Antiferromagnetic ordering in the expanded (NH$_3$)Rb$_3$C$_{60}$ fulleride

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Abstract

The magnetic behavior of the ammoniated alkali fulleride (NH$_3$)Rb$_3$C$_{60}$ is studied by means of $\mu$ + spin relaxation ($\mu$ +SR) spectroscopy. The observation of a strongly damped oscillating component in the low-temperature zero-field $\mu$ +SR spectra reveals that its ground state is that of an ordered antiferromagnet, characterized by large spatially inhomogeneous effects. The temperature dependence of the $\mu$ + spin precession frequency is consistent with that of a conventional 3D Heisenberg antiferromagnet ($T_N \approx 51$ K). The cooling rate of the sample affects sensitively the ordering of the magnetic moments, a behavior that can be attributed to the influence of the orientational order of the fullerene units on the exchange interactions.

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I. Introduction

Intercalation of the K$_{3-x}$Rb$_x$C$_{60}$ superconducting fullerenes with ammonia results in an anisotropic lattice expansion (the crystal structure changes from face-centered cubic, FCC, to face-centered orthorhombic, FCO) and suppression of superconductivity [1]. The proximity of these systems to a metal–insulator transition has been ascribed to the combined effects of increased interfullerene separation and crystal symmetry lowering. Large interfullerene separations lead to reduced widths, $W$, of the $t_{1u}$ conduction band and result in large ($U/W$) ratios (where $U$ is the on-ball Coulomb repulsion energy), while crystal symmetry lowering lifts the triple degeneracy of the $t_{1u}$ C$_{60}$ molecular orbitals and significantly decreases the critical value, ($U/W$)$_c$ (from $\sim 2.5$ to $\sim 1$) for the transition to a Mott insulating state [2]. Positive-muon spin relaxation ($\mu$ +SR) studies had revealed that the ground state of the (NH$_3$)K$_3$C$_{60}$ fulleride is antiferromagnetic (AF) with a Néel temperature, $T_N \approx 40$ K [3]. In addition, electron paramagnetic resonance (EPR)
measurements have shown that as the Rb concentration, $x$ increases in the $(\text{NH}_3)_x\text{K}_{3-x}\text{Rb}_x\text{C}_{60}$ series, $T_N$ first increases and then decreases [4]. This result is in accordance with that expected from the Mott–Hubbard phase transition diagram with an AF ground state, where $T_N$ increases for relatively small $U/W$ (itinerant regime) and decreases for larger $U/W$ (localized regime) [5].

Below $T_S\approx 150$ K, the parent $(\text{NH}_3)_3\text{K}_3\text{C}_{60}$ fulleride undergoes an orientational ordering transition to an orthorhombic structure derived by doubling the lattice constants of the high-temperature phase along all the three axes [6]. The K$^+$–NH$_3$ pairs orient along the $\langle 110 \rangle$ direction in an antiferroelectric fashion [6], while the C$_{60}$ units adopt two distinct orientations related by 90$^\circ$ about $c$ and are antiferrorotationally ordered along $a$ and $b$ (Fig. 1) [7]. There is a remarkable correlation between the orientational ordering motif of C$_{60}$ and the observed 3D AF structure, which arises through alternate stacking of 2D sheets of C$_{60}$, which order ferrorotationally (antiferromagnetically) along $\langle 110 \rangle$ and antiferrorotationally (ferromagnetically) along $\langle 1\overline{1}0 \rangle$ [7].

In the present work, we have characterized the AF ground state of the $(\text{NH}_3)_3\text{Rb}_3\text{C}_{60}$ fulleride with the $\mu^+$ SR technique. The effect of the cooling protocol on the magnetic ordering transition has been also studied.

2. Experiments

$(\text{NH}_3)_3\text{Rb}_3\text{C}_{60}$ was synthesized by dissolving a stoichiometric amount of C$_{60}$ and Rb metal into dry liquid ammonia kept at $-65^\circ$C. Subsequently, ammonia was evaporated very slowly over about 1 week, while the excess ammonia was removed by a 10-min annealing at 100$^\circ$C to obtain almost phase pure samples [4].

The zero-field (ZF) and the longitudinal-field (LF) $\mu^+$ SR measurements were carried out at the Paul Scherrer Institute (PSI), Villigen, Switzerland. The powder samples were sealed under an argon atmosphere in silver sample holders equipped with indium seals and Mylar windows. The samples were placed inside a continuous-flow helium cryostat for measurements at temperatures down to 1.7 K. Two experiments were performed for which the sample was cooled from room temperature at cooling rates of 0.6 (slow cooling) and 2.8 K/min (rapid cooling), respectively.

3. Results and discussion

The time evolution of the ZF $\mu^+$ spin polarization, $P_\mu(t)$ of $(\text{NH}_3)_3\text{Rb}_3\text{C}_{60}$ at low (circles) and high (squares) temperatures after slow (a) and rapid cooling (b) is presented in Fig. 2. Above 60 K, the $\mu^+$ SR spectra were described with a double relaxation function (the product of an exponential and a Gaussian function). The exponential function describes the $\mu^+$ spin relaxation due to fluctuating electron spins, while the Gaussian depolarization is due to the presence of weak quasi-static hydrogen nuclear magnetic dipole moments, frozen into a disordered spin configuration with a field distribution, $\langle \Delta B^2 \rangle^{1/2} \sim 0.6$ Oe.

As the temperature decreases for the slowly cooled sample, a short-lived heavily damped component appears in the $\mu^+$ SR spectra, whose
depolarization gradually increases. Its shape is very similar to those observed in related fullerides, like (ND₃)K₃C₆₀ [3] and (TDAE)C₆₀ [8], showing a rapid decay at time $t \lesssim 0.6 \mu$s, a minimum between 0.7 and 0.9 $\mu$s, and a recovery at $t > 0.9 \mu$s. At long times ($t \gg 1.5 \mu$s), it continues to relax at an increasing rate with increasing temperature. These characteristics are reminiscent of the dynamic Kubo–Toyabe relaxation function, which could provide an appealing description of the low-temperature magnetic phase. However, it was deemed inappropriate on the evidence of complementary LF-μSR data (500 Oe), which reveal a complete recovery of the asymmetry. As the effect of applied LFs is the decoupling of the depolarization due to dynamic or fluctuating moments from that due to static components, we conclude that the origin of the observed relaxation in ZF is quasi-static in nature.

The data were thus fit using a two-component function, which incorporates a strongly damped oscillating and a slowly relaxing non-oscillating component:

$$P_\mu(t) = A_1 \left\{ (1/3) \exp\left( -\frac{1}{2} \sigma_1^2 t^2 \right) + (2/3) \exp\left( -\lambda_1 t \cos(2\pi \nu_\mu t + \phi) \right) \right\} \ + A_2 \exp\left( -\frac{1}{2} \sigma_2^2 t^2 \right),$$

(1)

where $A_1$ and $A_2$ are the asymmetries of the two components, $\nu_\mu$ is the Larmor frequency of the $\mu^+$ spin precession and $\phi$ its phase, while $\lambda_1$, $\sigma_1$, and $\sigma_2$ are the relaxation rates of the exponential and the Gaussian components, respectively. The physical origin of the first term in Eq. (1) lies with the fact that on average, for a completely random distribution of the directions of the internal field in a polycrystalline sample, 1/3 of all muons will experience an internal field along their initial spin direction and consequently they will not precess. The relaxation of this 1/3-tail is normally due to fluctuating field components perpendicular to the $\mu^+$ spin and is typically described by an exponential. Unusually, in the present case, where the LF data also reveal purely static behavior, the damping of the 1/3-tail is best fit by a Gaussian function. On the other hand, the damping, $\lambda_1$ of the oscillating term in Eq. (1) reflects the influence of static field inhomogeneities, which lead to loss of phase coherence of the precessing muons. Finally, the slowly relaxing component (third term in Eq. (1), $\sigma_2 \sim 0.08 \mu$s$^{-1}$) reflects the persistence of paramagnetic domains to the lowest temperature.

The appearance of the oscillating signal in the ZF-μSR spectra implies the onset of AF order at low temperatures, while the strong damping of the oscillating component reflects spatial disorder and inhomogeneity effects. The $\mu^+$ spin precession frequency is $\nu_\mu = 0.48(1)$ MHz at 2 K, corresponding to a static local field at the $\mu^+$ site, $\langle B_\mu \rangle = 35.7(7)$ Oe. The magnitude of $\langle B_\mu \rangle$ is marginally larger than the width of the local field distribution, $\langle \Delta B^2 \rangle^{1/2} = 30.9(9)$ Oe, extracted from the depolarization rate of the oscillating component, $\lambda_1 = 2.63(8)$ $\mu$s$^{-1}$. The large value for the ratio $\langle \Delta B^2 \rangle^{1/2}/\langle B_\mu \rangle$—a characteristic feature of all magnetic fullerides studied up to
now [3,8]—reveals the existence of large spatial inhomogeneities of the local field due to a number of physical reasons, including orientational disorder effects of the C₆₀ molecules. The temperature dependence of \( n_m \) is illustrated in Fig. 3(a). The solid line through the data points is a fit using the expression \( n_m = n_0 \left[ 1 - (T/T_N) \right]^{-\beta} \), with \( n_0 = 0.54(1) \) MHz, \( T_N = 51(1) \) K and \( \beta = 0.35(6) \). The critical exponent \( \beta \) approaches the value expected for a three-dimensional (3D) Heisenberg antiferromagnet (\( \beta = 0.367 \)). We note that the ordering temperature extracted from ZF-\( \mu^+ \)SR data at temperatures above 10 K were fitted with a heavily damped exponential function superimposed on the Gaussian component due to the quasi-static nuclear moments and are consistent with quasistatic magnetic order of a random nature as the muons experience a local field that peaks close to zero. Still the temperature at which freezing of the electronic spins occurs \( (T_f \sim 50 \) K) is comparable to that observed for the slowly cooled sample.

In addition, as the temperature decreases below \( T_N \), the volume fraction of the magnetically ordered domains grows at the expense of the paramagnetic ones, reaching a value of \( \sim 43\% \) at the lowest temperature for the slow-cooled sample. The coexistence of AF and PM domains in the samples even at very low temperatures reveals the inhomogeneous form of the magnetism. This is even more pronounced after fast cooling, when the volume fraction of the magnetic domains reaches only \( \sim 32\% \).

In conclusion, we have shown that \((\text{NH}_3)\text{Rb}_3\text{C}_60\) displays a transition below \( \sim 51 \) K to an ordered antiferromagnetic state, characterized by considerable spatially inhomogeneous effects. Rapid cooling does not affect the onset temperature of spin freezing but increases substantially the local field inhomogeneities to the point that the magnetic state is best characterized by random quasistatic order.
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