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MAGNETIC SUSCEPTIBILITY OF $(Zr_{80}Co_{20})_{1-x}H_x$ METALLIC GLASSES

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Dedicated to Professor Kseno Ilakovac on the occasion of his 70$^{\mathbf{th}}$ birthday

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The magnetisation of hydrogen-doped $(Zr_{80}Co_{20})_{1-x}H_x$ metallic glasses has been measured in the temperature range 1.7 K -100 K for various dopant concentrations. The system is paramagnetic and becomes superconducting at $T_c = 3.98$ K. The magnetic susceptibility of the undoped sample above T_c is strongly temperature dependent and shows the Curie-Weiss behaviour, whereas in the doped amples it is temperature independent. It has been also found that the magnetic susceptibility at 100 K, $\chi(100\text{ K})$, decreases with hydrogen concentration. The low-temperature upturn in the undoped sample most likely results from a small amount of magnetic impurities. Doping the sample with small hydrogen concentration results in the screening of magnetic impurities thus reducing the Curie-Weiss contribution to the magnetic susceptibility. The form and magnitude of the observed temperature dependence of the magnetic susceptibility are well accounted for by the sum of the Curie-Weiss term and the quantum corrections to the susceptibility.

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1. Introduction

Our previous resistivity and magnetoresistivity results [1] show that in the $Zr_{80}Co_{20}$ metallic glass hydrogen doping reduces the effective electron diffusion constant, D, the electron density of states at the Fermi level, $N(E_F)$, and the screening of the Coulomb interaction, F, leading to a decrease in conductivity and suppression of the T_c.

In this paper we present the results and a detailed quantitative analysis for magnetic susceptibilities of the $(Zr_{80}Co_{20})_{1-x}H_x$ metallic glasses. We compare these with our magnetic susceptibility results for $(Zr_{67}Co_{33})_{1-x}H_x$ [2], and $(Zr_{80}Fe_{20})_{1-x}H_x$ [3], which also show a strong influence of the hydrogen dopant on the magnetic properties and electronic structure in these systems. For instance, the magnetic susceptibility at 100 K, $\chi(100\text{ K})$, of hydrogen-doped $(Zr_{80}Fe_{20})_{1-x}H_x$ [3] and $(Zr_{67}Co_{33})_{1-x}H_x$ [2] decreases with increasing hydrogen concentration.

2. *Experimental methods*

Ribbons of $Zr_{80}Co_{20}$ metallic glass were prepared by rapid solidification of the melt on a single-roll spinning copper wheel in an argon atmosphere. The samples cut from the ribbons were 5 – 8 mm long, 1.7 – 2.2 mm wide, and 25-30 μm thick. The hydrogenation was carried out electrolytically. During hydrogenation, the ribbons curl up because the gas enters preferentially trough the surface, which has been in contact with the quenching wheel. As hydrogen diffuses into the sample, the ribbons straighten out and are then used in the measurements. The hydrogen concentrations were determined volumetrically using a McLeod manometer.

The structures of the as-quenched and hydrogenated samples were examined by X-ray diffraction (XRD) using Cu Kα radiation to verify that they were amorphous.

The magnetisation was measured in the temperature range 1.7 K -100 K using Quantum Design's Magnetic Property Measurement System which uses a SQUID amplifier as a sensitive magnetic field detector. It is capable of resolving variations in magnetic moments as small as 10^{-11} J/T.

3. *Results and discussion*

The measured magnetisation of $Zr_{80}Co_{20}$ metallic glass vs. magnetic field at different temperatures ($T = 5$ K, 10 K, 20 K, 40 K, 60 K, 80 K and 100 K) is shown in Fig. 1. The magnetisation is linear with the magnetic field up to 3 T for temperatures $T > 20$ K and the values of the magnetic susceptibilities were determined from that linear part. The linear behaviour of the magnetisation vs. magnetic field was obtained for all measured samples of $(Zr_{80}Co_{20})_{1-x}H_x$ metallic glasses ($x = 0$, 0.05, 0.12). The magnetisation above $T_c = 3.98$ K strongly increases with decreasing temperature for the undoped sample due to the presence of magnetic impurities. For the doped samples, the temperature dependence of magnetisation is weak. The magnetic susceptibilities, χ(T), (Table 1) of $(Zr_{80}Co_{20})_{1-x}H_x$ metallic glasses vs. temperature below 100 K, are shown in Fig. 2. The solid lines are the best fits to the experimental data of Eq. (4). The magnetic susceptibility of the undoped sample above T_c is strongly temperature dependent and shows the Curie-Weiss behaviour, whereas in the doped samples it is temperature independent. It has been also found that the magnetic susceptibility at 100 K, $\chi(100\text{ K})$, decreases with hydrogen concentration. The value of the magnetic susceptibility at 100 K, $\chi_{\text{exp}} = (160 \pm 1)10^{-5}$ $\text{JT}^{-2}\text{mol}^{-1}$ for $Zr_{80}Co_{20}$, whereas for $(Zr_{80}Co_{20})_{0.88}H_{0.12}$, $\chi_{\text{exp}} = (128 \pm 1)10^{-5}$ $\text{JT}^{-2}\text{mol}^{-1}$ (where mole refers to a mole of metallic atoms, 80% Zr and 20% Co).

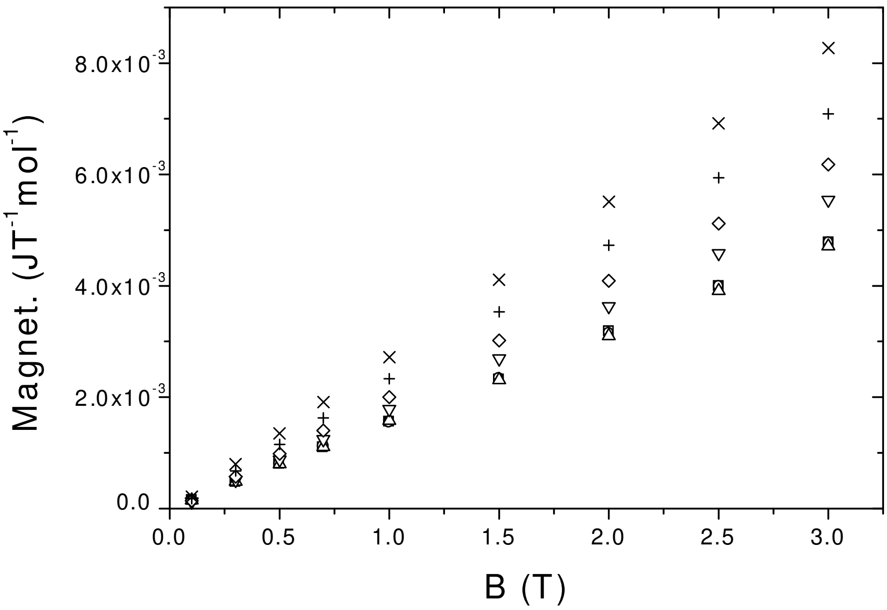

Fig. 1. Measured magnetisation of $Zr_{80}Co_{20}$ *metallic glass vs. magnetic field at different temperatures for* $T = 5$ K $(\times)$, 10 K $(+)$, 20 K $(\diamond)$, 40 K $(\bigtriangledown)$, 60 K $(\triangle)$, 80 K $(\circ)$ *and* 100 K $(\square)$.

TABLE 1. Magnetic susceptibility data for $(Zr_{80}Co_{20})_{1-x}H_x$ *metallic glasses. The experimental magnetic susceptibility at* $T = 100$ K, $\chi_{\rm exp}$*(100* K*), the Pauli spin susceptibility,* $\chi^{\rm d}_{\rm P\,0} = \mu_B^2 N_0(E_F)$*, the enhanced Pauli spin susceptibility,* $\chi^{\rm d}_{\rm P}$*, (where mole refers to a mole of metallic atoms, 80%* Zr *and 20%* Co*), the Stoner factor,* $1/(1-I)$*, the electron-phonon coupling constant,* λ*, and the electronic density of states at the Fermi level,* $N_0(E_F)$*.*

Sample $(Zr_{80}Co_{20})_{1-x}H_x$

x ± 0.01	$\chi_{\rm exp}$ $\pm\,10^{-5}$	$\chi^{\rm d}_{\rm P\,0}$ $\pm\,10^{-5}$	$\chi^{\rm d}_{\rm P}$ $\pm\,10^{-5}$	$\frac{1}{1-I}$ ± 0.1	λ ± 0.01	$N_0(E_F)$ ± 0.01
	$\left(\frac{\rm J}{\rm T^2 mol}\right)$	$\left(\frac{\rm J}{\rm T^2 mol}\right)$	$\left(\frac{\rm J}{\rm T^2 mol}\right)$			$\left(\frac{\rm States}{\rm eV\,at.}\right)$
0	$1.60 \cdot 10^{-3}$	$0.47 \cdot 10^{-3}$	$0.77 \cdot 10^{-3}$	1.6	0.73	1.44
0.05	$1.30 \cdot 10^{-3}$	$0.47 \cdot 10^{-3}$	$0.59 \cdot 10^{-3}$	1.3	0.67	1.45
0.12	$1.28 \cdot 10^{-3}$	$0.46 \cdot 10^{-3}$	$0.60 \cdot 10^{-3}$	1.3	0.65	1.43

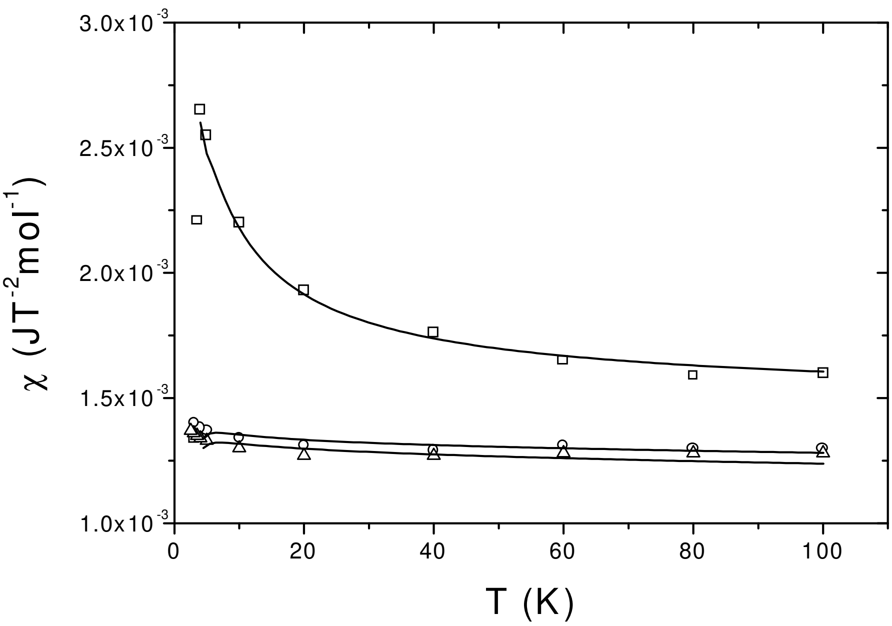

Fig. 2. Magnetic susceptibility of $(Zr_{80}Co_{20})_{1-x}H_x$ *metallic glasses vs. temperature below* 100 K *for* $x = 0$ (□), *0.05* (○) *and 0.12* (△).

The experimental magnetic susceptibility is given as:

$$\chi_{\rm exp} = \chi_{\rm P}^{\rm s} + \chi_{\rm P}^{\rm d} + \chi_{\rm ion} + \chi_{\rm orb} + \chi_{\rm cw}\,, \tag{1}$$

where $\chi_{\rm P}^{\rm s}$ is the Pauli paramagnetism of s-electrons, $\chi_{\rm P}^{\rm d}$ is the Pauli paramagnetism of d-electrons, $\chi_{\rm ion}$ is the ionic-core diamagnetism, $\chi_{\rm orb}$ is the orbital paramagnetism with the Landau contribution included and $\chi_{\rm CW}$ is the Curie-Weiss susceptibility, $\chi_{\rm cw} = C_1/(T + \Theta)$. The Pauli paramagnetism of s-electrons is

$$\chi_{\rm P}^{\rm s} = \mu_B^2\, N_0^s(E_F)\,, \tag{2}$$

where μ_B is the Bohr magneton and $N_0^s(E_F)$ is the bare density of states of s-electrons at the Fermi level. The Pauli paramagnetism of the d-band, $\chi_{\rm P}^{\rm d}$, which is enhanced over the free-electron value due to the Stoner exchange interaction is given by

$$\chi_{\rm P}^{\rm d} = \frac{\mu_B^2\, N_0^d(E_F)}{1 - I_{\rm eff} N_0^d(E_F)}\,, \tag{3}$$

where $I_{\rm eff}$ is the effective exchange integral within the d-band and $N_0^d(E_F)$ is the bare density of states of d-electrons at the Fermi level.

Since the dominant contribution to the electronic density of states at the Fermi level in the transition metals comes from the d-electrons, $\chi_{\rm P}^{\rm s}$ is an order of magnitude smaller than the values of $\chi_{\rm P}^{\rm d}$. The core susceptibilities of the two elements are small ($\chi_{\rm ion} = -20 \times 10^{-5}$ JT^{-2}mol^{-1} for Zr and $\chi_{\rm ion} = -29 \times 10^{-5}$ JT^{-2}mol^{-1} for Co) and we estimate $\chi_{\rm ion} = -22 \times 10^{-5}$ JT^{-2}mol^{-1} of the $(Zr_{80}Co_{20})_{1-x}H_x$. The orbital magnetic moments of the electrons are not completely quenched for partly filled degenerate bands and their contribution to the paramagnetic susceptibility is estimated from the values $\chi_{\rm orb}(\rm Zr) \approx 115 \times 10^{-5}$ JT^{-2}mol^{-1} and $\chi_{\rm orb}(\rm Zr) \approx 50 \times 10^{-5}$ JT^{-2}mol^{-1} [4,5]. Thus, the value of the orbital susceptibility for the $Zr_{80}Co_{20}$ system is estimated to be $\chi_{\rm orb}(Zr_{80}Co_{20}) = 102 \times 10^{-5}$ JT^{-2}mol^{-1}. The Curie-Weiss susceptibility, $\chi_{\rm cw} = C_1/(T + \Theta)$, was calculated using the parameters of the fit C_1 and Θ given in Table 2. Subtraction of $\chi_{\rm ion}$, $\chi_{\rm orb}$ and $\chi_{\rm cw}$ from $\chi_{\rm exp}$ gives the Pauli spin susceptibility $\chi_{\rm P}^{d} = (77 \pm 1)\, 10^{-5}$ JT^{-2}mol^{-1} for the $Zr_{80}Co_{20}$ and $\chi_{\rm P}^{d} = (60 \pm 1)\, 10^{-5}$ JT^{-2}mol^{-1} for the $(Zr_{80}Co_{20})_{0.88}H_{0.12}$.

TABLE 2. A, B, C_1, Θ and C_2 are the coefficients of the fit to the experimental data of Eq. (6), the superconducting transition temperature, T_c.

Sample $(Zr_{80}Co_{20})_{1-x}H_x$

x	A	B	C_1	Θ	C_2	T_c
± 0.01	$\pm 0.1\, 10^{-5}$	$\pm 0.5\, 10^{-5}$	$\pm 0.5\, 10^{-5}$	± 1	$\pm 0.5\, 10^{-5}$	± 0.02
	$\left(\frac{\rm J}{\rm T^2 mol\, K^{\frac{1}{2}}}\right)$	$\left(\frac{\rm J}{\rm T^2 mol\, K^{\frac{1}{2}}}\right)$	$\left(\frac{\rm JK}{\rm T^2 mol}\right)$	(K)	$\left(\frac{\rm J}{\rm T^2 mol}\right)$	(K)
0	$0.3 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$9 \cdot 10^{-3}$	4	$158 \cdot 10^{-5}$	3.98
0.05	$0.5 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$0.5 \cdot 10^{-3}$	2	$140 \cdot 10^{-5}$	3.24
0.12	$0.6 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$0.5 \cdot 10^{-3}$	3	$135 \cdot 10^{-5}$	2.98

The summary of measured and calculated values is given in Table 1. The lowering of the magnetic susceptibility at 100 K, $\chi_{\rm exp}(100\ \rm K)$, upon hydrogenation can be explained as due to the influence of hydrogen on the electronic density of states at Fermi level and Stoner factor and/or its possible effect on the orbital moments.

The values of the bare density of states at Fermi level, $N_0(E_F)$, derived from the relation, $N_0(E_F) = M/[e^2 \rho D(1+\lambda)d]$ are given in Table 1. M is the molecular weight, ρ is the electrical resistivity, D is the electron diffusion constant, λ is the electron-phonon coupling constant and d is the density of the sample. The values of the ρ and the D were used from Ref. [1], while λ was derived from McMillan relation [6] (see Table 1). The obtained values of the bare electronic density of states at the Fermi level, $N_0(E_F)$, and the values of the Stoner factor derived from the relation, $1/(1-I) = \chi_{\rm P}^{\rm d}/(\mu_B^2 N_0(E_F))$, are given in Table 1. The Stoner factor $1/(1-I)$ decreases with the increase of hydrogen concentration. This has been observed also in the $(Zr_{80}Fe_{20})_{1-x}H_x$ [3] and $(Zr_{67}Co_{33})_{1-x}H_x$ [2] systems. Doping the samples with hydrogen decreases the Pauli susceptibility, $\chi_{\rm P}^{\rm d}$ (see Table 1).

The corrections to the magnetic susceptibility in a disordered system that are weakly temperature dependent arise from the spin-splitting and orbital effects [7,8]. It has been shown that the interplay of disorder and the electron-electron interactions results in the spin-diffusion constant being suppressed, which in turn leads to an enhancement of the spin susceptibility at low temperatures. Aslamazov and Larkin [7] were the first to show that, in the presence of disorder, superconducting fluctuations give rise to the corrections in the diamagnetic susceptibility that persist high above the transition temperature. Moreover, the anomalous temperature dependence of the susceptibility has also been found in normal metals, when the interaction between the electrons is repulsive. This correction is enhanced for transition metals by the Stoner factor (Table 1).

We have fitted the temperature-dependent magnetic susceptibility by the relation

$$\chi(T) = -A\sqrt{T} + \frac{B\sqrt{T}}{\ln(T_c/T)} + \frac{C_1}{T+\Theta} + C_2\,, \tag{4}$$

where the first term on the right-hand side is a correction due to the spin-splitting effect in the diffusion channel [8], the second term contains the corrections in the particle-particle channel due to both, the orbital effect and to the spin susceptibility [7, 8], the third term on the right-hand side is the Curie-Weiss susceptibility. The parameter C_2 contains the temperature independent part of the measured magnetic susceptibility. The solid lines in Fig. 2 represent the fit of the experimental data to Eq. 4.

The values of the parameters of the fit A, B, C_1, C_2 and the superconducting transition temperature, T_c, are given in Table 2. The best fit yields $A = 0.3 \times 10^{-5}$ $\mathrm{JT^{-2}mol^{-1}K^{-1/2}}$ and $B = 1 \times 10^{-5}$ $\mathrm{JT^{-2}mol^{-1}K^{-1/2}}$ for the undoped sample, whereas for $(Zr_{80}Co_{20})_{0.88}H_{0.12}$, $A = 0.6\times10^{-5}$ $\mathrm{JT^{-2}mol^{-1}K^{-1/2}}$ and $B = 2\times10^{-5}$ $\mathrm{JT^{-2}mol^{-1}K^{-1/2}}$. The values of both parameters A and B increase upon hydrogenation (see Table 2), through the lowering of the diffusion constant [1]. The hydrogen dopant also reduces the orbital term (which enters the coefficient B) because it enhances the localisation by providing additional centres for quasielastic scattering. The enhancement of the spin susceptibility relatively to the orbital part upon hydrogenation is in agreement with our magnetoresistivity data [1] which show that the hydrogen reduces the spin-orbital scattering rate τ_{so}^{-1}, thus reducing the mixing of spin-up and spin-down subbands. A decrease of the superconducting transition temperature reduces the contributions of the superconducting fluctuations to the diamagnetic moment through the $1/\ln(T_c/T)$ term.

The most likely explanation of the strongly temperature-dependent magnetic susceptibility, Fig. 2, of $Zr_{80}Co_{20}$ metallic glass is that they result from a small amount of magnetic impurities in the nominally pure host. Doping the sample with a small hydrogen concentration results in screening of magnetic moments associated with impurities, which reduces the Curie-Weiss contribution to the magnetic susceptibility. This is consistent with the values of the parameter C_1 obtained from Eq. (4). The best fit yields $C_1 = (9 \pm 1)\,10^{-3}$ $\mathrm{JT^{-2}mol^{-1}K}$ for the undoped sample, whereas for $(Zr_{80}Co_{20})_{0.88}H_{0.12}$ $C_1 = (0.5 \pm 1)\,10^{-3}$ $\mathrm{JT^{-2}mol^{-1}K}$. A numerical estimate of the relative number of spins present in the undoped sample, $C_1/C = 2.4 \times 10^{-3}$, where $C = 3.76$ JT^{-2}mol^{-1} assuming $S = 1/2$, shows that even the smallest hydrogen concentration used is greater than this relative spin number. A suppression of local magnetic moments with hydrogen doping has been observed in the magnetoresistivity results of $(Zr_{68}Fe_{32})_{1-x}H_x$ [9], where hydrogen changed the small negative magnetoresistance, due to the spin-scattering at the local magnetic moments in fields lower than 0.4 T, to a positive one.

4. *Conclusion*

We have analysed the magnetic susceptibility data as a function of hydrogen concentration in $(Zr_{80}Co_{20})_{1-x}H_x$ metallic glass. The system is paramagnetic and becomes superconductive at $T_c = 3.98$ K. The magnetic susceptibility of the undoped sample above T_c is strongly temperature dependent and shows the Curie-Weiss behaviour whereas in the doped samples it is temperature independent. It has been also found that the magnetic susceptibility at 100 K, $\chi(100\ \mathrm{K})$, decreases with hydrogen concentration. The Curie-Weiss behaviour of the undoped sample is primarily due to the contribution of magnetic impurities. Doping the sample with a small hydrogen concentration results in the screening of these magnetic moments and reduces the Curie-Weiss contribution to the magnetic susceptibility. The form and magnitude of the observed temperature dependence of the magnetic susceptibility are well accounted for by the sum of the Curie-Weiss term and the quantum corrections to the susceptibility.

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MAGNETSKA SUSCEPTIBILNOST METALNOG STAKLA $(Zr_{80}Co_{20})_{1-x}H_x$

Mjerili smo magnetizaciju vodikom punjenih metalnih stakala $(Zr_{80}Co_{20})_{1-x}H_x$ u području temperatura 1.7 K – 100 K za razne koncentracije vodika. Taj je sustav paramagnetičan a postaje supravodljiv na $T_c = 3.98$ K. Magnetska je susceptibilnost nepunjenog uzorka iznad T_c jako ovisna o temperaturi i pokazuje Curie-Weissova svojstva, dok je u punjenim uzorcima neovisna o temperaturi. Također smo našli da na 100 K magnetska susceptibilnost, $\chi(100\ \mathrm{K})$, opada s koncentracijom vodika. Niskotemperaturni obrat u nepunjenom uzorku vjerojatno nastaje zbog malih količina magnetskih nečistoća. Punjenje uzorka malom koncentracijom vodika uzrokuje zasjenjivanje magnetskih nečistoća pa se smanjuje Curie-Weissov doprinos magnetskoj susceptibilnosti. Oblik se i iznos opažene temperaturne ovisnosti magnetske susceptibilnosti dobro opisuje zbrojem Curie-Weissovog člana i kvantnim popravkama susceptibilnosti.