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MAGNETIC PROPERTIES OF MILLED AND THERMAL RELAXED $YBa_2(Cu_{1-x}Fe_x)_3O_y$

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The influence of the mechanical milling and subsequent thermal relaxation on magnetic and superconducting behaviour of $YBa_2(Cu_{1-x}Fe_x)_3O_y$ system has been studied. Two methods of heat treatment were used: Set I — slow cooling from 980°C in flowing O_2 and Set II — reducing at 770°C in flowing Ar_2 followed by reoxidation in flowing O_2 below 400°C. The transition to superconductivity, diamagnetic response, critical current density and the effective magnetic moment in the normal state have been estimated. Our measurements indicate that the reducing atmosphere preparation is less detrimental on superconducting properties. The results are discussed in terms of occupancy Cu sites by Fe and redistribution of oxygen atoms.

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A substitution of Fe for Cu in $YBa_2(Cu_{1-x}Fe_x)_3O_y$ has attracted a large interest because of the iron influence on superconductivity, microstructure and magnetic properties. The microstructure of doped samples is twinned for $x < 0.015$, twinned and tweed for $0.015 < x < 0.03$, and tweed for $x > 0.03$, where tweed is a fine scale orthogonal microstructure [1]. It is known that there are two different Cu crystallographic sites in the structure Cu(1) chains and Cu(2) plane and it is conceivable that the site occupancies may vary as a function of concentration or a specific sample preparation method. A synthesis of $YBa_2(Cu_{1-x}Fe_x)_3O_y$ under relatively reducing conditions (inert atmosphere) and subsequent careful low-temperature annealing in O_2 produce material with a lower ratio of Fe in the Cu(1) and Cu(2) site compared with a conventionally prepared material [2]. On the other hand, the accumulation of crystal strain during milling is changing the lattice parameter, sinterability, transport and magnetic properties [3,4].

In this paper we are reporting superconducting and magnetic properties of milled and thermal relaxed $YBa_2(Cu_{1-x}Fe_x)_3O_y$ ($x = 0.0$ and 0.04) powder after different thermal treatments in superconducting and normal state.

Powders of nominal composition $YBa_2(Cu_{1-x}Fe_x)_3O_y$ were prepared in crushed, milled and milled & relaxed states [5]. The sintered powders were treated by two methods. The conventional method (denoted as Set I) involved annealing

in flowing O_2 from 980 to 900°C by rate 2°C/min, from 900 to 500°C by 1°C/min, from 500 to 350°C by 0.1°C/min and then slow cooling to room temperature. The second method (denoted as Set II) involved annealing in flowing Ar at 770°C for 65 hours with slow cooling to room temperature by 4°C/min. Annealing in flowing O_2 from 400 to 300°C by rate 1.5°C/hour and slow cooling to room temperature followed subsequently. As the prepared samples were crushed and a part of them was milled in a low intense rotary mill with zircon cylinders for 24 hours. Some amounts of the milled samples have been then thermally relaxed at 400°C for 1 hour. The temperature dependence of magnetization was studied by a vibrating sample magnetometer in an applied magnetic field with induction $\mu_0 H = 2$ mT (a superconducting state) and $\mu_0 H = 400$ mT (a normal state). The superconducting state was studied in both field-cooled (FC) and zero-field-cooled (ZFC) conditions. The hysteresis loops were measured at 4.2 K and in the fields with magnetic induction up to 5.5 T.

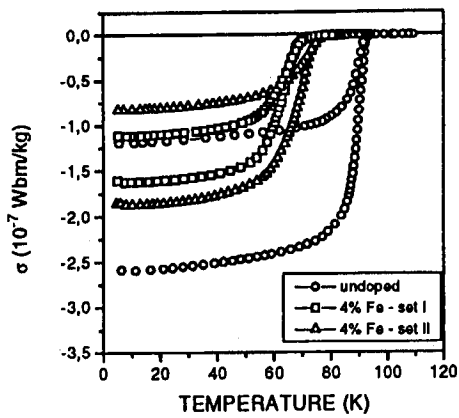

Fig. 1. Temperature dependence of ZFC and FC magnetization at $\mu_0 H = 2$ mT.

The magnetization data for both types of synthesis are shown in Fig. 1. The transition to superconductivity in both types of material is broader than in a conventionally undoped sample, but no signs of phase separation appear. The superconducting transition onset temperature T_c always decreases with Fe substitution and with any mechanical treatment. For the samples from the Set II the decrease in T_c is lower than for the Set I. The superconducting volume fraction of samples (Set II) is higher. The obtained data are collected in Table.

The normal state susceptibility was measured in the temperature range $T_c < T < 300$ K. The susceptibility data obeys the Curie–Weiss law and are collected in Table. The Curie–Weiss temperature Θ was found to be negative. This negative value of Θ indicates an antiferromagnetic correlation in samples. The antiferromagnetic correlations are more pronounced in the samples from Set II. The similar values were obtained by other authors [6, 7]. The invariance upon the substitution level could be due to the formation of Fe clusters whose structure would not be dependent upon Fe concentration. It is known that the thermal treatment

TABLE

Transition temperature T_c [K], the ZFC magnetization at 4.2 K, M_s [10^{-7} Wb m kg^{-1}], Curie constant C [10^{-6} K m^3/kg], the Curie–Weiss temperature Θ [K], the effective magnetic moment per magnetic ion $\mu_{\rm eff}$ ($\mu_{\rm B}$), critical current density at 4.2 K (in magnetic field 1 T) $J_c^{4.2\,\rm K}$ [10^5 A/cm^2], and transition width ΔT [K].

	Crushed			Milled			Relaxed		
	123	Set I	Set II	123	Set I	Set II	123	Set I	Set II
T_c	93	78	82	93	73	80	93	72	79
M_s	3.9	2.6	3.1	2.8	1.8	2.1	2.6	1.6	1.9
C	–	5.39	4.35	–	6.46	5.95	–	5.21	5.01
Θ	–	−1.6	−23	–	−21	−40	–	−17	−42
$\mu_{\rm eff}$	–	3	2.7	–	3.7	3.4	–	3.2	3.2
$J_c^{4.2}$	1.21	0.2	0.43	1.75	0.46	0.38	1.53	0.32	0.51
ΔT	8.7	18	15.7	17	21.5	22.7	21.8	17	24

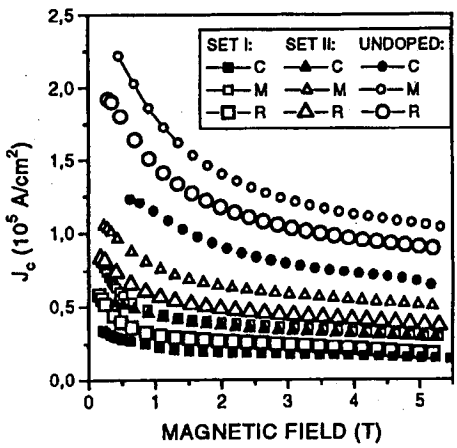

Fig. 2. Critical current density vs. magnetic field at 4.2 K after different mechanical and thermal treatments (C — crushed, M — milled, R — relaxed).

affects the occupancy of sites Cu(1) and Cu(2) by Fe [2] and on the other hand the value of Θ is strongly dependent on the occupancy. The results support our assumption that the treatment denoted as Set II leads to a lower degradation of superconducting properties in the Fe-doped samples.

Figure 2 shows the dependence of critical current density J_c on magnetic field. The J_c values were taken from hysteresis loops using the Bean critical state model. From Fig. 2 it is evident that J_c decreases for doped samples. This fact corresponds with the experimental results of Lan et al. [8]. After milling J_c increases and is higher than for crushed samples. It is remarkable that the value of J_c for

a sample from the Set II is two times higher than for the samples from the Set I at $\mu_0 H = 1$ T. The similar behaviour was observed by Smith et al. [9] as a consequence of more pronounced Fe clusters in a reduced and reoxidised sample which enhance flux pinning potential relative to the conventionally prepared sample. On the other hand the higher value of J_c can be connected with a microstructure of doped samples. It was suggested by Xu et al. [1] that the transformation of a twinned microstructure by Fe substitution of the Cu(1) site reduces the effective pinning potential of the twin planes. The reduction and reoxidation thermal treatment keeps the twinned microstructure at higher concentration of Fe and on higher pinning potential too. The changes of J_c for Fe doped samples after mechanical processing can be explained by the change in the point defect concentration [5]. This one increases by milling (extra oxygen atoms from (1/2 0 0) site formed by the separation of twin boundaries from Fe atoms) and is significantly reduced after thermal relaxation by oxygen vacancies annihilation via the extra oxygen atoms. The differential scanning calorimetry study showed [10] that the defects introduced by milling are associated with diffusive redistribution of oxygen.

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