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THE USE OF HYDROGEN AS A PROBE TO STUDY QUANTUM INTERFERENCE AT DEFECTS IN METALLIC GLASSES

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The electrical resistivity and the magnetic susceptibility of hydrogen-doped disordered Zr-Ni alloys have been measured at temperatures between 1.7 K and 300 K and in magnetic fields up to 6 T for various dopant concentrations. The temperature and magnetic field dependence of the measured properties have been analysed using the theoretical models of weak-localization and electron-electron interaction in disordered three-dimensional conductors. Doping the samples with hydrogen increases the disorder. Thus, we have found that hydrogen strongly enhances quantum interference at deffects. As a result the effective diffusion constant of the electrons and the screening of the Coulomb interaction are reduced. This leads to an increase in resistivity, suppression of the superconducting transition temperature, and to enhanced spin susceptibility at low temperatures. The Maki-Thompson interaction as well as the spin-orbit contribution to the magnetoresistivity are also depressed.

1. *Introduction*

Metallic glasses offer an exellenct matrix in which to study the behaviour of electrons in highly disordered systems. Their high resistivities span the region of values from those of crystalline alloys to the limit of metallic conduction. The observed anomalous low temperature resistivity and magnetic susceptibility as well as the huge magnetoresistivity of metallic glasses have been associated with the onset of electron localization[1,2] and enhanced electron-electron interaction[3] in the presence of disorder.

We have developed a method[4,5] of using hydrogen as an atomic probe to gain an insight into the way the atomic microenvironment influences the electronic properties of the system. Thus, by changing the hydrogen concentration, the effects of electron localization and electron-electron interaction have been continuously varied and their interplay studied in a controlled way.

In the presence of strong scattering the electron motion through the metal becomes diffusive, and basically all aspects of the Boltzmann behaviour become lost. In the past decade new theoretical models[6] have been developed which treat the disorder in a fundamental way, and are based on the concept of Anderson localization[7] and the interaction between electrons in the presence of a random potential.

In strongly disordered conductors electron momentum relaxation is determined by elastic collisions. At low enough temperatures, where the elastic scattering time is a few orders of magnitude shorter than the inelastic scattering time the quantum corrections to the Boltzmann conductivity arising from the interference of the electronic wave functions are very important because they lead to anomalous dependence of the conductivity on temperature, sample dimensions and external fields.

It has been shown that constructive interference of "uncharged" electrons can only be expected in a backscattering geometry. This quantum interference effect will produce an increase of the sample resistivity. The magnitude of this additional contribution at a given temperature is reduced by the presence of spin-orbit or spin-flip scattering, since they destroy the constructive interference. The inelastic processes destroy the phase coherence and lead to the negative temperature coefficient of the resistivity. An external magnetic field also causes dephasing of partial waves generating particular behaviour in magnetoresistivity. The diffusive character of electrons in highly disordered materials also leads to reduced screening of the electron-electron interaction. This gives rise to a second quantum correction termed interaction correction and an increase of the resistivity. Owing to its weak temperature dependence ($\simeq T^{1/2}$) this correction is restricted to the low temperature region. The interaction correction also gives rise to the low temperature magnetoresistivity that originates from the spin and orbital character of the electronic wave function.

In this paper we present experimental results for the electrical resistivity, magnetoresistivity and magnetic susceptibility of highly disordered Zr-Ni metallic glass doped with hydrogen.

The data were analysed using the above mentioned theoretical models and it was found that they describe well, both qualitatively and quantitatively, the measured properties.

2. *Experimental*

The Zr-Ni alloys were prepared by melt-spinning on a single copper wheel under an argon atmosphere. The ribbons produced were typically 3 mm wide and 30 μm thick. The samples $3-4$ cm long were then cut from the ribbon and electrolitically doped with warious hydrogen concentrations. The details of the method used have been given elsewhere[8]. The amount of absorbed hydrogen was determined using a previously established method[8] between the gain in resistance and volumetrically determined hydrogen concentration.

The structure of the as-quenched and doped samples had been examined by means of an X-ray diffractometer with Cu Kα radiation and found to be amorphous.

The electrical resistance was measured with a standard four-probe DC technique in the temperature range from 1.7 K to 300 K with a precision of a few parts in 10^6. The contacts were made by spot welding or by a silver paint.

The magnetoresistance measurements were carried out in a 6 T superconducting magnet. For this measurement the samples were cut to 10 mm $\times$ 1 mm $\times$ 30 μm and were mounted on an orientable sample holder situated in a separate He-bath. A low frequency, $\simeq$ 20 Hz, four-probe ac-method was used in conjunction with a PAR lock-in amplifier. The temperature range covered was from 1.7 K to 4.2 K in magnetic fields up to 6.5 T.

The magnetic susceptibility measurements were carried out by the Faraday method: the force excerted on the sample by an inhomogeneous magnetic field was measured using a Cahn electrobalance combined with a conventional magnet in fields up to 0.94 T. A sensitivity of 10^{-7} JT^{-2} mol^{-1} was maintained in these measurements and the temperature range covered was from 2 K to 300 K.

3. *Results and discussion*

3.1. *Magnetic field dependence of the electrical resistivity*

The experimental magnetoresistance data of $(Zr_2Ni)_{1-x}H_x$ ($x = 0$; 0.1; 0.2; 0.25; 0.3) samples at 4.2 K in the magnetic fields up to 6 T are shown in Fig. 1. The magnetoresistance was found to be independent of the sample orientation with respect to the magnetic field, as expected for disordered 3D systems.

The magnetoresistance is positive for all systems investigated due to the large spin-orbit scattering at Zr-sites. Namely, the sign of the localization magnetoresistivity is a function of the strength of the spin-orbit interaction, being negative in the absence of this mechanism.

The magnetoresistance slopes are lowered with increasing hydrogen concentration and the saturation is shifted to lower fields.

The magnetoresistivity is dominated by the localization effect and is predicted to be[9)]

$$\Delta\rho = \rho(H,T) - \rho(0,T) = -A\rho^2 \Bigg\{ h^{1/2}\left[F_3\left(\frac{1+t}{h}\right) - \beta F_3\left(\frac{t}{h}\right)\right] + 0.5\left(\frac{h}{1-\gamma}\right)^{1/2}\left[F_3\left(\frac{t_+}{h}\right) - F_3\left(\frac{t_-}{h}\right)\right] - \frac{1}{(1-\gamma)^{1/2}}\left(t_-^{1/2} - t_+^{1/2}\right) + t^{1/2} - (1+t)^{1/2} \Bigg\}, \tag{1}$$

with

$$A = \frac{e^2}{2\pi^2\hbar}(D\tau_{s0})^{-1/2}, \qquad \gamma = \left(\frac{g^*\mu_B H\tau_{s0}}{2\hbar}\right)^2,$$

$$h = \frac{eDH\tau_{s0}}{\hbar}, \qquad t = \frac{\tau_{s0}}{4\tau_i},$$

$$t_\pm = t + 0.5\left[1 \pm (1-\gamma)^{1/2}\right],$$

and

$$F_3(z) = \sum_{n=0}^{\infty}\left\{2\left[(n+z+1)^{1/2} - (n+z)^{1/2}\right] - \left(n+z+\frac{1}{2}\right)^{-1/2}\right\},$$

where $D = v_F^2\tau/3$ is the diffusion constant, τ, τ_i and τ_{s0} are the elastic, inelastic and spin-orbit scattering times, respectively, g^* is the effective g-factor and μ_B is the Bohr magneton. The term proportional to β is the Maki-Thompson magnetoresistance due to superconducting fluctuations. The approximated field dependence of β is contained in the coupling parameter, g, on which β depends[10)]

$$(g(T,H))^{-1} = \ln\left(\frac{T_c}{T}\right) + \Psi\left(\frac{1}{2}\right) - \Psi\left(\frac{1}{2} + \frac{DeH}{2\pi k_B T}\right), \tag{2}$$

where Ψ is the digamma function. When g is calculated from Eq. 2 one can use Larkin's tabulation[11)] to obtain $\beta(T,H)$.

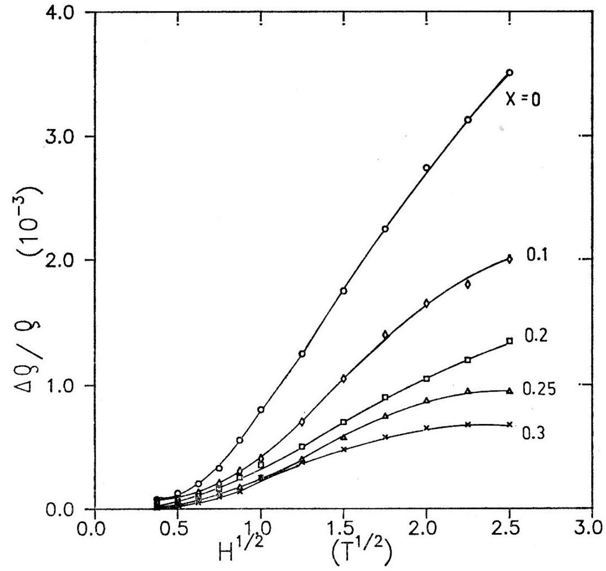

Fig. 1. Magnetoresistance of $Zr_{0.67}Ni_{0.33}H_x$ *metallic glasses, for different values of hydrogen concentration* x*, obtained at 4.2* K*. Full lines are theoretical fits of the sum of Eq. (1), (3) and (4).*

There are also corrections to the magnetoresistivity from Coulomb interaction which is modified in the presence of disorder. These corrections are important, only, at very low temperatures and high magnetic fields. There are two types of corrections: the spin-splitting in the diffusion channel has been given by Lee and Ramakrishnan[12)]

$$\Delta\rho = \rho^2 \frac{e^2}{4\pi^2\hbar} F \left(\frac{k_B T}{2\hbar D}\right)^{1/2} g_3 \left(\frac{g\mu_B H}{k_B T}\right), \quad (3)$$

with

$$F^* = \frac{32F}{3}\left(\left(1-\frac{F}{2}\right)^{3/2} - \left(1-\frac{3F}{4}\right)\right),$$

where F is the averaged screened Coulomb potential ($0 < F < 1$), and the orbital part in the Cooper channel which has been given by Altshuler et al.[13)]

$$\Delta\rho = \rho^2 g(T,H) \frac{e^2}{8\pi^2\hbar}\left(\frac{eH}{\hbar}\right)^{1/2} \Phi_3\left(\frac{2DeH}{\pi k_B T}\right). \quad (4)$$

The functions F_3, g_3 and Φ_3 are simmilar in form resulting in an H^2 dependence of the magnetoresistivity at low fields going over to an $H^{1/2}$ dependence at higher fields.

The magnitude of the resistivity change is set by the parameter ρ, but the field and temperature scales are fixed by the scattering parameters.

The localization contribution depends on the relative magnitude of the respective scattering lengths, $(D\tau_s)^{1/2}$ compared to the Landau length $(\hbar/eH)^{1/2}$. As can be seen from Eq. (3), the spin-splitting term depends on the usual $g\mu_B H/k_B T$ factor, and the orbital interaction (Eq. (4)) follows the quotient of the thermal diffusion length to the Landau length $\big((\hbar D/k_B T)/(\hbar/eH)\big)^{1/2}$.

The solid curves fitted to the experimental points in Fig. 1 are derived from the sum of the relations (1), (3) and (4). The inelastic scattering time τ_i, the spin-orbit scattering time τ_{s0}, the superconducting transition temperature T_c, the diffusion constant D and the screening parameter F have been used as fitting parameters. The dominant contribution (92%) to the measured magnetoresistivity comes from the localization term (Eq. (1)). The contribution from the spin-splitting term (Eq. (3)) is greatly reduced by the spin-orbit scattering and it amounts to 5% of the measured values. The orbital contribution (Eq. (4)) is even smaller (2%). From the analysis of the data we have determined the reasonable values of τ_i, τ_{0s}, D and F (Table 1).

It can be seen from Table 1 that the diffusion constant and the spin-orbit scattering rate are both lowered with increasing dopant concentration. The reduction of the effective spin-orbit contribution to the magnetoresistivity by the dopant can be taken as evidence that the hydrogen atoms migrate mainly to the Zr-rich sites.

TABLE 1

Sample	$D(10^{-5}\,\mathrm{m^2s^{-1}})$	$\tau_i(10^{-11}\mathrm{s})$	$\tau_{s0}(10^{-12}\mathrm{s})$	F	β (4.2 K)
$Zr_{0.67}Ni_{0.33}$	2.8	3.3	2.44	0.45	3.97
$Zr_{0.67}Ni_{0.33}H_{0.1}$	2.7	3.4	3.44	0.2	1.32
$Zr_{0.67}Ni_{0.33}H_{0.2}$	2.65	4.8	4.37	0.2	1.035
$Zr_{0.67}Ni_{0.33}H_{0.25}$	2.55	5.7	6.71	0.19	0.59

Values of the diffusion coefficient (D), the inelastic scattering time (τ_i), the spin-orbit scattering time (τ_{s0}), the screening parameter (F) and the Maki-Thompson coefficient (β) as determined from the magnetoresistivity data.

The inelastic scattering time, τ_i, increases with hydrogen concentration (Table 1). The inelastic scattering comes from the electron-electron interaction at lowest temperatures and from the electron-phonon interaction at higher temperatures.

We can compare the observed values of τ_i with the ones calculated from theoretical predictions.

Schmid[14)] has given the expression for the inelastic scattering time coming from the electron-electron interaction

$$\tau_{i(e-e)} = h\left(\frac{\pi E^2}{8E_F} + \frac{3^{1/2}E^{3/2}}{2E_F^{1/2}}(k_F l)^{3/2}\right)^{-1}, \tag{5}$$

where $E = k_B T$. With $T = 4.2$ K, $E_F = 6.75$ eV, $k_F = 1.335\ 10^{10}$ $\mathrm{m^{-1}}$ and $l = 3\,10^{-10}$ m, we obtain $\tau_i = 1.91\,10^{-8}$ s. This is three orders of magnitude greater than the observed values (Table 1). This discrepancy emphasizes the large enhancement factor of the electron-electron interactions due to atomic disorder.

Takayama[15)] has calculated the inelastic scattering time due to the electron-phonon scattering

$$\tau^{-1}_{i(e-e)} = 2\pi^2\lambda\,\frac{(k_BT)^2}{k_F l\hbar^2\omega_D}, \tag{6}$$

with λ electron-phonon coupling constant and ω_D Debye frequency.

If we use the known values of parameters for $(Zr_{0.67}Ni_{0.33})_{1-x}H_x$ metallic glass: $x = 0$; $\lambda = 0.6$, $k_F = 1.335\ 10^{10}$ $\mathrm{m^{-1}}$, $l = 3\ 10^{-10}$ m, $T = 4.2$ K and $\omega_D = 3.06\ 10^{13}$ $\mathrm{s^{-1}}$, and for $x = 0.2$: $k_F = 1.295\ 10^{10}$ $\mathrm{m^{-1}}$ and $\omega_D = 3.3\ 10^{13}$ $\mathrm{s^{-1}}$, we obtain $\tau_i = 3.39\ 10^{-11}$ s for $x = 0$ and $\tau_i = 3.55\ 10^{-11}$ s for $x = 0.2$. Thus, we can conclude that the increase of the inelastic scattering time comes partly from an increase of the Debye temperature and a decrease of the electron-phonon coupling constant with the hydrogen concentration which was observed in the specific-heat measurement[16)].

Since inelastic scattering presents one of the mechanisms (others being the spin-flip and spin-orbit scattering) by which a phase coherence of two partial electron waves traveling along time reversed electron paths is destroyed, we can try to calculate the phase coherence time, τ_φ, as a function of hydrogen concentration. In the strong scattering limit coming from the zero point motion of the atoms, it is given as[17)]

$$\tau_\varphi = \frac{M\Theta_D D\hbar}{mT_F D_0 E_F}\left(\frac{\zeta}{a}\right)^4, \tag{7}$$

with m the electron mass, M is the ionic mass, $D_0 = \hbar/m$, Θ_D is Debye temperature, T_F is Fermi temperature, a is interatomic distance and $\zeta = (D/\omega_D)^{1/2}$.

Using the known parameters for $(Zr_{0.67}Ni_{0.33})_{1-x}H_x$ metallic glass: $x = 0$, $M = 135\ 10^{-27}$ kg, $\Theta_D = 234$ K, $D = 2.8\ 10^{-5}$ m^2 s^{-1}, $\zeta = 9.6\ 10^{-10}$ m, $a = 3.3\ 10^{-10}$ m, $E_F = 6.75$ eV, and for $x = 0.2$: $\Theta_D = 250.44$ K, $D = 2.65\ 10^{-5}$ m^2 s^{-1}, $E_F = 6.4$ eV, $\zeta = 9\ 10^{-10}$ m, $a = 1.8\ 10^{-10}$ m we obtain from Eq. (7), the phase coherent times: for $x = 0$, $\tau_\varphi = 2.91\ 10^{-12}$ s and for $x = 0.2$ $\tau_\varphi = 7.1\ 10^{-12}$ s. Thus, we can say that the hydrogen effectivelly enhances the phase-coherent time by providing additional centers for the elastic scattering. The enhancement of τ_φ is consistent with the observed (Table 1) increase of the inelastic scattering time, τ_i, with the dopant.

The value of the Maki-Thompson parameter $\beta(T, H)$ (Table 1) decreases with increasing hydrogen concentration. This agrees with the observed lowering of the superconducting transition temperature T_c under similar conditions[5)].

We have observed earlier[5)] that the suppresion of T_c is very fast at smaller dopant concentrations and is saturated at hydrogen concentration $x \geq 0.5$. The reduction of T_c was found[5)] to be accompanied by the increase in the resistivity. The saturation of the resistivity at $x \geq 0.5$ has been explained[5)] by the tendency of the electron mean free path to converge to the interatomic spacing (Ioffe-Regel limit[18)]).

Anderson et al.[19)] have estimated the resistivity dependence of the superconducting transition temperature in the case of strong static and nonmagnetic disorder ($k_F l \simeq 1$). They found that the slowing down of electron diffusion enhances the Coulomb repulsive interaction and this reduces T_c. In this case the Coulomb pseudopotential in 3D system is given as[19)]

$$\mu^* = \frac{\mu'}{(1 + \mu' \ln(\varepsilon_F/\omega_D) - (\mu' - \mu)\ln(\alpha^{1/2}\varepsilon_F\tau)}, \tag{8}$$

with

$$\mu' = \mu[1 + 9\pi/(4k_F^2 l^2)\ln\alpha],$$

and

$$\alpha = (g_c\rho/l)^3 = (\rho/\rho_c)^3,$$

and T_c becomes the "universal" decreasing function of ρ/ρ_c (ρ_c being the critical resistivity which is an order of magnitude smaller than the Mott's critical resistivity.)

The experimental data in Fig. 2 are fitted by the McMillan's relation[20)]

$$T_c = \frac{\omega_D}{1.45} \exp\left(- \frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right). \tag{9}$$

The parameters of the fit are: the electron-phonon coupling constant λ_{ph}, the effective Coulomb potential μ, the electron mean-free path l and the residual resistivity ρ_c. To calculate μ^* from Eq. (8) we have used for $(Zr_{0.67}Ni_{0.33})_{1-x}H_x$ the values: $x = 0$, $k_F = 1.335\ 10^{10}$ m^{-1}, $\Theta_D = 234$ K; $x = 0.5$ $k_F = 1.24\ 10^{10}$ m^{-1}, $\Theta_D = 272$ K. We have used a linear interpolation to calculate k_F and Θ_D for the hydrogen concentrations $0 < x < 0.5$. The values of the parameters extracted from the fit are: for $x = 0$, the mean free path $l = 4.6\ 10^{-10}$ m the electron-phonon coupling constant $\lambda_{ph} = 0.6$, $\mu = 0.13$ and $\rho_c = 20$ $\mu\Omega$cm, and for $x = 0.5$ $l = 2.9\ 10^{-10}$ m.

The value of the mean-free path decreases with hydrogen concentration, it's magnitude being somewhat higher than the Zr-Zr nearest neighbours distance ($3.3\ 10^{-10}$ m) and Zr-H distance ($1.8\ 10^{-10}$ m) for the undoped and doped samples, respectively. Thus, we can conclude that the Ioffe-Regel limit is indeed reached in the systems investigated and can explain the observed resistivity saturation.

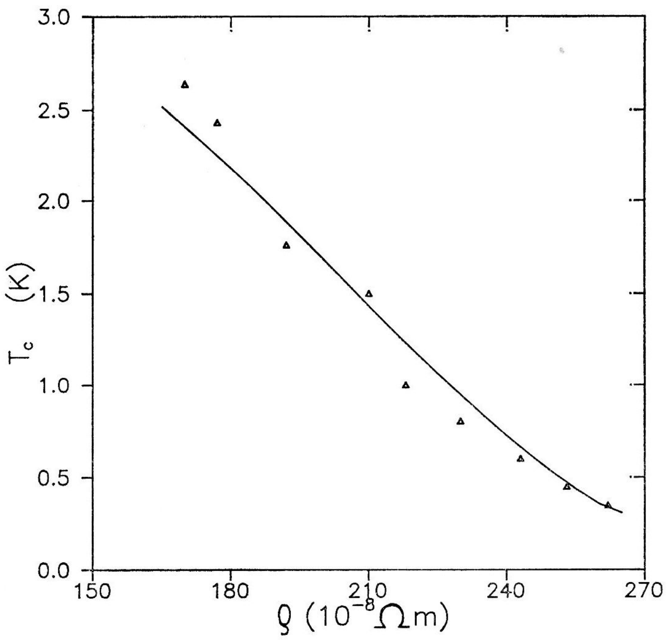

Fig. 2. Superconducting transition temperature, T_c, of $Zr_{0.67}Ni_{0.33}H_x$*, vs. the electrical resistivity. The lines are the best fits obtained from Eq. (9).*

The fit to the experimental data of Eq. (9) could be improved by taking into account a decrease of the electron-phonon coupling constant, λ_{ph}, in the presence of hydrogen. This was indeed observed[5,16] and was explained as due to the increase of the Debye temperature. Therefore, we conclude that the depression of T_c with the dopant is caused partly by the increase of Θ_D and partly by the increase of the effective Coulomb potential as a result of the interplay between the interaction and disorded, and is a localization effect.

3.2. *Temperature dependence of the electrical resistivity*

The phase breaking of the electron coherence takes place throught the inelastic scattering processes characterized by τ_i. In the presence of spin-orbit scattering, characterised by τ_{s0} this results in the conductivity corrections[9]

$$\sigma(T) = \frac{e^2}{2\pi^2\hbar}\left[3\left(\frac{1}{D\tau_{s0}} + \frac{1}{D\tau_i}\right)^{1/2} - \left(\frac{1}{D\tau_i}\right)^{1/2}\right]. \tag{10}$$

τ_{s0} is constant and τ_i is found to follow T^{-2} in metallic glasses at low temperature. This gives the localization correction proportional to T.

The Coulomb interaction term takes the following form[21]

$$\sigma_{e-e} = \frac{1.3e^2}{4\pi^2\hbar}\left(\frac{4}{3} - 2F^* - \frac{2}{\ln(T_0/T)}\right)\left(\frac{k_B T}{D\hbar}\right)^{1/2}, \tag{11}$$

where $F^* = F - \lambda_{ph}$ and with D, F, T_c and λ_{ph} defined in Sec. 3a.

In contrast to the magnetoresistivity, the temperature dependence of the resistivity at low temperature ($T < 20K$) is dominated by the interaction effects. The localization term is small at low temperatures, because the phase-breaking caused by the inelastic scattering processes falls off with decreasing temperature.

The experimental data for temperatures 5 K $< T <$ 80 K are fitted by the relation

$$\frac{\Delta\rho(T)}{\rho} = -A\big[3(B + C^2T^2)^{1/2} - CT + ST^{1/2}E\big], \tag{12}$$

which is a summation of Eq. (10) and Eq. (11). In Eq. (12) $A = e^2/2\pi^2\hbar$ is constant, and $B = 1/D\tau_{s0}$, $C = (1/4D\alpha)^{1/2}$, $\tau_i = \alpha T^{-2}$, $E = (k_B/D\hbar)^{1/2}$ and

$$S = \frac{1.3}{2}\left[\frac{4}{3} - 3F^* - \frac{2}{\ln(T_c/T)}\right]$$

are parameters of the fit.

The values of D, τ_i, τ_{s0} and T_c as determined from the fit are given in Table 2. Their magnitude and concentration dependence are in agreement with that obtained from the magnetoresistivity data.

TABLE 2

Sample	$D(10^{-5}\,\mathrm{m^2s^{-1}})$	$\tau_i(10^{11}\mathrm{s})$	$\tau_{s0}(10^{12}\mathrm{s})$	T_c
$Zr_{0.67}Ni_{0.33}H_{0.004}$	2.94	3	3.4	2.57
$Zr_{0.67}Ni_{0.33}H_{0.04}$	2.81	2.5	3.6	2.45
$Zr_{0.67}Ni_{0.33}H_{0.108}$	2.78	2.8	4.41	2.43

Values of the diffusion coefficient (D), the inelastic scattering time (τ_i), the spin-orbit scattering time (τ_{s0}) and the superconducting transition temperature (T_c) as determined from the temperature dependence of the resistivity.

The experimental data (points) and the fit of Eq. (12) (solid lines) are shown in Fig. 3 versus the square root of temperature for temperatures up to 25 K and in Fig. 4 versus the temperature up to 80 K. We can conclude that the quantum corrections to the resistivity are proportional to $T^{1/2}\ln^{-1}(T_c/T)$ from 5 K to 16 K as predicted by the Coulomb interaction model and to $-T$ from 16 K to 80 K due to electron localization.

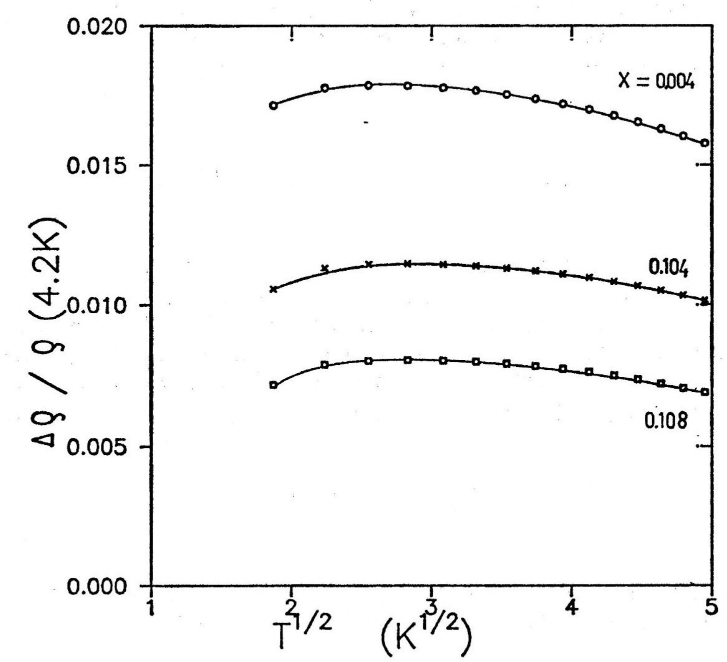

Fig. 3. The change of resistivity ($\Delta\rho$(T) − $\Delta\rho$(4.2 K)) normalized to the value at 4.2 K vs. the square root of temperature below 25 K for $Zr_{0.67}Ni_{0.33}H_x$ metallic glasses. The lines are the best fits obtained from Eq. (12).

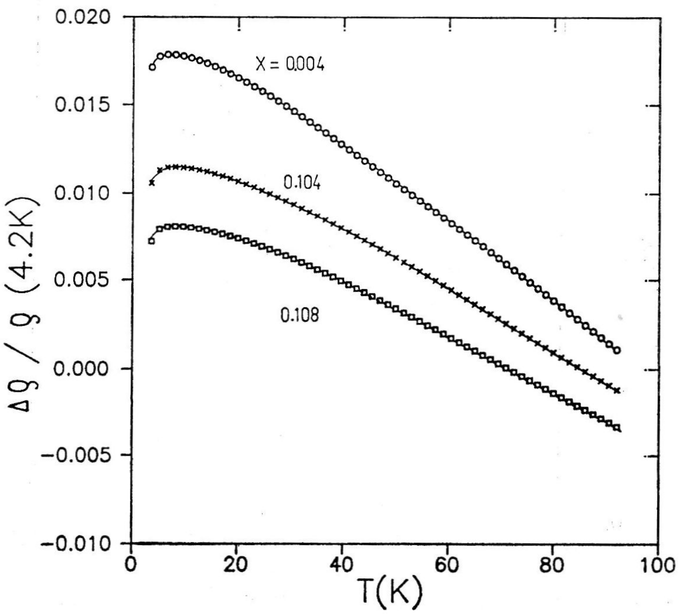

Fig. 4. The change of resistivity $(\Delta\rho(\mathrm{T}) - \Delta\rho(4.2\ \mathrm{K}))$ *normalized to the value at* 4.2 K *as a function of temperature below* 80 K. *The lines are the best fits obtained from Eq. (12).*

The data pertaining to the resistivity in the vicinity of the superconducting transition temperature are shown in Fig. 5.

The fluctuating conductivity dominates over the localization conductivity for $T_c < T < 1.05T_c$. This excess electrical conductivity consists of two distinct terms

$$\Delta\sigma = \sigma_{AL} + \sigma_{MT} \tag{13}$$

where σ_{AL} is the Aslamazov-Larkin[22)] term which originates from the virtual Cooper pairs created by thermal fluctuations and σ_{MT} is the Maki-Thompson[23)] term coming from the interaction of normal conducting electrons and the superfluid. In amorphous superconductors the coherence length is an order of magnitude smaller than in crystalline superconductors due to the small electron mean free path which is of the order of interatomic spacings in the former. (For example, in amorphous Zr_2Ni, $\zeta_0 = 6\ 10^{-9}$ m while $\zeta_0 = 10^{-7}$ m in most crystalline superconductors.) This permits rather localized fluctuations of the order parameter involving a relatively smaller region of material than in the crystalline case. Thus, such fluctuations involve a smaller volume free energy. As a result, the effects of fluctuations are observable over a much broader temperature range in amorphous superconductors. At the same time the “normal” part of the conductivity is two orders of magnitude smaller in amorphous superconductors so that $\Delta\sigma/\sigma = 10^{-3}$ in contrast to 10^{-6} in crystalline ones. This permits us to measure the fluctuating conductivity with enough precision.

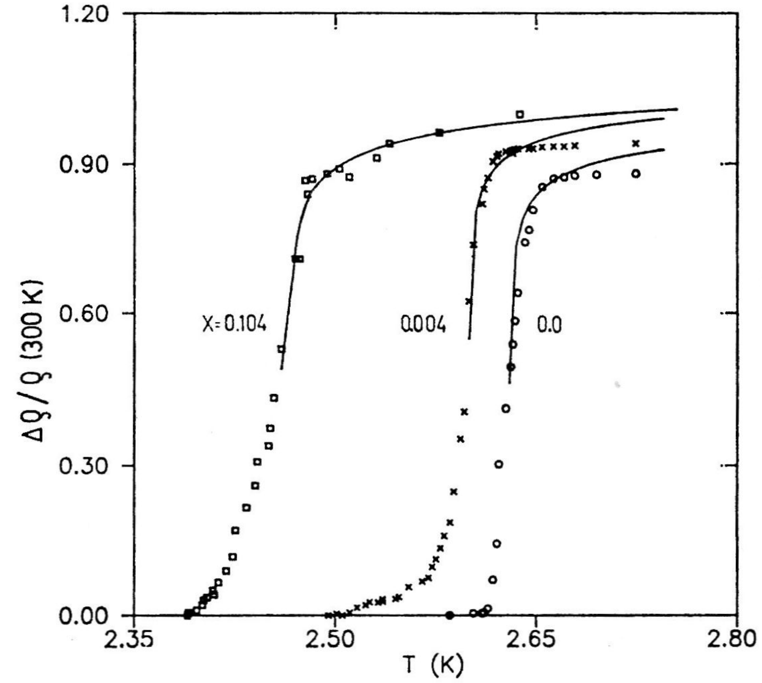

Fig. 5. The electrical resistivity of $Zr_{0.67}Ni_{0.33}H_x$ *metallic glasses for temperature* $T_c < T < 1.1T_c$. *The lines are the best fits obtained from Eq. (17).*

In a 3D superconductor the Aslamazov-Larkin term is[22)]

$$\sigma_{AL} = \frac{e^2}{32\xi t^{1/2}}, \tag{14}$$

with $t = (T - T_c)/T_c$ the normalized reduced temperature and ξ the coherence length.

The Maki-Thompson contribution, in the case for small pair breaking parameter δ, is given as[23)]

$$\sigma_{MT} = \frac{e^2}{8\xi t^{1/2}}, \tag{15}$$

so that σ_{MT} is four times larger than σ_{AL}. If the pair-breaking parameter is included the Maki-Thompson term becomes[24)]

$$\sigma_{MT} = \frac{e^2}{8\xi t^{1/2}} \frac{1}{1 + (\delta/\varepsilon_0)^{1/2}}, \tag{16}$$

with $\varepsilon_0 = 8(T - T_c)/\pi$. In the case of inelastic scattering, the pair-breaking parameter is

$$\delta = \frac{8}{\pi} T_c \varepsilon_c,$$

and

$$\varepsilon_c = \frac{\pi h}{8 k_B T_c \tau_i},$$

where τ_i is the inelastic scattering time.

The experimental data in Fig. 5 are fitted (solid line) by the relation

$$\Delta\rho/\rho = A - B \frac{T_c^{1/2}}{(T - T_c)^{1/2}} \left(1 + \frac{4}{1 + C/(T - T_c)} \right), \tag{17}$$

with A a free parameter, $B = e^2/32\xi$ and $C = \pi\hbar/8k_B\tau_i$. T_c value is parameter of the fit, and $\xi = 6\ 10^{-9}$ m.

The value of τ_i calculated from C is 3.03 10^{-11} s which is in good agreement with the one obtained from the magnetoresistance measurements (Table 1).

3.3. *Temperature dependence of the magnetic susceptibility*

It has been shown[5,25] that the interplay of the disorder and electron-electron interactions results in the suppresion of the spin-diffusion constant which in turn leads to the enhancement of the spin susceptibility at low temperatures.

The quantum corrections to the magnetic susceptibility arise from the spin-splitting and orbital effects.

The spin-splitting term in both the Cooper, $\delta\chi_s^c$, and the diffusion channel, $\delta\chi_s^\nu$, in 3D systems is given as[25]

$$\delta\chi_s = \delta\chi_s^c + \delta\chi_s^\nu = \frac{\zeta(1/2)(g\mu_B)^2}{16\pi^{3/2}2^{1/2}(D\hbar)^{3/2}}\, T^{1/2} \left[2\left(\ln\left(\frac{T_c}{T}\right)\right)^{-1} - \lambda^{(j=1)} \right], \tag{18}$$

where $\lambda^{(j=1)}$ is a dimensionless constant for the electron-hole interaction ($\lambda^{(j=1)} > 0$) for an attractive interaction), $\zeta(x)$ is the Riemann zeta function.

The correction to the orbital magnetic susceptibility due to the correction in the density of states at the Fermi level is given as[25]

$$\delta\chi = -2\chi_0 \left(\frac{\pi}{6}\right)^{1/2} \zeta\left(\frac{1}{2}\right) \left(\frac{T\tau}{h}\right)^{1/2} \left(\ln\left(\frac{T_c}{T}\right)\right)^{-1}, \tag{19}$$

where $\chi_0 = -(2/3)\beta^{*2}N_0$ is the diamagnetic susceptibility of electrons, $\beta^* = \hbar e/(2m^*c)$, N_0 is the density of states at E_F for one spin orientation and τ is the momentum relaxation time.

The magnetic susceptibility results for paramagnetic $Zr_{0.67}Ni_{0.33}H_x$ ($x = 0$; 0.13; 0.33) samples are shown in Fig. 6 versus the square-root of temperature. The values of the susceptibilies were found to be field independent up to 0.94 T, thus confirming the absence of magnetic impurities. The susceptibilities are only weakly temperature dependent, except below 30 K where a small increase is observed. There is a shallow minimum between 60 K and 115 K. The susceptibility is lowered by the dopant, the increase at low temperature is enhanced and the position of the minimum is shifted to higher temperatures.

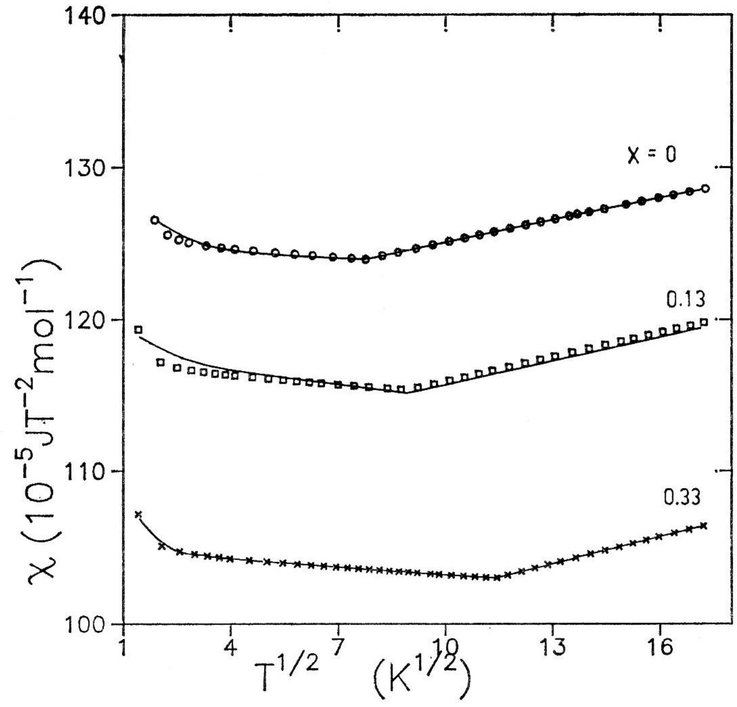

Fig. 6. The magnetic susceptibility of hydrogen doped $Zr_{0.67}Ni_{0.33}H_x$ *metallic glasses as a function of the square-root of temperature. The lines are the best fits obtained from Eqs. (20) and (21).*

The influence of hydrogen on the lowering of the room temperature susceptibility has been explained in detail elsewhere[5]. We have concluded[5] that it can be mainly attributed to the change of the Pauli paramagnetism through the lowering of the electronic density of states at the Fermi level, $N(E)$. Namely, hydrogen atoms migrate to the Zr-rich sites where their s-electron hybridize with the zirconium d-band. This leads to a formation of bound states close to the bottom of the valence band and to a decrease in $N(E_F)$[26].

We have fitted the temperature-dependent magnetic susceptibility for temperatures $T_c < T < T_{\min}$, ($T_{\min}$ is the temperature of the minimum in the susceptibility) by the relation

$$\delta\chi = -AT^{1/2} - BT^{1/2}\left(\ln\left(\frac{T_c}{T}\right)\right)^{-1} + C_1, \tag{20}$$

where the first term on the right-hand side is a correction due to the spin-splitting effect in the diffusion channel and the second one contains the corrections in the Cooper channel due to the orbital effect and to the spin susceptibility.

For temperatures $T > T_{\min}$ the data have been fitted by the relation

$$\delta\chi = -BT^{1/2}\left(\ln\left(\frac{T_c}{T}\right)\right)^{-1} + C_2, \tag{21}$$

where A and B are the temperature-independent parameters of the fit and $C_2 = C_1 - AT_{\min}$. This is because the inelastic relaxation time τ_i becomes comparable to the elastic scattering time τ at about 100 K (τ_i is $\simeq 5\ 10^{-15}$ s at 100 K and $\tau \simeq 5\ 10^{-15}$ s from a diffusion constant) and localization effects can be neglected above that temperature.

TABLE 3

Sample	A (10^{-5}) $(\mathrm{JT^{-2}mol^{-1}K^{-\frac{1}{2}}})$	B (10^{-5}) $(\mathrm{JT^{-2}mol^{-1}K^{-\frac{1}{2}}})$	C_2 (10^{-5}) $(\mathrm{JT^{-2}mol^{-1}})$	$T_{\min}$ (K)	T_c (K)
$Zr_{0.67}Ni_{0.33}$	0.6	4.0	115.5	60	2.5
$Zr_{0.67}Ni_{0.33}H_{0.13}$	0.85	4.4	106.3	80	0.95
$Zr_{0.67}Ni_{0.33}H_{0.33}$	1.15	4.95	91.7	115	0.85

The coefficient of fit to magnetic susceptibility data by Eqs. (20) and (21).

The values of the parameters A, B, C_2 as well as T_c and $T_{\min}$ are given in Table 3. The best fit gives $A = 0.6\ 10^{-5}\ \mathrm{JT^{-2}mol^{-1}K^{-1/2}}$ and $B = 4\ 10^{-5}\ \mathrm{JT^{-2}mol^{-1}K^{-1/2}}$ for the undoped sample. The value of B calculated from Eq. (19) and from χ_s^c part of Eq. (18) using the value of the diffusion coefficient $D = 2.8\ 10^{-5}\ \mathrm{m^2s^{-1}}$ are $2\ 10^{-5}$ $\mathrm{JT^{-2}mol^{-1}K^{-1/2}}$ and $1.92\ 10^{-5}\ \mathrm{JT^{-2}mol^{-1}K^{-1/2}}$, respectively, and together give $3.92\ 10^{-5}\ \mathrm{JT^{-2}mol^{-1}K^{-1/2}}$, in good agreement with the experimental value. The value of $A_{\exp}$ is also found to agree well with that estimated from χ_s^ν part of Eq. (18) which is $0.57\ 10^{-5}\ \mathrm{JT^{-2}mol^{-1}K^{-1/2}}$.

It can be seen from Table 3. that both A and B increase upon hydrogenation through the lowering of the diffusion constant. At the same time A, which gives the localization correction, is enhanced relatively to B, which represents the corrections due to the change of the Coulomb interaction.

This relative increase of A with respect to B is caused by a reduction of the spin-orbit scattering rate $1/\tau_{s0}$ (Table 1) upon hydrogenation, so that the mixing of the spin-up and spin-down subbands is reduced. The hydrogen dopant also reduces the orbital term (which enters B) because it enhances localization by providing additional centers of quasielastic scattering (see 3a). T_c also decreases, so that the contribution of the superconducting fluctuations to the diamagnetic moments through the $\ln^{-1}(T_c/T)$ term is reduced. The shift of $T_{\min}$ to a higher temperature is a consequence of the increase of the inelastic scattering time by the dopant (Table 1). The observed increase of the magnetic susceptibility at low temperatures cannot be attributed to the "normal" temperature dependence of the Pauli susceptibility which is a result of the increase of the density of states at low temperatures $(N(1 - \pi^2 k_B T^2)/12\mu_0)$, because the latter is two orders of magnitude smaller and goes like T^2. Since, the density of states is lowered in the doped samples this "classical" variation of the Pauli susceptibility would be in the opposite direction of what we have observed.

4. *Conclusion*

We have measured and analysed the magnetic and transport properties of Zr-Ni-H metallic glasses as a function of disorder which has been increased by doping the samples with hydrogen.

The observed anomalous temperature dependence of the resistivity and magnetic susceptibility, as well as the anomalous magnetoresistivity and a decrease of the superconducting transition temperature with disorder, as measured by the resistivity, were explained using the theoretical models of quantum interference in disordered systems.

Positive magnetoresistivity has been explained as being due to weak-localization in the presence of strong spin-orbit scattering and Maki-Thompson fluctuations. Both the spin-orbit scattering rate and the Maki-Thompson contributions are strongly suppressed with increased hydrogen concentration. At the same time hydrogen atoms present additional centres for the quasielastic scattering which leads to a reduction of a diffusion constant. This, on the other hand, reduces the screening of the effective Coulomb interaction resulting in a decrease of the superconducting transition temperature with the dopant.

The temperature dependence of the resistivity for temperatures below 16 K is found to be dominated by the interaction effects and for temperatures between 16 K and 80 K by the localization effects as predicted by theoretical models.

It has been found that the increase of the magnetic susceptibility at low temperatures which is proportional to hydrogen concentration can be well understood in terms of the slowing down of spin diffusion in the presence of enhanced disorder.

In conclusion, we have developed a method of using hydrogen as an atomic probe to study quantum interference at deffects in highly disordered systems. The method has proved very effective and we have been able to interpret our data both qualitatively and quantitatively. Thus, reasonable values of β, τ_i, τ_{s0}, D and F have been determined from the analysis of the data.

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UPOTREBA VODIKA KAO PROBE ZA PROUČAVANJE KVANTNE INTERFERENCIJE NA DEFEKTIMA U METALNIM STAKLIMA

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Prikazani su rezultati mjerenja električne otpornosti i magnetske susceptibilnosti (Zr-Ni)-H ultrabrzo kaljenih metalnih stakala u temperaturnom intervalu od 1.7 K do 300 K te u magnetskim poljima do 6 T u ovisnosti o koncentraciji absorbiranog vodika. Anomalna ovisnost mjerenih svojstava o temperaturi i magnetskom polju interpretirana je u svjetlu novijih teorijskih modela slabe lokalizacije i elektron-elektron interakcije u neuređenim trodimenzionalnim vodičima. Dopiranje vodikom povećava nered u sistemu, a time i kvantnu interferenciju na defektima. Kao rezultat toga dolazi do smanjenja difuzione konstante elektrona i smanjenja zasjenjenja efektivne Coulombove interakcije. Ovo dovodi do opaženog povećanja otpornosti, smanjenja temperature supervodljivog prijelaza te povećanja magnetske susceptibilnosti na niskim temperaturama. Također su smanjeni doprinosi spin-orbitalnog raspršenja i Maki-Thompsonove interakcije magnetootpornosti.