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Superconductivity at 18 K in potassium-doped C_{60}

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THE synthesis of macroscopic amounts of C_{60} and C_{70} (fullerenes)[1] has stimulated a variety of studies on their chemical and physical properties[2,3]. We recently demonstrated that C_{60} and C_{70} become conductive when doped with alkali metals[4]. Here we describe low-temperature studies of potassium-doped C_{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_xC_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_{60} in sealed tubes either in high vacuum or under a partial pressure of helium. The C_{60} was purified by chromatography[1] of fullerite[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[5]. Preliminary tests indicated that only the K-doped C_{60} showed a response consistent with a superconducting transition (Fig. 1). For this reason, together with the fact that K_xC_{60} showed the highest film conductivity[1], we focused our studies on the K-doped compound.

The conductivity measurements were performed on potassium-doped films of C_{60} that were prepared in a one-piece all-glass version of the apparatus described previously[4]. This reaction vessel was sealed under a partial pressure of helium before reaction. This configuration allowed both *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_xC_{60} film. The film was doped with potassium until the resistivity had fallen to 5×10^{-3} 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 ($<10^{-4}$ 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^{-2}.

A bulk polycrystalline sample of nominal composition K_3C_{60} was prepared by reaction of 29.5 mg of C_{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_{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^{-2} torr of helium to serve later as a thermal-exchange gas for low-temperature measurements. With the C_{60}-containing end of the tube at room temperature,

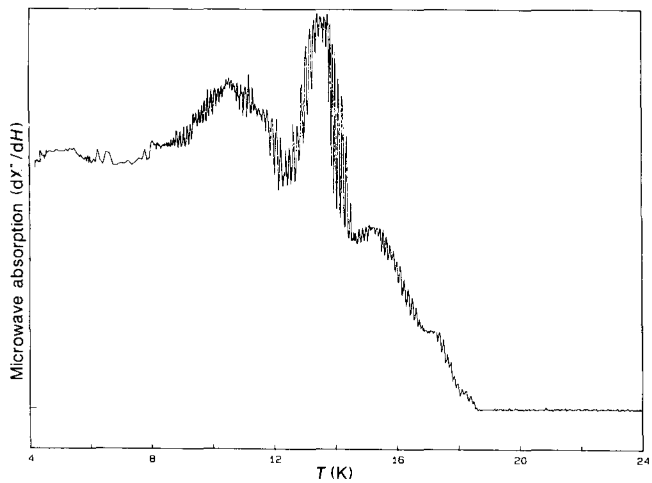

FIG. 1 Microwave loss as a function of temperature for K_xC_{60} in a static field of 20 Oe.

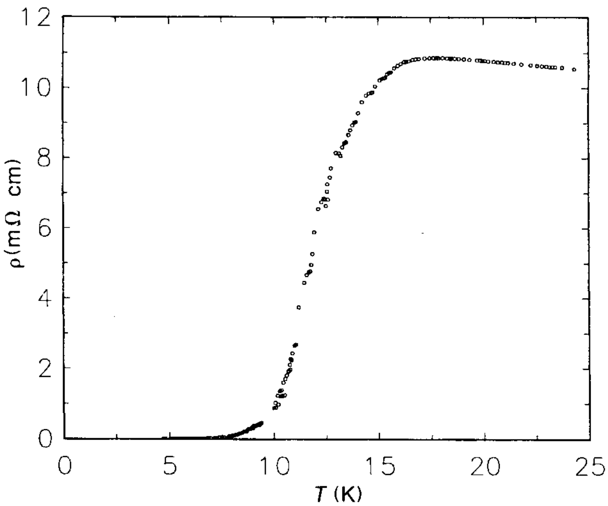

FIG. 2 Temperature dependence of the electrical resistivity of a 960-Å-thick film of K_xC_{60}.

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_3C_{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,

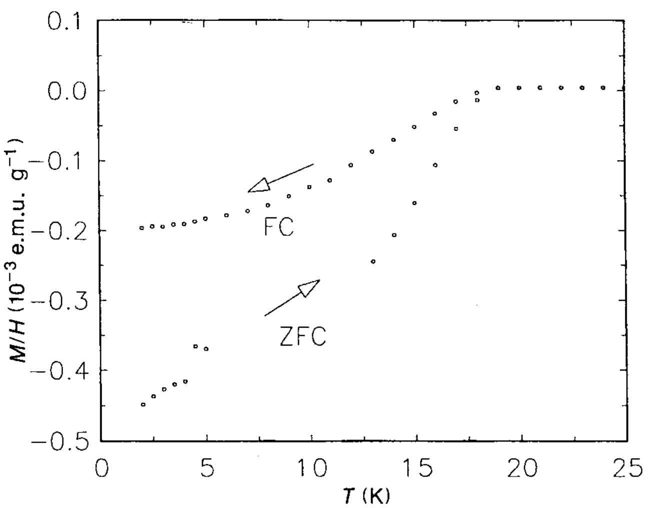

FIG. 3 Temperature dependence of the magnetization of a K_xC_{60} crystalline sample. The direction of temperature sweep in the field-cooled (FC) and the zero-field-cooled (ZFC) curves is indicated by the arrows.

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_xC_{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[6]. We expect that optimization of composition and crystallinity will lead to further improvement in the superconducting properties. □

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