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Superconductivity at 28.6 K in a Rubidium–C_{60} Fullerene Compound, Rb_xC_{60}, Synthesized by a Solution-Phase Technique

Introduction. An impressive achievement in the development of new molecular superconducting materials is the recent discovery by Hebard and associates[1] of superconductivity at 18 K in a potassium-doped, buckminsterfullerene C_{60} compound, K_xC_{60}, where x represents a presently unknown stoichiometry. In a previous communication,[2] we reported on an efficacious solution-phase synthesis of this superconductor and a confirmation of a superconducting transition temperature of $T_c = 18.0 \pm 0.1$ K. This solution-phase synthesis is much simpler to employ than the originally reported vapor-transport route,[1] and it is easily adaptable to a number of obvious chemical variations. In this communication, we describe the use of this solution-phase technique in the synthesis of an Rb-containing product of the C_{60} fullerene Rb_xC_{60}, having the considerably higher T_c of 28.6 ± 0.1 K.

Synthetic Procedures. Samples of C_{60} were prepared from graphite soot and purified by column chromatography, as described in detail in our previous communication.[2] The purity of the C_{60} was confirmed by mass spectral analysis. The rubidium–C_{60} compound was synthesized by following the solution-phase technique previously described.[2] The purified C_{60} and Rb (99.7% purity, Aldrich) were loaded into a dry Schlenk flask inside of an argon-filled drybox in the amounts of 24.8 mg (0.034 mmol) of C_{60} and 174 mg (2.04 mmol, 60-fold excess) of Rb. The flask containing this mixture was evacuated and back-filled with Ar three times. Toluene was freeze-thaw-degassed three times; then 30 mL was added to the C_{60}/Rb mixture, and the solution was brought to refluxing temperature. The mixture turned from a purple solution (pure C_{60}) to a black suspension of precipitate in about 30 min, but the refluxing was continued for a total of 2 h. After refluxing, the precipitate was filtered off under Ar and vacuum-dried at room temperature. Unreacted Rb beads (~138 mg) were removed from the dried powder, and the final product was stored under vacuum or under Ar until needed for further study.

Superconductivity. Magnetization measurements on two different samples from the same synthetic batch were carried out with the use of two different SQUID (superconducting quantum interference device) instruments. One sample specimen was sealed under vacuum in a quartz ampule, and the magnetization was measured with both zero-field (zfc) and field cooling (fc) in a magnetic field of 5 Oe. The results of these measurements, expressed as the mass susceptibility χ in cm^3/g, are illustrated in Figure 1. The superconducting onset temperature for the material was found to be $T_c = 28.6 \pm 0.1$ K. As shown in the figure, the superconducting transition is extremely broad, somewhat similar to that found for the potassium-doped compound, K_xC_{60}.[1,2] The shielding susceptibility (zfc experiment) indicates about 7% (with remnant field correction) volume superconductivity, based on a density of 2 g/cm^3 and a zero demagnetization factor. This is higher than the approximate 1% volume superconductivity reported for the potassium-doped product.[1,2] The Meissner fraction amounts to about 14%. The second sample was loaded into an open container, which was sealed with parafilm inside an argon-filled drybox. The magnetization of this sample was determined immediately after loading, with zero-field cooling only, and then redetermined after the sample was exposed to the normal atmosphere at ambient temperature for about 12 h. There was no discernible change in the superconducting onset temperature for the first determination of the magnetization. After the prolonged (12 h) exposure to air, the sample was no longer superconducting at any temperature down to 5 K, the lowest temperature achieved in this study.

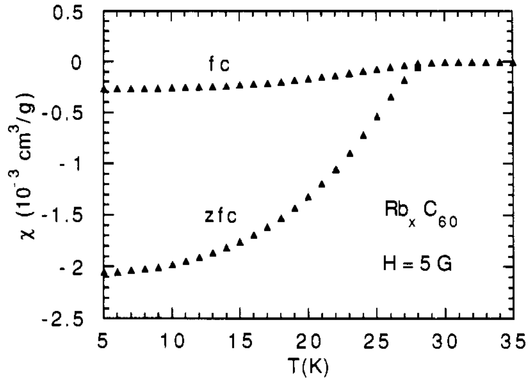

Figure 1. Temperature dependence of the mass susceptibility χ (cm^3/g) at an applied magnetic field of 5 Oe (G) for a field-cooled (fc) and zero-field-cooled (zfc) sample of Rb_xC_{60}, showing an onset $T_c = 28.6 \pm 0.1$ K.

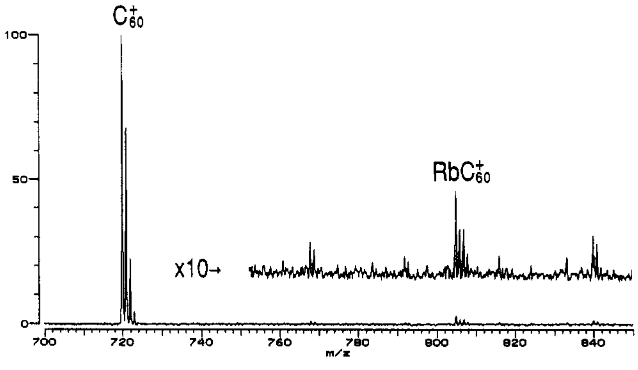

Figure 2. Laser desorption/Fourier transform mass spectrum of an Rb_xC_{60} superconducting sample.

Mass Spectral Analysis. The laser desorption/Fourier transform mass spectrometer includes a superconducting solenoid (~7 T), a LiF laser port, a 2 × 2 × 3 in^3 ICR cell for storing and detecting the laser-desorbed ions, an Ionspec Omega data collection system, and a cryopump (base pressure ~10^{-10} Torr). The Rb_xC_{60} sample was placed on a tantalum foil by using double-sided Scotch tape and inserted into the FTMS load lock under dry N_2 to prevent atmospheric contamination. The 532-nm-focused output of a Q-switched, mode-locked Nd^{3+}:YAG laser was used to desorb the Rb_xC_{60} from the substrate. The data were acquired by use of rf chirp excitation with an analog to digital conversion rate of 1 MHz and 64K data points acquired for each transient.

Figure 2 displays the positive-ion mass spectrum after 1000 averages. C_{60}^+ and RbC_{60}^+ are clearly evident in the spectrum. The isotope abundances observed for both of these species agree well with the predicted values.[3] For the C_{60} species, the observed relative intensities are 100:68:22:4, which is in excellent agreement with the predicted values of 100:67.3:20.6:4.3. This indicates that the amount of H_xC_{60} present in the sample is less than 2%. Hydrogen-containing C_{60} species have been observed from a Birch reduction[4] under experimental conditions similar to those used here for the preparation of the superconducting sample. For the RbC_{60}^+ species the predicted relative intensities are 100:67:61:37 for masses 805–808, which is comparable to the observed intensities of 100:53:53:25. No $Rb_2C_{60}^+$ or $Rb_3C_{60}^+$ was observed at

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(3) Percent relative abundances: ^{12}C, 98.9%; ^{13}C, 1.1%; ^{85}Rb, 72.2%; ^{87}Rb, 27.8%.

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a detection level of 0.5%. Although we cannot conclusively identify the superconducting phase from the mass spectrometric data presented here, it is interesting to note that the signal for RbC_{60}^+ is ~3% of the signal for C_{60}^+. This is close to the ratio observed for the amount of the superconducting phase present in this sample. We have performed similar experiments on a K_xC_{60} sample that was shown to be superconducting at the <1% level.[2] No detectable $K_xC_{60}^+$ species was observed at the detection limit of 1% in the mass spectrum. It is possible that the superconducting phase of the alkali-metal–C_{60} superconductors is a MC_{60} species (M = K, Rb), but we were only able to observe the species in the Rb sample because the concentration of the species was well above our detection limit. We have also performed postionization time-of-flight mass spectrometry[5] on the Rb_xC_{60} superconducting sample. Neutral Rb_xC_{60} species in the laser-desorbed plume were postionized with 266-nm, 5-ns quadrupled Nd^{3+}:YAG pulses. RbC_{60}^+ was observed in the mass spectrum. This experiment shows that RbC_{60} is present as a neutral species in the laser-desorbed plume and is not solely formed from an ion–molecule reaction between C_{60} and Rb^+ during the laser desorption.

Conclusions. We have demonstrated the usefulness of our previously described solution-phase technique for the synthesis of a second alkali-metal–C_{60} fullerene superconducting compound, Rb_xC_{60}, with $T_c = 28.6 \pm 0.1$ K. The preparation time is quite rapid, and the method is easily adaptable to the synthesis of other similar materials. It is interesting, and no doubt significant, that the superconducting products for both the K- and Rb-doping are formed in only small concentrations, and, at least in the case of the Rb_xC_{60} product, that the superconducting phase is unstable is moist air.

Our experiments show that T_c increases with increasing size of the cation, K^+ to Rb^+, in M_xC_{60}. This circumstance is analogous to that of the β-$(ET)_2X$ organic superconducting salts, where T_c increases with increasing size of the anion, $X^- = IBr_2^-$, AuI_2^-, and I_3^- [ET is the radical-cation organic donor molecule bis(ethylenedithio)tetrathiafulvalene]. In the case of these β-phase salts, the increase in T_c is attributed to an enlargement of the lattice and a softening of the interactions, thus enhancing the electron–phonon coupling.[6] A similar lattice-softening effect may occur with the alkali-metal fullerenes. Thus, one might expect a further increase in T_c with substitution of Cs^+, although this trend might be disrupted by unfavorable changes in crystallographic structure. The next important step in developing an understanding of these superconductors is the synthesis of highly crystalline materials that can be structurally well characterized.

Note Added in Proof. We have measured the pressure dependence of T_c in Rb_xC_{60} in a solid He pressure medium to 6 kbar and find $dT_c/dP = -0.7$ (±0.1) K/kbar. This result is nearly identical with our value for dT_c/dP in K_xC_{60} (*Physica C*, in press) and indicates that T_c will be still higher with a larger constituent such as Cs.

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