ERRATA

Molecular Dynamics of the Muonium-C_{60} Radical in Solid C_{60} [Phys. Rev. Lett. 68, 1347 (1992)]

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The notation μ^+-C_{60} was mistakenly typeset as a substitution for muonium-C_{60} or MuC_{60}, where Mu stands for muonium atom, the neutral atom composed of a muon and an electron.

This substitution unfortunately occurred throughout the paper. The corrected Letter is reprinted below.

Molecular Dynamics of the Muonium-C_{60} Radical in Solid C_{60}

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The molecular dynamics and electronic structure of the muonium-C_{60} radical in crystalline C_{60} have been studied using muon spin rotation and relaxation. At room temperature muonium-C_{60} appears to be in a state of quasifree rotation. At the critical temperature $T_S=260$ K the local electronic structure and molecular dynamics change discontinuously as expected for a first-order phase transition. The correlation times for reorientation are remarkably close to those determined by recent NMR experiments on C_{60}, suggesting that the molecular dynamics of muonium-C_{60} are strongly coupled to those of its C_{60} neighbors.

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The observation of C_{60} and other fullerenes by Kroto *et al.* [1] has led to wide variety of studies of closed carbon clusters. The subsequent production of bulk quantities of relatively pure C_{60} has greatly accelerated the process [2]. An intense effort is being made to understand the unique structural and electronic properties of pure crystalline C_{60}, which is a semiconductor, and C_{60} doped with other atoms. High-resolution x-ray diffraction [3] has determined that pure C_{60} at room temperature has an fcc crystal structure in which the large weakly interacting C_{60} molecules are orientationally disordered. Below 249 K there is a transition to an orientationally ordered phase accompanied by a small change in the lattice constant of 0.044 Å [4]. Although early calorimetry studies [5] indicated the transition is second order, heat-capacity anomalies have now been reported at 260 [3] and 252 K [6], which are characteristic of a first-order transition. Information on the molecular dynamics has been obtained principally from NMR studies [7,8], which show a very narrow ^{13}C line at room temperature, indicating rapid rotation of the C_{60} molecules. This is confirmed by recent quasielastic neutron scattering [9]. As the temperature is lowered below about 190 K the NMR line gradually broadens due to a gradual slowing down of the motion. Although no anomaly is observed in the $1/T_2$ linewidth or the chemical-shift tensor, at the transition there is a sharp but continuous increase in the $1/T_1$ spin-relaxation rate below 260 K [7].

Little is known about the electronic structure and molecular dynamics of simple isolated impurities in C_{60}, such as atomic hydrogen. In conventional semiconductors muon spin rotation (μSR) and related methods have been used to obtain detailed information on the structure and dynamics of isolated muonium (μ^+e^-), whose properties are closely related to those of hydrogen [10]. A previous muon-spin-rotation experiment revealed signals from two distinct paramagnetic centers in a commercial sample of C_{60} which had a 10%–15% C_{70} contamination [11]. One signal has a large isotropic muon hyperfine parameter of 4256 MHz, which is 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 muonated radicals [12]. In this Letter we report a study of the molecular dynamics and electronic structure of the 325-MHz center in a highly crystalline sample of pure C_{60}. We show that the 325-MHz signal at room temperature is a muonium-C_{60} (MuC_{60}) radical in crystalline C_{60} undergoing quasifree rotation. Clear discontinuities are observed at $T_S=260$ K, confirming that the phase transition is first order. The correlation times for reorientation of MuC_{60} above and below the phase transition are almost identical to the NMR results on C_{60} [7,8].

The experiment was performed on the M15 beam line at TRIUMF, which provides a beam of nearly 100% spin-polarized muons with a momentum of 28 MeV/c. Muons were stopped in a 500-mg sample of high-purity C_{60} powder prepared using standard techniques [2]. The sample was vacuum dried overnight at 250 °C, a process which results in 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} and no trace of $C_{60}O$. The sample was cooled using a He-gas-flow cryostat.

Conventional transverse-field μSR data [13] were taken in an applied magnetic field of 1.5 T. We assume that the MuC_{60} radical has an axial hyperfine interaction and that gyromagnetic ratios for the muon and electron ($2\pi\gamma_\mu$ and $2\pi\gamma_e$, respectively) are isotropic. For a fixed orientation of the symmetry axis with respect to a large external magnetic field $\mathbf{H}$ the muon spin will precess about an effective magnetic field whose components parallel and perpendicular to $\mathbf{H}$ are approximately

$$H_\parallel^\mu = H \mp [A_s - A_p(1-3\cos^2\theta)]/2\gamma_\mu\,, \tag{1}$$

$$H_\perp^\mu = \pm 3A_p\sin\theta\cos\theta/2\gamma_\mu\,, \tag{2}$$

where A_s and A_p are the isotropic (s) and anisotropic (p) hyperfine parameters, θ is the angle between $\mathbf{H}$ and the axis of symmetry, and the upper or lower sign corresponds to the projection of the electron spin along $\mathbf{H}$. If θ is random with respect to $\mathbf{H}$ and $A_p \ll A_s$, then one expects a powder-pattern line shape for each of the two possible muon precession frequencies, a higher one ν^- and a lower one ν^+. On the other hand if $H_\perp$ is fluctuating with an autocorrelation time τ_c due to reorientation, such that $2\pi A_p \ll 1/\tau_c \ll 2\pi\nu^-$, one expects a Lorentzian line shape, which for ν^+ has a width

$$1/T_2 = \sigma_\parallel^2\tau_c + \tfrac{1}{2}\sigma_\perp^2\tau_c/[1+(2\pi\nu^+\tau_c)^2]\,, \tag{3}$$

where the second term is the $1/T_1$ contribution arising from the fluctuating transverse components of the effective field. The parameters $\sigma_\perp^2 = \frac{3}{10}(2\pi A_p)^2$ and $\sigma_\parallel^2 = \frac{1}{5}(2\pi A_p)^2$ are proportional to the mean-squared deviations for $H_\parallel^\mu$ and $H_\perp^\mu$, respectively.

Figure 1 shows the Fourier transform of the μSR spectrum at various temperatures in the region of the lower frequency ν^+. Near room temperature the μSR lines are very narrow with a width close to that measured for muonated organic radicals in liquids [12]. Below $T_S=260$ K a new signal appears which is characterized by a

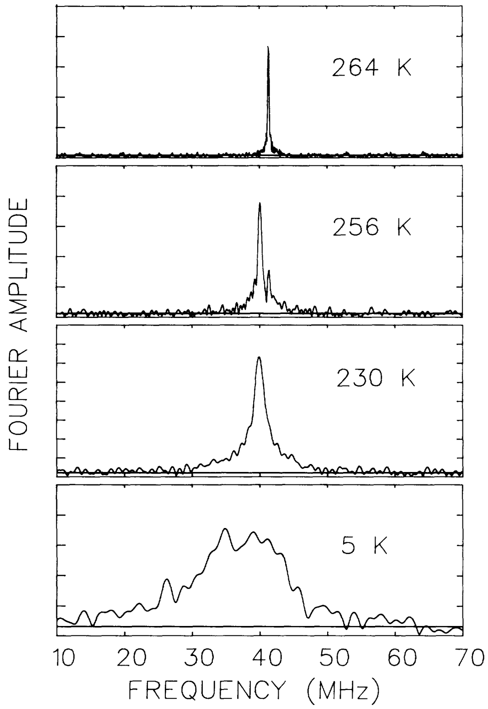

FIG. 1. μSR frequency spectra MuC_{60} in solid C_{60} near ν^+. Below the phase transition at $T_S=260$ K a new line appears at a slightly lower frequency and with increased linewidth.

slightly larger A_s and significant line broadening, attributed to slowing down of the reorientation. There is a region of temperature between 242 and 265 K where the signals coexist. The observation of a significant coexistence region for a first-order transition implies that part of the high-T phase is pinned by defects or (undetected) impurities during cooling. The Gaussian line shape at 5 K indicates that a distribution of hyperfine parameters, arising from inequivalent orientations of the symmetry axis with respect to the crystalline axes, effectively smears the powder pattern. The overall width of the line indicates that A_p is a few MHz which is typical for muonated radicals [14]. Figures 2(a) and 2(b) show the discontinuity in the fitted Lorentzian linewidth $1/T_2$ and the average hyperfine parameter A_s at 260 K.

The correlation times for reorientation below T_S [see Fig. 2(c)] were estimated by fitting the time evolution of the muon spin polarization using the formula [15]

$$G_{xx}(t)=\exp[-\sigma_\parallel^2\tau_c^2(e^{-t/\tau_c}-1+t/\tau_c)] \qquad (4)$$

to describe the dephasing and resulting decay of the amplitude of precession. Although this expression neglects the $1/T_1$ contribution to the linewidth in Eq. (3), it is valid for arbitrarily large τ_c. Note that the Fourier transform of $G_{xx}(t)$ is the line shape. In all the fits the static linewidth parameter $\sigma_\parallel=21.2(1.1)$ μs^{-1} was obtained from an average of the lowest-temperature runs so that the only free parameter was τ_c. The correlation times between 200 and 250 K were fitted with an Arrhenius law, $1/\tau_c=\Lambda\exp[-E_a/k_BT]$, yielding $\Lambda=6.4(2.4)\times10^{12}\ s^{-1}$ and $E_a=219(7)$ meV. At 200 K, $\tau_c=52(17)$ ns which is remarkably close to the NMR result [7] of 64 ns for C_{60}. This is surprising considering that the added Mu atom is estimated to be approximately a C-H bond length on the outside of the C_{60} molecule [16] where it would be expected to hinder the reorientation of the molecule. This suggests that the reorientation of MuC_{60} is coupled to the motion of its C_{60} neighbors such that the molecular dynamics of the MuC_{60} impurity are controlled by those of its neighbors. At 200 K there appears to be a slight change in slope in the temperature dependence of A_s and $1/\tau_c$. One possibility is that at lower temperatures the MuC_{60} is no longer able to execute large-angle reorientations but is restricted to jumps within a finite solid angle. Although an additional phase transition is also a possibility there is no evidence for such a transition from other studies. There are several calculations on the nature of the orientational ordering in C_{60} [17-20]. Most of them predict a single first-order transition below room temperature whereas one calculation [20] finds an additional second-order transition at lower temperatures [20]. However, none of the calculations is accurate enough yet to predict the simple-cubic phase indicated by x-ray diffraction [3].

Figure 3 shows the field dependence of the measured muon $1/T_1$ spin-relaxation rate as a function of magnetic field for two temperatures below T_S. The solid curves are fits with the second term in Eq. (3). Note that the peak position occurs at a magnetic field where $\nu^+=0$, whereas

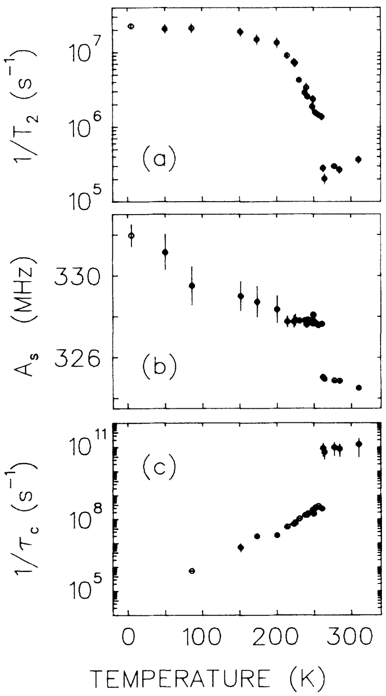

FIG. 2. (a) The μSR $1/T_2$ linewidth, (b) the isotropic hyperfine parameter, and (c) the reorientation rate of the MuC_{60} radical in crystalline C_{60}. Note the clear discontinuity at 260 K.

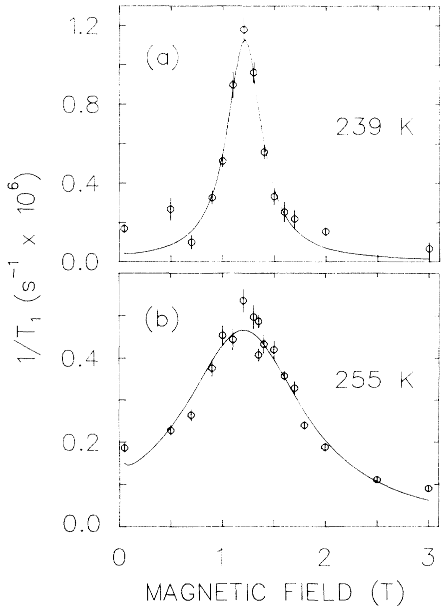

FIG. 3. The $1/T_1$ muon spin-relaxation rate of MuC_{60} as a function of magnetic field.

the width of the peak is determined by τ_c. The correlation times measured in this way agree within a factor of 2 with those obtained from the transverse-field data, confirming that the fluctuating hyperfine field is the dominant source of muon spin relaxation and line broadening below T_S.

Above T_S the motion changes suddenly as evidenced by the discontinuous behavior of $1/T_2$ and A_s [see Figs. 2(a) and 2(b)]. There is good evidence that $\mathrm{MuC_{60}}$ is in a state of quasifree rotation in the high-temperature phase, as has been proposed for the $\mathrm{C_{60}}$ molecules [7,8]. For instance, the linewidth for $\mathrm{MuC_{60}}$ above T_S is close to that observed for other muonated organic radicals in liquids [12] and increases with increasing temperature. The latter observation cannot be explained by Eq. (3) which predicts a monotonic decrease in the linewidth for increasing $1/\tau_c$ or temperature. On the other hand if there is very rapid rotation of the radical the contribution from the fluctuating hyperfine field is negligible and the μSR linewidths are dominated by electron-spin relaxation induced by the coupling of the electron spin to the molecular-rotational-angular momentum [21]. The muon $1/T_2$ linewidth in this case can be approximated as

$$1/T_2=\sigma_{\mathrm{SR}}^2\tau_c/[1+(2\pi\nu_e\tau_c)^2]\,, \tag{5}$$

where σ_{SR} is the electron-spin-molecular-rotation coupling constant and $\nu_e=\gamma_e H$ is the Zeeman frequency of the electron. The relaxation-rate data above T_S were fitted with Eq. (5) assuming an Arrhenius behavior for $1/\tau_c$, yielding $\sigma_{\mathrm{SR}}=4.9(1.0)\times10^8\ \mathrm{s^{-1}}$, $\Lambda=5.1(7)\times10^{12}\ \mathrm{s^{-1}}$, and $E_a=98(16)$ meV. The correlation times above T_S shown in Fig. 2(c) were obtained from the measured $1/T_2$ linewidths using this fitted value for σ_{SR}. At 300 K, $\tau_c=8.5(2.0)$ ps. This is in good agreement with NMR results [7,8], although we find the preexponential factors for $\mathrm{MuC_{60}}$ are about the same above and below T_S with the main change occurring in the activation energy.

The discontinuous change in the isotropic hyperfine parameter at T_S shows that the electronic structure of $\mathrm{MuC_{60}}$ changes suddenly at the phase transition. Based on what is known about structure and intramolecular motion of muonated radicals [22] it is reasonable to assume that at the phase transition there is a sudden change in the C-Mu bending motion and/or C-Mu bond length. Since the lattice constant at T_S changes by only a small amount (0.044 Å) [4] it suggests that there is a change in the distribution of angles between the C-Mu bond and the crystalline axes which are being sampled over the path of rotation. This is consistent with a sudden change in the motion from one characterized by jumping between specific crystalline directions to one involving quasifree rotation.

In conclusion, we have carried out a μSR investigation of the molecular dynamics of the $\mathrm{MuC_{60}}$ radical in solid $\mathrm{C_{60}}$. Above the structural phase transition at $T_S=260$ K the radical appears to rotate rapidly as if it were in a liquid with correlation times of about 10 ps, whereas just below T_S the correlation time is more than a 100 times longer. The molecular dynamics of $\mathrm{MuC_{60}}$ appear to be controlled by those of its $\mathrm{C_{60}}$ neighbors indicating strong dynamic correlations. Clear discontinuities in both the local electronic structure and in the molecular dynamics are observed at T_S, confirming that the orientational ordering at 260 K is a first-order transition.

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