Detection by NMR of a “local spin-gap” in quenched CsC$_{60}$

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We present a $^{13}$C and $^{133}$Cs NMR investigation of the CsC$_{60}$ cubic quenched phase. Previous ESR measurements suggest that this phase is metallic, but NMR reveals contrasting electronic behavior on the local scale. The $^{13}$C spin-lattice relaxation time ($T_1$) exhibits a typical metallic behavior down to 50 K, but indicates that a partial spin-gap opens for $T < 50$K. Unexpectedly, $^{133}$Cs NMR shows that there are two inequivalent Cs sites. For one of these sites, the NMR shift and $(T_1T)^{-1}$ follow an activated law, confirming the existence of a spin-gap. We ascribe this spin-gap to the occurrence of localized spin-singlets on a small fraction of the C$_{60}$ molecules.

The electronic properties of the alkali fullerenes A$_x$C$_{60}$ seem contradictory at first sight. A simple independent electron approach predicts metallic behavior for any n between 1 and 5, because of the threefold degeneracy of the conduction band (denoted t$_{1u}$ from its symmetry). However, for even n (Na$_2$C$_{60}$ and A$_4$C$_{60}$) insulating behavior is observed and may correspond to a band gap associated with a lifting of the degeneracy of the t$_{1u}$ level and/or electronic correlations. For half-filling (n = 3), a series of metallic compounds are found, which suggests that the electronic correlations are not as large as expected because of the narrow electronic bands. The A$_3$C$_{60}$ family exhibit superconductivity which can be described in the framework of a conventional phonon-mediated mechanism. From this, one would also expect a simple metallic (perhaps superconducting) behavior for the AC$_{60}$ composition. On the contrary, the cubic high-temperature (CHT) phase of the AC$_{60}$ compounds has a Curie-like susceptibility, suggesting electronic localization. This is consistent with the nearly T independent NMR relaxation rates, which indicate further very weak exchange constants between the localized electrons. Early optical conductivity measurements, however, found metallic conductivity.

The occurrence of a structural transition in AC$_{60}$ from cubic to orthorhombic symmetry below about 350 K leads to the formation of a polymerized phase. To extend the study of the CHT phase to lower T, attempts were made to preserve the cubic symmetry by quenching. For KC$_{60}$ and RbC$_{60}$, a phase formed of C$_{60}$ dimers was obtained first. More recently, it has been found that a cubic phase (CQ phase for Cubic Quenched) can be maintained in CsC$_{60}$ (and RbC$_{60}$ for faster quenching below 100 K), which transforms irreversibly into the dimer phase above 130-150 K. In the CHT phase, the C$_{60}$ are freely rotating (space group Fm3n), whereas in the CQ phase they are static and orientationally ordered (space group Pn3m). Because the ESR spin susceptibility ($\chi_{\text{esr}}$) of this phase exhibits no significant T dependence, unlike the CHT phase, it was concluded to be metallic. The inconsistency between the CHT and CQ phases indicates that the properties of fullerenes with one electron per C$_{60}$ are not clear at all, and calls for more detailed investigations of the CQ phase, which is the only one that can be studied at low T.

The $^{13}$C and $^{133}$Cs NMR data in the CQ phase presented here not only evidence a distinct electronic behavior from the CHT phase, but also show that the results cannot be explained in a simple metallic framework. A partial opening of a spin-gap is detected at low T, which is not associated with any long range magnetic ordering. Such behavior has not been observed previously in metallic fullerenes, and thus indicates a new class of competing electronic instabilities in these compounds. Unexpectedly, we also find by $^{133}$Cs NMR investigation that there are two inequivalent Cs sites in the CQ phase. The local electronic susceptibility sensed by one of these Cs sites is dominated by the existence of the spin-gap, suggesting that the origin of the two $^{133}$Cs sites is related with the gap.

The CQ phase was obtained by immersing the sample directly into liquid nitrogen after one hour thermalization at 530 K. NMR measurements have been performed on the same sample in the polymer, dimer and CHT phases and are consistent with other results in the literature. ESR and X-ray diffraction measurements on the sample also confirmed published results for the CQ phase. No impurity phases could be singled out by either X-rays or NMR.

An irreversible transition at 135 K between the CQ and dimer phase is clearly evidenced by $^{13}$C NMR. In the dimer phase, the lineshape is identical to that of the RbC$_{60}$ dimer, i.e. a typical powder pattern due to anisotropic chemical shifts of sp$_2$ carbons. In the CQ phase, the spectrum is also broad, indicating that molecular motion is frozen, but it is more symmetric, as observed in metallic fullerenes where an electronic contribution adds to the chemical shift tensor. This electronic shift is however hard to extract, and the study of the $^{13}$C relaxation rates ($T_1^{-1}$) is more straightforward.

Figure 1 shows $^{13}$C $(T_1T)^{-1}$ in the CQ phase as a function of temperature. As in other fullerenes, the relaxation curves are not exponential, but they possess the same functional form over the whole T range (see inset of Figure 1), so that the T dependence of $(T_1T)^{-1}$ is unaffected by the choice of the fit function. In a conventional metal, the NMR relaxation rates usually follow the Korringa relation $(T_1T)^{-1} = \text{ cst}$. Neglecting the increase of $(T_1T)^{-1}$ above 110 K which will be discussed later,
(T_1T)^{-1} is nearly constant between 110 K and 50 K, in agreement with the metallic character suggested by the Pauli-like \(\chi_{\text{esr}}\), and its value lies in the range of other metallic fullerides \[^{13}\]. On the other hand, \( (T_1T)^{-1} \) falls by a factor 3 between 50 K and 10 K. Such a reduction of \( (T_1T)^{-1} \) indicates a loss of weight in the low energy density of electronic excitations and shows that the CQ phase does not remain a simple metal down to low \( T \).

\(^{133}\)Cs NMR experiments help to clarify the anomalous behavior found by \(^{13}\)C NMR. The spectrum is shown for several temperatures in Fig.2. The most prominent feature of these spectra is that there are two \(^{133}\)Cs lines, even though X-ray data demonstrate that there is a single Cs site in the structure (the octahedral interstitial site of the fcc lattice) \[^{17}\]. We estimate that the intensities of the two lines correspond to equal numbers of sites within 10\% \[^{10}\]. This ratio is similar in the three other samples investigated. One line exhibits an unusually large shift of about 800 ppm at 130 K, we denote it hereafter “S” line for Shifted. The other line is centered at -100 ppm, which is a typical shift for Cs in fullerides (hereafter “NS” line for Non-Shifted). Although the NS line appears at roughly the same position as that of the dimer, it can be unambiguously distinguished from the dimer as it is narrower and its \( T_1 \) is two orders of magnitude smaller at 120 K. The two lines disappear irreversibly above 135 K, where a single line characteristic of the dimer phase appears. Thus, the two lines S and NS are intrinsic to the CQ phase.

To rule out any macroscopic phase separation, we have carried out a double resonance experiment (SEDOR \[^{14}\][\(^{15}\)] that allows to detect sizable dipolar coupling between the two lines. In this experiment, we observe selectively the spin-echo of the S line. Normally, the dephasing caused by dipolar coupling with NS nuclei is refocused and contributes to the echo intensity. However, when a pulse is applied to NS at a time \( \tau \) after the first pulse on S, a fraction of the S magnetization, which is determined by the dipolar coupling between this S site and its NS neighbors, does not refocus. This reduction of the echo intensity called the sedor fraction (SF) is presented on the inset of fig. 2 for the S line, and follows SF \( \propto \Delta^2 \tau^2 \), where \( \Delta^2 \) is determined by the dipolar coupling between S and NS sites. Since dipolar coupling decays as 1/\( r^3 \), the very fact that we detect a SEDOR effect implies that the two sites are mixed on the microscopic scale \[^{14}\].

Why do these lines have such different shifts ? Recall that the shift \( K \) of a NMR line is proportional to the local electronic susceptibility (\( \chi_{\text{loc}} \)) through a hyperfine coupling, which is constant for a given environment and usually \( T \) independent. Different shifts could thus arise from different \( \chi_{\text{loc}} \) and/or different hyperfine couplings. In both cases, the sites must be structurally inequivalent, which is very puzzling in our case, since a thorough X-ray investigation of the same sample showed no deviation from the orientationally ordered Pa\( \overline{3} \) cubic structure \[^{17}\]. The situation is somewhat reminiscent of the A\( _3 \)C\( _{60} \) case, for which three different alkali NMR lines are observed at low \( T \), instead of the expected two lines corresponding to filled octahedral and tetrahedral sites \[^{18}\].

The \( T \) dependence of the shifts in the CQ phase is shown in Figure 3 together with the shifts in other CsC\( _{60} \) phases for comparison. It is immediately clear that neither CQ lines has a \( T \) dependence that could be extrapolated to the Curie law of the CHT phase. Hence, the two cubic phases have markedly different properties, despite their structural similarity. However, whereas the shift in the CHT phase scales with the Curie-like \( \chi_{\text{esr}} \), the shift of the \(^{133}\)Cs S line falls sharply below 80 K, at variance with the nearly T independent \( \chi_{\text{loc}} \). This corresponds to a very large \( T \) variation of \( \chi_{\text{loc}} \) at the S site, since the reference chemical shift should be around -200 ppm. For the NS line, the shift is very small, so that it is rather hard to determine the \( T \) dependence of \( \chi_{\text{loc}} \) and to decide whether the two sites differ only by hyperfine coupling.

Relaxation measurements allow an easier comparison between the different sites.

Figure 4 shows \( (T_1T)^{-1} \) on a logarithmic scale for \(^{13}\)C and the two \(^{133}\)Cs lines. Let us notice first that above 110 K, near the CQ-dimer transition, all the relaxation rates undergo rapid changes. The NS \( (T_1T)^{-1} \) increases by two orders of magnitude, so that the two \(^{133}\)Cs lines have similar relaxation rates at 130 K. Note that the formation of a small fraction of dimer phase would, in contrast, lead to a decrease of the NS line relaxation rate. No differences could be found in X-ray spectra recorded at 25 K and 125 K \[^{17}\]. The convergence of \( (T_1T)^{-1} \) for the Cs lines should then be ascribed to an exchange process between the two \(^{133}\)Cs sites above 110 K. Such an exchange would produce electronic fluctuations, that could explain the concomitant increase of \( (T_1T)^{-1} \) for \(^{13}\)C above 110 K.

Below 110 K, \( (T_1T)^{-1} \) decreases with decreasing temperature for all the nuclei. The effect is clearest for the S line, and moreover the \( T \) dependence of \( (T_1T)^{-1} \) for this site is identical to that of its shift, which shows that the static and dynamic properties are similarly affected. For the NS line, \( (T_1T)^{-1} \) only decreases slightly with decreasing \( T \), but as \( T_1 \) is already very long at 110 K, it might be dominated at low \( T \) by extrinsic contributions. Even though the \(^{13}\)C and \(^{133}\)Cs S relaxation rates both decrease with temperature, it is puzzling to find that they do not scale. For the S line, \( (T_1T)^{-1} \) starts decreasing below 90 K and saturates below 20 K, whereas for \(^{13}\)C it begins to decrease below 50 K and does not saturate down to 10K. Although we are not able to resolve different types of \(^{13}\)C sites, the splitting of the \(^{133}\)Cs spectrum implies the existence of inequivalent C\( _{60} \), so the observed \(^{13}\)C relaxation is probably an average of two different behaviors. Better experimental accuracy in \(^{13}\)C NMR might allow us to distinguish contributions from different C\( _{60} \) balls. Finally, the combination of the low \( T \) decrease of the shift and \( (T_1T)^{-1} \) of the S line and of the \(^{13}\)C \( (T_1T)^{-1} \) arg in favor of the existence of a spin-gap. In the same \( T \) range, the \(^{13}\)C and \(^{133}\)Cs spectra do
not broaden, ruling out any magnetic ordering.

These results imply that the electronic properties of the CQ phase are microscopically inhomogeneous, with coexistence of metallic and spin-gap behavior. Because the spin-gap behavior is strongest for the S line, weaker for $^{13}$C, and not presently detected by ESR within experimental accuracy, we ascribe it to a small fraction of C$_{60}$ molecules, strongly coupled to the neighboring Cs nuclei, which we identify as S sites. Although only a fraction of the C$_{60}$ are involved in the spin-gap, let us emphasize that the existence of two very well defined and non-overlapping $^{133}$Cs lines is very unusual and implies an underlying order. Disorder typically broadens an NMR line, while the appearance of two NMR lines implies at least a short range ordering.

The formation of a super-structure seems at first counter-intuitive in this 3D system, in which a strong distortion is ruled out by structural studies. X-ray investigation of our sample [7] shows that the only possible source of symmetry lowering is the existence of two orientations corresponding respectively to 85% and 15% of the C$_{60}$, as in other C$_{60}$ Pa3 compounds. Orientational correlations could be responsible for a super-structure, with a large unit cell, that could easily be missed in structural measurements of powder samples. However, if the gap originates in the band structure of an orientational superlattice, then it should be sensed equivalently by the different nuclei, and not preferentially by the Cs S site.

On the other hand, the occurrence of localized singlets strongly differentiates between the sites depending on their position with respect to this local perturbation and is in better accordance with our results. Hence, we use here the denomination of “local spin-gap”. These singlets could either be formed in dilute C$_{60}$ dimers or by localization of two electrons on a ball. In the first case, the dimers would be very weakly bound as the gap is much smaller than in the quenched dimer phase, for example. There is no apparent mechanism to stabilize such dimers, and furthermore, there would be more than two inequivalent Cs sites surrounding such a structure.

We therefore conclude that the spin-singlets are localized on a C$_{60}$ molecule. The nearest neighbor sites of a C$_{60}^{-2}$ are strongly coupled to the molecular spin-singlet and constitute the S sites on the observed spectrum. Since the octahedral Cs site is six-fold coordinated, the intensity of the S line requires about 10% of C$_{60}^{-2}$. Refined ESR experiments [3] are compatible with a decrease by 10% of the ESR susceptibility at low T, which is expected in this model. Such local electron pairing could be stabilized by a Jahn-Teller (JT) distortion. In these materials, the energy gain due to a JT distortion is predicted to be larger for a C$_{60}^{-2}$ with even n, leading to an effective attractive interaction between electrons for odd n [4]. Consequently, in the case of A$_3$C$_{60}$, dynamic JT distortions may favor superconductivity by reducing Coulomb repulsion. However, in CQ CsC$_{60}$, the two Cs lines indicate that the singlets are static. In this case, an ordered ground state with alternating C$_{60}^{2-}$ and neutral C$_{60}$ seems at first more natural than the dilution of 10% C$_{60}^{-2}$ in a metallic phase. The apparent rigorous stability of this dilute singlet phase (indicated by the reproducible Cs intensities) may be the result of frustration in the fcc lattice together with electrostatic repulsion between C$_{60}^{2-}$, which could make the occurrence of near neighbors C$_{60}$ energetically unfavorable. Whether these dilute C$_{60}^{2-}$ balls actually form a long-range super-structure remains an open question.

In conclusion, we have shown that the CQ phase of CsC$_{60}$ is not a simple metal but that a spin-gap in the electronic structure exists at low T. We attribute this spin-gap to the formation of localized spin-singlets on a small fraction of the C$_{60}$, possibly stabilized by a Jahn-Teller distortion of the C$_{60}^{-2}$ molecules. A structural evidence for the presence of such JT distorted balls would be welcome, but this may prove difficult given their low concentration (≈10%). Although the role of JT distortions has often been invoked to explain the properties of fullerides - both in the metallic A$_3$C$_{60}$ and insulating A$_2$C$_{60}$ compounds - there is no unambiguous evidence of their importance. Our results suggest that, in metallic A$_{2p+1}$C$_{60}$, an insulating cooperative JT ground state consisting of alternating C$_{60}^{2-}$ and C$_{60}^{(2p+2)-}$ molecules may actually be competing in the extreme case with a superconducting ground state. We would like to acknowledge P.W. Stephens and G. Bendele for the X-ray experiment, M. Héritier and A. MacFarlane for helpful discussions. Financial support from the TMR Programme of the European Comission (Research Network ‘FULPROP’ ERBFMRXVT970155) is acknowledged.

FIG. 1. 1/T$_1$/T measured by standard saturation recovery methods for $^{13}$C in the CQ phase. The relaxation curves are integrated over the whole spectrum and fitted with a stretched exponential (exp(-(t/T$_1$)$^\beta$)) with $\beta = 0.65$). Inset shows that this fitting procedure holds from 10 K to 125 K.

FIG. 2. $^{133}$Cs spectra in the CQ phase at 10 K, 50 K and 120 K in a 7T field. Inset : SEDOR fraction at 80 K for the S line as a function of the time $\tau$ when a $\pi$ pulse is applied to the NS line. The line is a fit to SF = a+$\Delta^2\tau^2$.

FIG. 3. Shifts of the $^{133}$Cs lines with respect to that of a diluted CsCl solution in the different phases of CsC$_{60}$. The dotted line extrapolates the Curie behavior of the CHT phase.

FIG. 4. Comparison of 1/T$_1$/T on a logarithmic scale for $^{13}$C and the two $^{133}$Cs lines in the CQ phase. For $^{133}$Cs, the relaxation curves are exponential even at low temperatures when they begin to merge together.
[1] M. Knupfer and J. Fink, Phys. Rev. Lett. 79, 14, 2714 (1997) and references therein.
[2] For a review see: O. Gunnarsson, Rev. Mod. Phys. 69, 575 (97)
[3] O. Chauvet et al., Phys. Rev. Lett. 72, 2721 (1994)
[4] R. Tycko et al., Phys. Rev. B 48, 9097 (1993).
[5] M.C. Martin et al., Phys. Rev. B 49, 10818 (1994).
[6] G. Oszlanyi et al., Phys. Rev. B 51, 12228 (1995), Q. Zhu et al., Phys. Rev. B 51, 3966 (1995).
[7] M. Kosaka et al., Phys. Rev. B 51, 17, 12018 (1995).
[8] A. Lappas, M. Kosaka, K. Tanigaki and K. Prassides, J. Am. Chem. Soc. 117, 7560-7561 (1995).
[9] G. Baumgartner, F. Simon, L. Forro et al., unpublished.
[10] We found that the pulse lengths optimizing the echo intensity were similar for the two lines, and indicative of small first order quadrupole effects, which do not distort significantly the measured intensities.
[11] K.F. Thier, M. Mehrling and F. Rachdi, PRB 55, 124 (1997)
[12] K. Holczer et al., Europhysics letters 23, 63 (1993)
[13] Y. Maniwa et al., Phys. Rev. B 54, 10, R6861 (1996)
[14] C.P. Slichter, Principles of Magnetic Resonance (Springer-Verlag, 1989)
[15] C.H. Pennington et al., Phys. Rev. B, 54.10, R6853 (1996)
[16] To irradiate selectively one line, we reduce the power of the NMR pulses. This leads to incomplete saturation of the lines, and systematically lowers the intrinsic value of $\Delta^2$, making a detailed quantitative analysis unreliable. However, we obtain a lower bound for $\Delta^2$ corresponding to more than 2 NS first nearest neighbors for S, which unambiguously rules out macroscopic phase separation.
[17] G. Bendele, P.W. Stephens, in preparation
[18] R.E. Walstedt, D.W. Murphy and M. Rosseinsky Nature 362, 611 (1993)
[19] W. Victoroff and M. Héritier, J. Phys. I France 6, 2175-2180 (1996); O. Gunnarson PRB 51, 3493 (1995); N Manini, E. Tosatti and A. Auerbach, Phys. Rev. B 45, 13008 (1994)
