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Granularity and upper critical fields in K_3C_{60}

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Abstract

The magnetoresistance of superconducting K_3C_{60} samples with different granularity has been measured in fields up to 7.5 T. The upper critical field $H_{c2}(T)$ is dependent on the grain size of the K_3C_{60} regions within the sample: $dH_{c2}(T)/dT$ varies from -2.18 to -2.8 T/K near the superconducting transition temperature. At low temperatures, a small grain size leads to an apparent enhancement in $H_{c2}(0)$.

1. Introduction

Superconductivity in alkali metal fullerides has attracted extensive experimental and theoretical interest. Although the occurrence of superconductivity is well established [1,2], the nature of the phenomenon in this novel system still remains unclear. Determination of normal and superconducting state parameters is essential in the understanding of the mechanism of the superconductivity. In a type-II superconductor, the upper critical field $H_{c2}(T)$ relates directly to the Ginzberg–Laudau coherence length ξ by the relation $H_{c2}(T) = \Phi_0/2\pi\xi(T)^2$. Various techniques have been used to measure $H_{c2}(T)$ in K_3C_{60} powder [3–6], thin film [7], and single-crystal [8] samples. These measurements have yielded very different values of dH_{c2}/dT, from -1.34 to -5.5 T/K. The extrapolated zero-temperature upper critical field $H_{c2}(0)$ varies from 17.5 to 49 T. This immediately raises the question as to what is the intrinsic value of the upper critical field in K_3C_{60}.

Here we report our measurements of $H_{c2}(T)$ in K_3C_{60} samples of varied quality obtained by controlling the doping and annealing time. We find that the measured upper critical field is dependent on the grain size of K_3C_{60}. In contrast to bulk K_3C_{60} single-crystal samples which display a very sharp resistive transition width and a small value of $dH_{c2}(T)/dT$ [8], we find a wider transition width and higher $dH_{c2}(T)/dT$ in samples that are off the global stoichiometry of K_3C_{60} or non-uniformly doped. In conjunction with excess conductivity (paraconductivity) measurements, this result is ascribed to a granularity-enhanced upper critical field effect operative when the grain size is smaller than the Ginzberg–Landau coherence length $\xi(T)$.

2. Experiments and results

High-quality single crystals of pure C_{60} were grown employing a vapor sublimation method. K_3C_{60} samples were obtained using two-zone high-temperature doping–annealing cells. The temperature of crystals was kept at 250°C, while the dopant temperature was

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about 200°C to 300°C. The doping rate was controlled by adjusting the temperature gradient between the crystal and dopant. During doping and annealing, the resistance of the sample was monitored. Fig. 1 shows a typical plot of sample resistance versus doping and annealing time. From Fig. 1, we see that at the early doping and annealing stage, the resistance drops very fast, by a few orders of magnitude, and then the dropping rate decreases as the resistance of the sample reaches a minimum.

The formation of the K_3C_{60} phase and the phase diagram of doped C_{60} are important in understanding the normal state and superconducting properties. Previous X-ray and neutron diffraction studies [9,10] indicate a line-phase diagram for A_xC_{60} (where A is K or Rb): pristine C_{60}, metallic A_3C_{60}, and insulating A_4C_{60} and A_6C_{60} phases. Thus, during the vapor-phase doping, K_3C_{60} nucleates and grows as islands during intercalation of the K atoms. In principle a sample with an exact global stoichiometry K_3C_{60} can be obtained if all of the islands coalesce and all of the C_{60} is converted to K_3C_{60}. But in practice, because K_3C_{60} is not a saturated phase, the samples will not always reduce to a uniform K_3C_{60} metallic phase, particularly if the doping and annealing cycle are not terminated at the right time. Moreover, we find that sample homogeneity and defect density are dependent on synthesis conditions, such as doping temperature, doping rate, annealing time, and cooling rate. The properties of non-uniformly doped samples suggestive of the line-phase and granular growth picture as discussed above.

In the normal state above T_c, we find a discontinuity in the electrical resistivity at about 260 K for slightly underdoped samples ($x<3$), as shown in Fig. 2. In contrast, in our best samples with very low room-temperature resistivities of about 1 mΩ cm, there is no discontinuity. This discontinuity near 260 K in inhomogeneous doped samples is attributed to the strain effect of pristine C_{60} on the surrounding metallic K_3C_{60} phase as the pristine C_{60} undergoes an order–disorder phase transition which leads to a few percent decrease in the lattice constant [11] of the pristine materials. Despite the discontinuity at 260 K, the inhomogeneous samples have the same normalized temperature-dependent resistivity as do the homogeneous samples (see inset, Fig. 2). This similarity is expected in the line-phase picture since the transport in the inhomogeneous samples will be dominated by the same metallic phase when the percolation path is formed.

Single crystals of K_3C_{60} or samples with grain size much larger than $\xi(T)$ are uniform three-dimensional superconductors according to the excess conductivity measurements [12]. However, for non-uniformly doped samples, the temperature-dependent excess conductivity has a functional form $\sigma' = At^{-2}$, where $t = (T - T_c)/T_c$ is the reduced temperature. This indicates that those samples are zero-dimensional (0D) superconductors. Similar results

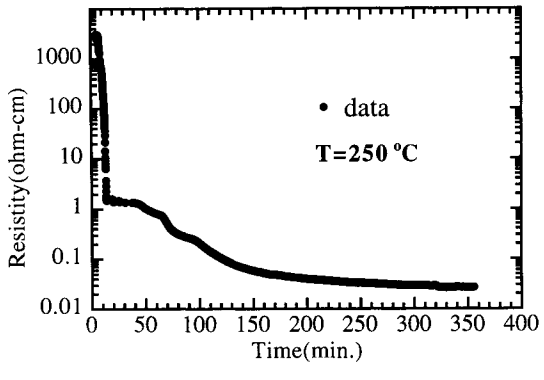

Fig. 1. Time dependence of the resistivity of a K_xC_{60} sample during the doping and annealing process. The doping time is very short compared to the annealing time. The sample temperature was kept at 250°C, while the dopant temperature was controlled between 200°C and 300°C.

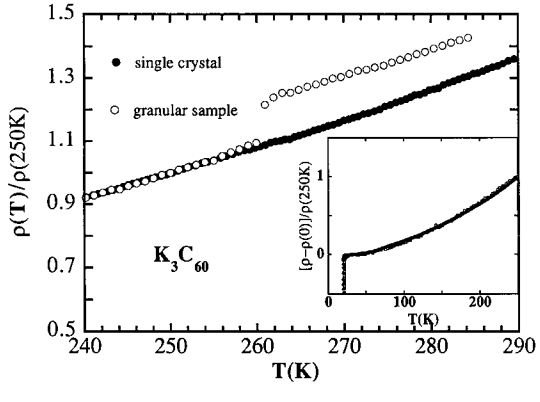

Fig. 2. R vs. T plots for a non-uniformly doped sample and a single-crystal sample. At about 260 K, there is a discontinuity in resistivity for the underdoped sample. But both samples have the same normalized temperature-dependent resistivity at lower temperature (inset).

have also been reported for K_3C_{60} thin-film samples [7]. In Fig. 3 we plot the 0D excess conductivity data vs. reduced temperature for a granular sample, together with 3D single-crystal data for comparison. In a superconductor 0D fluctuations will be observed when the grain size is less than about three times of the Ginzberg–Landau coherence length $\xi(T)$ [13]. The observation of 0D fluctuation provides direct evidence of sample granularity.

We find that the onset superconducting temperatures are almost identical for all granular samples, measured in zero magnetic field. However, the resistive transition width differs for different samples. Defining the full resistive transition width (ΔT_c) as twice the temperature interval from the peak in dR/dT to the temperature when the resistance drops to zero, we find that ΔT_c varies from about 0.35 to 0.9 K for samples with different quality. We believe the broadening is a direct indication of the extent of sample granularity. Usually the grain size of the sample can be estimated from the reduced temperature at which 3D to 0D takes place. But in our measurements, no clear sign of 3D to 0D cross-over was observed in any of our granular samples. This implies that the grain size in these samples is very small, causing the cross-over to take place at temperature too high for excess conductivity to be measured. However, the average grain size in these samples can be estimated from the relation [14] $\Delta T_c \approx T(k_B/D^3\Delta C_p)^{1/2}$, where D is the grain size. Using the electronic specific heat term $\gamma=\Delta C_p/1.43=70$ mJ/mol K for K_3C_{60} [15], the grain size of different samples can be obtained and the results are listed in Table 1. The errors come largely from the uncertainties in the determination of ΔT_c.

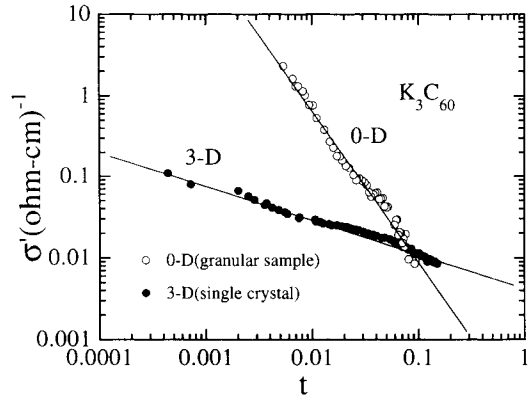

Fig. 3. Plots of excess conductivity vs. reduced temperature. Open circles are the data obtained from a granular sample ($\sigma^*=At^{-2}$); black dots are for a single crystal with 3D fluctuations ($\sigma^*=At^{-1/2}$).

In contrast to the single-crystal K_3C_{60} samples with no excessive broadening of the magnetoresistive transition near T_c, granular samples have wider resistive transition widths and higher onset field-dependent transition temperatures under high magnetic field. If we define $T_c(H)$ as the temperature where the resistance drops to one-half of the normal resistance ($R(T_c)=0.5R_n$), the T–H critical lines of different samples can be obtained. The linear fits to $H_{c2}(T)$ yield the values of dH_{c2}/dT from -2.18 to -2.8 T/K. Using the Werthermer–Helfond–Hohenberg formula [16], the zero-temperature extrapolated values of $H_{c2}(0)$ can also be obtained. These results are also listed in Table 1 together with the values corresponding to single-crystal and thin-film samples for comparison. From the table, one can see that the smaller the grain size, the higher the measured upper critical fields $H_{c2}(0)$ are. Moreover, if we compare the magnetoresistance data of a sample with the same doping level before and after long-time annealing, we find that long-time heat treatment can reduce the apparent upper critical field, presumably due to smaller grains coalescing into larger grains or improving the sample homogeneity. An example of this effect is shown in Fig. 4.

A granularity-enhanced upper critical field effect also occurs in conventional superconductors. For examples, Al granular films have an upper critical field which is about two orders of magnitude larger than that of the bulk samples [17]. The theory of upper critical fields in granular conventional superconductors is well established. Usually three regimes can be distinguished in the behavior of upper critical fields: (a) Coupling between the grains is extremely weak, and the measured upper critical field is that of isolated grains, (b) the coupling is strong, and the system can be described as a dirty superconductor, (c) in the intermediate regime, the temperature dependence of H_{c2} exhibits an upturn point at a temperature below which the grains become weakly coupled. Deutscher et al. [18] indicate that in the extreme weak-coupling limit, the upper critical field has a characteristic $(T_c-T)^{1/2}$ temperature dependence if

Table 1
Transition width ΔT_c, average grain size D, and upper critical field $H_{c2}(0)$ in different K-doped C_{60} samples

Sample	ΔT_c (K)	D (Å)	$dH_{c2}(T)/dT$ (T/K)	$H_{c2}(0)$ (T)
1, film [a]	2	70	−5.5	50
2, granular	0.9±0.1	150	−2.8	40
3, granular	0.5±0.05	250	−2.33	33
4, granular	0.35±0.03	310	−2.18	28
5, single crystal [b]	0.25	>6000	−1.34	17.5

[a] Data from Ref. [7]. [b] Data from Ref. [8].

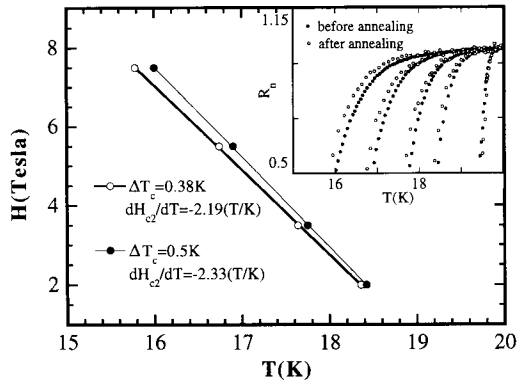

Fig. 4. Plots of $dH_{c2}(T)/dT$ in the same sample before and after long-time annealing. The inset shows the magnetoresistance under magnetic fields. The upper critical field is reduced after long-time annealing.

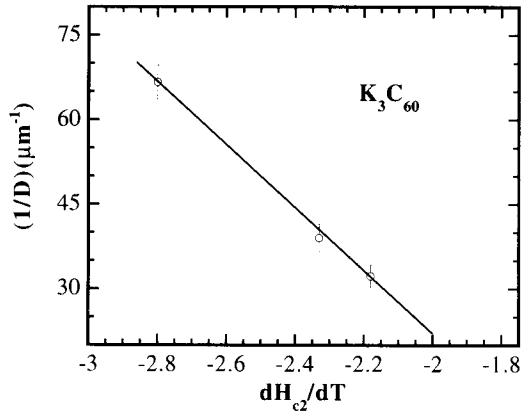

Fig. 5. Plot of $dH_{c2}(T)/dT$ vs. inverse average grain size $(1/D)$. The linear relation indicates that the behavior of the upper critical field in K_3C_{60} is similar to that of conventional granular superconductors.

the Landau–Ginzburg theory is used. The linear relationship of upper critical field vs. temperature in all our granular samples indicates that there may be a strong coupling between the grains in K_3C_{60}. Abeles et al.'s [17] proposed model for a strongly coupled system suggests Josephson tunneling between adjacent grains. In this model, the upper critical field is a function of the grain size D, the coupling strength t_c between the grains and the temperature T

$$H_{c2}(T)=\frac{\phi_0}{2\pi(0.72)\xi_0 D t_c T_c}(T_c-T)\,, \qquad (1)$$

where ξ_0 is the Pippard coherence length and ϕ_0 is the quantum flux. In Fig. 5, we plot $dH_{c2}(T)/dT$ vs. $(1/D)$ where the open circles are the data of granular samples, and the line is the linear fit of the data. The error bars come from uncertainties in the determination of transition width. The linear relationship between the granular data indicates that the upper critical field behavior of granular K_3C_{60} is similar to that of conventional superconductors. From Eq. (1), the coupling strength can be determined from the slope of the dH_{c2}/dT vs. $(1/D)$. Using the Pippard coherence length $\xi_0=135$ Å [8], t_c can be estimated to be in the order of 0.01. Comparing to the values of Al, Sn and Ga films where $0.04<t_c<0.1$, the coupling between the grains is relatively weak in K_3C_{60} granular samples.

In conclusion, we have measured the upper critical fields in K_3C_{60} granular samples. We find that the value of $H_{c2}(T)$ is dependent on the grain size of K_3C_{60}. Coupling between the grains is consistent with Josephson tunneling and the behavior of the upper critical field is similar to that of conventional granular superconductors.

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