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Hydrogen-induced degradation of T_c in Zr-Ni and Zr-Cu metallic glasses

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We have studied the effect of hydrogen doping of Zr-3*d* metallic glasses on the superconducting transition temperature T_c. It is shown that the degradation of T_c is well accounted for by Anderson localization in highly disordered systems.

I. INTRODUCTION

It has been known for a long time[1,2] that the superconducting transition temperature, T_c, of various metallic films decreases sharply with thickness and disorder, that is with the increase of the film resistance. It is also known that in the case of *A* 15 superconductors[3] (such as Nb_3Ge, Nb_3I, V_3Si) T_c decreases with disorder (increasing resistivity).

The classical theory of disordered superconductors formulated by Anderson[4] and Gorkov,[5] predicts that the superconducting transition temperature is unaffected by static and nonmagnetic disorder.

As the approach to Anderson localization is better understood, the effects of disorder on the superconducting properties have been reexamined by the recent theories of the localization of electrons in both the weakly localized regime[6] and in the case of strong disorder.[7]

It has been shown by Maekawa and Fukuyama[8] (for two-dimensional disordered systems) and Fukuyama, Ebisawa, and Maekawa[6] (FEM) (for three-dimensional systems) that in interacting electron systems, even in the weakly localized regime (for $\varepsilon_F\tau \gg 1$, ε_F and τ being the Fermi energy and lifetime of the electron, respectively), quantum corrections depress the superconducting transition temperature. They have also predicted the observed enhancement of the upper critical field[9] above the standard Werthamer-Helfand-Hohenberg-Maki[10] curves. Their result shows that there exist two different contributions to the suppression of T_c. One is due to the fact that the electron density of states at the Fermi level is depressed due to charge density fluctuations, and the other is caused by the enhancement of the Coulomb interaction. The enhancement of the upper critical field occurs as a result[11,12] of magnetic-field-induced delocalization effects on the Coulomb repulsive interaction.

II. THEORETICAL BACKGROUND

The result of FEM theory for the correction to the superconducting transition temperature in the weakly localized regime is given to the lowest order in $\lambda=(2\pi\varepsilon_F\tau)^{-1}$ by[6,13]

$$\ln\frac{T_c(H)}{T_{c0}(H)}=\frac{\delta K(T_c,H)}{N(\varepsilon_F)}+\psi\left[\frac{1}{2}+\frac{a}{4\pi T_{c0}(H)}\right]-\psi\left[\frac{1}{2}+\frac{a}{4\pi T_c(H)}\right], \tag{1}$$

where $T_c(H)$ is the measured critical temperature of a disordered system in applied field *H*, with the effects of localization included, $T_{c0}(H)$ is the corresponding critical temperature (hypothetical) if localization effects were absent, and $\delta K(T,H)$ is

$$\delta K(T,H)=-\frac{3^{1/2}3}{2}\pi\lambda^2N(0)\times\left\{\left[\frac{1}{g^*}\right]^2+2\pi\left[g^{-1}-(\mu^*/g)^2\ln\omega_D\tau-\frac{a}{12\pi T}\psi'\left[\frac{1}{2}+\frac{a}{4\pi T}\right]\right]\right\}, \tag{2}$$

where $a=4DeH/c$,

$$g^*=g\frac{1+\mu\ln(\epsilon_F/\omega_D)}{1+\mu\ln\epsilon_F\tau}, \tag{3}$$

g is the BCS interaction

$$-g=-(\lambda_{\rm ph}-\mu^*),$$

and ψ is the digamma function.

Anderson, Muttalib, and Ramakrishnan[7] (AMR) have, on the other hand, examined the effect of strong disorder ($k_Fl>1$, where k_F is the Fermi wave vector and l the mean free path) on T_c in three-dimensional systems. They have found that the slowing down of electron diffusion enhances the Coulomb repulsive interactions thus reducing T_c. The suppression of T_c was found to be proportional to the increment of disorder as measured by the resistivity ratio ρ/ρ_c (ρ_c being the critical resistivity).

The increase of the Coulomb pseudopotential was found to be

$$\mu^*=\frac{\mu'}{1+\mu'\ln(\epsilon_F/\omega_D)-(\mu'-\mu)\ln(\alpha^{1/2}\epsilon_F\tau)}, \tag{4}$$

where

$$\mu' = \mu[1 + (9\pi/4k_F^2 l^2)\ln\alpha] , \tag{5}$$

and $\alpha = (\rho/\rho_c)^3$.

III. RESULTS AND DISCUSSION

The superconducting transition temperature, T_c, for Zr-Ni and Zr-Cu metallic glasses is shown in Fig. 1 and Table I as calculated from our magnetoresistivity results.[14] In Ref. 14 we have shown that hydrogen incorporated in Zr-3d metallic glasses reduces both the effective electron diffusion constant and the screening of the Coulomb interaction. The experimental details are given in Ref. 14. The values of T_c were derived from the parameter β (at $T=4.2$ K and $H=0$) arising from the Maki-Thompson interaction, using the weak-localization expression[15] for the magnetoresistivity. The good agreement found between the experimental results and theoretical curves[14] shows that weak localization has provided us with a reliable tool to determine very low superconducting transition temperatures from data taken at much higher temperatures. The superconducting transition temperature for the doped samples lower than 1.7 K could not be measured with the available low-temperature equipment.

The values of T_c determined as described above are shown in Fig. 1 as a function of hydrogen concentration and in Fig. 2 as a function of the sample resistivity.

The suppression of T_c by the dopant is observed to be very fast at smaller hydrogen concentrations and then levels off at $x > 0.5$. (The same has been shown[16] for Zr_2PdH_x, where T_c was determined from the specific-heat measurements.)

TABLE I. Values of the hydrogen concentration x, the resistivity ρ, the electron-phonon coupling constant λ_{ph}, the superconducting transition temperature T_c, and the Coulomb pseudopotential μ^*, for $(Zr_{0.67}Ni_{0.33})_{1-x}H_x$, $(Zr_{70}Cu_{30})_{1-x}H_x$, and $(Zr_{60}Cu_{40})_{1-x}H_x$ metallic glasses. Values of λ_{ph} and μ^* were determined from the fit of experimental data to the Eq. (6). See the text for details.

x	ρ ($\mu\Omega$ cm)	λ_{ph}	T_c (K)	μ^*
		$(Zr_{0.67}Ni_{0.33})_{1-x}H_x$		
0	172.3	0.588	2.5	0.141
0.09	188.4	0.571	1.98	0.149
0.21	209.1	0.550	1.38	0.163
0.33	229.8	0.528	0.86	0.174
0.39	239	0.519	0.67	0.179
0.48	255.1	0.502	0.4	0.189
		$(Zr_{0.7}Cu_{0.3})_{1-x}H_x$		
0	161	0.536	1.63	0.149
0.08	177.8	0.524	1.15	0.154
0.25	200.5	0.508	0.65	0.17
		$(Zr_{0.6}Cu_{0.4})_{1-x}H_x$		
0	172	0.527	1.27	0.153
0.16	200.5	0.508	0.65	0.173
0.28	221	0.494	0.33	0.189

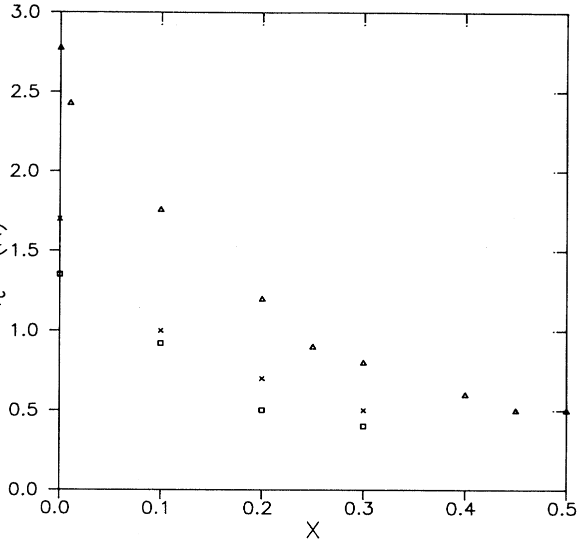

FIG. 1. Superconducting transition temperature T_c of △-$(Zr_{0.67}Ni_{0.33})_{1-x}H_x$, x −$(Zr_{0.7}Cu_{0.3})_{1-x}H_x$, and □-$(Zr_{0.6}Cu_{0.4})_{1-x}H_x$ as a function of hydrogen concentration.

We have analyzed the data from Fig. 2 using the FEM result[6] [Eqs. (1) and (2)]. The values of the parameters entering Eqs. (1) and (2) for the undoped $Zr_{0.67}Ni_{0.33}$ sample were the Fermi wave vector $k_F = 1.335\times10^{10}$ m^{-1} and the density of states at the Fermi level $N(\varepsilon_F) = 1.3$ st/eV at. The value of k_F was derived from the relation $k_F = (3\pi N\rho_s Z/A)^{1/3}$ where N is the Avogadro's number, ρ_s is the sample density, Z is the effective number of the electrons (we have used 2 e/at. for the Zr atom, and 0.6

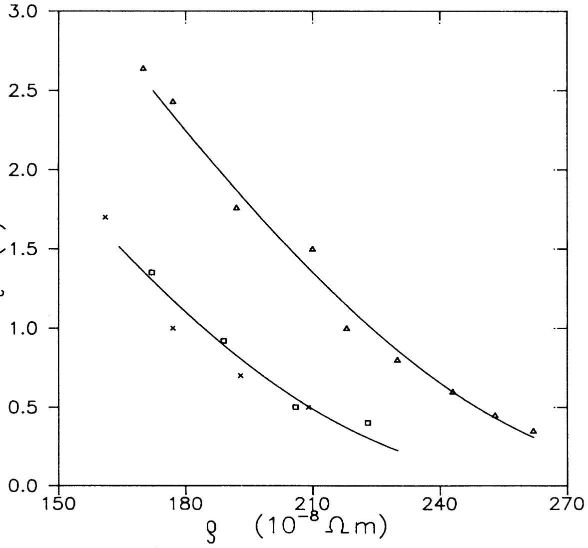

FIG. 2. Superconducting transition temperature T_c of △-$(Zr_{0.67}Ni_{0.33})_{1-x}H_x$, x-$(Zr_{0.7}Cu_{0.3})_{1-x}H_x$, and □-$(Zr_{0.6}Cu_{0.4})_{1-x}H_x$ as a function of resistivity. Full lines are theoretical fits to Eqs. (4)–(6).

e/at. for the Ni atom), and A is the atomic weight. The value of $N(\varepsilon_F)$ was derived from our magnetic susceptibility results.[14] The Debye temperature $\theta_D=234$ K was taken from the specific-heat results.[16] The value of the interaction constant was $g=0.44$ and the elastic relaxation energy was $E_\tau=4.14$ eV. (This energy corresponds to the elastic relaxation time $\tau=10^{-15}$ s derived from the fit of the experimental magnetic susceptibility data to the theoretical expression.[14]) For the doped sample $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{0.8}\mathrm{H}_{0.2}$ the parameters used were $k_F=1.29\times10^{10}$ m^{-1}, $N(\varepsilon_F)=1.16$ st/eV at., $\theta_D=250.4$ K, $g=0.37$, and $\tau=6.5\times10^{-16}$ s. Using these values of the parameters, Eq. (1) gives $T_c^{\mathrm{UD}}/T_{c0}=0.16$ and $T_c^{\mathrm{D}}/T_{c0}=0.024$ for the undoped (UD) and doped (D) sample, respectively. Because T_{c0} is equal in both samples, we obtain $T_c^{\mathrm{D}}/T_c^{\mathrm{UD}}=0.15$ from Eq. (1), while the measurements give 0.57. Thus, the theoretical prediction for the suppression of T_c by localization effects gives T_c values that are much smaller ($T_c^{\mathrm{D}}=0.37$ K) than the ones observed experimentally ($T_c^{\mathrm{D}}=1.43$ K) (Fig. 1). This is because Eq. (1) was derived perturbatively for the case of weak disorder $[(k_F l)^{-1} \ll l]$. This condition is not fulfilled in our samples ($k_F l=4.4$ for the undoped sample).

It can be seen from Fig. 2 that the reduction of T_c is proportional to the sample resistivity, which increases with the hydrogen concentration, and the leveling off of T_c is accompanied by saturation in the resistivity.[14] The resistivity saturation can be explained by the tendency of the electron mean free path, l, to converge to a constant value, i.e., to the interatomic distance. If we calculate l using the relation $\rho^{-1}=e^2N_0(\varepsilon_F)v_F\frac{1}{3}$, we obtain for $\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33}$ $l=3.5\times10^{-10}$ m, which corresponds to Zr-Zr nearest neighbors.[17]

We have also fit the experimental data in Fig. 2 to McMillan's relation[18]

$$T_c=\frac{\omega_D}{1.45}\exp\left[-\frac{1.04(1+\lambda_{\mathrm{ph}})}{\lambda_{\mathrm{ph}}-\mu^*(1+0.62\lambda_{\mathrm{ph}})}\right]. \tag{6}$$

The parameters of the fit are electron-phonon coupling constant λ_{ph}, the effective Coulomb potential μ, the electron mean free path l, and the critical resistivity ρ_c. To calculate μ^* from Eq. (4), we have used for $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{H}_x$ the values $x=0$, $k_F=1.335\times10^{10}$ m^{-1}, $\theta_D=234$ K, and $\mu=0.13$; for $x=0.48$, $k_F=1.24\times10^{10}$ m^{-1}, and $\theta_D=272$ 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 $l=4.6$ Å, $\mu^*=0.141$, $\rho_c=60$ $\mu\Omega$ cm, and the electron-phonon coupling constant $\lambda_{\mathrm{ph}}=0.588$. In the theoretical approach used it is assumed that λ_{ph} does not change with disorder. However, for the systems investigated, specific-heat results show[16] that λ_{ph} decreases with the hydrogen concentration for $x<0.5$. The experimental results were fit to Eq. (6) assuming λ_{ph} being either constant[19] or changing with the hydrogen concentration. In the latter case a better fit is achieved. This fit yields an empirical relation for λ_{ph}:

$$\lambda_{\mathrm{ph}}=-0.00104\rho+0.76715\ .$$

On this basis λ_{ph} has been found to decrease from the value of 0.588 to 0.502 for hydrogen concentration $x=0$ and $x=0.48$, respectively, while T_c changes from 2.50 to 0.4 K, μ^* from 0.141 to 0.189, and ρ from 172.3 to 255.1 $\mu\Omega$ cm. A decrease of λ_{ph} is consistent with magnetoresistivity results,[14] which show an increase of the inelastic scattering time with the hydrogen concentration. The value of the mean free path also decreases with hydrogen concentration. Thus, for the undoped sample ($x=0$) $l=4.6$ Å, which is somewhat higher than the Zr-Zr nearest-neighbors distance (NND) (3.3 Å), while for the doped sample ($x=0.48$) $l=2.9$ Å approaching the value of the Zr-H NND (1.8 Å), which is the smallest NND in the doped sample. Thus, we can conclude that the Ioffe-Regel limit is indeed reached in the systems investigated and can explain the observed resistivity saturation.

The same analysis has been applied to the $(\mathrm{Zr}\text{-}\mathrm{Cu})_{1-x}\mathrm{H}_x$ system. The values of the parameters used are $x=0$, $k_F=1.29\times10^{10}$ m^{-1}, $\theta_D=255$ K, $\lambda_{\mathrm{ph}}=0.536$, $\mu=0.13$, $l=3.5$ Å, $\rho_c=50$ $\mu\Omega$ cm, and $E_\tau=2$ eV; for $x=0.25$, $k_F=1.28\times10^{10}$ m^{-1}, $\theta_D=260$ K, and $l=3.35$ Å. λ_{ph} has been found to decrease according to the relation

$$\lambda_{\mathrm{ph}}=-0.0065\rho+0.64894\ .$$

Thus, for example, λ_{ph} changes from 0.536 to 0.508 for hydrogen concentration $x=0$ and $x=0.25$, respectively, while T_c diminishes from 1.63 to 0.65. At the same time μ^* is enhanced from 0.149 to 0.170 and ρ from 161 to 200.5 $\mu\Omega$ cm.

The electron-phonon coupling constant is given as

$$\lambda_{\mathrm{ph}}=\frac{N_0(\varepsilon_F)\langle I^2\rangle}{M\langle\omega^2\rangle}\ , \tag{7}$$

where $N_0(\varepsilon_F)$ is the bare density of states at ε_F, $\langle I^2\rangle$ is an average of the squared electron-phonon matrix element, M is the ionic mass, and $\langle\omega^2\rangle$ is an average squared phonon frequency, which is taken as varying as θ_D^2.

In a previous paper,[14] we have explained why the product $N_0(\varepsilon_F)\langle I^2\rangle$ should stay constant and, which has also been confirmed experimentally (Ref. 37 in 14), in the case of amorphous Zr-Ni and Zr-Cu alloys. Thus, a decrease of λ_{ph} is caused by an increase in the Debye temperature, θ_D,[16] with hydrogen concentration.

In conclusion, we have analyzed the suppression of the superconducting transition temperature, T_c, in hydrogen-doped Zr-Ni and Zr-Cu metallic glasses. The experimental data derived from the magnetoresistivity results[14] were fit both to the results of FEM theory [Eqs. (1) and (2) derived in the weakly localized regime] and AMR theory [Eq. (4) derived for the case of strong disorder]. We have shown that FEM theory does not fit our data well because the condition $(k_F l)^{-1} \ll 1$ is not satisfied in our samples. On the other hand, the experimental results have been successfully fit to the AMR theory. We have found that μ^* increases with hydrogen concentration, which is consistent with the observed decrease of the diffusion constant.[14] That is why we believe that the suppression of T_c with the hydrogen is caused partly by the increase of θ_D (and thus the decrease of λ_{ph}) and partly by an increase of the effective Coulomb interaction μ^* as a result of the interplay between the interaction and disorder as predicted by Anderson, Muttalib, and Ramakrishnan.[7]

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