Evidence for Endohedral Muonium in K_xC_{60} and Consequences for Electronic Structure

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Positive muons injected into solid C_{60}, K_4C_{60}, and K_6C_{60} form vacuumlike muonium (μ^+e^-) with a (6–12)% probability. Observation of coherent spin precession of muonium establishes that all three materials are nonmagnetic and nonconducting at low temperatures. From the temperature dependence of the signals we estimate the electronic band gaps in K_4C_{60} and K_6C_{60} to be considerably smaller than in C_{60}. The similarity of the muonium centers supports a model in which a muonium atom is caged inside the C_{60} molecule in pure C_{60} or the $C_{60}{}^{-x}$ molecular ion in K_xC_{60}.

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The observation of C_{60} [1] and the subsequent production of bulk quantities of relatively pure C_{60} [2] has led to tremendous interest in the structural, electrical, and magnetic properties of C_{60} and related compounds. Pure C_{60} forms an fcc lattice at 300 K in which the C_{60} molecules are rotating almost freely [3–5]. Below 260 K there is a first-order transition to an orientationally ordered phase in which the C_{60} molecules reorient less rapidly and acquire a time-averaged orientation with respect to one another [6]. Compounds produced by doping with alkali-metal atoms exhibit interesting transport properties. For example, pure C_{60} is nonconducting whereas K_3C_{60} is metallic with a superconducting transition at $T_c = 19$ K [7]. Band-structure calculations find that pure C_{60} and K_6C_{60} are semiconductors with band gaps of about 1.5 and 0.48 eV, respectively [8,9], whereas K_3C_{60} and K_4C_{60} are predicted to be good metals [10,11]. Interesting magnetic properties have also been predicted. Chakravarty, Gelfand, and Kivelson have used a Hubbard model to take into account electron-electron correlations within the C_{60} molecule itself and predict ferromagnetic and antiferromagnetic phases under some doping conditions [12]. With a similar model it has also been predicted that undoped C_{60} has an exotic magnetic ground state [13]. There is also a report that C_{60} doped with a strong organic reducing agent tetrakisdimethylaminoethylene (TDAE) is a soft ferromagnet [14].

The positive muon is a sensitive probe of internal magnetic fields, capable of detecting small magnetic moments on the order of a nuclear magneton or less [15]. Information on electronic structure can also be obtained under certain circumstances. For example, in intrinsic semiconductors and insulators the muon often forms paramagnetic muonium centers [16] whose spin precession signals are very sensitive to the presence of free carriers [17]. The electronic structure of a muonium center is closely related to that of atomic hydrogen with small differences due to the larger zero-point motion of muonium ($m_\mu \approx \frac{1}{9} m_p$). Muonium centers in fullerenes were first observed in a sample of C_{60} containing (10–15)% C_{70} [18]. One signal had a larger isotropic muon hyperfine parameter close to the value for a muonium atom (μ^+e^-) in vacuum (4463 MHz), whereas the second signal had an isotropic hyperfine parameter of 325 MHz which is typical of muonium-substituted free radicals [19]. Recently we confirmed the presence of the latter in high purity C_{60} and identified it as a neutral C_{60}-muonium radical (C_{60}Mu) reorienting at a rate close to that of C_{60} itself [5]. In this Letter we report the presence of vacuumlike muonium (Mu) in high-purity samples of C_{60}, K_4C_{60}, and K_6C_{60}. The characteristic muonium spin precession signals establish that all three materials are nonconducting and nonmagnetic at 5 K. The similarity of the observed centers at low temperature indicates that the Mu is endohedral, i.e., inside the C_{60} cage in pure C_{60} or the $C_{60}{}^{-x}$ ion in K_xC_{60}.

The experiment was performed on the M15 and M13 beamlines at TRIUMF which provide nearly 100% spin-polarized positive muons with a momentum of 28 MeV/c. The starting material of high-purity C_{60} powder was prepared using standard techniques [2] and showed no detectable infrared lines attributable to solvent molecules. High-resolution powder x-ray diffraction yielded a crystallite size of greater than 1500 Å and high-performance liquid chromatography showed better than 99.5% pure C_{60} with no trace of $C_{60}O$. The process for K doping is described elsewhere [20]. In order to prevent any exposure to air, the K_4C_{60} and K_6C_{60} powdered samples were sealed in an atmosphere of 90% Ar and 10% He inside an aluminum vessel (20 mm diameter by 2 mm deep) with a 0.05-mm-thick Al window.

Conventional transverse field muon-spin rotation (μSR) data [15] were taken in external magnetic fields between 0.5 and 10 mT. Figure 1 shows the Fourier transforms of the μSR spectra for C_{60}, K_4C_{60}, and K_6C_{60}. The lines labeled Mu are attributed to a center with a spin Hamiltonian close to that of free Mu characterized by a large isotropic muon-electron hyperfine interaction A_μ. The two observed frequencies correspond to the allowed magnetic dipole transitions between the spin-triplet states of Mu which are split by the Zeeman interaction with the applied magnetic field H. The sum of the frequencies $\nu_{12}+\nu_{23}=g_e\mu_B H/h$ is approximately the Larmor frequency of a free electron, whereas the difference provides a measure of A_μ [21]:

$$A_\mu=\frac{1}{2}\left[\frac{(\nu_{12}+\nu_{23}+2\nu_\mu)^2}{\nu_{23}-\nu_{12}}+\nu_{12}-\nu_{23}\right], \qquad (1)$$

where $\nu_\mu=0.1355\ \text{MHz/mT}\times H$ is the Larmor frequency of a free muon. The observed characteristic precession signals for Mu establish that all three samples are nonmagnetic and nonconducting at low temperatures. If there were any free carriers at the level of about 10^{15} cm^{-3} we would expect the Mu electron to undergo spin exchange leading to substantial line broadening. At much higher concentrations of carriers one expects to see a single precession frequency close to ν_μ, as reported for metallic K_3C_{60} [22]. Similarly, if there were a dense concentration of electronic magnetic moments (static or fluctuating), one would expect an exchange interaction with the Mu electron which would either broaden the lines substantially or alter dramatically the frequency spectrum. Our observations exclude these possibilities.

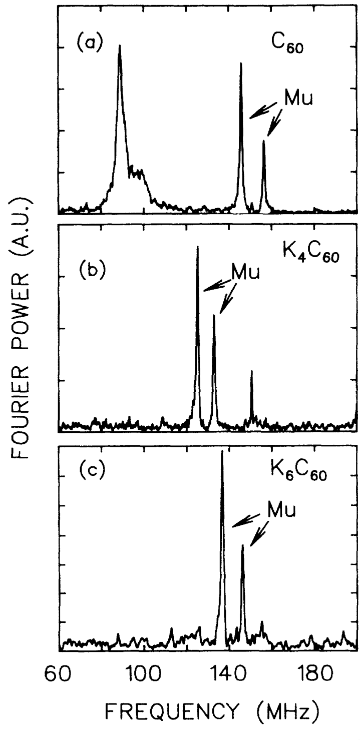

FIG. 1. μSR frequency spectra in (a) C_{60}, (b) K_4C_{60}, and (c) K_6C_{60} at a temperature of 5 K in transverse magnetic fields of 10.7, 9.6, and 10 mT, respectively. The signals labeled Mu are attributed to endohedral muonium. The line at 150 MHz in (b) is an instrumental artifact.

In pure C_{60} [see Fig. 1(a)] there is an additional broad line centered at about 90 MHz which is due to the C_{60}Mu radical. In K_4C_{60} and K_6C_{60}, which are essentially ionic compounds of K^+ and $C_{60}{}^{-x}$, the formation of a radical is suppressed. Instead the majority of the muons form a diamagnetic center, i.e., with no unpaired electron spin density and therefore no magnetic hyperfine interaction. Such a center, which is characterized by a precession frequency close to that of a free muon (ν_μ), was observed in all three materials but is not shown in Fig. 1. The probabilities for forming the different species can be estimated from the coherent precession amplitudes and are given in Table I. The fact that the sum of the probabilities is less than 100% implies there is a fraction of the muon spin polarization which is not observed. This missing fraction is a common observation in nonmetals.

Unlike the radical, Mu is remarkably insensitive to the presence of K and the accompanying change in the bonding characteristics. Our estimates of the muon-electron hyperfine parameters A_μ obtained from Eq. (1) are given in Table I. Note that the A_μ values are very similar and a few percent less than that of a Mu atom in vacuum (4463 MHz). The small negative shift in A_μ is typical for a van der Waals solid where there is only weak interaction between Mu and the host molecules [23]. While this may be understandable in C_{60} it is surprising that the ionic environment in K_xC_{60} does not have a more pronounced effect on the electronic structure and consequently on A_μ. It is interesting to note that the region of weakest electric fields in the K-doped material is on the inside a charged $C_{60}{}^{-x}$ cage.

Figure 2 shows the temperature dependence of the muonium T_2^{-1} linewidth parameter obtained by fitting

TABLE I. Fraction of injected muons which form a diamagnetic center (f_D), muonium (f_{Mu}), or radical (f_R) at 5 K. A_μ is the muon-electron hyperfine parameter of muonium and α and E_g are fitted parameters as defined in Eq. (2).

	f_D (%)	f_{Mu} (%)	f_R (%)	A_μ (MHz)	α [a] ($\text{eV}^{-1}\text{s}^{-1}$)	E_g (eV)
C_{60}	2(5)	12(2)	60(10)	4341(24)	···	···
K_4C_{60}	68(5)	7(2)	···	4342(66)	$5(4)\times10^{14}$	0.33(2)
K_6C_{60}	69(5)	6(2)	···	4230(63)	$5(4)\times10^{14}$	0.27(2)

[a] A single value of α was used to fit the data for both K_4C_{60} and K_6C_{60}.

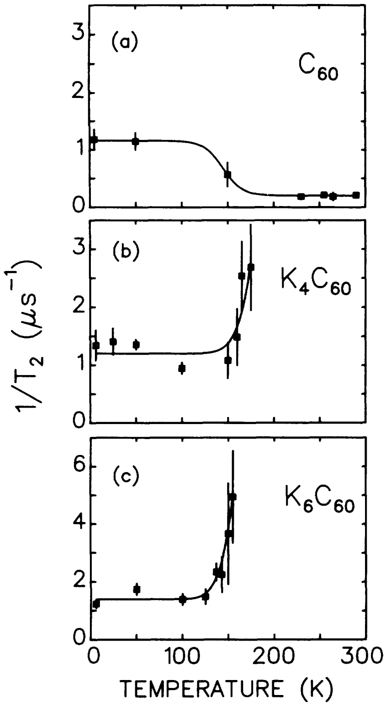

FIG. 2. (a) The T_2^{-1} linewidths of muonium in C_{60}, K_4C_{60}, and K_6C_{60}. The data were taken in a transverse magnetic field of 10.7 mT for C_{60} and at 0.5 mT for K_4C_{60} and K_6C_{60}. The curve in (a) is a guide to the eye, whereas in (b) and (c) the curves are fits to Eq. (2).

the μSR time spectra assuming an exponential decay of the muonium precession amplitude $R_{\mathrm{Mu}}(t)=\exp[-t/T_2]$. In pure C_{60} the linewidth at low temperature [1.1(2) μs^{-1}] is close to that observed in the K-doped material even though the naturally abundant isotopes of K have nuclear moments. The weak influence of the K on the linewidth and muon-electron hyperfine parameter leads us to a model in which a Mu atom is trapped on the inside of the C_{60} cage. In this case the dominant source of line broadening at low temperatures is likely to be the weak magnetic dipolar interaction with ^{13}C nuclei which have a natural isotopic abundance of 1.1%. The magnitude of the observed relaxation rate is about twice that expected from a simple calculation of the average nuclear dipolar field at the center of the C_{60} molecule, indicating there may be additional effects from the zero-point motion of muonium, the extended nature of the muonium electron, and the influence of more distant neighbors. Note from Fig. 2(a) that the linewidth in pure C_{60} decreases above about 100 K. This is consistent with motional averaging of the anisotropic nuclear dipole interaction as a result of the reorientation of the C_{60} cage which occurs above this temperature [5].

Note that the linewidths in K_4C_{60} and K_6C_{60} have distinctly different temperature dependences [see Figs. 2(b) and 2(c)]. Above about 175 K in K_4C_{60} and 150 K in K_6C_{60} the muonium lines broaden abruptly and are not observable at higher temperatures. Considering that the expected band gap in K_6C_{60} is predicted to be small (0.48 eV) [9], a reasonable explanation for the line broadening is that it is due to interaction with thermally excited carriers. In this case the linewidth may be written

$$T_2^{-1}=\sigma v n+\lambda_0=a(k_BT)^2\exp[-E_g/2k_BT]+\lambda_0\,, \qquad (2)$$

where σ is the total cross section for spin exchange or charge transfer, n is the number density of thermally excited carriers [24], v is the mean thermal velocity of the carriers, λ_0 is the background relaxation, a is a constant, and E_g is the electronic band gap. The values of E_g in Table I should be considered a lower limit on the real band gap, since there may be other mechanisms for line broadening which have a lower activation energy—for example, interaction with bound excitons or muonium ionization. The lack of any enhancement in T_2^{-1} in pure C_{60} up to 300 K is reasonable since the band gap in pure C_{60} observed by photoemission [25] is considerably larger (about 2.1 eV). Figures 2(b) and 2(c) suggest that the electronic structures of K_4C_{60} and K_6C_{60} are similar, i.e., they are both nonconductors with relatively small band gaps. It is interesting to note that the gap values in Table I are close to the gap or pseudogap seen in photoemission studies on K-doped thin films of C_{60} [25]. Our result for K_4C_{60} is in striking disagreement with band-structure calculations [11], which indicate that K_4C_{60} should be a good metal. It should be noted that the NMR $1/T_1$ spin relaxation rate in Rb_4C_{60} is non-Koringa-like, indicative of a nonmetal, but is unusually large [26]. One possible explanation for the insulating behavior of K_4C_{60} is that electron-electron correlations are important in this class of material. A naive application of the results in Ref. [12] to K_4C_{60} suggests that it may be a Mott-Hubbard insulator with a gap of a few hundred meV [27]. There are other possibilities. For example, it has been speculated that a gap opens up at the Fermi surface as a result of a distortion caused by a charge-density wave [28], but so far there is no confirmation of this.

Finally, we note that molecular-beam and mass spectrometer experiments [29] have demonstrated that it is possible to form large carbon clusters such as C_{60} with atoms such as La, K, Ne, and He trapped inside the carbon cage. However, little structural information is presently available on such endohedral complexes and even less is known about the physical properties of compounds produced from such complexes. Our results on muonium highlight the dramatic differences one may expect in the local electronic structure depending on the location of the impurity atom. They also suggest it may be possible to form endohedral complexes efficiently in the solid state by ion implantation.

In conclusion, we have carried out a μSR investigation of positive muons implanted into C_{60}, K_4C_{60}, and K_6C_{60}. In all three cases a fraction of the implanted muons form paramagnetic centers with large isotropic hyperfine parameters which are close to that of a muonium atom in vacuum. The similarity of the centers suggests that the muonium atom is endohedral. The mere observation of muonium establishes that all three materials are nonmagnetic and nonconducting at low temperatures.

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