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INFLUENCE OF HYDROGEN ON THE SUPERCONDUCTING AND THE  
PARAMAGNETIC PROPERTIES OF SOME Zr-3d METALLIC GLASSES

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**Dedicated to Professor Mladen Paić on the occasion of his 90<sup>th</sup> birthday**

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We present the experimental results on the effects of hydrogen doping on the superconducting and paramagnetic properties of zirconium-rich ( $x > 0.66$ )  $Zr_x3d_{1-x}$  metallic glasses.  $Zr_{0.70}Cu_{0.30}$ ,  $Zr_{0.67}Ni_{0.33}$  and  $Zr_{0.67}Co_{0.33}$  are superconductors with a superconducting transition temperature in the vicinity of 2 K, while  $Zr_{0.68}Fe_{0.32}$  is a paramagnet down to very low temperatures because of pronounced spin-fluctuations. The magnetoresistivity data are analysed using theoretical models of weak localization and electron-electron interactions. Doping with hydrogen reduces the superconducting transition temperature in  $Zr_{0.70}Cu_{0.30}$ ,  $Zr_{0.67}Ni_{0.33}$  and  $Zr_{0.67}Co_{0.33}$  metallic glasses. The magnetoresistivity enhancement of hydrogen-doped  $Zr_{0.68}Fe_{0.32}$  has been attributed to the increase of the Stoner factor,  $(1-I)^{-1}$ . That increase indicates an enhancement of spin fluctuations with hydrogen.

## 1. Introduction

Early transition-metal (ETM) – late transition-metal (LTM) glasses can often be formed over wide composition ranges, and provide a means for the study of their properties as a function of composition. For example, Zr-3d amorphous al-

loys exhibit superconductivity in Zr-rich compositions but exhibit various magnetic phases for some 3d-rich compositions. It has also been shown [1], that for a given  $Zr_x$  concentration ( $x = 0.70$ ) superconductivity is destroyed as the LTM changes from Cu to Fe.

Photoemission spectroscopy studies [2] have shown that the valence band spectra of Zr-3d metallic glasses are characterized by a two-peak d-band structure for Zr concentration in the range of 60–75 at%. The high-banding-energy peak has been identified with the states of the LTM and the peak near the Fermi level with d-states of zirconium. Thus, it is the density of Zr 4d-states at the Fermi level,  $N_d(E_F)$ , which mainly influences physical properties of these alloys that depend on  $N(E_F)$ . The separation the two d-band peaks decreases on going to the left in the 3d transition metal series. Thus, the contribution of the 3d density of states to the  $N(E_F)$  increases as one goes from Cu to Fe. One would then expect, for a given Zr concentration, higher  $T_C$  in the Zr-Fe than in the Zr-Ni alloy. That is opposite to what is observed experimentally. This has been explained [1] by the pronounced spin fluctuations in alloys containing Fe atoms. Spin fluctuations tend to enhance the parallel spin orientation and thus destroy the superconductivity.

Soft-X-ray spectroscopy measurements of Zr-Ni and Zr-Ni-H metallic glasses have shown [3] that the Zr 4d-band is strongly modified by hydrogen. The addition of hydrogen reduces the height of the emission spectra peak at  $E_F$  and produces a subband at about 6.5 eV below the  $E_F$ . This subband has been attributed to the formation of Zr-H bound states. On the other hand the emission spectrum of Ni shows no sign of Ni-H bond formation.

In our earlier work [4,5], we have demonstrated that hydrogen can be used to vary continuously the transport and paramagnetic properties of Zr-3d (3d being Cu, Ni, Co and Fe) metallic glasses. We have explained in detail the changes of the resistivity, the magnetoresistivity, the magnetic susceptibility, and the superconducting transition temperature upon hydrogenation. We have observed an increase of the resistivity, a decrease of the room temperature magnetic susceptibility (and hence the  $N(E_F)$ ), and a decrease of the superconducting transition temperature with increasing hydrogen concentration.

In this paper we present the results of some new magnetoresistance measurements of hydrogen doped  $Zr_{0.67}Co_{0.33}$  and  $Zr_{0.68}Fe_{0.32}$  metallic glasses.  $Zr_{0.68}Fe_{0.32}$  is, unlike Zr-Cu, Zr-Ni and Zr-Co of the same composition, paramagnetic down to very low temperatures ( $< 1$  K) because of pronounced spin fluctuations. We analyse quantitatively the magnetoresistivity results of  $(Zr_{0.67}Co_{0.33})_{1-x}H_x$  using the weak-localization (WL) [6], and electron-electron interaction (EI) [7,8] expressions for 3D disordered transition-metal alloys. In the case of  $(Zr_{0.68}Fe_{0.32})_{1-x}H_x$ , these expressions have to be renormalized [9]. The renormalization takes into account the enhancement of exchange of the spin-splitting contributions (through the Stoner factor) to the WL and EI terms. This enhancement is caused by the presence of spin-fluctuations in these alloys.

We also summarize our earlier results [4,10] on superconducting properties of hydrogen-doped Zr-Cu, Zr-Ni and Zr-Co amorphous alloys to show the effects of hydrogen doping on both the superconductivity and spin-fluctuations in these materials.

## 2. Experimental

Samples of amorphous Zr-3d alloys were prepared by the usual method of melt spinning. The ribbons were cut into stripes 4 cm long and electrolytically loaded with hydrogen to various concentrations. The details of the method, by which the hydrogen concentration in the sample was determined, have been given elsewhere [4].

The magnetoresistance was measured by a low-frequency (23.2 Hz), four-probe AC method, with a relative precision of  $10^{-6}$ , in magnetic fields up to 0.7 T of a superconducting magnet.

## 3. Results and discussion

The magnetoresistance results pertaining to  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{0.952}\text{H}_{0.048}$  for two different temperatures  $T_1 = 2.7$  K and  $T_2 = 4.2$  K are shown in Fig. 1. Figure 2 shows the magnetoresistivity of  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$  as a function of the magnetic field for various hydrogen concentrations ( $x = 0; 0.02; 0.048; 0.12$ ). The magnetoresistance was found to be independent of the sample orientation with respect to the magnetic field as predicted by the WL model for 3D disordered systems.

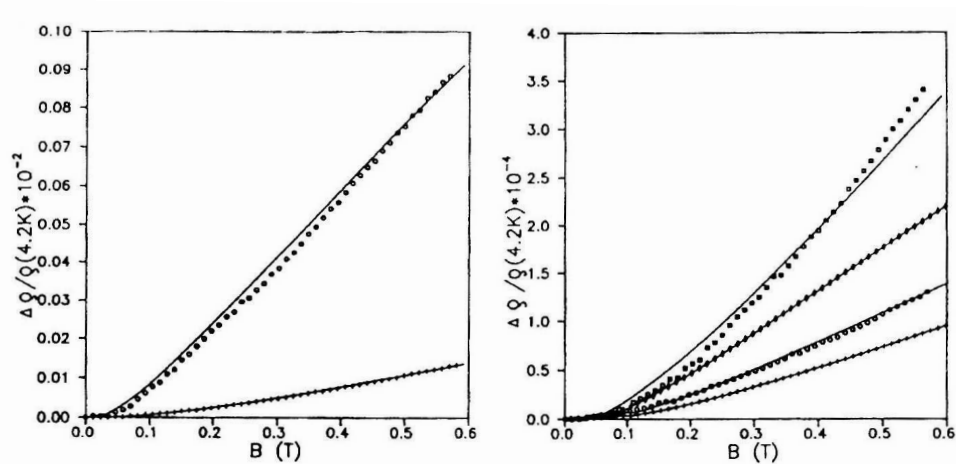


Fig. 1. Magnetoresistivity of  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{0.952}\text{H}_{0.048}$  at  $T = 2.7$  K ( $\circ$ ), and  $T = 4.2$  K ( $+$ ). Solid lines are the best fits of the WL and EI expressions (Ref. 4).

Fig. 2. Magnetoresistivity of  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$  at  $T = 4.2$  K ( $\square$  -  $x = 0$ ;  $\diamond$  -  $x = 0.02$ ;  $\circ$  -  $x = 0.048$ ;  $+$  -  $x = 0.12$ ). Solid lines are the best fits of the WL and EI expressions (Ref. 4) (right).

From Fig. 1, it can be inferred that magnetoresistivity increases as temperature decreases and approaches  $T_c$ . This reflects the fact that the Maki-Thompson contribution to the magnetoresistivity increases in the vicinity of the superconducting transition temperature.

The increase of hydrogen concentration leads to a lowering of the magnetoresistance slopes, and hence of the Maki-Thompson contribution and  $T_c$ , as shown in Fig. 2.

Solid lines are the theoretical fits to the experimental data of the well-known expression for the WL correction [6] to the magnetoresistivity in the presence of superconducting fluctuations and spin-orbit scattering. It has been shown that, in the case of superconductors, the dominant part to the WL term above  $T_c$  comes from the Maki-Thompson interaction through the parameter  $b$ . The spin-splitting contribution [8] to the magnetoresistivity amounts only 5% [4] and the orbital contribution [7] is only 2% [4]. It is the variation of the Maki-Thompson term that mainly determines the change of the magnetoresistivity of  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$  with both hydrogen concentration and temperature. The parameters of the fit are the diffusion constant  $D$ , the inelastic scattering time  $\tau_i$ , the spin-orbit scattering time  $\tau_{so}$  and  $T_c$  and are given in Table 1.

TABLE 1.

Values of the hydrogen concentration,  $x$ , the diffusion constant,  $D$ , the inelastic scattering time,  $\tau_i$  (4.2 K), the spin-orbit scattering time,  $\tau_{so}$ , the superconducting transition temperature,  $T_c$ , and the Stoner factor,  $(1 - I)^{-1}$ , of  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$ , and  $(\text{Zr}_{0.68}\text{Fe}_{0.32})_{1-x}\text{H}_x$  metallic glasses.

$x$	$D$ $10^{-5} \text{ m}^2\text{s}^{-1}$	$\tau_i$ $10^{-11} \text{ s}$	$\tau_{so}$ $10^{-13} \text{ s}$	$T_c$ K	$(1 - I)^{-1}$
$(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$					
0	6.4	3.38	1.1	2.74	
0.02	6.3	4.5	1.12	2.6	
0.048	6.25	1.76	1.13	2.35	
0.12	6	1.57	1.17	1.7	
$(\text{Zr}_{0.68}\text{Fe}_{0.32})_{1-x}\text{H}_x$					
0	3	0.69	0.71		2.65
0.017	2.95	2.79	2		2.75
0.067	2.9	1.19	3.85		2.7
0.077	2.85	0.97	6.3		3.05

On the other hand in  $\text{Zr}_{0.68}\text{Fe}_{0.32}$  a positive contribution to the WL magnetoresistance from the Zeeman splitting becomes dominant and is enhanced by spin fluctuations.

Although  $\text{Zr}_{0.68}\text{Fe}_{0.32}$  has a higher density of states at the Fermi level than  $\text{Zr}_{0.67}\text{Co}_{0.33}$ , it is not superconducting. It has been shown [11] that  $dT_c/dx$  ( $x$  being the Zr concentration) actually diverges close to  $x = 0.71$ ;  $T_c$  being 0.6 K for  $x = 0.72$  and less than 0.06 K for  $x = 0.71$ . The collapse of  $T_c$  is accompanied by an increase of susceptibility and hence of the Stoner factor, and has been explained by the occurrence of spin fluctuations and the formation of localized magnetic moments at the Fe sites. For  $x < 0.62$   $\text{Zr}_x\text{Fe}_{1-x}$ , amorphous alloys are ferromagnetic.

The magnetoresistivity data of hydrogen-doped  $(\text{Zr}_{0.68}\text{Fe}_{0.32})_{1-x}\text{H}_x$  ( $x = 0, 0.01, 0.067$  and  $0.077$ ) samples at  $T = 4.2$  K are shown in Fig. 3. The undoped sample has a small negative magnetoresistance for fields lower than  $0.4$  T. This negative magnetoresistance may indicate the presence of spin-disorder scattering or the Kondo-effect. In samples doped with hydrogen the observed magnetoresistance is positive even for the smallest hydrogen concentration ( $x = 0.017$ ) and it increases with hydrogen concentration.

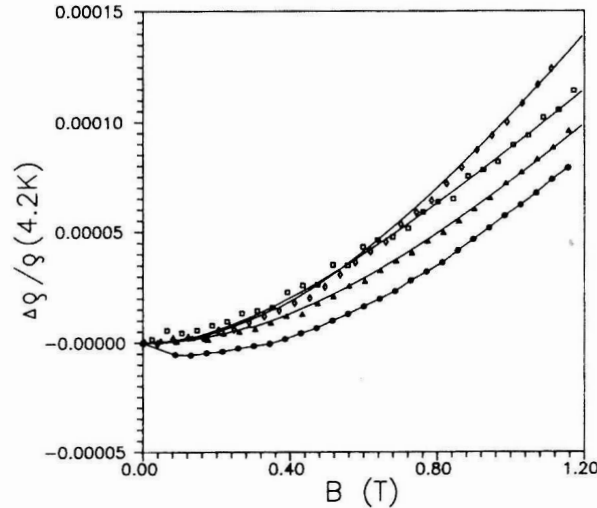


Fig. 3. Magnetoresistivity of  $(\text{Zr}_{0.68}\text{Fe}_{0.32})_{1-x}\text{H}_x$  at  $T = 4.2$  K:  $\circ$  -  $x = 0$ ;  $\triangle$  -  $x = 0.017$ ;  $\square$  -  $x = 0.066$ ;  $\diamond$  -  $x = 0.077$ . Solid lines are the best fits of the WL and EI expressions (Ref. 4).

Although the WL and EI theories describe well, both qualitatively and quantitatively, the magnetoresistivity of superconducting transition-metal amorphous alloys, significant deviations occur in magnitude and temperature dependence for nonsuperconducting systems. Trudeau et al. have shown [12] that the size and form of the magnetoresistivity for paramagnetic Zr-Fe alloys vary rapidly as a result of the increasing Stoner factor,  $(1 - I)^{-1}$ . They found that their experimental data were well described by the exchange-enhanced spin-splitting contributions to the usual WL and EI terms. Thus, we have fitted to our experimental data for hydrogenated  $\text{Zr}_{0.68}\text{Fe}_{0.32}$  metallic glasses the renormalized expression for the magnetoresistivity. The results of the fit are given as solid lines in Fig. 3. The parameters of the fit are the diffusion constant  $D$ , the inelastic scattering time  $\tau_i$ , the spin-orbit scattering time  $\tau_{so}$  and the Stoner factor  $(1 - I)^{-1}$ . They are given in Table 1. In the following we will concentrate mainly on the behaviour of the Stoner factor.

Table 1 shows that the Stoner factor increases with increasing hydrogen concentration (e.g.,  $(1 - I)^{-1} = 2.65$  in  $\text{Zr}_{0.68}\text{Fe}_{0.32}$  and  $3.05$  in  $(\text{Zr}_{0.68}\text{Fe}_{0.32})_{0.923}\text{H}_{0.077}$ ). Our resistivity measurements for the same samples have shown that hydrogen produces a pronounced positive anomaly in the resistivity below about  $25$  K, leading

to a maximum in  $\rho(T)$  before the curve resumes a monotonic decrease with increasing temperature, characteristic for ETM-LTM metallic glasses. This anomaly, together with the present results that show an increase of the Stoner factor with hydrogen concentration, can be explained by the enhanced spin-fluctuations in  $(\text{Zr}_{0.68}\text{Fe}_{0.32})_{1-x}\text{H}_x$  metallic glasses.

Since  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$  alloys are superconductors for all the hydrogen concentrations measured, the Stoner factor (calculated from the magnetic susceptibility measurements) is much smaller. It cannot be determined from the present magnetoresistivity measurements, because the dominant part in the WL magnetoresistivity correction is the Maki-Thompson term.

The values of the superconducting transition temperatures,  $T_c$ , for hydrogen doped Zr-Cu, Zr-Ni and Zr-Co metallic glasses are shown in Fig. 4 as a function of resistivity,  $\rho$ , and in Table 2 as a function of hydrogen concentration and of the sample resistivity. The results for Zr-Cu and Zr-Ni are taken from our earlier work.

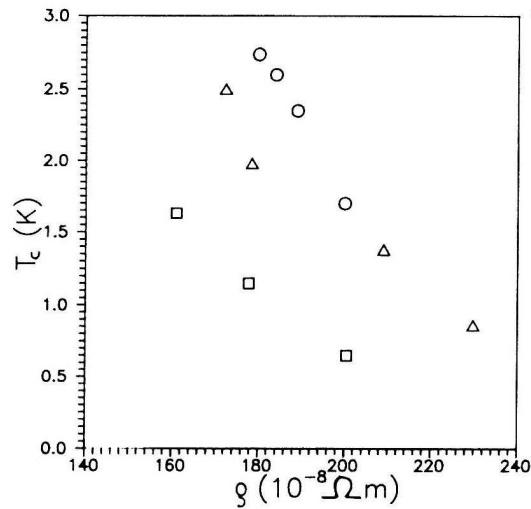


Fig. 4. Plot of the superconducting transition temperature  $T_c$  vs. resistivity for  $\circ$ —  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$ ,  $\Delta$ —  $(\text{Zr}_{0.67}\text{Ni}_{0.33})_{1-x}\text{H}_x$  and  $\square$ —  $(\text{Zr}_{0.7}\text{Cu}_{0.3})_{1-x}\text{H}_x$  metallic glasses.

Figure 4 shows that the reduction of  $T_c$  is proportional to the sample resistivity that increases with the hydrogen concentration.

The superconducting transition temperatures were calculated from the magnetoresistivity results using the expression for weak-localization [4]. It is noteworthy that  $T_c$  values obtained in this way are in good agreement with the ones obtained directly from the resistivity measurements as a function of temperature. Thus, we were able to determine very low superconducting transition temperatures from magnetoresistivity data taken at much higher temperatures. This is important because the superconducting transition temperature of the doped samples lower than 1.7 K could not be measured with the available low-temperature equipment.

Figure 4 shows that a decrease of  $T_c$  with  $\rho$  (and hence hydrogen concentration) is more pronounced for Zr-Co-H than for the Zr-Cu-H system. This enhanced affinity for hydrogen atoms, as one goes from Cu to Ni, Co and Zr, can be attributed to the difference in the extension of d-states and to a band structure of the alloy. As has been said before, the density of states of Zr-3d amorphous system at the Fermi level is dominated by the Zr 4d-states. Since Zr d-band is only partly filled it can accommodate the surplus hydrogen electrons more easily. In the case of Cu the 3d-band is completely filled and lies well below the Fermi level. As one goes

TABLE 2.

Values of the hydrogen concentration,  $x$ , the resistivity,  $\rho$ , and the superconducting transition temperature,  $T_c$ , for  $(\text{Zr}_{0.7}\text{Cu}_{0.3})_{1-x}\text{H}_x$ ,  $(\text{Zr}_{0.67}\text{Ni}_{0.33})_{1-x}\text{H}_x$  and  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$ , metallic glasses.

$x$	$\rho$ (295 K) ( $10^{-8}$ $\Omega\text{m}$ )	$T_c$ (K)
$(\text{Zr}_{0.70}\text{Cu}_{0.30})_{1-x}\text{H}_x$		
0	161	1.63
0.08	177.8	1.15
0.25	200.5	0.65
$(\text{Zr}_{0.67}\text{Ni}_{0.33})_{1-x}\text{H}_x$		
0	172.3	2.5
0.09	178.3	2.5
0.21	209	1.38
0.33	229.8	0.86
$(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$		
0	180	2.74
0.02	184	2.6
0.048	189	2.35
0.12	200	1.7

from Cu to the left in the transition-metal series the peak position of the 3d-band moves towards the Fermi level thus increasing the contribution of the 3d density of states at the Fermi level. That is why  $T_c$  for  $\text{Zr}_{0.67}\text{Co}_{0.33}$  is slightly higher ( $T_c = 2.74$  K) than for  $\text{Zr}_{0.67}\text{Ni}_{0.33}$  ( $T_c = 2.5$  K) although the Zr concentration is the same.

#### 4. Conclusion

We have analysed our magnetoresistivity data for  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$  metallic glasses using the theoretical models of weak-localization and electron-electron interaction in 3D disordered systems. For the  $(\text{Zr}_{0.68}\text{Fe}_{0.32})_{1-x}\text{H}_x$  system, we had to include the enhancement of these contributions due to the presence of spin fluctuations.

We have included also some of our earlier results on the superconducting properties of hydrogen-doped Zr-Ni and Zr-Cu metallic glasses.



It has been shown that the magnetoresistivity slopes of  $(\text{Zr}_{0.67}\text{Co}_{0.33})_{1-x}\text{H}_x$  samples are lowered by the hydrogen dopant. The lowering of the Maki-Thompson term is caused by the lowering of the superconducting transition temperature with hydrogen. The values obtained for  $D$ ,  $\alpha_i$  and  $\tau_{so}$  are consistent with those obtained earlier for  $(\text{Zr-Cu})_{1-x}\text{H}_x$  and  $(\text{Zr-Ni})_{1-x}\text{H}_x$  metallic glasses. The increase of the magnetoresistivity slopes of  $(\text{Zr}_{0.68}\text{Fe}_{0.32})_{1-x}\text{H}_x$  samples with hydrogen dopant are due to an increase of the Stoner factor. This indicates an enhancement of the spin fluctuations with increasing hydrogen concentration.

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## UTJECAJ VODIKA NA SUPRAVODLJIVA I PARAMAGNETSKA SVOJSTVA NEKIH Zr-3d METALNIH STAKALA

Prikazuju se eksperimentalni rezultati utjecaja vodika na supravodljiva i paramagnetska svojstva  $\text{Zr}_x\text{3d}_{1-x}$  metalnih stakala bogatih cirkonijem ( $x > 0.66$ ).  $\text{Zr}_{0.70}\text{Cu}_{0.30}$ ,  $\text{Zr}_{0.67}\text{Ni}_{0.33}$  i  $\text{Zr}_{0.67}\text{Co}_{0.33}$  su supravodiči s temperaturom supravodljivog prijelaza oko 2 K, dok je  $\text{Zr}_{0.68}\text{Fe}_{0.32}$  paramagnetičan i na veoma niskim temperaturama zbog prisustva spinskih fluktuacija. Rezultati magnetootpora analizirani su primjenom teorijskih modela slabe lokalizacije i elektron-elektron interakcije u neuređenim sistemima. Dopiranje vodikom dovodi do sniženja temperature supravodljivog prijelaza u  $\text{Zr}_{0.70}\text{Cu}_{0.30}$ ,  $\text{Zr}_{0.67}\text{Ni}_{0.33}$  i  $\text{Zr}_{0.67}\text{Co}_{0.33}$  metalnim staklima. Povećanje magnetootpora u  $\text{Zr}_{0.68}\text{Fe}_{0.32}$  dopiranim vodikom uzrokovano je povećanjem Stonerovog faktora. Ovo povećanje ukazuje na povećanje spinskih fluktuacija pod utjecajem vodika.