Role of dynamic Jahn-Teller distortions in Na$_2$C$_{60}$ and Na$_2$CsC$_{60}$ studied by NMR

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Through $^{13}$C NMR spin lattice relaxation ($T_1$) measurements in cubic Na$_2$C$_{60}$, we detect a gap in its electronic excitations, similar to that observed in tetragonal A$_2$C$_{60}$. This establishes that Jahn-Teller distortions (JTD) and strong electronic correlations must be considered to understand the behaviour of even electron systems, regardless of the structure. Furthermore, in metallic Na$_2$CsC$_{60}$, a similar contribution to $T_1$ is also detected for $^{13}$C and $^{133}$Cs NMR, implying the occurrence of excitations typical of JT distorted C$_{60}$ (or equivalently C$_{60}^4$). This supports the idea that dynamic JTD can induce attractive electronic interactions in odd electron systems.

It has been known, almost since the discovery of alkali doped fullerene, that A$_4$C$_{60}$ is insulating, while A$_2$C$_{60}$ is metallic and superconducting [1]. This contrasts with expectations for a rigid band filling model, as the C$_{60}$ lowest unoccupied molecular $t_{1u}$ level should form a triply degenerate band. All A$_n$C$_{60}$ with n<6 should either be metals if the strength of the Coulomb repulsion U is small compared to the band width W or Mott insulators if U is larger. In fullerides, U/W is close to the critical ratio where a metal-insulator transition is expected [2], but the observation of both metals and insulators within this family is puzzling.

An attractive explanation [3,4] is that the presence of Jahn-Teller distortions (JTD) could create effective electronic interactions which would modulate U, so that different compounds could be on different sides of the metal-insulator transition. More precisely, the computation of $U_{\text{eff}} = E(n+1)+E(n-1)-2E(n)$, where n is the number of electrons per C$_{60}$, supports this idea when the larger gain of electronic energy associated with the JTD of an evenly charged C$_{60}$ ball is taken into account [3,4]. It follows that in even electron systems JT effects add to the Coulomb repulsion to localize electrons, whereas for odd electrons systems they oppose the Coulomb repulsion and favor delocalization. Hence, A$_{2n}$C$_{60}$ could be insulating whereas A$_{2n+1}$C$_{60}$ could become metallic despite the strong electronic correlations. To give some experimental support to this idea, a large amount of work has been devoted to the search of JTD in fullerides, but without success up to now. However, the distortion is expected to be very small and possibly dynamic, which makes it difficult to detect directly. Alternatively, recent models have suggested that the different properties between A$_4$C$_{60}$ (body centered tetragonal) and A$_3$C$_{60}$ (face cubic centered) are due to their different structures [1].

In order to sort out the relevant parameters for the physics of A$_n$C$_{60}$, we present here an NMR study of Na$_2$C$_{60}$ and Na$_2$CsC$_{60}$, as they have the same cubic structure but even and odd stoichiometries. Na$_2$C$_{60}$ is the only compound with n=2 known so far, but experimental studies are still limited and controverted. The first ESR studies [7] concluded that its electronic properties were identical to K$_4$C$_{60}$ but more recently, another ESR investigation claimed that it was metallic with a metal-insulator transition at 50 K [8]. We present the first NMR study of Na$_2$C$_{60}$, which allows to detect singlet-triplet excitations of JTD C$_{60}$ balls, as found in A$_2$C$_{60}$ [1,4]. This rules out a strong dependence of the electronic properties on the structure, as one expects similar properties for n = 2 and 4 due to electron-hole symmetry in the $t_{1u}$ band. We then extend our investigation to Na$_2$CsC$_{60}$, which superconducts below $T_c = 12 K$ [4]. In the metallic phase, we evidence an anomalous contribution to the $^{13}$C and $^{133}$Cs NMR spin-lattice relaxation rate $1/T_1$. As it is similar to that found in Na$_2$C$_{60}$, we assign it to the presence of Jahn-Teller distorted C$_{60}^{(2,4)-}$. This demonstrates the importance of dynamic JTD in metallic fullerides also and suggests that the metallic character of A$_3$C$_{60}$ could be related to an enhanced stability of C$_{60}^{(2,4)-}$.

The Na$_2$C$_{60}$ and Na$_2$CsC$_{60}$ samples were prepared by conventional solid-state reaction. Phase purity was checked by X-ray diffraction. At high T, both compounds have the same structure as other A$_n$C$_{60}$ systems (face centered cubic structure (fcc) with space group Fm$ar{3}$m) but they undergo below room T an orientational order transition like pure C$_{60}$ (the symmetry is reduced to simple cubic (sc) with Pa$ar{3}$ space group) [1,4,3].

NMR measurements were carried out in a 7 T field and spin-lattice relaxation measurements were obtained with usual saturation recovery sequences.

Figure 8 shows that $1/T_1$ for $^{13}$C in Na$_2$C$_{60}$ increases very steeply and can be modelled by an activated law $1/T_1 \propto \exp(-E_a/k_BT)$ with $E_a = 140 \pm 20$ meV. This contrasts with the linear T dependence (the Korringa law) expected for simple metals [3] and indicates that a gap $E_a$ separates the ground state from the excited states of the system. This is similar to the insulating A$_4$C$_{60}$ systems, where an activated behaviour dominates the relaxation with $E_a \approx 50 - 75$ meV [1,4,3,4]. Besides this central fact, more features are evident:

i) There is a peak at 180 K which is typical of a
esr of the system. Therefore, we have measured with NMR should give us further insight into the properties between 200 and 300 K [7] and a quantitative comparison expected for T \text{low} \[18\]. This is again similar to A _\text{Na}^2\text{C}_60 part and a Curie-Weiss contribution. The intrinsic part _\text{chi}_{\text{int}}_ \text{of C}_60 decomposed into an intrinsic part and a Curie-Weiss contribution.

contribution due to the slowing down of C_60 molecular motions [17] as shown in more details elsewhere [18].

ii) At low temperature, 1/T_1 is enhanced with respect to the activated law. On Figure 4, it can be more clearly seen that (T_1/T)^{-1} tends to a constant value. If intrinsic, such a contribution could indicate a residual metallic character with a small density of states _n(E_F) \approx 1 \text{ eV}^{-1}\text{spin}^{-1} [18]. A very similar behaviour was in fact observed in Rb_2\text{C}_60, where an additional relaxation mechanism becomes efficient at low T, which was assigned to a small gap (∼ 20 meV) [14]. This gap is easily closed by applying pressure and a growing linear contribution to the relaxation is observed with increasing pressure that coexists with the activated contribution [16]. By analogy, Na_2\text{C}_60 would be equivalent to Rb_2\text{C}_60 under an applied pressure of roughly 1 kbar.

The relaxation behaviour does not change down to 10 K, implying that there is no transition to an ordered ground state. In particular, we do not observe any anomaly at 50 K that might be assigned to a metal-insulator transition as claimed in ref. [8]. Hence, the ground state is non-magnetic, which is confirmed by the absence of magnetic broadening of the NMR spectra at low T [15]. This is again similar to A_4\text{C}_60.

iii) Above 300K, 1/T_1 saturates, which would only be expected for T \gtrsim E_a/k_B \approx 1600 \text{ K}. As the structural transition from sc to fcc takes place at 310 K, it is natural to wonder whether there is an associated change of the electronic properties, for example a smaller gap in the fcc phase. Data at higher temperatures would be needed to conclude this unambiguously.

Like 1/T_1, the ESR susceptibility \chi_{\text{esr}} increases between 200 and 300 K [8] and a quantitative comparison with NMR should give us further insight into the properties of the system. Therefore, we have measured \chi_{\text{esr}} in our sample (see inset of Fig. 1), with results analogous to those of ref. [8]. The intrinsic part \chi_{\text{int}} of \chi_{\text{esr}} is difficult to extract precisely below 250 K as a large Curie contribution is always observed in Na_2\text{C}_60. From a low T fit, we deduce a Curie-Weiss contribution C/(T + T_\chi) with T_\chi = 8 K corresponding to 2.3 % impurities per C_60. As can be seen in Fig. 4, the remaining part \chi_{\text{int}} tends to a constant value of 6.1 \times 10^{-5} \text{ emu/mol} at low T. Although direct conductivity measurements will be necessary to conclude about a possible weak metallicity of this compound, we note that such a Pauli contribution in \chi_{\text{int}} would be consistent with the constant (T/(T)^{-1} found at low T that we have previously discussed. The T dependent contribution \chi to \chi_{\text{int}} can then be compared to 1/T_1 (see right scale of Fig. 1). The simplest way to relate 1/T_1 and \chi is to assume that both are associated with electronic excitations characterized by a spin correlation function with an exponential decay time \tau. In the limit \omega_{\text{c}} \tau << 1, where \omega_{\text{c}} is the electronic Larmor frequency, one expects [19]:

\[
\frac{1}{T_1} = \left( \frac{A}{\hbar} \right)^2 \frac{\chi}{N_A \mu_B^2} \omega_{\text{c}}^2 k_B T \tau
\]

where A is the hyperfine coupling and N_A the Avogadro number. Fig. 4 evidences the validity of this scaling between 1/T_1 and \chi. Unfortunately, the limited T range of the experiment does not allow to probe efficiently the T dependence of \tau. Assuming that it is constant and using A = 4 \times 10^{-20} \text{ erg} [18], we obtain \tau \approx 8 \times 10^{-14} \text{sec}, which has the same order of magnitude as that found in Rb_2\text{C}_60 and is consistent with \omega_{\text{c}} \tau << 1.

To summarize, we conclude that there are strong similarities between Na_2\text{C}_60 and A_4\text{C}_60. To describe the weakness of the metallic character of these compounds, models involving a (dynamic) JTD of the C_60 molecule that lifts the degeneracy of the t_{1u} levels are the most likely, as they naturally yield a non-magnetic ground state. Indeed, although it could be singlet or triplet, depending on the nature of the JTD, molecular calculations indicate that the singlet state has the lowest energy [4] for both n=2 and n=4. However, as Hund’s rules favor the triplet state, the two states lie close in energy and singlet-triplet like excitations would take place when one molecule goes from one distortion to the other. The 140 meV value of the gap observed in 1/T_1 corresponds to the molecular estimate for this “spin-gap” [20]. We can then attribute the relaxation to a coupling between the NMR nuclei and the thermally populated triplet states, which have a spin lifetime \tau. While ref. [18] predicts the same spin-gap for C_5\text{C}_60 and C_{60}^{2-}, the experimental difference between Na_2\text{C}_60 and A_4\text{C}_60 could be due to their different structures, as suggested by the saturation in 1/T_1 observed here at the structural transition. Alternatively, electron-hole symmetry in the t_{1u} level might be broken when excitations to higher electronic levels (t_{1g}) are taken into account [20].

The fact that molecular properties on an energy scale of 140 meV are not smeared out by the formation in the solid of bands of typically 500 meV width requires strong electronic correlations. This was recognized by
FIG. 2. $1/T_1 T$ for $^{13}$C as a function of temperature in Na$_2$C$_{60}$ and Na$_2$CsC$_{60}$. Below 200 K, the recovery curves for the magnetization are not exponential and $T_1$ is defined as the mean value of a double exponential fit.

FIG. 3. Left scale : $1/T_1 T$ for $^{133}$Cs as a function of temperature in Na$_2$CsC$_{60}$. The recovery curves are exponential through the full T range. As shown by the line, the relaxation can be divided into $1/T_1 T = \lambda + B/T^* \exp(-E_0/T)$ with $E_0 = 110$ meV. Right scale : $\chi^2$ as a function of T.

Fabrizio et al. [31], who qualified these systems as “Mott Jahn-Teller insulators”. They emphasized that the splitting between $t_{1u}$ levels induced by the JT distortion, estimated to be 500 meV (and observed experimentally as an “optical gap” in $\Delta C_{60}$ [22,23]), is too small to lead to a band insulator. Electron correlations increase the average time spent by one electron on a C$_{60}$ ball, so that “molecular physics”, such as the JT distortions, can take place even before complete localization. This might be the case in Na$_2$C$_{60}$, where a residual metallic character is suggested by our low $T$ data.

We now turn to the study of Na$_2$CsC$_{60}$, for which Fig. 2 shows $(T_1 T)^{-1}$ compared with Na$_2$C$_{60}$. Below 150K, $(T_1 T)^{-1}$ in Na$_2$CsC$_{60}$ is dominated by a $T$ independent contribution, in agreement with its metallic character, which is nearly suppressed in Na$_2$C$_{60}$. But at higher $T$, $(T_1 T)^{-1}$ departs from the metallic behaviour and surprisingly, its overall behaviour is very similar to that of Na$_2$C$_{60}$. We want to argue here that this is not accidental but reveals a similar relaxation mechanism in the two compounds. We will restrict our discussion to the $sc$ phase of Na$_2$CsC$_{60}$ ($T < 300$ K), since it was recently suggested that the $fcc$ phase might be insulating [24].

The strong deviation from the Korringa law in Na$_2$C$_{60}$ had already been observed previously [22,24]. It was attributed to an increase of the density of states associated to the lattice expansion plus a peak due to molecular motions around 300 K. We present here new experimental data to refute this hypothesis. First, to avoid completely a contribution of the C$_{60}$ molecular motions to the relaxation, we have performed measurements on $^{133}$Cs which is not coupled to these motions. As can been seen on Fig. 3, $(T_1 T)^{-1}$ for $^{133}$Cs does not exhibit any molecular motion peak around 180 K. Such a peak, already discussed for Na$_2$C$_{60}$, is also present in the $^{13}$C relaxation of Na$_2$CsC$_{60}$ but was missed in the study of ref. [22,24]. On the other hand, as for $^{13}$C, $(T_1 T)^{-1}$ for $^{133}$Cs does deviate above 150 K from the Korringa law, ensuring that this deviation is not due to molecular motions but to electronic excitations. Second, to determine an eventual $n(E_f)$-related increase of $(T_1 T)^{-1}$,

we have measured $\chi_{esr}$ in our sample. It does not follow a simple Pauli law, but increases slightly above 100 K. The increase of $(T_1 T)^{-1}$ should scale with $\chi^2$, if both were related to a variation of $n(E_f)$ [15], but Fig. 3 shows that $(T_1 T)^{-1}$ increases much more steeply, already at 200 K, well into the $sc$ phase. Hence, the increase of $(T_1 T)^{-1}$ in Na$_2$CsC$_{60}$ is related to an additional relaxation channel. It can be fitted by an activated law with $E_0 = 110 \pm 5$ meV, as sketched on Fig. 3.

It is then natural to propose that this additional relaxation mechanism is similar to that proposed for Na$_2$C$_{60}$. For a JT distorted C$_{60}$, there are no possibilities for singlet-triplet transitions directly similar to the ones of a C$_{60}$. Therefore we believe that the similarity between Na$_2$C$_{60}$ and Na$_2$CsC$_{60}$ comes directly from the presence of C$_{60}$- in Na$_2$CsC$_{60}$, or C$_{60}$ which are equally likely to be formed when electrons jump from ball to ball in the metal [27]. As the gap observed by NMR in Na$_2$C$_{60}$ is related to individual excitations of C$_{60}$ and not to a band gap, similar excitations might occur in Na$_2$CsC$_{60}$ as well, if $C_{60}^{-2}$ exist within the metal for times $\tau_{pair}$ sufficiently long compared to the spin lifetime $\tau$ of an excited state. This does not imply a static charge separation in Na$_2$CsC$_{60}$, which is ruled out by the $^{23}$Na NMR spectra (not shown) which display one narrow line shifted from the position of Na$_2$C$_{60}$.

Using Eq. 1, $\tau$ can be extracted from $(T_1 T)^{-1}$ if the singlet-triplet component in $\chi$ is known. We assume a similar $T$ dependence as that found in Na$_2$C$_{60}$, which scales as $\chi = \alpha T^{-1} \exp(-E_a/T)$ in the experimental $T$ range and the gap value $E_a = 110$ meV determined accurately from $^{133}$Cs NMR. Such a contribution to the susceptibility can only be smaller than the increase of $\chi_{esr}$, which implies $\alpha \lesssim 2$ and yields $\tau \approx 10^{-14}$ sec. On the other hand, the time $\tau_{esr}$ spent by one electron in the vicinity of one C$_{60}$, which is a lower limit for $\tau_{pair}$, can be estimated by $\tau_{esr} \approx \hbar n(E_f) \approx 6.10^{-15}$ sec in Na$_2$CsC$_{60}$, which is only slightly shorter than $\tau$. Electronic correlations, Jahn-Teller effects, as well as scattering on a C$_{60}$ ball, would all increase $\tau_{esr}$ compared to this simple es-
timate, so that we are likely in the limit $\tau_{\text{pair}} > \tau$ where the $C^{2(4)-}_{60}$ can contribute to the NMR relaxation.

Both the gap value and $\tau$ are reduced compared with Na$_2$C$_{60}$. The same trend was observed in Rb$_3$C$_{60}$, where $\tau$ and the gap decrease with increasing pressure, i.e., increasing density of states $[14]$. This suggests a direct relation between $\tau$ and $n(E_f)$, which raises the question of the origin of the relaxation time $\tau$ for triplet states. One could expect such a trend if the triplet states are relaxed by conduction electrons, although the triplet state is formed by “potential” conduction electrons, making it difficult to distinguish different spin species. This would also predict that for higher density of states like in K$_4$C$_{60}$ and Rb$_3$C$_{60}$, the contribution of triplet states to the relaxation almost disappear. We note that although a “better” Korringa law is observed in these compounds $[28]$, a 20%-30% decrease of $(T_1T)^{-1}$ was still noticed between 100 K and 300 K. It could in fact have a similar origin, so that the presence of $C^{2(4)-}_{60}$ might be a common feature of metallic A$_3$C$_{60}$ compounds.

In conclusion, we have shown that Na$_2$C$_{60}$ has a non-magnetic ground state and that its low energy electronic excitations are characterized by a 140 meV spin-gap. This is very similar to A$_3$C$_{60}$ systems and supports the “Mott JT scenario” $[21]$ to describe fullerides with 2 or 4 electrons per C$_{60}$. Furthermore, we evidence very similar electronic excitations in Na$_2$CsC$_{60}$, coexisting with typically metallic ones. In both cases, we assign the spin-gap to singlet-triplet excitations between two JT distortions of C$_{60}^{2n-}$ balls ($n = 1$ or 2). Because the triplet state provides a very efficient relaxation mechanism for NMR, we could indirectly detect here for the first time the presence of dynamic JTD in a superconducting fulleride. Our study also implies that Na$_2$CsC$_{60}$ undergoes rapid charge fluctuations (on a time scale of $10^{-14}$ sec) which create preferentially C$_{60}^{2(4)-}$. We suggest that this can be rationalized as a consequence of the JTD which stabilizes evenly charged C$_{60}$.

A first indication of the role played by JTD in the electronic properties of fullerides was the observation in the metallic cubic quenched CsC$_{60}$ of localized C$_{2n}^{2-}$ $[22]$. Although this large difference of charge lifetime remains to be understood, these behaviours suggest that the key feature behind the physics of cubic fullerides is due to an interplay between strong electronic interaction and “JT mediated electronic interactions”. Electronic correlations are essential for molecular excitations, such as the JTD, to exist in the solid. JT mediated electronic interactions play in turn a crucial role in determining the insulating or metallic character of a given compound, by inducing repulsive interactions in even electron systems and attractive interactions in odd electron systems, in order to promote the existence of $C^{2n-}_{60}$. The recent discovery of a way of doping continuously the C$_{60}$ t$_{1u}$ level through a field-effect device might open a new path for checking this original behaviour more systematically $[30]$.

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