and δ^2 is the variance of the distribution. Regions with $\eta < 0$ (the hatched regions in Fig. 1) have an activated conductivity $\Delta\sigma(\eta) \propto \exp(\eta/T)$. Since the contribution of the semiconducting regions to the total conductivity is small, i.e., since the relative size of the low-temperature anomalies satisfied $\Delta\sigma/\sigma_0 \sim 10^{-3} \ll 1$ and constitutes a small increment in the metallic conductivity, we can deal with it by taking a sum over all regions with $\eta < 0$:

$$\frac{\Delta\sigma}{\sigma_0} = \int_{\eta<0} g(\eta)\exp(\eta/T)d\eta = \frac{1}{2}\left[1 - \phi\left(\bar{\eta}^* + \frac{1}{2T^*}\right)\right]\exp\left[\frac{1}{T^*}\left(\bar{\eta}^* + \frac{1}{4T^*}\right)\right],$$

where $\phi(z) = (2/\sqrt{\pi})\int_0^z \exp(-t^2)dt$, $\bar{\eta}^* \equiv \bar{\eta}/\delta$, $T^* \equiv T/\delta$, and σ_0 is the conductivity of the metallic regions with $\eta > 0$. Using the expansion $\sqrt{\pi}/2[1-\phi(z)] \approx \exp(-z^2)/2z$ at $z \gg 1$ (this case corresponds to low temperatures), we find

$$\frac{\Delta\sigma(T)}{\sigma_0} = \frac{1}{2\sqrt{\pi}\left(\bar{\eta}^* + {}^1/_{2T^*}\right)}\exp(-\bar{\eta}^{*2}).$$

Since we have $(\Delta\sigma/\sigma_0) \approx (\Delta R/R_0) \ll 1$ for metallic glasses, the $R(T)$ dependence at low temperatures takes the form

$$R(T) = R_0 - \Delta R\frac{T}{T+\xi}, \qquad (1)$$

where $\xi = \delta^2/2\bar{\eta}$, $\Delta R/R_0 = 1/2\sqrt{\pi}\bar{\eta}^*\exp(-\bar{\eta}^{*2})$. Figure 2 shows the results of measurements of[2] $R(T)$ for two metallic glass samples, differing in the concentration of the metalloid: I–$Ni_{60}B_{40}$; II–$Fe_{81.8}Mn_{1.6}B_{16.6}$. Also shown here are theoretical curves plotted from expression (1) with the following parameter values: I–$R_0 = 333.1$ $\mu\Omega\cdot$cm, $\Delta R = 1.60$ $\mu\Omega\cdot$cm, $\xi = 19.1$ K; II–$R_0 = 137.416$ $\mu\Omega\cdot$cm, $\Delta R = 0.596$ $\mu\Omega\cdot$cm, $\xi = 0.46$ K. We see that function (1) describes the experimental data over a wide temperature range. The deviation of the points from the curve for sample II stems from the small value $\xi = 0.46$ K and the need to incorporate the next term in the expansion for $\phi(z)$ at $T \gg \xi$. The quantity $\Delta R/R_0$ in equal to the ratio of the volume of the semiconducting clusters to the total volume of the sample, and we have $\Delta R/R_0 \approx 5\times10^{-3}$ for both samples. We thus find (for sample I) $\bar{\eta} = 132$ K and $\delta = 71$ K and (for sample II) $\bar{\eta} = 3.25$ K and $\delta = 1.73$ K.

The small values found for $\bar{\eta}$ agree with the model of Ref. 7, where it was pointed out that if the Fermi energy lies at a minimum of the state density, there should be an

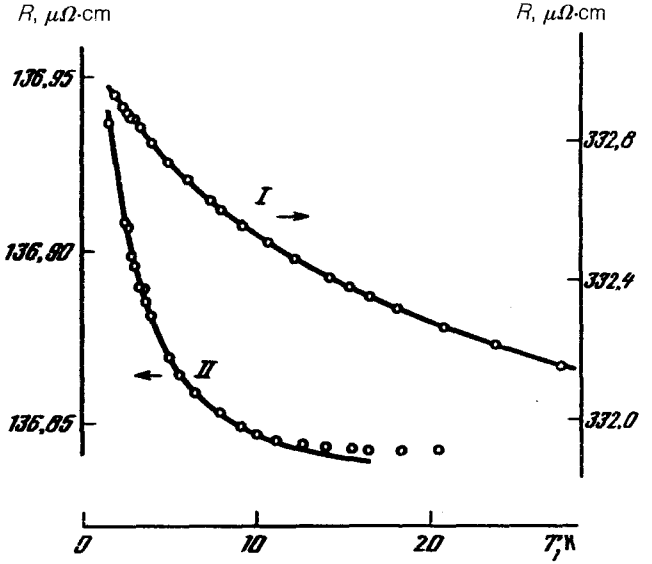

FIG. 2. Temperature dependence of the resistance, $R(T)$, for two metallic glass samples, I and II. The curves are plotted from expression (1). The values of the constants are given in the text proper.

elevated stability with respect to crystallization. That model also agrees with the values found for $\bar{\eta}$ and δ for alloys I and II. For sample II, whose composition is close to the stablest alloy, of the $A_{80}B_{20}$ type, the values of $\bar{\eta}$ and δ are substantially smaller than those for sample I, with 40 at. % of boron. The increase in δ with increasing concentration of the metalloid is evidence of a blurring of the band edge due to a nonuniformity of the glasses. The quantity $\bar{\eta}^* = \bar{\eta}/\delta \simeq 2$ remains essentially constant.

In order to correctly analyze the relationship between the structural irregularities in glasses, on the one hand, and the low-temperature resistance anomalies, on the other, it would be worthwhile to measure the dependence $R(T)$ of a series of $A_{1-x}B_x$ alloys over a wide x interval. It would thus become possible to find curves of $\bar{\eta}(x)$ and $\delta(x)$, which would characterize the structure and electronic properties of the glasses.

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