NMR Evidence for 1D Antiferromagnetic Properties in Cs_1C_{60} and Rb_1C_{60} Polymers

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We have performed ^{13}C NMR measurements on the three phases of A_1C_{60} ($A = $ K, Rb, Cs) and alkali NMR in Cs_1C_{60} (^{133}Cs) and Rb_1C_{60} (^{87}Rb). We show that, for Rb_1C_{60} and Cs_1C_{60}, strong antiferromagnetic (AF) fluctuations persist up to room temperature, suggesting a one-dimensional character. However, K_1C_{60} behaves as an ordinary three-dimensional metal. NMR also reveals a magnetic transition at about 25 K in the Rb and Cs polymers. Comparison of the ^{133}Cs and ^{13}C spectra supports the occurrence of a spin-flop AF phase. Simulations of the ^{133}Cs spectrum due to a distribution of dipolar fields are consistent with moments $m \simeq 0.5\mu_B$ ordered in AF chains. [S0031-9007(96)00161-5]

It is by now well established that the A_1C_{60} compounds display an orthorhombic (o)-phase below room temperature, where the C_{60} balls form polymerized chains in the a direction [1,2]. Yet the consequences of this strongly one-dimensional (1D) structure on the symmetry of the electronic properties of these systems are still debated. Shortly after the synthesis of this new phase, Chauvet *et al.* argued [1], interpreting their ESR measurements, that (o)-Rb_1C_{60} is a quasi-1D conductor, where spin or charge density wave (SDW or CDW) instabilities lead to an insulating ground state. A transition at about 50 K has actually been confirmed for Rb_1C_{60} and Cs_1C_{60} through various experiments [ESR, conductivity [3], and muon spin resonance (μSR) [4–6]]; such a transition is not detected in K_1C_{60} either by ESR or by conductivity despite the structural similarity [3], although the eventual occurrence of a CDW state is controversial [3,7]. The exact nature of the transition in Rb_1C_{60} and Cs_1C_{60} is still unclear: μSR seems to favor a highly disordered magnetic state. On the other hand, Erwin, Krishna, and Mele claim that from band structure calculations [8] in the polymer phase the electronic density at the bonding sites between C_{60} balls is small, and therefore the transfer integral along the chain is too weak to display a 1D character. As a consequence, the electronic properties should remain three dimensional (3D).

In this context, local magnetic probe studies are highly desirable. We present here a thorough study of the various nuclear spins, which allows us to extract a 1D antiferromagnetic (AF) component of the spin fluctuations in the Rb and Cs polymers. In Cs_1C_{60}, the comparison between the ^{133}Cs and ^{13}C low T spectra leads us to conclude that the broadening is not due to static hyperfine fields and is better explained by dipolar fields in a spin-flop AF phase.

The ^{13}C relaxation data shown in Fig. 1 demonstrate immediately that T_1 behaves quite differently in Rb_1C_{60} and Cs_1C_{60}, on one hand, and K_1C_{60}, on the other hand. In K_1C_{60}, both $T_1T = 300$ sec K and the spin susceptibility

[3] are T independent, which is the usual situation for an ordinary 3D metal. On the contrary, $(T_1T)^{-1}$ increases with decreasing T, as T_1 *is nearly T independent* in the Rb and Cs polymers. This difference is very likely related to the existence of a magnetic ground state in these compounds, and would then indicate the occurrence of strong magnetic fluctuations. *The persistence of these fluctuations up to 300 K seems characteristic of a reduced dimensionality of the electronic properties,* since, in this case, the energy scale for the magnetic fluctuations, related to the strong low-dimension couplings, is much larger than that of the 3D couplings, which drive the transition. Moreover, χ increases only slightly with decreasing T for both
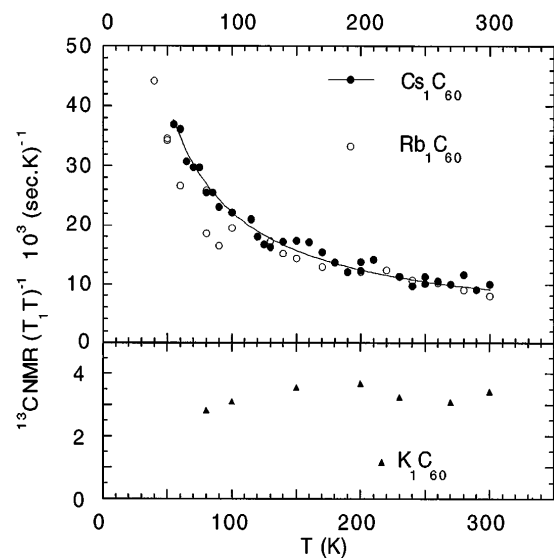

FIG. 1. T dependence of $(T_1T)^{-1}$ for ^{13}C in the three A_1C_{60} systems. T_1 is the slope at the origin of the magnetization recovery (MR) curve, measured on a narrow window on the low frequency side (20–90 ppm) of the spectrum. Although the MR curves are not exponential, they keep a similar shape in the displayed T range, so that the way T_1 is defined changes its absolute value but not its temperature dependence. For Cs_1C_{60}, the fit by Eq. (3) is $(T_1T)^{-1} = 1.7 + 1430T^{-0.95}$ (sec K)$^{-1}$.

compounds [9,10]. The fact that T_1 and χ are nearly constant cannot be understood in a 3D picture. This situation is reminiscent of that found in 1D organic compounds [11] or in the two-dimensional (2D) cuprates [12], and indicates that electronic correlations are important.

NMR alkali relaxation in Rb_1C_{60} and Cs_1C_{60} (Fig. 2) allows one to get indications on the q dependence of these fluctuations. Since the electrons are mainly located on the C_{60} ball, ^{13}C senses directly the spin fluctuations at any wave vector q. In contrast, components at $q \neq 0$ may partially cancel at the alkali site because of its symmetry with respect to the neighboring C_{60}. Figure 2 shows indeed that, contrary to the ^{13}C relaxation, a constant term dominates the alkali $(T_1T)^{-1}$ at high T, as already mentioned by Tycko *et al.* for Cs_1C_{60} [13]. Our measurements at low T reveal an extra contribution which increases as for ^{13}C. The slight relative increase of ^{87}Rb relaxation rate at high T with respect to ^{133}Cs might be associated with a small quadrupolar contribution on ^{87}Rb (cf. Fig. 2 caption). For ^{133}Cs, which has a small quadrupole moment, the relaxation is purely magnetic, so that our detailed analysis will be done for Cs_1C_{60}. The fact that the T-dependent term is the same for ^{13}C and ^{133}Cs is emphasized by the linear relationship between $^{Cs}(T_1T)^{-1}$ and $^{C}(T_1T)^{-1}$ (Fig. 2, inset). The extra constant term for the alkali implies that the spin fluctuations are not homogeneous in q space and that *the fluctuations probed by ^{13}C have a strong AF character*.

A quantitative analysis of the relaxation rates above 60 K for the ^{13}C and ^{133}Cs nuclei allows us to separate the AF contribution. Very generally, one can write for a nucleus α, where α stands for ^{13}C or ^{133}Cs:

$$^{\alpha}(T_1T)^{-1} = \frac{k_B\,^{\alpha}\gamma^2}{2}\sum_q |^{\alpha}A_q|^2 \frac{\chi''_\perp(q,\omega_0)}{\omega_0}, \qquad (1)$$

where $^{\alpha}A_q$ is the hyperfine constant per μ_B at wave vector q. For ^{13}C, $^{C}A_q$ exhibits no q dependence, while for ^{133}Cs the symmetry of the alkali site yields

$$^{Cs}A_q = 4A_1 \cos(q_xa/2)\cos(q_yb/2) + 2A_2\cos(q_zc/2), \qquad (2)$$

where A_1 is the coupling with the four C_{60} in a plane, and A_2 with the two C_{60} in a vertical direction (Fig. 3). For AF fluctuations in the a-b plane, the first term of Eq. (2) vanishes, implying that the alkali only senses the fluctuations of the two C_{60} in a vertical direction.

From the symmetry of the structure, it is hard to imagine a 2D behavior, and assuming a 1D electron gas model is quite natural, although the 1D direction might be either along or perpendicular to the polymer chains, depending upon the strength of the overlapping integrals. Two terms in the sum over q of Eq. (1) are relevant in 1D, those related to the excitations at $q = 0$, and at $q = 2k_F = \pi/a$ (or π/b), for AF fluctuations along (or perpendicular to) the chains [16]. The T dependence of these two terms is different. As suggested by the plot inserted in Fig. 2, we assume that $\chi''(0,\omega_0)/\omega_0$ is a constant, while the term at
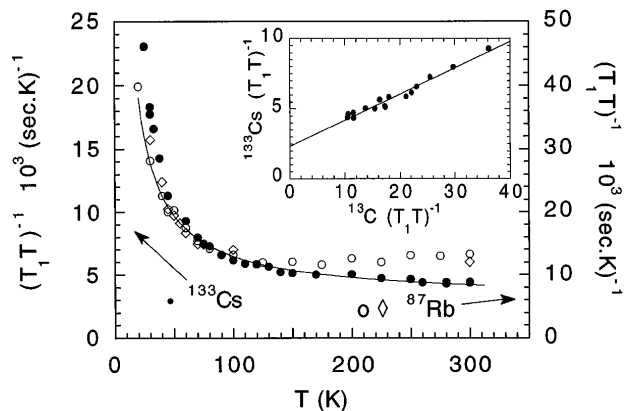

FIG. 2. T dependence of $(T_1T)^{-1}$ for ^{87}Rb and ^{133}Cs. The static quadrupole effects are small for ^{133}Cs (spin 7/2), so that all the transitions are flipped by the NMR pulses, and we consequently observe an exponential MR [14]. For ^{87}Rb (spin 3/2), the static quadrupole effects are large, and only the central transition is flipped; the MR is well described by $M(t) = M_0[1 - 0.9\exp(-6t/T_1) - 0.1\exp(-t/T_1)]$, expected in case of magnetic relaxation [15]. For Cs_1C_{60}, the fit by Eq. (3) for $T = 60$ K is $(T_1T)^{-1} = 3 + 280T^{-0.95}$ (sec K)$^{-1}$. The deviation at lower T is related to 3D critical effects. A plot of the ^{133}Cs data as a function of $^{C}(T_1T)^{-1}$ is inserted.

$2k_F$ is known to become singular at low temperature with $\chi''(2k_F,\omega_0)/\omega_0 \propto T^{\kappa_\rho-1}$, where κ_ρ is an exponent characteristic of the correlation strength. In such a model, we expect for both nuclei

$$^{\alpha}(T_1T)^{-1} = \,^{\alpha}\gamma^2(a|^{\alpha}A_0|^2 + b|^{\alpha}A_{2k_F}|^2 T^{\kappa_\rho-1}). \qquad (3)$$

We will assume in the following $A_1 \simeq A_2 = \,^{Cs}A$, which yields from Eq. (2), $^{Cs}A_0 = 6\,^{Cs}A$ and $^{Cs}A_{2k_F} = 2\,^{Cs}A$. The reduced value of $^{Cs}A_{2k_F}$ explains that the relative magnitude of the T independent contribution to $(T_1T)^{-1}$ is enhanced at the alkali site. The data for Cs_1C_{60} are fitted by Eq. (3) for the two nuclei with a fixed ratio $^{Cs}A_0/^{Cs}A_{2k_F} = 3$, which yields a consistent determination of a, b, and κ_ρ. The good agreement of the fits of Figs. 1 and 2 supports this model, and especially that the spin
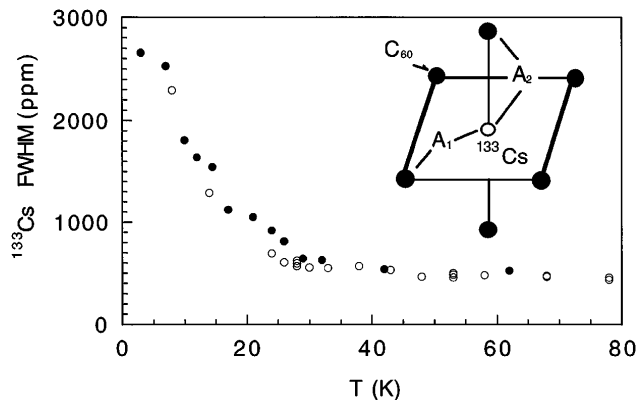

FIG. 3.   Temperature dependence of the ^{133}Cs full width at half maximum. The different symbols refer to different samples. Inset: geometry of the ^{133}Cs site, the chain direction is represented by thick lines.

susceptibility is peaked at $q = 0$ and $q = 2k_F$, which is characteristic of a 1D system. Despite the metallic character of the polymers, we obtain a very small value $\kappa_\rho = 0.05$, near the strong correlation limit $\kappa_\rho = 0$.

Below 60 K, $(T_1T)^{-1}$ increases sharply and deviates from the 1D fit, as can be seen in Fig. 2 for the alkalis. In the same T range, the shape of the recovery curves changes for ^{13}C, implying a distribution of relaxation rates. These features might be correlated with the appearance of 3D critical fluctuations near the transition.

As for the static effects, we will first focus on Cs_1C_{60}, since it appears to be more sensitive to the magnetic order than Rb_1C_{60} [17]. The ^{13}C spectrum is significantly modified only below 25 K. As ^{13}C is a spin 1/2, it is only sensitive to magnetic local fields, which definitely establishes the magnetic nature of the transition. A broad tail appears gradually below 25 K, while a narrow line, unbroadened compared to the paramagnetic phase, persists down to 5 K (Fig. 4). At 5 K, the broad tail represents half the signal intensity and reaches a width of 3000 ppm. However, the ^{133}Cs line does not break into two components, its linewidth increases *as a whole* by a factor of 5 between 25 and 4 K (Figs. 3 and 5). These features are intrinsic to the system, as measurements for two different Cs_1C_{60} samples (Fig. 3) gave identical results. As all the C_{60} balls are equivalent in the orthorhombic structure, it is quite unexpected that only half the ^{13}C sites sense the magnetic order. However, these sites belong to the magnetic phase, since the ^{133}Cs spectrum does not contain a signal similar to the one of the paramagnetic phase. A quadrupolar broadening on ^{133}Cs, which would be due to a structural distortion associated with the magnetic transition, can be excluded as quadrupolar effects are small on ^{133}Cs [14].

The maximum values of the local magnetic fields on the ^{133}Cs and ^{13}C nuclei in the magnetic phase are of the same order of magnitude. As we will see below, this is puzzling since the hyperfine coupling should be much stronger for some ^{13}C sites than for ^{133}Cs. A simple picture for a magnetic phase is that each C_{60} bears a localized spin with a direction fixed by the interactions with its neighbors. This moment m induces a local field on the ^{13}C: $H_{loc\parallel} = {}^CA m \cos(\theta)$, where θ is the angle between the applied NMR field H_0 and m, and ^CA is the hyperfine constant of the site. m is *a priori* oriented at random with respect to H_0 for a powder sample, so that a broadening is expected. From the shift of the different sites as revealed by the ^{13}C magic angle spinning–(MAS-) NMR spectrum [18], we know that ^CA ranges from 0 to 2500 Oe/μ_B. Contrary to ^{13}C, the local field on ^{133}Cs is sensitive to the local magnetic structure, and writes $^{Cs}H_{loc\parallel} = m \sum_i A_i \cos(\theta_i)$, where the sum runs over the six nearest C_{60} neighbors of ^{133}Cs. The value of the isotropic Knight shift $K = 6^{Cs}A\chi$ in the paramagnetic phase, yields an upper estimate $^{Cs}A = 100$ Oe/μ_B [19]. Among all the possible magnetic structures, a phase with completely disordered frozen moments would lead to the larger ^{133}Cs coupling ($\simeq \sqrt{6}^{Cs}A$). Even in this case, the ^{133}Cs broadening is at least 5 times too large compared with that of the tail of the ^{13}C spectrum. *Therefore the large ^{133}Cs broadening is inconsistent with an ordered or disordered magnetic phase where the electron spins are randomly oriented with respect to H_0.*

To avoid this contradiction between the ^{13}C and ^{133}Cs spectra, it is natural to assume that *the electron spins orient perpendicularly to H_0 ($\theta = \pi/2$) in the spin-flop phase of the AF state.* In such a phase, we are in a rather unusual situation, as *the isotropic hyperfine fields are negligible and the broadening is then mainly due to dipolar fields.* The residual effect of the hyperfine fields will cause a NMR shift similar to the one of the paramagnetic phase as χ is not much modified below the transition. Also, as the main component of the hyperfine local field is now perpendicular to H_0, each spin senses the same field $(H_0^2 + H_{loc\perp}^2)^{1/2}$, and the additional corresponding shift would be small in the 7T NMR field even for 1μ_B per C_{60}, and consistent with the data within experimental accuracy for both ^{13}C and the alkali.

In order to evaluate the magnitude and the distribution of the dipolar fields at the alkali site, we consider only
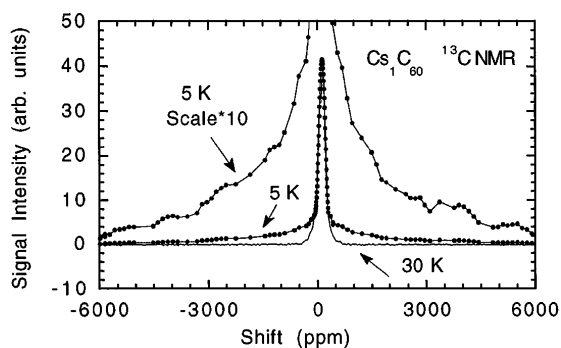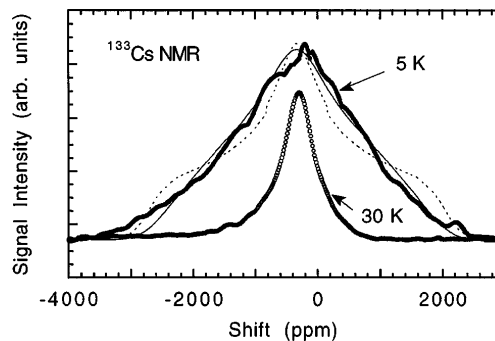

FIG. 4. Comparison of the ^{13}C spectra at 5 and 30 K in Cs_1C_{60}. The tail which appears below 25 K is magnified by a factor of 10. The spectra were taken point by point, by sweeping the frequency, to ensure detection of all the spins.

FIG. 5. ^{133}Cs spectra at 5 and 30 K. Calculated dipole field spectra in the spin-flop AF phase for uncorrelated AF chains (solid line) and for the in-plane ferromagnetic structure [8] (dashed line). In both cases, $m = 0.5\mu_B$, and a convolution of the computed spectra with a Gaussian fit with the 30 K spectrum has been performed.

the dominant contribution of the six C_{60} nearest neighbors of ^{133}Cs, as the contributions from more distant neighbors decrease rapidly and will vanish because of the AF order at long distance. We then compute the distribution of the component of the dipolar field parallel to H_0 for all the positions of the crystalline axis with respect to H_0, assuming different types of magnetic order. The structure of the simulated spectra are quite sensitive to the local magnetic order around ^{133}Cs, but the overall broadening will always correspond to a large value of the moment ($\simeq 0.5\mu_B$). The best fit of the ^{133}Cs spectrum (Fig. 5) has been obtained with $m = 0.5\mu_B$ for AF chains, assuming no magnetic order between them. The fit is still good if the AF chains order AF within the a-b plane. On the other hand, for the in-plane ferromagnetic structure proposed in [8], the spectrum should exhibit singularities (Fig. 5) which are not observed. The ^{13}C spectrum brings less information as the twelve C_{60} neighbors yield smaller dipolar fields. In both cases considered above, a rough simulation, which ignores the different locations of the ^{13}C sites on the C_{60} ball, displays a narrow line and a tail of 800 ppm linewidth (for $0.5\mu_B$). The ^{13}C spectrum is therefore less sensitive to the magnetic order. Further, additional broadening could arise from the anisotropic dipolar part of the on-ball hyperfine coupling, which has a similar magnitude for some ^{13}C sites [18].

Although previous μSR studies [4–6] conclude that m is rather small, this estimate is not reliable as long as the location of the muon is not well known Both μSR and NMR sense a large distribution of static local magnetic field only below 25 K. The small broadening at 75 K detected by μSR [4] is not seen in NMR on either nuclei, so it is probably a minor effect. On the other hand, the ESR signal intensity starts decreasing at 50 K for Rb_1C_{60} and at 40 K for Cs_1C_{60} [3]. As the time scale of the ESR experiment is much shorter than that of μSR and NMR, we are tempted to associate the modification of the ESR signal to the 3D critical fluctuations, probed below 60 K by our T_1 measurements.

In conclusion, we have shown that K_1C_{60} behaves the same as an ordinary 3D metal. However, the Rb and Cs polymers display original magnetic properties. They are quite identical at high T, as shown by the similarity of their MAS-NMR ^{13}C spectra [18] and of the T_1 data presented here, which can be explained by large AF 1D fluctuations occurring on a large T range above the 3D transition temperature. We suggest a crossover between the 1D and 3D regimes below 60 K. However, the slight increase of the susceptibility at low T is anomalous with respect to the 1D picture, which predicts a slight decrease of χ as usually observed in organic conductors [11]. Detailed electronic structure calculations in the lines of [8] will be required to understand the specificity of these alkali polymer systems and the changes of magnetic couplings in the series. A magnetic order develops progressively below 25 K and is shown in the case of Cs_1C_{60} to be consistent with a spin-flop AF phase, in which the spins are ordered AF

in one direction. In the magnetic phase, the ^{13}C spectra are also similar, but the alkali ones differ significantly; the ^{87}Rb spectrum breaks into two components as for ^{13}C [17], while the ^{133}Cs one broadens as a whole. The weak 3D couplings which drive the transition could be slightly different in Rb_1C_{60} and Cs_1C_{60} and would lead to a different 3D magnetic order of the AF chains, which can only be sensed by the alkali. It is quite clear that neutron scattering experiments are needed to probe the validity of the present analysis and to allow the refinement of our knowledge of the magnetic order.

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[14] The quadrupole frequency ν_q is much larger for ^{87}Rb ($I = 3/2$, $\nu_q \simeq 2.5$ MHz [15]) than ^{133}Cs ($I = 7/2$, $\nu_q \simeq 7$ kHz). If the ^{133}Cs broadening below 30 K were due to first order quadrupolar effects, the second order ^{87}Rb linewidth would be $\simeq 1$ MHz, while the observed broadening, probably of magnetic origin, does not exceed 20 kHz.

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[19] The ^{133}Cs line occurs at -230 ppm with respect to a molar solution of CsCl. The ^{133}Cs resonance (-250 ppm) in the superconducting state (where $K \simeq 0$) of Rb_2CsC_{60} [V. A. Stenger et al., Phys. Rev. B **48**, 9942 (1993)] is less shifted than the position of the ^{133}Cs$^+$ ion in the gas phase (-330 ppm). With this value as a reference chemical shift, we then deduce upper estimates for $K = 100$ ppm and $A = 100$ Oe/μ_B.