Superconductivity at 18 K in potassium-doped C\textsubscript{60}

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The synthesis of macroscopic amounts of C\textsubscript{60} and C\textsubscript{70} (fullerenes)\textsuperscript{1} has stimulated a variety of studies on their chemical and physical properties\textsuperscript{2,3}. We recently demonstrated that C\textsubscript{60} and C\textsubscript{70} become conductive when doped with alkali metals\textsuperscript{4}. Here we describe low-temperature studies of potassium-doped C\textsubscript{60} both as films and bulk samples, and demonstrate that this material becomes superconducting. Superconductivity is demonstrated by microwave, resistivity and Meissner-effect measurements. Both polycrystalline powders and thin-film samples were studied. A thin film showed a resistance transition with an onset temperature of 16 K and essentially zero resistance near 5 K. Bulk samples showed a well-defined Meissner effect and magnetic-field-dependent microwave absorption beginning at 18 K. The onset of superconductivity at 18 K is the highest yet observed for a molecular superconductor.

The sensitivity to air of alkali-metal-doped fullerenes (A\textsubscript{x}C\textsubscript{n}) limits the choice of sample preparation and characterization techniques. To avoid sample degradation, we carried out reactions with the alkali metal vapour and C\textsubscript{60} in sealed tubes either in high vacuum or under a partial pressure of helium. The C\textsubscript{60} was purified by chromatography\textsuperscript{1} of fullerite\textsuperscript{2} and was heated at 160°C under vacuum to remove solvents. Small amounts of the individual fullerenes (~0.5 mg) were placed in quartz tubes with alkali metals and sealed under vacuum. These samples were subjected to a series of heat treatments and tests for superconductivity by 9-GHz microwave-loss experiments\textsuperscript{5}. Preliminary tests indicated that only the K-doped C\textsubscript{60} showed a response consistent with a superconducting transition (Fig. 1). For this reason, together with the fact that K\textsubscript{x}C\textsubscript{60} showed the highest film conductivity\textsuperscript{1}, we focused our studies on the K-doped compound.

The conductivity measurements were performed on potassium-doped films of C\textsubscript{60} that were prepared in a one-piece all-glass version of the apparatus described previously\textsuperscript{4}. This reaction vessel was sealed under a partial pressure of helium before reaction. This configuration allowed both \textit{in situ} doping and low-temperature studies of thin films. All measurements were made in a four-terminal Van der Pauw configuration using a 3-μA a.c. current at 17 Hz. Figure 2 shows the temperature dependence of the resistivity of a 960-Å-thick K\textsubscript{x}C\textsubscript{60} film. The film was doped with potassium until the resistivity had fallen to 5 x 10\textsuperscript{-4} Ω cm. The resistivity increases by a factor of two on cooling the sample to near 20 K. Below 16 K, the resistivity starts to decrease; zero resistivity (<10\textsuperscript{-4} of the normal state) is obtained below 5 K. The 10-90% width of the transition is 4.6 K. At 4 K we measured the lower bound to the critical current to be 40 A cm\textsuperscript{-2}.

A bulk polycrystalline sample of nominal composition K\textsubscript{3}C\textsubscript{60} was prepared by reaction of 29.5 mg of C\textsubscript{60} with 4.8 mg potassium. The amount of potassium was controlled volumetrically by using potassium-filled pyrex capillary tubing cut to size in a dry box. The reaction was run with the C\textsubscript{60} in a 5-mm fused silica tube joined to a larger tube in which the potassium-containing capillary was placed. The tube was sealed after being evacuated and refilled with 10\textsuperscript{-2} torr of helium to serve later as a thermal-exchange gas for low-temperature measurements. With the C\textsubscript{60}-containing end of the tube at room temperature,

FIG. 1 Microwave loss as a function of temperature for K\textsubscript{x}C\textsubscript{60} in a static field of 20 Oe.
the potassium was distilled from the capillary in a furnace at 200 °C. Some reaction of the potassium with the quartz tube, visible as a dark brown discoloration, was observed at this temperature. Unreacted potassium was observed after this period. Following distillation of the potassium to the C_{60} end, the tube was shortened by sealing to about 8 cm and heated to 200 °C for 36 h. Finally, the tube was resealed to a length of about 4 cm for magnetic measurements.

The temperature dependence of the d.c. magnetization of the sample with nominal composition K_{3}C_{60} was measured in a SQUID magnetometer (Fig. 3). On zero-field cooling the sample to 2 K, a magnetic field of 50 Oe was applied. On warming, this field is excluded by the sample to 18 K; this verifies the presence of a superconducting phase. The bulk nature of superconductivity in the sample is demonstrated unambiguously by cooling in a field of 50 Oe. A well defined Meissner effect (flux expulsion) develops below 18 K. The shape of the magnetization curve, in particular the temperature-independent signal at low temperature, indicates good superconducting properties for this sample. Also noteworthy is the relatively narrow transition width. The magnitude of the flux exclusion for the zero-field-cooled curve corresponds to 1% volume fraction. This small fraction is possibly due to non-optimal doping or the granular nature of the sample. The large value of the Meissner effect for the field-cooled curve relative to the total exclusion, however,

indicates bulk superconductivity in the electrically connected regions.

The universally accepted tests for superconductivity, namely a transition to zero resistance and a Meissner effect showing the expulsion of magnetic field, demonstrate unequivocally the existence of superconductivity in K_{3}C_{60}. The 18-K transition temperature is the highest yet reported for a molecular superconductor. This may be compared with the previously reported occurrence of superconductivity at 0.55 K in potassium-intercalated graphite. We expect that optimization of composition and crystallinity will lead to further improvement in the superconducting properties.


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FIG. 2 Temperature dependence of the electrical resistivity of a 960-Å-thick film of K_{3}C_{60}.

FIG. 3 Temperature dependence of the magnetization of a K_{3}C_{60} crystalline sample. The direction of temperature sweep in the field-cooled (FC) and the zero-field-cooled (ZFC) curves is indicated by the arrows.