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Influence of the preparation conditions on the diamagnetic response of high-T_c $YBa_2Cu_3O_x$ superconductor

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ABSTRACT : Prolonged ~~that~~ treatments in oxygen lead to a substantial increase of the diamagnetic signal of superconducting $YBa_2Cu_3O_x$ due to the decrease of the amount of defects and to the development of Josephson-like contacts between homogeneous superconducting regions in the sample. The superconducting-glass features are expected to be considerably reduced in well crystallized samples at least at liquid nitrogen temperature.

Introduction

The recent discovery of high T_C copper oxide-based superconductors /1,2/ has mulated enormous worldwide interest in their physical and technological potential. The magnetic response of these materials is a field of intensive studies and the first published perimental results /3-7/ clearly indicated the existence of superconducting grains weakly upled together. The magnetic data for the La-Ba-Cu oxides /3,4/, show all the aspects of e behaviour of superconducting clusters as predicted in /8/, where a similarity in the haviour of such clusters to that of spin-glases was emphasized. This is related to ustation" of clusters with closed loops to find, in an applied magnetic field, a state which multaneously minimizes the energies of all pairs of coupled superconducting grains. The alogy with a spin-glass leads to the concept of superconductive-glass state /3/ whose sential features are the difference in field-cooled and zero-field-cooled diamagnetic sponses, the existence of a quasi de Almeida-Thouless line separating metastable from able regimes and nonexponential time dependences. Glassy features for Y-Ba-Cu oxide ve been also reported, but the glass temperature has a field dependence which differs bstantially from that observed in spin glasses. In the case of granular superconductors creasing the field increases the system's frustration, and therefore enhances its glassy haviours, whereas for a real spin glass the magnetic field supresses the spin-glass phase by igning the spins /9/.

In this paper we report a significant increase of both the Meissner signal and the hielding" magnetization of superconducting $YBa_2Cu_3O_x$ after prolonged heat treatments oxygen. We also show that the superconducting-glass features seem to be reduced in well ystallized samples.

The $YBa_2Cu_3O_x$ material is of particular importance from the point of view of a ry high T_C which allows some experiments in liquid nitrogen to be performed and from the ct that single-phase specimens can easily be made /10,11/.

II. Sample preparation and characterization

Samples were prepared from reagent grade Y_2O_3, $BaCO_3$ and CuO by mixing the constituents and reacting in alumina crucibles for various times at temperatures between 920 and 960°C in air and/or flowing oxygen at normal pressure. The cooling time to ambient temperature was always of 2.5 h. Two types of samples were investigated: in a first protocol the starting mixture was calcined at 920°C in air for 17 h. The product was lightly grinded, the resulting powder was compacted at 5 kbar into a 10x5x4 mm^3 pellet and sintered in air at 950°C for 17 h (sample 1a). The same specimen was then maintained at 960°C for 15 h in oxygen (sample 1b) and finally annealed at 960°C also in oxygen for another 15 h (sample 1c). The second type of samples (2-8) were obtained by firing the starting mixtures in air or in oxygen, the temperature and the time of firing increasing in the sample-sequence 2 to 8. For example, the sample 2 was prepared by firing the mixture in air at 920°C for 12 h, whereas for the sample 8 the initial mixture was reacted in oxygen at 960°C for 60 h with three intermediate grindings. After a final light grinding the powders were pressed in cylindrical plastic buckets (6 mm in diameter and 12 mm long).

The samples in the powder form (2-8) were investigated by X-ray diffraction using a Siemens Kristalloflex IV diffractometer provided with a copper target and scanning electron microcopy (SEM). All the samples were single-phase and orthorhombic in crystal structure but exhibited significant variation of the width of the diffraction peaks. We calculated the integral breadth (in 2θ scale) of the peak (020)/(006) which accounts mainly for the defects situated along the b and c axes. The peak width was corrected for the instrumental factors by means of a NaCl reference sample. The pure diffraction breadth (β_{cor}) was used as an indicator of the amount of defects. Large values of β_{cor} correspond to large densities of defects.

Experimental results and discussion

The d.c. magnetization curves were traced at liquid nitrogen temperature. The samples were zero-field-cooled and subsequently a longitudinal magnetic field up to 800 Oe was applied by means of a copper solenoid with a sweeping rate of 50 Oe/sec. The shielding magnetization was continuously registered using an electronic integrating amplifier. Cooling the samples in magnetic field the Meissner signal at 77 K was also measured.

In figure 1 we show the magnetization curves for the bulk sintered samples 1a, 1b and 1c. Both the absolute value of the magnetization and the field value at which the magnetization minimum appears increase with time of sintering. As it is known /8/ a similar field dependence of the magnetic moment is characteristic for frustated superconducting clusters. The low-field limit to reach a complete Meissner effect is $H_{c1} = \Phi_0/2S$, where Φ_0 is the flux quantum and S is the homogeneous superconducting area /3/. However, increasing the sintering time in oxygen is expected to increase S and therefore the magnetization minimum should be shifted towards lower magnetic field values. The results from figure 1 do not corroborate this.

The d.c. magnetization curves for the samples 2-8 are presented in figure 2. The same increase of the shielding magnetization signal with time of firing was observed.

A significant increase of the Meissner signal for well crystallized samples appears. In figure 3, the flux expulsion data at 300 Oe as a function of the parameter β_{cor} were plotted. While X-ray diffraction studies revealed single phase specimens, the flux expulsion data show that - due to the variation in composition or in the oxygen defect ordering - only the homogeneous regions in the crystallites expel the flux. The effective volume of such regions increase at prolonged heat treatments.

Our picture invokes homogeneous superconducting regions coupled together via Josephson-like contacts which can be driven normal by the applied magnetic field. Figure 4 shows that our powdered samples consist essentially from large assemblies of crystallites sintered together (grains). Contacts between homogeneous superconducting regions in the crystallites, between the crystallites inside the grain and between grains (in bulk sintered samples) can exist. The contacts between grains which are driven normal at very low field values explain the anomalies in M(H) curves traced for bulk sintered samples /5/ and the low critical current density measured on polycrystalline specimens /12/. In the case of our samples 1a, 1b and 1c such anomaly (not illustrated in fig.1) appears at 10-15 Oe and, of course, disappears on powdering.

At moderate heat treatments (samples 2-5 in fig.2) only relative weak contacts were developed and the position of the magnetization minimum is mainly dictated by the Meissner signal. Prolonged heat treatments produce the strengtnening of the contacts, increase their number and, consequently, the shielding magnetization signal increases and the minimum is shifted towards higher field values.

At even higher field values, most of the contacts were driven normal and the shielding magnetic moment approaches the Meissner signal (fig.5).

The real picture seems to be, however, not so simple. The complications arise from the great anisotropy of these layered superconductors and dimensional effects. As shown in /13/ from experiments performed on single-crystal specimens a large anisotropy in the H_{cl} values appears. The crystallites with the Cu-O planes oriented perpendicular to the magnetic field have a H_{cl} value larger than those with the Cu-O planes oriented parallel to the field. The random orientation of the crystallites, the complicated distribution of the internal magnetic field, different values of the "internal" demagnetization factor and dimensional effects (the mean dimension of the homogeneous superconducting regions is comparable with the penetration depth) lead to the large maximum observed in the magnetic field dependence of the absolute value of the Meissner signal (fig.5).

In order to explain the temperature dependence of the initial slope in the magnetization curves of La-Ba-Cu oxide a model based on an array of weakly coupled, roughly spherical superconducting grains whose average radius is comparable with the penetration depth has been proposed /6/. In /7/ the temperature dependence of the magnetic susceptibility was found to be in excellent agreement with this model. However, the assumption of complete isolation of the crystallites is ~~far to be~~ not correct in our samples and

We believe that the contacts also play an important role in describing the low field magnetization curves of ceramic superconductors.

In conclusion, we observed a significant increase of the diamagnetic signal of superconducting $YBa_2Cu_3O_x$ after prolonged heat treatments in oxygen. This is mainly caused by the increase of the effective volume which expels the flux and by the development of Josephson-like contacts between homogeneous superconducting regions in the sample. The superconducting-glass features are expected to be considerably reduced in these samples.

It is worth noting that prolonged heat treatments in oxygen also lead to an extremely sharp superconducting transition /14/. For example, the powder which constituted the sample 8 compacted at 5 kbar and sintered in oxygen at 960°C for 15 h shows a resistive transition width (between the 90% and 10% signals) $\Delta T_c < 0.5$ K.

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FIGURE CAPTIONS

Fig. 1 Weak-field magnetization curves of the bulk sintered samples 1a, 1b and 1c.

Fig. 2 Weak-field magnetization curves of the powdered samples 2-8.

Fig. 3 The dependence of the maximum Meissner signal at 300 Oe on the diffraction breadth.

Fig. 4 Scanning electron micrograph of the sample no.8.

Fig. 5 The shielding magnetization (M) and the Meissner signal (•) versus applied magnetic field for the samples no.2 and no.8.

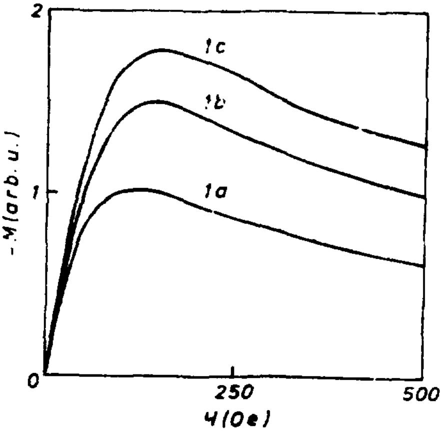

Fig.1

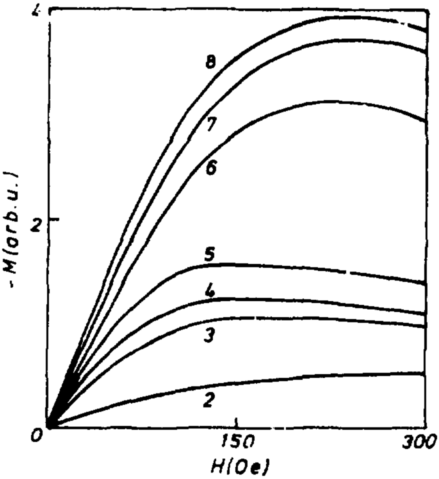

Fig.2

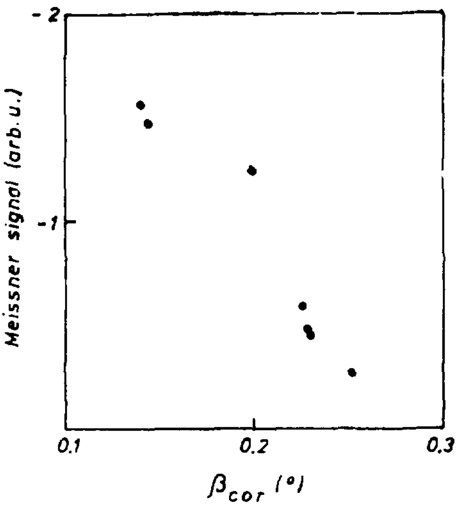

Fig.3

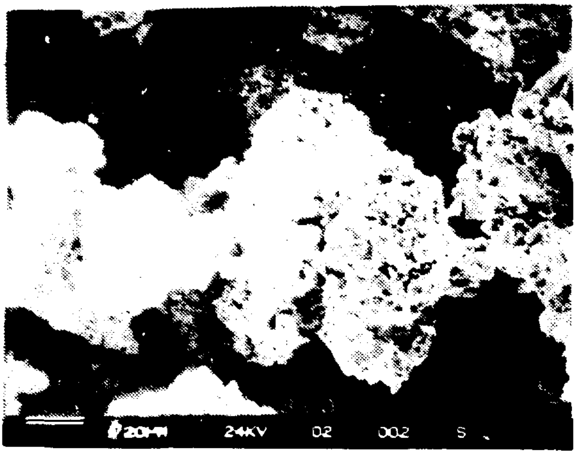
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Fig.4

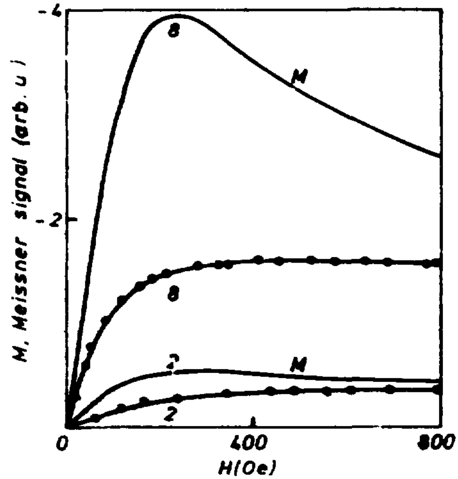
-4
-2
0
400
800
H(Oe)
M, Meissner signal (arb. u.)
8
M
8
2
M
2

Fig.5