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THE ELECTRICAL RESISTIVITY AT LOW TEMPERATURES AND DURING TRANSITION TO CRYSTALLINE STATE AND THE SEEBECK COEFFICIENT OF METAL GLASSES

J. VAJDA[1], P. ŠVEC[2], Š. VARGA[1], J. KREMPASKÝ[1], Bratislava

Some low-temperature anomalies in the temperature dependence of electrical resistivity in metal glasses were calculated on the basis of the theory of the modified relaxation time. The theory also enables to explain the temperature dependence of the Seebeck coefficient and both its signs. A simple mechanism of the electrical resistivity change during transition to the crystalline state is presented. A way of a more realistic approach to the model is suggested in the discussion.

НИЗКОТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ ЭЛЕКТРИЧЕСКОГО УДЕЛЬНОГО СОПРОТИВЛЕНИЯ И КОЭФФИЦИЕНТА ТЕРМОЭЛЕКТРОДВИЖУЩЕЙ СИЛЫ В ПРОЦЕССЕ КРИСТАЛЛИЗАЦИИ МЕТАЛЛИЧЕСКИХ СТЕКОЛ

В работе на основе модели модифицированного времени релаксации рассчитаны некоторые низкотемпературные особенности электрического сопротивления металлических стекол. Модель позволяет также объяснить температурную зависимость коэффициента термоэлектродвижущей силы одновременно с его знаками. Кроме того, предложен простой механизм изменения электрического сопротивления в процессе кристаллизации. Обсуждается также попытка сделать модель более реалистичной.

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I. INTRODUCTION

Metal glasses represent solids which make it possible to investigate theoretically and experimentally, the influence of the absence of long-range order on various transport properties. The most important feature of these materials in comparison with universally known glasses is a substantial content of metallic elements.

[1] Dept. of Physics, Faculty of Electrical Engineering, Slovak Technical University, Gottwaldovo nám. 19, 812 19 BRATISLAVA, Czechoslovakia.
[2] Inst. of Physics of the Centre of Electro-Physical Research, Slovak Academy of Sciences, Dúbravská cesta, 842 28 BRATISLAVA, Czechoslovakia.

Analysis of several experimental data suggests that, in spite of the nonexistence of crystalline structure, metal glasses retain all typically metallic properties.

Electrical transport properties of metal glasses are no exception from the mentioned rule, e.g. the temperature dependence of mean electrical resistivity $\varrho(T)$ has a typically metallic character, although it presents some unusual common traits like a low temperature coefficient of resistivity of both signs and several others. One of the most discussed subjects is the origin of a minimum in the temperature dependence $\varrho(T)$ of certain metal glasses. In contrast with the discovery of this phenomenon in crystalline alloys there are several definite distinctions discussed in more detail in [1]. This has been the reason of some new theories suggesting the structural origin of this anomaly [1, 2] differing from a group of theories of a resistivity minimum based on magnetic dispersion mechanisms.

The theoretical model of the temperature dependence of metal glass resistivity was proposed and analysed in [1]. Comparison of theoretical predictions with known experimental results showed the possibility of the model to explain general traits of the $\varrho(T)$ dependence of metal glasses as well as a great number of anomalies observed in some types of glasses. It is remarkable that the model enables us to explain also a so-far unknown anomaly, the so-called "jumps" in the low -temperature dependence of $\varrho(T)$.
These facts stimulated a further analysis of the model. The authors present results of theoretical calculations which are continuations of [1]; in the following there are results for 1) the low-temperature part of the curve $\varrho(T)$ with emphasis on the already mentioned resistivity "jumps" minima and maxima, 2) the temperature dependence of the Seebeck coefficient of metal glasses and 3) resistivity-time curves representing a simulation of the transition to the crystalline state.

Applications of a more realistic approach to calculations of the $\varrho(T)$ curves of metal glasses within the framework of the proposed model are analysed in the discussion.

II. THEORY

Characteristic features of the theoretical approach are explained in [1]. The theory is based on the idea of the so-called modified relaxation time. Formulae for calculation of different transport coefficients are formally similar to those well -known from the theory of crystalline solids. Thus for mean electrical resistivity there holds

$$\varrho=\frac{m}{ne^2}\frac{1}{\langle\tau\rangle} \tag{1}$$

and for the Seebeck coefficient $\alpha(T)$

$$\alpha=\frac{1}{eT}\left(\frac{\langle E\tau\rangle}{\langle\tau\rangle}-E_F\right), \tag{2}$$

where m is the effective mass, e the charge, E the energy and n the concentration of electrons; T is the temperature, E_F the Fermi energy and τ the relaxation time of scattering. The symbol $\langle\rangle$ will be explained below.

The dispersion on both thermal oscillations and impurities was considered in the calculations. Disorderliness of structure was taken into account by introducing rectangular potential barriers through which electrons either tunnel or are dispersed by them. The approach in [1] thus gives for the relaxation time in metal glasses the relation

$$\tau(E,T)=\tau_{cryst.}(E,T)\frac{1}{1+\frac{l_k(E,T)}{d}\frac{1-Q(E)}{Q(E)}} \tag{3}$$

where $\tau_{cryst.}$ is the "crystalline" relaxation constant, l_k the mean free path of charge carriers, d is the distance between barriers and

$$\begin{aligned} Q(E)&=\exp\left(-\frac{2\pi}{\hbar}d_B\sqrt{W-E}\right) \quad &\text{for } E<W\\ Q(E)&=1 &\text{for } E\geq W \end{aligned} \tag{4}$$

is the transition probability for the rectangular barrier of height W and thickness d_B.

III. ELECTRICAL RESISTIVITY AT LOW TEMPERATURES

The analysis of the given formulae was done on a digital computer, as the symbol $\langle\tau\rangle$ is represented by the integral [3]

$$\langle\tau\rangle=E_F^{-3/2}\int_0^\infty E^{3/2}\tau(E)\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E, \tag{5}$$

which, due to the presence of the Fermi–Dirac distribution f_0 cannot be evaluated analytically.

Fig. 1a shows a typical example of the "jumps" in the $\varrho(T)$ curve of metal glasses. In contrast with the preceding publication [1] it was demonstrated that this "jump" is part of a complicated anomaly observed only recently at low temperatures in the metal glass of the $Fe_{20}Pd_{60}Si_{20}$ type [4]. It is obvious from Fig. 1b that the model provides at low temperatures an unusually sharp and relatively deep extreme, which, however, could only be obtained by a proper choice of model parameters. As in [5] it was shown that the model accounts for a number of other unknown irregularities in the dependence $\varrho(T)$ of metal glasses; some of these have already been experimentally observed [12].

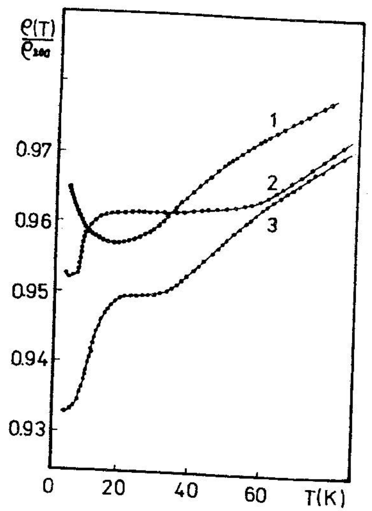


Fig. 1a. Experimental temperature dependence of electrical resistivity of metallic glass $Co_{15}Pd_{65}Si_{20}$. (1) – unannealed sample, (2) – sample annealed for 2 h at 150 °C, (3) – sample annealed for 2 h at 250 °C. Full circles represent the measured values. (According to Ref. [1]).

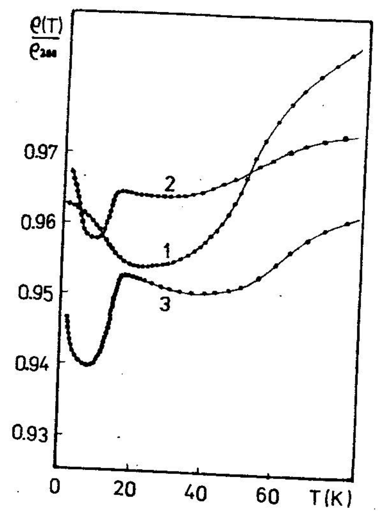


Fig. 1b. $\varrho(T)$ calculated for input parameters $T_x = 300$ K, $R = 1.5\times10^{-16}$s, $d = 1$ nm. (1) – $E_F = 7.5$ eV, $W = 8$ eV, $d_B = 1$ nm; (2) – $E_F = 9.2$ eV, $W = 10$ eV, $d_B = 0.5$ nm; (3) – as (2), $d_B = 0.25$ nm. Full circles represent the calculated values of ϱ at the temperature T. Parameter T_x denotes the temperature at which the phonon and impurity scattering mechanisms equally contribute to $\varrho(T)$ and thus there is $R = \tau_{phonon}(E_F, T_x) = \tau_{impurity}(E_F, T_x)$.

Figs. 2a and 3a represent two other low temperature anomalies: a minimum and a maximum in $\varrho(T)$. While the first of these is well known from numerous experimental measurements, the resistivity maximum has only rarely been observed [6]. The appearance of the resistivity maximum in metal glasses has not been satisfactorily explained so far by any other theory.

IV. THE SEEBECK COEFFICIENT $\alpha(T)$

Up to date there exist only a few experimental data about the temperature dependence of $\alpha(T)$ in metal glasses. Some characteristic experimental curves for $\alpha(T)$ are schematically drawn in Figs. 4a, 5a [7, 16]. It thus becomes apparent that relatively very small Seebeck coefficients of both signs have been observed.

Relation (2) provides for the Seebeck coefficient within the framework of the modified relaxation time theory curves depicted in Figs. 4b, 5b. Comparing with Figs. 4a, 5a one can see good agreement with experiment.

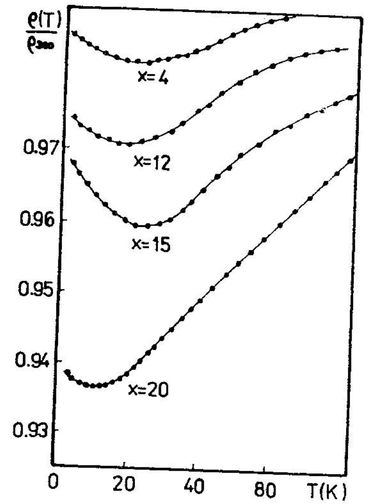


Fig. 2a. Resistivity minimum in metallic glasses $Pd_{80-x}Co_xSi_{20}$. Experimental dependence taken from Ref. [15].

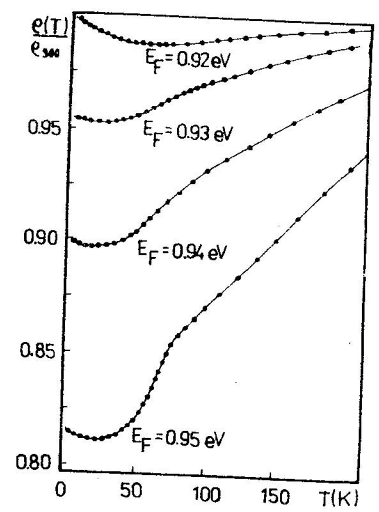


Fig. 2b. $\varrho(T)$ calculated for various E_F. Input parameters: $W = 1.0$ eV, $R = 10^{-15}$ s, $d_B = d = 1$ nm, $T_x = 120$ K. Full circles represent the calculated values of ϱ at the temperature T.

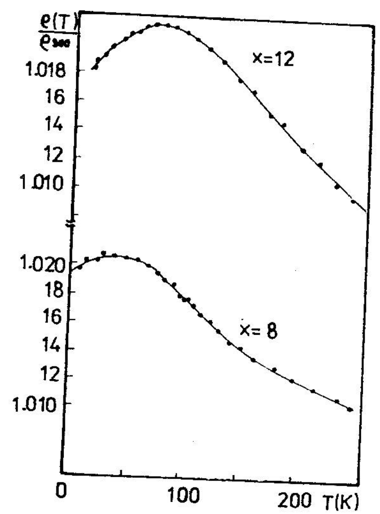


Fig. 3a. Resistivity maxima observed on amorphous $Zr_{40}Cu_{60-x}Fe_x$ [14].

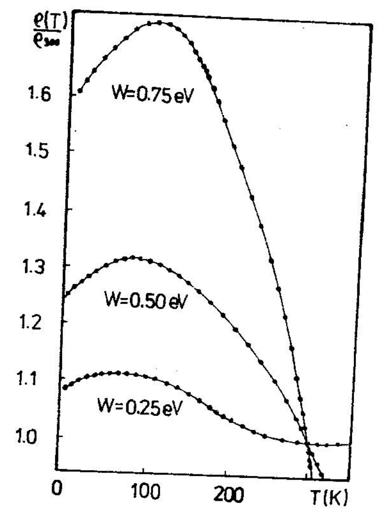


Fig. 3b. Influence of W on $\varrho(T)$ calculated for input parameters $E_F/W = 0.92$, $d_B = d = 1$ nm, $R = 8\times10^{-15}$s, $T_x = 90$ K. Full circles represent the calculated values of ϱ at the temperature T.

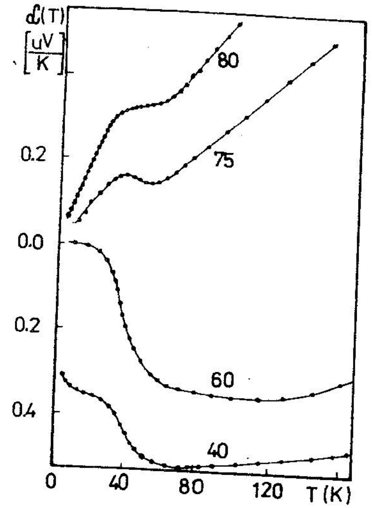
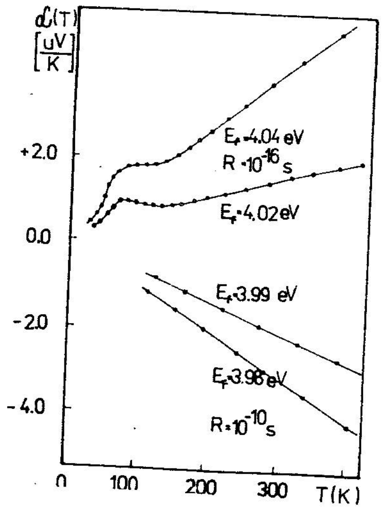


Fig. 4a. Thermopower $\alpha(T)$ for amorphous thin film SnCu (drawn schematically). Numbers denote percentual content of Cu in samples [16].



4b. $\alpha(T)$ of both signs calculated for $W=4$ eV, $d_B = d = 1$ nm, $T_x = 1$ K. Full circles represent the calculated values of α at the temperature T.

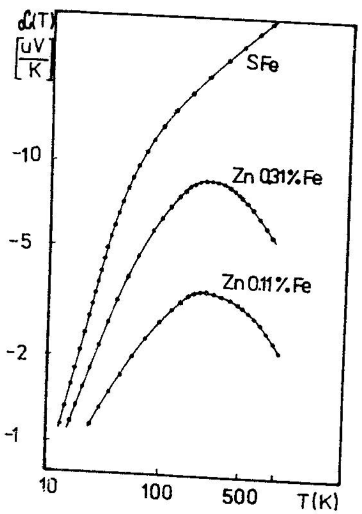


Fig. 5a. Temperature dependences of thermopower measured in various amorphous samples (drawn schematically according to [7]).

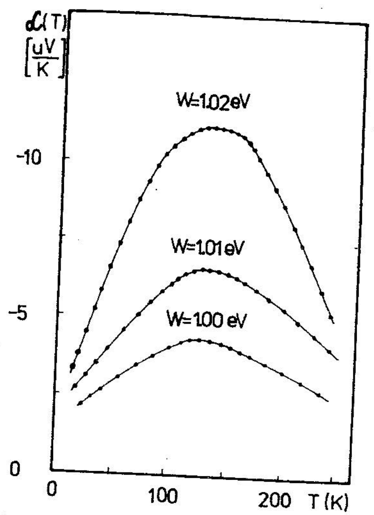


Fig. 5b. Influence of W on the shape of theoretical $\alpha(T)$ – curve. Calculated points (full circles) for input parameters $E_F = 1$ eV, $R = 10^{-15}$s, $T_x = 1$ K, $d_B = d = 1$ nm.

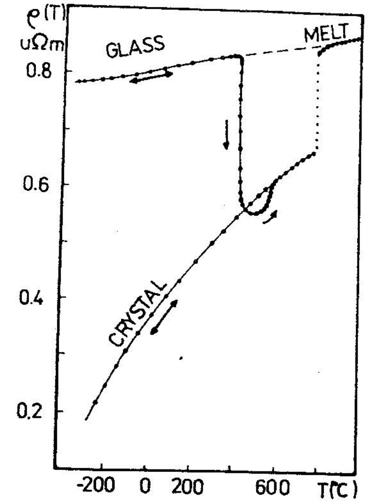


Fig. 6a. Temperature dependence of electrical resistivity of metallic glass $Pd_{80}Si_{20}$ during glassy-to-crystalline phase transition. Linear heating regime 1.5 K/min. [8].

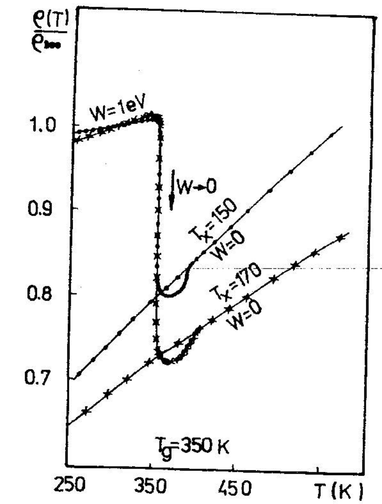


Fig. 6b. The calculated $\varrho(T)$ – curve for various values of parameter T_x at high temperatures. For $T = T_x$ the numerical values of barrier height W start to decrease continously. For low W the calculated points of ϱ (dots and crossed dots) lie below the points corresponding to the case without barriers ($W=0$). The case $W=0$ represent the crystalline state.

V. ELECTRICAL RESISTIVITY DURING TRANSITION TO CRYSTALLINE STATE

The least coped with theoretical problem in metal glasses has been the transition to the crystalline state. So far no theory has been able to supply satisfactory curves of $\varrho(T)$ during the initial stage of crystallization. It is, however, well known experimentally [8] that the dependence $\varrho(T)$ exihibits here a characteristic decrease (Fig. 6a) which may also consist of some "steps". Above all it is remarkable that in some metal glasses in the vicinity of transition to the crystalline state the resistivity value of glass in the process of crystallization decreases below the value of a stable crystalline phase. This observation has not been explained yet.

Accepting a simple notion that at a certain temperature the height W of our model barriers starts to decrease continuously due to crystallization, one can obtain a curve as shown in Fig. 6b; surprisingly enough, there appears an interval of temperatures with $\varrho(T)$ below the value of resistivity of the crystalline specimen. It should be noted that the decrease of the barrier height is not the only parameter which can change during the process of crystallization. The influence of changes in some other parameters on the shape of the $\varrho(T)$ curve was analysed in a previous publication [1].

VI. DISCUSSION

The fundamental problem of the presented model is to find a reason for the existence of potential barriers. Some possible dispersion mechanisms of charge carriers in metal glasses having the character of potential barriers are proposed in [1]. One of the possibilities is the assumption that metal glasses are composed of basic "structural units" -the so-called icosahedral microclusters [9], separated from each other by less ordered regions which, from the point of wiev of electron transport appear as potential barriers. This situation could be modified further by another possibility: addition of a certain amount of "magnetic" impurity to a non-magnetic alloy might allow for the tendency to form regions rich in this impurity [10]. The interface between these magnetic clusters and a surrounding matrix could have the character of an obstacle similar to a potential barrier.

Due to the fact that the used value of height W of potential barriers has been relatively high, there has been an attempt at "lowering" the value W. The relation (4) supposes that for electron energies $E \geqq W$ the electron does not "feel" the presence of barriers. A more realistic approach allows for the dispersion of electrons at the barriers even for $E \geqq W$. Quantum mechanics give the appropriate relation for $Q(E)$ describing this case in the form

$$Q(E) = \frac{1}{1 + \dfrac{W^2 \sin^2 \beta\, d_B}{4E(E-W)}}, \qquad \beta = \sqrt{\frac{2m(E-W)}{\hbar^2}}. \tag{6}$$

A detailed analysis has shown [11] that all above-mentioned curves remain principally unchanged by the introduction of rel. (6); the value of W at which several extremes in $\varrho(T)$ start to appear, however, is by 30 – 40 % lower than in the preceding cases. Another way is a different choice of the shape or a change in the width d_B of the potential barriers. Thus one can see that there are various ways of making these model assumptions more realistic.

VII. CONCLUSION

The analysis of the model approach has shown that it is possible to explain satisfactorily several anomalies in the dependence $\varrho(T)$ of metal glasses within the framework of the proposed model. The paper also presents the first attempt to simulate the resistivity change during the transition of the metal glass to the crystalline state. The theory has also been successful in the case of the temperature dependence of the Seebeck coefficient $\alpha(T)$ as it enables to explain the shape of

the curves as well as both signs of $\alpha(T)$. A more realistic approach to the model has also been suggested.

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