PHYSICAL REVIEW B VOLUME 38, NUMBER 10 1 OCTOBER 1988

Granular superconductivity in $R_1Ba_2Cu_3O_{7-\delta}$ thin films

P. England and T. Venkatesan
Bell Communications Research, 331 Newman Springs Road, Red Bank, New Jersey 07701

X. D. Wu and A. Inam
Physics Department, Rutgers University, Piscataway, New Jersey 08855

(Received 17 March 1988; revised manuscript received 13 May 1988)

Present methods of fabricating thin films and bulk samples of the high-T_c oxide superconductor $R_1Ba_2Cu_3O_{7-\delta}$ frequently produce a granular morphology with stoichiometric grains separated by weakly superconducting material, Josephson, or proximity effect junctions. In these films, the bulk superconducting properties (transition width, critical current density) are controlled primarily by the strength of coupling between the grains and not by the superconductivity of the grains themselves. We have examined the I-V characteristics of thin-film oxide superconductors as a function of temperature and find evidence for a coherence transition in which isolated grains couple to form a bulk superconductor. The transition manifests itself in the scaling behavior $V \sim (I-I_c)^x$ where x changes abruptly at coherence. The magnetotransport is in support of the model.

Present methods of fabricating thin films of the high-transition-temperature superconductors $R_1Ba_2Cu_3O_{7-\delta}$ (where $R=$Y, Er, Eu, etc.) include pulsed laser deposition,[1] e-beam and thermal evaporation from one or multiple sources,[2] sputtering,[3] solution, and sol-gel techniques.[4,5] All of these techniques frequently produce films with a granular morphology with grains of the correct stoichiometry separated by grain boundaries and/or material of a different phase. It is also found that high-temperature annealing, which is often needed to produce the correct crystal structure and to incorporate oxygen, can result in microscopic cracking of the thin film. These observations suggest that most thin-film R-Ba-Cu-O superconductors consist of rather weakly connected superconducting islands. This view is supported by measurements on single crystals of Y-Ba-Cu-O, which show qualitatively different behavior from multigranular films and bulk materials.[6] Therefore, it seems clear that in multicrystalline material, the bulk superconducting properties of critical current and transition width are largely controlled by intergrain coupling.

In this paper, we describe experiments that support the view that some R-Ba-Cu-O films can be described as weakly coupled granular superconductors. In particular, we report a scaling behavior in the current-voltage (I-V) characteristics of the films which is evidence for a transition in which uncoupled superconducting grains couple together to produce bulk superconductivity. Magnetotransport measurement in the films are also indicative of the granular nature of the material.

Granular superconductors have been studied for many years, and demonstrate a variety of interesting physical effects.[7] In particular, (at least) two superconducting transitions are seen as a bulk granular superconductor is cooled.[8,9] At, or just below, the transition temperature of the superconducting material which comprises the grains (T_{c0}), a nonzero order parameter develops on individual grains. Close to T_{c0}, thermal fluctuations ensure that the phase of the order parameter on nearby grains is unrelated. However, if nearby grains are coupled by the proximity effect or Josephson tunneling, there exists a coupling energy $E=\hbar i_c/2e$ (where i_c is the intergrain critical current), which, as the temperature is lowered, can exceed thermal fluctuations. This can result in a second transition to a bulk superconducting state in which the phase on nearby grains becomes equal: the coherent state.

Theoretical descriptions of granular superconductors generally assume a Josephson coupling between grains $E=\hbar i_c/2e[1-\cos(\theta_i-\theta_j)]$, where θ is the phase of the order parameter on individual grains. Noting that for planar spins, $\mathbf{S}_i \cdot \mathbf{S}_j \sim \cos(\theta_i-\theta_j)$, we see the model is isomorphic to the X-Y model of magnetism with an explicitly temperature-dependent coupling energy, enabling us to use standard results to describe the granular system.[10] The details of the transition to the coherent state are sensitive to the dimensionality of the system, the degree of disorder and the strength of the intergrain coupling; but all systems show an abrupt change in the I-V characteristics of the system at the coupling transition temperature T_c.[8,10,11] To briefly summarize, in two dimensions ($d=2$), the coupling transition can be described by the Kosterlitz-Thouless theory of phase transitions.[12] In particular, at the transition temperature T_{KT}, bound vortex-antivortex pairs dissociate and then become free and may contribute to dissipation. Experimentally, the I-V characteristics follow the form $V \sim I^x$, where x changes abruptly from $x=1$ to $x=3$ at $T=T_{KT}$. However, in a clean (no resistance to flux flow) $d=2$ system, a critical current cannot be defined, as arbitrarily small transport currents can dissociate the most weakly bound vortex pairs.

The transition in three-dimensional systems is to a state in which thermal fluctuations of the phase on individual grains is strongly suppressed; the almost exact analogy is the transition to a ferromagnetic state in the X-Y model of magnetism. The $d=3$ granular superconductor *can* support a supercurrent, since we can develop a phase gradient along the material without disrupting the temporal phase coherence, and, from the second Josephson relation, $V = \hbar\dot{\theta}/2e$, only a time varying phase difference causes dissipation. Below T_{c0}, and above T_c, increasing correlations of the order parameter cause an increasing paraconductivity which diverges at T_c.

$Y_1Ba_2Cu_3O_{7-\delta}$ has already been shown to exhibit some of the characteristics of granular superconductors. In particular, the high-field magnetic susceptibility is that of uncoupled superconducting grains of size comparable to the magnetic penetration depth of the grains themselves.[13] Of more interest here, the susceptibility in low fields (~1 mOe) shows evidence of a grain coupling transition, significantly below the isolated grain transition temperature.[14] In addition, the current-voltage characteristics of bulk, multicrystalline Y-Ba-Cu-O has shown similar characteristics to those described here, over a correspondingly narrower temperature region.[15] Both the results themselves, and their interpretation differ somewhat from the present work. However, the presence of stoichiometric grains separated by grain boundaries are essential to both interpretations.

The $Er_1Ba_2Cu_3O_7$ thin films under study were grown by pulsed laser deposition from pellets of the same stoichiometry. A KrF excimer laser operating at 1.5 $J\,cm^{-2}$/shot on the pellet and 30 nS full width at half maximum (FWHM) was used. The samples described here were both grown on $SrTiO_3$ ⟨100⟩ substrates, the details of the growth process and subsequent annealing have been described in detail elsewhere.[1]

A scanning-electron-microscope morphological analysis of the *R*-Ba-Cu-O film shows irregularly shaped grains of size (0.75 ± 0.3) μm. There is no evidence of macroscopic inhomogeneity of the film which could possibly mask critical behavior, beyond the fact that the average grain size varies by about 5% over the region of study. Cross-sectional transmission electron microscopy shows that grains form as platelets, of thickness ~0.1 μm, shrinking slightly in size away from the substrate. Grains adjacent to the substrate show perfect epitaxy, and all grains have perfect crystal structure and the correct 1:2:3 stoichiometry.[16] However, the regions between the grains are amorphous with typical thickness < 50 Å, and it is this material which provides the intergrain coupling essential for the observation of a bulk superconducting state. Finally, we make contact to the film with silver paint extending completely across the superconducting region. The voltage probes are 0.6 mm apart, and the current carrying area is $\sim 10^{-5}\ cm^2$.

The approximation we will adopt in this paper is that individual grains acquire bulk superconductivity at the bulk 1:2:3 transition temperature; close to 90 K. As the temperature is lowered, a coupling develops between nearby grains. This coupling increases with reducing temperature for two (related) reasons. First, and most importantly in this material, we expect the surfaces of the grains to be slightly off stoichiometry. This means that the size of the superconducting part of the grain is increasing with decreasing temperature, and so the coupling between adjacent grains increases. Second, all forms of weak link show an enhancement of the critical current as the temperature is lowered. In either case, at some lower temperature, the coupling between nearby grains will be sufficient to force the system into a state where the superconducting phase on all the grains in the system is the same. The semi-idealized model we will use is an assembly of weakly connected superconducting regions extending essentially infinitely in the plane of the film, and 4 or 5 grains thick. For the purposes of simplicity, we will further simplify this to an isotropic infinite three-dimensional (3D) system where each grain has six nearest neighbors (cubic).

The resistive transition of one of the samples under study is shown in Fig. 1. It demonstrates an onset temperature of 92 K and a 10%–90% transition width of 35 K. While better films are currently available [< 1-K transition width, and $\approx 10^5\ A/cm^{-2}$ critical current density at 77 K (Ref. 17)], we intentionally chose to work with films with a relatively wide transition to make a detailed examination of the critical region possible. The critical current density is also shown in Fig. 1. Using the 1 μV/mm criterion, we see that bulk superconductivity occurs at $T \approx 60$ K. The measured critical current density in the films rises to 700 A/cm^2 at 4.2 K.

The transition to the coherent state should occur when the grain coupling energy is equal to the energy available in thermal fluctuations. That is, $ZE_J(T_c) = k_BT_c$, where E_J, Z, and k_B are the intergrain coupling energy, the number of nearest neighbors surrounding a grain, and the Boltzmann constant, respectively.[7] The coupling energy may be related to the intergrain critical current i_c through the relation $E_J = \hbar i_c/2e$. Assuming $Z=6$, we obtain $i_c = 0.42$ μA at $T=60$ K. It is not straightforward to obtain the bulk critical current from the intergrain critical current since we do not know the dissipation process (flux flow, isolated normal regions, etc.). However, if we assume a parallel array of junctions, each carrying i_c, we arrive at a bulk critical current of $I_c \approx 5$ mA which is consistent with that observed. Note that above T_c, short-range correlations of the order parameter still exist, and

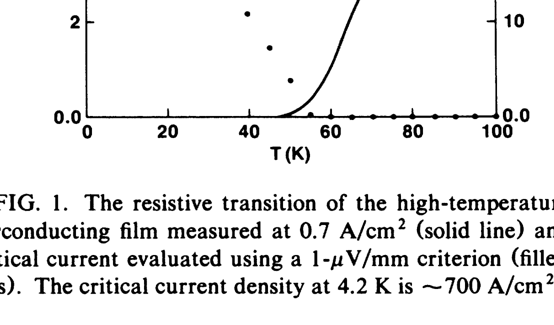

FIG. 1. The resistive transition of the high-temperature superconducting film measured at 0.7 A/cm^2 (solid line) and the critical current evaluated using a 1-μV/mm criterion (filled circles). The critical current density at 4.2 K is ~700 A/cm^2.

these are reflected in the sharply rising paraconductivity.

We have studied the current-voltage characteristic of these films over 7 orders of magnitude in voltage to obtain the characteristics shown in Fig. 2. In pursuance of the analogy with conventional granular superconductors we have examined the data for scaling behavior in the I-V characteristic. In particular, we find $V \propto (I-I_c)^x = I_S^x$ over 4 orders of magnitude in V above I_c. Representative behavior is shown in Fig. 3, and the temperature dependence of the critical exponent x is shown in Fig. 4. The system is essentially Ohmic above $T_c \approx 60$ K, with $x = 1$ and $I_c = 0$ (although because of correlations in the order parameter, the resistance close to 60 K is much less than the resistance at 90 K). There is an approximately 10-K wide transition to a bulk superconducting state in which x rises to ~ 2. As the temperature is lowered further, x rises more gradually to $x \sim 3$ at the lowest temperature studied. Similar scaling behavior has been seen in the second sample of similar morphology. However, films grown at lower temperatures which do not appear to be granular,[17] do not show the scaling behavior.

We turn now to an explanation of this behavior within existing models of granular superconductors. Above T_c, the I-V characteristics should resemble that of a series and parallel connected assembly of *uncorrelated* Josephson junctions biased above their critical current. In this case, the I-V characteristics should be Ohmic ($I_c = 0$, $x = 1$). However, the sample resistance will depend on the strength of the intergrain coupling, which in turn depends on the intergranular material. This qualitatively explains the high-temperature characteristics. Below T_c, because of the strong suppression of fluctuations in the order parameter in the 3D x-y model, a critical current should exist. The details of the coherence transition in 3D granular superconductors have been studied both theoretically and experimentally by Rosenblatt and co-workers.[18] By drawing an analogy between the 3D x-y model of magnetism and the present case, they have been able to show that if the temperature dependence of the intergrain critical current is not too large close to the coupling transition, then, for small voltages, $V \propto (I-I_c)^x$, where $x = (d+1)/(d-1+\eta)$ at T_c and η is the exponent characterizing the order-parameter correlation function $\langle \theta(r)\cdot\theta(0)\rangle \sim r^{d-2+\eta}$. Unfortunately, η is not directly accessible to experiment. However, various theoretical predictions exist. In particular, for the $d = 3$ X-Y model we expect $\eta \approx 0$; hence, $x = 2$; whereas from a time-dependent Ginzburg-Landau analysis of fluctuations we expect $x = \frac{3}{2}$ in three dimensions, at low fields and close to T_c.[18] The jump from $x = 1$ to $x \sim (2.2 \pm 0.1)$ seen in our granular high-T_c materials is suggestive, if not conclusive evidence that the $d = 3$ X-Y model is appropriate for describing the coupling transition. It has also been found to be the most appropriate model in the case of conventional granular superconductors where, an almost identical transition has been observed in compacted composites of tantalum grains.[18] In this system $x(T_c)$ is found to be (2.1 ± 0.2), in complete agreement with the high-T_c film case.

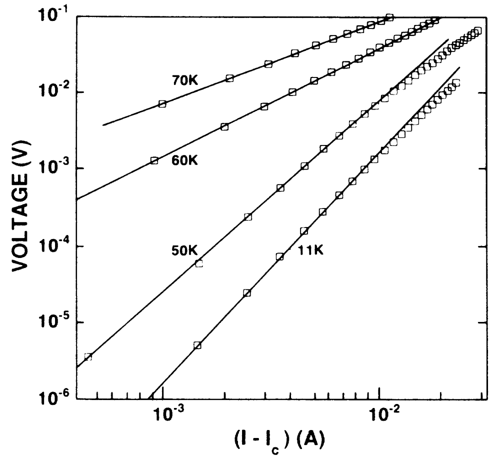

FIG. 3. The current voltage characteristics of the film both below (11 K, 50 K) and above (60 K, 70 K) the coherence transition.

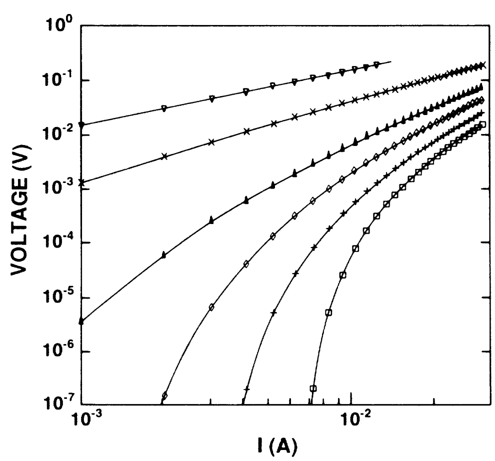

FIG. 2. The current voltage characteristics of the high-temperature superconducting film recorded at a sequence of temperatures. From the bottom: 11, 30, 40, 50, 60, and 80 K.

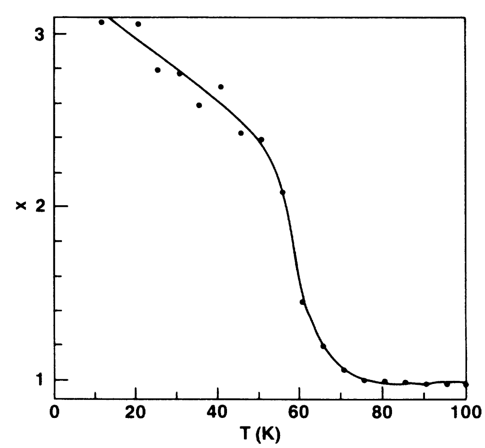

FIG. 4. Behavior of the critical parameter x which appears in $V \sim (I-I_c)^x$ as a function of temperature. The sharp rise from ~ 1 to ~ 2 at $T_c \sim 60$ K is interpreted as the coherence transition.

We have also studied magnetotransport in the films. Figure 5 shows how the critical current is monotonically reduced by application of a perpendicular magnetic field; whereas the scaling behavior $V \sim I_c^x$ is preserved and the critical exponent is essentially unchanged to the point where bulk superconductivity is extinguished. The effect of a magnetic field on a granular superconductor is twofold: it will reduce the strength of the intergrain coupling directly since both the Josephson effect and proximity effect are field dependent. It will also set up microscopic circulating currents around each flux line or bundle in the film to ensure that the superconducting phase remains single valued. Unfortunately, the nature of the intergrain coupling (Josephson, proximity effect, etc.) is not yet clear,[19] and so the effect of a magnetic field on i_c, the intergrain critical current, cannot be quantified. However, the circulating currents interfere with the phase transition to the coherent state by "frustrating" the simultaneous reduction of energy at all points in the assembly.[20] Complete frustration occurs when each unit cell in the random system contains approximately one flux quantum ϕ_0. We expect complete frustration in this sample at $\sim$40 Oe, using the average grain size from scanning electron microscopy (SEM) analysis. This corresponds quite well with the observed extinction field of $\sim$80 Oe. In an ordered system, the critical current would be periodic in field with period ϕ_0 per cell; however, in a random system, a monotonic reduction is expected.

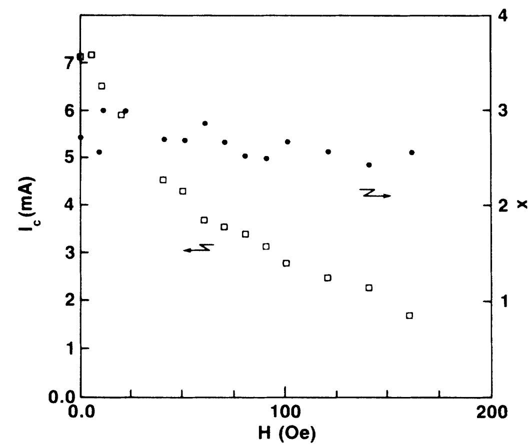

FIG. 5. The behavior of the critical current (squares) and the parameter x (filled circles), as a function of the perpendicular field intensity H at $T = 4.2$ K.

In summary, we have demonstrated that the electrical properties of $Er_1Ba_2Cu_3O_{7-\delta}$ films grown by pulsed laser deposition can be described within existing models of granular superconductivity. We have observed scaling behavior in the I-V characteristic which is indicative of the grain coupling transition which is essential for bulk superconductivity. The magnetotransport is in support of this picture.

[1]D. Dijkkamp, T. Venkatesan, X. D. Wu, S. A. Shaheen, N. Jiswari, Y. H. Min-Lee, W. L. McLean, and M. Croft, Appl. Phys. Lett. **51**, 619 (1987).

[2]R. B. Laibowitz, R. H. Koch, P. Chaudhari, and R. J. Gambino, Phys. Rev. B **35**, 8821 (1987); P. M. Mankiewich, J. H. Scofield, W. J. Skocpol, R. E. Howard, A. H. Dayem, and E. Good, Appl. Phys. Lett. **51**, 1753 (1987); D. K. Lathrop, S. E. Russek, and R. A. Buhrman, *ibid.* **51**, 1554 (1987).

[3]Y. Enomoto, T. Murakami, M. Suzuki, and K. Moriwaki, Jpn. J. Appl. Phys. **26**, L1248 (1987); K. Char, A. D. Lent, A. Kapitulnik, M. R. Beasley, and T. H. Geballe, Appl. Phys. Lett. **51**, 1370 (1987).

[4]P. Barboux, J. M. Tarascon, L. H. Greene, B. G. Bagley, and G. W. Hull, in *High-Temperature Superconductors, Fall 1987,* edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller, Materials Research Society Symposia Proceedings, Vol. A99 (Materials Research Society, Pittsburgh, 1988).

[5]C. E. Rice, R. B. Vandover, and G. J. Fisanick, Appl. Phys. Lett. **51**, 1842 (1987).

[6]S. Z. Tozer, A. W. Kleinsasser, T. Penney, D. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1768 (1987).

[7]*Inhomogeneous Superconductors,* edited by D. U. Gubser, T. L. Francaville, A. Wolf, and J. R. Laibowitz (American Institute of Physics, New York, 1979).

[8]A. Raboutou, P. Peyral, and J. Rosenblatt, in Ref. 7.

[9]D. W. Abraham, C. J. Lobb, M. Tinkham, and T. M. Klapwijk, Phys. Rev. B **26**, 5268 (1982).

[10]Chang-Keng Ma, *Modern Theory of Critical Phenomena* (Benjamin-Cummings, Reading, MA, 1976).

[11]P. England and A. D. Caplin, J. Phys. F **17**, 447 (1987).

[12]J. M. Kosterlitz and D. M. Thouless, J. Phys. C **6**, 1181 (1973).

[13]D. E. Farrel, M. R. DeGuire, B. S. Chandrasekhar, S. A. Alterowitz, P. R. Aron, and R. L. Fagaly, Phys. Rev. B **35**, 8797 (1987).

[14]A. Raboutou, P. Peyral, J. Rosenblatt, C. Lebeau, O. Pena, A. Perrin, C. Perrin, and M. Sergent, Europhys. Lett. **4**, 1321 (1987).

[15]M. A. Dubson, S. T. Herbert, J. J. Calabrese, D. C. Harris, B. R. Patton, and J. C. Garland, Phys. Rev. Lett. **60**, 1061 (1988).

[16]D. M. Hwang, L. Nazer, T. Venkatesan, and X. D. Wu, Appl. Phys. Lett. **52**, 1834 (1988).

[17]X. D. Wu, A. Inam, T. Venkatesan, C. C. Chang, E. W. Chase, P. Barboux, J. M. Tarascon, and B. Wilkens, Appl. Phys. Lett. **52**, 754 (1988).

[18]C. Lebeau, J. Rosenblatt, A. Raboutou, and P. Peyral, Europhys. Lett. **1**, 313 (1986); J. Rosenblatt, C. Lebeau, P. Peyral, and A. Raboutou, in *Josephson Effects: Achievements and Trends,* edited by A. Barone (World Scientific, Singapore, 1985).

[19]S. B. Ogale, D. Dijkkamp, T. Venkatesan, X. D. Wu, and A. Inam, Phys. Rev. B **36**, 7210 (1987).

[20]M. Tinkham, D. W. Abraham, and C. J. Lobb, Phys. Rev. B **28**, 6578 (1983).