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Magnetism and microstructure of $YBa_2Cu_3O_{7-x}$ superconductors produced by rapid solidification

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The superconducting $YBa_2Cu_3O_{7-x}$ phase has been produced through a novel rapid solidification processing route yielding a high-quality granular superconducting phase. A detailed study of the magnetic properties indicates important features relevant to current carrying capacity. Low-field magnetization data reveal that weakly coupled superconducting grains decouple at fields of approximately 20 Oe so that the magnetization measurements at higher fields are reflective of intragranular processes exclusively. The high-field data reveal significant irreversibility as well as nonergodic susceptibility behavior consistent with the recently proposed superconducting glass state.

The use of rapid solidification techniques in ceramic processing is well-documented[1,2] with benefits arising from the ability to quench in high temperature or amorphous phases, to produce materials with nonequilibrium defect concentrations or cation distributions,[3] to accommodate improved microstructural control, and to improve chemical homogeneity through the prevention of chemical segregation. We have used rapid solidification to produce $YBa_2Cu_3O_{7-x}$ which after a short (1 h) post anneal in oxygen yields the orthorhombic 1:2:3 superconducting phase. The material thus produced is notable in its fairly uniform grain size and long-lived superconducting properties which include a significant diamagnetic response, a narrow resistive transition and large irreversibility in low-temperature magnetization behavior.

Magnetic measurements have been performed at low and moderate fields revealing that the grains decouple in relatively weak fields (20 Oe) interupting intergranular supercurrents. This decoupling has its own characteristic irreversible magnetization process with a remanence which can be related to the critical current density of the bulk polycrystalline sample. This low-field decoupling of the grains implies that the rest of the magnetization curve in these materials is reflective of intragranular response and thus should parallel single-crystal behavior. The response of the noninteracting aggregate of grains will be shown to be consistent with the superconducting glass state model.[4] The observed decoupling of the grains is consistent with Müller's assertion that the glass state length scale is smaller than the grain size. Thus the glass state in these materials describes coupling between coherent superconducting domains within the grains. The data also reveal the irreversible nature of the magnetization process at low temperatures which is of technical importance in determining single grain critical current densities. The remanent magnetization M_r and lower critical field H_{c1} show an unusual temperature dependence. The implications of the temperature dependence of M_r on the critical current density for single crystals will also be discussed as well as a possible microscopic origin for the unique temperature dependence of H_{c1}.

Thin flakes of amorphous $YBa_2Cu_3O_7$ were produced by the crucibeless[5,6] melting of a sintered pellet of the 1:2:3 phase and rapid solidifying in an oxygen-rich atmosphere. These amorphous flakes were then annealed in oxygen at various temperatures. Metallic resistances at room temperature and high-T_c superconductivity were only observed after annealing at 950 °C in oxygen, which is the temperature at which the 1:2:3 phase was formed. Annealed flakes were crushed and cold pressed into pellets. The resulting material was confirmed both by x-ray diffraction and TEM to be single phase. Samples were subsequently cut from the pellets for resistance and magnetic measurements. Resistance measurements reveal a T_c of 91 K with a $\Delta T_c \approx 1$ K (measured between 10% and 90% of the resistive transition). Magnetization data were collected using an SHE squid magnetometer. The magnetic properties of our material remained consistent over the four months in which they were examined. This long life was attained without any special handling precautions (such as storing the samples in desiccators).

The low-field behavior of our material has been investigated between 0–250 Oe for the temperatures 5, 10, 30, 80, 85, 88, and 89 K. Figure 1(a) shows the low-field response at 5 K. Notable in this response is the large initial susceptibility followed by a turning over of the curve at 25 Oe to a new constant susceptibility. This behavior is similar to that observed by Kwak, Venturini, Ginley, and Fu,[7] and is attributed to grain decoupling. Below 25 Oe our superconducting grains remain coupled (presumably through weak Josephson links) and the initial slope, corrected for demagnetization, is that of a perfect diamagnet. Above a certain field, $H_d \approx 25$ Oe in Fig. 1(a), some flux is able to penetrate the intergranular regions as they can no longer accommodate the screening currents. Figure 1(b) illustrates that the grain decoupling is a strongly irreversible magnetization process contributing to a remanence of ≈ 0.22 emu/g, which corresponds to a critical field[8] of $J_c \sim 30 M_r/R$ ~ 500 A/cm^2, using $R \approx 0.08$ cm, a typical sample dimension. This critical current density agrees well with electrical measurements on bulk polycrystalline samples.[9] Figure 1(c) shows that this magnetization process (when the constant background slope is removed) resembles a bulk magnetization

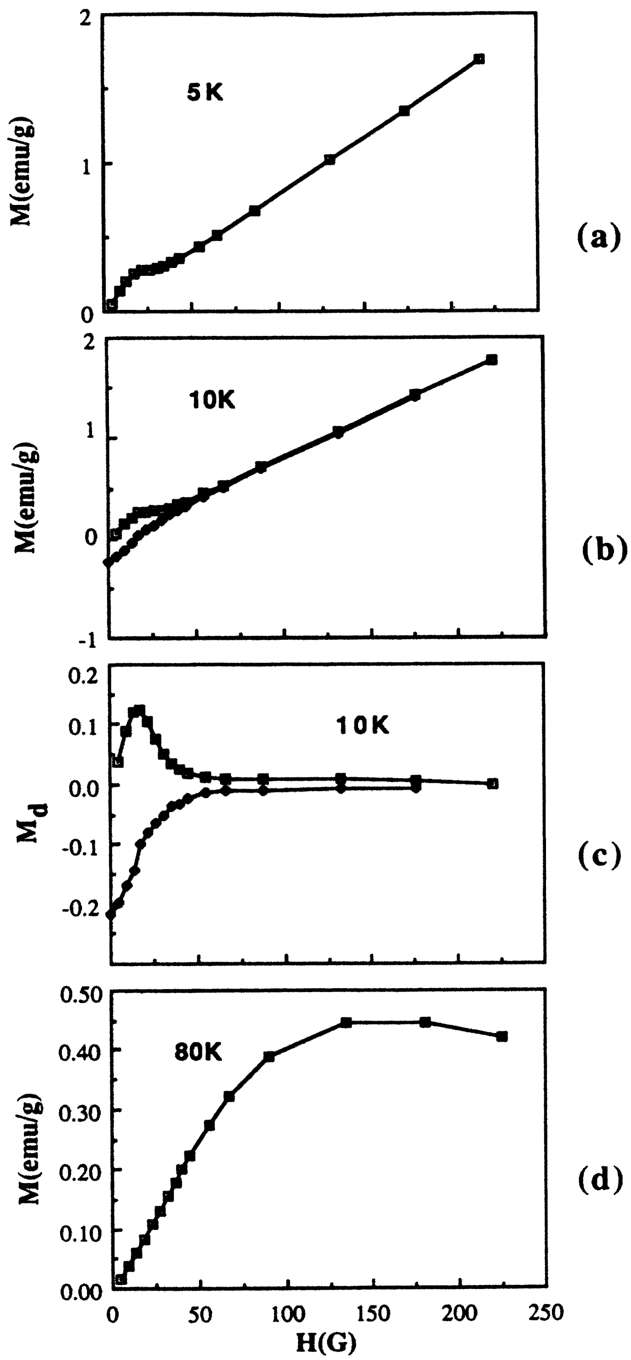

FIG. 1. Field dependence of magnetization (a) at 5 K and (b) at 10 K showing irreversibility of low-field anomaly. Panel (c) shows data of (b) with linear portion removed. Panel (d) shows the low-field anomaly to be absent at 80 K.

curve but on much smaller field and magnetization scales. The temperature dependence of H_d, though not completely characterized, is also of interest. For T=5, 10, and 30 K the decoupling field decreased and for $T \geq 80$ K decoupling phenomena is not observed [Fig. 1(d)], indicating that H_d has a different temperature dependence as compared with the bulk superconductor. Thus a temperature exists between 30 and 80 K at which the grains are decoupled in zero field (note that Kwak, Venturini, Ginley, and Fu[7] observed a different temperature dependence in that they observe a significant H_d at 77 K).

An obvious consequence of this grain decoupling phenomena is that the magnetization curves of our materials above ~25 Oe at all temperatures consist almost entirely of intragranular contributions and thus can be modeled as arising from an aggregate of randomly oriented noninteracting grains.[10,11] SEM on our samples has revealed them to consist of orthorhombic shaped grains 2–5 μm wide and ~10 μm in length. The grains are heavily twinned with twin spacings of ~200–1000 Å.

In a recent Letter, Müller, Takashige, and Bednorz[4] describe the diamagnetic response of a frustrated, granular superconductor La_2CuO_{4-y}:Ba as a superconducting glass state, as originally elucidated by Ebner and Stroud.[12] According to Müller, Takashige, and Bednorz the superconducting glass state is characterized by nonergodicity with respect to field cooling versus zero-field cooling of the magnetic susceptibility and time-dependent (but nonexponential) decays in the susceptibility upon applying a field to a zero-field cooled sample below the ergodic temperature $T^* < T_c$. These features are also

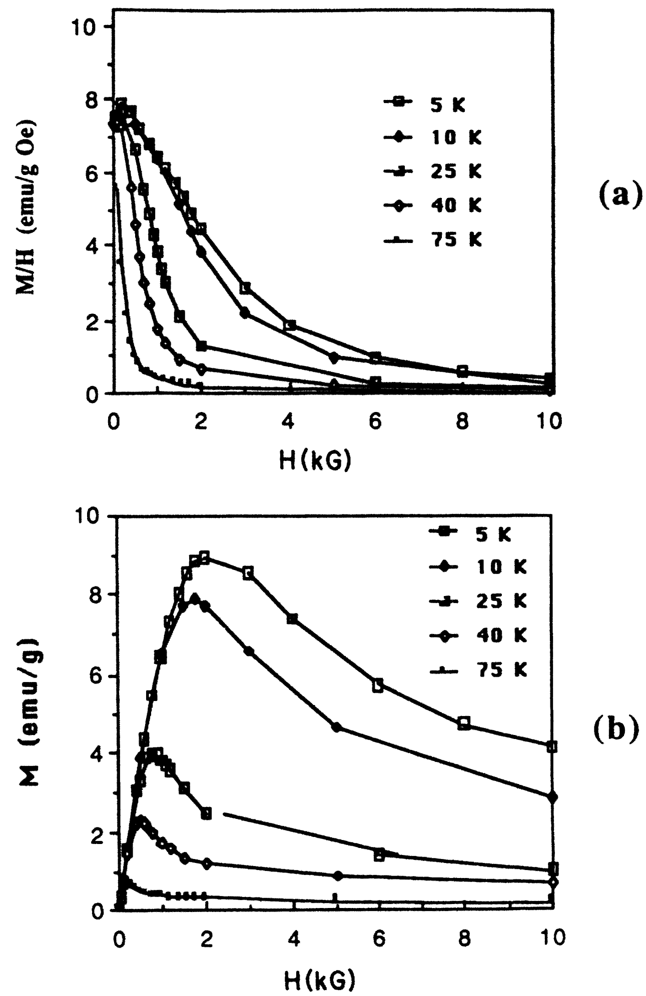

FIG. 2. (a) Susceptibility and (b) magnetization in increasing fields (note greater field range as compared to Fig. 1) for several temperatures below T_c.

present in our $YBa_2Cu_3O_{7-x}$ samples. Figure 2(a) illustrates the field dependence of the susceptibility observed for our sample with the characteristic increasing χ with decreasing applied field strength.

Nonergodicity in the zero-field cooled diamagnetic response is also observed and will be discussed below (Fig. 3). Figure 2(b) shows the zero-field cooled magnetization curves as a function of increasing field for various temperatures. These curves exhibit linear response at low fields with deviation from linearity above H_{c1}. In the language of the superconducting glass state model H_{c1} signifies the point of departure between the ac and dc susceptibilities. We define for later use H_{c1}^* as the field where $dM/dH=0$. From H_{c1}, it is possible to calculate the homogeneous superconducting area S using the relation $H_{c1}=\phi_0/2S$ as proposed by Ebner and Stroud.[12] At 5 K $S=0.02$ μm^2 and at 80 K $S=0.20$ μm^2 both much smaller than the smallest cross section of a typical grain (~ 10 μm^2). It is thus clear from both the low-field decoupling behavior and the fact that the homogeneous superconducting area is much smaller than the grain size for all temperatures that the superconducting glass state in this material describes a coupling between coherent superconducing domains of size smaller than the $YBa_2Cu_3O_{7-\delta}$ grains.

With the glass state response in mind we now examine the irreversibility of the high-field magnetization and the critical current densities and flux pinning. Figures 3(a), 3(b) and 3(c) illustrate magnetization versus field curves at 5, 40, and 85 K, respectively. The behavior at 5 K shows significant irreversibility consistent with previous

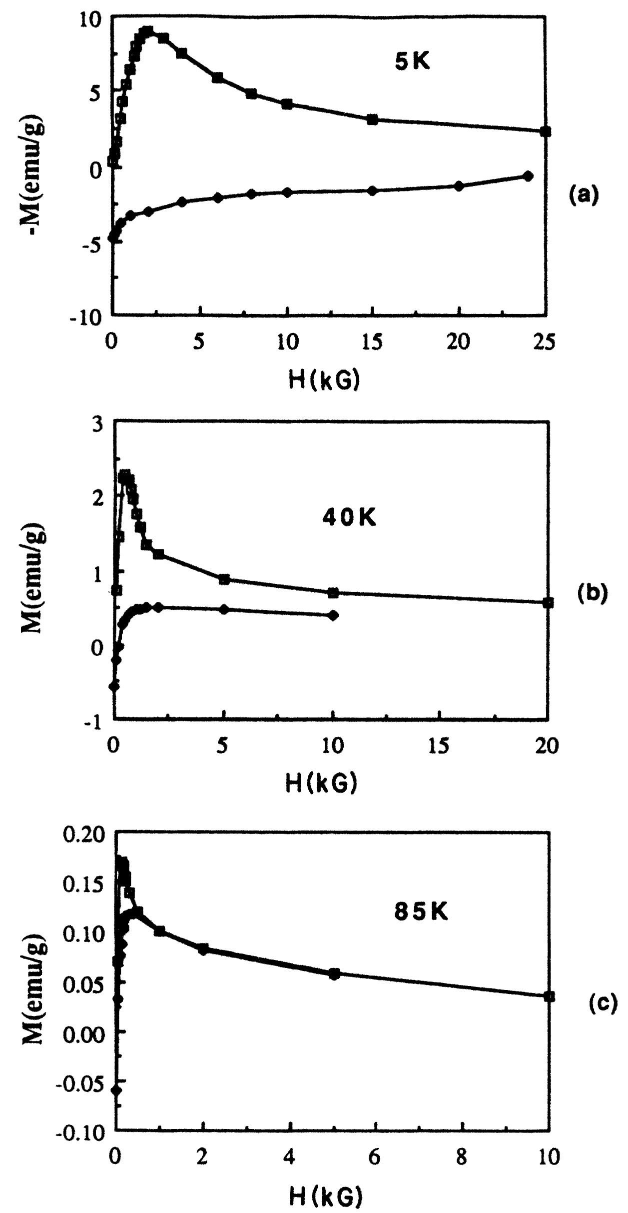

FIG. 3. Magnetization in increasing and decreasing applied fields for three temperatures below T_c. Note different field scales and increasing reversibility as T approaches T_c.

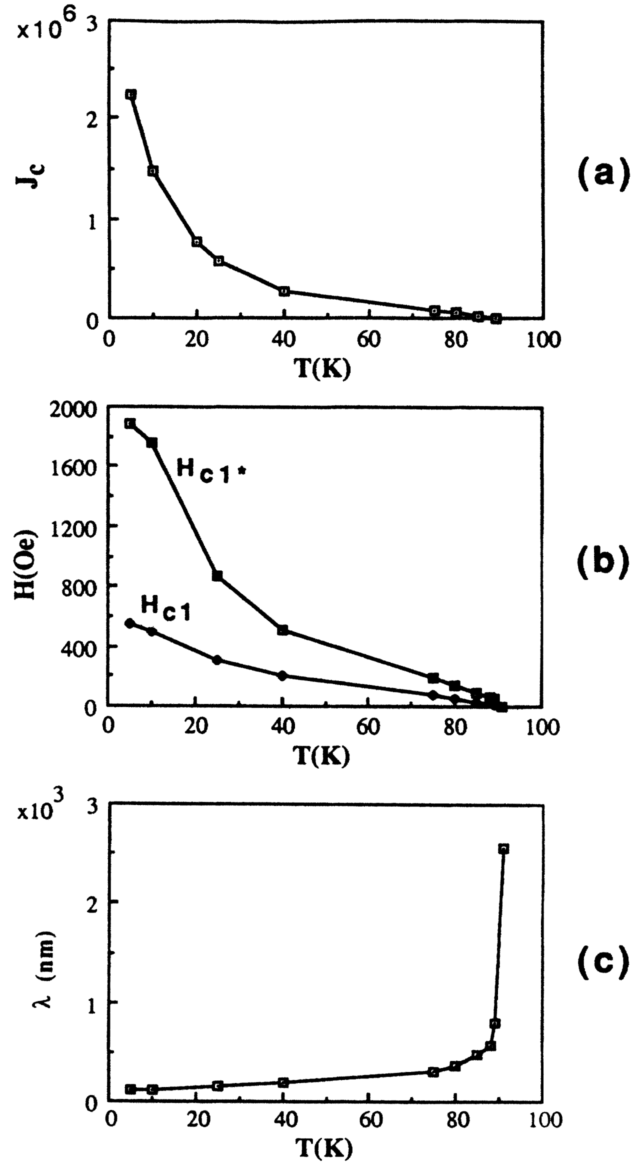

FIG. 4. Temperature dependence of (a) critical current density as derived from the remanent magnetization ($J_c \sim 30$ M_r/R), (b) lower critical field H_{c1} and H_{c1}^* (where $dM/dH=0$), and (c) London penetration depth derived from the lower critical field $\lambda=(\phi_0/\pi H_{c1})^{1/2}$.

observations[13,14] and a large remanence of 31.5 G. At 40 K the first reversible response (below 50 kG) is noted in that with decreasing field the slope dM/dH begins to follow that observed in the increasing-field branch. Thus ergodic susceptibility behavior is observed over part of the M-H loop at 40 K. At higher temperatures, as shown in Fig. 3(c) for 85 K, the loops become increasingly more reversible. The field at which the decreasing-field magnetization first deviates from that of the increasing-field curve is identified as H^* by Müller, Takashige, Bednorz.[4] This field defines a point in the $H-T$ plane on the de Almeida–Thouless[15] phase boundary between the superconducting glass state and random uncoupled superconducting domains. It is observed for our materials that for all but the highest temperatures this field is larger than 50 kG. From the high-temperature data we determine that the de Almeida–Thouless line for our material is 6–10 times steeper than that observed in Müller's $LaCuO_4$:Ba sample.

The irreversibility of the magnetization curves at low temperatures is indicative of a strong flux pinning mechanism. This strong pinning is important to determining the critical current density in single grains of these materials and thus is reflective of the J_c to be expected in single crystals. The critical current density at a given field can be related to the difference in magnetization between increasing and decreasing field curves and therefore the critical field at $H=0$ is related to the remanent magnetization. From the simple magnetostatic relationship used above $J_c \approx 30M_r/R$ (where R is now the grain dimension) it is possible to derive a value of $J_c \approx 2\times10^6$ A/cm^2 for 5 K in excellent agreement with values attained for single-crystal superconductors.[14]

Figure 4(a) shows the behavior of the critical current density as that derived from the remanent magnetization as a function of temperature. It is very interesting to note the behavior of H_{c1} and H_{c1}^* vs T (remembering H_{c1}^* to be defined as the field where $dM/dH=0$) in Fig. 4(b). Both the Hc_1 and H_{c1}^* are shown to have large values at low temperature dropping sharply with increasing temperature with a crossover at 30–50 K to more modest values. The technical importance of high-J_c values is apparent and the origin of such a crossover effect is also of great interest. We point out that 40 K is the temperature above which some reversibility of the magnetic response is seen. We believe that the explanation of this bifurcation in the superconducting behavior is related to the fact that the coherent area S ($\sim$0.05 μm^2 at 40 K) corresponds closely to A the area per twin observed within the grains of our material. The physical model that emerges from such considerations is as follows.

(1) For $T \lesssim 40$, $S < A$, and therefore the twin boundaries act as effective flux pinning sites. The critical field H_c^* and critical current density J_c are large due to the irreversibility of the magnetization process induced by these sites.

(2) For $T \gtrsim 40$, K $S > A$, and the flux is no longer effectively pinned by the twin boundaries. Thus, H_c^* and J_c are significantly reduced because of the more reversible magnetization process.

The bifurcation in the critical field data is also source to an anomalous temperature dependence of the penetration depth as illustrated in Fig. 4(c), where the penetration depth is calculated from the expression $\lambda = (\phi_0/\pi H_{c1})^{1/2}$. The penetration depth varies smoothly with temperature but fails to follow the typical $[1-(T/T_c)^4]^{1/2}$ dependence, as it also fails in La–Cu–O.[16]

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[1]G. Kalonji, J. McKittrick, and L. W. Hobbs, in *Proceedings of the Second International Meeting on ZrO₂*, Stuttgart, Germany, 1983 [Adv. Ceram. **12**, 816 (1984)].

[2]M. R. DeGuire, R. C. O'Handley, M. D. Dyer, and G. Kalonji, J. Non-Cryst. Solids **81**, 351 (1986).

[3]M. R. DeGuire, R. C. O'Handley, M. D. Dyer, and G. Kalonji, J. Magn. Magn. Mater. **54-57**, 1357 (1986).

[4]K. A. Müller, M. Takashige, and J. G. Bednorz, Phys. Rev. Lett. **58**, 1143 (1987).

[5]J. McKittrick, G. Kalonji, and T. Ando, J. Non-Cryst. Solids (to be published).

[6]J. McKittrick, L. Q-.Chen, S. Sasayama, M. E. McHenry, G. Kalonji, and R. C. O'Handley, Adv. Ceram. Mater. **2**, 353 (1987).

[7]J. R. Kwak, E. L. Venturini, D. S. Ginley, and W. Fu, in *Novel Superconductivity,* Proceedings of the International Workshop on Novel Mechanisms of Superconductivity, Berkeley, 1987, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 983.

[8]C. P. Bean, Phys. Rev. Lett. **8**, 250 (1962).

[9]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[10]D. K. Finnemore, R. N. Shelton, J. R. Clem, R. W. McCallum, H. C. Ku, R. E. McCarley, S. C. Chen, P. Klavins, and V. Kogan, Phys. Rev. B **25**, 5319 (1987).

[11]D. E. Farrell, M. R. DeGuire, B. S. Chandrasekhar, S. Alterovitz, P. Aron, and R. Fagaly, Phys. Rev. B **35**, 8797 (1987).

[12]C. Ebner and A. Stroud, Phys. Rev. B **31**, 165 (1985).

[13]M. S. Osofsky, W. W. Fuller, L. E. Toth, S. B. Qadri, S. H. Lawrence, R. A. Hein, D. U. Gubser, S. A. Wolf, C. S. Pande, A. K. Singh, E. F. Skelton, and B. A. Bender (unpublished).

[14]T. R. Dinger, T. K. Worthington, W. J. Gallagher, and R. L. Sandstrom, Phys. Rev. Lett. **58**, 2687 (1987).

[15]J. R. de Almeida and D. J. Thouless, J. Phys. A **11**, 983 (1978).

[16]G. Aeppli, R. J. Cava, E. J. Ansaldo, J. H. Brewer, S. R. Kreitzman, G. M. Luke, D. R. Noakes, and R. F. Kiefl, Phys. Rev. B **35**, 7129 (1987).