Reports

^{13}C NMR Spectroscopy of K_xC_{60}: Phase Separation, Molecular Dynamics, and Metallic Properties

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The results of ^{13}C nuclear magnetic resonance (NMR) measurements on alkali fullerides K_xC_{60} are reported. The NMR spectra demonstrate that material with $0 < x < 3$ is in fact a two-phase system at equilibrium, with $x = 0$ and $x = 3$. NMR lineshapes indicate that C_{60}^{3-} ions rotate rapidly in the K_3C_{60} phase at 300 K, while C_{60}^{6-} ions in the insulating K_6C_{60} phase are static on the time scale of the lineshape measurement. The temperature dependence of the ^{13}C spin-lattice relaxation rate in the normal state of K_3C_{60} is found to be characteristic of a metal, indicating the important role of the C_{60}^{3-} ions in the conductivity. From the relaxation measurements, an estimate of the density of electronic states at the Fermi level is derived.

The recent discovery that electrically conducting (*1*) and superconducting (*2, 3*) alkali fullerides with general formula M_xC_{60} (M = K, Rb, Cs) can be prepared by reacting solid C_{60} [buckminsterfullerene (*4, 5*)] with alkali metals has stimulated widespread interest in the properties of these materials. Crystal structures of K_3C_{60} (*6*) and K_6C_{60} (*7*) have been reported. It is generally believed (*1–3, 8*), that the K_3C_{60} phase is responsible for superconductivity in K_xC_{60}, while the K_6C_{60} phase is an insulator. At present, substantial questions remain concerning the structure, stability, and electronic properties of intermediate phases, that is, phases with $x \neq 0, 3, 6$. In this paper, we report ^{13}C nuclear magnetic resonance (NMR) measurements on alkali fullerides with nominal stoichiometry K_xC_{60}. We find distinctive spectral features for the K_3C_{60} and K_6C_{60} phases. Our NMR spectra demonstrate that, for $x \leq 3$, only the C_{60} and K_3C_{60} phases are stable. We show that this finding is consistent with the calculated electrostatic energies of the $x = 1, 2$, and 3 phases. The NMR lineshapes indicate that C_{60}^{3-} ions rotate rapidly in K_3C_{60} at room temperature and that C_{60}^{6-} ions are static in K_6C_{60} at room temperature. Finally, we present measurements of the ^{13}C spin-lattice relaxation time (T_1) in K_3C_{60} in the temperature range from 133 K to 363 K that reveal behavior characteristic of a metal and provide an experimental determination of the local density of electronic states at the Fermi level.

Powder samples of K_xC_{60} were prepared as described previously (*3, 5, 8*). Briefly, the appropriate amounts of C_{60} powder and K were sealed in pyrex tubes in vacuo. The tubes were heated at 225°C for 3 to 5 days to form the potassium fulleride compounds. The samples were then resealed in ≤20 torr $He_{(g)}$ and annealed at temperatures between 250° and 300°C for periods ranging from 10 to 25 days. NMR measurements are reported for four samples, with nominal stoichiometries $K_{1.5}C_{60}$ (sample I), $K_{2.0}C_{60}$ (sample II), $K_{3.1}C_{60}$ (sample III), and $K_{6.0}C_{60}$ (sample IV). Superconducting fractions, as determined by magnetic flux expulsion measurements, were 16, 33, 32, and 0% for samples I to IV, respectively. In all cases, a single superconductivity transition at 19.0 ± 0.5 K was observed. NMR spectra were obtained at a ^{13}C frequency of 100.5 MHz (9.39-T field). Frequencies are reported in parts per million with respect to tetramethylsilane. The total mass of carbon that contributes to the NMR spectrum was determined for each K_xC_{60} sample by comparing the initial amplitude of the free induction decay (FID) signal with that of a known weight of $CH_3OH_{(l)}$. In all cases, the entire mass of the sample was accounted for in the NMR spectrum to within the accuracy of the calibration (±15%). T_1 values were determined using the saturation-recovery technique. Recovery curves were well fit by a single exponential.

NMR spectra were taken of pure solid C_{60} and of samples I through IV at room temperature after the above preparation (Fig. 1). As reported earlier (*9–11*), the spectrum of C_{60} (Fig. 1a) shows a single line at 143 ppm, with a width of 2.5 ppm. The spectrum of sample III (Fig. 1d) also shows a single line, but centered at 186 ppm and with a width of 15 ppm. We assign this line to C_{60}^{3-} in the K_3C_{60} phase. The spectra of samples I and II show only the K_3C_{60} and C_{60} lines. We see no evidence for resonances from intermediate phases. The ratio of the areas of the two lines in the spectrum of sample I is 1:1, precisely what one would predict if the intermediate phases were un-

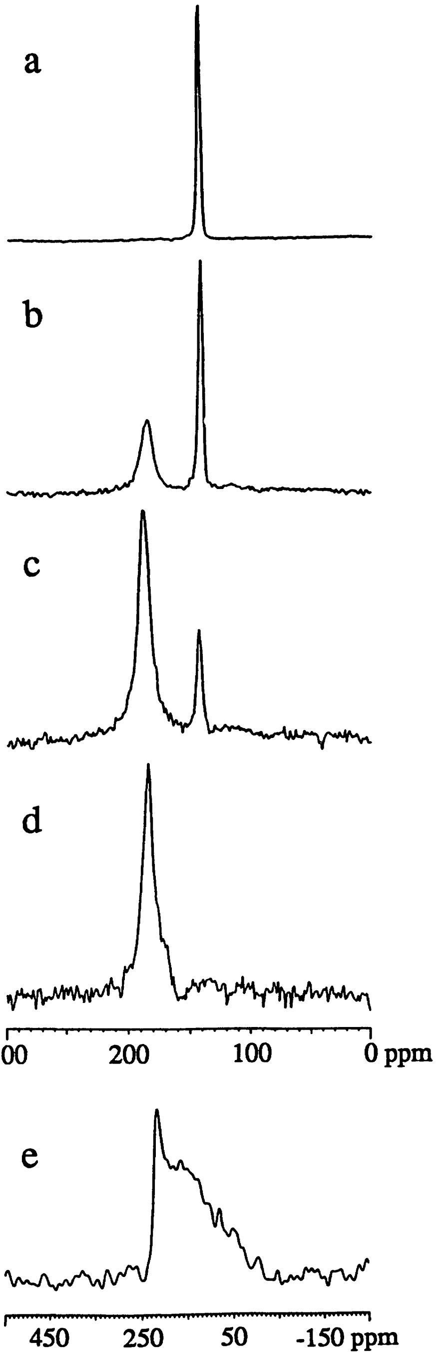

Fig. 1. ^{13}C NMR spectra of C_{60} powder (**a**) and K_xC_{60} with nominal values of x = 1.5 (**b**), 2.0 (**c**), 3.1 (**d**), and 6.0 (**e**). T = 300 K; sample weights ≈ 30 mg; number of shots = 16, 256, 256, 128, 780 (a–e); delay between shots = 300, 180, 180, 30, 120 s (a–e).

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stable with respect to disproportionation into K_3C_{60} and C_{60} phases. The area ratio is 5:1 in the spectrum of sample II, indicating an actual stoichiometry $K_{2.5}C_{60}$.

X-ray powder diffraction patterns were also acquired for C_{60} and for samples I, III, and IV (Fig. 2). The similarity of the patterns for samples I and III is attributable to the fact that there is virtually no change in the lattice parameters or symmetry between C_{60} and K_3C_{60} (*6, 12*). Thus, x-ray powder diffraction without profile analysis is of marginal utility in distinguishing between phase separation and the formation of a solid solution for $0 < x < 3$. The diffraction pattern for sample IV is in good agreement with the x-ray data for K_6C_{60} reported previously (*7*).

To check that equilibrium was established in our K_xC_{60} samples, we examined the NMR spectrum of sample I after further heating. Spectra were taken after initial preparation (Fig. 3a, same as Fig. 1b), after an additional 24 hours at 350°C (Fig. 3b), and after an additional 72 hours at 400°C (Fig. 3c). Although the width of the K_3C_{60} line changes upon heating, the ratio of the areas of the K_3C_{60} and the C_{60} lines remains roughly 1:1. In addition, we see the development of a broad, low-intensity feature in the spectrum. X-ray powder diffraction at this point shows a substantial broadening and weakening of the diffraction peaks. We attribute these observations to sample decomposition. We conclude that the spectra in Fig. 1 are those of the equilibrium phases.

The narrowness of the K_3C_{60} line in Figs. 1 and 3 indicates that C_{60}^{3-} ions rotate rapidly in K_3C_{60} at room temperature, thereby averaging out the ^{13}C chemical shift anisotropy (CSA) as previously observed for C_{60} molecules in the undoped solid (*9, 10, 13*). In contrast, the spectrum of sample IV (Fig. 1e) shows a broad, poorly defined CSA powder pattern lineshape. The fact that the ^{13}C CSA is not averaged out in K_6C_{60} indicates that large amplitude reorientations of C_{60}^{6-} ions in K_6C_{60} at room temperature are infrequent on the time scale of the inverse of the CSA width (roughly 50 μs). Once the C_{60}^{6-} ions are static, the individual carbon nuclei are no longer all magnetically equivalent. The NMR lineshape in Fig. 1e is then a superposition of CSA powder patterns from inequivalent, but similar, carbon sites. Refinement of the x-ray diffraction data for K_3C_{60} and K_6C_{60} indicates that the data is better fit in both cases by structures in which C_{60} ions are orientationally ordered, rather than rotationally averaged (*6, 7*). Our NMR lineshapes then imply that the dynamics of C_{60}^{3-} ions are better described by jump motion among symmetry-equivalent orientations, as observed in the orientationally ordered phase of undoped C_{60} (*13, 14*), rather than by continuous rotational diffusion.

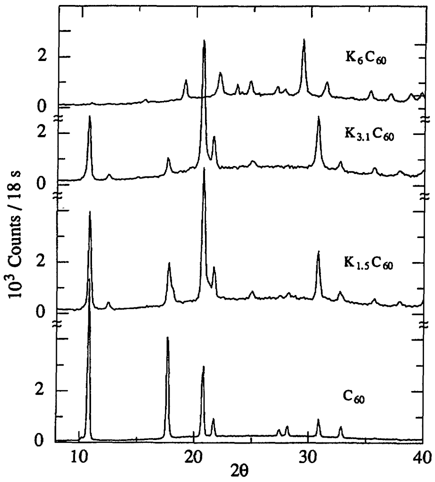

Fig. 2. X-ray powder diffraction patterns (Cu K_α radiation) for K_xC_{60} with indicated nominal stoichiometries.

The two-phase behavior of K_xC_{60} with $0 < x < 3$ can be understood in terms of electrostatic forces. Pure, undoped C_{60} adopts a structure in which C_{60} molecules are positioned with their centers of mass on a face-centered-cubic (fcc) lattice (*12*). In K_3C_{60}, K^+ ions occupy the one octahedral and the two tetrahedral holes per C_{60}^{3-} ion in the fcc lattice (*6*). Assuming that the ions act as point charges, we calculate a total electrostatic (Madelung) energy ME_3 of -22.4 eV per K_3C_{60} unit. The electrostatic energies of a putative K_1C_{60} structure, in which K^+ ions occupy only the octahedral holes and only C_{60}^{-} ions are present, and a putative K_2C_{60} structure, in which K^+ ions occupy only the tetrahedral holes and only C_{60}^{2-} ions are present, are $ME_1 = -3.5$ eV and $ME_2 = -11.8$ eV per K_1C_{60} and K_2C_{60}, respectively. In addition to the Madelung energies, we must take into account the electron-electron repulsions on individual C_{60} ions. We take the electron affinity of an isolated C_{60} neutral molecule to be $EA = 2.6$ eV, as determined experimentally (*15*). We assume that a second electron is bound by $EA - RE_2$, where RE_2 is the electron-electron repulsive energy per C_{60}^{2-} ion. Taking for RE_2 the minimum energy of two point charges on a sphere, RE_2 has the value $e^2/2R = 2.1$ eV ($R = 3.5$ Å, the radius of a C_{60} molecule). This gives a net binding energy of 0.5 eV for the second electron. Similarly, the interaction energy of a third electron is assumed to be $-EA + RE_3 - RE_2$, where RE_3 is the repulsive energy per C_{60}^{3-} ion. We assume that RE_3 has the value $\sqrt{3}e^2/R = 7.1$ eV, corresponding to the minimum energy of three point charges on a sphere. With this assumption, addition of a third electron is energetically unfavorable by 2.5 eV. Even with this strongly repulsive value for the energy of placing a third electron on C_{60}, electrostatic energies favor the K_3C_{60} phase. The electrostatic energy of disproportionation of K_1C_{60} into one-third K_3C_{60} and two-thirds C_{60} is $(ME_3 - 3ME_1 + RE_3)/3 = -1.6$ eV. The energy of disproportionation of K_2C_{60} into two-thirds K_3C_{60} and one-third C_{60} is $(2ME_3 - 3ME_2 + 2RE_3 - 3RE_2)/3 = -0.4$ eV.

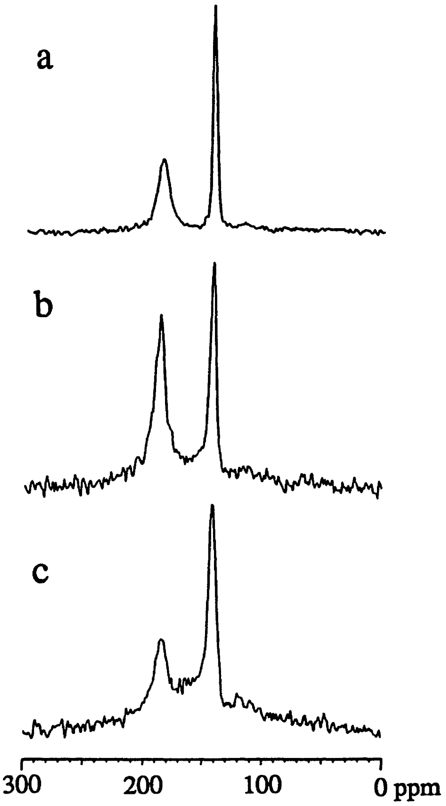

Fig. 3. ^{13}C NMR spectra of $K_{1.5}C_{60}$ after initial preparation (**a**), an additional 24 hours of annealing at 350°C (**b**), and an additional 72 hours at 400°C (**c**).

Relaxation time (T_1) measurements were made on the K_3C_{60} line in sample II between 133 K and 363 K (Fig. 4). For $T \leq 273$ K, the T_1 data can be fit to the form $T_1T = \kappa$, as expected for a metal (*16*), with $\kappa = 140$ K-s. This result provides experimental evidence that molecular orbitals on C_{60} molecules contribute to the conduction band in K_3C_{60}, as anticipated, and that the normal state of K_3C_{60} is a Fermi liquid. Above 273 K, T_1T is reduced. We also see an increase in the NMR linewidth, from 15 ppm to 100 ppm, with decreasing temperature in the range from 300 K to 220 K. We therefore attribute the reduction in T_1T above 273 K to a contribution to the spin-lattice relaxation rate from rotation of C_{60}^{3-} ions (*9, 13*), which vanishes when the rotational motion freezes out and the line broadens. Using $\kappa = 140$ K-s and the standard

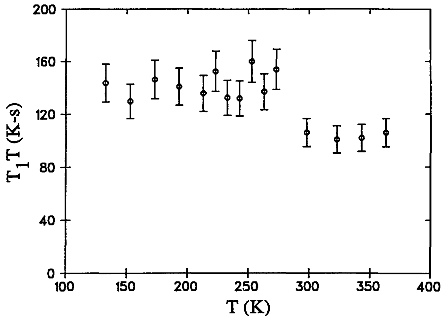

Fig. 4. Temperature dependence of the ^{13}C spin-lattice relaxation time T_1 in K_3C_{60}, plotted as T_1T versus T. Error bars are standard deviations estimated from five T_2 measurements at 298 K.

expression for spin-lattice relaxation by a contact hyperfine interaction (*16*),

$$\frac{1}{\kappa} = \frac{64}{9}\pi^3 k\hbar^3\gamma_e^2\gamma_n^2|\Psi(0)|^4\rho^2(E_f) \qquad (1)$$

where γ_e and γ_n are the gyromagnetic ratios of the electron and the ^{13}C nucleus, we calculate the local electron density of states at the Fermi level and at a carbon nucleus in the normal state of K_3C_{60} to be $|\Psi(0)|^2\rho(E_f) = 7.6 \times 10^{24}$ eV^{-1} cm^{-3} per C_{60}^{3-} ion. We estimate $|\Psi(0)|^2$, the average electron density at a carbon nucleus for an orbital at the Fermi level (normalized to 1 for each C_{60} molecule), to be of order 4×10^{23} cm^{-3}. This value is determined from unrestricted Hartree-Fock calculations of the ratio of the unpaired spin density in carbon 2*s* orbitals in C_{60}^{3-} to that in planar methyl radical (*17*) and from the measured isotropic ^{13}C hyperfine coupling in methyl radical (*18*). 2*s*-2*p* hybridization (*19*) associated with the nonplanarity of C_{60} and core polarization make comparable contributions to $|\Psi(0)|^2$. We then derive a density of states at the Fermi level $\rho(E_f) = 20$ eV^{-1} per C_{60}^{3-} ion.

We interpret the 43 ppm downfield shift of the K_3C_{60} ^{13}C NMR resonance relative to the C_{60} resonance to be primarily a Knight shift attributable to hyperfine coupling between ^{13}C nuclei and conduction electron spins. A downfield shift of only 14 ppm relative to neutral C_{60} has been observed for a diamagnetic C_{60} anion of unknown charge in solution (*20*), suggesting a small orbital contribution to the shift in K_3C_{60}. With $\kappa = 140$ K-s, the Korringa relation for a Fermi gas of noninteracting electrons predicts a ^{13}C Knight shift of 170 ppm. The discrepancy between the observed and predicted shifts raises the possibility that orbital couplings (*21*) make a substantial contribution to the relaxation rate.

In conclusion, our ^{13}C NMR spectra of K_xC_{60} provide strong evidence for phase separation in material with $0 < x < 3$. The NMR lineshapes demonstrate the presence of rapid, large amplitude molecular reorientations at room temperature in K_3C_{60} and the absence of such reorientations in K_6C_{60}. NMR relaxation measurements indicate the central role played by C_{60}^{3-} ions in the conductivity of K_3C_{60} and suggest that ^{13}C NMR will be an important probe of the superconducting state of K_3C_{60} and other alkali fullerides. Further low temperature measurements are in progress.

Note added in proof: We find the ^{13}C NMR T_1T to be 69 ± 8 K-s in Rb_3C_{60} between 213 K and 344 K, indicating that $\rho(E_f)$ is 40% larger than K_3C_{60}.

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$(Rb_xK_{1-x})_3C_{60}$ Superconductors: Formation of a Continuous Series of Solid Solutions

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By means of an approach that employs alkali-metal alloys, bulk single-phase $(Rb_xK_{1-x})_3C_{60}$ superconductors have been prepared for all x between 0 and 1. For $x = 1$ it is shown that the maximum superconducting fraction, which approaches 100% in sintered pellets, occurs at a Rb to C_{60} ratio of 3:1. More importantly, single-phase superconductors are formed at all intermediate values of x, and it is shown that the transition temperature (T_c) increases linearly with x in this series of materials. The formation of a continuous range of solid solutions demonstrates that the rubidium- and potassium-doped C_{60} superconducting phases must be isostructural, and furthermore, suggests that the linear increase in T_c with x results from a chemical pressure effect.

THE RECENT FINDING OF SUPERCONDUCTIVITY in K-doped C_{60} (*1*) has been followed by an intense effort directed toward understanding the chemistry and physics of alkali metal–doped C_{60} solids (*2*–*12*). In particular, studies of the K-doped superconducting phase, K_3C_{60}, have yielded insight into the structure (*8*), coherence length and penetration depth (*11*), and pressure dependence of T_c (*9*, *10*). The success of these physical measurements has in large part been due to the development of a method for preparing K-doped C_{60} samples that contain predominantly the superconducting phase (*4*). In the case of Rb_xC_{60}, which has a significantly higher transition temperature (T_c) than K_3C_{60} (28 versus 18 K), the reported yields of superconducting phase have been much lower, and thus have precluded the clear identification of the composition and key properties of this superconducting phase.

Understanding the origin of superconductivity in doped C_{60} will require, however, experimentalists to characterize the properties of other alkali metal–doped C_{60} superconductors, and importantly to elucidate the relationship between these phases. To this end we have undertaken the study of C_{60} doped simultaneously with Rb and K, and herein report the synthesis and characterization of bulk superconducting $(Rb_xK_{1-x})_3C_{60}$ materials for x = 0 to 1. In previous studies of M_xC_{60} materials most researchers have relied upon the direct reaction of alkali-metal vapor with C_{60} (*1*–*4*). While this approach results in the formation of high yields of K_3C_{60} (*4*), only small fractions of Rb-doped and no Cs-doped C_{60} superconducting phase fabricated with this method have been reported (*3*, *4*). To enable greater control

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