Electronic Transport Properties of K_3C_{60} Films

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(Received 23 October 1991)

We report the longitudinal resistivity and Hall-effect data of thin films of K_3C_{60} in the normal and superconducting states in magnetic fields up to 12.5 T. The resistivity is 2.5 mΩ cm at room temperature and near the metal-to-insulator transition. The Hall coefficient is small as expected for a half-filled conduction band, and changes sign at 220 K. The resistivity is interpreted in terms of the granularity of the film which leads to zero-dimensional superconductivity in these systems with a length scale of 70 Å. We find a superconducting coherence length of $\sim$26 Å, which we interpret as a single-grain property. The Pippard coherence length, i.e., in the absence of granularity, is estimated to be $\sim$150 Å.

PACS numbers: 74.70.Mq, 74.70.Kn

The discovery of superconductivity [1,2] in conducting alkali-doped C_{60} phases [3] yielded the second group of materials besides the oxide superconductors [4] to overcome the historic limit of $T_c = 23$ K in intermetallic compounds [5]. This breakthrough has created an intense experimental and theoretical effort to understand the nature of both the superconducting and normal-state properties of these new conductors. We report the dc longitudinal and Hall resistivities of K_3C_{60} in the normal and superconducting states. The absence of reliable transport data on doped C_{60} phases has led to wide discrepancies in estimates of the conduction bandwidth and associated Fermi-level density of states. Early magnetization experiments [6] found an upper critical field of $\sim$45 T, corresponding to a small value of the superconducting coherence length of $\sim$26 Å. This small coherence length was interpreted as arising from a very narrow band with a width of only 500 K. However, it was not verified whether the clean-limit analysis they employed is valid, or whether the coherence length was reduced by a small mean free path. Recent magnetic susceptibility measurements [7] of the compounds $K_xRb_{1-x}C_{60}$ were interpreted with a density of states arising from a much wider band, and the small coherence length was ascribed to a small mean free path of the order of the size of a C_{60} molecule. Assuming weak-coupling BCS theory, local-density approximation (LDA) band-structure calculations of the Fermi velocity v_F yield a clean-limit coherence length in the range 100–200 Å [8,9].

Our electrical transport data show that our films have a minimum resistivity of $\sim$2.5 mΩ cm, which corresponds to an effective mean free path of $\sim$3 Å and would validate the dirty-limit analysis. However, detailed analysis of our data shows unambiguously that the high resistivity does not arise from microscopic disorder, but comes about from the granular nature of our films [10]. We find a grain size of $\sim$70 Å, and we interpret the experimentally observed short coherence length as a single-grain property, which is significantly reduced from the bulk value by finite-size effects. Using theoretical results pertaining to granular superconductors, we can estimate the clean-limit (Pippard) coherence length, $\xi_0 \approx 150$ Å. The Hall data show that the Hall coefficient is small, as expected for a half-filled band. However, the charge of the carriers changes sign at 220 K, which can be ascribed to a temperature dependence of the inelastic scattering rate.

The C_{60} thin films were grown by thermal evaporation of pure C_{60} onto a glass substrate of $\sim 10 \times 10$ mm^2. Prior to evaporation, four contacts for van der Pauw measurements were made by evaporating Ag, and connecting Pt wires with Ag epoxy. The K doping was performed in a custom UHV stainless-steel reaction cell, with feedthroughs on one end and a metal-to-glass seal at the other end. This reaction cell contained besides the thin film, a SAES K dispenser and a sublimation getter. The cell was evacuated and sealed off after the getter was activated, and the undoped film was annealed at 200 °C. The doping was performed at room temperature. As K_3C_{60} is very reactive, the cell was designed to be cooled within the bore of a 14.5-T magnet. The temperature was monitored by a carbon-glass thermometer, and the resistance of the sample was measured using an ac resistance bridge operating at a frequency of 17 Hz.

The undoped film had a resistivity larger than 10^5 Ω cm. The film was doped in discrete steps by resistively heating the K dispenser for one minute and then waiting until the resistivity of the film was constant. The resistivity is affected both by the doping process and by radiative heating of the film due to the hot dispenser. The relaxation time of the doping process is relatively slow, about 200 s for a 1600-Å-thick film, corresponding to a diffusion constant of $\sim 10^{-16}$ m^2/s [10]. The lowest resistivity obtained on this 1600-Å film was 2.5 mΩ cm, only 10% larger than values obtained under UHV conditions on similar films [10]. Good homogeneity was obtained in this film as the two components of the van der Pauw resistance differed by less than 5%.

Figure 1 shows the temperature dependence of the electrical resistivity between 4 and 300 K. At room temperature the resistivity has a positive temperature coefficient of 0.8×10^{-3} K^{-1}. However, the temperature coefficient changes sign at $\sim$250 K, and the resistivity increases by 30% before reaching the superconducting state at 12.8 K. The inset of fig. 1 shows the superconducting transition in detail. The temperature dependence of the

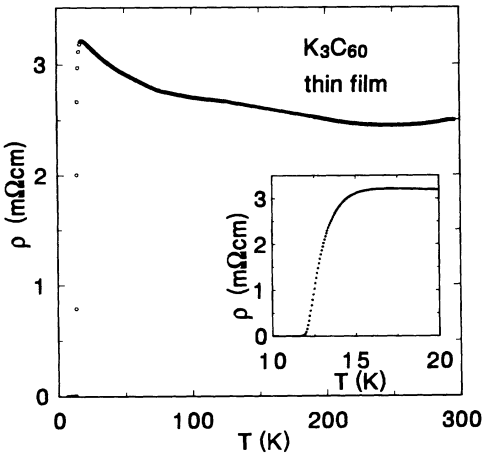

FIG. 1. Temperature dependence of the electrical resistivity of a 1600-Å thin film of K_3C_{60} between 4 and 300 K. The inset shows an expanded scale of the superconducting transition between 10 and 20 K.

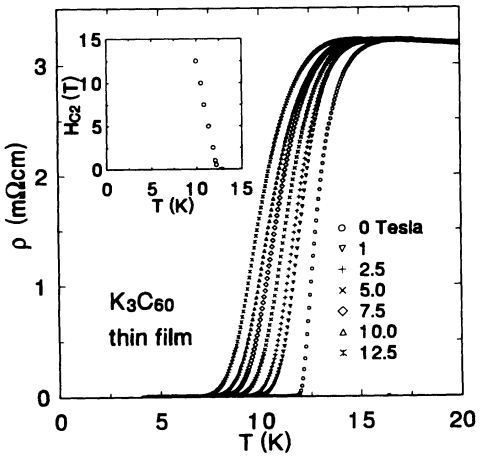

FIG. 2. Temperature dependence of the electrical resistivity of K_3C_{60} in dc magnetic fields of 0, 1, 2.5, 5.0, 7.5, 10.0, and 12.5 T. Inset: Temperature dependence of the upper critical field H_{c2} determined from the midpoints, giving a slope of 5.5 T/K.

normal-state resistivity is negligible on this scale. Therefore, we define the superconducting transition temperature T_c as the midpoint value. The transition is sharp with a 50% to 90% width of only 0.6 K. The onset of the transition is considerably broader, at least part of which is intrinsic to this material (see below).

In Fig. 2 we show the shift of the resistive transition on application of a magnetic field up to 12.5 T. The field was applied perpendicular to the film. Although the transition broadens slightly in a magnetic field, this change is so small that the midpoint is a reasonable estimate of T_c. The inset of Fig. 2 shows the magnetic-field dependence of T_c. We attribute the small upturn at low fields to sample imperfection, and therefore we take the upper-critical-field slope from the high-field data. We obtain a value of 5.5 T/K, which results [11] in a very large upper critical field of ~ 47 T and a Ginzburg-Landau coherence length $\xi_{GL} \approx 26$ Å, in good agreement with magnetic measurements [6,7].

In Fig. 3 we show the Hall coefficient between 30 and 260 K. The Hall coefficient is at low temperatures a factor of 5 smaller than expected from three electrons per C_{60}, which gives $1/ne = -1.5\times10^{-9}$ m^3/C. With increasing temperature we observe that the Hall coefficient increases and changes sign at 220 K. Typically one expects electronlike behavior for an almost empty band, and holelike behavior for an almost filled band, based on the energy dispersion in these cases. Near half filling the sign of the charge of the carriers is difficult to predict, and the sign change at 220 K is further evidence that these films are near half filling. This is in agreement with recent band-structure calculations that show both electron and hole orbitals, effectively reducing the Hall coefficient [8]. However, because of the granular microstructure (discussed below), interpretation of the Hall voltage in terms of a carrier density is questionable.

First let us assume that the high resistivity is caused by microscopic disorder. Since the Hall data indicate multiple conduction bands, we assume for simplicity three carriers per C_{60}. This results in an effective scattering time $\tau = m/\rho ne^2 = 3\times10^{-16}$ s. Using the theoretical [8] Fermi velocity, $v_F \approx 1.8\times10^5$ m/s, we find an effective mean free path l of the order of the interatomic distance. This means that the Ginzburg-Landau coherence length ξ_{GL} is reduced from the Pippard coherence length, $\xi_0 = 0.18\hbar v_F/k_B T_c \approx 200$ Å, by mean-free-path effects, $\xi_{GL} \approx 0.85(\xi_0 l)^{1/2} \approx 20$ Å, in good agreement with our experimental value. Since l is of the order of interatomic distances, the system is near the metal-insulator transition. Even though these parameters give a reasonable

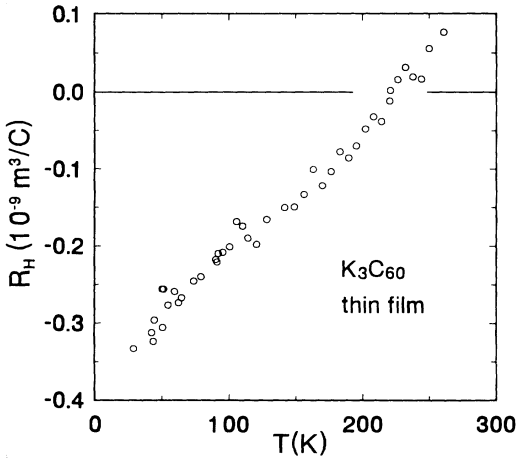

FIG. 3. Temperature dependence of the Hall coefficient between 30 and 260 K. For three electrons per C_{60} the Hall coefficient is -1.5×10^{-9} m^3/C.

description of several normal- and superconducting-state properties, we have compelling evidence that this picture is inappropriate for our films.

We will show that the high resistivity is not caused by microscopic disorder, but by the granular nature of the films. The granularity is evidenced by the observation of zero-dimensional fluctuations in the conductivity, as shown below. Further support of this model is the x-ray linewidth broadening of the pristine films [12], giving an estimated grain size of 60 Å. A granular model has previously been used to model the activated ($x \neq 3$) transport properties above room temperature, using an activation energy derived from electrostatic charging energies of 80-Å-diam grains [10]. We also note that our films have a temperature coefficient of the resistivity that approaches zero at optimum doping [10]. This means that we are near a metal-insulator transition. Imry and Strongin [13] use scaling arguments to propose a critical value at the transition, $\rho_c = (\hbar/e^2)D$, with D the grain size. Using the experimentally observed resistivity of 3 mΩ cm, we can estimate a grain size of ~ 75 Å. Finally, we can estimate the particle size from the width of the resistive transition [14], $\Delta T \approx T_c (k_B/D^3 \Delta C_p)^{1/2}$. Using the experimental width $\Delta T_c \approx 2$ K and the electronic specific-heat term $\gamma = \Delta C_p/1.43 = 70$ mJ/mol K^2 [7], we find that the particle size is ~ 70 Å.

Usually, superconducting fluctuations [15] in 3D materials are confined to an extremely narrow temperature interval near T_c. However, the small coherence length $\xi_{GL} \approx 26$ Å and the high resistivity in these films makes the fluctuations observable as excess (or para) conductivity in a wide regime above T_c. We have analyzed the zero-field data in more detail in Fig. 4, plotting the excess conductivity as a function of the reduced temperature. The normal-state conductivity can be fitted between 20 and 75 K with the empirical formula, $\sigma_n = 2.1 \times 10^2 + 80 \log_{10}(T)$ $(\Omega\,\mathrm{cm})^{-1}$. Plotting then the excess conductivity versus the reduced temperature $t = (T - T_c)/T_c$, we find power-law behavior for $T_c = 11.75$ K, corresponding to the onset of resistivity. The slope of the data yields a power of -2.2, and is rather insensitive to the value of T_c.

Excess conductivity in superconductors σ' has been extensively studied [15] and depends on the dimensionality d of the system: $\sigma' \propto t^{(d-4)/2}$. For a 3D system the proportionality factor is $\frac{1}{32} e^2/\hbar\xi(0)$ and depends only on the coherence length. Using $\xi(0) = 26$ Å we expect $\sigma' = 3 \times 10^3 t^{-1/2}$, as indicated by the solid line in Fig. 4. It is clear that this functional form cannot account for the data. Moreover, the 3D fluctuation contribution is even larger than the experimental excess conductivity for $t > 0.2$. This means that the experimental curve has a narrower transition than that expected for the 3D fluctuation model and therefore we can exclude the possibility of resistive broadening due to a spread in T_c. The experimentally observed power $(d-4)/2 \approx -2$ suggests that these films exhibit zero-dimensional fluctuations for

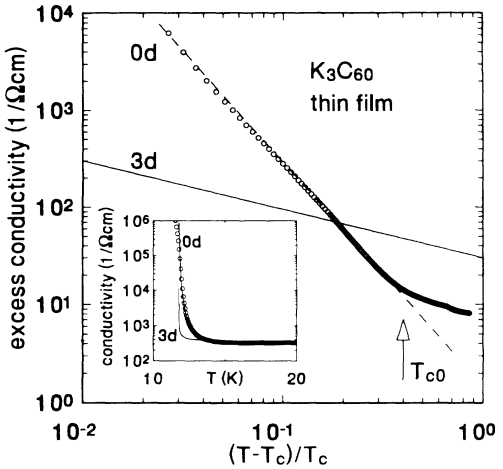

FIG. 4. Excess conductivity vs reduced temperature of K_3C_{60}. The slope of this curve has been proposed for a zero-dimensional system. A three-dimensional system exhibits fluctuation conductivity indicated by curve "3D," based on the measured coherence length $\xi_{GL}(0) = 26$ Å. Inset: The divergence of the conductivity in unrenormalized quantities. The two lines indicate the theoretical prediction for a 0D and a 3D system, respectively. The arrow indicates the mean-field transition temperature T_{c0}.

$t < 0.4$. For $t > 0.4$ the slope of the curve is $\sim -\frac{1}{2}$, which indicates the transition to 3D behavior at the mean-field transition temperature $T_{c0} = 18$ K.

Zero-dimensional fluctuations can be observed in systems in which the conduction is mediated by superconducting particles that are weakly coupled, i.e., granular materials [16]. Furthermore, the grain size must be smaller than the superconducting coherence length $\xi_{GL}(T)$. Inside each grain the superconducting order parameter is well established, but the long-range phase coherence is destroyed by the weak coupling between the particles. Experimentally, the $\sigma \propto t^{-2}$ behavior has been observed in granular Sn [17] and NbN [18]. As $\xi(T)$ diverges at T_c the particle size can be a few times $\xi_{GL}(0) = 26$ Å. The origin of the granularity [10] may be inherent in the growth of the pristine film or could be related to the phase separation of undoped C_{60}, K_3C_{60}, and the fully doped K_6C_{60} [19]. We emphasize that the present film growth procedures consistently give room-temperature resistivities of 2.5 mΩ cm, and the films are completely stable at room temperature.

The reduction of T_c in our films with respect to the bulk value can be ascribed to Coulomb charging effects of the grains. It has been shown that T_c can be substantially reduced, before H_{c2} is affected [20]. The origin of this effect is that for our resistivities larger magnetic fields are required to quench the Josephson coupling compared to the isolated-grain superconductivity [21]. It is well known that for small particles the critical field is a single-grain property, and depends on the size of the grain [22]. Deutscher, Entin-Wohlman, and Shapira

[21] find that in strong magnetic fields and weak coupling the upper critical field is given by $H_{c2}=(5/12\pi^2)^{1/2}\phi_0/\xi_R$, with R the radius of the grain. The appropriate coherence length is that of the single grain [21], $\xi_{\text{grain}}=0.85\xi_0 l[T_c/(T_c-T)]^{1/2}$, and we can take $l\approx R$. Using $H_{c2}(0.9)=6.5$ T, we find a Pippard coherence length $\xi_0\approx 150$ Å. (The error bar on this value is mostly related to the determination of the grain size $D\approx 70$ Å.) This coherence length is in good agreement with the LDA calculations [8,9], but, of course, much larger than the single-grain value.

In conclusion, we have characterized thin-film K_3C_{60} to be a granular superconductor, with a typical grain size of 70 Å. The granularity of our films is clearly shown by the presence of zero-dimensional fluctuations above T_c. The grain size of 70 Å leads to a metal-to-insulator transition near a normal-state resistivity of 3 mΩ cm. The upper critical field is strongly affected by the grain size of the film, and using the theory of granular superconductors, we find a Pippard (clean limit) coherence length of $\sim$150 Å, in good agreement with recent theoretical calculations. The sign of the carriers changes with temperature, which shows that in this material at half filling both electron and hole conduction are present.

We gratefully acknowledge stimulating discussions with E. Abrahams, B. Batlogg, S. J. Duclos, D. R. Harshman, G. P. Kochanski, P. B. Littlewood, A. P. Ramirez, S. H. Glarum, D. W. Murphy, M. J. Rosseinsky, and M. Schluter, and technical assistance from A. V. Makhija. J. Zaanen acknowledges financial support from the Foundation for Fundamental Research on Matter (FOM), which is sponsored by the Netherlands Organization for the Advancement of Pure Research (NWO).

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