Direct observation of magnetic ordering in the $(CH_3NH_2)K_3C_{60}$ fulleride†

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The zero-field muon-spin-relaxation (ZF-μ^+SR) technique provides direct observation of the development of antiferromagnetic long range order in the hyperexpanded methylaminated fulleride salt, $(CH_3NH_2)K_3C_{60}$ below $T_N \sim 10$ K—coherent ordering of the electronic magnetic moments leads to a local field of ~25 G at the muon site at 1.2 K.

Superconducting transition temperatures, T_c are as high as 33 K at ambient pressure for chemically intercalated fullerides.[1] Despite the apparent simplicity of these materials, key features of their electronic properties, including the comparable magnitudes of the Fermi and phonon energies and the role of the large electron correlations are of considerable theoretical interest.[2] The metallic nature of cubic A_3C_{60} fullerides can be rationalised in terms of the triple orbital degeneracy of the LUMO t_{1u} states. No transition to a Mott–Hubbard insulator occurs and metallic behaviour is observed when the on-site Coulomb repulsion, U is smaller than ~2.5 W, where W is the t_{1u} bandwidth.[2] Noting that W in fullerides depends sensitively on the interfullerene separation, a transition to an AF Mott insulating state is anticipated when electron correlation effects become dominant. This occurs when the t_{1u} orbital degeneracy is removed through crystal symmetry lowering and/or the interfullerene separation increases sufficiently for (U/W) to exceed ~2.5. Ammoniation of alkali fullerides has been the only effective method till now to achieve large expansions of the fulleride unit cells, as neutral NH_3 molecules coordinate to the alkali ions in the octahedral sites of the cubic structure of A_3C_{60}.[3] The resulting $(NH_3)A_3C_{60}$ (A = K, Rb) phases in which the fulleride units both retain a charge of −3 and remain in electronic contact have proven key compounds for providing a test bed of existing theories of the metal–insulator (MI) transition at large interfullerene spacings.

We have recently reported the first successful attempt to insert in fulleride lattices a larger unit than ammonia‡—co-intercalation of K_3C_{60} with methylamine affords the phase $(CH_3NH_2)K_3C_{60}$ and retains a structure related to close-packing with significant electronic interactions between the $C_{60}{}^{3-}$ anions.[4] The orthorhombic $(CH_3NH_2)K_3C_{60}$ structure features a significantly anisotropic lattice expansion accompanied by a volume inflation of ~7% compared to K_3C_{60} (Fig. 1) with both effects expected to have a profound influence on the electronic properties of the fulleride phase. Magnetic susceptibility measurements have provided tentative evidence for the possible occurrence of a transition to an antiferromagnetic state at low temperature but these data suffer from contamination by paramagnetic impurity (defect) contributions, as commonly encountered in crystalline powders of fullerides which prevent precise identification of the ordering temperature. Here we report the unambiguous authentication of the low-temperature electronic state of $(CH_3NH_2)K_3C_{60}$ as that of a long-range-ordered antiferromagnet using the zero-field muon-spin-relaxation (ZF-μ^+SR) technique (see ESI†). The spin moment of the muon acts as a sensitive local probe of magnetism which produces coherent precession in the presence of static magnetic order.[5] Unexpectedly, the Néel temperature, T_N is found to be only ~10 K, drastically smaller than the ordering temperatures of the analogous ammoniated alkali fullerides[6,7] and consistent with much weaker exchange interactions between the $C_{60}{}^{3-}$ anions despite the comparable interfullerene spacings. This suggests that methlyamine coordination produces a qualitatively new mechanism for controlling the electronic properties of fullerides.

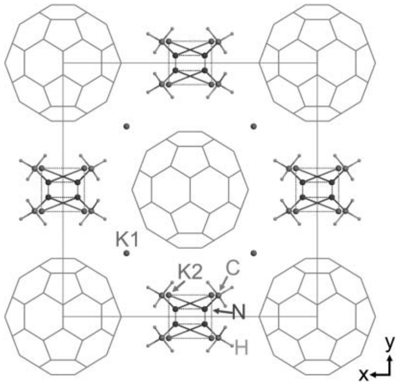

Fig. 1 Basal-plane projection of the structure of $(CH_3NH_2)K_3C_{60}$. Four K^+–NH_2-CH_3 units are disordered over the corners of two interpenetrating rectangles per octahedral site. The unit cell volume of K_3C_{60} expands by ~7% upon CH_3NH_2 co-intercalation with the expansion being strongly anisotropic (C_{60}–C_{60} long/short contact = 1.057).

In Fig. 2, we show the ZF time-dependent μ^+SR spectra of $(CH_3NH_2)K_3C_{60}$ at temperatures 1.2, 6.2, 11.1 and 99.7 K. There is clear evidence of the presence of a ZF heavily-damped spontaneous muon precession at low temperatures, signalled by the minimum in the evolution of the asymmetry in the 1.2 K data and implying the existence of coherent ordering of the $C_{60}{}^{3-}$ electronic moments. No oscillating signal is seen at 9.3 K and above. Instead, there is a slow depolarisation of the μ^+ spin evident, gradually disappearing with further increase in temperature.

The ZF-μ^+SR spectra in the high-temperature range of the experiments are characteristic of the presence of weak static

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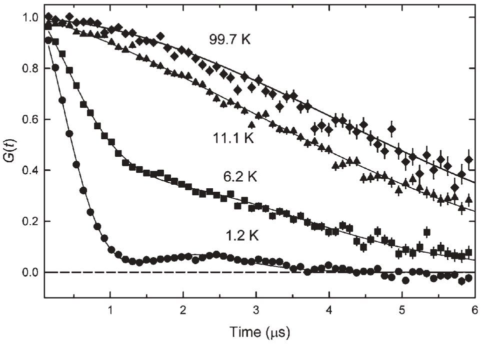

Fig. 2 ZF muon spin relaxation function $G(t)$ observed in $(CH_3NH_2)K_3C_{60}$ at 1.2 K (●), 6.2 K (■), 11.1 K (▲) and 99.7 K (◆). The solid lines represent the fit to the model function of eqn (1) (1.2 and 6.2 K) and to the product $\exp(-\lambda_d t)\exp(-\frac{1}{2}\sigma^2 t^2)$ (11.1 and 99.7 K), as described in the text.

nuclear dipole moments which result in a small depolarisation rate, $\sigma = 0.229(4)\ \mu s^{-1}$. These are frozen into a disordered spin configuration, producing a temperature-independent distribution of local fields with a width, $<\Delta B^2>^{1/2} \approx 2.7$ G. However, an additional very slow relaxation of the μ^+ spin polarisation is present, arising from fluctuating electronic moments. Thus the spectra were fitted with the product of a Gaussian (σ) relaxation, representing the frozen nuclear moments and an exponential (λ_d) relaxation, accounting for the fluctuating $C_{60}{}^{3-}$ moments. The relaxation rate λ_d is 0.015(1) μs^{-1} at 99.7 K, implying extremely rapid fluctuations. Cooling down towards the freezing temperature leads to an enhanced slowing-down of the $C_{60}{}^{3-}$ spin dynamics within the paramagnetic domains. The spectra are still described well with the same functional form and the dynamic depolarisation rate λ_d reaches a value of 0.212(2) μs^{-1} at 9.3 K. The temperature dependence of λ_d above T_f can be described by $(T/(T - T_f))^\eta$ with a critical exponent $\eta = 0.55(3)$.

Below 9.3 K, the ZF-μ^+SR spectra (Fig. 2) are dominated by a short-lived oscillating signal whose depolarisation gradually increases with decreasing temperature. The solid lines in Fig. 2 are fits to the data of the two-component function

$$G_\mu(t) = A_1 \exp(-\tfrac{1}{2}\sigma_1{}^2 t^2) + A_2 \exp(-\lambda_2 t)\cos(2\pi\nu_\mu t + \phi) \quad (1)$$

$G_\mu(t) = A(t)/A_0$ is the muon relaxation function with A_0 the initial asymmetry at $t = 0$, A_1 and A_2 are amplitudes reflecting the fractions of the muons contributing to the two components, ν_μ is the μ^+ Larmor frequency and ϕ its phase, and σ_1 and λ_2 are relaxation rates associated with the two components. The physical origin of the function of eqn (1) lies with the fact that on average, for a random distribution of the directions of the internal field in a polycrystalline sample, ⅓ of all muons will experience an internal field along their initial spin direction and consequently will not precess, giving rise to the first component in eqn (1) and resulting in an ideal ratio of $A_1/A_2 = 0.5$. σ_1 is a measure of the relaxation caused by field components perpendicular to the μ^+ spin, while λ_2 reflects the influence from static field inhomogeneities and fluctuating-field components along the μ^+ spin direction.

The observation of a spontaneous precession frequency, ν_μ in zero applied field at low temperatures for $(CH_3NH_2)K_3C_{60}$ indicates unambiguously the onset of long range magnetic order, where the static internal field at the muon site, $<B_\mu>$ is proportional to ν_μ. The frequency is 0.322(5) MHz at the lowest measured temperature of 1.2 K and corresponds to $<B_\mu> = 23.8(4)$ G. In addition, the depolarisation rate λ_2 reaches a value of 1.14(1) μs^{-1} at 1.2 K, implying a distribution of local fields with a width $<\Delta B^2>^{1/2} = 13.4(1)$ G—only smaller than $<B_\mu>$ by a factor of 1.8. This is reminiscent of what has been observed by ZF-μ^+SR for other magnetically ordered fullerides—namely, $<B_\mu>/<\Delta B^2>^{1/2}$ is ∼1.4 and 1.7 in the $(TDAE)C_{60}$ ferromagnet ($T_C = 16$ K) and the $(NH_3)K_3C_{60}$ antiferromagnet ($T_N = 37$ K), respectively.[7,8] It implies that although the static internal field in $(CH_3NH_2)K_3C_{60}$ peaks at a non-zero average value, there is considerable variation in its magnitude from site to site and different muons precess at slightly different frequencies, thereby becoming progressively dephased. The large spatial inhomogeneities of the local field experienced in $(CH_3NH_2)K_3C_{60}$ should be associated with orientational disorder effects of the fullerene and the K^+–NH_2-CH_3 units inherent in the structure, consistent with MAS NMR evidence concerning hindered methyl group rotational dynamics.[4] Alternatively, spin glass-type effects could also co-exist with the long-range magnetic order. Finally, we note that the low-temperature ZF-μ^+SR spectra display features similar to those of the dynamic Kubo–Toyabe relaxation function, appropriate for a Gaussian distribution of fluctuating random fields whereby the large damping of the oscillation originates from spin fluctuations.[5] However, such a description is inappropriate on the evidence of the complementary LF-μ^+SR data. The effect of applied longitudinal fields (LF) is to decouple the depolarisation of the μ^+ spin due to dynamic or fluctuating moments from that due to quasi-static internal fields. Fig. 3 shows the LF-μ^+SR data at 1.2 K. There has been a complete recovery of the asymmetry at long times with no evidence for any remaining dynamic fields. Hence static magnetic order with a broad local field distribution is established in $(CH_3NH_2)K_3C_{60}$.

Fig. 4 shows the temperature evolution of the ZF spontaneous precession frequency, ν_μ in the ordered state with its value approaching zero above 9.2 K. The observed variation can be described by the equation $\nu_\mu = \nu_0\,[1 - (T/T_N)]^\beta$, with $\beta = 0.39(6)$ and $\nu_0 = 0.33(1)$ MHz. The critical exponent, β is close to what is expected for a 3D Heisenberg antiferromagnet ($\beta = 0.367$). In addition, the ratio A_1/A_2 (where A_1 and A_2 are the volume fractions of the non-oscillating and oscillating components, respectively) remains roughly near 0.5, as expected for a polycrystalline sample between 1.2 and 5 K. However, as the temperature increases towards T_N, A_1 begins to dominate

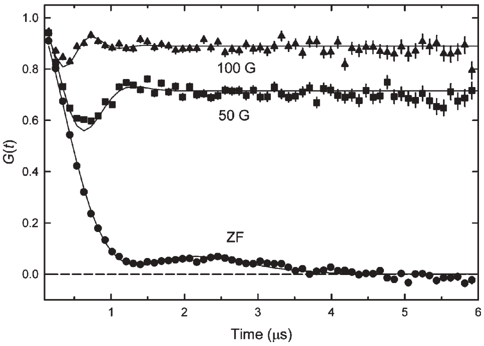

Fig. 3 Longitudinal-field muon spin relaxation function $G(t)$ observed in $(CH_3NH_2)K_3C_{60}$ at 1.2 K for applied external fields of 50 G (■) and 100 G (▲). The solid lines represent the expected decoupling in LF if the initial depolarisation were due mainly to a distribution of static fields.

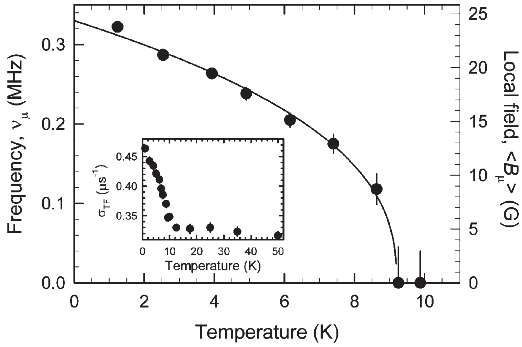

Fig. 4 Temperature dependence of the ZF muon precession frequency, ν_μ and of the local field at the muon site, $<B_\mu>$ in $(CH_3NH_2)K_3C_{60}$. The solid line is a fit of the data to a critical law, $\nu_\mu \propto [1 - (T/T_N)]^\beta$ with β = 0.39(6) and T_N = 9.2 K. The *inset* shows the temperature dependence of the depolarisation rate, σ_{TF} at an applied TF of 600 G.

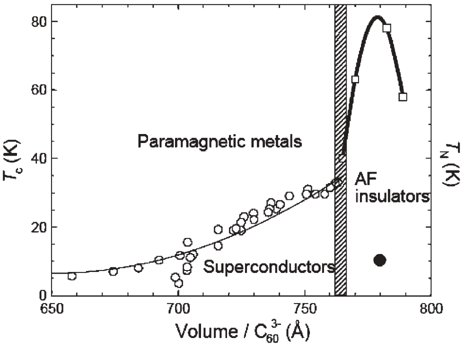

Fig. 5 Electronic phase diagram of C_{60}^{3-} compounds, including T_c values for superconducting fullerides (○) and T_N values for AF $(NH_3)K_{3-x}Rb_xC_{60}$ (□) and $(CH_3NH_2)K_3C_{60}$ (●). The shaded area denotes the metal(superconductor)–insulator (AF) boundary.

implying the emergence of paramagnetic domains. This may reflect the presence of a broad distribution of exchange constants (and ordering temperatures) arising from the orientational disorder of the fulleride ions. Finally, both depolarisation rates σ_1 and λ_2 in eqn (1) decrease with increasing temperature. Complementary evidence for the onset of magnetic order also comes from the temperature dependence of TF-μ^+SR spectra collected at an applied transverse field of 600 G as the depolarisation rate, σ_{TF} increases rapidly with decreasing temperature below ~10 K (Fig. 4 inset).

The prominent point arising from the present μ^+SR results is that $(CH_3NH_2)K_3C_{60}$ displays an electronic phenomenology—the appearance of ordered magnetic moments with large spatial inhomogeneities at low temperatures—akin to the ammoniated fulleride analogues despite the insertion of the larger CH_3NH_2 molecules. This is consistent with the survival of substantial electronic contact between the fulleride anions even at these hyperexpanded interfullerene spacings—a significant finding for the ongoing search for electronically active systems lying close to the Mott–Hubbard metal–insulator boundary that can be driven to a metallic/high-T_c superconducting state by the judicious choice of chemical and physical (application of pressure) means.

An additional significant and surprising finding, which forces re-evaluation of the role of the molecules coordinating to metal cations in controlling the electronic properties of complex fullerides is that the onset of long range AF order in $(CH_3NH_2)K_3C_{60}$ occurs at a much lower temperature (~10 K) than those encountered in $(NH_3)K_{3-x}Rb_xC_{60}$ ($0 \leqslant x \leqslant 3$) (Fig. 5). This is particularly surprising as especially the volume per C_{60}^{3-} anion, V in $(NH_3)KRb_2C_{60}$ (T_N ~ 76 K) is comparable to that of $(CH_3NH_2)K_3C_{60}$ and a naïve use of the rigid-band picture for the fullerides—where the width of the t_{1u}-derived band, $W \propto (1/V)$—would lead to comparable magnitudes of the exchange constants (and of T_N) if the new $(CH_3NH_2)K_3C_{60}$ was simply another orthorhombic fulleride with a different unit cell volume. The drastic reduction of T_N thus implicates either the increased anisotropy of the fulleride sublattice, driven by the more elongated nature of the complex cation due to the extra CH_3 group of the coordinating molecule, or the role of non-classical hydrogen bonding contacts in the ammonia case in propagating exhange interactions. Given the importance of anion orientational ordering in controlling orbital order and exchange interactions in the (TDAE)C_{60} system, it is possible that CH_3NH_2 drives a different orientational ground state and resulting exchange paths compared to the more symmetrical NH_3 molecule through determination of the orbital ordering on adjacent anions. These observations thus motivate further exploration of the control of fulleride electronic properties by the generation of complex counterions.

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Notes and references

‡ The $(CH_3NH_2)K_3C_{60}$ sample was prepared by reaction of single-phase K_3C_{60} powder with CH_3NH_2 vapour, as described before.[4] Phase purity was confirmed by powder XRD using a Stoe Stadi-P diffractometer. Zero-field (ZF), longitudinal-field (LF) and transverse-field (TF) μ^+SR data were collected at ISIS with the MuSR spectrometer. The powder sample (522 mg) was sealed under Ar in a Ti sample holder of 25 mm diameter, equipped with a knife-edge sharp seal and mylar windows, and placed inside a continuous-flow helium cryostat. ZF measurements were performed in the temperature range 1.2–100 K, with data collection (~6×10^7 events) taking ~3 h per dataset, except for a 12 h run (~2.5×10^8 events) at 4 K. Complementary LF (5 to 250 G) and TF (600 G) μ^+SR data were collected at 1.2 K and between 1.2 and 150 K, respectively.

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