

of magnitude higher than that measured in a typical YBCO SQUID with similar parameters.

The feasibility demonstration of Hg-based cuprate SQUIDS operating above 110 K appears promising and expands the possibility of utilizing integrated microcooling techniques, such as Joule-Thompson or on-chip thermoelectric refrigeration, for superconducting electronic applications. Joule-Thompson microcoolers that operate at temperatures down to 77 K are commercially available. On the other hand, more development work is necessary to allow operation of cryogenic thermoelectric coolers at temperatures below 150 K.

The design of composite systems consisting of a battery of thermoelectric coolers for operation at lower temperatures has recently been proposed (11).

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Single-Crystalline $(K_{C_{60}})_n$: A Conducting Linear Alkali Fulleride Polymer

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Single crystals of a linear cycloadduct conducting polymer, $(K_{C_{60}})_n$, have been grown that are a few tenths of a millimeter in length. Partial oxidation under toluene transformed these crystals into bundles of fibers. The degree of polymerization exceeded 100,000.

The large-scale production (1) of C_{60} has initiated an intensive research effort for the isolation of higher fullerenes (2) and the synthesis of fullerene derivatives with interesting physical and chemical properties (3). Rao *et al.* (4) reported a photoinduced polymerization of C_{60} films and hypothesized that it resulted from the formation of a [2 + 2] cycloadduct linkage. The synthesis of conducting alkali fullerides (5) also opened a new field of research. Recently, the unusual physical properties of A_3C_{60} ($A = K, Rb, \text{ and } Cs$) compounds came into focus. A rather unusual phase transition has been observed at about 400 K in optical (6) and electron spin resonance (7) (ESR) spectra and in differential scanning calorimetry (8). The initial suggestion of Winter and Kuzmany (6) that the high-temperature phase has a face-centered cubic (fcc) "rock salt" structure with C_{60} ions surrounded by eight alkali metal ions was confirmed by the x-ray

diffraction (XRD) studies of Zhu *et al.* (8). Chauvet *et al.* (9) showed that the low-temperature structure of Rb_3C_{60} is orthorhombic ($o\text{-}Rb_3C_{60}$) with an unusually short separation of 9.1 Å between the centers of C_{60} molecules along the crystallographic c direction. An isostructural phase of K_3C_{60} was observed at ambient temperature in XRD studies (10).

Pekker *et al.* (11) suggested that the anions in the orthorhombic phase of A_3C_{60} compounds are linear polymers formed by an ionically induced reversible [2 + 2] cycloaddition reaction of the fulleride ions in the solid state at about 400 K. It was argued that the forbidden [2 + 2] cycloaddition of ground-state neutral molecules is thermally allowed between the singly charged fulleride anions. The proposed structure of the cycloadduct polyanion (Fig. 1) is supported by a Rietveld refinement (12) of powder XRD data. In this report, we provide further evidence for the polyanions. We have grown large single crystals of orthorhombic K_3C_{60} that are unexpectedly stable in air. Long fibers of orthorhombic K_3C_{60} apparent in crystals that were treated with organ-

ic solvents in air are evidence for a high degree of polymerization.

The K_3C_{60} single crystals were prepared by a new coevaporation method. Stoichiometric amounts of C_{60} and K were sealed in a quartz tube that was heated in a gradient furnace. The temperatures of C_{60} and K were 600° and 150°C, respectively. A microcrystalline film of K_3C_{60} coated the wall of the tube at about the 300°C zone within a few hours, and single crystals embedded in a microcrystalline matrix grew in 3 days. A typical region with a few single crystals is shown in the optical micrograph in Fig. 2. The typical dimensions of the largest crystals are 200 μm by 100 μm by 100 μm. Only microcrystalline alkali metal salts of C_{60} have been prepared by coevaporation previously (13).

In Fig. 3 we compare the temperature dependence of the ESR linewidths of a few large coevaporated single crystals to that of a K_3C_{60} powder composed of a few crystallites in the micrometer size range. The powder was prepared in a usual way (5) by solid-state reaction of a stoichiometric mixture of C_{60} and K in a sealed quartz capillary at 260°C for 80 days. The ESR spectrum of the coevaporated single crystals shows that they are indeed $o\text{-}K_3C_{60}$. The ESR linewidths of the single crystals and the powder K_3C_{60} sample are nearly the same, and both show a hysteretic transition in the temperature range of the polymerization. The magnetic spin susceptibility decreases by a factor of 2 during the polymerization. A similar narrowing of the linewidth and a small decrease of susceptibility with decreasing temperature was observed (7, 9) upon polymerization of Rb_3C_{60} . Although we have no XRD evidence, the magnetic characteristics and the phase transition above 350 K make it very likely that the single crystals are composed of K_3C_{60} .

We have studied the stability of the crystals against oxygen and solvents. We exposed a few coevaporated single crystals to air and monitored the variation of the ESR signal at room temperature. The intensity of the signal was constant over a few

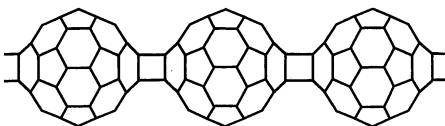


Fig. 1. Molecular view of the [2 + 2] cycloadduct $(C_{60})_n$ polyanion.

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days, implying that $\text{o-K}_1\text{C}_{60}$ is stable in air. This conclusion was confirmed by a detailed study of ESR, optical, and x-ray properties of air-exposed K_1C_{60} and Rb_1C_{60} samples (14). On the other hand, the single crystals disintegrated to bundles of fibers when treated with organic solvents in air. K_1C_{60} single crystals embedded in microcrystalline matrix were exposed to air and kept under toluene for a few days. The solvent gradually turned magenta from the dissolved C_{60} , but part of the material remained insoluble. The residue was washed consecutively with toluene, ethanol, and pentane. Thin-layer chromatography of the toluene solution showed that the dissolved material is pure C_{60} . The residue was insoluble in a variety of solvents such as CS_2 , xylene, and methylnapthalene. The ESR measurements performed on a bundle of fibers show a temperature-independent



Fig. 2. Optical micrograph of K_1C_{60} single crystals embedded in a microcrystalline matrix (size $340\ \mu\text{m}$ by $500\ \mu\text{m}$).

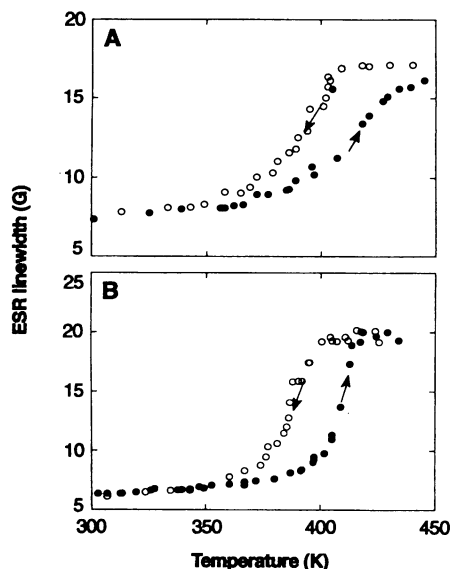


Fig. 3. The hysteric change of the ESR linewidth indicating the polymerization-depolymerization transition (A) in microcrystalline K_1C_{60} powder synthesized by standard methods and (B) for a few coevaporated single crystals.

Pauli susceptibility and a narrow line characteristic of the metallic $\text{o-A}_1\text{C}_{60}$ phases (9). Neutralization of the polymer by oxidation is expected to lead to a strong decrease in intensity, because neither pure C_{60} nor neutral $(\text{C}_{60})_n$ polymer are ESR active.

The fibrillar morphology of the residue (Fig. 4) reveals the polymeric nature of $(\text{KC}_{60})_n$ in a spectacular way. The structure of the fibers may be a modified $\text{o-K}_1\text{C}_{60}$ structure; ESR measurements show that the modifications must be of minor importance. The original contours of a partially disintegrated crystal are easily visible in the transmission optical micrograph (Fig. 4A). Parallel to the contours of the original crystal, bundles of thin fibers extend from one end to the other. Figure 4B shows some individual fibers. The sharp parallel edges of the typically 2- to $5\text{-}\mu\text{m}$ -thick fibers suggest single crystals. If we assume that the polymer chains are parallel to the fibers, the polymerization degree n may be greater than 100,000.

The ESR intensity shows that $(\text{KC}_{60})_n$ has a Pauli susceptibility, and recent microwave conductivity measurements (15) confirm that this material is a metal. It is somewhat surprising that the light brown fibers (Fig. 4) are transparent to visible light. In most cases metals reflect light, and even for sample thicknesses of a few micrometers are not transparent. Systems with quasi-one-dimensional electronic structure are expected to be transparent to light polarized with the electric field perpendicular to the conducting chains. We have not observed, however, this effect under

polarized light in the $(\text{KC}_{60})_n$ fibrils, and we do not yet know the origin of the transparency to visible light.

We devised an experiment to show that the oxidation of the nonpolymeric fcc- K_1C_{60} under toluene does not result in an insoluble residue. As shown by XRD (9), ESR (7), and optical transmission measurements (16), the polymerization of Rb_1C_{60} may be prevented by quenching from 500 K to below 280 K. In the quenched state, the structure at 270 K is the same fcc structure as at 500 K. Our present ESR studies on microcrystalline powders show that quenching has a similar effect on K_1C_{60} and Rb_1C_{60} . We heated coevaporated crystalline K_1C_{60} to 250°C in a sealed tube and quenched it to -25°C . After opening the tube, the sample was kept under toluene in air at -25°C in a refrigerator. Within 5 days, the material dissolved completely and the characteristic magenta solution of C_{60} appeared. Thus, oxygen neutralizes completely the monomer anions of fcc- K_1C_{60} ; insoluble residue is only formed from the polymeric $\text{o-K}_1\text{C}_{60}$. The disintegration of the polymer single crystals into fibers may be related to the neutralization and solution of a small amount of nonpolymeric C_{60} ions in between the polymeric fibers.

We have prepared long single-crystalline fibers that show clearly the polymeric nature of $\text{o-K}_1\text{C}_{60}$ and from which a polymerization degree greater than 100,000 can be estimated. In contrast to the polymer, fcc- K_1C_{60} crystals were completely dissolved in toluene due to oxidation.

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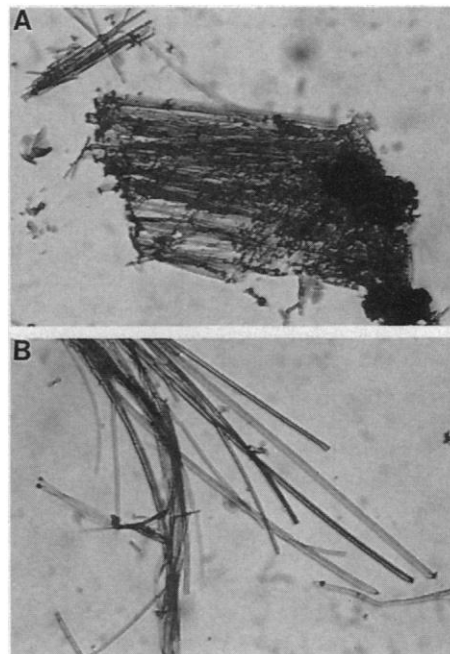


Fig. 4. Transmission optical micrographs of the fibrillar polymer formed by partial oxidation of K_1C_{60} single crystals (size $85\ \mu\text{m}$ by $125\ \mu\text{m}$). (A) Parallel bundles of fibers showing the contours of the original crystal. (B) Individual single crystalline fibers.