Diamagnetic properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ presintered powders: critical current densities and a.c. losses

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The intrinsic diamagnetic response of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ presintered powders obtained by the citrate pyrolysis method has been studied. The techniques applied were: a.c. susceptibility at zero d.c. field, low field d.c. susceptibility, isothermal magnetization and a.c. susceptibility at varying bias fields up to 5 T. To investigate intragrain links, powders of known sizes were used directly, dispersed in oil and finally in the sintered form. Intragrain inductive critical currents and critical field values are derived. Finally, the experimental results are discussed within the framework of weak link models and flux pinning effects.

Keywords: high T_c superconductivity; critical currents; weak links; Y-Ba-Cu-O compounds

In the study of the physical properties of ceramic high temperature superconductors (HTSC) a wide range of critical temperatures, magnetic behaviour and critical currents has been found which depends on synthesis and sintering processes.

For a homogeneous HTSC ceramic material, i.e. one with correct stoichiometry and oxygen content throughout, the onset temperature of the superconducting phase, T_c , is well defined. The granular character of the sample influences its macroscopic thermodynamic and transport properties below T_c . In particular, a.c. magnetic susceptibility measurements have demonstrated the existence of two regimes in the magnetic response, the intergrain shielding dominating the low temperature behaviour and the intragrain effects dominating the response near T_c . The same conclusions were reached for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ¹⁻⁴ and $\text{TmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ⁵ sintered materials, irrespective of rare earth substitution.

A recent experiment on the transport properties across the individual boundaries of two $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin film single crystal grains⁶ (c-axis normal) has shown that perfect contact of grains, except for a small crystallographic misalignment ($\leq 5^\circ$) in the basal plane, yields intergrain critical current density values, J_{cJ} , which are very sensitive to magnetic field. This result is consistent with a superconductor-normal-superconductor type of weak link at intergrain contact. It certainly justifies the model which considers a ceramic sample as a network of weak links, each of them with a different characteristic

critical current. Any measurement on a macroscopic sample will be related to the detection of a distribution of J_{cJ} values.

As a consequence of the existence of a complex weak link network in sintered samples, the magnetic and electric transport properties are strongly influenced by the sintering conditions²⁻⁴. To avoid the influence of the pelletizing and sintering process, in the present paper a complete set of susceptibility and magnetization experiments have been performed as a function of temperature and external field on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powdered samples (δ being undetermined but close to zero) of well-defined particle sizes. For HTSC powdered systems magnetic susceptibility for a.c. and d.c., $\chi_{a.c.}(B, T)$ and $\chi_{d.c.}(B, T)$, respectively, and magnetization measurements, $M(B, T)$, allow one to locate the onset of superconductivity, T_c , and to derive inductive critical current and critical field values. The data have been interpreted in terms of the intrinsic effects due to magnetic flux pinning.

Experimental details

Synthesis and characterization

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders were obtained by the citrate synthesis method followed by pyrolysis to obtain a fine and homogeneous powder⁷. The preparation proceeds as follows: stoichiometric amounts of Y_2O_3 , BaCO_3 and CuO are dissolved in nitric acid. After adding citric acid,

the solution is neutralized with ammonia to a pH value of 6.8. A small volume is heated, until spontaneous combustion occurs. This technique gives a homogeneous powder with significantly less impurities than that prepared via the normal solid state reaction procedure. Grains of 50–100 nm and of the proper 1-2-3 stoichiometry are obtained. Because of the fine powder size, the subsequent solid state reaction is very effective and is quickly executed. This solid state reaction is necessary to obtain the correct orthorhombic structure. Depending on the reaction temperature and the time allowed, the typical particle size varies from 1 to 500 μm . The oxygen content, δ , of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder depends on the rates of warming up and cooling down used.

Magnetic measurements were performed on the following $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders: sample I which has particle sizes ranging from 5 to 10 μm with a wide distribution function, the particles being commonly formed by a conglomerate of smaller single crystal grains; and sample II which is obtained after milling the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders of sample I with agate balls in an isopropyl alcohol slurry, producing an average particle size of 3 μm with a standard deviation of 2 μm . A third set of measurements was performed on sample I powder dispersed in paraffin oil. The particle size distribution function was determined from photographs of optical microscopy.

A.c. susceptibility at zero d.c. field

For sample I, measurements of the in phase, $\chi'(T)$, and out of phase, $\chi''(T)$, components of the a.c. susceptibility were performed at four different values of applied a.c. field amplitude, $\mu_0 h_0$, between 1.1 μT and 1.1 mT, for a frequency, $\nu = 120$ Hz, and in the presence of the d.c. earth magnetic field. The results are shown in Figures 1a and b (curves I to IV, hereafter called $\chi_I, \dots, \chi_{IV}$). All the curves have, within experimental error, the same onset temperature, $T_c = (91.2 \pm 0.5)\text{K}$. The same $\chi_{a.c.}(T)$ measurements were performed on sample II. For the sake of simplicity, only the $\chi'(T)$ and $\chi''(T)$ components for the highest value $\mu_0 h_0 = 1.1$ mT have been represented as curve V, χ_V , in Figures 1a and b.

To analyse the influence of the particle to particle contacts produced by the loose packing of the powder grains in the sample holder, the susceptibility of sample I, further prepared by dispersion of the grains in paraffin oil followed by rapid solidification by immersion in liquid nitrogen, was monitored under the same experimental conditions and $\mu_0 h_0 = 1.1$ mT. The results (curve VI in Figure 1a and b hereafter χ_{VI}) are very similar to χ_{IV} ; actually, the differences are negligible above 80 K and amount to a maximum of 7% at the lowest temperature measured (4.2 K).

As could be expected for powder samples, all six $\chi'(T)$ curves depicted in Figure 1a show a sudden decrease at T_c followed by a progressive tendency to an asymptotic constant value at low temperatures, even for the lowest $\mu_0 h_0$ applied, i.e. no curve shows the usually characteristic inflexion point caused by the onset of intergrain coherent superconductivity in sintered samples⁵. It is more surprising that the $\chi''(T)$ curves for sample I (5–10 μm particles) still possess the $\mu_0 h_0$ sensitive low temperature maximum, characteristically provoked by magnetic losses

Figure 1 (a) In phase, χ' , and (b) out of phase, χ'' , components of the a.c. initial magnetic susceptibility of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Exciting field amplitudes, $\mu_0 h_0$ (in mT), for sample I (5–10 μm powders): curves I, 1.1×10^{-3} ; II, 1.1×10^{-2} ; III, 0.11; IV, 1.1. Curves V are the results for the powdered sample II and curves VI correspond to sample I dispersed in paraffin oil (both measured at the highest a.c. field applied, $\mu_0 h_0 = 1.1$ mT)

in a weak link network. The maximum height is, nevertheless, lower (30%) than in the sintered compound. The reduction of particle size by a factor of three in sample II almost completely quenches the low temperature maximum of χ''_V (6% of the values for sintered samples). On the other hand, a second maximum in χ'' , at $T = T_{\text{high } \chi'' \text{ max}}$, near T_c is observed in all cases measured. To clarify the discussion, in Figure 2 an expanded view of the $\chi''(T)$ component in the region close to T_c for samples I and II, is shown.

Low field d.c. susceptibility

Zero field cooled (ZFC, open symbols) and in-field cooled (FC, filled symbols) d.c. susceptibility, $\chi_{\text{d.c.}}(\mu_0 H, T)$ measurements of samples I and II at low fields $\mu_0 H = 3.9$ mT, were also performed and the results are presented in Figure 3. The T_c value observed in this experiment coincides with that obtained from $\chi_{\text{a.c.}}(T)$. Moreover, the $\chi_{\text{d.c.}}(T)$ -ZFC results for sample II (triangles) overlap with $\chi'_V(T)$, whereas there are differences, which increase upon cooling, between analogous results for sample I (squares) and the corresponding $\chi'_V(T)$ curve. The $\chi_{\text{d.c.}}(T)$ -FC results of both samples coincide over the full temperature

Figure 2 Enlarged plot of $\chi''(T)$ near the superconducting onset temperature, T_c . For key to curve labelling, refer to Figure 1 caption

Figure 3 Zero field cooled (open symbols) and in-field cooled (filled symbols) d.c. magnetic susceptibility, $\chi_{\text{d.c.}}$, derived at $\mu_0 H = 3.9$ mT on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders. ■, □, Sample I; ▲, △, sample II. Continuous lines labelled IV and V correspond to the $\chi_{\text{IV}}(T)$ and $\chi_{\text{V}}(T)$ results

range; thus the percentages of flux expulsion of sample I and sample II are almost the same. Furthermore, the FC and ZFC curves coincide at temperatures higher than $T_{\text{irr}} = (90.4 \pm 0.5)$ K. In fact, this temperature effectively separates the a.c. field dependent irreversible region at low temperature from the reversible one above. The coincidence of T_{irr} with $T_{\text{high } \chi'' \text{ max}}$ deduced from $\chi''(T)$ should be noted.

Isothermal magnetization and a.c. susceptibility at high fields

At selected temperatures, 4.2, 60 and 87 K, isothermal magnetization, $M(\mu_0 H, T)$, and a.c. susceptibility, $\chi_{\text{a.c.}}(\mu_0 H, T)$, measurements at $\nu = 120$ Hz and $\mu_0 h_0 = 0.11$ mT were performed up to a maximum applied field of $\mu_0 H_{\text{max}} = 5$ T. The $M(\mu_0 H)$ isotherms for sample I are presented in Figure 4.

The $M(\mu_0 H)$ curves start to deviate smoothly from the $M = -H$ line at a value usually identified with the lower critical field, H_{c1} . The value obtained for 4.2 K, $\mu_0 H_{c1} = 36$ mT, is 50% lower than the value reported for a sintered

Figure 4 Isothermal magnetization curves, $M(\mu_0 H, T)$, at three different temperatures: (a) 4.2 K; (b) 60 K; and (c) 87 K, for 5–10 μm particle sizes (sample I) versus external induction field, B , up to 5 T. Arrows indicate increase or decrease of external field

and crushed $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample measured with the same technique, $\mu_0 H_{c1} = 80$ mT, and almost coincident with the value $\mu_0 H_{c1} = 30$ mT found for a second set of powdered samples⁸. Upon increasing the field, the $M(\mu_0 H)$ isotherms show a minimum at a field $\mu_0 H_{\min} = 250$ mT and 45 mT for 4.2 and 60 K, respectively, eventually reaching an asymptotic straight line.

On the contrary, once the minimum is passed, the $M(\mu_0 H)$ 87 K isotherm is qualitatively different since it increases monotonically, becoming positive at $\mu_0 H \approx 1$ T, and tending to an asymptotic line of positive slope. Undoubtedly, the sample reaches the normal state for $\mu_0 H_{c2} \approx 1\text{--}2$ T, becoming paramagnetic. The slope at $H_{\max}$ yields a value of $\chi' = 5.03 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, which agrees quite well with the paramagnetic susceptibility at 100 K ($\chi' = 4.65 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$) measured elsewhere⁹ for a sample prepared by the citrate pyrolysis method, which is thus comparable to the sample studied here.

As the applied field starts to diminish from $H_{\max}$, the $M(\mu_0 H)$ isotherm at 4.2 K jumps to positive values showing clear irreversibility effects, as expected for strong or moderate flux pinning and trapping (see Figure 4a). Upon further decrease of the field, the $M(\mu_0 H)$ 4.2 K isotherm continuously increases, yielding an opposite remanent magnetization, $\mu_0 M_r = 48.2$ mT, at $H = 0$.

The 60 K magnetization isotherm is almost reversible down to the field $\mu_0 H_{\text{irr}}$, i.e. the increasing and decreasing curves differ by less than 10% of the total magnetization. Below $\mu_0 H_{\text{irr}} = 2.5$ T, the decreasing curve begins to separate from that for an increasing field, yielding $\mu_0 M_r = 5.86$ mT, a value an order of magnitude smaller than for 4.2 K. The behaviour of the decreasing field $M(\mu_0 H)$ isotherm at 87 K is qualitatively the same as the 60 K one, though $\mu_0 H_{\text{irr}} = 200$ mT is an order of magnitude lower, i.e. it only shows irreversibility below 100 mT. In addition, $\mu_0 M_r = 0.26$ mT is also an order of magnitude smaller.

The $\chi'(\mu_0 H)$ isotherms measured for sample I are represented in Figure 5. Furthermore, for comparative purposes the characteristic values of the $\chi'(\mu_0 H)$ curves are collected in Table 1, together with the results reported above for $\chi'(T)$ at zero d.c. field in all the samples used. From this, one observes that the $\chi'(\mu_0 H = 0)$ values at 4.2 and 60 K agree very closely with the values of column χ'_{III} , which correspond to the same sample and exciting a.c. field amplitude. For small d.c. fields, $H \ll H_{c1}$, the $\chi'(\mu_0 H)$ isotherms at 4.2 and 60 K decrease steeply in amplitude, bending sharply in a kink at H_k . At this field, χ' has a value which corresponds quite well to the χ'_V column, i.e. for 3 μm particle size measured at the highest a.c. field. Moreover, it also agrees, at the corresponding temperatures, with the ratio M/H derived for $H \rightarrow 0$ in the magnetization isotherms. Thus, one can conclude that

the application of small d.c. fields destroys the inter-particle weak link network just as effectively as the mechanical disaggregation of the powder does.

However, for the 87 K isotherm there is no quantitative agreement with the $\chi'(T)$ corresponding values (see Table 1). The reason for this discrepancy is that the applied field is very close to the lower critical field and, as a consequence, it may penetrate the grains giving rise to irreversible intrinsic effects.

For fields higher than H_k , in the 4.2 and 60 K cases, the $\chi'(\mu_0 H)$ curve smoothly diminishes in absolute value with increasing H , towards an asymptotic constant slope

Figure 5 In phase $\chi'(\mu_0 H, T)$ component of a.c. susceptibility of sample I versus external induction field, B , up to 5 T, at given constant temperatures: $\square$, 4.2 K; $\blacklozenge$, $\triangle$, 60 K; and $\diamond$, 87 K. Arrows indicate variation of field. Inset shows an expansion of low field region

Table 1 Selected χ' values of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder sample I, χ'_{IV} (5–10 μm particles, $\mu_0 h_0 = 1.1$ mT), compared to χ'_{VI} , when dispersed in paraffin oil. Values taken from $\chi'(\mu_0 H)$ isotherms at the earth magnetic field, $H = 0$, at the kink field, H_k , and at $H = 0$ after magnetizing up to $H_{\max} = 5$ T and demagnetizing, are compared to the zero d.c. field, $\chi'(T)$, data for sample I, χ'_{III} (5–10 μm particles, $\mu_0 h_0 = 0.11$ mT), sample II, χ'_V (3 μm particles, $\mu_0 h_0 = 1.1$ mT). Linear slope of the magnetization isotherm determined at $H < H_{c1}$ for sample I is also included. Similarities are highlighted by division of the table into groups. Units of $\chi' = 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and experimental error is $\leq 10\%$

T (K)	χ'_{IV}	χ'_{VI}	χ'_{III}	$\chi'(H = 0) \uparrow$	χ'_V	M/H	$\chi'(H_k)$	$\chi'(H = 0) \downarrow$
4.2	1.59	1.72	2.06	2.26	1.22	1.18	1.38	1.38
60	1.23	1.33	1.81	1.88	1.07	1.08	1.25	1.25
87	0.73	0.75	0.75	0.30	0.57	0.19	—	—

which diminishes with the trend of increasing temperature isotherms. This result is expected since in these two cases the field region corresponds to $H_{c1} < H < H_{c2}$ and, consequently, in this mixed normal-superconducting state, the size of the perfectly diamagnetic volume continuously decreases for increasing field and increasing temperature. On the other hand, the $\chi'(\mu_0 H)$ for 87 K decays sharply to a small positive (paramagnetic) value, crossing the zero line at $\mu_0 H \approx 300$ mT, in reasonable agreement with the magnetization measurements.

Upon reduction of the field, the $\chi'(\mu_0 H)$ curves are almost reversible down to $H \approx H_{c1}$, except for the 60 K isotherm, where minor hysteresis effects are observed. For lower fields, the χ' curve decreases continuously with a constant slope. Extrapolating linearly to $H = 0$ one obtains the values $\chi'(H = 0)$ listed in the last column of Table 1, which compare very well with $\chi'(H_k)$, i.e. after the weak link structure has been destroyed by the applied field (see insert in Figure 5).

Analysis of results

For sample I, the results of $\chi'(T)$ and $\chi''(T)$ for particles packed loosely and the oil dispersed specimens are almost coincident and prove that there are no effects due to particle-particle contacts. Thus, the observed behaviour is attributable to the response of individual particles. However, in spite of the close similarity, the $\chi'(T)$ and $\chi''(T)$ values are slightly larger for the oil dispersed samples. It is known that in these samples the preferential stacking of their platelet-like grains induce anisotropy and, consequently, different demagnetizing factors between the powder sample particles and the randomly orientated ones dispersed in oil, thus explaining the observed difference.

The optical microscopy shows that most of the powder particles of sample I are formed by a conglomerate of grains, whereas in sample II the number of conglomerates is much lower. Thus, the experimental finding that $\chi'(T)$ for particle sizes of 5–10 μm is larger than the same results for 3 μm particles, $\chi'_v(T)$, is explained by the presence of screening superconducting currents flowing through intraparticle but otherwise intergrain weak links. Indeed, since the screened volume is larger for a larger particle, its absolute volume susceptibility at low temperatures will be larger. Moreover, the reduction in height of the low temperature $\chi''_v(T)$ and $\chi''_v(T)$ maxima from sample I to sample II points to the same idea. Only the losses due to weak links formed by the intergrain material (in this case, also intraparticle) is highly sensitive to the very small a.c. exciting fields applied in this case^{4,5}.

The measurements of $\chi_{d.c.}(T)$ -FC and ZFC were performed at $H = 3.9$ mT, which is the value of H_{c1} at $T = 87$ K. This implies that below this temperature the linear regime is in effect. The FC data yield a measure of flux expulsion upon reaching the superconducting state, thus the coincidence of both samples indicates that the relative volume penetrated by the field is the same. This can only happen if the larger particles of sample I are actually built up of the same smaller grains that are disgregated in sample II. Then, such a low field is capable of penetrating via the intergrain weak link lattice existent in each sample I particle. For the same reason one may conjecture that the amount of flux pinning per unit volume is also the same.

The ZFC measurements yield flux exclusion which is different for both samples. The larger effect observed for sample I than for sample II indicates that the remaining weak links between the grains of the particles support a superconducting current which shields a relatively larger volume for the larger particles. The difference between ZFC and FC results, even for the smaller particles, indicates that pinning centres are effective within the intraparticle, intergrain, weak link lattice, and the penetrated superconductor volume.

The upper temperature $\chi''(T)$ maxima near T_c (see Figure 2) does not change upon reduction in particle size. Recently this anomaly has been related to the existence of weak links inside the single crystal domains¹¹, the twin boundaries being the most likely physical agent. The results reported here agree with such an idea since the distance between twin planes, for example 0.12 μm for polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ¹¹, is more than an order of magnitude smaller than our smallest particle size and, consequently, the structure of the twinned domains within each grain will remain unmodified after crushing.

If the dominant mechanism giving rise to magnetic losses is flux pinning, Clem¹² has proposed that the maximum in $\chi''(T)$ may be related to the condition when the a.c. field penetrates to the centre of a hypothetically cylindrical grain of radius R , for fixed h_0 . This occurs due to the progressive increase in penetration length with increasing temperature. In the present experiments for sample I one observes two peaks in $\chi''(T)$. Since they must be related to single particles, it is proposed that an interstitial material exists between well crystallized regions formed by the twinned domains. Then, $J_{cJ}(T)$ associated with the whole particle and $J_{cg}(T)$ ascribed to the crystallites may be calculated from the expressions

$$J_{cJ}(T_{\text{low } \chi'' \text{ max}}) = \frac{ch_0}{4\pi R_J}, \quad J_{cg}(T_{\text{high } \chi'' \text{ max}}) = \frac{ch_0}{4\pi R_g}$$

where: h_0 = amplitude of the applied a.c. field; T_{max} = temperature of the $\chi''(T)$ maximum; and $R_J = 4 \mu\text{m}$ and $R_g = 1.5 \mu\text{m}$ values identified with the particle and grain radii, respectively.

The $J_{cJ}(T)$ data so obtained are depicted in Figure 6 versus the relative temperature, $T_c - T$, and are compared to the values obtained elsewhere for sintered samples. In particular, good concordance is found between two sets of data^{11,13} and for the present authors' previously

Figure 6 Double logarithmic plot of $J_{cJ}(T)$ deduced from the peak at $T_{\text{low } \chi'' \text{ max}}(K)$, versus $T_c - T$. $\square$, This work with $R = 4 \mu\text{m}$; *, same material after sintering; $\blacksquare$, sintered material in Reference 13; $\blacklozenge$, material in Reference 11; +, values currently deduced from data of Reference 2

published sintered sample result¹. There seems to be a certain common weak link behaviour among the sintered ceramic samples when they behave as a large superconducting cylinder, notwithstanding the different preparations. However, the values derived from the published $\chi''(T)$ data in Reference 2 are discrepant, though these correspond to a thin, flat sample, i.e. of different shape to the others in question, a fact that could explain the difference.

On the other hand, the values of $J_{c1}(T)$ obtained here are one to two orders of magnitude higher than for the sintered samples, as may be observed in Figure 6. Since in the present analysis particle radius needs to be considered, it is possible that a low estimation of the effective radius would artificially enhance the J_{c1} values. However, if one derives this effective radius considering J_{c1} for the sintered materials, one arrives at $R_1 = 0.4$ mm, i.e. a radius not supported physically by any entity in the dispersed powder sample. Since the present sample has not been subject to sintering, the explanation is that the J_{c1} detected must be related to types of weak links other than those in the sintered case; perhaps intraparticle, intergrain contacts.

The values of J_{c2} deduced from this method are again one order of magnitude larger than the same parameter deduced for a larger particle¹¹. In fact, the J_{c2} values tend to increase with decrease in grain size. This has been attributed to the twin boundaries which, due to the small coherence length, act as weak links, reducing the actual R_g radius.

In the $M(\mu_0 H)$ and $\chi(\mu_0 H)$ isotherms of Figures 4 and 5, and for the fields reached, H_{c1} divides the behaviour into two regions. For $H < H_{c1}$, a complete Meissner state should be observed which means $B = 0$ inside the sample and thus: $M = -H$, then $\chi'(\mu_0 H) = -1/4\pi\rho(1 - N)$ (where ρ = density and N = demagnetizing factor) and $\chi''(\mu_0 H) = 0$. However, upon the application of an external field, for $H < H_{c1}$ a sharp reduction in the $\chi'(\mu_0 H)$ values are observed which could be ascribed to the break-down of the weak link network within the particle and the associated disappearance of the shielding provided by it. Decreasing the field below H_{max} , the differences between the values of $\chi'(\mu_0 H)$ and the previous levels are due to the pinning of the magnetic flux. This will be discussed later.

Between H_{c1} and H_{c2} , magnetic flux quanta, $\Phi_0 = (hc/2e)$, can penetrate the sample^{14,15} and vortices pin at the lattice defects (mainly at the twin boundaries). This pinning is deemed as the main cause for the observed irreversibility in $M(\mu_0 H)$ ^{16,17}. The degree of pinning of the vortex lattice is intermediate, as could be inferred from the $M(\mu_0 H)$ isotherms at 60 and 87 K, compared to a semireversible type II conventional superconductor (such as PbIn) and a completely irreversible one (such as VTi)¹⁸. Finally, pinned vortices have been observed in a well ordered Abrikosov lattice in defect- or twin-free regions of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal, besides those pinned at the twin boundaries¹⁹. The former, proposed to be produced by an intrinsic pinning mechanism, are thermally disordered as the temperature rises, while the latter seem to be in deeper potential wells.

Defining the irreversible magnetization, $\Delta M(\mu_0 H) = [M^+(\mu_0 H) - M^-(\mu_0 H)]/2$, where $M^+(\mu_0 H)$ and $M^-(\mu_0 H)$ are the isothermal magnetization increasing and decreasing the field, respectively, any reversible contributions are eliminated in $\Delta M(\mu_0 H)$. Then the critical

current associated to the crystallite is derived to be

$$J_{cg}(\mu_0 H) = \frac{3000 \Delta M(\mu_0 H)}{4\pi R_g} \quad (\text{Bean Model})$$

where ΔM is in mT, R_g is in mm and J_{cg} is in A cm^{-2} . These results are presented in Figure 7. $\Delta M(\mu_0 H)$ is more than two orders of magnitude lower at 60 K than at 4.2 K. This may be interpreted as due to progressive softening of the superconducting material upon warming. In fact, it has been argued from the temperature dependence of the inductive to transport current ratio that the pinning centres at 4.2 K become weak links at 60–70 K²⁰. On the other hand, thermally assisted flux creep may occur when the temperature is high enough to overcome the pinning potential barrier, even at small driving forces and this could also cause similar irreversibility in the magnetization temperature dependence²⁰.

For the $J_{cg}(\mu_0 H)$ curve at 4.2 K, the behaviour is qualitatively similar to values measured using the same technique²¹, or by flux penetration measurements using Campbell's method¹¹. However, the actual values given by those authors are nearly an order of magnitude lower than those from the present determination. The discrepancy probably arises from the grain radius ($1.5 \mu\text{m}$) applied here in the London-Bean formula, justified by the known particle size used, while the grain radius in Reference 11 was $13 \mu\text{m}$, i.e. an order of magnitude larger.

The 60 K curve is, on the contrary, qualitatively different, since here no maximum is observed at ≈ 3 T, while both other authors did so. The appearance of a minimum in $J_{cg}(B)$ is explained in Reference 11 as being produced by the crossover from the dominant intragrain

Figure 7 Critical currents, $J_{cg}(T)$, on logarithmic scale versus external induction field of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powdered sample I, deduced from the magnetization isotherms. Curve a, $T = 4.2$ K; b, $T = 60$ K; c, $T = 87$ K. Isolated point reflects same parameter deduced from χ'' high temperature maximum at $T = 90.4$ K

weak link regime at low fields, to the pinning regime at higher ones. Then, for particle size an order of magnitude lower, as with the present sample, the first regime will be destroyed by the mechanical grinding down to the subregion boundaries, where the intrinsic response actually dominates. In favour of this interpretation is the fact that at $\mu_0 H = 4$ T, which the previous authors claim to be in the pinning regime, the present value of $J_{\text{cg}} = 2 \times 10^4$ A cm⁻² agrees quantitatively with their results.

It is worth mentioning that for films made by electron beam co-evaporation²² the $J_{\text{cg}}(\mu_0 H)$ values determined from the irreversibility in the magnetization hysteresis loops are in quantitative agreement with the present results. In that case, it was also taken as proof of substantial pinning in the film sample.

For comparative purposes, the $J_{\text{cg}}(H=0) = 5.8 \times 10^4$ A cm⁻² value determined at 90.4 K from the $\chi''(T)$ high temperature peak has been presented in Figure 7. The value is very large compared to the result derived from the $M(\mu_0 H)$ 80 K isotherm. The methods of determining J_{cg} seem to be discrepant, probably due to lack of accuracy in determining the effective dimensions. Unfortunately, the present authors do not have data at the same temperature to compare both determinations more precisely.

In principle, $\chi'_{\text{a.c.}}$ measures the $M(H)$ slope and, from the data presented here, it is obvious that $\partial M(H, T)/\partial H$ (Figure 4a) does not yield $\chi'(\mu_0 H, T = 4.2$ K) for $H > H_{c1}$ in Figure 5. In fact, $\chi'(\mu_0 H)$ values follow a smooth variation with the induction field and do not show anomalous or irreversibility effects. When $h_0 \ll H$, $\chi'(\mu_0 H)$ is proportional to the maximum of $(d\Phi/dt)_{\text{max}}$, where Φ is the magnetic flux through the sample caused by the d.c. and a.c. fields²³. At the relatively slow frequency applied, the depth of the a.c. field penetration, $x_{\text{max}}(h_0)$, is proportional to $(d\Phi/dt)_{\text{max}}$

$$x_{\text{max}} \approx \frac{\chi'(\mu_0 H, T)}{\mu_{\text{eq}}(\mu_0 H)}$$

and

$$\mu_{\text{eq}}(\mu_0 H) = \mu_0 \left[1 + \frac{dM(H, T)}{dH} \right]$$

For fields above 1 T, $\mu_{\text{eq}}(\mu_0 H)$ is almost constant; here the almost constant value of $\chi'(\mu_0 H)$ indicates that the penetration depth of the a.c. field is field independent. In other words, only a small crust of the grain is affected by the a.c. field in the increasing and decreasing $\chi'(\mu_0 H)$ curves, for high enough fields.

It can be concluded that both inter- and intracrystalline monodomain weak link effects are already present in the particles of HTSC powders before they undergo any mechanical treatment. By grinding the particles their number decreases, but the size of crystallites in sample II (3 μm) is not small enough to have monodomain (untwinned) single crystal particles. For a fixed size, in the measurements at 4.2 K, there is evidence of a moderate amount of irreversibility which could be caused by the pinning of the flux in medium potential barriers, whereas at 60 and 87 K, the pinning centres do not act so effectively and a softening of the superconducting behaviour is observed.

In a recent paper²⁴, the particle radius $R_g = 10$ μm has been determined as a boundary below which the magnetic

measurements are related to the bulk properties; while above it the granularity dominates the measurements. In the present paper the particles are below this limit. Consequently, the high J_{cg} values obtained in the present work are consistent with that result, since they reflect the intrinsic, bulk properties of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample.

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