Coherence Peak and Superconducting Energy Gap in Rb_3C_{60} Observed by Muon Spin Relaxation

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Muon spin relaxation resulting from spin exchange scattering of endohedral muonium (μ^+e^-) with thermal electronic excitations has been observed in the fullerene superconductor Rb_3C_{60}. The temperature dependence of T_1^{-1} shows a coherence peak just below T_c and can be fit to the conventional Hebel-Slichter theory for spin relaxation in a superconductor with a broadened BCS density of states. The average energy gap for electronic excitations, $\Delta/k_B = 53(4)$ K or $2\Delta/k_BT_c = 3.6(3)$, is consistent with the BCS weak-coupling limit.

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Solid C_{60} and the family of related compounds exhibit fascinating structural and electrical properties. Perhaps most surprising is the fact that A_3C_{60} (where A is an alkali metal) undergoes a superconducting transition [1] with a T_c which is surpassed only by the cuprates. It is not yet clear to what extent these materials are related to exotic superconductors such as heavy fermions and cuprates. The nature of the superconducting ground state is often revealed through studies of the low energy electronic excitations. For example, the BCS theory predicts an energy gap (2Δ) for excitations which in the weak coupling limit satisfies $2\Delta/k_BT_c = 3.52$. There is still uncertainty about the value of the gap and the superconducting density of states (SDOS) in A_3C_{60}. The most direct method, point contact tunneling, finds a very large gap in both K_3C_{60} and Rb_3C_{60} corresponding to $2\Delta/k_BT_c = 5.2$ [2] and evidence for a broadened BCS-like density of states. Measurements of the far infrared reflectivity on Rb_3C_{60} have determined that $2\Delta/k_BT_c$ is in the range 3-5 [3]. Recent absolute reflectivity measurements indicate $2\Delta/k_BT_c$ equals 3.6 and 2.98 for K_3C_{60} and Rb_3C_{60}, respectively, and thus is close to the BCS weak-coupling limit [4]. These values are also near those obtained from nuclear spin relaxation measurements in Rb_3C_{60} and K_3C_{60} where $2\Delta/k_BT_c$ equals 3.1 and 4.0, respectively [5]. However, the coherence peak or Hebel-Slichter peak in T_1^{-1}, which is a characteristic feature of conventional superconductors [6,7], is not observed. Since the already small NMR relaxation rate in fullerene superconductors may be influenced by nonelectronic processes (e.g., molecular reorientation as in pure C_{60} [8]), it is important to have results from other microscopic spin probes.

The positive muon is an alternative probe. However, because of its short lifetime (2.2 μs) it is generally insensitive to slow spin relaxation resulting from the interaction with electronic excitations in a normal metal (i.e., Korringa relaxation). Although a muonium atom (μ^+e^-) should have a much greater sensitivity [9] due to the large hyperfine interaction with a single bound electron, no such state in a metal has been identified until now. Apparently the conduction electrons in a metal act to screen the positive charge of the muon such that no local electronic moment exists on the muon. Our recent identification [9] of endohedral muonium (a muonium atom trapped inside the C_{60} cage denoted by Mu@C_{60}) in the insulating phases C_{60}, K_4C_{60}, K_6C_{60} led us to the present experiment to search for Mu@C_{60} in the metallic phase Rb_3C_{60}. Since the conduction electrons in this unusual metal are confined to the carbon shell it seemed reasonable that a muon in the middle region of the cage could form a stable bound state with a single electron giving rise to unusually large T_1^{-1} spin relaxation.

In this paper we report the observation of muon T_1^{-1} spin relaxation in the normal and superconducting states of Rb_3C_{60}, which we attribute to endohedral muonium undergoing spin exchange scattering with electronic excitations. The temperature dependence of T_1^{-1} fits the theory of Hebel and Slichter [6,7] for spin relaxation in a BCS superconductor with a broadened density of states. The gap for electronic excitations $\Delta/k_B = 53(4)$ K corresponds to $2\Delta/k_BT_c = 3.6(3)$ which is consistent with the BCS weak-coupling limit.

The experiment was performed on the M15 beam line at TRIUMF which provides nearly 100% spin-polarized positive muons with a momentum of 28 MeV/c. The starting material was high purity C_{60} powder prepared using standard techniques [10]. The process for Rb doping is described elsewhere [11]. There was evidence for a small impurity phase (5%) whose x-ray lines could be indexed to those of Rb_4C_{60}. This is unimportant for the present measurements since the muon spin relaxation (μSR) signals from Rb_4C_{60} and Rb_3C_{60} are clearly distinguished. The magnetization curve showed an onset of superconductivity at 29.4 K with shielding and Meissner

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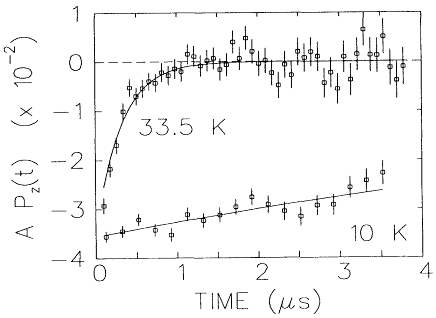

FIG. 1. Muon spin relaxation of endohedral muonium in Rb_3C_{60} above and below T_c in a longitudinal magnetic field of 1.5 T. The y axis is the muon spin polarization $P_z(t)$ of muonium multiplied by an experimental constant A which is negative for our geometry.

fractions of about 60% and 8%, respectively.

In order to prevent any exposure to air the sample, in the form of a lightly pressed pellet (15 mm diameter) weighing approximately 100 mg, was sealed in an Al vessel in an atmosphere of 90% Ar and 10% He. The vessel had thin 25 mm diam Capton windows which allowed stray muons which missed the sample to trigger a veto scintillation detector directly behind the sample. In this way the background signal from such muons was effectively eliminated. The temperature measurements were made with a calibrated carbon glass resistor located 2.5 cm downstream of the sample vessel in a flow of cold He gas.

Conventional muon spin rotation/relaxation spectra [12] were taken with the muon spin polarization both transverse and parallel to the applied magnetic field. The transverse field (TF)-μSR spectra at 1 T showed a single precession signal at a frequency close to that of a free muon but with an amplitude about 70% of that in a normal metal such as Al. This reduced precession amplitude, which is similar to that reported in K_4C_{60} and K_6C_{60} [9], is indirect evidence for muonium in Rb_3C_{60}. Direct detection of muonium in a metal via TF-μSR is difficult because precession signals are rapidly damped due to electron-electron spin exchange. The linewidth of the observed signal under conditions of field cooling increased sharply at 29 K, the T_c determined from magnetization. This broadening is attributed to field inhomogeneities resulting from the Abrikosov flux lattice in a type II superconductor [7]. From the fitted rms deviation in the internal field $\Delta B = 0.72$ mT we estimate the London penetration depth to be 3700 Å which is close to a previous μSR measurement of 4200 Å for Rb_3C_{60} [13].

In order to observe muonium directly a large magnetic field was applied along the initial direction of muon spin polarization. Just above T_c a fast relaxing component of the muon spin polarization was present which we attribute to muonium undergoing spin exchange with the conduction electrons (see Fig. 1). From the amplitude of the

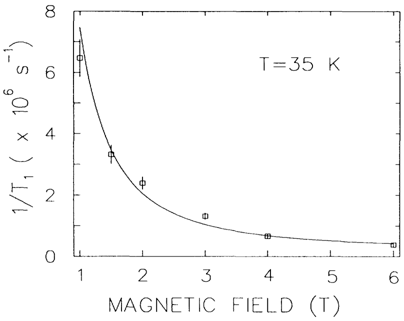

FIG. 2. The magnetic field dependence of T_1^{-1} in Rb_3C_{60}. The solid curve is a fit to the muonium spin exchange model (see text).

relaxing component we estimate that about 15% of the implanted muons contribute to the signal, which is similar to the fraction of muons which form endohedral muonium in the insulating phases of K_xC_{60} [9]. The field dependence of T_1^{-1} shown in Fig. 2 is characteristic of a paramagnetic species undergoing electron spin exchange [14] in which case

$$T_1^{-1} \approx \frac{A_\mu^2 \lambda_{ex}}{2[A_\mu^2 + (\gamma_\mu + \gamma_e)^2 H^2]}, \tag{1}$$

where A_μ is the muon-electron hyperfine coupling, λ_{ex} is the electron spin exchange rate, γ_μ and γ_e are the gyromagnetic ratios for the muon and electron, respectively, and H is the applied magnetic field. Equation (1) may be understood by noting that the coupling between the muon spin and the conduction electrons is indirect,

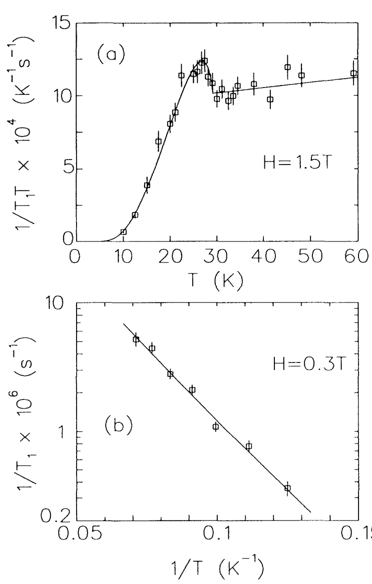

FIG. 3. (a) $(T_1T)^{-1}$ in Rb_3C_{60} at a magnetic field of 1.5 T. The solid curve is a fit to the theory of Hebel and Slichter with a broadened density of states. (b) Arrhenius plot of T_1^{-1} in a magnetic field of 0.3 T.

acting through the bound electron via the muonium hyperfine interaction. Increasing H effectively decouples the muon and electron spins of muonium and thus suppresses the muon spin relaxation rate. Spin exchange scattering with electronic excitations is possible for $Mu@C_{60}$ because the conduction electron wave functions have the $2p_z$ character of carbon atoms and thus have a finite amplitude at the interior surface of the C_{60} cage. The observed field dependence was not as strong as predicted from our model for the spin relaxation, for which Eq. (1) is only an approximate solution. A slightly better fit to the data was obtained by including a small field independent term $2.2(4)\times10^5$ s^{-1} (see solid curve in Fig. 2) with $\lambda_{ex}=6(1)\times10^8$ s^{-1} and A_μ fixed at 4340 MHz the value found in C_{60} and K_4C_{60} [9]. A small direct coupling between the muon and conduction electron spins could account for such a field independent term but this does not affect our results provided that T_1^{-1} scales with λ_{ex} as is apparent from the temperature dependence of $(T_1T)^{-1}$ shown in Fig. 3.

The solid curve in Fig. 3(a) is a fit to the following functional form:

$$(T_1T)^{-1}=a+bT;\quad T>T_c\,,$$
$$=(a+bT)\frac{1}{k_BT}\int_0^\infty f(E)[1-f(E')][N_s(E)N_s(E')+M_s(E)M_s(E')]dE;\quad T<T_c\,, \tag{2}$$

where

$$N_s(E)=\mathrm{Re}\{(E-i\Gamma)/[(E-i\Gamma)^2-\Delta^2]^{1/2}\}\,, \tag{3}$$

$$M_s(E)=\mathrm{Re}\{\Delta/[(E-i\Gamma)^2-\Delta^2]^{1/2}\}\,, \tag{4}$$

and $f(E)$ is the Fermi-Dirac function and $E'-E=hA_\mu/2$ is the energy difference between the initial and final scattering states. $N_s(E)$ is the BCS superconducting density of states broadened by a phenomenological parameter Γ [15] whereas $M_s(E)$ is an additional term [6,7] arising from the BCS coherence factor. The fitted parameters $a=1.0(2)\times10^5$ K^{-1}s^{-1} and $b=4(2)\times10^2$ K^{2}s^{-1} are determined by the relaxation rate in the normal state. Below T_c we assume $\Delta(T)$ has the conventional BCS form [16]. The value for $\Delta(T=0)$ depends slightly on the temperature dependence we assume for Γ. For example, if $\Gamma(T)=\Gamma_0(T/T_c)^n$ with $n=0$, 1, or 3 we obtain $\Delta/k_B=56$, 58, or 65 K, respectively, and $\Gamma_0/k_B=5.8$, 7.0, 8.3 K, respectively. The fitted transition temperature $T_c=29.2$ K agrees with that determined from the T_2^{-1} line broadening mentioned above. Note that in the normal state $(T_1T)^{-1}$ increases slightly with temperature. This deviation from the Korringa relation has also been observed in the NMR relaxation rate in A_3C_{60} [8,17] and attributed to the influence of lattice expansion on the density of states at the Fermi energy [17].

Just below T_c $(T_1T)^{-1}$ peaks at about 1.25 times the extrapolated normal state value compared with the ratio of 2.8 predicted from Eq. (2) if there were no broadening, i.e., $\Gamma=0$. Such a coherence peak is predicted in the Hebel-Slichter (HS) theory for a BCS superconductor [6,7]. It arises from the divergent nature in the SDOS at the gap edge which tends to enhance the spin exchange scattering rate just below T_c. At much lower temperatures the presence of a gap leads to an exponential reduction in the number of quasiparticle excitations and thus suppresses the spin relaxation rate. In a conventional single band BCS superconductor the SDOS can be broadened by gap anisotropy or by a short quasiparticle lifetime leading to a reduced amplitude of the HS peak [7]. Simple gap anisotropy is unlikely to be effective in reducing the HS peak here since the short mean free path in A_3C_{60}, resulting from the orientational disorder [18], should eliminate the gap structure and resultant broadening in the SDOS. Quasiparticle lifetime broadening is not normally observed in weakly coupled BCS superconductors although the high transition temperature in A_3C_{60} might enhance this effect [19]. Band structure effects may also broaden the SDOS. Mele and Erwin have developed a model for nodeless d-wave pairing in orientationally ordered A_3C_{60} using a realistic Fermi surface and find a broad SDOS [20]. Recently the possible influence of multiband superconductivity has been considered and used to explain the high value of $2\Delta/k_BT_c$ seen in tunneling [21]. This added structure in the SDOS should also diminish the HS peak compared to a single band model.

Our estimate of the gap depends on the assumptions we make for the temperature dependence of Δ and Γ. In order to get a more precise value for $\Delta(T=0)$ measurements were also performed at lower temperatures where these dependencies are less important. This was achieved by lowering the magnetic field so that $(T_1T)^{-1}$ is increased [see Eq. (1) and Fig. 2] and thus observable down to lower temperatures. Figure 3(b) shows the Arrhenius plot of T_1^{-1} at 0.3 T. The solid curve is a fit to the HS theory with the ratio of a/b fixed at the value from the data taken at 1.5 T. The best fit yields $a=8.5(1.0)\times10^5$ K^{-1}s^{-1} and $\Delta/k_B=53(4)$ K where the error on Δ is dominated by the uncertainty in $\Gamma(T)$ discussed above. For comparison, a fit to an Arrhenius law gives an activation energy of $E_a/k_B=51(3)$ K. Our best estimate for $2\Delta/k_BT_c$ is then 3.6(3), which is consistent with the BCS weak-coupling limit and similar to that obtained from far infrared reflectivity and NMR. It does not agree with point contact tunneling experiments [2] where $2\Delta/k_BT_c=5.2$, although we do find evidence for significant broadening in the density of states near T_c.

In conclusion, we have observed muon spin relaxation in Rb_3C_{60} which we attribute to endohedral muonium. The temperature dependence of T_1^{-1} is consistent with a picture in which muonium undergoes spin exchange scattering with thermal electronic excitations. The data are consistent with the Hebel-Slichter theory for spin relaxation in a conventional superconductor with a broadened BCS density of states. The ratio of $2\Delta/k_B T_c = 3.6(3)$ is consistent with the BCS weak-coupling limit.

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