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EVALUATION OF EFFECTS OF NANOSCALE INHOMOGENEITIES ON THE  
SUPERCONDUCTING TRANSITION TEMPERATURE IN HYDROGEN-DOPED  
Zr-Co METALLIC GLASSES

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**This paper is dedicated to Professor A. Bonefačić on the occasion  
of his 70<sup>th</sup> birthday**

We present the results of measurements of electrical resistivity on hydrogen-doped Zr-Co metallic glass in the vicinity of the superconducting transition temperature,  $T_C$ , in the temperature range 1.5 K – 4.2 K. The hydrogen dopant lowers the superconducting transition temperature. At the same time, the superconducting transition region is broadened and “steps” appear in the resistance curve at the transition. Scanning proton microprobe and p-p scattering have been used to determine areal distributions of hydrogen and depth profiles in the samples studied. Hydrogen depth profiles at particular positions have been deconvoluted using cubic splines. We discuss the effects of different hydrogen environments on the superconducting transition temperature of Zr-Co-H metallic glasses.

## 1. Introduction

In evaluating the effects of higher-order diagrams in the perturbation models dealing with electronic properties of disordered systems, such as 4d-3d metallic glasses, we use the hydrogen dopant as an atomic probe to test the contribution of various interactions [1]. Since these highly disordered alloys contain atoms of widely different properties, one may expect considerable variations in the chemical short-range order, which is in fact

observed. These systems may thus be regarded as heterogeneous on the nanoscale. It is, therefore, of great importance to be able to characterize the sample nanotopology and nanomorphology before and after the dopant is introduced. More specifically, the question of homogeneity of the dopant distribution is of primary interest before further investigation of its influence on the nanoscale can be performed in a quantitative way. In order to address this question, we have undertaken a study of samples of Zr-Co metallic glass doped with various concentrations of hydrogen introduced into the metal matrix. Here we discuss the effects of different hydrogen environments on the superconducting transition temperature of Zr-Co-H metallic glasses.

## 2. Experimental

Samples were prepared by the usual method of melt spinning [2]. The ribbons, typically  $30\ \mu\text{m}$  thick and 3 mm wide, were cut into strips 4 cm long, and were electrolytically charged with hydrogen. During hydrogenation, the ribbons curl up because the gas enters preferentially through the surface which had been in contact with the quenching wheel. As the hydrogen diffuses into the sample, the ribbons straighten out and are then used in the measurements. The structures of the as-quenched and hydrogenated samples were examined by X-ray diffraction using Cu  $K\alpha$  radiation to verify that they were amorphous.

In our earlier work, the relationship between the volumetrically determined hydrogen concentration in the sample and its resistance has been found to be linear for the range of concentrations used [3]. Here we apply the same method by correlating the dopant concentration with the change in the sample resistance at  $0\ ^\circ\text{C}$  and it is expressed in those terms.

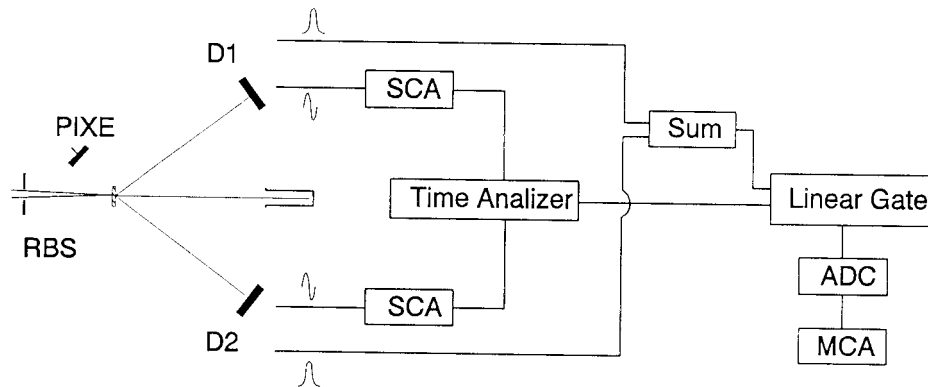


Fig. 1. Schematic presentation of the experimental setup. Detectors D1 and D2 are used for detection of elastically scattered protons. Detectors PIXE and RBS are used for detection of X-rays and backscattered protons, respectively. Bipolar pulses from D1 and D2 are used in coincidence, while unipolar pulses are summed for the pulse-height analysis in ADC/MCA.

The resistance was measured by low-frequency (23.2 Hz) four-probe AC-method in

the temperature range 1.5 K – 4.2 K. The precision of these measurements extends to a few parts in  $10^6$ .

The scanning proton microprobe and p-p scattering were used to investigate the hydrogen areal distributions and depth profiles in the samples studied. The hydrogen depth profiles at particular positions were deconvoluted using cubic splines. The layout of the scanning proton microbeam facility at the “Rudjer Bošković” Institute is shown schematically in Fig. 1. The experimental details of this new method for 3D hydrogen profiling as well as the deconvolution technique applied on the experimental spectra measured at different sample points have been described elsewhere [4].

### 3. Results and discussion

The temperature-dependent parts of the electrical resistivity of  $Zr_{0.67}Co_{0.33}H_x$  metallic glasses, ( $x = 0; 0.01; 0.02; 0.07$ ), in the vicinity of the superconducting transition temperature are shown in Fig. 2. As the hydrogen enters into the Zr-Co matrix, the superconducting transition region not only broadens, but “steps” appear so that three transition temperatures can be associated with each sample (see Table 1). Thus, in  $Zr_{0.67}Co_{0.33}H_{0.01}$ , there are three steps, at  $T_{C1} = 2.74$  K,  $T_{C2} = 2.68$  K and  $T_{C3} = 2.58$  K. As the hydrogen concentration rises, the steps become more pronounced and shift to lower temperatures (e.g., in  $Zr_{0.67}Co_{0.33}H_{0.07}$ ,

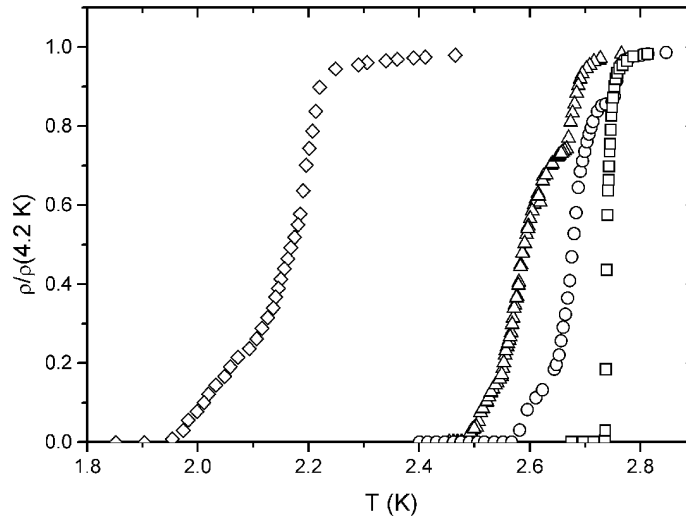


Fig. 2. The temperature-dependent resistivity relative to its value at 4.2 K versus temperature below 3 K of hydrogen-doped  $Zr_{0.67}Co_{0.33}H_x$  metallic glasses:  $x = 0$  ( $\square$ ), 0.01 ( $\circ$ ), 0.02 ( $\triangle$ ) and 0.07 ( $\diamond$ ).

TABLE 1. Values of the electrical resistivity,  $\rho(290\text{ K})$ , and the superconducting transition temperatures,  $T_{C1}$ ,  $T_{C2}$  and  $T_{C3}$  of hydrogen-doped  $\text{Zr}_{0.67}\text{Co}_{0.33}\text{H}_x$  metallic glasses.

$x$	$\rho(\mu\Omega\text{cm})$	$T_{C1}(\text{K})$	$T_{C2}(\text{K})$	$T_{C3}(\text{K})$
0	180	2.74		
0.01	182	2.74	2.68	2.58
0.02	184	2.69	2.59	2.50
0.07	192	2.21	2.17	1.98

$T_{C1} = 2.21\text{ K}$ ,  $T_{C2} = 2.17\text{ K}$  and  $T_{C3} = 1.98\text{ K}$ ). The occurrence of several “steps” associated with the onset of superconductivity could be due to the presence of several superconducting “phases” which are due to differences in the local environment of the hydrogen atoms in the matrix. Of course, this phenomenon may (at least in principle) be due to the possible inhomogeneity in the doped sample and/or different glassy phases. If the steps were due to inhomogeneities, they would have to be very large so as to effectively divide the sample into several series-connected samples, since inhomogeneities on a small scale are expected to insure percolation to each “phase”, and should not cause the steps. Besides, large inhomogeneities would produce very different and irregular transitions in samples containing different concentration of hydrogen.

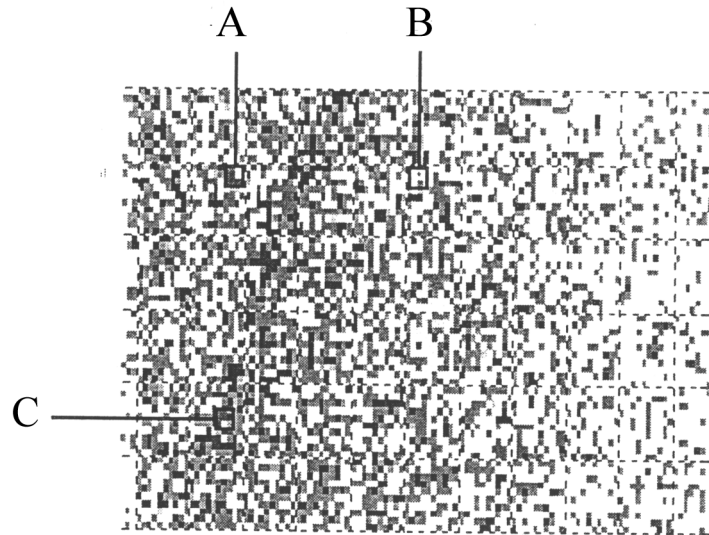


Fig. 3. Areal density map of  $\text{Zr}_{0.67}\text{Co}_{0.33}\text{H}_{0.10}$  sample. Scan size is  $700\mu\text{m} \times 1000\mu\text{m}$ .

The samples were scanned with 6 MeV proton microbeam to determine if the hydrogen areal densities were uniform (Fig. 3). Since the samples were more than  $30\mu\text{m}$  thick, the protons scattered at  $45^\circ$  in the first few microns could not emerge through the back of the samples to give a coincidence in the counters. For deeper collisions, the energy loss of the scattered particles decreases, and at one point they begin to give coincidences.

The closer the origin of the scattering gets to the back surface of a given sample, the greater the probability of the particles to reach the coincidence counter, and, conversely, the further from the back surface the scattering event takes place, the greater the probability that multiple scattering of the emerging particles will cause coincidence losses. The signal yield thus decreases as we move from the back surface of the sample toward its front surface i.e. toward “shallower” (as viewed from the front surface) collision depths. This can be observed from Fig. 4. A large exponential decrease of events is observed as we move toward the lower energies i.e. toward the front of the target. An assumed constant exponential factor  $\alpha$  was fitted to the slope of the energy spectrum for the last  $10\ \mu\text{m}$  of the sample thickness. Three depth profiles at the points marked in Fig. 3, and deconvoluted with 11 cubic splines, are shown in Fig. 5. Points A) and C) have the same thickness, but at C), there is a line-shaped surface contamination (also visible in Fig. 3), probably due to traces of formvar glue. Points A) and B) have the same hydrogen concentration, but at B), the sample is thicker and the coincidence loss is higher. This causes a false decrease in areal concentration seen in Fig. 3. Inside the sample, all the three points have the same hydrogen concentration.

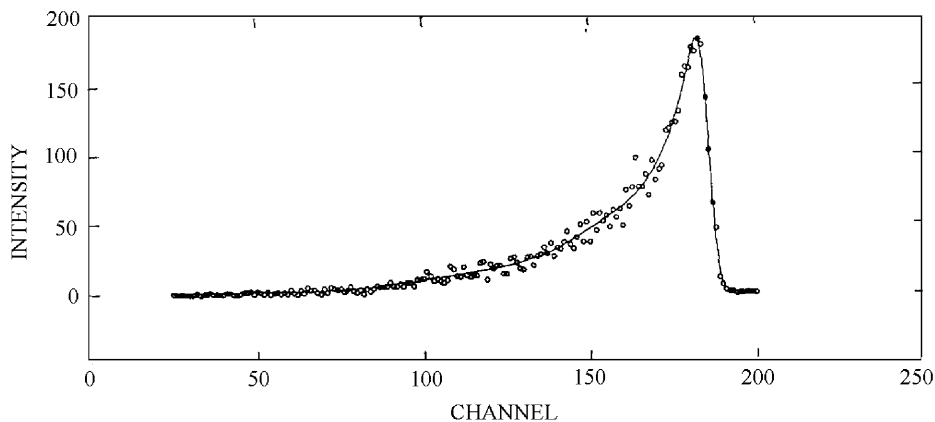


Fig. 4. The 6 MeV proton-proton coincidence spectrum of the  $\text{Zr}_{0.67}\text{Co}_{0.33}\text{H}_{0.10}$  sample.

Thus, only the last  $10\ \mu\text{m}$  of the sample can be reliably analysed, and by reversing the sample, we have obtained the profile data pertaining to the two outer  $10\ \mu\text{m}$  layers.

We thus conclude that, within the limits of this method, the dopant concentration in our sample was remarkably uniform, lending credence to the doping method used. There is still no guarantee that this uniformity extends to the nanoscale.

According to the structural analyses [5,6] of hydrogen doped Zr-3d amorphous alloys, the hydrogen atoms tend to occupy preferentially tetrahedral holes surrounded by four Zr atoms, for small hydrogen concentration, while tetrahedral sites defined by three Zr atoms begin to be occupied at higher hydrogen concentration. Consequently, the electronic states around Zr atoms, which contribute mainly to the electronic density at the Fermi level,  $E_F$ , are modified substantially [7]. Thus, a subband forms at 6.5 eV below the Fermi level,

which has been attributed to the formation of Zr-H bound states. This results in a reduction of the Zr 4d-density of states at  $E_F$ , as observed earlier [1,8]. Because of this preferential Zr-H bonding, the Co 3d-states would shift towards the  $E_F$  (the effect opposite to that observed on alloying Co with Zr), leading to the enhancement of spin fluctuations in the doped sample. Thus, both effects lead to the suppression of the superconducting transition temperature  $T_C$ . The effects are similar to those observed in Zr-Co metallic glasses on going from Zr-rich to Co-rich alloys [9].

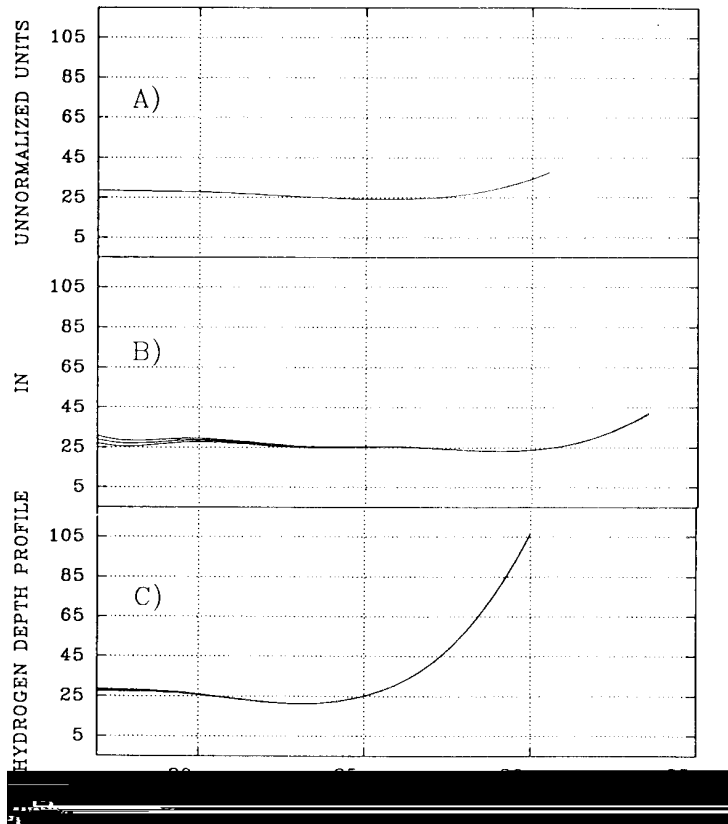


Fig. 5. Hydrogen depth profile of  $Zr_{0.67}Co_{0.33}H_{0.10}$  sample at three different points shown in Fig. 3. The thickness increases as one moves upwards, causing a false decrease of areal density. Point C) lies on an intense areal density line but the depth profile shows that this enhancement is caused by surface contamination.

In the undoped sample, the onset of superconductivity is established by percolation through the Zr-rich part of the matrix ( $T_C = 2.74$  K). As hydrogen concentration increases, the sites with less and less Zr atoms begin to be occupied. Thus, for  $x = 0.01$ , the hydrogen atoms are probably trapped at tetrahedral holes defined by four Zr atoms (step at  $T_C = 2.74$  K), or three Zr atoms and one Co atom (step at  $T_C = 2.68$  K), or two Zr atoms and two Co atoms (step at  $T_C = 2.58$  K). This is in contrast to the hydrogen-doped Zr-Ni amorphous

alloys where sites defined by there Zr atoms and one Ni atom begin to be occupied at much higher hydrogen concentrations [10]. For the Zr-Cu system, this concentration is even higher [1]. This enhanced affinity for hydrogen atoms as one goes from Cu to Ni, and 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 d-states which are only partly filled and, thus, can accommodate the surplus hydrogen electrons more easily. In the case of Cu, the d-band is completely filled and lies well below the Fermi level. This is consistent with the resistivity results [1,3] in the vicinity of the superconducting transition temperatures, which show no evidence of “steps” in hydrogen-doped Zr-Ni and Zr-Cu alloys.

We can assume that introduction of hydrogen tends to suppress percolation in the Zr-rich part of the matrix, and superconductive currents are also directed through the Co-richer domains where spin fluctuations are increasingly influential, owing to a decreasing coherence length,  $\xi$ , found earlier [11] (i.e.,  $\xi = 35 \times 10^{-10}$  m in the undoped sample, and  $\xi = 27 \times 10^{-10}$  m for  $x = 0.12$ ). The existence of spin fluctuations in hydrogen - doped Zr-Co metallic glasses is confirmed in our magnetic measurements [12] which show an increase of the magnetic susceptibilities at temperatures below 20 K, proportional to the hydrogen concentration. Again, if we compare the present results with those for Zr-Ni-H and Zr-Cu-H [1,3], we see that superconductivity is more rapidly suppressed in the Zr-Co-H due to enhanced spin fluctuations.

#### 4. Conclusion

The scanning microprobe and p-p scattering results show a uniform distribution of hydrogen atoms in Zr-Co-H metallic glasses. Although there is no guarantee that this uniformity extends to the nanoscale, we have proposed that the observed “steps” in the resistivity curves at the superconducting transition are caused by different hydrogen environments in the metallic matrix. The effect of hydrogen on the lowering of the superconducting transition temperature is through the decrease of the Zr 4d-density of states at the Fermi level and enhancement of the spin-fluctuations at Co-richer sites.

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#### UTJECAJ NEHOMOGENOSTI NA NANOSKALI NA TEMPERATURU SUPRAVODLJIVOG PRIJELAZA U Zr-Co METALNOM STAKLU DOPIRANOM VODIKOM

Prikazuju se rezultati mjerenja električne otpornosti Zr-Co metalnog stakla dopiranog vodikom u blizini temperature supravodljivog prijelaza,  $T_c$ , u temperaturnom području 1.5 – 4.2 K. Povećanjem koncentracije vodika smanjuje se temperatura supravodljivog prijelaza. Istovremeno se širi područje supravodljivog prijelaza i pojavljuju se stepenice u krivuljama otpora na prijelazu. Prostorna raspodjela vodika, kako površinska tako i dubinska, određena je skenirajućom protonskom mikroprobom i p-p raspršenjem. Dubinska raspodjela vodika na pojedinim mjestima dekonvoluirana je pomoću kubne prilagodbe. Raspravlja se utjecaj razlika u raspodjeli atoma matrice u okolini vodikovih atoma na temperaturu supravodljivog prijelaza u Zr-Co metalnim staklima.