Evidence for Bulk Superconductivity in K_3C_{60} Single Crystals

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A detailed study of the supercurrent flow in K_3C_{60} single crystals is presented. From dc magnetization and ac susceptibility measurements we obtain the sample dimension over which the superconducting currents flow. We find that this dimension is identical to the sample size and, therefore, demonstrates the bulk nature of superconductivity in fullerenes in an unambiguous way. [S0031-9007(98)07504-8]

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For many years, only powder samples were available for experimental investigations of fullerene superconductors (FS). This imposed considerable restrictions on the investigation of the basic properties of FS, because the average grain size in powders is typically of the order of 1 μm, which is comparable to the magnetic penetration depth, λ. Therefore, many important features of the magnetic properties of FS are possibly masked by the small grain size, especially because measurements of the critical current density, J_c, can be done only by magnetic methods. The critical current densities of bulk single crystals are typically by 2 orders of magnitude smaller than those of powders (see, for instance, Table I in Ref. [1]). If we compare them with those of $YBa_2Cu_30_{7-\delta}$ single crystals, the material with the lowest anisotropy of all high-T_c superconductors, we find again that the critical current density J_c of the FS is significantly smaller (by about a factor of 100, see, e.g., Ref. [2]). This represents a serious problem, because flux pinning depends only on a few intrinsic parameters, such as the thermodynamic critical field, H_c, and the coherence length, ξ, both of which are comparable to $YBa_2Cu_30_{7-\delta}$ and on the size and the density of the defects. The defect size can hardly be much smaller than the lattice parameter and, therefore, has to be comparable to ξ in the fullerenes. This would leave only a small density of defects as an explanation for the low J_c in the fullerenes. However, typical fullerene samples are far from being perfect single crystals and are expected to have many defects, especially since the C_{60} lattice is damaged by the diffusion of the alkali metal atoms during the doping procedure. Therefore, pinning in single crystals is not expected to be much weaker than in powders or in high-T_c crystals. The only possible alternative for explaining the observed low J_c would be an "automatic" breakup of the sample into many small superconducting grains. In fact, some experimental results [3] could be explained *only* by the assumption of an "intrinsic granularity" in FS with grain sizes ≤ 1 μm.

However, this assumption of intrinsic granularity cannot be understood easily, unless we assume *molecular superconductivity*, i.e., superconductivity that is restricted to the C_{60} molecules, and transport currents that are due only to Josephson coupling between these molecular grains. In this case, the grain size should be equal to the radius of the C_{60} molecule and be the same for all samples, crystals, or powders. However, if experimental results on J_c obtained on different samples of both K_3C_{60} and Rb_3C_{60} [4–6] are compared, a certain decrease of J_c with sample size is observed (Table I in Ref. [1]), although not exactly as expected from Bean's critical state model [7]. According to this model, J_c is proportional to the width of a hysteresis loop, $\Delta M = M_+ - M_-$, and inversely proportional to the radius, R, of the region screened by the supercurrent,

$$J_c = \frac{3}{2}\,\frac{M_+ - M_-}{R}\,, \tag{1}$$

where $M[\mathrm{A/m}] = m/V$ is the magnetization, and m is the magnetic moment of a cylindrical sample with volume V. M_+ and M_- denote the magnetization measured at a certain magnetic field in increasing and decreasing fields, respectively. The calculation of J_c requires the knowledge of the correct value of R. For a bulk single crystal, the supercurrent screens the whole sample and R is equal to the sample radius R_s. J_c in powders is usually calculated under the assumption of R being equal to the average grain size, which is of the order of 1 μm.

In order to distinguish between the bulk and the molecular nature of fullerene superconductivity, special experiments and evaluation methods are needed, which are directly sensitive to the size of the regions screened by the supercurrent. The most direct experiment would be to measure the magnetization of a bulk single crystal ($R \gg \lambda$) without structural granularity and weak links and then to crush the crystal. This reduces the "grain size" only if the crystal is a true bulk superconductor. From a comparison of the calculated J_c values before and after crushing, any intrinsic granularity can be detected. However, this method does not preserve the precious original crystal and is, therefore, only the last step in a series of experiments.

In this Letter we report on a detailed investigation of K_3C_{60} single crystals, which is based on dc and ac magnetic measurements in superconducting quantum interference device magnetometers. Two K_3C_{60} crystals

(K5 and K27) were measured in the "as-grown" state and carefully analyzed. Then K27 was crushed and remeasured. We will show, for the first time, that only the existence of bulk superconductivity in FS can consistently explain all the data.

A detailed description of the sample preparation can be found in Refs. [8–10]. The samples were very irregularly shaped, their approximate physical dimensions were $2.3 \times 1.5 \times 0.8$ mm^3 (K5) and $2.5 \times 2 \times 1.2$ mm^3 (K27). dc and ac magnetic measurements confirmed that both crystals were fully superconducting ("100% superconducting fraction"), but the out-of-phase signal of the ac susceptibility revealed granularity in K5 and none in K27.

The first approach to obtain the characteristic dimension R is to do magnetization measurements in fields high above the Bean penetration field, H^*, at which the flux reaches the center of the sample. In this case, the internal field and the critical current density can be assumed to be constant. As discussed by Angadi *et al.* [11], the initial slope of the magnetic moment dm/dH, along the reverse leg of a hysteresis loop right after the field reversal, is a direct measure of R. This holds over only a very small field range and, therefore, requires the measurement of the magnetization in closely spaced field steps after the field reversal. For a uniform disc of radius R_s, $R_s = R$, and thickness, t, the initial slope of the reverse leg [11] is given by

$$\frac{dm}{dH} = -\frac{\pi^2 R^3}{\Theta}, \tag{2}$$

where $\Theta = \ln(8R_s/t) - 1/2$. The experimental uncertainty in the ratio R_s/t does not lead to large errors in R (for a single crystal with $R_s/t = 1$, e.g., $\Theta \sim 1.5$, and for a thin film with $R_s/t = 103$, $\Theta \sim 6.5$).

A granular sample with radius R_s contains N regions of large critical currents connected by low-J_c weak links. This can be approximated by a sample consisting of an array of N circular islands, each with radius R. The initial slope of the reverse leg for this system is given by

$$\frac{dm}{dH} = -\frac{\pi^2 R^3}{\Theta_1} = -\frac{R_s^2 R \pi^2}{\Theta_1}, \tag{3}$$

where $\Theta_1 = \ln(8R/t) - 1/2$. Equation (3) is appropriate for both granular ($R \neq R_s$) and nongranular ($R = R_s$) samples and will be used later on.

The experimental magnetization loops of the samples K5 and K27 are shown in the two upper panels of Fig. 1. The reverse leg for K27 is smooth and wide, while it is much steeper and steplike in K5. According to [11], the return leg of the hysteresis follows an exponential law in a sample with $R \sim R_s$, while in a granular sample ($R \ll R_s$) the magnetic moment changes linearly with the field and is much steeper. These features are exactly displayed by the reverse legs obtained on our samples, i.e., K5 is granular and K27 is a bulk crystal. The

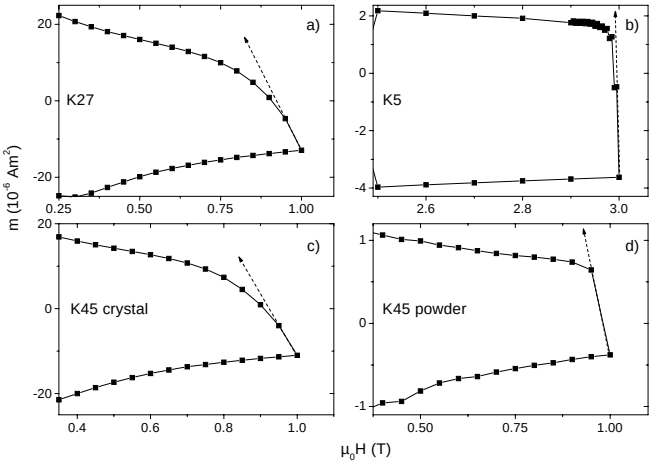

FIG. 1. Hysteresis loops for (a) K27, (b) K5, (c) K45 before crushing, and (d) A45 (K45 after crushing). All data refer to $T = 5$ K.

same result was obtained from our ac characterization mentioned above. From Eq. (3), the corresponding radii are found to be $R \simeq 580$ μm for K27 and $R \simeq 30$ μm for K5.

The second possibility is to estimate R from measurements of the trapped magnetic moment $m_{\rm tr}$ at low external fields near the lower critical field, $H_a \simeq H_{c1}$ [12]. As discussed there, bulk single crystals show a field dependence of $m_{\rm tr}$, $m_{\rm tr} \propto H_a^2$ at fields $H_a \geq H_{c1}$. However, granular crystals (such as K5) show a strong kink in $m_{\rm tr}(H_a)$ at some characteristic field. An example of this kind, measured at $T = 5$ K, is shown in Fig. 2. If we assume that the kink appears at the full penetration field H^*, the grain size can be estimated [13]. In this model $J_c(B)$ is assumed to be related to B by a power law, $J_c(B) = CB^{-n}$, where

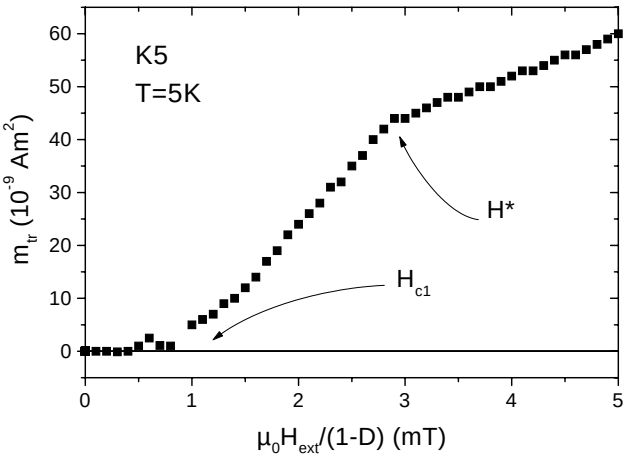

FIG. 2. Trapped magnetic moment vs magnetic field, corrected by the demagnetizing factor D, for K5 at $T = 5$ K. The lower critical field H_{c1} and the full penetration field H^* are indicated by arrows.

$C = J_c(\mu_0 H_{c1})^n$. H^* is then calculated from

$$H^* = H_s - H_b\left[1 + \frac{CR(n+1)}{\mu_0^n H_b^{n+1}}\right]^{1/(n+1)}, \quad (4)$$

where H_a is the externally applied field corrected by the demagnetizing factor, H_b is the experimental field step, which is usually a fraction of H_{c1}, and $H_s = H_{c1} - H_b + \Delta H_{\mathrm{en}}$, where ΔH_{en} is the flux entry barrier introduced by Clem [14]. C and n can be temperature dependent.

In order to decrease the number of parameters in Eq. (4), we fit the data with $n = 1/2$ and $\Delta H_{\mathrm{en}} = 0$. As found in [13] and in agreement with our data, the best fit occurs for $n = 1/2$ and changes of n do not substantially improve the fit. Therefore, we keep only one adjustable parameter C. This gives a first rough estimate of R from Eq. (4), if we assume J_c to be between 10^8 and 10^9 A/m^2 [1] and $\mu_0 H_{c1} = 1.27$ mT [12]. With these parameters we obtain $1.2 < R < 14$ μm for sample K5.

In order to make the calculation more precise, we fit the experimental trapped magnetic moment of a sample with volume V to the predicted $M_{\mathrm{tr}}(H)$ dependence [13]

$$M_{\mathrm{tr}} = \frac{m_{\mathrm{tr}}}{V} = \frac{2\mu_0^n}{CR(n+2)}\left[\frac{1}{2}(H^* - H_s)^{n+1} + \frac{1}{2}H_b^{n+1}\right]^{(n+1)/(n+2)} - H_b^{n+2}. \quad (5)$$

Here C is the only fit parameter. From this procedure we obtain $R = 12 \pm 6$ μm, which agrees well with the upper limit for R obtained from the previous rough estimate ($R = 14$ μm for $J_c \sim 10^9$ A/m^2 and corresponds reasonably well to the value $R = 30$ μm obtained from the slope of the reverse leg of the hysteresis loop.

Crystal K27, which seemed to be a single grain bulk single crystal judging from the ac experiments, was also analyzed according to Eq. (3). As mentioned above, we find $R \simeq 580$ μm instead of its macroscopic dimension (diameter $\sim$2.5 mm). Consequently, we suspected that the crystal might have consisted of a few smaller subcrystals separated by macroscopic cracks along the (111) planes [10]. Indeed, when the crystal was removed from the capsule and a very small mechanical pressure applied, it split into four pieces with sizes of $2R \simeq 500$ μm each. The cleaved pieces were then sealed separately (sample codes K41, K42, K45, and K46) and remeasured. The widths of the magnetization loops $\Delta M(H)$ in the subcrystals were almost the same as that of the original crystal K27 (Fig. 3). This shows that the shielding radius R before and after splitting remained almost unchanged. From the reverse legs of the loops, the shielding radii were calculated to be 280 (K41), 240 (K42), 260 (K45), and 350 μm (K46), respectively, which roughly corresponds

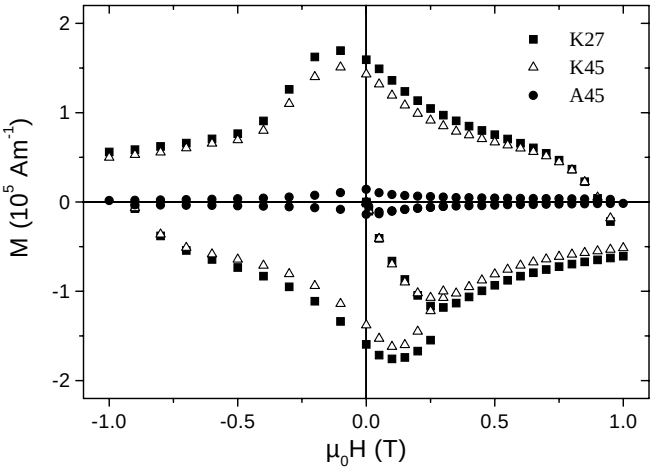

FIG. 3. Hysteresis loops at $T = 5$ K for K27 (squares), K45 (triangles), and A45 (circles).

to the macroscopic dimensions of the subcrystals. Therefore, these four samples can definitely be considered to be single crystals in terms of the supercurrent flow.

The last and most decisive step of this investigation was to crush one of these single crystals (K45). If there is no intrinsic granularity in fullerene superconductors, the width of the magnetization loop and the reverse leg before and after powdering (code K45 $\rightarrow$ A45) should reflect the sharp decrease of R_s. Indeed, ΔM_{K45} of the single crystal K45 is by a factor of $\sim$30 larger than ΔM_{A45} after crushing. This implies that R_{A45} is of the order of 10 μm. The shape of the reverse leg of the hysteresis loop is shown in the two bottom panels of Fig. 1. Instead of a smooth and wide curve in the single crystal (Fig. 1c) we find a sharp jump from the positive to the negative branch of the loop. Equation (3) allows us to recalculate the grain radius in the powdered sample A45 to be $R_{\mathrm{A45}} \simeq 6$ μm. The actual measurement of the grain size with an optical microscope shows a distribution of R between 2 and 12 μm, with 85% of the particles having sizes from 5 to 10 μm, and very few larger particles having sizes of up to 30 μm. This corresponds nicely to the value of $R \simeq 6$ μm obtained from the magnetic measurements.

Finally, the knowledge of R in K45 allows us to calculate the critical current density for the K_3C_{60} single crystal from Eq. (1). At $T = 5$ K and $\mu_0 H = 0.15$ T the critical current density is 1.26×10^9 A/m^2. This value is similar to those obtained on powders and comparable to that of cuprates [2]. We can therefore safely conclude that the low-J_c values deduced from previous experiments on fullerene single crystals have been caused by macroscopic cracks ("hidden granularity"), which cannot be detected even by ac measurements.

In summary, single crystals of the fullerene superconductor K_3C_{60} were investigated by dc and ac magnetic techniques. Several evaluation methods (such as the slope

of the hysteresis loop upon reversing the field, the field dependence of the trapped moment and of the trapped magnetization) were employed to obtain the relevant dimension of the crystals for unimpeded supercurrent flow. Finally, one of the crystals was crushed into powder. A consistent description of our results can be achieved only by invoking bulk superconductivity in the fullerenes. Discrepancies pertaining to the seemingly low critical current densities in these materials are also removed. The data presented in this study are, therefore, suited to rule out "exotic" forms of superconductivity in the fullerenes and to establish its bulk character in an unambiguous way.

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[1] V. Buntar, F. M. Sauerzopf, and H. W. Weber, in *Proceedings of the Symposium on Recent Advances in Chemistry and Physics of Fullerenes and Related Materials*, edited by K. Kadish and R. F. Ruoff (Electrochemical Society, Pennington, NJ, 1997), Vol. 5, p. 495.

[2] F. M. Sauerzopf, H. P. Wiesinger, W. Kritscha, H. W. Weber, G. W. Crabtree, and J. Z. Liu, Phys. Rev. B **43**, 3091 (1991).

[3] R. D. Boss, J. S. Briggs, E. W. Jacobs, T. E. Jones, and P. A. Mosier-Boss, Physica (Amsterdam) **243C**, 29 (1995).

[4] M. Baenitz, M. Heinze, E. Straube, H. Werner, R. Schlögl, V. Thommen, H.-J. Güntherodt, and K. Lüders, Physica (Amsterdam) **228C**, 181 (1994).

[5] S. H. Irons, J. Z. Liu, P. Klavins, and R. N. Shelton, Phys. Rev. B **52**, 15 517 (1995).

[6] S. Chu and M. E. McHenry, Phys. Rev. B **55**, 11 722 (1997).

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

[8] V. Buntar, F. M. Sauerzopf, H. W. Weber, J. E. Fischer, H. Kuzmany, and M. Haluska, Phys. Rev. B **54**, 14 952 (1996).

[9] V. Buntar, Physica C (to be published).

[10] M. Haluska, V. Buntar, C. Krutzler, and H. Kuzmany, in *Proceedings of the Symposium on Recent Advances in Chemistry and Physics of Fullerenes and Related Materials*, edited by K. Kadish and R. F. Ruoff (Electrochemical Society, Pennington, NJ, 1998), Vol. 6, p. 436.

[11] M. A. Angadi, A. D. Caplin, J. R. Laverty, and Z. X. Shen, Physica (Amsterdam) **177C**, 479 (1991).

[12] V. Buntar, F. M. Sauerzopf, and H. W. Weber, Phys. Rev. B **54**, R9651 (1996).

[13] M. W. McElfresh, Y. Yeshurun, A. P. Malozemoff, and F. Holtzberg, Physica (Amsterdam) **168A**, 308 (1990).

[14] J. Clem, J. Appl. Phys. **50**, 3518 (1979).