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SUPERCONDUCTING PROPERTIES OF THERMALLY-RELAXED  $Zr_{80}Co_{20}$   
METALLIC GLASS

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**Dedicated to the memory of Professor Zvonko Ogorelec**

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We have studied the effect of thermal relaxation on the superconducting properties of  $Zr_{80}Co_{20}$  metallic glass by means of differential scanning calorimetry and electrical resistivity measurements in the vicinity of the superconducting transition temperature  $T_c$ . Experimental values for the crystallisation temperature and activation energy of the crystallisation processes were derived by studying these processes at different heating rates. The  $T_c$  of the  $Zr_{80}Co_{20}$  metallic glass thermally relaxed with a heating rate of 60 K/min to slightly below its first crystallisation exotherm is higher than in unrelaxed  $Zr_{80}Co_{20}$  metallic glass, whereas in all other thermally relaxed samples  $T_c$  decreases with decreasing heating rates and increasing temperature of relaxation. The homogeneity of the thermally relaxed  $Zr_{80}Co_{20}$  metallic glass is discussed by using the superconducting transition width as a criterion. The superconducting transitions of thermally relaxed  $Zr_{80}Co_{20}$  metallic glass samples are characterised by a sharp fall in electrical resistance. This suggests that the samples are homogeneous on a spatial scale of less than the zero-temperature coherence length  $\xi_0$ .

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## 1. Introduction

It has been found that the presence of crystallites in amorphous superconductors can enhance the superconducting transition width above that obtained in homo-

geneous sample [1]. Thus, superconductivity provides a rather sensitive tool for probing the microscopic state of amorphous alloys. Many studies have been carried out in order to understand the effect of structural relaxation on the  $T_c$  of metallic glasses [1,2]. The  $T_c$  of  $Zr_2X$  ( $X= Co, Ni, Pd$ ), and  $Zr_3X$ , ( $X= Ni, Pd, Rh$ ), metallic glasses have been found to decrease their values for the as-quenched state [1]. This decrease in  $T_c$  upon annealing has been linked to the decrease in the electron-phonon coupling constant,  $\lambda_{ph}$ , created by a hardening of phonon modes as a result of relaxation of the quenched-in strains or redistributions of the defects created by rapid quenching. The increase in  $T_c$  upon annealing in Zr-Fe metallic glasses, however, has been related to the decrease in the spin-fluctuations mass enhancement,  $\lambda_{sp}$  [2].

The purpose of this experiment was to study the effect of thermal-relaxation on the short-range order in  $Zr_{80}Co_{20}$  metallic glass using thermal analysis, electrical resistivity and the measurements of the  $T_c$ .  $Zr_xCo_{1-x}$  metallic glasses are characterised by high room-temperature resistivities, they are paramagnetic [3] and become superconducting at temperatures below 4 K.

## 2. Experimental

Ribbons of  $Zr_{80}Co_{20}$  metallic glass were prepared by rapid solidification of the melt on a single-roll spinning copper wheel (60 m/s) in an argon atmosphere. The samples, 5 mm long, 1 mm wide and 25  $\mu m$  thick, were then cut from the ribbon. The thermal stability of the  $Zr_{80}Co_{20}$  metallic glass was measured by means of a calibrated Perkin-Elmer DSC-4 differential scanning calorimeter using an atmosphere of purified argon gas. Heating rates of 60 K/min, 30 K/min and 10 K/min were employed. The samples were examined by X-ray diffraction, using Cu  $K\alpha$  radiation.

The electrical resistance was measured by a low-frequency (23.2 Hz) four-probe ac method in the temperature range of 2–290 K; the precision extended to a few parts in  $10^6$ . The critical magnetic field ( $H_{c2}(T)$ ) measurements were performed at temperatures down to 2.5 K in magnetic fields up to 1 T, oriented transversely to the sample.

## 3. Results and discussion

The values of specific heat,  $c_p$ , determined from the DSC measurements of the  $Zr_{80}Co_{20}$  metallic glass in the temperature range of 298–723 K at the heating rates of 60 K/min, 30 K/min and 10 K/min are shown in Fig. 1. The DSC trace shows two clearly resolvable exothermal peaks: the small first peak and the high, sharp second peak. The crystallisation peak temperatures  $T_{px}$  corresponding to the maximum of the first exotherm are designated  $T_{p1}$  and those corresponding to the maximum of the second exotherm are designated  $T_{p2}$ . The values of  $T_{p1}$  and  $T_{p2}$  observed with the heating rates  $s = 10$  K/min, 30 K/min and 60 K/min are shown

in Fig. 1. The dependence of the temperatures  $T_{p1}$  and  $T_{p2}$  on the heating rate,  $s$ , was used to determine the activation energy of crystallisation  $E_{a1}$  and  $E_{a2}$ . For this purpose, we used the adaptation of the method of Kissinger [4]. The values of  $E_{a1}$

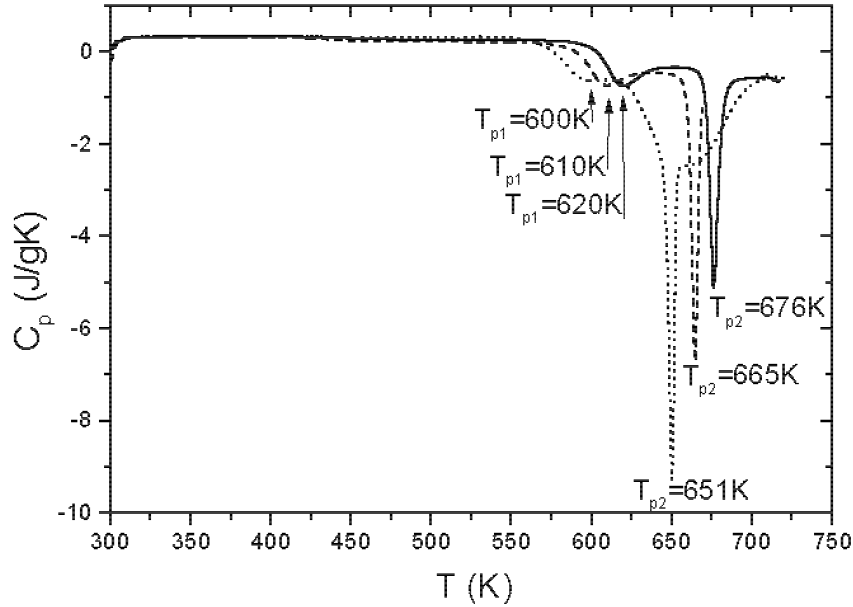


Fig. 1. The temperature dependence of  $C_p$  of the  $Zr_{80}Co_{20}$  metallic glass in the temperature range of 298 – 723 K at the heating rates,  $s$ :  $s = 60$  K/min (full line),  $s = 30$  K/min (dashed line),  $s = 10$  K/min (dotted line).

and  $E_{a2}$  are:  $E_{a1} = (2.67 \pm 0.05)$  eV and  $E_{a2} = (2.51 \pm 0.05)$  eV. Comparing our thermal data with those previously published, we find good agreement in  $T_{px}$ , and  $E_a$  with results of Buschow ( $E_{a2} = 2.69$  eV) [5] and Altounian et al. ( $E_{a2} = 2.9$  eV) [6].

The change in the temperature-dependent electrical resistivity, relative to its value at 290 K,  $\Delta\rho/\rho(290\text{ K})$ , of the thermally relaxed  $Zr_{80}Co_{20}$  samples for the temperature range of 5 – 290 K is shown in Fig. 2. The temperature coefficient of the resistivity (TCR) of the samples thermally relaxed in the heating temperature range of 298 – 563 K is negative. The TCR changes sign and becomes positive for the heating temperature higher than  $T_{p1}$ . The TCR values of the thermally relaxed samples increase as the temperature of heating increases. The temperature-dependent electrical resistivity relative to its value at 4.2 K,  $\Delta\rho/\rho(4.2\text{ K})$ , of  $Zr_{80}Co_{20}$  metallic glass in the vicinity of  $T_c$  is shown in Fig. 3. The  $T_c$  was determined as the midway point on the resistivity versus temperature transition. The experimental data are

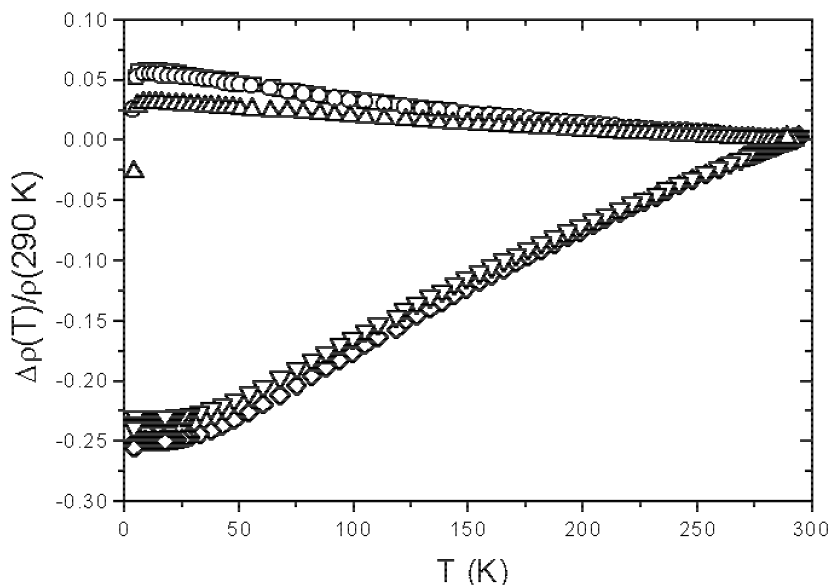


Fig. 2. The change in the temperature-dependent part of the electrical resistivity relative to its value at 290 K  $(\rho(T) - \rho(290 \text{ K}))/\rho(290 \text{ K})$  of  $\text{Zr}_{80}\text{Co}_{20}$  metallic glasses: unrelaxed ( $\square$ ), the thermally relaxed up to 563 K with  $s = 60 \text{ K/min}$  ( $\circ$ ), the thermally relaxed up to 563 K with  $s = 10 \text{ K/min}$  ( $\triangle$ ), the thermally relaxed up to 618 K with  $s = 10 \text{ K/min}$  ( $\nabla$ ), the thermally relaxed up to 653 K with  $s = 60 \text{ K/min}$  ( $\diamond$ ).

given in Table 1. It can be seen from Table 1 and Fig. 3 that all superconducting transitions are very sharp and the temperature difference between the 90% and 5% points of the resistivity change is typically less than 20 mK. The  $T_c$  of the samples thermally relaxed at a temperature of heating below the first exotherm changes slightly with decreasing heating rate. The  $T_c$  of the thermally relaxed  $\text{Zr}_{80}\text{Co}_{20}$  metallic glass that underwent a heating rate of 60 K/min to slightly below the first exotherm (Fig. 1) is higher than in the unrelaxed  $\text{Zr}_{80}\text{Co}_{20}$  metallic glass, whereas in all other thermally relaxed samples,  $T_c$  decreases with decreasing heating rates and increasing heating temperatures. Using the modified form of the McMillan equation [7], it can be shown that this change in  $T_c$  upon annealing is related to a decrease in the electron-phonon coupling constant,  $\lambda_{\text{ph}}$ , and the spin fluctuation mass enhancement parameter,  $\lambda_{\text{sf}}$ . The decrease in  $\lambda_{\text{ph}}$  created by a hardening of phonon modes as a result of relaxation of the quenched-in strains or redistribution of the defects will decrease  $T_c$ , while the decrease in  $\lambda_{\text{sf}}$  increases  $T_c$ . Thus, we can conclude that for the heating rate of 60 K/min, the thermal-relaxation in the thermally-relaxed sample decreases both  $\lambda_{\text{ph}}$  and  $\lambda_{\text{sf}}$ , but the decrease in  $\lambda_{\text{sf}}$  is dominant, hence the  $T_c$  increases. The modification in the chemical short-range order due to heating above the first crystallisation exotherm resulting in evolution of the  $\omega$ -Zr phase, which coexists with Co-enriched nanocrystal matrix as seen in

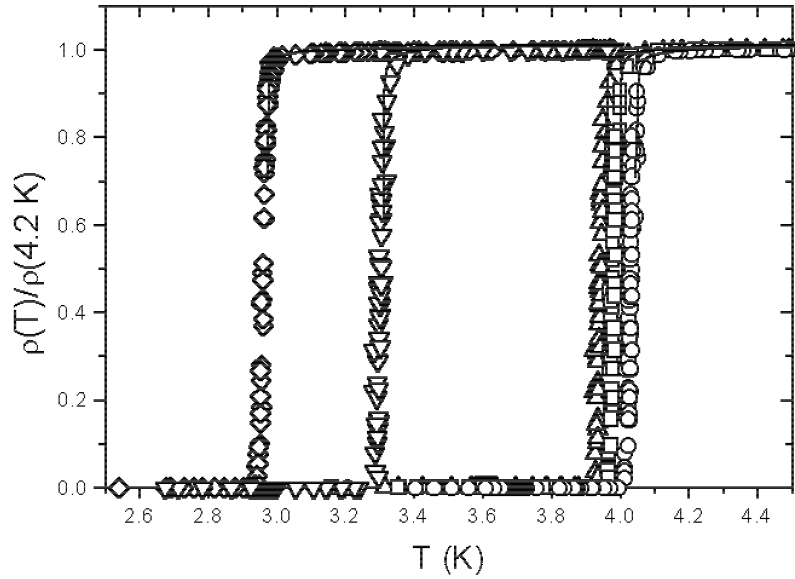


Fig. 3. The temperature-dependent electrical resistivity relative to its value at 4.2 K,  $\rho(T)/\rho(4.2\text{ K})$ , versus temperature below 4.5 K of  $\text{Zr}_{80}\text{Co}_{20}$  metallic glasses: unrelaxed ( $\square$ ), the thermally relaxed up to 563 K with  $s = 60$  K/min ( $\circ$ ), the thermally relaxed up to 563 K with  $s = 10$  K/min ( $\triangle$ ), the thermally relaxed up to 618 K with  $s = 10$  K/min ( $\nabla$ ), the thermally relaxed up to 653 K with  $s = 60$  K/min ( $\diamond$ ).

TABLE 1. Values of the heating temperature,  $T_a$ , the heating rate,  $s$ , the electrical resistivity,  $\rho(290\text{ K})$ , the temperature coefficient of the resistivity,  $(1/\rho)\partial\rho/\partial T$ , the superconducting transition temperature,  $T_c$ , the superconducting transition width,  $\Delta T_c$ , the value of the  $(\partial H_{c2}/\partial T)_{T_c}$  as determined from the slope of the measured  $H_{c2}$  versus  $T_c$  curve at  $T_c(0)$ , the density of states at the Fermi-level,  $N^\gamma(E_F)$ , the electron diffusion constant,  $D$  and the zero-temperature coherence length,  $\xi_0$ .

$T_a$	$s$	$\rho(290\text{ K})$	$\frac{1}{\rho} \frac{\partial \rho}{\partial T}$	$T_c$	$\Delta T_c$	$\frac{\partial H_{c2}}{\partial T}$	$N^\gamma(E_F)$	$D$	$\xi_0$
$\pm 1$		$\pm 5$	$-0.1 \times 10^{-4}$	$\pm 0.01$	$\pm 0.005$	$\pm 0.1$	$\pm 0.1$	$\pm 0.1$	$\pm 5$
K	K/min	$\mu\Omega\text{ cm}$	1/K	K	K	T/K	sta./eV at.	$10^{-5}\text{ m}^2/\text{s}$	$10^{-10}$
295	0	170	$-3.3 \times 10^{-4}$	3.98	0.020	-3.5	2.4	3.27	42
563	60	168	$-3.3 \times 10^{-4}$	4.03	0.015	-3.4	2.3	3.37	42
563	10	160	$-1.9 \times 10^{-4}$	3.95	0.015	-3.2	2.3	3.47	43
618	10	132	$18.9 \times 10^{-4}$	3.30	0.015	-3.0	2.5	3.7	52
653	60	115	$20.9 \times 10^{-4}$	2.95	0.017	-2.4	2.5	4.7	58

the X-ray diffraction measurements [8], plays an important role in determining the

$T_c$  of thermally-relaxed samples subjected to different heating temperatures. Their superconducting properties are characterised by a somewhat sharper electrical resistive transition than observed in an unrelaxed sample (Table 1). This suggests that the thermally-relaxed samples are homogeneous on a spatial scale of less than the zero-temperature coherence length  $\xi_0$ . The value of  $\xi_0$  was estimated by fitting Eq. (1) to the experimental data given in Fig. 3 and is given in Table 1. The results of the fit are shown as solid lines in Fig. 3. The fluctuating conductivity in the vicinity of the  $T_c$  consists of two terms: the Aslamazov-Larkin term [9] which originates from the virtual Cooper pairs created by thermal fluctuations and the Maki-Thompson term [10] coming from the interaction of normal conducting electrons and the superfluid

$$\frac{\rho(T)}{\rho(4.2\text{K})} = A - \frac{e^2 T_c^{1/2} \rho(4.2\text{K})}{32 \xi_0 (T - T_c)^{1/2}} \left( 1 + \frac{4}{1 + [C/(T - T_c)]^{1/2}} \right), \quad (1)$$

where  $A$  is a free parameter,  $e^2 = 2.43 \times 10^{-4} \Omega^{-1}$ ,  $C = \pi \hbar / 8 k_B \tau_i$ , and  $\tau_i = \alpha_i T^{-2}$  is the inelastic scattering time. The value of  $\alpha_i = (1.5 \pm 0.2) \times 10^{-10} \text{ sK}^2$ , as determined from the fit, is in good agreement with the one obtained from the electrical resistivity measurements at higher temperatures [11].

The values of the density of electron states at the Fermi level,  $N^\gamma(E_F)$ , derived from Eq. (2), are given in Table 1,

$$N^\gamma(E_F) = -9.451 \cdot 10^{-10} \frac{M}{\rho d} \left[ \frac{\partial H_{c2}}{\partial T} \right]_{T_c}, \quad (2)$$

where the prefactor in Eq. (2) is chosen so that  $N^\gamma(E_F)$  comes out in states/(eV atom),  $M$  is the molecular weight in grams,  $d = 6.9 \text{ g/cm}^3$  the density of sample,  $\rho$  the electrical resistivity in  $\Omega\text{cm}$  and  $(\partial H_{c2}/\partial T)_{T_c}$  is assumed in  $\text{O}/\text{K}$ . The value of the  $(\partial H_{c2}/\partial T)_{T_c}$  was determined from the slope of the measured  $H_{c2}$  versus  $T_c$  curve at  $T_c(0)$  and is given in Table 1. The absolute value of  $(\partial H_{c2}/\partial T)_{T_c}$  decreases with decreasing heating rates and increasing heating temperatures (Table 1). The values of the electron diffusion constant,  $D$ , are derived from the relation  $D = (e^2 N^\gamma(E_F) \rho)^{-1}$  and are given in Table 1. It can be seen from Table 1 that the values of  $D$  increase with increasing relaxation temperature and decreasing heating rate.

#### 4. Conclusion

We have studied the effect of thermal relaxation on the superconducting properties of  $\text{Zr}_{80}\text{Co}_{20}$  metallic glass by means of differential scanning calorimetry and electrical resistivity measurements in the vicinity of the superconducting transition temperature,  $T_c$ . The value of  $T_c$  of the thermally relaxed  $\text{Zr}_{80}\text{Co}_{20}$  samples, using a heating rate of 60 K/min to slightly below its first crystallisation exotherm, is higher than in unrelaxed  $\text{Zr}_{80}\text{Co}_{20}$  samples, whereas in all other thermally-relaxed

samples, the  $T_c$  decreases with decreasing heating rates and increasing heating temperature. The homogeneity of the thermally relaxed  $Zr_{80}Co_{20}$  metallic glass is judged to be high as evidenced by a small superconducting transition width and sharp electrical resistive transition. This suggests that the homogeneity is on a spatial scale of less than the zero-temperature coherence length  $\xi_0$ . The resistivity decrease of the thermally-relaxed  $Zr_{80}Co_{20}$  is caused mostly by the increase of the electron diffusion constant,  $D$  (Table 1).

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SUPRAVODLJIVA SVOJSTVA TOPLINSKI-OPUŠTENOG METALNOG  
STAKLA  $Zr_{80}Co_{20}$ 

Proučavali smo učinak toplinskog opuštanja na supravodljiva svojstva metalnog stakla  $Zr_{80}Co_{20}$  pomoću diferencijalne pretražne kalorimetrije i mjerenjem električnog otpora oko temperature supravodljivog prijelaza  $T_c$ . Odredili smo eksperimentalnu temperaturu kristalizacije i aktivacijsku energiju kristalizacijskih procesa njihovim proučavanjem pri različitim brzinama zagrijavanja. Iznos  $T_c$  toplinski opuštenog metalnog stakla  $Zr_{80}Co_{20}$  pri brzini grijanja 60 K/min do malo ispod njegove prve isotermne kristalizacije veći je nego u neopuštenom metalnom staklu  $Zr_{80}Co_{20}$ , dok se u svim ostalim toplinski opuštenim uzorcima  $T_c$  smanjuje pri usporenom zagrijavanju i povećanoj temperaturi opuštanja. Raspravljamo homogenost toplinski opuštenog metalnog stakla  $Zr_{80}Co_{20}$  na osnovi širine supravodljivog prijelaza. Značajka supravodljivih prijelaza uzoraka toplinski opuštenih metalnih stakala  $Zr_{80}Co_{20}$  jest nagao pad električnog otpora. To ukazuje na homogenost uzoraka u njihovim djelićima koji su manji od duljine koherencije na apsolutnoj nuli,  $\xi_0$ .