Critical Magnetic Fields in the Superconducting State of K_3C_{60}

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We have measured the temperature dependence of the lower and upper critical fields in superconducting K_3C_{60}. From the measurements, we have evaluated the penetration depth ($\lambda = 2400$ Å) and superconducting coherence length ($\xi = 26$ Å). The parameters are in agreement with a superconducting state formed by a narrow band.

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The material C_{60}, also called buckminsterfullerene, upon reacting with donors, like alkali metals, forms a new class of molecular solids. Several of them are conductors, and superconductivity was repored for K_3C_{60} with a critical temperature [1] $T_c = 18$ K and Rb_3C_{60} with $T_c = 30$ K [2]. So far, practically nothing is known about the normal and superconducting states of these materials, although the first findings are suggestive of type-II superconductivity. In this paper we report on our measurements of the critical magnetic fields of the K_3C_{60} compound, and evaluate the penetration depth λ and coherence length ξ. We also briefly discuss the implications of our results.

The samples were prepared from solid-phase reaction of high-purity C_{60} powder with potassium in a way similar to that reported originally by the AT&T group [1]. A wide range of composition was explored and different heat treatments were applied to maximize the superconducting fraction of the resulting material. In the case of the sample used in this study, a starting composition of K_4C_{60} was heated in a vacuum at 200 °C for 22 h. The material was subsequently annealed in He atmosphere at 200 °C for 24 h, followed by another annealing at 250 °C for another 6 h. This procedure leads to a maximum shielding fraction of about 15% of the perfect diamagnetism. Throughout the whole preparation, extreme care has been taken to avoid oxygen contamination. A detailed study of the reaction kinetics and of the determination of the stoichiometry of the superconducting compound is published elsewhere [2]. We believe that we have measured K_3C_{60}.

dc magnetization was measured with a Quantum Design SQUID magnetometer in fields up to 5 T and temperatures down to 2 K. The pickup coils were arranged in a second gradiometer geometry in order to eliminate any spurious gradient of the applied magnetic field. The powder of K_3C_{60} was sealed in a Pyrex capillary under 1 atm of helium as an exchange gas. The powder can be approximated by a set of independent spheres. In this case the magnetic field inside the sample is related to the externally applied magnetic field by

$$\mathbf{H}_{\text{in}} = \frac{\mathbf{H}_{\text{ext}}}{1-n}, \quad \mathbf{M} = -\frac{1}{4\pi}\frac{\mathbf{H}_{\text{ext}}}{1-n}, \tag{1}$$

where n is the demagnetization factor, a geometrical constant equal to $\frac{1}{3}$ for a sphere. In all the measurements, care was taken to ensure that the sample was not exposed to a field gradient larger than $\pm 0.03\%$ of the applied field.

We have evaluated the lower critical field from the magnetic-field dependence of the zero-field-cooled dc magnetization. From the normal phase ($T = 55$ K), the sample was cooled down to the superconducting phase ($T < T_c$) in zero field (magnetic field below 1 Oe). Once the desired temperature was reached, the dc magnetization was measured as a function of increasing applied field. The lower critical field $H_{c1}(T)$ was defined as $1/(1-n)$ times the lowest value of the applied field which leads to a departure from a linear behavior in the dc magnetization. The accuracy of the determination of the lower critical field was found to be around ± 5 Oe at low temperature and ± 10 Oe near T_c (the linear regime narrows and thus becomes difficult to evaluate).

The upper critical field $H_{c2}(T)$ was evaluated from the temperature dependence of the field-cooled magnetization. From the normal phase, the sample was cooled to the superconducting state in an external magnetic field (2 kOe $< H_{\text{ext}} <$ 50 kOe). We monitored the magnetization while heating the sample until the normal state is reached, with the applied field held constant. The intercept of a linear extrapolation of the magnetization in the superconducting state with the normal-state base line defines the transition temperature T, and the upper critical field $H_{c2}(T)$ is equal to the applied field.

In Fig. 1 we display the zero-field-cooled (ZFC) and field-cooled (FC) temperature dependence of the dc mag-

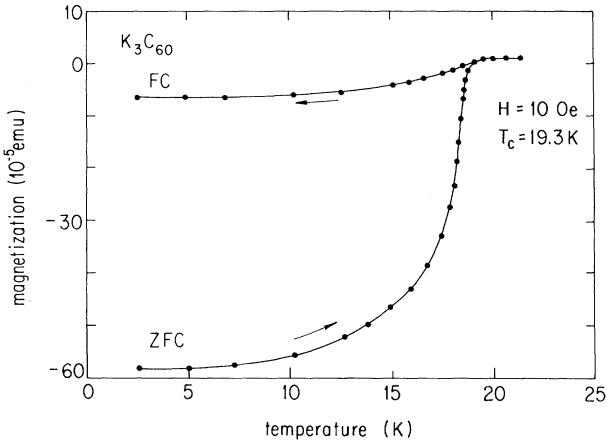

FIG. 1. Temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) dc magnetization with a fixed applied field of 10 Oe. The mass of the sample was $m = 0.013$ g.

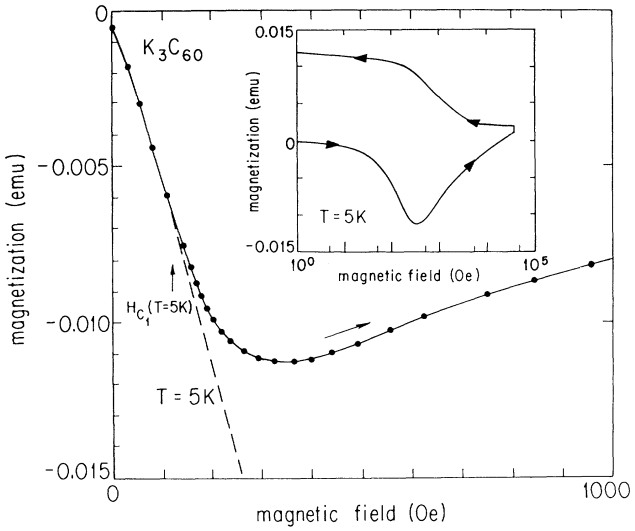

FIG. 2. Magnetic-field dependence of the magnetization at a fixed temperature $T = 5$ K. The zero offset is due to the Pyrex capillary in which the sample was sealed.

netization at a fixed field of 10 Oe. The protocol was the following: From its normal state ($T = 55$ K) the sample was first cooled to 2 K with no field applied; we then monitored the dc magnetization as the sample was heated above the critical point under an applied field of 10 Oe (ZFC). We then cooled the sample to $T = 2$ K under the same field, 10 Oe (FC). The onset of a diamagnetic transition occurs at $T = 19.3$ K. The magnetic transition (10%–50% diamagnetic shielding) is narrow, less than 1 K, suggesting that the superconducting transition is relatively homogeneous. From the ZFC curve one can compute the diamagnetic shielding fraction. Assuming the powder is made of independent spheres, this leads to a shielding fraction of 15% of the perfect diamagnetism, a much higher figure than the one first reported [1]. Hysteresis between the FC and ZFC measurement indicates that flux is trapped in the sample as it is cooled below the transition temperature.

In Fig. 2 we display the magnetic-field dependence of the dc magnetization at a fixed temperature $T = 5$ K. From the normal state, the sample was cooled to $T = 5$ K in zero field ($H_{ext} < 1$ Oe) and the dc magnetization was monitored as the field was increased up to 40 kOe and then back to zero. The hysteresis found suggests the presence of substantial flux pinning, i.e., critical current density, that decreases strongly with applied field. One can get an order of magnitude for the critical-current density using the hysteresis curve in Fig. 2. If we assume that we have a cylindrical specimen of radius R, then we can use the formula [3]

$$J_c(H)(\mathrm{A/cm^2}) = 15\frac{M_+ - M_-(\mathrm{emu/cm^3})}{R(\mathrm{cm})}, \qquad (2)$$

where M_+ and M_- are the hysteretic magnetizations at a given field H. Using a typical grain size of the powder, determined using an optical microscope, $R = 1$ μm, we evaluate $J_c(H = 10\ \mathrm{kOe}) = 1.2 \times 10^5$ A/cm^2.

In Fig. 3 we have plotted the temperature dependence of the upper and lower critical fields, determined as described earlier. For the upper critical field we observe that, except in the vicinity of the critical temperature

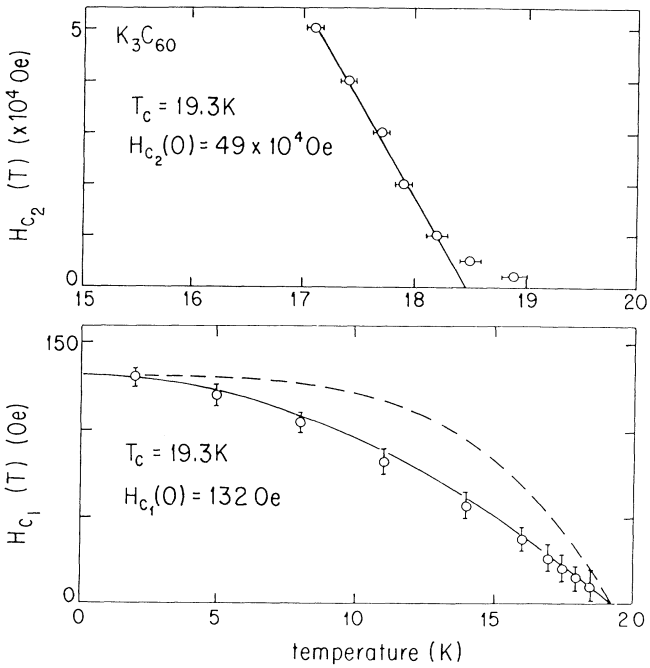

FIG. 3. Temperature dependence of the upper and lower critical fields. For the upper panel, the solid line is a linear fit of the temperature dependence; the slope of the fit is -3.73 T/K. For the lower panel, we compare the temperature dependence of H_{c1} to $H_{c1}(T)/H_{c1}(0) = 1 - (T/T_c)^n$, where $n = 2$ corresponds to the empirical law (solid line) and $n = 4$ is appropriate for the two-fluid model (dashed line).

($T_c = 19.3$ K), a linear dependence adequately fits the temperature dependence of H_{c2}. The critical-field slope from the linear fit is -3.73 T/K. The critical field extrapolated to $T=0$ K using the Werthamer-Helfand-Hohenberg (WHH) formula [4]

$$H_{c2}(0) = 0.69 \left(\frac{\partial H_{c2}}{\partial T} \right) \Big|_{T_c} T_c \qquad (3)$$

is $H_{c2}(0) = 49^{+5}_{-10}$ T. This large value exceeds the Pauli limit [5] of 35 T assuming no electron-phonon enhancement of the Pauli field, H_P [6]. Rigorously, Eq. (3) is only valid in the dirty limit. In the clean limit, the value of $H_{c2}(0)$ computed from the WHH formula is higher by a few percent than the one in the dirty limit [7]. If one includes effects of Pauli spin paramagnetism [3], the value of $H_{c2}(0)$, extrapolated from the slope near T_c (WHH formula), will be greatly reduced. Direct measurement of $H_{c2}(0)$ would be particularly informative in this regard. Using the relation [8]

$$H_{c2}(0) = \phi_0 / 2\pi\xi^2 , \qquad (4)$$

this corresponds to a zero-temperature coherence length of $\xi = 26^{+4}_{-2}$ Å for $H_{c2}(0) = 49$ T. If the applied field is below 5 kOe, then $\partial H_{c2}/\partial T$ is smaller than the slope expected from the linear fit shown in Fig. 3. Such behavior is found commonly in conventional superconductors and attributed to slight variations in the local T_c.

The temperature dependence of the lower critical field follows within a few percent the empirical law [8]

$$H_{c1}(T) = H_{c1}(0)[1 - (T/T_c)^2] . \qquad (5)$$

From the fitting we extrapolate the lower critical field at zero temperature $H_{c1}(0) = 132^{+10}_{-20}$ Oe and using the formula [8]

$$H_{c1}(0) = (\phi_0 / 4\pi\lambda^2) \ln(\lambda/\xi) , \qquad (6)$$

we estimate $\lambda_L = 2400^{+100}_{-200}$ Å. For comparison we have also plotted in Fig. 3 the temperature dependence of H_{c1} expected by assuming that λ/ξ is independent of temperature and that $H_{c1}(T) \propto \lambda(T)^{-2}$. Using the two-fluid temperature dependence for $\lambda(T)$ gives

$$H_{c1}(T) = H_{c1}(0)[1 - (T/T_c)^4] . \qquad (7)$$

Shown in Fig. 4 are two sets of raw data used to determine H_{c2}. Below T_c, the slopes are $\partial M/\partial T = 0.063$ and 0.089 G/K for the $H = 5$ and 2 kOe data sets, respectively. In calculating these slopes, we used the sample mass $m = 0.013$ g and the x-ray density [9] of K_3C_{60}, $\rho = 1.91$ g cm^{-3}, to arrive at the conversion $M(\mathrm{G}) = 4\pi(\rho/m)M$ (emu). These slopes can be compared to that calculated from [10]

$$\frac{\partial M}{\partial T} = - \left[\frac{1}{4.64\pi(2\kappa^2 - 1)} \right] \frac{\partial H_{c2}}{\partial T} , \qquad (8)$$

where $\kappa = \lambda/\xi = 92$ and $\partial H_{c2}/\partial T = -1.6$ T/K from Fig. 3. Equation (8) gives $\partial M/\partial T = 0.063$ G/K $\pm 10\%$, with the assumption that κ is temperature independent and the Pyrex capillary contributes negligibly to the slope at these low fields. The agreement is rather good, confirming consistency in our estimate of H_{c2}. At higher fields, the latter assumption is no longer valid and direct comparison is not possible.

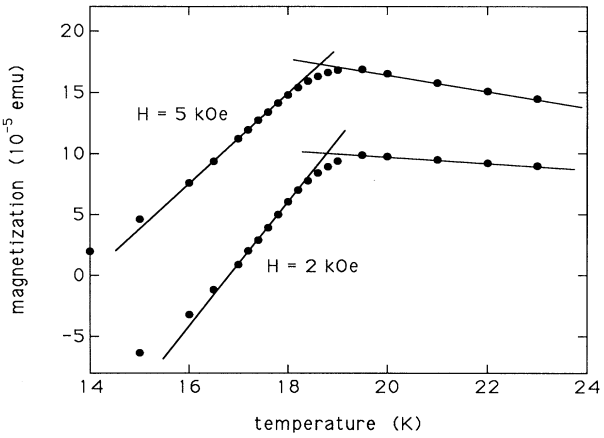

FIG. 4. Magnetization vs temperature measured near T_c in applied fields of 5 and 2 kOe. The intersection of the linear extrapolations made both below and above T_c defines $H_{c2}(T)$.

The electronic structure of C_{60} can be described crudely by a tight-binding approach, and the overlap of the neighboring C_{60} units can be accounted for by an overlap integral t_1. The fact that the coherence length exceeds the diameter d ($\simeq 10$ Å) of the C_{60} spheres suggests that the appropriate starting point for understanding the superconducting state is not that of a weakly Josephson coupled unit but that of a conventional superconducting state where the relevant normal-state parameter is the transfer integral t_1. The coherence length can be written as [11]

$$\xi/d = D/\Delta , \qquad (9)$$

where the relevant bandwidth D equals $8t_1$ in three dimensions. The measured coherence length, together with a weak-coupling expression for the superconducting gap $\Delta = 3.52 k_B T_c$, leads to a bandwidth $D = 200$ K. The clean-limit expression of the penetration depth [8]

$$\lambda = \frac{c}{\omega_p} , \quad \omega_p = \left(\frac{4\pi n e^2}{m_{\mathrm{eff}}} \right)^{1/2} , \qquad (10)$$

where $n = 1.9 \times 10^{21}/\mathrm{cm}^3$ is the number of carriers (assuming one conduction electron per C_{60}) and m_{eff} is the effective band mass, gives $m_{\mathrm{eff}} = 4m_e$, i.e., a slightly enhanced effective mass, a situation similar to that encountered in high-temperature superconductors, and in full agreement with our previous conclusion on the bandwidth D. Taking one conduction electron per C_{60} is equivalent to assuming that the threefold-degenerate Fer-

mi level of the pure C_{60} splits with doping. In the case where degeneracy holds, then we have to take a density of carriers 3 times larger, leading to an effective mass $m_{\text{eff}}=12m_e$.

In conclusion, our experiments on the critical magnetic fields in K_3C_{60} show a strongly type-II superconducting state with the temperature dependence of the parameters well described by mean-field theory. The coherence length and the penetration depth are in agreement with the picture of a superconducting state that develops within a relatively narrow band, which we believe is controlled by the overlap of the wave functions of the neighboring C_{60} units. The $T=0$ upper critical field, extrapolated from the WHH model, exceeds the Clogston limit, suggesting that $H_{c2}(0)$ is Pauli paramagnetically limited as might be expected for a material with a modestly large density of states at the Fermi level. We note that the superconducting properties of K_3C_{60} are rather similar to those of conventional A15 superconductors [6] (e.g., Nb_3Sn). Also throughout this paper we have assumed that the electronic structure is isotropic, and both the normal and superconducting states have a three-dimensional character. The extent to which K_3C_{60} deviates from three-dimensional character and influences our conclusions remains an open question.

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