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Anomalous metallicity and electronic phase separation in the CsC$_{60}$ polymerized fulleride

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^{133}Cs and ^{13}C-NMR have been used to study the electronic properties of the polymerized phase of CsC$_{60}$ at ambient and under hydrostatic pressure. The salient result of this study is the finding of fluctuations in the local field at ^{133}Cs site, which are independent of the applied pressure and due to thermally activated changes in the local electronic environment of ^{133}Cs nuclei. We establish that the phase separation between magnetic and nonmagnetic domains observed in the low-temperature state at ambient pressure is the result of a slowing down of these fluctuations likely related to polaronic-charge excitations on the polymers.

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I. INTRODUCTION

When the fcc phase of A_1C$_{60}$ (A=K, Rb, Cs) compounds is slowly cooled from 400 K, one-dimensional polymerization of C$_{60}$ molecules spontaneously occurs along the (110) cubic direction and leads to an orthorhombic phase.[1] A drastic change in the electronic properties is observed at the structural transition.[2,3] Indeed, the fcc phase was shown to be a paramagnetic insulator,[2,3] whereas in the orthorhombic phase a plasma frequency was measured in optical experiments.[4] However, the density of carriers is likely to be rather low or their effective mass very large since the plasma frequency is equal to 0.1 eV in KC$_{60}$ polymer and even lower for RbC$_{60}$ and CsC$_{60}$.[4] In addition, the low-frequency conductivity of both RbC$_{60}$ and CsC$_{60}$ decreases smoothly over a broad temperature range, at variance with KC$_{60}$ that remains conducting down to 4.2 K.[4] Furthermore, the temperature dependence of the ^{13}C spin-lattice relaxation rate shows that strong magnetic fluctuations are present up to room temperature in RbC$_{60}$ and CsC$_{60}$[5] and the sharp decrease of the uniform static susceptibility (measured from EPR line intensity) below 50 K for RbC$_{60}$ and 40 K for CsC$_{60}$ (Ref. 4), suggests that both compounds undergo magnetic transitions at these respective temperatures. The occurrence of spin ordering is also evident from NMR experiments:[5,6] the slowing down of magnetic fluctuations gives rise to a divergent relaxation rate below 40 K. However, the nature of the spin order is less obvious. On one hand, EPR experiments[7,8] suggest the onset of a spin density wave ground state as a result of a possible one-dimensional (1D) character of the band structure. On the other hand, muon spin resonance (μSR) studies[9,10] show a gradual transition towards a highly disordered magnetic phase and do not rule out the possibility of a random spin freezing below 40 K.

In a recent NMR work,[11] we have shown that some of the ^{133}Cs sites remain unaffected by the onset of the spin ordering in the low-temperature state, magnetic and nonmagnetic domains being spatially distributed. At the temperature of 13.8 K the occurrence of a charge redistribution and a concomitant decrease of the local electronic susceptibility inside these nonmagnetic domains have been observed.[11] In agreement with this latter result, detailed analysis of the EPR linewidth at ambient pressure also suggests that two distinct magnetic environments coexist in the low-temperature state of RbC$_{60}$ and CsC$_{60}$ polymers[12,13] and insofar as a charge redistribution occurs in the nonmagnetic domains at 13.8 K,[11] the spontaneous thermal contraction recently observed at 14 K by x-ray diffraction in CsC$_{60}$[14] strongly supports the fact that these inhomogeneities are intrinsic.

In this manuscript, we give experimental evidence showing that the ‘‘conducting’’ state of the CsC$_{60}$-polymerized phase cannot be understood within the framework of an electronic band conductor as claimed earlier.[3–5,7,8,18] We report the temperature dependence of the spin-lattice relaxation rate $(T_1)^{-1}$ for both ^{13}C and ^{133}Cs nuclei at different pressures up to 9 kbar, indicating that in the temperature domain above 80 K two different mechanisms govern the relaxation of ^{13}C and ^{133}Cs nuclei, respectively. As far as ^{133}Cs is concerned, $^{133}(T_1)^{-1}$ decreases linearly down to about 80 K though remaining pressure independent up to 9 kbar. This behavior is in sharp contrast with the ^{13}C nuclei for which $^{13}(T_1)^{-1}$ strongly decreases under pressure up to 9 kbar while remaining almost temperature independent. The difference between ^{133}Cs and ^{13}C nuclei exists *independently* of the nature of the ground state of the system. More insight into these peculiar properties is then obtained using quadrupolar echo experiments performed on the ^{133}Cs nucleus that enable us to analyze with great accuracy the temperature dependence of the NMR spectrum at 1 bar. We show that the NMR spectrum of the two phases (magnetic and nonmagnetic) is motional narrowed above 100 K because of the fast motion of the local environment around the ^{133}Cs sites. The evolution of the line shape with temperature reveals that the static coexistence of two different ^{133}Cs sites below 15 K arises from a gradual freezing of these fluctuations in the local environment.

II. EXPERIMENTAL DETAILS

The measurements have been conducted on two powdered samples with entirely consistent results, one of them (10%) ^{13}C enriched. The pressure setup is a homemade double-stage copper-beryllium cell using fluor-inert as the pressure medium. This enables us to correct for each temperature the loss of pressure within the sample chamber due to the gradual freezing of the fluor-inert.

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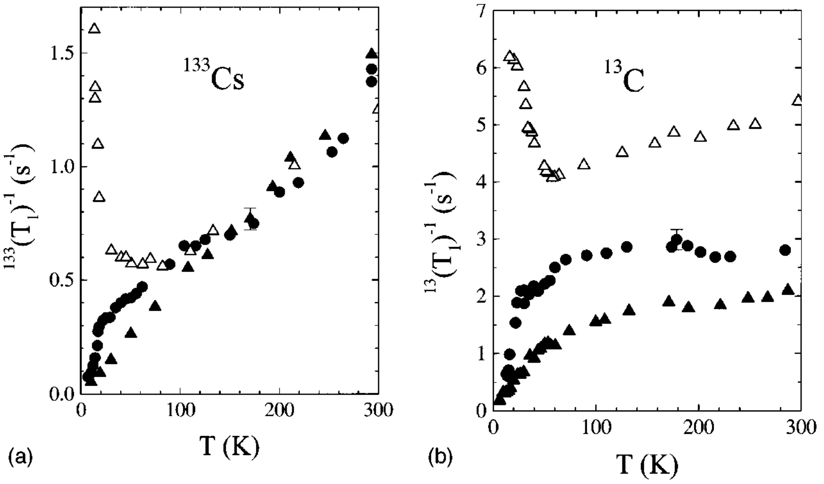

FIG. 1. Temperature dependence of T_1^{-1} for (a) ^{133}Cs (at 8 T) and (b) ^{13}C (at 9 T), at 1 bar (empty triangles), 5 kbar (black circles) and 9 kbar (black triangles). At 1 bar and below 40 K, the magnetization recovery curves are biexponential for both ^{133}Cs and ^{13}C but only the rapid component is reported versus temperature.

The spin-lattice relaxation were measured by monitoring the recovery of the magnetization after saturation with a series of $\pi/2$ pulses. The recovery curve is exponential for ^{133}Cs and ^{13}C[15] at room temperature. At ambient pressure, the recovery curve gradually becomes biexponential for both nuclei below 40 K. A large distribution of fast relaxation rates is observed giving raise to a recovery curve of the following shape $1-e^{(-t/T_1)^{\beta}}$ with a value of β of the order of 0.5 at the lowest temperature investigated, i.e., 4 K. At 5 kbar the recovery curve for ^{133}Cs is exponential down to 4 K. Not so for ^{13}C, since a nonexponential recovery is observed below 20 K. Different fit procedures did not help us to determine without ambiguity the shape of the recovery but no significant changes were observed on the qualitative temperature dependence of $^{13}(T_1)^{-1}$. The relaxation rates $^{13}(T_1)^{-1}$ shown in Fig. 1(b) at 5 kbar are therefore deduced below 20 K from a fit of the recovery curve assuming it to be exponential as above 20 K. At 9 kbar, the recovery curve is exponential for ^{133}Cs and ^{13}C in the all temperature range investigated.

Finally, we should point out that despite the presence of a static quadrupole splitting[16] for the NMR line of ^{133}Cs in the orthorhombic phase, the smallness of the quadrupole frequency, which is of the order of 5 kHz, enables us to saturate all the transitions at once. Therefore, the nuclear levels are initially equally populated establishing a well-defined spin temperature. In that case no deviation from an exponential behavior is expected for the relaxation of the magnetization[17] whose perfect exponential recovery at room temperature is a proof of the homogeneity of the samples.

III. ^{13}C AND ^{133}Cs-NMR UNDER PRESSURE

We report in Figs. 1(a) and 1(b) the temperature dependence of the relaxation rate for ^{133}Cs and ^{13}C nuclei at ambient pressure, 5 kbar and 9 kbar. The large enhancement of $^{133}(T_1)^{-1}$ and $^{13}(T_1)^{-1}$ below 40 K is due to a slowing down of magnetic fluctuations that is completely suppressed at 5 kbar. At this pressure, both $^{133}(T_1)^{-1}$ and $^{13}(T_1)^{-1}$ decrease exponentially below 20 K revealing the opening of a spin gap at $T_C \approx 20K$, the ground state being homogeneous and nonmagnetic. The effect of an applied pressure on this long-range order has been carefully investigated by ^{133}Cs-NMR. The temperature dependence of $^{133}(TT_1)^{-1}$ at 5, 5.5, 5.7, and 9 kbar is shown in Fig. 2. The well-defined instability at 5 kbar gives rise to a sharp peak on $^{133}(TT_1)^{-1}$ at T_C. Quite remarkably, a slight increase of the applied pressure strongly reduces the amplitude of the spin gap, without any significant change in T_C itself [as given by the position of the $^{133}(TT_1)^{-1}$ peak, see Fig. 2]. However, a smooth decrease of the temperature T_{mag} at which the slowing down of magnetic fluctuations occurs has been observed

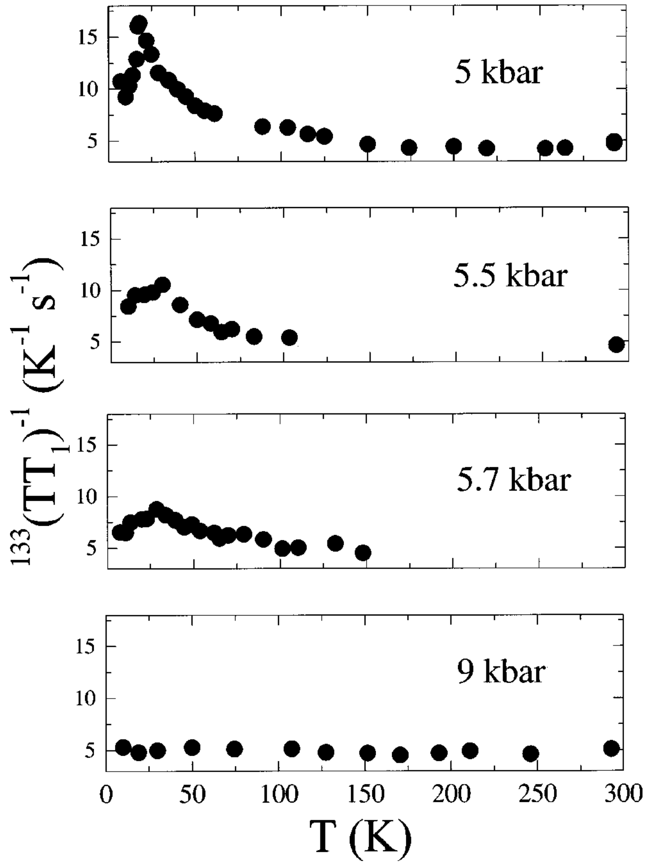

FIG. 2. Temperature dependence of $^{133}(TT_1)^{-1}$ at 5 kbar, 5.5 kbar, 5.7 kbar and 9 kbar.

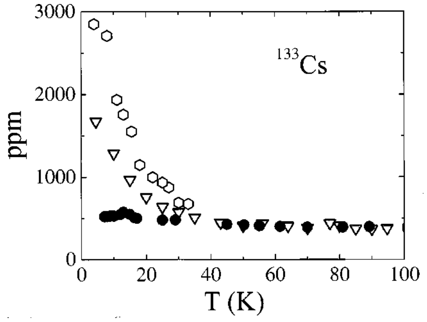

FIG. 3. Temperature dependence of the linewidth of the ^{133}Cs-NMR line at 1 bar from Ref. 5 (empty hexagons), at 3 kbar (present study, empty triangles), and at 5 kbar (present study, full circles).

by EPR experiments under pressure up to 4 kbar.[22] This fact is also evident from the temperature dependence of the linewidth of the ^{133}Cs-NMR line shown at different pressures in Fig. 3. Thus, as the pressure increases, T_{mag} drops continuously along a transition line that does not exist for the case of the spin-singlet ground state. Henceforth, we can infer that the sharp suppression of the spin gap below 20 K, which in turn gives rise to a metallic state, is not due to continuous changes in the magnitude of the electronic interactions but may reflect some structural changes above 5 kbar as suggested by dc conductivity measurements performed under pressure.[19,20]

Another striking feature in the response of the polymerized phase CsC_{60} to high pressure appears at glance in Figs. 1(a) and 1(b). Indeed, a clear distinction has to be made between the two temperature domains 4.2–80 K and 80–300 K. Below 80 K, $^{133}(T_1)^{-1}$ and $^{13}(T_1)^{-1}$ exhibit a similar pressure and temperature dependence. This is, however, no longer true above 80 K, where $^{133}(T_1)^{-1}$ and $^{13}(T_1)^{-1}$ behave in complete different ways. In particular, we can see in Fig. 1(a) that above 80 K, $^{133}(T_1)^{-1}$ exhibits no pressure dependence up to 9 kbar unlike $^{13}(T_1)^{-1}$, which is shown in Fig. 1(b). Within the first five kilobars, the relaxation of ^{13}C nuclei is strongly affected by pressure in two manners: (i) an overall depression is observed under pressure following the depression of the uniform spin susceptibility (χ) measured by EPR[22] that drops at a rate of about 10% per kbar, (ii) a weakly temperature dependent contribution to $^{13}(T_1)^{-1}$ (20% decrease from 300 to 40 K) is suppressed at 5 kbar.

Broadly speaking, the spin-lattice relaxation rate for a given nucleus and the static electronic spin susceptibility are linked together by the following relation: $(T_1T)^{-1} \propto \Sigma_q |A(\vec{q})|^2 \chi''_{\perp}(\vec{q})$, where $A(\vec{q}) = \Sigma_i A_i e^{i\vec{q}\cdot\vec{r}_i}$ is the form factor of the hyperfine interaction between a given nucleus and the electronic spins located at the neighboring sites. Unlike ^{133}Cs whose environment is octahedral, there is no particular symmetry for ^{13}C sites. If both nuclei are coupled to the same electronic spins then, that $^{13}(T_1)^{-1}$ and $^{133}(T_1)^{-1}$ display a different pressure and temperature dependence above 80 K, might be attributed to the presence of a spatially dependent electronic spin susceptibility that dominates the relaxation of ^{13}C nuclei. However, as previously shown for RbC_{60},[6] the decrease of $^{13}(T_1)^{-1}$ follows the decrease of the uniform spin susceptibility deduced from EPR[22] within at least the first five kilobars. This reveals that in the low-pressure regime, the dominant contribution to the relaxation of ^{13}C above 80 K is due to enhanced magnetic fluctuations at the wave vector $\vec{q}=0$ and therefore, the differences described above between ^{13}C and ^{133}Cs cannot be ascribed to the form factor of the alkali site in the polymerized phase.

As it is, one can draw the following conclusions. First, the absence of pressure dependence observed for $^{133}(T_1)^{-1}$ above 80 K shows that the dominant contribution to the fluctuating field at ^{133}Cs site in this temperature range is unrelated to the electronic spins involved in the relaxation of ^{13}C nuclei. Second, the fact that above 80 K, $^{13}(T_1)^{-1}$ is weakly temperature dependent at ambient pressure and constant at 5 kbar suggests that the electronic spins are localized. This latter conclusion is in agreement with the calculated band structure of the polymer $(C_{60}^{-})^{n}$[21] that displays a dispersionless 1D half-filled band at the Fermi level but in apparent contradiction with transport measurements[19,20] performed in the similar compound RbC_{60}. One can therefore conclude that a model based on a single electron species is inadequate for describing the electronic properties of the polymerized phases RbC_{60} and CsC_{60}.

In a previous work,[11] we have shown that the use of quadrupolar spin echoes of ^{133}Cs nuclei enables to reveal the presence of nonmagnetic domains within a magnetic background. However, whether this inhomogeneous state results from the existence of static structural defects along the chains or is purely electronically driven, e.g., as proposed for underdoped cuprates[23] and spin-ladders compounds,[24] remained an open question. In what follows, we address this problem with the aid of quadrupolar spin echoes in order to determine how the inhomogeneous state at low temperature arises from the high temperature one.

IV. ^{133}Cs-NMR AT AMBIENT PRESSURE

In a similar way as in the reference,[11] the spin echoes of ^{133}Cs have been obtained after a $(\pi/2-\tau-\pi/8)$ in-phase rf pulse sequence,[25] maintaining fixed echo delay τ at 40 μs. Half of the spin-echo at 3τ is then Fourier transformed. This procedure gives rise to a spectrum containing two lines $5/2 \rightarrow 3/2$ and $-3/2 \rightarrow -5/2$ split by an amount $4\nu_Q$, where ν_Q is the quadrupole frequency of ^{133}Cs nuclei in the polymerized phase.[11,26] The evolution of the ^{133}Cs spectrum is displayed in Fig. 4 at different temperatures between 100 and 4.2 K. The expected doublet spectrum corresponding to a single ^{133}Cs site is observed at 100 K, but as T approaches 40 K the shape becomes asymmetric and a fine structure gradually develops. At 25 K, the coexistence of two different ^{133}Cs sites is evident in Fig. 4, with a frequency difference in the local field of the order of $4\nu_Q$. This means therefore that two distinct magnetic environments are spatially distributed at this temperature. As the temperature is further lowered, the situation with a single quadrupolar split is recovered and thus only one ^{133}Cs site contributes to the spin echo signal below 15 K. The amplitude of the spin echo refocused at 3τ

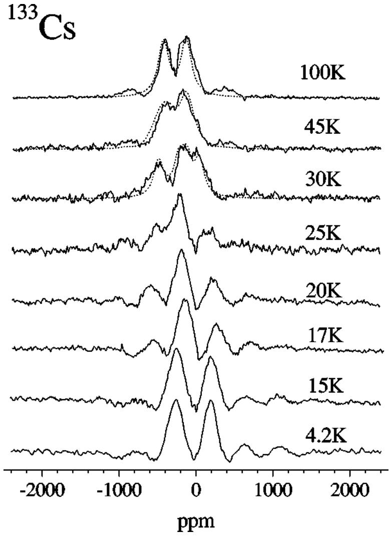

FIG. 4. Evolution of the line shape of the ^{133}Cs quadrupolar normalized splitting from 100 K down to 4.2 K. Because we take the Fourier transform of half of the spin echo at 3τ, the other spin echoes induce distortion of the base line.

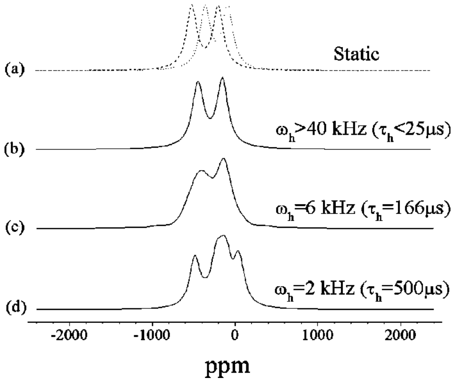

FIG. 6. Simulation of the shape of the ^{133}Cs quadrupolar spectrum. (a) In the static case, for each of the two configurations, both the quadrupole frequency ν_Q and the frequency shift K compare to the Larmor frequency are determined from the spectrum at 100 K, i.e., in the fast motion limit. This gives the respective values: $\nu_Q = 4.17$ kHz and $K = -350$ ppm (dashed line), $\nu_Q = 3.57$ kHz, $K = -209$ ppm (dotted line). (b) In the fast motion limit, $\delta\omega\tau_h \ll 1$. (c) In the slow motion limit, $\delta\omega\tau_h \approx 1$. (d) For a *quasistatic* distribution, $\delta\omega\tau_h \gg 1$.

is proportional to $e^{-3\tau\gamma\Delta H(T)}$ where $\Delta H(T)$ is the width of the local field distribution due to the static electronic moments at a given temperature T. Considering two distinct populations of ^{133}Cs nuclei below 30 K, N_m and N_{nm} that are coupled to the local field inhomogeneity $\Delta H(T)$ and located inside the nonmagnetic domains, respectively, the total number of ^{133}Cs sites contributing to the spin echo signal at 3τ can be expressed as: $N(T) = N_m / \{1 + [3\tau\gamma\Delta H(T)]^2\} + N_{nm}$. If the condition $3\tau\gamma\Delta H(T) \gg 1$ is fulfilled, only a fraction N_{nm} of the nuclei contribute to a spin echo at 3τ since this experiment selects those Cs sites that are entirely decoupled from the onset of local magnetism. Let $I(T)$ be the integrated intensity of the Fourier transform performed on this spin echo. The temperature dependence of $N(T)$ [equal to $I(T)T$] is reported in Fig. 5. We observe that a majority of the ^{133}Cs nuclei is gradually wiped out of the signal below 40 K. A minimal value for N_{nm} is reached at 15 K and amounts to about 10% of the total number of nuclei at 40 K. However, the estimated ratio between the two phases from the ^{13}C spectrum suggests that approximately half of the ^{13}C sites do not see the magnetic moment distribution in the low-temperature state.[5] We may solve this puzzle by considering that the ^{13}C spins probe the very local properties within each C_{60} chains carrying the electronic spins, whereas only ^{133}Cs sites far from any magnetic domain will contribute to the echo signal refocused at 3τ. This would mean that the boundary surface is large compared to the domains size suggesting that the phase separation sets on a microscopic scale.

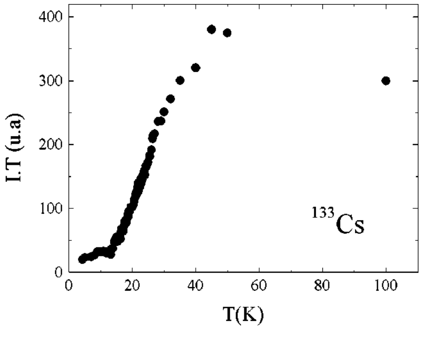

FIG. 5. Temperature dependence of $N(T) = I(T).T$ where $I(T)$ is the integrated intensity of the Fourier transform of half of the spin echo refocused at 3τ.

To gain insight into the driving force of this process, more attention must be paid to what happens above the spin ordering temperature. In particular, we see in Fig. 4 that the splitting of the ^{133}Cs spectrum displays a fine structure near 40 K although the NMR spectrum corresponding to two ^{133}Cs sites is not yet resolved. This can be understood if we assume that the local field of a ^{133}Cs nucleus jumps randomly from one value to the other in the ''conducting'' state. Indeed, using only the difference between the resonance frequencies $\delta\omega$ and the hopping time τ_h, we can propose the following scenario. At high temperature, $\delta\omega\tau_h \ll 1$ and the spectrum is motional narrowed, which means that only one doublet is visible. When the temperature is lowered, the jump frequency $(1/\tau_h)$ decreases and the condition $\delta\omega\tau_h \approx 1$ becomes fulfilled with a fine structure developing in the NMR spectrum. Finally, when $\delta\omega\tau_h \gg 1$, the quadrupolar splitting of the two sites is well resolved, i.e., one for ^{133}Cs sites in the magnetic domains and the other for ^{133}Cs sites in the nonmagnetic ones. We simulate each of the three cases and our simulations at fixed $\delta\omega$ are shown in Fig. 6 for different correlation times τ_h and superimposed (dotted line) on the experimental spectra in Fig. 4. Clearly, the calculated spectra bear a strong resemblance with the experimental ones displayed in Fig. 4 between 100 and 30 K. We can thus infer the existence of a thermally activated change in the local environment of ^{133}Cs sites that may become the dominant contribution to $^{133}(T_1)^{-1}$ when the frequency $1/\tau_h$ is of the order of the Larmor frequency (43 MHz) of the ^{133}Cs nuclei. Therefore, from the results presented in this section, we can conclude the existence of another degree of freedom besides the fluctuations of the electronic spins located in the C_{60} molecules, and possibly related to spontaneous local structural changes in the polymerized phase.

V. DISCUSSION

As emphasized above, one of the difficulties aroused by our work is to bring together the conducting nature of the polymerized phase established by optical and transport measurements[4,19,20] with the pressure and temperature dependence of $^{13}(T_1)^{-1}$ that strongly suggest that electrons are localized. It, therefore, turns out natural to question ourselves about the possible relationship between the local structural change around ^{133}Cs nuclei and the presence of charge-degrees-of-freedom-like polarons in the polymerized phase. On the basis of the above NMR results and anticipating results described further on, we suppose that the mobility of a charge carrier in the polymerized phase mainly depends upon the occurrence of a local structural distortion in its vicinity. From a point of view, which is somewhat naive, one may consider that at thermal equilibrium the charge carriers diffuse through the lattice under the action of a random force $F(t)$ that takes on only two discrete values $\pm f_0$. For our particular purpose, the relevant physical quantity to be considered is the spectral density $F(\omega)$ defined as the Fourier transform of the correlation function $\langle F(t)F(t+\tau)\rangle$—the brackets indicating an ensemble average. In our case, $\langle F(t)F(t+\tau)\rangle$ can be assumed to be of the form:[28] $f_0^2 e^{-|t|/\tau_h}$, which leads to the following spectral density: $F(\omega)=\tau_h/[1+(\omega\tau_h)^2]$. Because any excited state of the charge carriers is to relax due to the random force $F(t)$, the spectral density $F(\omega)$ will lead to a strong frequency dependence in the response function of the carriers to external oscillating fields. It is therefore of great interest to focus on ac resistivity measurements[20] performed at ambient pressure in both KC_{60} and RbC_{60}. For KC_{60} that does not exhibit a slowing down of spin fluctuations, ac and dc resistivities display a similar temperature dependence. This is, however, not true for RbC_{60} since a frequency-dependent peak is clearly observed in ac resistivity. The peak shifts from 35 K at 1.1 kHz down to 25 K at 43 Hz, the order of magnitude of these frequencies being in good agreement with the value we deduced from our simulated spectra in the same temperature range for CsC_{60} (cf. Fig. 6). The fact that the electronic properties of RbC_{60} and CsC_{60} display similar electronic and structural features as opposed to KC_{60} allow us to extrapolate the results obtained by Zhou *et al.* for RbC_{60} to the case of CsC_{60}. Thus experiments show that in the two polymerized phases RbC_{60} and CsC_{60}, the dissipation reaches a maximum when the hopping frequency of the local environment of the alkali ion becomes equal to the ac frequency. Such a coincidence can be hardly fortuitous and suggests that the mobility of the charge carriers in the polymerized phase is strongly coupled to the environment of the alkali ion. In this context, it is worthwhile to mention that polaronlike distortions such as $C_{60}{}^{-1-x}-C_{60}{}^{-1+x}$ have been predicted to be energetically favorable in the charged polymer $(C_{60}{}^{-})^n$ that exhibits a tendency to undergo a charge density wave transition.[27] In that particular case, the conduction mechanism would be due to an intramolecular property of the polymer itself and that would drastically change our expectations regarding the pressure effect on the electronic properties of the polymerized phase. However, on the sole basis of the NMR experiment described above we cannot address the microscopic mechanism at the origin of the spontaneous formation of polarons in the polymerized phase.

In the light of the above considerations, it is interesting to shortly reconsider the pressure effect on the spin-lattice relaxation rate $^{13}(T_1)^{-1}$ of ^{13}C nuclei in the low-pressure regime. As mentioned above, $^{13}(T_1)^{-1}$ shows at room temperature a similar pressure decrease than the electronic spin susceptibility deduced from EPR[6] that suggests that magnetic fluctuations at the wave vector $\vec{q}=0$ dominate $^{13}(T_1)^{-1}$ at ambient pressure. One possible explanation for the origin of these enhanced uniform fluctuations might be that polarons acting as local defects induce disorder in the AF exchange coupling J along the chain leading to the formation of spin clusters.[29] It was indeed shown theoretically[29] that the low-energy-magnetic fluctuations (i.e., when $T \ll J$) of a disordered AF spins chain are merely governed by clusters with an odd number of spins, each one acting as a nearly free localized (1/2) spin. In such a case the *reversible* suppression at 5 kbar of a weak temperature dependent term in $^{13}(T_1)^{-1}$ could be ascribed to the suppression with applied pressure of disorder in the magnetic coupling along the chain whose presence would be henceforth closely related to the slowing down of spin fluctuations in the low-temperature state. Much more experimental inputs are, however, required to go beyond this statement.

As it is, the phase separation occurring in the low-temperature state at ambient pressure appears to be the logical outcome of the twofold nature of the polymerized phase CsC_{60}, that is, mobile polarons spontaneously form aside from localized electrons and compete with a 3D magnetic order imposed by the transverse dipolar coupling between the chains. Note that the presence of nonmagnetic domains is in itself a strong hint that polarons are not randomly spatially distributed within the magnetic background but may form collective structures developing a long-range order below 14 K as suggested by NMR (Ref. 11) and x-ray experiments.[14]

VI. CONCLUSION

The work described in this manuscript deals with the electronic properties of the polymerized phase CsC_{60} extensively studied by NMR of ^{13}C and ^{133}Cs nuclei. The salient result is that the electronic properties of the polymerized phase CsC_{60} involve two degrees of freedom: one related to localized spins, the other related to mobile charges whose mobility is strongly entangled to the local environment of the Cs ion. The polymerized phase CsC_{60} is therefore dynamically inhomogeneous and as shown by NMR under pressure, this feature persists up to 9 kbar.

At ambient pressure static inhomogeneities gradually develop below 40 K concomitantly with a slowing down of spin fluctuations. At 5 kbar, the polymerized phase CsC_{60} undergoes a nonmagnetic transition at T_c equal to 20 K. The ground state is homogeneous and a spin gap opened below 20 K. Finally, a dramatic decrease of the amplitude of the spin gap is observed above 5 kbar without any significant decrease of T_c. The presence of magnetism, therefore, appears to be closely related to the occurrence of static inhomogeneities. How does the applied pressure suppress these inhomogeneities and stabilize a homogeneous, nonmagnetic ground state cannot be addressed by the present work, but remains an important issue to be solved.

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[1] P.W. Stephens *et al.*, Nature (London) **370**, 636 (1994).

[2] R. Tycko, G. Dabbagh, D.W. Murphy, Q. Zhu, and J.E. Fischer, Phys. Rev. B **48**, 9097 (1993).

[3] O. Chauvet *et al.*, Phys. Rev. Lett. **72**, 2721 (1990).

[4] F. Bommeli *et al.*, Phys. Rev. B **51**, 14 794 (1995).

[5] V. Brouet, H. Alloul, Y. Yoshinari, and L. Forró, Phys. Rev. Lett. **76**, 3638 (1996).

[6] P. Auban-Senzier, D. Jérome, F. Rachdi, G. Baumgartner, and L. Forró, J. Phys. I **6**, 1 (1996).

[7] A. Jánossy *et al.*, Phys. Rev. Lett. **79**, 2718 (1997).

[8] M. Bennati, R.G. Griffin, S. Knorr, A. Grupp, and M. Mehring, Phys. Rev. B **58**, 15 603 (1998).

[9] W.A. MacFarlane, R.F. Kiefl, S. Dunsiger, J.E. Sonier, and J.E. Fischer, Phys. Rev. B **52**, 6695 (1995).

[10] Y.J. Uemura *et al.*, Phys. Rev. B **52**, 6691 (1995).

[11] B. Simovič, D. Jérome, F. Rachdi, G. Baumgartner, and L. Forró, Phys. Rev. Lett. **82**, 2298 (1999).

[12] V.A. Atsarkin, V.V. Demidov, and G.A. Vasneva, Phys. Rev. B **56**, 9448 (1997).

[13] C. Coulon, J. Duval, C. Lavergne, A.L. Barra, and A. Pénicaud, J. Phys. I **10**, 205 (2000).

[14] S. Rouzière, S. Margadonna, K. Prassides, and A.N. Fitch, cond-mat/0002419 (unpublished).

[15] We can always fit the recovery curve with the expression $M(t) = M_{eq}(1-e^{(-t/T_1)^{\beta}})$, M_{eq} being the equilibrium magnetization and β a dimensionless coefficient comprised between 0.5 and 1. At room temperature and at any pressure investigated β is equal to 1 for ^{133}Cs whereas a substantial deviation from an exponential recovery is observed, i.e., $\beta \approx 0.72$ for ^{13}C. Because of the possible presence of a small amount of pure amorphous C_{60}, such deviation might be extrinsic. Therefore, we talk about ‘‘exponential recovery’’ for ^{13}C as opposed to the dramatic changes in the recovery curve observed at low temperature and whose occurrence is unambiguously related to some intrinsic properties of the polymerized phase.

[16] The presence of a quadrupole splitting does not imply a quadrupole relaxation but is consequent to the noncubic symmetry of the local environment of ^{133}Cs site. For a cubic symmetry the three components of the electric field gradient are strictly equal to zero that implies no quadrupole splitting. However, any fluctuations leading to a substantial deviation from the cubic symmetry may lead to a quadrupole relaxation depending upon the magnitude of the quadrupolar coupling compared to others. For the particular case of ^{133}Cs, the possibility of a quadrupole contribution in the relaxation of the magnetization can be easily ruled out because of the remarkably small value of its quadrupole moment.

[17] A detailed analysis of the magnetization recovery for nuclear spin $I > 1/2$ can be found in the following reference: A. Suter, M. Mali, J. Roos, and D. Brinkmann, J. Phys.: Condens. Matter **10**, 5977 (1998).

[18] S.C. Erwin, G.V. Krishna, and E.J. Mele, Phys. Rev. B **51**, 7345 (1995).

[19] K. Khazeni, V.H. Crespi, J. Hone, A. Zettl, and M.L. Cohen, Phys. Rev. B **56**, 6627 (1997).

[20] W.Y. Zhou, S.S. Xie, L. Lu, E.S. Liu, and Z. Peng, J. Phys. Chem. Solids **61**, 1159 (2000).

[21] S. Stafström, M. Boman, and J. Fagerström, Europhys. Lett. **30**, 295 (1995).

[22] L. Forró *et al.*, in *Progress in Fullerene Research*, edited by H. Kuzmany *et al.* (World Scientific, Singapore 1996).

[23] O. Zachar, S.A. Kivelson, and V.J. Emery, Phys. Rev. B **57**, 1422 (1998).

[24] S.R. White and D.J. Scalapino, Phys. Rev. B **55**, 14 701 (1997).

[25] For a given nucleus, the amplitude of the spin echoes strongly depends upon the angle of the rotation applied by the second pulse to the magnetization as well as the relative phase between the two pulses. For the in-phase pulse sequence $(\pi/2-\tau-\pi/8)$ applied on ^{133}Cs nuclei, the calculated (Ref. 26) amplitude of the spin echo is maximal at 3τ and strongly reduced at $5\tau/2$ and 4τ.

[26] B. Simovič, Thesis, Université Paris-Sud, Orsay, 1999.

[27] M. Springborg, Phys. Rev. B **52**, 2935 (1995).

[28] C.P. Slichter, *Principles of Magnetic Resonance*, 3 ed., (Springer-Verlag, Berlin, 1990), Appendix C.

[29] G. Theodorou, Phys. Rev. B **16**, 2264 (1977).