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The effect of concentration on some superconducting properties of small grain systems of $GdBa_2Cu_3O_{7-\delta}$ embedded in solid epoxy

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Abstract. We present the effect of intergrain interactions, at $T = 75$ K, on the intragranular critical current density and on the susceptibility of a system consisting of small superconducting grains of $GdBa_2Cu_3O_{7-\delta}$ embedded in solid epoxy. The critical current density in a single grain is unaffected by the intergrain interactions. We also found that the magnetic screening volume susceptibility, χ, varies linearly with the grain concentration, ε, of the system. Non-interacting models can be used to describe the magnetic phenomena of such systems. Finally the variation of $-\chi$ with ε was found to be strong near the first critical field H_{c1} and $-\chi$ becomes insensitive to ε in the neighbourhood of H_{u}, which we call the cut-off field.

1. Introduction

In the past five years a great deal of activity has occurred in superconductivity because of the potential impact on technology of ultra-high-temperature superconductors (see, for example, [1]). Many compounds, almost always containing CuO_2 planes in their crystal structure, have exhibited superconductivity with superconducting transition temperatures T_c ranging from 7 to 125 K. The hole-doped superconductors such as $La_{2-x}M_xCuO_4$ with M = Ba, Ca or Sr [2, 3] and at $x = 0.15$ have their T_c not exceeding 42 K. While the compounds $RBa_2Cu_3O_7$ (R = Y or a lanthanide element except Ce, Pm, Pr and Tb) [4, 5, 6] have their T_c not exceeding 96 K. Compounds such as Bi–Pb–Sr–Ca–Cu–O [7] have their T_c around 100 K and Tl–Ba–Ca–Cu–O [8] have a maximum T_c around 125 K. However the electron-doped superconductors such as $Ln_{2-x}M_xCuO_{4-y}$ (Ln = Pr, Nd, Sm, Eu, Gd; M = Ce, Th; $y = 0.02$) [9, 10, 11, 12] at $x = 0.15$ have their T_c not exceeding 27 K. In general, all the above values of T_c were mainly obtained using either the electrical resistivity or the magnetic susceptibility measurements [13]. Another quantity of extreme technological importance is the critical current density J_c. J_c is either obtained electrically, which we call transport J_c, or is obtained using the Bean model [14, 15] applied to magnetic hysteretic measurements, which we refer to as the intrinsic J_c.

Many studies on the above quantities in the various superconducting compounds have been done either on polycrystalline samples or on single crystals.

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Some studies, such as the work done by Maury and co-workers [16] and Shimizu and co-workers [17] have dealt with the effect of changing the grain size, for a superconducting powder, on the hysteresis loops and on the critical current density of such systems.

However, little attention is paid to the effect of the intergrain interactions in a well dispersed powder sample where identical small superconducting grains of the powder are embedded in a solid matrix.

It is interesting to see if there is any noticeable change in the intragranular critical current density and in the susceptibility of such systems due to the variation in the concentration of these systems and consequently due to the change in the intergrain interactions. The concentration of such systems can be measured through the volumetric packing fraction ε which is defined by

$$\varepsilon = NV_g/V_s \tag{1}$$

where N is the number of grains in the system, V_g is the volume of the grain and V_s is the sample volume.

In the present work we are studying the effect of intergrain interaction, at $T = 75$ K, on the intragranular critical current density and on the susceptibility of a system of small superconducting grains of $GdBa_2Cu_3O_{7-\delta}$ embedded in solid epoxy.

2. Experimental details

Polycrystalline $GdBa_2Cu_3O_{7-\delta}$ is prepared by mixing high purity (99.99%) powders of Gd_2O_3, $BaCO_3$, and CuO in the proper proportions using the solid state reaction technique. The mixture is fired at about 900 °C for seven days with seven intermediate grindings. The resulting compound is pressed into pellets at about 5 kbar pressure. The pellets are then put into a flow of oxygen inside a furnace at about 950 °C for 48 h and then at 450 °C for 24 h. The ramping of the temperature is always done slowly each time at least over a period of 10 h (i.e. about 0.8 °C min^{-1}). Finally, most of the pellets are ground into fine particles with a grain size range of 1 to 2 μm.

X-ray powder diffraction measurements showed that the $GdBa_2Cu_3O_{7-\delta}$ compound is single-phase and has the same crystal structure as $YBa_2Cu_3O_{7-\delta}$. The iodometric titration indicated that $\delta = 0.08 \pm 0.02$.

The electrical resistivity measurements were done using a four-probe AC resistance bridge on a bar-shaped sample with dimensions $1 \times 2 \times 6$ mm^3 which had been cut from the annealed pellet. The results of the measurements gave a mid-point critical transition temperature of 94 K and a transition width ΔT_c of 1.6 K.

We prepared five samples by mixing thoroughly specific amounts of small grains of $GdBa_2Cu_3O_7$ with epoxy which solidifies in 6 min. These samples (numbers 2–6) are listed in table 1, along with their concentrations ε. Sample number 1 has been slightly compressed with no epoxy in it. To make sure that the powder is well dispersed throughout the epoxy, we took several orthogonal thin slices of a dilute sample and looked at them under the optical microscope. We observed that the grains were homogeneously dispersed with a minimum of grain agglomeration. This ensures that in our study we are indeed looking at the effect of the intergrain interactions, rather than the effect of the interactions between agglomerates of grains. Hence, any concentration dependence, other than what theory predicts, of a physical quantity such as the magnetic susceptibility may be interpreted in terms of intergrain interactions. Finally, magnetic measurements

Table 1. Small grain systems of $GdBa_2Cu_3O_{7-\delta}$ embedded in solid epoxy (excluding sample number 1). The sample number is in the first column, the concentration or volumetric packing fraction ε is in the second column and ΔM at T = 75 K, as defined in figure 1(*a*) is in the third column.

Sample no	Conc. ε	ΔM ($A\ m^{-1}$)
1	0.283	645
2	0.069	165
3	0.037	110
4	0.033	87
5	0.021	62
6	0.007	30

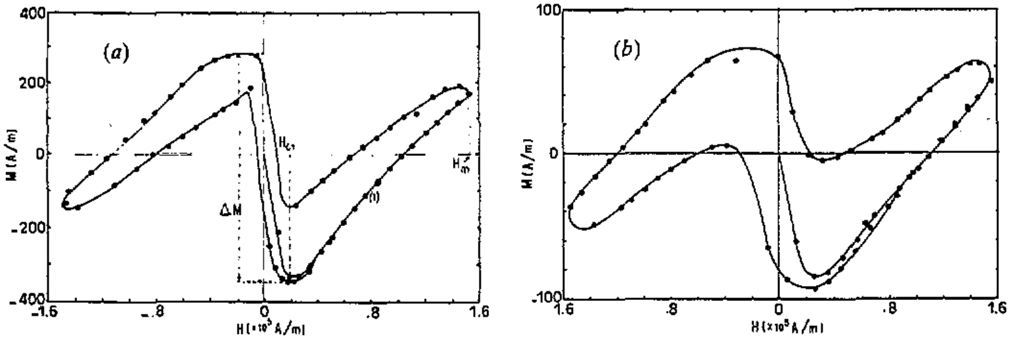

Figure 1. Hysteresis loop of the magnetization M ($A\ m^{-1}$) versus internal field intensity H ($A\ m^{-1}$) at $T = 75$ K for samples of $GdBa_2Cu_3O_{7-\delta}$ small grain system with (*a*) concentration $\varepsilon = 0.283$ (sample 1) and (*b*) $\varepsilon = 0.069$ (sample 2). ΔM, H_{C1} and H_m are indicated.

were performed using an Oxford Instruments Faraday balance [18] equipped with a continuous flow cryostat covering the temperature range of 70 to 500 K.

3. Results and discussion

Figures 1(*a*) and (*b*) display the hysteresis loops of the magnetization M versus the magnetic field intensity H for two $GdBa_2Cu_3O_7$ small grain samples with concentrations $\varepsilon = 0.283$ and 0.069 respectively at $T = 75$ K. The maximum field H_m ($\sim 1.6 \times 10^5\ A\ m^{-1}$) indicated in figure 1(*a*) is chosen in the intermediate range that is not too large (~Telsa) and not too small (~Oersted) where these extreme ranges were used by Senoussi and co-workers [19] to study the hysteresis loops of pressed samples of $La_{1.85}Sr_{0.15}CuO_4$. Similar behaviour for the other samples mentioned in table 1 have been obtained. The magnetization due to epoxy has been subtracted from the total magnetization of every sample. The paramagnetic component of the magnetization for the relatively higher magnetic fields, $H_{C1} < H < H_m$ (H_{C1} is shown in figure 1(*a*)), have not been subtracted from our results. The paramagnetism is mostly coming from the gadolinium ions in the small grains and its effect, for example, on the susceptibility or the magnetization of the system can be predicted from the formulae given in solid state textbooks [20, 21]. In our study this paramagnetic effect is rather small and can be neglected. Therefore any deviation from the expected non-interacting behaviour can be

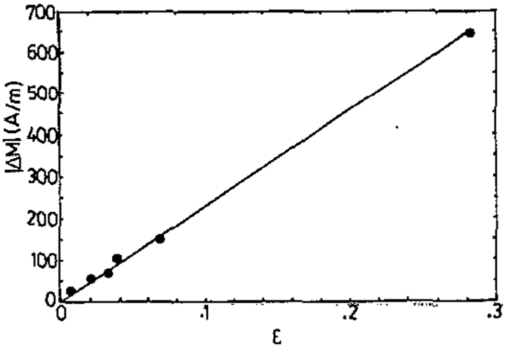

Figure 2. Variation of ΔM (A m^{-1}) with ε at $T = 75$ K.

attributed to the intergrain interactions between the magnetic moments induced by supercurrents in the small grains.

A common behaviour for these hysteresis loops is that at fields greater than H_{Cl} as indicated by line (1) in figure 1(*a*) the variation of the magnetization M versus the magnetic field intensity H is approximately linear, such that we can assume

$$M = a + bH \tag{2}$$

where a and b depend on the concentration ε and on the size of the grains.

We define ΔM (see figure 1(*a*)) as the sum of the magnitudes of the maximum diamagnetic magnetization of the fourth quadrant for positive fields and the second quadrant for negative fields. ΔM for all six samples is tabulated in table 1 and is plotted against ε in figure 2. It is clearly seen in figure 2 that ΔM varies linearly with ε. That is

$$\Delta M = A\varepsilon \tag{3}$$

where A is independent of ε.

The magnetic moment, Δm, that corresponds to ΔM is given by

$$\Delta m = \Delta M V_s = A V_s \varepsilon \tag{4}$$

where V_s is the volume of the sample.

Equation (3) leads us to the conclusion that the effect of intergrain interactions on the intragranular critical current density J_c (i.e. J_c for a single grain) is negligible and if this effect exists then it is extremely small.

This result can be understood using the Bean model [14, 15] for a single grain such that

$$J_c = 15\Delta I/R \tag{5}$$

where R is the radius of the grain and ΔI is defined in a similar manner as ΔM but for a single grain. Let $\Delta\mu$ be the magnetic moment of a single grain that has the same definition as Δm for a small grain system. Then

$$\Delta\mu = \Delta I V_g. \tag{6}$$

For a system of N identical small grains

$$\Delta\mu = \Delta m/N. \tag{7}$$

Substituting equations (4) and (1) into equation (7) yields

$$\Delta\mu = A V_g. \tag{8}$$

From equations (6) and (8) we find that

$$\Delta I = A \tag{9}$$

and therefore equation (5) becomes

$$J_c = 15A/R \tag{10}$$

which shows that J_c is independent of ε and consequently the effect of interactions on the critical current density is negligible.

If a sample is cooled from the normal to the superconducting state passing through the transition temperature in a zero magnetic field, then we obtain what is called zero-field-cooled (ZFC) state. Then, by applying a magnetic field, we obtain the ZFC magnetization of the screening magnetization. But, if the sample is transformed from the normal state to the superconducting state in the presence of a magnetic field, then this gives the field-cooled (FC) state. The FC state is a true expression of the Meissner effect.

The basic difference between ZFC and FC states is that, in the case of ZFC state, the flux is initially absent inside the sample and the observed diamagnetism after applying the magnetic field excludes the flux from inside the grains while in the FC case the flux is expelled from the interior of the small grains.

In general, the diamagnetic magnetization of the ZFC state is larger, for a given field, than that obtained in the FC state for a single grain (i.e. bulk effect). However, in this work we are interested in the effect of intergrain interactions and not in the volumetric fraction of superconductivity. Therefore, we must look for the states in which the intergrain interaction is larger and this can be accomplished by studying the ZFC susceptibility rather than the FC one.

In various studies [22, 23] on magnetic fine particle systems, the importance of the interparticle interactions can easily be observed through studying the variation of the magnetic susceptibility with the volumetric packing fraction, ε, or concentration. Hence, following the same attitude for our present superconducting systems, we define the screening or ZFC volume susceptibility as

$$\chi = M/H \tag{11}$$

where M is the ZFC magnetization at the internal magnetic field intensity H which is corrected for shape demagnetization.

Figures 3(*a*) and 3(*b*) show the variation of the negative ZFC susceptibility, $-\chi$, with H for the six samples at $T = 75$ K. The results show that the variation of $-\chi$ with H for a given ε is non-linear and $-\chi$ decreases as H increases. This behaviour is due to the field penetration in the superconducting grains. Also, as H becomes greater than H_{C1}, the superconducting grains transform to the mixed state with the formation of normal cores in each grain, which lead to the decrease of $-\chi$ as H increases.

The variation of $-\chi$ with the concentration ε for five different magnetic field intensities at $T = 75$ K are shown in figure 4. It is clear that, for a particular field H, $-\chi$ varies linearly with ε. This linear relationship predicts that the intergrain interaction is negligible which can be explained in the following simple model.

Suppose that we have N non-interacting superconducting small grains system. The magnetic moment μ for a single grain is given by

$$\mu = IV_g \tag{12}$$

where I is the bulk magnetization (i.e. magnetization of a single grain). The magnetic moment, m, for N such grains is given by $m = \mu N$ or

$$m = IV_gN. \tag{13}$$

Substituting for N from equation (1), we get

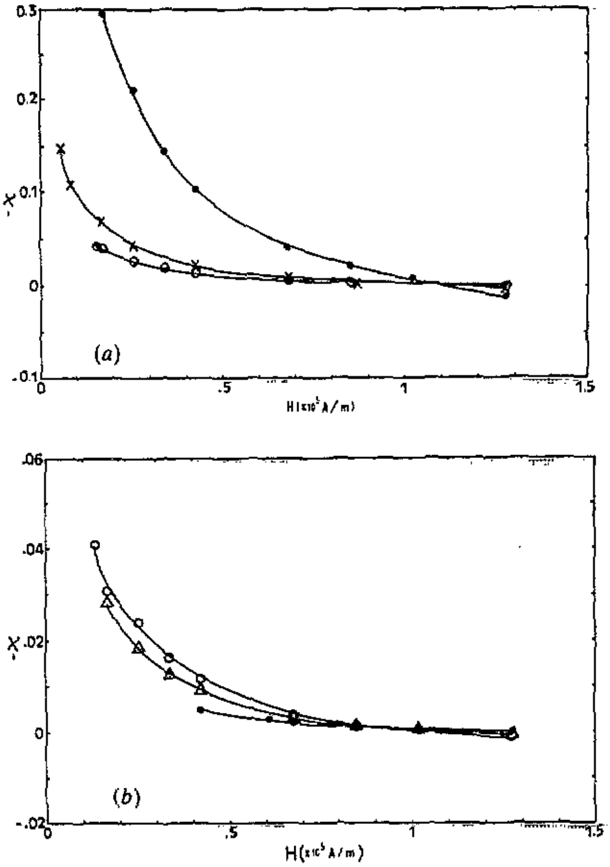

Figure 3. Negative ZFC susceptibility $-\chi$, at $T = 75$ K, versus internal magnetic field intensity H (A m^{-1}), where (*a*) full circles are for $\varepsilon = 0.283$, crosses for $\varepsilon = 0.069$ and open circles for $\varepsilon = 0.037$; (*b*) open circles for $\varepsilon = 0.033$, open triangles for $\varepsilon = 0.021$, and solid circles for $\varepsilon = 0.007$.

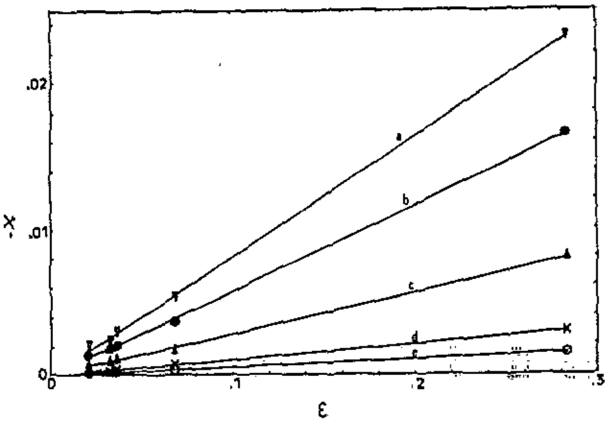

Figure 4. Variation of $-\chi$, at $T = 75$ K, with ε for internal field intensities of: a, 17.0×10^3; b, 25.5×10^3; c, 42.5×10^3; d, 68.0×10^3; e, 85.0×10^3 A m^{-1}.

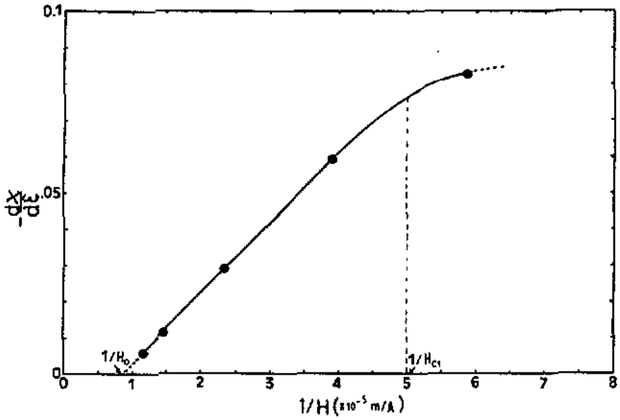

Figure 5. Variation of $-\mathrm{d}\chi/\mathrm{d}\varepsilon$, at $T = 75$ K, obtained from figure 4 with $1/H$. $1/H_{\mathrm{C}1}$ and $1/H_0$ are indicated.

$$m = IV_{\mathrm{s}}\varepsilon. \tag{14}$$

The magnetization M of the sample is given by

$$M = m/V_{\mathrm{s}} = I\varepsilon. \tag{15}$$

Therefore the susceptibility χ becomes

$$\chi = M/H = I/H\varepsilon \tag{16}$$

where I/H is the susceptibility of the bulk which is independent of ε. Equation (16) shows that the effect of intergrain interactions on $-\chi$ is negligible, since it is the result of a non-interacting model.

Finally we plot in figure 5, the slopes of the lines shown in figure 4, that is $-\mathrm{d}\chi/\mathrm{d}\varepsilon$ versus the inverse of the magnetic field intensity $(1/H)$. The results show that $-\mathrm{d}\chi/\mathrm{d}\varepsilon$ varies linearly with $1/H$ in the range of $H_{\mathrm{C}1} < H < H_{\mathrm{m}}$. This behaviour can be predicted from equation (2) with

$$\chi = M/H = a/H + b. \tag{17}$$

From figure 4 we see that a and b are each directly proportional to ε such that $a = \alpha\varepsilon$ and $b = \beta\varepsilon$ where α and β are independent of ε and can be determined using figure 5.

From figure 5 we also notice that as H increases, $-\mathrm{d}\chi/\mathrm{d}\varepsilon$ decreases and therefore the dependence of $-\chi$ on ε becomes weaker. We also observe a cut-off field, H_0, near which the ZFC susceptibility becomes quite insensitive to the variation in ε.

4. Conclusions

In this work we found that the effect of the concentration (and consequently the effect of intergrain interactions) of a system made of small superconducting grains of $GdBa_2Cu_3O_{7-\delta}$, on the intragranular critical current density J_c is negligible at $T = 75$ K. Also because the negative of ZFC susceptibility, $-\chi$, varies linearly with ε and by using a simple non-interacting model we deduced that the effect of the intergrain interaction on $-\chi$ is negligible. This is an important result, since it suggests that one can use a non-interacting model to describe various magnetic phenomena in the small grain superconducting systems.

Finally, we note that $-\chi$ varies strongly with ε near H_{C1}. However, $-\chi$ is insensitive to ε in the neighbourhood of a cut-off field H_0. Where H_0 is determined from the intercept of the straight line of $-\mathrm{d}\chi/\mathrm{d}\varepsilon$ versus $1/H$ when $-\mathrm{d}\chi/\mathrm{d}\varepsilon = 0$.

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References

[1] See, for example, Ginsberg D M (ed) 1989 *Physical Properties of High Temperature Superconductors* vol I (Singapore: World Scientific)
[2] Bednorz J G and Muller K A 1986 *Z. Phys.* B **64** 189
[3] Cava R J, van Dover R B, Batlogg B and Rietman E A 1987 *Phys. Rev. Lett.* **58** 408
[4] Wu M K, Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q and Chu C W 1987 *Phys. Rev. Lett.* **58** 908
[5] Maple M B, Dalichaouch Y, Ferreira J M, Hake R R, Lee B W, Neumeier J J, Torikachvili M S, Yang K N, Zhou H, Guertin R P and Kuric M V 1987 *Physica* B **148** 155
[6] Yang K N, Lee B W, Maple M B and Laderman S S 1988 *Appl. Phys.* A **46** 229
[7] Chavira E, Escudero R, Rios-Jara D and Leon L M 1988 *Phys. Rev.* B **38** 9272
[8] Sheng Z Z and Hermann A M 1988 *Nature* **332** 55
[9] Tokura Y, Takagi H and Uchida S 1989 *Nature* **337** 345
[10] Markert J T and Maple M B 1989 *Solid State Commun.* **70** 145
[11] Markert J T, Early E A, Bjornholm T, Ghamaty S, Lee B W, Neumeier J J, Price R D, Seaman C L and Maple M B 1989 *Physica* C **158** 178
[12] Early E A, Ayoub N Y, Beille J, Markert J T and Maple M B 1989 *Physica* C **160** 320
[13] Ayoub N Y, Markert J T, Early E A, Seaman C L, Paulius L M and Maple M B 1990 *Physica* C **165** 469
[14] Bean C P 1962 *Phys. Rev. Lett.* **8** 250
[15] Bean C P 1964 *Rev. Mod. Phys.* **36** 31
[16] Murray R, Fert A R, Redoules J P, Ayache J, Sabras J and Monty C 1990 *Physica* C **167** 591
[17] Shimizu E and Ito D 1989 *Phys. Rev.* B **39** 2921
[18] Cullity B D 1972 *Introduction to Magnetic Materials* (London: Addison-Wesley)
[19] Senoussi S, Oussena M and Ribault M 1987 *Phys. Rev.* B **36** 4003
[20] Van Vleck J H 1932 *The Theory of Electric and Magnetic Susceptibilities* (London: Oxford University Press)
[21] Kittel C 1976 *Introduction to Solid State Physics* 5th edn (London: Wiley)
[22] Ayoub N Y, Abu-Aisheh B, Laham N, Dababneh M, Popplewell J and O'Grady K 1988 *J. Physique Coll.* **49** 1841
[23] Popplewell J, Abu-Aisheh B and Ayoub N Y 1988 *J. Appl. Phys.* **64** 5852