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Superconducting Alkali Metal Fullerides: Development of a Versatile Solution-Phase Route from Soluble M_3C_{60} Precursors

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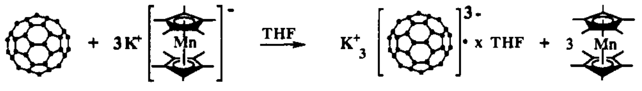
Considerable interest has focused on alkali metal fullerides as a result of the discovery of superconductivity in alkali metal M_3C_{60} salts at critical temperatures (T_c) that are surpassed only by those of the high-T_c copper oxides.[1] Superconducting M_3C_{60} materials have commonly been prepared by the vapor transport method, which involves combining C_{60} with the alkali metal[1-3] or M_6C_{60}[4] in a sealed tube under vacuum and heating at anywhere from 200 to 400 °C for several days to several weeks, depending on the particular procedure. Solution-phase routes to M_3C_{60} materials have several potential advantages over the vapor-phase routes: (i) shorter reaction times and lower temperatures; (ii) ease of handling and control of stoichiometry; (iii) increased homogeneity of the product; and (iv) control of deposition: solution routes may allow thin films and composite materials to be prepared more easily. A few solution routes to M_3C_{60} materials have been reported,[3,5,6] but they require the stoichiometric control of alkali metal or the use of liquid ammonia.[6] In addition, the M_3C_{60} solid is deposited directly from the reaction solution and no isolable precursor is involved, which limits the potential utility of these methods.

We report here a simple and versatile solution-phase synthesis of superconducting M_3C_{60} materials via soluble alkali metal–fulleride precursors that circumvents the usual problems of stoichiometric control. Our method involves the use of alkali metal salts of the strongly reducing 18-electron decamethylmanganocene anion, $[Mn(cp^*)_2]^-$ (cp* = pentamethylcyclopentadienide), to produce discrete THF-solvated alkali metal salts of the C_{60} trianion, $M_3C_{60}{\cdot}x$THF, in high yield.



The $M_3C_{60}{\cdot}x$THF salts serve as versatile precursors to the superconducting M_3C_{60} phases, since we have found that the THF can be removed by mild heating under vacuum, yielding a product with a high superconducting shielding fraction (vide infra). Results presented here focus on K_3C_{60}, although similar results have been obtained for Rb_3C_{60}.

$K^+[Mn(cp^*)_2]^-$ is a convenient reagent for the synthesis of K_3C_{60}, as well as other $K^+{}_xC_{60}{}^{x-}$ salts:[7] (i) the metallocene anion $Mn(cp^*)_2{}^-$ is a powerful one-electron reductant ($E_{1/2}{}^{0/1-} = -2.17$ V vs SCE for the Na^+ salt)[8] and is easily capable of reducing C_{60} to the $C_{60}{}^{3-}$ anion ($E_{1/2}{}^{2-/3-} = -1.3$ V vs SCE);[9] (ii) $K^+[Mn(cp^*)_2]^-$ is a well-defined crystalline material with a high equivalent weight relative to C_{60} and, thus, can be easily weighed out for precise control of stoichiometry; and (iii) the $Mn(cp^*)_2$ produced in the synthesis of $K^+{}_xC_{60}{}^{x-}$ salts can be recycled to $K^+[Mn(cp^*)_2]^-$.

$K^+[Mn(cp^*)_2]^-$ was prepared by potassium naphthalide reduction of $Mn(cp^*)_2$ in a similar fashion to the method reported for $Na^+[Mn(cp^*)_2]^-$.[8,10] $K_3C_{60}{\cdot}x$THF was prepared by adding a THF solution (60 mL) of $K[Mn(cp^*)_2]$ (109 mg, 0.30 mmol) dropwise to a stirred suspension of C_{60}[11] (72 mg, 0.10 mmol) in THF (10 mL) over 1.5 h. The resulting deep red solution was stirred for 0.5 h and filtered, and the volume of the filtrate was reduced to ca. 20 mL, upon which deep red crystals began to precipitate. Hexane (20 mL) was slowly added to the solution, and the product was collected by filtration, leaving a yellow filtrate containing $Mn(cp^*)_2$. The product was washed with hexane (2 × 5 mL) to remove residual $Mn(cp^*)_2$, yielding 108 mg of microcrystalline material. Recrystallization from THF gives dark red plates, and elemental analysis is consistent with the heptasolvated salt, $K_3C_{60}{\cdot}7$THF.[12] The amount of THF in a given preparation of $K_3C_{60}{\cdot}x$THF varies since the solvated THF is easily lost, especially if the material is dried under vacuum. $K_3C_{60}{\cdot}x$THF is soluble in polar solvents such as THF and CH_3CN. The spectroscopic properties of this and other $K^+{}_xC_{60}{}^{x-}$ salts will be described in detail elsewhere.[13]

Low-temperature ac magnetic susceptibility measurements on $K_3C_{60}{\cdot}x$THF did not show any evidence of superconductivity, presumably due to the presence of the THF. Removal of nearly all of the THF by vacuum (0.1 mTorr) drying at room temperature, as evidenced by ^1H NMR, still did not result in the superconducting phase. However, annealing at 300 °C for 12 h under vacuum resulted in a dark black microcrystalline material with superconducting behavior. The superconducting transition in this material was verified by observation of the diamagnetic shielding associated with the superconducting state. As shown in Figure 1, the onset temperature is ca. 18 K, with a superconducting shielding fraction of 31% at 6.5 K. ^1H NMR of CD_3CN solutions of annealed K_3C_{60} did not show any evidence for residual THF. We investigated the effect of annealing temperature and found that superconducting K_3C_{60} can be prepared by annealing $K_3C_{60}{\cdot}x$THF under vacuum at as little as

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(12) Anal. Calcd for $C_{88}H_{56}O_7K_3$: C, 78.72; H, 4.20. Found: C, 79.73; H, 4.21. Mass loss on drying is also consistent with this formula.

(13) Liu, X; Wan, W. C.; Owens, S. M.; Broderick, W. E. In preparation.

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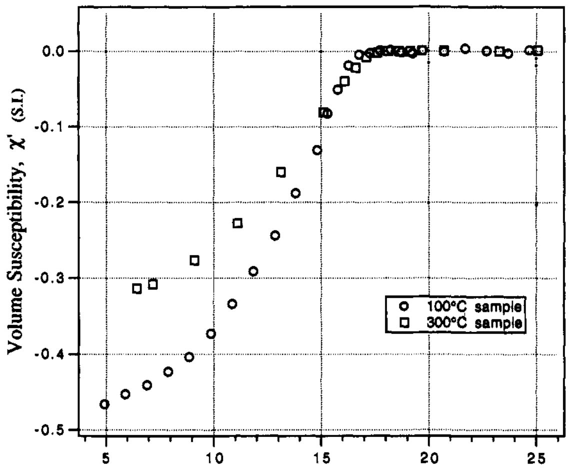

Figure 1. Temperature dependence of the real part of the ac magnetic susceptibility of K_3C_{60} microcrystalline samples prepared by annealing at the temperatures indicated.

100 °C! As shown in Figure 1, a microcrystalline sample annealed at this temperature for 18 h shows a T_c of ca. 18 K, with a superconducting shielding fraction of 47% at 5 K. The role of annealing in producing the superconducting phase appears to be 2-fold: to aid in the removal of residual THF and to promote reorganization of the lattice (after solvent loss) into the fcc superconducting K_3C_{60} phase. Differential scanning calorimetry (DSC) measurements on $K_3C_{60}\cdot x$THF that had been dried under vacuum for 24 h provide evidence for this latter point. As shown in Figure 2, the fairly sharp exothermic peak observed at ~103 °C is consistent with a recrystallization process from a metastable K_3C_{60} phase to the more stable fcc phase.

Our findings are somewhat surprising since it has been reported that removal of THF from nominal K_3C_{60} compositions obtained by reaction of C_{60} and K metal in THF require heating to 300 °C, and only small amounts of superconductivity were observed.[3] In addition, M_3C_{60} materials prepared from liquid ammonia required annealing for 24–48 h at 375 °C to obtain large superconducting fractions.[6] We attribute the low temperatures and relatively short annealing times of our method to the precise control of stoichiometry and homogeneity of the $K_3C_{60}\cdot x$THF precursor.

We have found a marked dependence of the shielding fraction on the crystallinity of the $K_3C_{60}\cdot x$THF, with larger crystal size giving higher shielding fractions. This is expected, since low values for the shielding fraction are obtained unless the grain size is much larger than the London penetration depth (~0.24–0.48 μm for K_3C_{60} and Rb_3C_{60}).[3,14] We are currently attempting to grow large single crystals of $K_3C_{60}\cdot x$THF for a structural analysis of the precursor and to see if 100% shielding fractions are obtainable without compaction. In addition, we are investigating the effect of solvent loss and annealing on crystallinity to see if this is a viable route to single-crystal K_3C_{60}, the latter of which has thus far only been prepared by vapor phase doping of C_{60} crystals.[15]

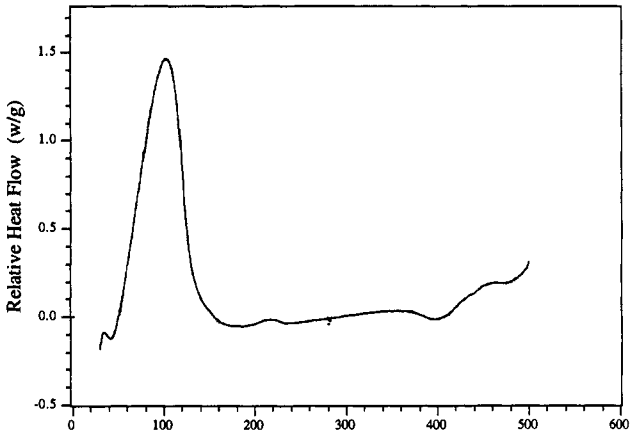

Figure 2. DSC thermogram of $K_3C_{60}\cdot x$THF that had previously been dried under vacuum for 24 h. Heating rate: 20 °C/min.

In summary, the use of strongly reducing alkali metal metallocene salts, $M^+[Mn(cp^*)_2^-]$, provides a versatile solution-phase route to superconducting M_3C_{60} materials. The soluble M_xC_{60} precursors, $M_3C_{60}\cdot x$THF, can be converted to the superconducting M_3C_{60} phase with large shielding fractions by annealing under very mild conditions (100 °C). In addition, these precursors provide greater versatility in the preparation and deposition of M_3C_{60} materials than the conventional vapor transport method and should allow the preparation of highly crystalline M_3C_{60}, as well as thin films.

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