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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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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, λ_{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, 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 $K\alpha$ 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}

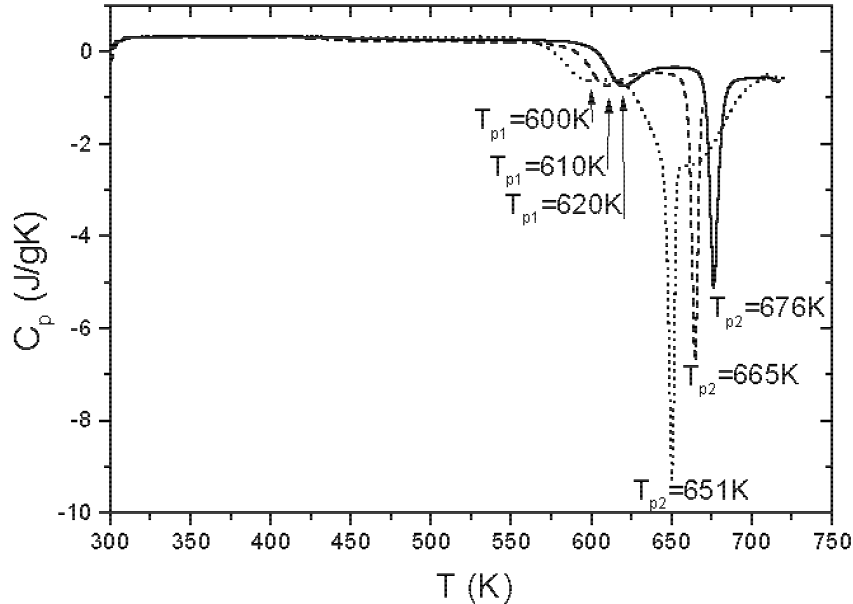


Fig. 1. The temperature dependence of C_p of the $Zr_{80}Co_{20}$ metallic glass in the temperature range of 298 – 723 K at the heating rates, s : $s = 60$ K/min (full line), $s = 30$ K/min (dashed line), $s = 10$ K/min (dotted line).

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

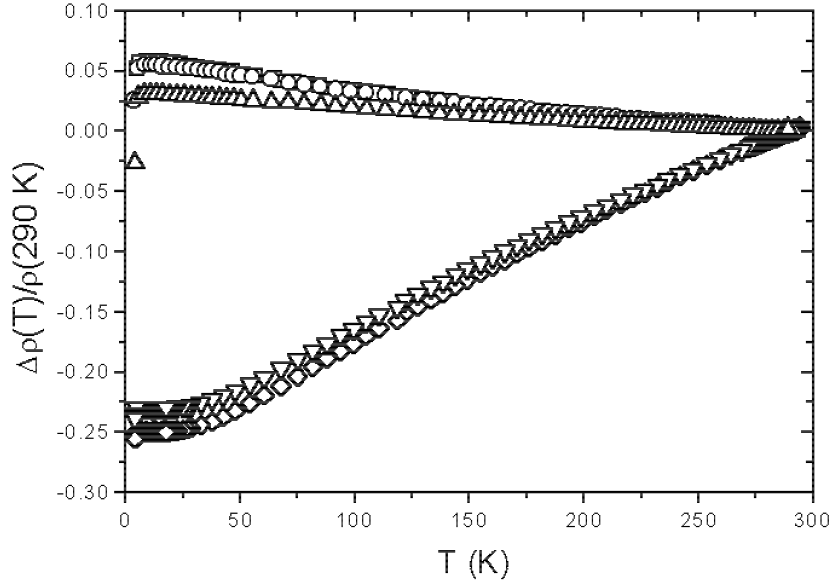


Fig. 2. The change in the temperature-dependent part of the electrical resistivity relative to its value at 290 K $(\rho(T) - \rho(290 \text{ K}))/\rho(290 \text{ K})$ of $\text{Zr}_{80}\text{Co}_{20}$ metallic glasses: unrelaxed (\square), the thermally relaxed up to 563 K with $s = 60 \text{ K/min}$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

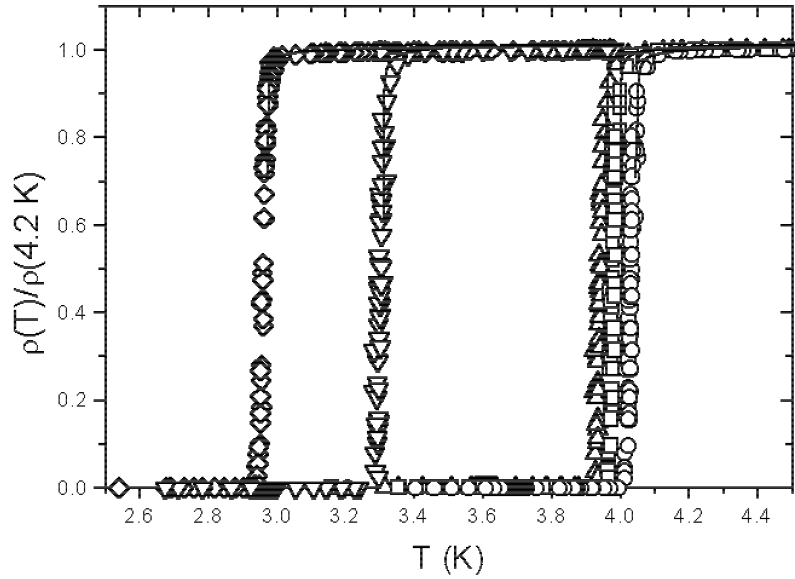


Fig. 3. The temperature-dependent electrical resistivity relative to its value at 4.2 K, $\rho(T)/\rho(4.2\text{ K})$, versus temperature below 4.5 K of $\text{Zr}_{80}\text{Co}_{20}$ metallic glasses: unrelaxed (\square), the thermally relaxed up to 563 K with $s = 60$ K/min (\circ), the thermally relaxed up to 563 K with $s = 10$ K/min (\triangle), the thermally relaxed up to 618 K with $s = 10$ K/min (∇), 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, 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	$\rho(290\text{K})$	$\frac{1}{\rho} \frac{\partial \rho}{\partial T}$	T_c	ΔT_c	$\frac{\partial H_{c2}}{\partial T}$	$N^\gamma(E_F)$	D	ξ_0
± 1		± 5	-0.1×10^{-4}	± 0.01	± 0.005	± 0.1	± 0.1	± 0.1	± 5
K	K/min	$\mu\Omega\text{cm}$	1/K	K	K	T/K	sta./eV at.	$10^{-5}\text{m}^2/\text{s}$	10^{-10}
295	0	170	-3.3×10^{-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

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

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, ρ the electrical resistivity in Ωcm and $(\partial H_{c2}/\partial T)_{T_c}$ is assumed in O/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 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 .