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1995 J. Phys.: Condens. Matter 7 L567

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J. Phys.: Condens. Matter 7 (1995) L567–L573. Printed in the UK

LETTER TO THE EDITOR

μ^+SR study of zero-field magnetic ordering in CsC_{60}

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Received 4 September 1995

Abstract. We have measured the zero-field muon spin relaxation (ZF μ^+SR) spectra of the quasi-one-dimensional fulleride conductor CsC_{60}. Static magnetic order of a random nature develops gradually below about 30 K. The local field distribution at the muon site has a Gaussian shape with a width of 48.3(7) G at 2.8 K. Muon spin rotation (TF μ^+SR) measurements at an applied transverse field of 6 kG also show the onset of magnetic order in the same temperature range.

Alkali intercalation of solid C_{60} leads to superconducting compositions A_3C_{60} [1]. The structures of these fulleride salts can be rationalized to a good approximation using simple cubic ionic crystal structure arguments with the alkali ions occupying the tetrahedral and octahedral interstices of a face-centred-cubic array of disordered C_{60}^{3-} ions [2]. Even though changing the size of the tetrahedral cations is found to affect the orientational ordering of the fulleride ions [3, 4] the structures remain three dimensional with inter-fullerene distances in excess of 3 Å. However, this relatively simple picture is not applicable when the metallic AC_{60} (A = K, Rb, Cs) salts are considered [5]. These adopt an orthorhombic structure with pronounced one-dimensional character and show unusually close contacts between the fulleride ions [6]; partial covalent bonding between fullerenes along the chains and their consequent molecular deformation from icosahedral symmetry have been postulated to account for these observations.

Moreover, the temperature evolution of the static susceptibility, χ_s of RbC_{60} as measured by EPR, revealed a sharp decrease to zero in the vicinity of 50 K, attributed to a spin density wave instability of the conducting C_{60}^{-} linear chains [7]. Below about the same temperature, a transition to an insulating state also occurs [8]. However, the origin and true nature of the low-temperature magnetic phase still remain the subject of controversy. Earlier zero-field μSR studies on two different RbC_{60} samples [9, 10] gave conflicting results but revealed frozen electronic moments in the low-temperature phase and the absence of spontaneous Larmor frequencies which would have implied long-range magnetic order, associated with antiferromagnetism or SDW formation.

In this letter, we report μ^+SR measurements on the quasi-one-dimensional fulleride CsC_{60}. The problem of the existence of non-zero internal local fields in the low-temperature phase of CsC_{60} is addressed using 100% spin-polarized positive muons (μ^+) in the absence

0953-8984/95/430567+07$19.50 © 1995 IOP Publishing Ltd

of external fields. These are implanted into the solid sample and after they come to rest at an interstitial site, they act as highly sensitive microscopic local magnetic probes. In the presence of local magnetic fields ($\langle B_\mu \rangle$), they will precess with a frequency given by

$$\nu_\mu = (\gamma_\mu/2\pi)\langle B_\mu \rangle$$

where

$$\gamma_\mu/2\pi = 13.55 \text{ kHz G}^{-1}.$$

In the absence of an applied external field, the appearance of a precession signals the onset of an ordering transition. Moreover, application of a magnetic field parallel to the initial muon spin polarization (longitudinal field) allows the decoupling of the μ^+ spin from the static internal fields. μ^+SR spectroscopy has proven extremely powerful before in the field of small-moment magnetism and in all instances when magnetic order is of a random, very-short-range, spatially inhomogeneous or incommensurate nature [11]. In CsC_{60}, we find that ZF measurements show the gradual development below about 30 K of static order only of random nature. Knight shift (K_μ) measurements in an applied 6 kG transverse field again show a similar transition in the same temperature range.

CsC_{60} powder samples were prepared by the reaction of stoichiometric amounts of C_{60} with Cs metal in sealed, evacuated quartz tubes [12, 13]. Final annealing was carried out at 800 K for four weeks. High-resolution synchrotron x-ray [12, 14] and neutron [13, 14] diffraction data established the purity of the present materials which were well crystalline and single phase with an orthorhombic structure and showed no evidence of any impurity phases. EPR measurements [12] confirmed the presence of the low-temperature transition reported earlier [7]. μ^+SR experiments were carried out both at the Paul Scherrer Institute (Villigen, Switzerland) and at the ISIS facility (Rutherford Appleton Laboratory, UK).

Experiments in ZF at the PSI were performed with the general purpose spectrometer using low-energy (surface) muons on the μ^+SR-dedicated πM3 beamline on the PSI 600 MeV proton accelerator. A 200 mg CsC_{60} powder sample was sealed under Ar in an Ag sample holder equipped with In seals and Mylar windows and placed inside a continuous-flow He cryostat, allowing measurements down to 2.8 K. TF data were also collected in the same temperature range at an applied field of 6 kG. Experiments in ZF and LF at ISIS were performed with a pulsed beam of positive muons using the EMU beamline. 300 mg CsC_{60} and RbC_{60} powder samples were sealed under Ar in Al sample holders equipped with In seals and Mylar windows and placed inside a continuous-flow He cryostat with a base temperature of 1.5 K.

Figure 1 presents representative ZF time-dependent μ^+SR spectra of CsC_{60} at various temperatures between 2.8 and 79.1 K. No oscillating signal is seen at any temperature. The μ^+SR spectra at 79.1 K are characteristic of the presence of weak static nuclear dipole moments, which result in a small depolarization rate, $\sigma_1 = 0.098(8)\,\mu s^{-1}$. The μ^+SR spectra above 30 K reflect the presence of random ^{133}Cs nuclear dipole moments (essentially static within the μSR time window) which produce a weak Gaussian field distribution at the μ^+ sites with a full width at half maximum (FWHM) of 1.3(1) G. The slight decrease of σ_2 from 0.14 μs^{-1} at 30 K to 0.10 μs^{-1} at 80 K (figure 2(a)) is most likely caused by some slow μ^+ diffusion or residual molecular motion of the fulleride units, rather than signalling another magnetic phase transition as has been suggested in [9, 10]. Below ~30 K, the shape of the time-dependent μ^+SR spectra changes, as a short-lived component appears. In fitting the data, we now employ a strongly damped polarization signal superimposed on a slowly relaxing component:

$$P_\mu(t) = A_1 \exp\left(-\tfrac{1}{2}(\sigma_1 t)^2\right) + A_2 \exp\left(-(\lambda_2 t)^\beta\right) \quad (1)$$

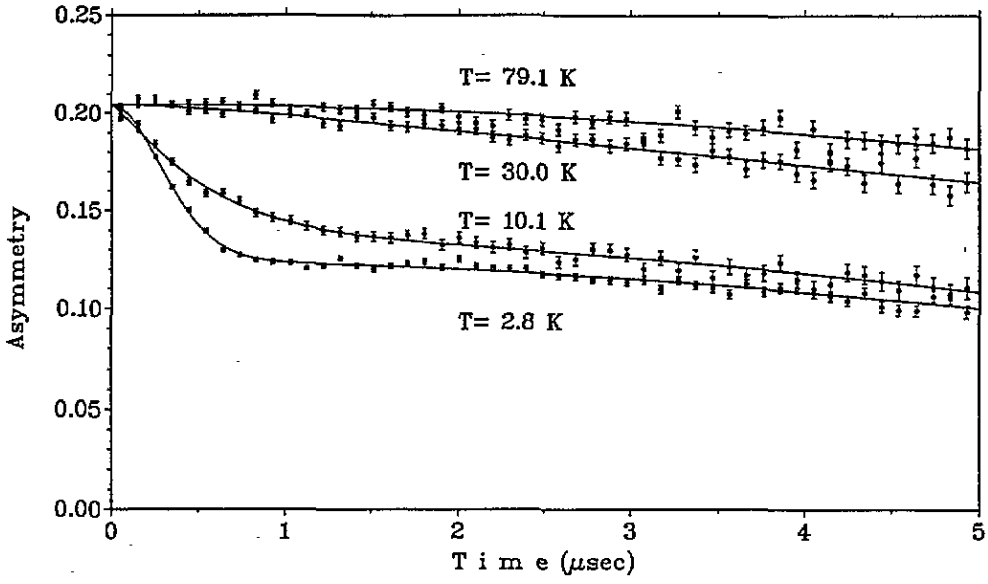

Figure 1. Zero-field μSR spectra at various temperatures for CsC_{60}. The solid line through the 79.1 K and 30.0 K data is a fit to a Gaussian function, reflecting the presence of weak static nuclear dipole moments; at 10.1 K and 2.8 K, the data are fitted to the two-component function of equation (1), representing the sum of a slowly relaxing Gaussian and a rapidly relaxing stretched exponential function.

where A_1 and A_2 are amplitudes reflecting the fractions of the muons contributing to the two components, and σ_1 and λ_2 are relaxation rates associated with the two components.

Figure 2(b) shows that as the temperature is lowered, the volume fraction of component No 1 becomes smaller, while the rapidly relaxing component No 2 begins to dominate at lower temperatures, as the volume fraction of the magnetic domains continuously increases at the expense of the paramagnetic ones. The data clearly imply an inhomogeneous form of magnetism even at 2.8 K with co-existing paramagnetic and random static local fields. The depolarization rate λ_2 continues to increase as the temperature is lowered, reaching a value of 2.47(3) μs^{-1} at 2.8 K. This implies a distribution of local fields with a FWHM of 48.3(7) G. The muons thus experience a local field that peaks close to zero and with large spatial inhomogeneities that may be due to a number of physical factors, including a wide distribution of $(C_{60}^{-})_n$ chain lengths and orientational disorder effects.

Of particular importance is the evolution with temperature of the fitted exponent β (equation (1)) of the contribution of component No 2 to the μ^+ spin polarization. Close to the freezing temperature $\beta \sim 1$, corresponding to a Lorentzian shape of the local field distribution; this changes smoothly (inset of figure 2(a)) as the temperature is lowered with $\beta \rightarrow 2$ at 2.8 K and the shape of the local fields best described by a Gaussian. This should reflect the gradual slowing down of the spin dynamics with completely static features evident only at the lowest temperatures.

Muon spin rotation data at an applied TF of 6 kG were also collected for the material in the temperature range 2.8–300 K. The μ^+ polarization was best fitted at high temperatures by a single oscillating component with an essentially temperature-independent Gaussian relaxation rate $\sim$0.07 μs^{-1}, reflecting again the nuclear dipole field spread as in ZF.

Below $\sim$50 K, the rms local field begins to increase, indicating the diminishing

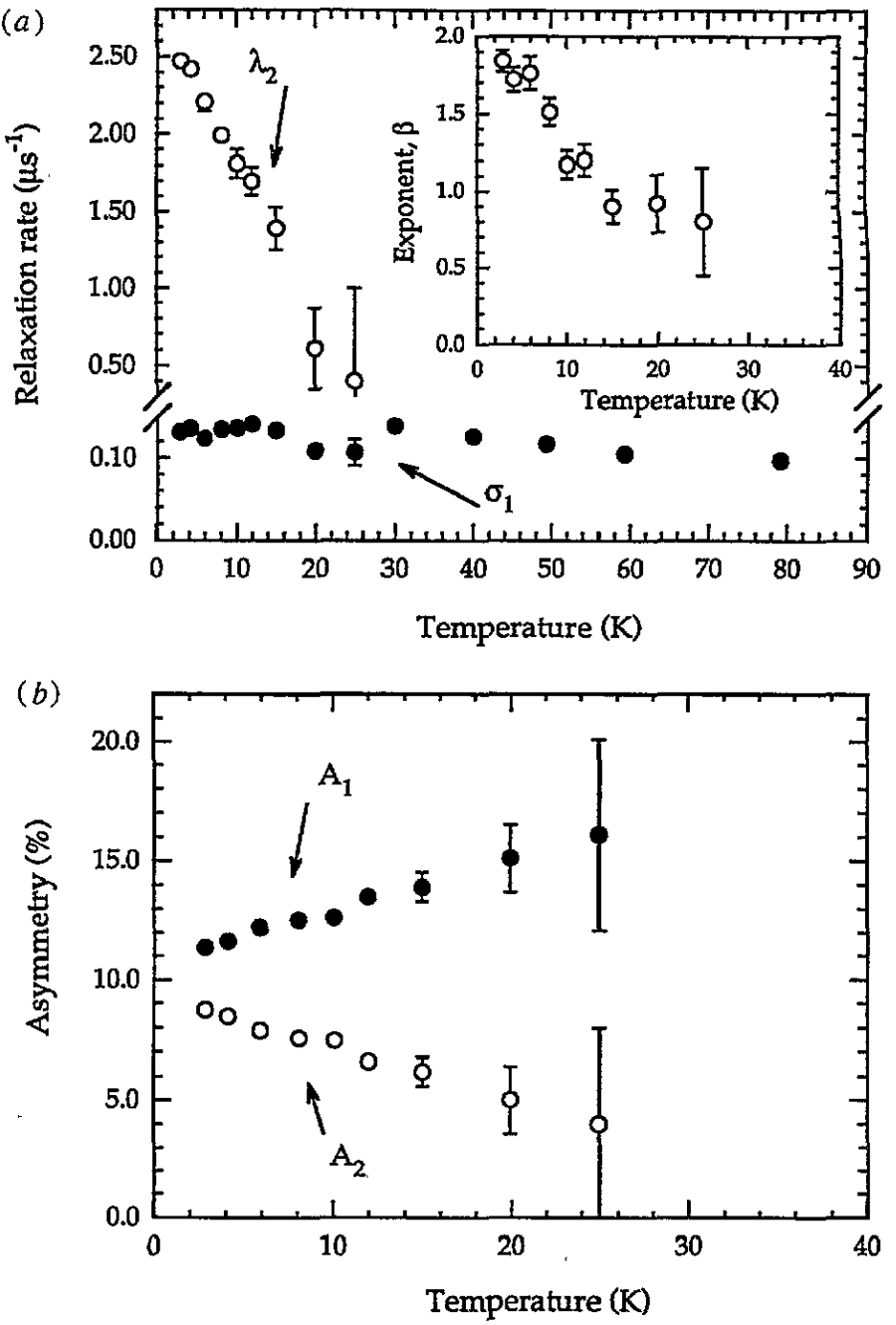

Figure 2. The temperature dependence of (a) the relaxation rates of the Gaussian, σ_1 (solid circles), and stretched exponential, λ_2 (open circles), components and (b) the asymmetries A_1 (solid circles) and A_2 (open circles) of the two components present in the ZF μSR spectra. The inset in (a) shows the temperature dependence of the exponent, β, of the rapidly relaxing stretched exponential component which gradually evolves from a Lorentzian to a Gaussian on cooling.

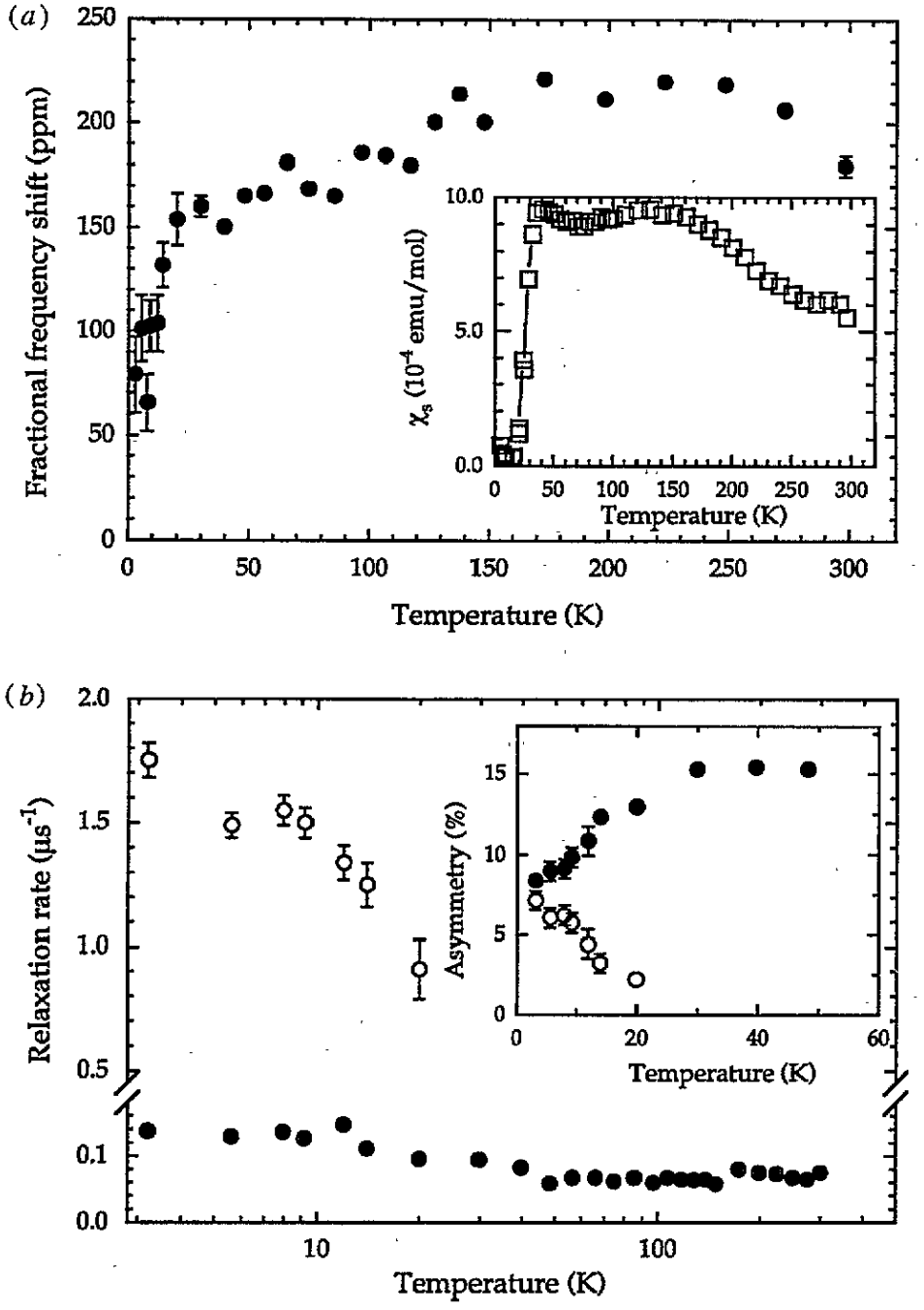

Figure 3. The temperature dependence of (a) precession frequency, ν_1 (solid circles), and (b) the relaxation rates of the two Gaussian, σ_1 (solid circles) and σ_2 (open circles), components present in the TF μSR spectra. The inset in (a) shows the temperature dependence of the static spin susceptibility, χ_s, measured by ESR and the inset in (b) shows the asymmetries A_1 (solid circles) and A_2 (open circles) of the two components.

importance of diffusion effects until, below ~30 K, a second rapidly relaxing component which was approximated in the fit by a Gaussian function becomes clearly evident. Both the relative fraction and the relaxation rate of component No 2 are smoothly increasing with decreasing temperature, mimicking the behaviour described earlier in ZF. The lowest temperature ratio of the relaxation rates of component No 2 in ZF and TF is approximately equal to 2, in agreement with the expected value of $5^{1/2}$ in the case of a random spin arrangement.

This may be contrasted with the corresponding ratio of relaxation rates for the slow component No 1 which is ~1, implying the existence of strong electric field gradients for the Cs nuclei. The temperature evolution of the relaxation rates of the two components and of the resulting fractional (Knight) shift in the μ^+ precession frequency are shown in figure 3(a) and 3(b). For comparison the inset in figure 3(a) shows the molar susceptibility, χ_s, of the present sample measured by ESR that displays a magnetic transition at ~35 K. Although the muon Knight shift reflects the behaviour of χ_s in the vicinity of 35 K, it does not scale with χ_s at higher temperatures.

In our attempts to explore the static or dynamic nature of the observed relaxation of the μ^+ spin polarization at various temperatures, measurements in applied LFs were also performed. These routinely confirmed the presence of static fields, as the μ^+ spin is readily decoupled (at an applied LF of 100 G) from the static internal fields resulting in complete recovery of the asymmetry.

In conclusion, the present μSR data for the quasi-one-dimensional conducting fulleride CsC_{60} are consistent with a transition below ~30 K to a magnetic state, characterized by random static order. No evidence for the development of long-range order associated with either antiferromagnetism or SDW formation is found in the ZF measurements.

We thank the EPSRC (UK) for financial support and access to ISIS, the Paul Scherrer Institute for provision of beam time and C A Scott and D Herlach for help with the experiments. This work was partially supported by the MRL Program of the National Science Foundation under Award No DMR-9123048.

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