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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 ξ_0.

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Keywords: $Zr_{80}Co_{20}$ metallic glass, thermal relaxation, superconductivity, transition temperature T_c, homogeneity, crystallisation exotherm, electrical resistance

1. Introduction

It has been found that the presence of crystallites in amorphous superconductors can enhance the superconducting transition width above that obtained in homogeneous 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, λ_{ph}, created by a hardening of phonon modes as a result of relaxation of the quenched-in strains or redistibutions 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, λ_{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 μm 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 Kα 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}

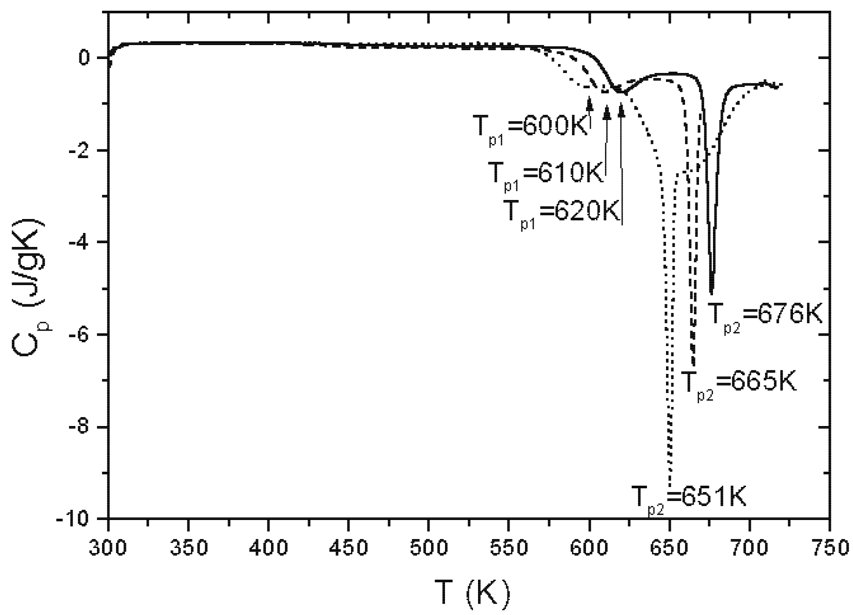

Fig. 1. The temperature dependence of C_p *of the* $Zr_{80}Co_{20}$ *metallic glass in the temperature range of* $298 - 723$ K *at the heating rates, s:* $s = 60$ K/min *(full line),* $s = 30$ K/min *(dashed line),* $s = 10$ K/min*) (dotted line).*

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

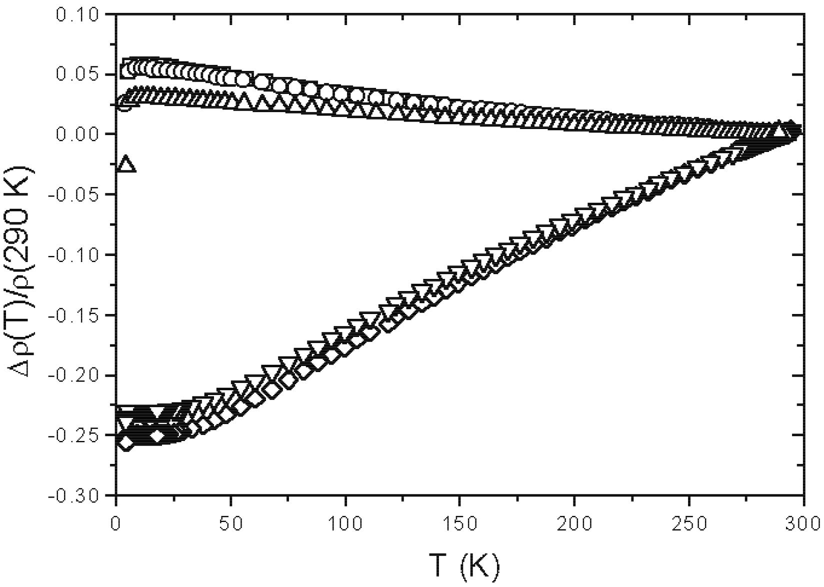

Fig. 2. The change in the temperature-dependent part of the electrical resistivity relative to its value at 290 K $(\rho(T) - \rho(290\,\mathrm{K}))/\rho(290\,\mathrm{K})$ *of* $Zr_{80}Co_{20}$ *metallic glasses: unrelaxed* (□)*, the thermally relaxed up to* 563 K *with* $s = 60$ K/min (○)*, the thermally relaxed up to* 563 K *with* $s = 10$ K/min (△)*, the thermally relaxed up to* 618 K *with* $s = 10$ K/min (▽)*, the thermally relaxed up to* 653 K *with* $s = 60$ K/min*)* (◇).

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 $Zr_{80}Co_{20}$ 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 $Zr_{80}Co_{20}$ 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, λ_{ph}, and the spin fluctuation mass enhancement parameter, λ_{sf}. The decrease in λ_{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 λ_{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 λ_{ph} and λ_{sf}, but the decrease in λ_{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 ω-Zr phase, which coexists with Co-enriched nanocrystal matrix as seen in

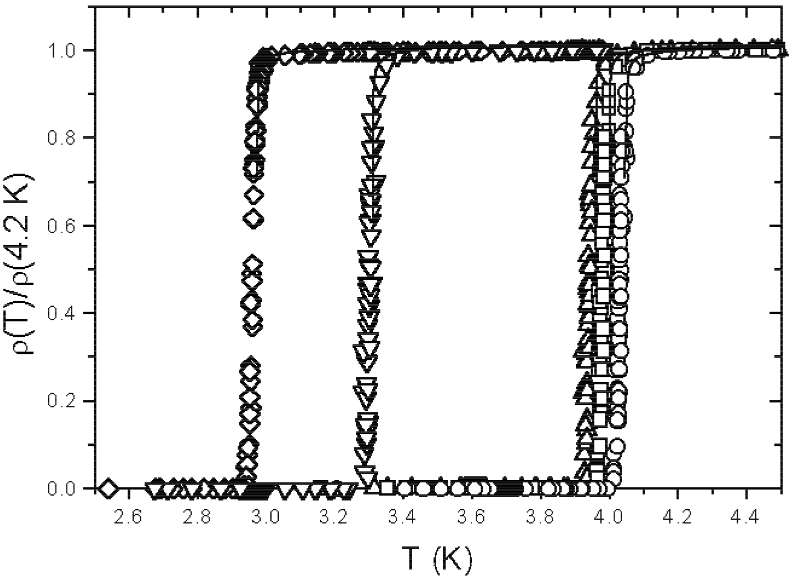

Fig. 3. The temperature-dependent electrical resistivity relative to its value at 4.2 K, $\rho(T)/\rho(4.2\,\mathrm{K})$, *versus temperature below* 4.5 K *of* $\mathrm{Zr_{80}Co_{20}}$ *metallic glasses: unrelaxed* (□), *the thermally relaxed up to* 563 K *with* s = 60 K/min (○), *the thermally relaxed up to* 563 K *with* s = 10 K/min (△), *the thermally relaxed up to* 618 K *with* s = 10 K/min (▽), *the thermally relaxed up to* 653 K *with* s = 60 K/min (◇).

TABLE 1. Values of the heating temperature, T_a*, the heating rate,* s*, the electrical resistivity,* $\rho(290\mathrm{K})$*, the temperature coefficient of the resistivity,* $(1/\rho)\partial\rho/\partial T$*, the superconducting transition temperature,* T_c*, the superconducting transition width,* ΔT_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,* ξ_0*.*

T_a	s	$\rho(290\mathrm{K})$	$\dfrac{1}{\rho}\dfrac{\partial\rho}{\partial T}$	T_c	ΔT_c	$\dfrac{\partial H_{c2}}{\partial T}$	$N^{\gamma}(E_F)$	D	ξ_0
±1		±5	-0.1×10^{-4}	±0.01	±0.005	±0.1	±0.1	±0.1	±5
K	K/min	μΩcm	1/K	K	K	T/K	sta./eV at.	$10^{-5}\mathrm{m^2/s}$	10^{-10}
295	0	170	-3.3×10^{-4}	3.98	0.020	-3.5	2.4	3.27	42
563	60	168	-3.3×10^{-4}	4.03	0.015	-3.4	2.3	3.37	42
563	10	160	-1.9×10^{-4}	3.95	0.015	-3.2	2.3	3.47	43
618	10	132	18.9×10^{-4}	3.30	0.015	-3.0	2.5	3.7	52
653	60	115	20.9×10^{-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 ξ_0. The value of ξ_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

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

where A is a free parameter, $e^2 = 2.43 \times 10^{-4}\ \Omega^{-1}$, $C = \pi\hbar/8k_B\tau_i$, and $\tau_i = \alpha_i T^{-2}$ is the inelastic scattering time. The value of $\alpha_i = (1.5 \pm 0.2) \times 10^{-10}$ 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,

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

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, $d = 6.9$ g/cm^3 the density of sample, ρ the electrical resistivity in Ωcm and $(\partial H_{c2}/\partial T)_{T_c}$ is assumed in Ø/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 $Zr_{80}Co_{20}$ metallic glass by means of differential scanning calorimetry and electrical resistivity measurements in the vicinity of the superconducting transition temperature, T_c. The value of T_c of the thermally relaxed $Zr_{80}Co_{20}$ samples, using a heating rate of 60 K/min to slightly below its first crystallisation exotherm, is higher than in unrelaxed $Zr_{80}Co_{20}$ 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 ξ_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, ξ_0.