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# ELECTRICAL TRANSPORT IN GLASSY Zr-3d ALLOYS

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Superconducting transition temperature, magnetic susceptibility and electrical resistivity of Zr-3d glassy alloy systems has been measured. The above properties are closely connected with the electronic structure of these alloys. Almost linear decrease of the magnetic susceptibility, temperature of the superconducting transition and the constant of the electron-photon interaction 1 with the concentration of 3d element show that the electronic density of states at the Fermi level is dominated with Zr d-states. These results are simply explained with the dilution effect due to increase of the concentration of 3d element. This claim has been verified with the results of the UPS experiments performed on Zr-3d alloys, and is also supported with the analysis of temperature dependence of the electrical conductivity. The calculation has shown that the electrical resistivity of glassy Zr-3d alloys can not be explained within the framework of the classical extended Ziman theory only.

## *1. Introduction*

Recently, glassy alloys of early transition metal-late transition metal type have been subject of considerable research interest. The reason for that is a wide composition range over which one can achieve the glassy state and can therefore investigate in some details influence of the individual constituent on physical properties of these alloys. The photoemission experiments[1)] have shown that Zr d-band lies very close to the Fermi surface since 3d states have much higher binding energies than Zr-4d states. Therefore the contribution of 3d constituent is rather small and the electronic density of states at the Fermi level is mainly determined by zirconium.

We have investigated over sufficiently wide composition range the following glassy Zr-3d alloy systems: $Zr_{100-x}Cu_x$ $(26 < x < 71)$, Zr, $Zr_{100-x}Ni_x$ $(22 < x <$

63) and $Zr_{100-x}Co_x$ ($19 < x < 35$). Few alloys with Fe addition have also been investigated.

## 2. Experimental

The amorphous Zr-3d alloys were prepared by melt-spinning in air. The samples were ribbons 2 to 4 mm wide, 30 to 50 $\mu$m thick and were cut into pieces 30 to 50 mm long for subsequent measurements. The glassy nature of the ribbons was checked by the X-ray diffraction.

The electrical resistance in the temperature range from 1.5 K to 300 K, the superconducting transition temperature $T_c$, the room temperature magnetic susceptibility and the temperature coefficient of resistivity at room temperature have been measured. The electrical resistivity was measured with the potentiometric technique with an accuracy of 5 ppm. The voltage and current contacts were made by spot welding the platinum wires of thickness 50 $\mu$m onto the samples. The magnetic susceptibility has been measured with the Faraday method on samples weighing few milligrams[2)].

## 3. Results and discussion

The temperature dependence of electrical conductivity of selected Zr-Ni, Zr-Cu and Zr-Co glassy alloys is shown on Fig. 1. Because of convenience the change in conductivity $\Delta\sigma = \sigma_T - \sigma_0$ ($\sigma_T$ is conductivity at temperature $T$, and $\sigma_0$ expected conductivity at $T = 0$ K obtained by the extrapolation of the low temperature variation) is shown. Since in our alloys the electronic mean free path is very short, we expect the contribution of the incipient localization to the temperature dependence of the electrical conductivity[3)]. The change in conductivity due to incipient localization is proportional to $(D\tau)^{-1/2}$ ($D$ is the diffusion constant, and $\tau$ is the time of the phase coherence). We expect that $\tau$ is in fact the inelastic scattering time, and in non-magnetic disordered alloys it is determined by the electron-phonon interaction. Above the Debye temperature (in practice usually above $\theta_D/3$) $\tau_i^{-1} \sim T$, and at lower temperatures $\tau_i^{-1} \sim T^2$. As the electron-phonon interaction determines $\tau_i$, we expect a linear dependence of conductivity with $T$ at lower temperatures and as $T^{1/2}$ at higher temperatures. Apparently, these predictions are in qualitative agreement with the experimental data shown in Fig. 1. The electrical conductivity of our alloys at temperatures lower than 100 K increases approximately linearly with $T$, whereas at temperatures above 100 K its dependence becomes proportional to $T^{1/2}$. Furthermore we expect that the temperature dependence of the conductivity of our alloys can be quantitatively described with Fukuyama-Hoshino expression[4)],

$$\Delta\sigma(T) = a\left[3\left(b + c^2T^2\right)^{1/2} - cT - 3b^{1/2} + dT^{1/2}\right], \tag{1}$$

where $a = a^2/\pi h$, $b = (D\tau_{50})^{-1}$, $c = (4D\beta)^{-1/2}$, $\beta\tau = T^2$, $d = 0.65(1.33 - 2F^* - 0.2)(2\pi k/Dh)^{1/2}$, $F^* = x^{-1}\ln(1+x) - \lambda$, $x = (2k_F/k_0)^2$, $\lambda$ is the electron-

phonon coupling constant, and $k_0$ is the screening length. Equation (1) includes the contributions from the localization, the spin-orbit scattering and from the electron-electron scattering. We used the magnetoresistance results[5)] in order to obtain $\tau_i$ (inelastic scattering time) and $\tau_{s0}$ (the spin-orbit scattering time). The diffusion constant $D$ was calculated from Einstein relation by using the experimental data for the electrical conductivity and the density of states at the Fermi level. Indeed for $Zr_{43}Cu_{57}$ alloy by using the experimental magnetoresistance data5' and the data for the electronic density states at the Fermi level[6)] we obtained very good agreement between the measured $\Delta\sigma$ and that calculated from Eq. (1) over a wide temperature range[7)].

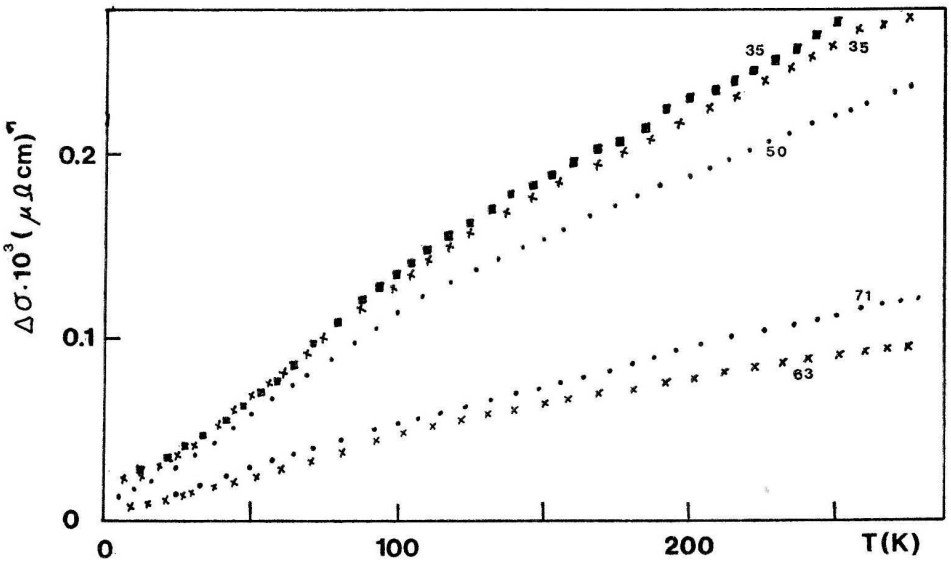


*Fig. 1. Change in electrical conductivity* $\Delta\sigma = \sigma_T - \sigma_0$ *for selected* Zr-3d *glassy alloys (*• =Zr–Cu, × =Zr–Ni, ■ =Zr–Co*) vs. temperature. Numbers denote 3d content.*

In Table 1 we list the data relevant to our alloys: $\rho_{273}$ (electrical resistivity at 273 K), room temperature coefficient of resistance $\alpha$, superconducting transition temperature $T_c$, coefficient $A$ of linear change of conductivity at temperatures below 100 K, coefficient $B$ of $T^{1/2}$ dependence of conductivity above 100 K, constant of electron-phonon interaction $\lambda$ and magnetic susceptibility at room temperature $\chi_P$. The constant of electron-phonon interaction has been calculated from the McMillan expression,

$$T_c = \frac{\Theta}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right]. \tag{2}$$

$\mu^*$ is the effective Coulomb potential which has the value 0.13. We calculated the

Debye temperature by using the experimental specific heat results. The specific heat results for Zr-Ni alloys were taken from Matsuura et al.[8], and those for Zr-Fe alloys from D. G. Onn et al.[9].

TABLE 1.

| | $10^6\ A$ $(\mu\Omega\text{cm})^{-1}$ $\text{K}^{-1}$ | $10^5\ B$ $(\mu\Omega\text{cm})^{-1}$ $\text{K}^{-1/2}$ | $B/A$ $\text{K}^{1/2}$ | $T_c$ K | $\lambda$ | $\alpha\ 10^4$ $\text{K}^{-1}$ | $\chi_p\ 10^3$ $\text{JT}^{-2}$ $\text{mol}^{-1}$ | $\rho_{273}$ $(\mu\Omega\text{cm})$ |
|---|---|---|---|---|---|---|---|---|
| $Zr_{70}Cu_{30}$ | 1.31 | 2.30 | 17.6 | 2.68 | 0.61 | -1.02 | 1.07 | 160.6 |
| $Zr_{60}Cu_{40}$ | 1.36 | 2.19 | 16.1 | 1.60 | 0.54 | -1.03 | 0.93 | 164.9 |
| $Zr_{50}Cu_{50}$ | 1.13 | 1.88 | 16.6 | 0.7 | 0.45 | -1.06 | 0.78 | 167.6 |
| $Zr_{42}Cu_{58}$ | 0.89 | 1.57 | 17.6 | 0.3 | 0.39 | -0.96 | 0.66 | 167.5 |
| $Zr_{33}Cu_{67}$ | 0.68 | 1.25 | 18.4 | 0.3 | – | -0.63 | 0.51 | 162.8 |
| $Zr_{29}Cu_{71}$ | 0.54 | 1.08 | 20.0 | – | – | – | 0.39 | 162.0 |
| $Zr_{76}Ni_{24}$ | 0.90 | 1.86 | 20.7 | 3.20 | 0.65 | -0.90 | 1.54 | 165.6 |
| $Zr_{72}Ni_{28}$ | 1.20 | 2.40 | 20.0 | 3.06 | 0.62 | -1.00 | 1.53 | 166.9 |
| $Zr_{67}Ni_{33}$ | 1.31 | 2.36 | 18.0 | 2.68 | – | -1.08 | 1.48 | 172.4 |
| $Zr_{65}Ni_{35}$ | 1.31 | 2.29 | 17.5 | 2.60 | – | -1.10 | – | 174.2 |
| $Zr_{62}Ni_{38}$ | 1.31 | 2.29 | 17.5 | 2.36 | 0.55 | -1.20 | 1.44 | 173.5 |
| $Zr_{37}Ni_{63}$ | 0.42 | 0.78 | 18.7 | 1.2 | 0.4 | -0.50 | 1.1 | 176.2 |
| $Zr_{81}Co_{19}$ | 1.68 | 2.84 | 16.9 | 3.90 | – | -1.10 | 1.81 | 162.2 |
| $Zr_{75}Co_{25}$ | 0.82 | 2.00 | 24.4 | 3.63 | – | -1.22 | 1.86 | 162.3 |
| $Zr_{67}Co_{33}$ | 0.74 | 1.85 | 25.0 | 2.80 | – | -1.35 | 1.92 | 175.9 |
| $Zr_{65}Co_{35}$ | 1.35 | 2.38 | 17.6 | 2.70 | – | -2.00 | 1.97 | 182.5 |
| $Zr_{76}Fe_{24}$ | 1.29 | 2.39 | 18.6 | 1.7 | 0.56 | -1.30 | 2.63 | 171.4 |

Table 1. Data relevant to Zr-3d alloys ($A$ is the coefficient of linear conductivity variation below 100 K, $B$ is the coefficient of $T^{1/2}$ conductivity variation above 100 K, $T_c$ is the superconducting transition temperature, $\lambda$ is the constant of electron-phonon interaction, $\alpha$ is the room temperature coefficient of resistance, $\chi_p$ is the magnetic susceptibility at room temperature and $\rho_{273}$ is the electrical resistivity at 273 K.

Figures 2 and 3 show the dependence of the coefficients $A$ and $B$ versus concentration of 3d constituent. The values of both coefficients increase with the zirconium concentration. Similar dependences show the superconducting transition temperatures, temperature coefficients of the resistivity at room temperature $\alpha$

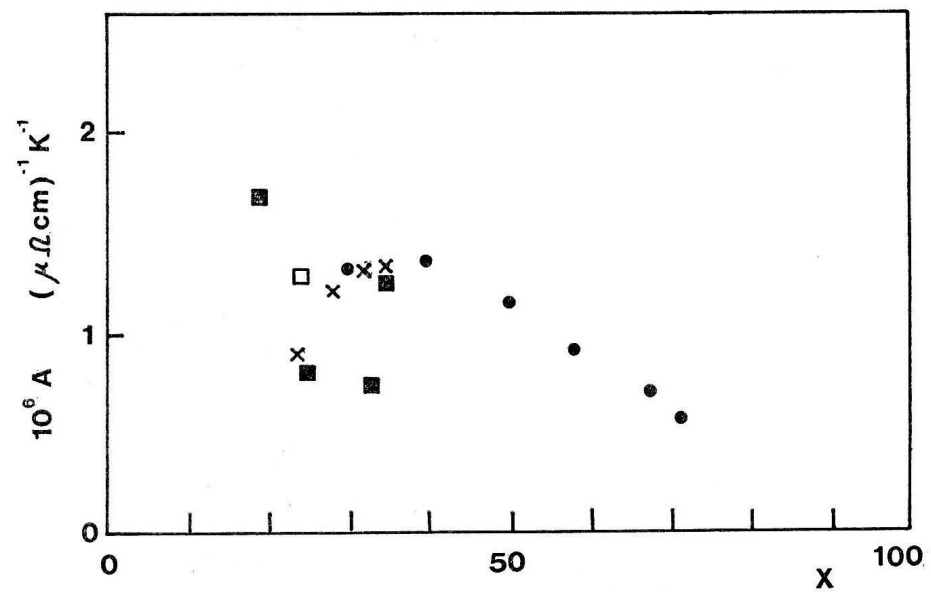


*Fig. 2. Coefficient A of a linear conductivity variation below 100* K *vs. x.* • =Zr–Cu, × =Zr–Ni, ■ =Zr–Co, □ =Zr–Fe, *glassy alloys.*

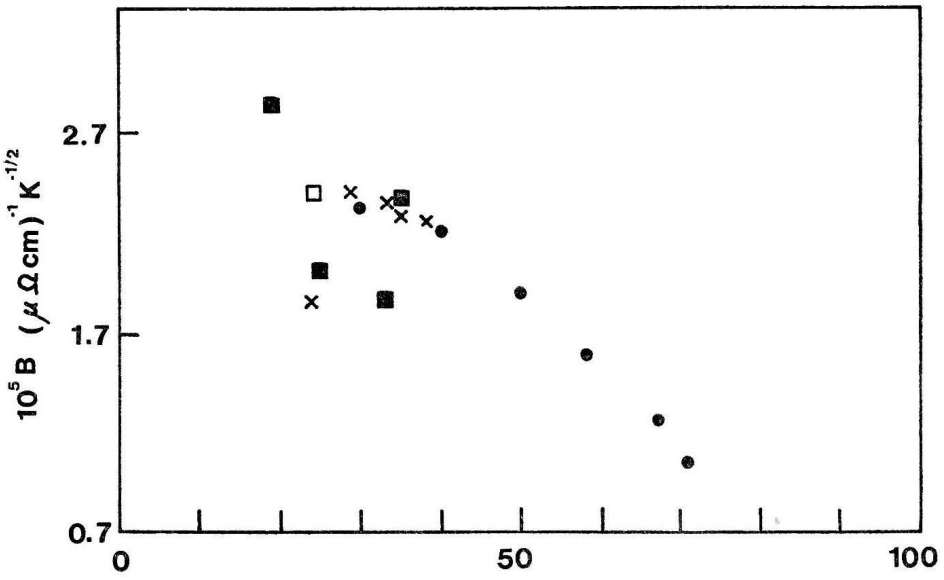


*Fig. 3. Coefficient B of a* $T^{1/2}$ *conductivity variation above 100 K vs. x.* • =Zr–Cu, × =Zr–Ni, ■ =Zr–Co, □ =Zr–Fe, *glassy alloys.*

and the constants of the electron-phonon interaction $\lambda$ (Table 1). Ratio $B/A$ is approximately equal to the square root from the Debye temperature. The magnetic susceptibility of Zr-Cu and Zr-Ni alloys decreases with decreasing Zr concentration. Zr-Co and Zr-Fe alloys have considerably higher magnitudes of susceptibility which is caused by the appearance of spin fluctuations in these alloys. All above, confirms the results of UPS experiments that the density of states at Fermi level is dominated by Zr d-states and that therefore the electronic structure of these alloys can approximately be described by the dilution of zirconium.

The electrical resistivity and temperature coefficients of resistivity at room temperature, calculated within the framework of the Ziman theory[10,11], do not agree well with the experimental results. The calculated resistivities are considerably larger than the measured ones, their concentration dependences are erroneous, and the temperature coefficients have wrong sign. The main problem in this theory is how to determine the number of free electrons per atom because it strongly influences the calculated quantities. The possible solution of these difficulties is in contribution of d-electrons to conductivity and the effect of s-d hybridization. Taking into consideration these effects it is hoped that satisfactory results for the electrical resistivity and temperature coefficient of resistivity can be obtained (including the right sign for $\alpha$)[12].

It is very interesting to examine the connection between the constant of electron-phonon interaction $\lambda$ and the derivative of electrical resistivity at room temperature $\mathrm{d}\rho/\mathrm{d}T$. The Ziman theory anticipates a linear dependence between $\lambda$ and $\mathrm{d}\rho/\mathrm{d}T$[13]

$$\lambda = k\frac{\mathrm{d}\rho}{\mathrm{d}t}\,. \tag{3}$$

Fig. 4 shows $\lambda$ versus $\mathrm{d}\rho/\mathrm{d}T$ for our alloys. The straight line $\lambda = -28\mathrm{d}\rho/\mathrm{d}T$

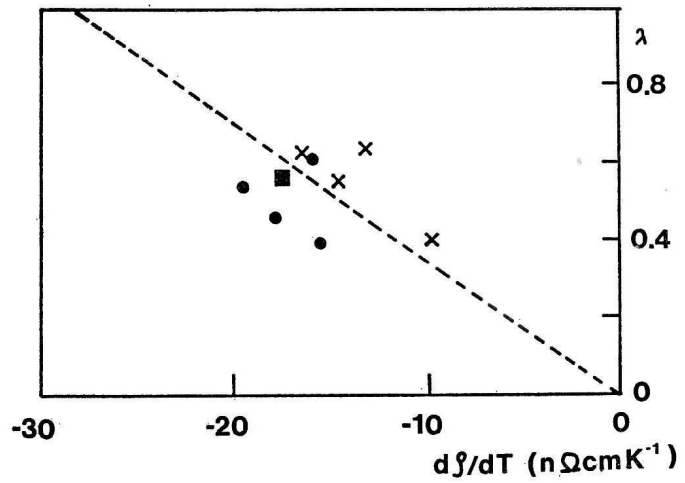


*Fig. 4. Constant of the electron-phonon interaction $\lambda$ vs. $\mathrm{d}\rho/\mathrm{d}T$ for some* Zr-3d *glassy alloys* (• =Zr–Cu, × =Zr–Ni, ■ =Zr–Co).

is drawn on this figure. The data lie rather close to this line but there is strong deviation from linear dependence (3). The reasons for deviation may be manifold: alloys at the end of concentration range may be partially crystalline, real values for effective Coulomb potential $\mu^*$ may be different from the chosen value 0.13, in some alloys spin fluctuation can exist, some alloys have very low superconducting transition temperatures $T_c$ which is hard to be determined correctly. The approximate validity of the expression (3) seems to indicate that the Ziman's theory, with the addition of d-conductivity and s-d hybridization, can be used for explaining the electrical transport at elevated temperatures in glassy Zr-3d alloys.

## *4. Conclusion*

The results of the measurements of electrical resistivity, superconducting transition temperature and magnetic susceptibility on a series of Zr-3d alloys show that the electronic band structure at the Fermi level of these alloys is dominated with that of zirconium. The concentration dependence of magnetic susceptibility, superconducting transition temperature and constant of electron-phonon interaction can be explained with the effect of dilution of Zr by the 3d element. The Ziman's theory does not give good results for the magnitudes of electrical resistivity and temperature coefficients of resistivity, but we think that taking into consideration d-conductivity and s-d hybridization we can get acceptable results. The temperature dependence of electrical resistivity at lower temperatures is affected by the incipient localization and can be explained by the Fukuyama-Hoshino expression.

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## ELEKTRIČNI TRANSPORT U STAKLASTIM Zr-3d SLITINAMA

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Mjerene su temperature supravodljivog prijelaza, magnetska susceptibilnost kao i električni otpor za niz Zr-3d slitina. Navedena mjerenja su usko povezana s elektronskom strukturom danih slitina. Gotovo linearno smanjenje magnetske susceptibilnosti, temperature supravodljivog prijelaza i konstante $\lambda$ elektron-fonon interakcije s koncentracijom 3d elementa pokazuju da je gustoća elektronskih stanja na Fermijevom nivou u tim slitinama dominirana Zr d-stanjima. Rezultati se jednostavno mogu objasniti efektom razređenja s povećanjem koncentracije 3d elementa. Tvrdnju potvrđuje i analiza temperaturne ovisnosti električne vodljivosti kao i rezultati dobiveni eksperimentima UPS fotoemisije na danim slitinama. Proračuni pokazuju da električni otpor staklastih Zr-3d slitina nije moguće objasniti u okviru klasične proširene Zimanove teorije.