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Coexistence of spin singlets and metallic behavior in simple cubic CsC_{60}

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We present a detailed nuclear magnetic resonance (NMR) study of simple cubic CsC_{60}, the only metallic cubic fulleride known so far besides A_3C_{60}, obtained by quenching from high temperature. ^{133}Cs NMR signals the presence of about 12–15 % of "anomalous" C_{60} balls, characterized by a 15-meV gap. We present different experimental observations supporting the idea that a spin singlet (i.e., a $C_{60}{}^{2-}$) is localized on these latter balls and stabilized by a Jahn-Teller distortion. A splitting of the ^{133}Cs spectrum into three different lines, with distinct electronic environments, is observed, which emerges naturally from such a situation. Quadrupole effects on ^{133}Cs confirm an inhomogeneous distribution of the charge between C_{60} molecules. Analysis of the relative intensities of the ^{133}Cs lines show that the spin singlets do not form clusters at the local scale, but are diluted within the lattice. This is probably to avoid the occurrence of neighboring $C_{60}{}^{2-}$ and minimize electrostatic repulsion between these balls. Through spin-lattice relaxation measurements, we detect chemical exchange between the Cs sites above 100 K. From this, we deduce that the lifetime of a spin singlet on a given ball decreases exponentially with increasing temperature (from 15 s at 100 K to 3 ms at 130 K) with an activation energy of 320 meV. The implications of the presence of such spin singlets for the nature of the metallic state is discussed, in relation with a decrease of $1/T_1T$ for ^{13}C at low temperatures, which indicates a deviation from a simple metallic model.

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I. INTRODUCTION

To investigate the electronic properties of fullerides, one would wish to vary freely the number of doped electrons between 0 and 6 in the triply degenerate t_{1u} band. It is rather difficult with chemical doping because only a limited number of phases appear to be stable. The field-effect transistor devices recently synthesized[1] might offer a more convenient way to do this, if the number of charge carriers injected in one C_{60} monolayer can be controlled through an applied gate voltage. However, although transport measurements are easily accessible, all investigations cannot be performed on these systems. Furthermore, it is not yet clear whether the properties of "bulk C_{60}" are similar to those of its surface[2] and a careful comparison between the two systems is extremely desirable.

The conventional chemical doping is obtained by inserting n alkali ions (A) in the C_{60} structure, leading to A_nC_{60} compounds, where the charge state of the C_{60} molecule is very close to $-n$. The direct influence of the alkali atoms on the electronic properties are thought to be negligible, although it could be a complication in some cases, mainly through structural modifications. Usually, only phases with an integer number of electrons per ball are formed. A_3C_{60} and A_4C_{60} were discovered first[3] and were consequently the most studied. A_3C_{60} are metals and superconductors at low temperatures, while A_4C_{60} are insulators. As both should be metals in a simple band-structure approach,[4] such a difference raises fundamental questions. Electronic correlation and/or electron-phonon interactions, both neglected in simple band calculations, must be important here. The fact that these two interactions are strong and have similar orders of magnitude is actually one of the most interesting aspects of the physics of fullerides. In view of the contrasted experimental situation, it seems important to extend investigations to other stoichiometries to estimate the relative importance of the different parameters. This paper is a second of a series of three papers devoted to this task, called hereafter I,[5] II, and III.[6]

Certain stoichiometries are more difficult to obtain for the following reasons.

(1) $n=1$ is stable (with $A=$K, Rb, Cs) but spontaneously polymerizes below 350 K,[7] leading to a rich but different physics, where low dimensionality could play a role. To avoid this problem, the cubic fcc phase ($T>350$ K) has been quenched to obtain metastable phases with cubic symmetry. A noncubic phase is usually formed with C_{60} dimers.[8] In the case of CsC_{60}, however, a cubic phase can be obtained by quenching to liquid nitrogen, and the detection by electron-spin resonance (ESR) of a Pauli-like susceptibility suggests it is metallic.[9] The purpose of this paper is to study in detail the electronic properties of this phase, called hereafter CQ for cubic quenched. On the other hand, the properties of the high-temperature cubic phase will be discussed in paper III.

(2) $n=2$ is not obtained with large alkali ions (K, Rb, Cs) that first fill the large octahedral site (forming A_1C_{60}) and then the two tetrahedral sites (forming A_3C_{60}). Na_2C_{60} is the only case where $n=2$ can be studied. As is the electron-hole symmetric of the insulating A_4C_{60} in the t_{1u} band, similar properties of these compounds would ensure that the insulating state is an intrinsic feature of these stoichiometries. This

is indeed the conclusion of a detailed comparative nuclear magnetic resonance (NMR) study of Na_2C_{60} and K_4C_{60}, presented in paper I.

(3) $n=5$ cannot be reached by inserting only alkali ions. A charge transfer of five electrons per C_{60} has been observed in ABa_2C_{60} (A=K, Rb, Cs) because Ba gives two electrons C_{60}.[10] We note that the first investigations indicate a metallic state; a Korringa law has, for example, been observed by NMR,[11] although more studies are still necessary because the t_{1u} band might be modified in this case by some hybridization with Ba orbitals.

This short review suggests that, beyond the opposition of A_3C_{60} and A_4C_{60}, compounds with an *even* number of electrons per C_{60} are insulators, while those with an *odd* number of electrons are metals. This is puzzling as, if the band picture fails because the Coulomb repulsion $U\approx 1$ eV is larger than the bandwidth $W\approx 0.5$ eV, all compounds with an integer number of electrons should be Mott insulators. The study presented here reveals the presence in CQ CsC_{60} of a small number of C_{60}^{2-}. This implies that there must be *an effective attractive interaction* at the local scale that helps to overcome the strong Coulomb repulsion. Understanding the actual mechanism for the formation of such pairs is then likely to shed light on how some of these phases can become metallic despite the large Coulomb repulsion. We will argue that a Jahn-Teller distortion (JTD) of the C_{60} molecule, which is a consequence of the electron-phonon coupling in these systems with a degenerate band, is the missing ingredient responsible for this behavior.

The difficulties introduced by the quench necessary to produce CQ CsC_{60} have limited so far experimental investigations, for example, there are no reported transport measurements. Also, the temperature range is restricted to $T<135$ K, above which the CQ phase transforms irreversibly into the dimer phase. Its structure is known to be orientationally ordered (sc $Pa\overline{3}$ symmetry).[12] As for its electronic properties, in addition to the Pauli-like ESR susceptibility, ^{13}C NMR spin-lattice relaxation follows a Korringa law down to 50 K, reinforcing the probability of a metallic character.[13] By analogy to A_3C_{60}, a superconducting ground state could then be expected, but no superconductivity has been detected down to 4 K.[9] We have suggested in Ref. 13 that it could be due to a competition with alternative ground states. Indeed, clear anomalies in the ^{133}Cs NMR spectrum indicate that *the electronic properties of CQ* CsC_{60} *are not homogeneous on the local scale*. The situation can be summarized by Fig. 1. Within a predominantly metallic phase, we proposed that two electrons get localized on some C_{60} balls (about 10%) and paired into a spin singlet. We will give in this paper experimental observations which support this scenario (Sec. II). To get more detailed information on this charge segregation phenomenon, we particularly focus our attention in this paper on some features that were not addressed in our previous report on this phase:[13] the distribution of the C_{60}^{2-} within the metal (Sec. III) and their lifetime (Sec. IV). Finally, we discuss the implications of the presence of C_{60}^{2n-} for the nature of the metallic state (Sec. V).

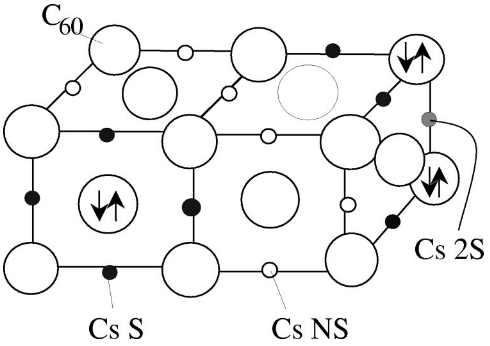

FIG. 1. Structural model of cubic quenched CsC_{60} describing the electronic properties as revealed by NMR. Spin singlets are localized on a fraction of the C_{60} balls (about 10%) leading to different types of Cs sites. They are called, respectively, NS, S, or $2S$ when zero, one, or two of the six C_{60} neighbors of one Cs site bears a singlet. The remaining electrons are delocalized over the other C_{60} balls.

II. THREE Cs LINES

In the ^{133}Cs spectrum of Fig. 2, obtained at 120 K and 7 T, three different lines are clearly resolved at -15 ppm, 800 ppm, and 1800 ppm, which we call by reference to their position with respect to a chemical reference,[14] i.e., their shift, NS (not shifted), S (shifted) and $2S$ (twice shifted), respectively. The latter line has a much smaller intensity ($6\pm 2\%$ of the total) than the two main lines and was not detected in Ref. 13. As shown hereafter, its detection allows to confirm and refine the model of Fig. 1.

Finding three Cs lines contradicts the expectations of structural studies, for which there is only one site for Cs in this phase, namely, the octahedral site.[12] With one site, only one NMR line should be observed, as in the high-temperature fcc phase.[15] The particular phase diagram of CsC_{60} allows to convince oneself rather directly that all these lines are intrinsic, because they all disappear irreversibly at the transition to the dimerized structure. In addition, SEDOR experiments reported in Ref. 13 demonstrate that the different Cs sites are mixed on the microscopic scale.

A. Local electronic environment of the three Cs lines

To understand the origin of the three different Cs sites, the study of the local electronic environment, as probed by the

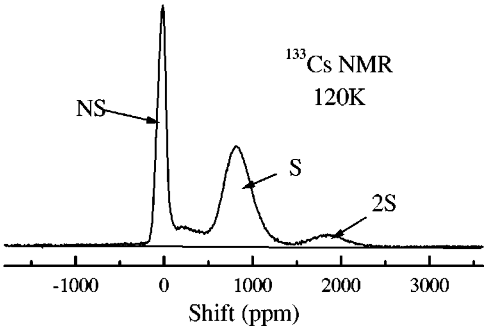

FIG. 2. ^{133}Cs NMR spectrum at 120 K in the cubic quenched phase showing the different Cs lines. The repetition time was 200 ms.

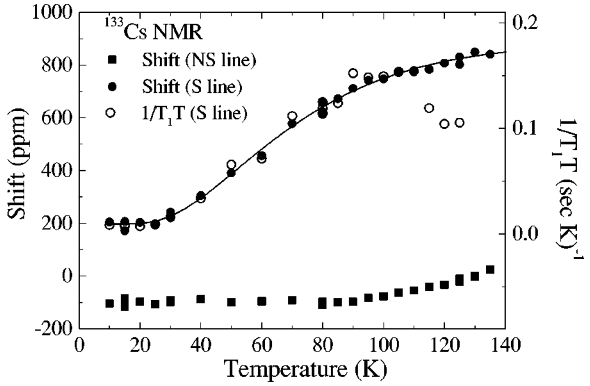

FIG. 3. ^{133}Cs NMR shifts with respect to a CsCl solution as a function of temperature for the two main Cs lines (NS and S) in cubic quenched $\mathrm{CsC_{60}}$. For the S line, $1/T_1T$ is also displayed by open symbols (right scale). The line is a fit to a law $A + B/T\exp(-E_a/k_BT)$ with $E_a = 15$ meV.

NMR shift K and the spin-lattice relaxation rate $1/T_1$, is very helpful. Figure 3 shows the shift for the NS and S lines together with $1/T_1$ for the S line, as a function of temperature. These data demonstrate that *the inequivalency between the Cs sites results from a local perturbation and that the three lines emerge from the coupling with zero (NS), one (S), or two (2S) "anomalous* C_{60}*."* Usually, the shift of one line is expected to read $K = \sigma + 6A\chi_{loc}$, where σ is the reference chemical shift, χ_{loc} is the local electronic susceptibility, and A is the hyperfine coupling between Cs and one of its six $\mathrm{C_{60}}$ first neighbors. If there are two types of balls, the shift will depend on the number of neighbors of each type. Calling χ_g and χ_m the susceptibilities of, respectively, one anomalous $\mathrm{C_{60}}$ and one metallic $\mathrm{C_{60}}$, A_g and A_m the hyperfine couplings between them and Cs, we expect the following relations.

$$K_{NS} = \sigma + 6A_m\chi_m,$$

$$K_S = \sigma + 5A_m\chi_m + A_g\chi_g,$$

$$K_{2S} = \sigma + 4A_m\chi_m + 2A_g\chi_g.$$

The small shift of the NS line, yielding $A_m\ \chi_m = 30$ ppm, is expected for Cs in metallic fullerides because electrons are almost completely transferred to the $\mathrm{C_{60}}$ balls. In addition, Fig. 3 shows that it is almost temperature independent according to a metallic susceptibility (the upturn above 100 K will be discussed in Sec. IV B). On the contrary, the two other lines exhibit unusually large shifts with large temperature dependences inconsistent with a metallic environment. This is because they are dominated by $A_g\ \chi_g$, which turns out to be much larger than $A_m\ \chi_m$. From the shift of the S line, we deduce $A_g\ \chi_g = 700$ ppm at 120 K, which implies $K_{2S} \approx 2K_S$ as observed in Fig. 2.

On the other hand, $1/T_1$ is proportional to the imaginary part of the local susceptibility $\chi''_{loc}(\omega_0)$ at the nuclear Larmor frequency ω_0 through A^2 (for ^{133}Cs, $\omega_0 = 40$ MHz at 7 T). Similar reasoning predicts that $(1/T_1)_{2S} \approx 2(1/T_1)_S$. At 80 K, we measure $^{2S}T_1 = 43$ ms $\pm$ 11 ms to be compared with $^{S}T_1 = 110 \pm 10$ ms for the S line, which definitively validates this interpretation.

Figure 3 also shows that there is a scaling between K and $1/T_1T$ for the S line up to 110 K, which ensures that they are both dominated in this temperature range by the same electronic excitations. This common behavior represents χ_g and is fitted in Fig. 3 by an activated law $(A/T)\exp(-E_a/k_BT)$ with $E_a \approx 15$ meV. This means that the anomalous $\mathrm{C_{60}}$ corresponds to a molecular arrangement with a gap E_a, and therefore electrons must be localized on these balls. The simplest idea would be that one electron is "trapped" by some defects, but in this case we should observe a paramagnetic behavior of this localized spin 1/2 at low temperatures, which we do not. The most plausible way to explain the vanishing susceptibility at low T is that *two* electrons are localized instead of one and paired up into a *singlet*. Molecular calculations[16] indeed predict that the singlet state wins over the triplet state (favored by Hund's rules) for $\mathrm{C_{60}}^{2-}$ in the presence of a JTD. In our opinion, this gain of energy associated with JTD is at the origin of the formation of $\mathrm{C_{60}}^{2-}$ within the metal. We note that there might be an additional temperature-independent contribution χ_0 to K as its low-temperature value is very different from our estimation of $\sigma = -300$ ppm or from the shift of the NS line.

$\mathrm{Na_2C_{60}}$ is a natural reference for the NMR behavior of the JTD $\mathrm{C_{60}}^{2-}$.[17] The gap measured on Cs S sites is much smaller than the 140 meV singlet-triplet gap of a $\mathrm{C_{60}}^{2-}$ measured through $1/T_1$ relaxation in $\mathrm{Na_2C_{60}}$. The limited stability of the CQ phase in temperature ($T < 135$ K) does not really allow to probe the existence of molecular excitations of this high energy. This 15-meV gap more likely corresponds to excitations of the singlets towards the metallic band. We have seen in paper I that the low-temperature behavior is governed by such band excitations for $\mathrm{Na_2C_{60}}$. The fact that the spin singlets cannot be viewed as an isolated entity might also explain why K and $1/T_1$ seem to tend to a constant value different from zero at low temperatures. More details will be given in Sec. V of this paper on the interactions between the singlets and the band.

B. Confirmation of local charge segregation

This inhomogeneous distribution of the charge among the $\mathrm{C_{60}}$ balls will create electric-field gradients (EFG) at the Cs S and $2S$ sites and, since ^{133}Cs is spin 7/2, it should sense them through its quadrupole moment Q. Actually, we show hereafter that the larger linewidth of the S line ($\Delta\nu \approx 16$ kHz at half-width) compared to the NS line ($\Delta\nu \approx 5$ kHz) is due to larger quadrupole effects on these sites.

In the presence of quadrupole effects, the different nuclear transition ($7/2 \leftrightarrow 5/2$, $5/2 \leftrightarrow 3/2$, etc.) acquire different frequencies, which results in a splitting of the spectra into a central line ($1/2 \leftrightarrow -1/2$ transition) and satellites for the other transitions. The position of the central line is unaffected to first order by the EFG, while satellites are shifted proportionally to a quadrupole frequency ν_Q, related to the strength of the EFG and the value of the quadrupole moment.

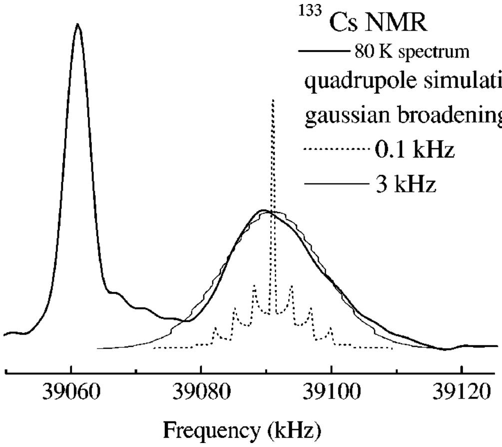

FIG. 4. ^{133}Cs spectrum at 80 K in the CQ phase (thick line). The other lines are quadrupole simulations of the S line shape explained in the text. The theoretical line shape is convoluted by a Gaussian of linewidth 0.1 kHz (dotted line) and 3 kHz (thin line).

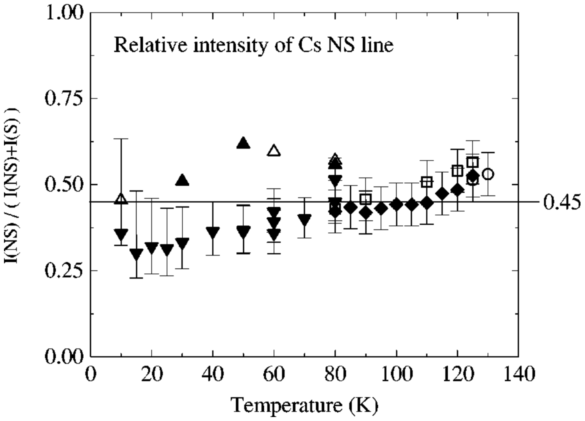

FIG. 5. Relative intensity of the ^{133}Cs NS line compared to that of the S line. This gives the percentage of NS sites as a function of temperature. The different symbols refer to different samples and/or different quench, showing a good reproducibility of this measurement. Error bars are larger at low temperatures when the two lines begin to overlap.

The precise line shape of the satellites depends on the symmetry of the EFG and on its orientation with respect to the NMR applied field. When ν_Q is very large, the satellite transitions sometimes become too broad to be observed. This is not the case here, the lengths of the NMR pulses optimizing the signal show that all nuclear transitions are detected.[18]

The shape of the spectrum expected for the S sites in our model can then be estimated by calculating the EFG, assuming a simple point-charge model in which the charge of C_{60} is localized at the center of the ball. If V is the electrostatic potential, the EFG is defined by its second derivative $V_{ii} = \partial^2 V/\partial i^2$, where $i = x, y, z$. The quadrupole frequency ν_q is then deduced form the largest component of the EFG (called V_{zz} by convention),

$$\nu_Q = \frac{3(1-\gamma_\infty)eV_{zz}Q}{2I(2I-1)h}, \tag{1}$$

where I is the nuclear spin and $(1-\gamma_\infty)$ is the Sternheimer antishielding factor.[19] The distribution of charges around one S site yields $\nu_Q \approx 6$ kHz. Furthermore, we obtain an axial EFG with $V_{xx} = V_{yy} = -1/2 V_{zz}$. A simulation of the spectra (with this powder sample, it has to be summed over all possible orientations[19]) is shown in Fig. 4 with two different broadenings of the theoretical curve. For the dotted line, a very small broadening is used, so that all satellite transitions are clearly visible; for the thin line, a realistic experimental broadening of 3 kHz (similar to the NS linewidth) allows a direct comparison with the experimental spectrum. The agreement is very good, which should only be taken as a proof of the consistency of our analysis. It is known that the EFG could vary significantly from this rough point-charge estimate, when a more realistic situation is considered, for example, an inhomogeneous distribution of the charge over the C_{60} molecule.

As for the $2S$ line, the linewidth is similar to that of S $(\Delta\nu \approx 18 \text{ kHz})$. This is consistent with the idea that the broadening is not of magnetic origin (for example, arising from a distribution of shift), in which case the linewidth should double. The quadrupole broadening for a $2S$ site in our model depends on the relative position of the ${C_{60}}^{2-}$ with respect to this Cs site. If they are on a straight line with respect to their common Cs neighbor, the point-charge calculation predicts that $\nu_Q[2S] = 2\nu_Q[S]$, while if they are in different directions $\nu_Q[2S] \simeq \nu_Q[S]$. This latter case would apparently be in better agreement with the data but, as already mentioned, the calculation of the EFG is somewhat rough and the lack of structure in the S and $2S$ line shape does not allow a refined analysis. Actually, the following section provides more reliable information on the distribution of the ${C_{60}}^{2-}$, which does not favor the arrangement, in which singlets are localized on the neighboring C_{60} balls. The detection of quadrupole effects on S and $2S$ sites is however essential to ensure a qualitative agreement with the model of Fig. 1.

III. DISTRIBUTION OF ${C_{60}}^{2-}$ WITHIN THE METAL

Following the model described in Fig. 1, the number of C_{60}^{2-} can be deduced from the relative intensities of the three lines, the area of one line being proportional to the number of sites resonating at this frequency. As can be seen in Fig. 5, the ratio between S and NS sites is nearly constant as a function of temperature, NS/S = 45/55. It is reproducible with different samples and/or different quench, so that it must correspond to a well-defined equilibrium. As there are six C_{60} neighbors to one Cs site, there must be roughly 10% of ${C_{60}}^{2-}$ to produce this ratio. With such a number, there is a non-negligible probability of finding a Cs site with two ${C_{60}}^{2-}$ neighbors, which correspond to our $2S$ sites.

A. Structural arrangement of the C_{60}^{2-}

More precisely, a closer look at the relative intensities, and especially the number of $2S$ sites, can help us to address the question of the *distribution* of ${C_{60}}^{2-}$ balls within the metal. In Fig. 6, we show the results of the calculations of the number of Cs sites as a function of the concentration of

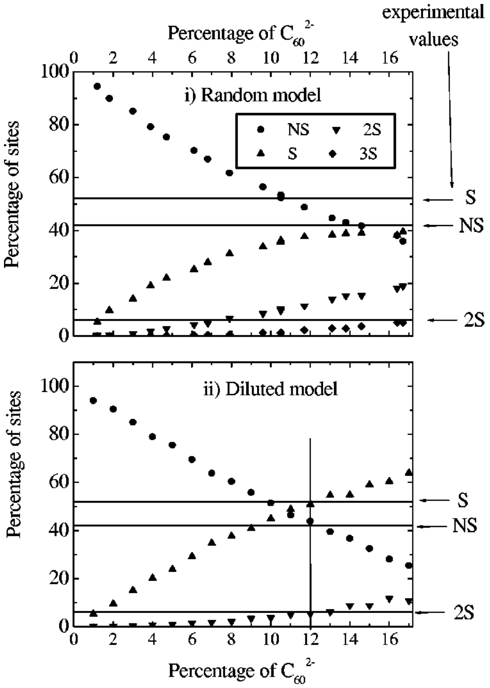

FIG. 6. Simulation of the number of NS, S, $2S$, and $3S$ Cs sites as a function of the percentage of $C_{60}{}^{2-}$ in two different situations: (i) the distribution of $C_{60}{}^{2-}$ is assumed to be random, (ii) a "diluted model" where two neighboring C_{60} molecules in a singlet state are excluded (in this case there are no $3S$ sites). Experimental values at 120 K are given by horizontal lines for comparison and the agreement with 12% $C_{60}{}^{2-}$ in the diluted case by a vertical line.

$C_{60}{}^{2-}$ in two different cases: (i) with a random distribution of $C_{60}{}^{2-}$, (ii) when neighboring $C_{60}{}^{2-}$ are excluded ("diluted" case).

To compare with the experiment, the number of S, NS, and $2S$ sites at 120 K are reported in Fig. 6. In the random case, the calculated intensities never quite reach the experimentally observed values. The fraction of $2S$ sites is rapidly higher than in the experiment and there are always more NS sites than S sites, contrary to the experiment. Furthermore, the intensity of a 3S line corresponding to C_{60} with three $C_{60}{}^{2-}$ neighbors would be sizable, although it is not observed.

In the diluted case, 12% of $C_{60}{}^{2-}$ almost exactly correspond to the experiment at 120 K, as shown by the vertical line. In this situation, the $3S$ configuration is forbidden, according to the experimental finding. Therefore, we conclude that *C_{60}^{2-} are diluted within the lattice to avoid a situation where they are first neighbors*. They do not segregate in superstructures that could be reminiscent of the formation of stripes. This last point is consistent with SEDOR experiments that rule out the formation of "clusters" of $C_{60}{}^{2-}$. This dilution could be favored because it minimizes the electrostatic repulsion between $C_{60}{}^{2-}$. As a function of decreasing temperature, comparison between Figs. 5 and 6 suggests an increase of the number of $C_{60}{}^{2-}$ to about 15%.

B. What limits the number of $C_{60}{}^{2-}$ to 10–15 %?

The experimental concentration of $C_{60}{}^{2-}$ appears a little bit puzzling at first, since one could expect that, if the $C_{60}{}^{2-}$ are more stable than $C_{60}{}^{-}$, there should be a total charge dismutation between C_{60} and $C_{60}{}^{2-}$. One problem with such a dismutated ground state is that it cannot be realized in this phase because of the inherent frustration of the fcc lattice. Furthermore, if first neighboring $C_{60}{}^{2-}$ are excluded, the maximum number of $C_{60}{}^{2-}$ is reduced to 25%. This would correspond to a completely ordered structure with a singlet on each corner of the cubic cell and none on the faces. With some disorder, this number would rapidly drop.

Maybe the $C_{60}{}^{2-}$ do not order collectively, because they are preferentially formed on some defects of the structure. A particular feature of the orientational order characterizing the sc phase is that there are two orientations for the C_{60} molecule. They are defined by an angle φ from which C_{60} are rotated with respect to the so-called "standard orientation" around one diagonal axis.[20] The value minimizing the C_{60} interactions occurs for $\varphi = 98°$ but a second minimum for $\varphi = 38°$ is nearly degenerate. The fit of the x-ray spectra can be improved in all sc phases (C_{60}, Na_2AC_{60}, and CQ CsC_{60}) by allowing 12–20 % of the balls at low T to be in a "minor orientation" corresponding to $\varphi = 38°$. For CQ CsC_{60} 16% gives the best fit at 4.5 K.[12] The closeness of this value with the number of singlets found here is such that one is tempted to consider that a ball in a minor orientation might be viewed as a disorder potential efficient in trapping a $C_{60}{}^{2-}$. It is indeed known that the overlap integrals between neighboring C_{60} are very sensitive to their relative orientations. In addition, in pure C_{60}, no correlation between the positions of the C_{60} in minor orientations could be found by x ray.[20] This is in agreement with the diluted model favored here for the singlets, which does not require an ordering between $C_{60}{}^{2-}$.

IV. MOTION OF SPIN SINGLETS ABOVE 100 K

The observation of three different lines indicates that the spin singlets are nearly static on well-determined C_{60} balls on the time scale of the NMR signal (roughly the inverse of the spectrum width, typically 100 μs here). However we show hereafter that other experimental observations, such as the NMR spin-lattice relaxation time T_1, allow to determine the lifetime of the spin singlets, which decreases with increasing temperature.

A. Relaxation behavior

As can be seen in Fig. 7, T_1 for the NS line changes dramatically between 110 K and 130 K, getting shorter by two orders of magnitude. At 130 K although the two main ^{133}Cs lines are perfectly resolved, they have almost the same T_1. This finding suggests that the nature (NS, S, or $2S$) of any Cs nucleus is changing with time, so that the properties of these sites become identical on the large time scale of the T_1 measurement (more than 50 ms). Such a chemical exchange between the S and NS lines could occur if a singlet jumps from a C_{60} ball to one of its neighbors.

This idea could, in principle, be directly tested by a two-dimensional NMR exchange experiment, similar to that used in Ref. 21. Here, we examine whether it could explain the variation of T_1 for the S and NS lines quantitatively. We

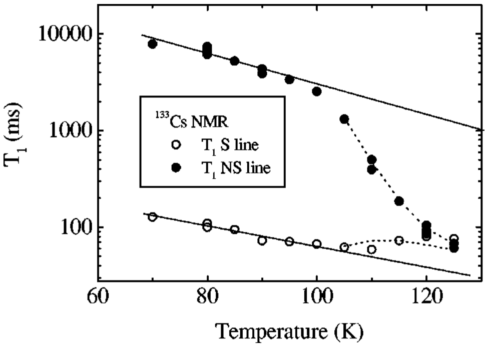

FIG. 7. T_1 for the two main ^{133}Cs NMR lines between 80 K and 135 K. The reduction of the NS T_1 for above 100 K is attributed to chemical exchange between the two sites. The straight lines extrapolate the temperature evolution of T_1 if there were no exchange. The other lines are a fit to our model of chemical exchange (see text).

assume that there is a probability p per unit time that such an electronic jump induces a change of a site S in NS and vice versa.[22] On the other hand, we suppose that for each situation (Cs neighboring a C_{60}^{2-} or not), there is a well defined relaxation rate W_S (W_{NS}). Let n_S (n_{NS}) be the number of S (NS) sites excited at the time $t=0$ by the saturation pulse of the T_1 experiment, the relaxation of the two spin species obeys the following coupled system:

$$\frac{dn_S}{dt}=-(W_S+p)n_S+pn_{NS},$$

$$\frac{dn_{NS}}{dt}=pn_S-(W_{NS}+p)n_{NS}.$$

For an infinite lifetime of the singlets, that is, for $p=0$, we recover the expected exponential decay with $(1/T_1)_S=W_S$ and $(1/T_1)_{NS}=W_{NS}$. When $W_{NS}\leqslant p\leqslant W_S$, the relaxation rate of the NS line is strongly reduced and tends to the value $(W_S+W_{NS})/2$ as p increases. By extrapolating the variation of W_S and W_{NS} by straight lines (see Fig. 7), we calculate with this model the value needed for p to obtain the experimental T_1 values. We can indeed reproduce the experimental results, as shown by the dashed lines in Fig. 7. For each temperature, the value of p that we have used is reported in Fig. 8. It follows an activated temperature dependence with $p=5\times10^{14}\exp(-3700/T)$, which sets a new energy scale for the sytem of about 320 meV, characterizing the energy barriers that trap the singlet. This magnitude is quite comparable with the activation energies usually found for the molecular rotations in A_nC_{60} compounds. The temperature range where we start to observe the motion of the spin singlets also roughly corresponds to the usual range for the onset of molecular motions. This reinforces the idea that the trapping of the singlets could be related to C_{60} in a minor orientation.

From the frequency of jumps between the two sites, we can deduce the characteristic lifetime of a spin singlet on a particular C_{60} ball. It changes from 15 s at 100 K to 3 ms at 130 K.

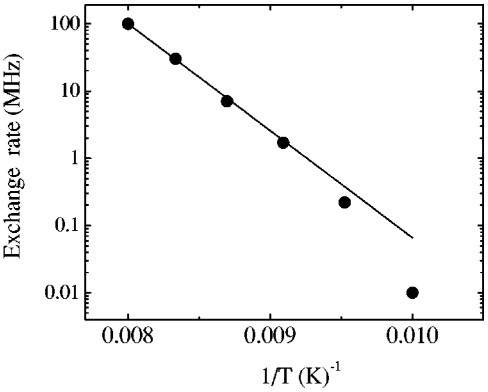

FIG. 8. Logarithmic plot of the value of the exchange parameter p used to obtain the line of Fig. 7 as a function of the inverse of the temperature. p can be fitted by an activated law as shown by the solid line.

B. Static spectrum

This characteristic time is still long compared to the time scale of the experiment, therefore the motions of the singlets do not show up clearly on the static spectra. However, in the range of temperatures for which the T_1 become identical, the scaling between the shift and the relaxation for the S line does not hold anymore (Fig. 3), which suggests that the jumps of the singlets begin to affect as well the resonance frequencies. If we could increase the temperature further, we could expect that p will become short enough to yield a *motional narrowing* of the static spectrum with three lines ultimately merging into one. From the data of Fig. 8, we can extrapolate that the two main lines would merge together at 150 K, when the frequency jump is comparable to the 30 kHz frequency separation of the two lines. This is a first step to reconcile the properties of CsC_{60} in its CQ and high-temperature phases, where only one Cs line is observed. The relation between these two cubic phases will be discussed in greater detail in paper III. The upturn of the NS shift above 110 K that can be noted on Fig. 3 might be a precursor sign of this effect.

V. INTERPLAY BETWEEN THE SPIN SINGLETS AND THE METALLIC STATE

Now that the existence of the electronic singlets has been established, one of course would like to understand how they coexist with the metallic band. Actually, in a metallic state with nominally one electron per C_{60}, one expects to find on each C_{60} either zero, two, or one electron, either with spin up or down, all states having equal probabilities if the on-site Coulomb repulsion is negligible. A 25% concentration of doubly charged C_{60}, or less if we include some Coulomb repulsion, is then quite natural. The particularity of CQ CsC_{60} is the increased lifetime of the electronic pairs, which

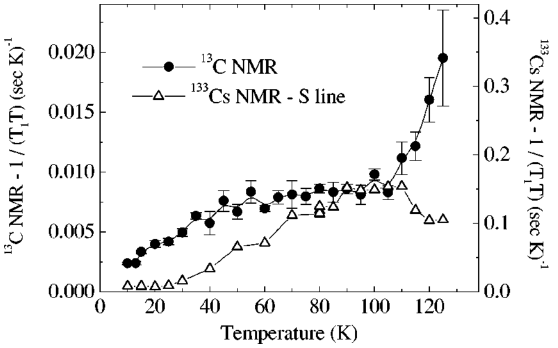

FIG. 9. $1/T_1T$ as a function of temperature for ^{13}C NMR (left scale) and ^{133}Cs NMR *S* line (right scale) in the CQ phase of CsC_{60}. While the ^{133}Cs *S* line behavior mainly reflects the properties of the gapped $C_{60}{}^{2-}$ ion, ^{13}C NMR is dominated by the metallic behavior, which becomes anomalous below 50 K.

we assign to the stability of the JTD $C_{60}{}^{2-}$. The pairs could then become trapped in the presence of any disorder potential, which seems to be the case in CQ CsC_{60}.

An important question that has been left aside so far is whether there is also 12% of static neutral C_{60} or if the unpaired electrons are delocalized on the 88% remaining balls. Although hypothetic, the possible "nonstoichiometrly" of the CQ phase is reminiscent of the discussions about the role of vacancies in A_3C_{60}. The physical model behind this idea was that A_3C_{60} would be a Mott insulator for integer filling because of the strong electronic correlations and that only the deviation from 3, introduced by a reproducible number of vacancies, allows the formation of a metal.[23] The same argument could be discussed for CQ CsC_{60}, namely, the metallicity at $T=0$ of this phase might arise solely from the holes induced by the nonstoichiometry associated with the localization of singlets if the C_{60} are not stabilized.

From the experimental point of view, we are not able to distinguish by ^{13}C NMR the signals of differently charged C_{60} balls, neither the signal of $C_{60}{}^{2-}$ nor that of possible neutral C_{60}, from that of the dominant fraction of $C_{60}{}^{-}$.[24] This is not surprising as it is well known that the spectra are broadened at low temperatures by an orbital contribution that dominates the electronic one.[25] Nevertheless, we do observe an anomaly in ^{13}C NMR, which could help us to understand the coupling between the band and the formation of $C_{60}{}^{2-}$. Figure 9 shows that $1/T_1T$ is not constant below 50 K, as would be expected for a simple metal, where $1/T_1T \propto n(E_f)^2$, but decreases. As emphasized by the comparaison with the ^{133}Cs *S* line in Fig. 9, this decrease is not related to the gap detected by the ^{133}Cs *S* line and then most likely reflects a change in the metallic properties. A decrease of $n(E_f)$, corresponding to the increase of the number of $C_{60}{}^{2-}$ at low temperatures detected in Fig. 5, would give a qualitative but not quantitative explanation [the decrease of $n(E_f)$ would be at most $\approx 5\%$]. To explain the strong decrease of $1/T_1T$, one has to assume that the change in the number of $C_{60}{}^{2-}$ dramatically affects the properties of the band, as could be expected for a strongly correlated metal near half-filling.

VI. CONCLUSION

We have shown that many independent NMR observations support the idea that spin singlets are present in the CQ phase of CsC_{60} on a small fraction of the C_{60} balls (10–15 %). The lifetime of these spin singlets on a given ball increases exponentially with decreasing temperature (from 3 ms at 130 K to 15 s at 100 K). We believe that they are formed randomly by hopping within the metallic phase and become trapped at low temperatures, maybe by the disorder potential associated with the existence of two different orientations for the C_{60} molecules in the sc phase.

The most important consequence of this study is that it reveals an *attractive interaction at the local scale*, which allows to form spin singlets despite the large Coulomb repulsion that should forbid a double occupancy of the same site. We propose that this interaction is mediated by Jahn-Teller distortions. Because the gain of energy associated with a JTD is larger for an evenly charged molecule, these configurations could be stabilized even in compounds with odd stoichiometries. It is natural to wonder whether this also plays a role in the case of A_3C_{60}.

As a matter of fact, the splitting of the ^{133}Cs spectrum, which directly results from the presence of $C_{60}{}^{2-}$, inevitably refers to the T' line observed in many fcc A_3C_{60} systems for the alkali in the tetrahedral site, albeit with a much smaller intensity.[26] Despite the large amount of work devoted to this problem, the origin of this line is still unclear. By analogy to CQ CsC_{60}, where the splitting is much clearer, it is tempting to argue that the T' line could correspond to a small fraction of about 3% localized $C_{60}{}^{2-}$ or $C_{60}{}^{4-}$ in A_3C_{60}, maybe trapped by some defects. This would mean that the peculiar properties of CQ CsC_{60} actually reveal a common trend in alkali fullerides.

Indeed, we will develop in paper III the idea that $C_{60}{}^{2-}$ and $C_{60}{}^{4-}$ are also formed in A_3C_{60} systems, but on very short time scales of the order of 10^{-14} s. The main difference between CQ CsC_{60} and these other compounds then resides in the *lifetime* of the $C_{60}{}^{2n-}$. The fact that neutral C_{60} is not stabilized by JTD could favor localization, because a jump of one electron is less likely to lead to a stable configuration than in A_3C_{60}. The quasilocalization of $C_{60}{}^{2-}$ in CQ CsC_{60} at low temperature could also explain why it is not superconducting. The difference of behavior should vanish as the singlets start to move more freely with increasing temperature. Above 300 K, CsC_{60} can be studied again in a cubic structure, but, unexpectedly, it appears to be insulating. We will show data at high temperature in paper III that allow to conclude that this behavior is in fact similar to that of some A_3C_{60} systems and can be explained by the presence of $C_{60}{}^{2-}$.

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