

## Persistence of molecular excitations in metallic fullerenes and their role in a possible metal to insulator transition at high temperatures

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We present  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spin-lattice relaxation measurements ( $1/T_1$ ) in  $\text{Na}_2\text{CsC}_{60}$  and  $\text{Rb}_3\text{C}_{60}$  from 10 to 700 K. The large temperature range of this measurement allows to define unambiguously an increase of  $1/T_1 T$  with increasing temperature, which is anomalous in a simple metallic picture, where the Korringa law predicts  $1/T_1 T = \text{const}$ . From the analogy with the relaxation data in  $\text{Na}_2\text{C}_{60}$  and  $\text{K}_4\text{C}_{60}$ , we suggest that this increase is associated with the existence of an additional relaxation channel related to singlet-triplet (ST) excitations of Jahn-Teller distorted  $\text{C}_{60}^{2-}$  and  $\text{C}_{60}^{4-}$ . The amplitude of the ST component is found to depend directly on the density of states, which indicates an interplay between metallic and molecular excitations. We propose a phenomenological model to describe the correlation between the two phenomena. The  $\text{C}_{60}^{2-}$  and  $\text{C}_{60}^{4-}$  would be formed within the metal on very short time scales ( $10^{-14}$  s) that do not imply static charge segregation. The interaction between metallic and molecular properties is also revealed by the high-temperature behavior of  $\text{Na}_2\text{CsC}_{60}$  and  $\text{CsC}_{60}$ , which we then discuss. A divergence between the behaviors of  $1/T_1$ , the NMR shift, and the electron-spin resonance susceptibility is interpreted as the result of a rapid increase of the lifetime of the charge carriers, signaling a tendency to charge localization. In our analysis, the particular stability of  $\text{C}_{60}^{2-}$  is then a common feature of all known metallic fullerenes and allows to reconcile apparently contradicting properties of these systems.

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### I. INTRODUCTION

The properties of strongly correlated materials have been in the focus of solid-state research for many years. To describe the competition between Coulomb and kinetic energies, the one-band Hubbard model is widely used. However, many real systems exhibit orbital degeneracy, which adds a degree of freedom that is not always taken into account. Fullerenes are one such example as the lowest unoccupied molecular orbital that forms the narrow  $t_{1u}$  conduction band in the solid is triply degenerate. Together with the strong electron-phonon coupling characteristic of these materials, this leads to the possibility of Jahn-Teller distortions (JTDs). Whereas predictions for the JTDs can be done quite accurately for a single molecule,<sup>1</sup> their role in the solid is less clear. The broadening of the molecular levels should at first sight reduce the gain of energy associated with JTDs. As it is estimated to be of the same order of magnitude as the gap opened by the JTDs, the survival of these distortions in the solid can be questioned.

Yet, JTDs appear to play a crucial role in many different fullerenes. This paper concludes a series of three papers devoted to nuclear magnetic resonance (NMR) studies of different stoichiometries of alkali fullerenes, where we have already seen evidence for such effects. It is widely believed that JTDs contribute to convert  $\text{Na}_2\text{C}_{60}$  and  $\text{A}_4\text{C}_{60}$ , which should be metals in a band picture, into nonmagnetic insulators. In our first paper<sup>2</sup> (called hereafter paper I), we have presented NMR data supporting this scenario and we refer

the reader to references therein to the various papers invoking JTDs in the properties of  $\text{A}_4\text{C}_{60}$ . Perhaps more surprisingly, they offer the most likely way for explaining the unexpected properties of the cubic quenched (CQ) phase of  $\text{CsC}_{60}$ , the only alkali cubic metallic fullerene phase known so far besides  $\text{A}_3\text{C}_{60}$ . In this phase, we have shown in Ref. 3 and paper II (Ref. 4) that the electronic properties are inhomogeneous on the local scale because spin singlets are trapped in about 10% of the  $\text{C}_{60}$  balls. We believe that these singlets are stabilized by a JTD of the  $\text{C}_{60}$  ball which is energetically more favorable for  $\text{C}_{60}^{2-}$  than  $\text{C}_{60}^{-}$ .

More generally, a simplified view of the effect of JTDs on the  $t_{1u}$  band as a function of its filling is sketched in Fig. 1. The gain of energy obtained from the JTDs is found to be always larger for evenly charged  $\text{C}_{60}$ . Then, JTDs

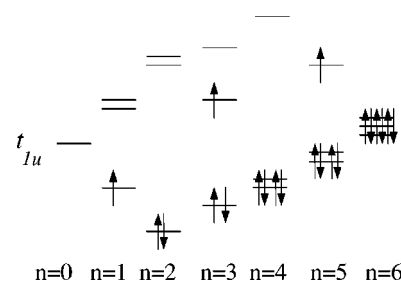


FIG. 1. Schematic representation of the splitting of the  $t_{1u}$  levels as a function of the  $\text{C}_{60}$  charge induced by Jahn-Teller distortions (adapted from Refs. 1 and 7). Only the most stable JTD is represented.

could induce attractive interactions for odd stoichiometries in order to promote the formation of the more stable  $C_{60}^{2n-}$  (hence, the presence of the spin singlet in CQ  $CsC_{60}$ ), whereas for even stoichiometries, they would induce repulsive interactions and favor localization (hence, the insulating  $Na_2C_{60}$  and  $A_4C_{60}$ ). This suggests an elegant way for rationalizing the different properties of even and odd stoichiometries<sup>1,5,6</sup> and the purpose of this paper is to determine to what extent this framework could be relevant for  $A_3C_{60}$ , extending ideas already presented for the case of  $Na_2CsC_{60}$ .<sup>8</sup>

Despite the possible survival of these unusual molecular properties in the solid, there is a general consensus that the electronic properties of  $A_3C_{60}$  can be understood in a rather conventional way, both for the metallic and superconducting states.<sup>9</sup> In the first part of this paper (Sec. II), we show that there are, however, in  $A_3C_{60}$  deviations with respect to the conventional metallic NMR behavior, which we attribute to an enhanced stability of  $C_{60}^{2-}$  and  $C_{60}^{4-}$ . The consequences of the formation of such “pairs” on the properties of the metal is an interesting issue to clarify. For this study, we choose two examples of superconducting fullerides  $Rb_3C_{60}$  ( $T_c = 29$  K) and  $Na_2CsC_{60}$  ( $T_c = 12$  K). While the structure of  $Rb_3C_{60}$  is face-centered cubic (fcc, space group  $Fm\bar{3}m$ ) through the whole temperature range,<sup>10</sup>  $Na_2CsC_{60}$  undergoes an orientational transition from fcc to simple cubic (sc, space group  $Pa\bar{3}$ ) around 300 K.<sup>11</sup> In the second part of this paper (Sec. III), we study the high-temperature properties of two metallic fullerides where  $C_{60}^{2-}$  have been detected,  $Na_2CsC_{60}$  and  $CsC_{60}$ . The behavior departs from that of a metal and can be best described by a progressive localization of the charge carriers with increasing temperature. This is likely related to a change of the role of the JTDs as a function of temperature. However, the most important conclusion of this study might be that it reveals an overall similar behavior in these two compounds, which simplifies greatly the understanding of fullerides by unifying apparently conflicting properties. Up to now,  $CsC_{60}$  was thought to be metallic in its low-temperature phase<sup>12</sup> and insulating in its high-temperature phase.<sup>13</sup> The connection between these two behaviors was not understood, which has forbidden so far a comparison with  $A_3C_{60}$  systems.

## II. DETECTION OF MOLECULAR EXCITATIONS THROUGH SPIN-LATTICE RELAXATION MEASUREMENTS IN SUPERCONDUCTING FULLERIDES

In this section, we demonstrate first that the deviation of  $1/T_1T$  from the simple metallic behavior is due to an additional relaxation channel. In Sec. II A, we show that it cannot be explained solely by a modification of the usual metallic relaxation process and discard some possibilities that were advocated so far. In Sec. II B, we suggest that the relevant excitations are singlet-triplet distortions of JTD  $C_{60}^{2-}$  and  $C_{60}^{4-}$ . A phenomenological model that correlates the spin lifetime of the triplet excitations to the metallic density of states is given. It allows to explain the data consistently, which gives some weight to it.

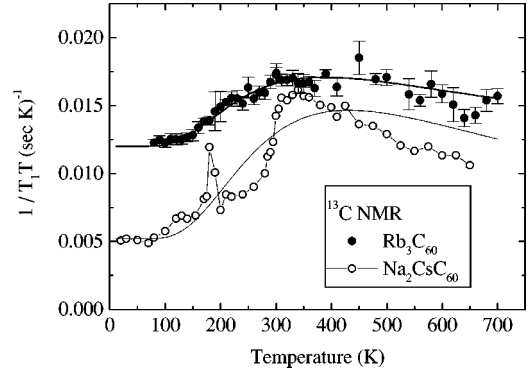


FIG. 2.  $^{13}C$  NMR  $1/T_1T$  as a function of the temperature for  $Rb_3C_{60}$  and  $Na_2CsC_{60}$ . The thick line ( $Rb_3C_{60}$ ) and thin line ( $Na_2CsC_{60}$ ) are fits to Eq. (2) of the text. The parameters of the fits are displayed in Table I.

### A. Origin of the non-Korringa relaxation

In a metal, the relaxation of nuclear spins is usually dominated by their coupling with conduction electrons. This leads to a simple dependence of the relaxation rate on the density of states  $n(E_f)$ , known as the Korringa law,<sup>14</sup>

$$\frac{1}{T_1T} = \frac{\pi k_B}{\hbar} A^2 n(E_f)^2, \quad (1)$$

where  $A$  is the hyperfine coupling (in erg) between  $^{13}C$  and conduction electrons. One anomaly in the NMR behavior of  $A_3C_{60}$  is that  $1/T_1T$  frequently deviates from the  $1/T_1T = cst$  law that one consequently expects. An increase of  $^{13}C$  NMR  $1/T_1T$  with increasing temperatures has been reported for nearly all  $A_3C_{60}$  compounds,<sup>15–18</sup> sometimes with moderate values [30% in  $Rb_3C_{60}$  (Ref. 15)] or very large ones [200% in  $Na_2CsC_{60}$  (Ref. 17)]. To probe these aspects further, we have taken data in these two extreme cases in identical experimental conditions, with a 7 T applied magnetic field and standard saturation recovery pulse sequences, and over an extended temperature range. The results are presented in Fig. 2. In both compounds, the relaxation curves for the NMR magnetization are not exponential below 150 K, which causes *a priori* a problem for defining  $T_1$  at low temperatures. However, we have shown in paper I that the nonexponentiality is small and does not change between 10 and 150 K so that it cannot affect significantly these results. Moreover, the region below 150 K is precisely that where the Korringa law is better obeyed. For the data presented here,  $T_1$  has been defined below 150 K as the mean value of a double exponential fit.

The narrow peak observed at 180 K in  $Na_2CsC_{60}$  is due to a coupling with slowing down molecular motions, as was also observed in the isostructural  $Na_2C_{60}$ .<sup>2</sup> As this shows that not only conduction electrons can contribute to the relaxation in our case, one could wonder whether similar peaks could be present (although not well resolved) in other temperature ranges or in  $Rb_3C_{60}$ . If so, could they explain part

of the increase of  $1/T_1T$ ? The large temperature range for the data presented here allows to discard such a possibility, because these peaks would be symmetric while the increase of  $1/T_1T$  is essentially steplike. We refer the reader to our paper I for a detailed discussion of the characteristics of these molecular motion peaks.

From Eq. (1), some temperature dependence of  $1/T_1T$  could be expected if  $n(E_f)$  is not strictly constant as expected for a standard Pauli susceptibility. This could indeed happen, if there are narrow features in the density of states near the Fermi level. Those could be progressively disclosed as thermal expansion increases the lattice constant with increasing temperature. Because they are molecular solids, bound by weak van der Waals interactions, fullerenes are actually very compressible materials and the temperature dependence of  $n(E_f)$  must be seriously considered. Some studies have concluded that it is sufficient to explain the observed increase of  $1/T_1T$  for certain compounds.<sup>18</sup> An obvious test to determine if the increase of  $1/T_1T$  is due to such an effect is to plot  $1/T_1T$  together with  $\chi^2$ , as we have done for  $\text{Na}_2\text{CsC}_{60}$  in Ref. 8. We have found that the temperature dependence of  $\chi^2$  is much too small to explain that of  $1/T_1T$ , so that the deviation must be due, at least in this case, to the presence of an *additional relaxation channel*.

We want to reinforce this conclusion here by taking advantage of the comparison between  $\text{Na}_2\text{CsC}_{60}$  and  $\text{Rb}_3\text{C}_{60}$ , over the large temperature range of the present experiments. The accuracy of the data presented on Fig. 2 at low temperature establishes that the increase is not regular. While  $1/T_1T$  is quite remarkably constant below 100 K ( $\text{Na}_2\text{CsC}_{60}$ ) or 150 K ( $\text{Rb}_3\text{C}_{60}$ ), it then increases up to room temperature, where it decreases ( $\text{Na}_2\text{CsC}_{60}$ ) or saturates ( $\text{Rb}_3\text{C}_{60}$ ). The lattice contraction on the other hand is expected to follow a smooth temperature dependence defined by the compressibility of the materials. Furthermore, the compressibility of sc and fcc phases are known to be quite similar,<sup>19</sup> so that the slightly different structure in the two compounds cannot explain such a difference. The thermal compressibility measured in  $\text{Rb}_3\text{C}_{60}$  [ $\kappa = d(\ln a)/dT = 3 \times 10^{-5} \text{ K}^{-1}$  (Ref. 20)] corresponds to an increase of the lattice parameter  $a$  by 0.16 Å between 10 and 400 K, very close to that measured in  $\text{Na}_2\text{CsC}_{60}$  [0.14 Å (Ref. 11)]. One could argue that even though the temperature dependence of  $a$  is the same,  $n(E_f)$  might display quite different variations with  $a$  in sc or fcc materials.<sup>21</sup> This idea has been proposed to explain the different variation of  $T_c$  with  $a$  in  $\text{Na}_2\text{AC}_{60}$  (sc) or  $\text{A}_3\text{C}_{60}$  (fcc) materials (with  $A = \text{K, Rb, Cs}$ ) because it is generally assumed that  $T_c$  depends on  $n(E_f)$  in a straightforward way according to the BCS theory. However, the variation of  $T_c$  with pressure was later found the same in fcc and sc phases,<sup>22</sup> so that the different variation of  $T_c$  is not related to  $n(E_f)$  but to an alkali effect. The comparison between  $\text{Na}_2\text{CsC}_{60}$  and  $\text{Rb}_3\text{C}_{60}$  is then legitimate and presents the advantage to cover a large variation in the density of states. An even more serious drawback with such an explanation is that our study evidences a much larger increase in  $\text{Na}_2\text{CsC}_{60}$  than in  $\text{Rb}_3\text{C}_{60}$ , although a direct measurement of the susceptibility below 300 K shows the opposite behavior.<sup>23</sup>

## B. Singlet-triplet excitations in $\text{A}_3\text{C}_{60}$

In  $\text{Na}_2\text{CsC}_{60}$ , the origin of the increase of  $1/T_1T$  was suggested by the comparison with  $\text{Na}_2\text{C}_{60}$ , which exhibits a very similar relaxation behavior at high  $T$  despite the fact that it is insulating (see Ref. 8 or Fig. 7). In this latter compound, the relaxation is due to singlet-triplet transitions between different JTDs of a  $\text{C}_{60}^{2-}$ . Theoretical calculations have shown that for an isolated  $\text{C}_{60}^{2-}$ , a JTD with a triplet ground state lies above the singlet JTD represented in Fig. 1 by  $E_a = 140 \text{ meV}$ , so that triplet states can be thermally populated.<sup>1</sup> Therefore, we have suggested that *singlet-triplet excitations persist in  $\text{Na}_2\text{CsC}_{60}$*  because  $\text{C}_{60}^{2-}$  and  $\text{C}_{60}^{4-}$  are formed there on very short time scales (about  $10^{-14} \text{ s}$ ), which creates an additional relaxation channel, explaining the increase of  $1/T_1T$  at high temperature. We now investigate if such an explanation could describe the evolution of the relaxation behavior between  $\text{Na}_2\text{CsC}_{60}$  and  $\text{Rb}_3\text{C}_{60}$ .

The data led us to suggest that the relaxation can be divided between two relaxation channels, a metallic Korringa-like channel and a molecular channel corresponding to localized singlet-triplet excitations. For this latter term, we assume that the imaginary part of the susceptibility, the quantity measured by  $1/T_1$  at the nuclear Larmor frequency (80 MHz for  $^{13}\text{C}$  in this measurement), can be described by a Lorentzian with a width  $1/\tau$ , where  $\tau$  is a lifetime characterizing the electronic excitations. This is a usual assumption for localized magnetic moments, which yields for small  $\omega$ ,  $1/T_1 \propto \chi\tau$ , where  $\chi$  is the static paramagnetic susceptibility of the localized moment.<sup>24</sup> This leads to the following expression:

$$\frac{1}{T_1T} = \frac{k_B}{\hbar} A^2 \left( \pi n(E_f)^2 + \frac{\chi_{ST}}{\mu_B^2} \frac{\tau_{st}}{\hbar} \right), \quad (2)$$

where  $\tau_{st}$  is the characteristic lifetime of triplet states and  $\chi_{ST}$  is an activated susceptibility describing the population of triplet states. In Eq. (2), the separation between the two terms is quite arbitrary, as the same electrons participate in both terms. Such a phenomenological decomposition should nevertheless capture the essential points of the physics as long as  $\tau_{st}$  is shorter than the lifetime  $\tau_p$  of a  $\text{C}_{60}^{2n-}$  in the metal. Some correlation between the parameters describing the “localized” states (such as  $\tau_{st}$ ) and the extended carriers states (such as  $n(E_f)$ ) can be expected as a result of this situation.

A source of inspiration for this correlation is the evolution of  $\text{Rb}_4\text{C}_{60}$  from an insulator to a metal with applied pressure.<sup>25</sup> This transition is not sharp, but a linear metallic term appears with increasing pressure *that coexists* with the localized activated one, as replotted in Fig. 3. As the metallic term grows, the molecular one can still be described by the same model, but the value of the gap and  $\tau_{st}$  have to be reduced. This legitimates the assumption of coexisting molecular and metallic excitations, which is also observed in  $\text{Na}_2\text{C}_{60}$ .<sup>2</sup> We believe that this property is actually essential to understand the originality of fullerenes, in which molecular features are retained because the large electronic correlations forces one electron to spend a “long” time on each molecule before being transferred to the next.

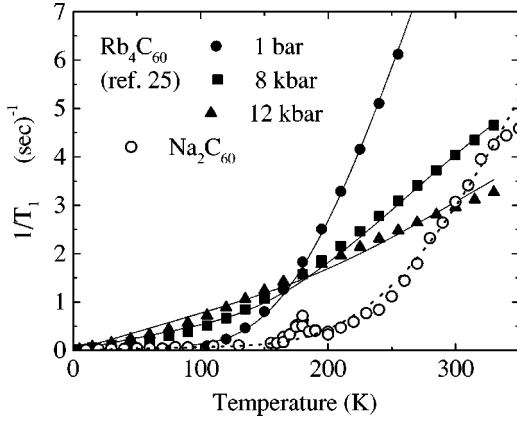


FIG. 3.  $^{13}\text{C}$  NMR  $1/T_1$  in  $\text{Rb}_4\text{C}_{60}$  for different applied pressure (from Ref. 25) and  $\text{Na}_2\text{C}_{60}$ . The curves are fitted to Eq. (2) with parameters displayed in Table I. They assume that the relaxation is the sum of a linear metallic component and an activated molecular one with fixed ratio.

The behavior in  $\text{Rb}_4\text{C}_{60}$  tells us that  $\tau_{st}$  directly depends on  $n(E_f)$ . This suggests that *the triplet states are relaxed by conduction electrons*. Assuming that the triplet state can be treated as a local impurity on the time scale of its existence, it will undertake a Korringa relaxation,<sup>24</sup>

$$\frac{1}{\tau_{st}} = \frac{\pi}{\hbar} k_B T J^2 n(E_f)^2, \quad (3)$$

where  $J$  would be the coupling between the triplet and conduction electrons.

To test this model, which reduces the number of free parameters in Eq. (2), we have tried to reproduce the pressure evolution of the two terms in  $\text{Rb}_4\text{C}_{60}$ . To model the susceptibility associated with singlet-triplet excitations, we choose

$$\chi_{st} = \frac{8\mu_B^2}{k_B T} \frac{\exp(-\Delta/T)}{2 + 3 \exp(-\Delta/T)}, \quad (4)$$

which was found in reasonable agreement with the susceptibility of  $\text{Na}_2\text{C}_{60}$ .<sup>2</sup> The coupling  $J$  is treated as a shared parameter between the three sets of data and the best fits are found for  $J = 10^{-13}$  erg. Fits using Eqs. (2)–(4) with this value for  $J$  are shown on Fig. 3. They are in fair agreement with the data, which supports this model. The density of

states and the value of the gap used in each case are displayed in Table I. This model can be applied as well to  $\text{Na}_2\text{C}_{60}$ . Figure 3 shows that, with a larger gap value already noticed previously<sup>8</sup> but keeping the same value for  $J$ , the data are also well reproduced.

Does this model also apply to the case of  $\text{A}_3\text{C}_{60}$ ? Equation (3) implies that the increase of  $1/T_1 T$  due to the localized term should show up more clearly when  $n(E_f)$  is small, which is in qualitative agreement with the evolution of  $1/T_1 T$  between  $\text{Na}_2\text{CsC}_{60}$  and  $\text{Rb}_3\text{C}_{60}$ . Remarkably, the previous fitting procedure *with the same  $J$  value* gives a correct order of magnitude for the increase of  $1/T_1 T$  in both compounds. In this model, the magnitude of the high-temperature increase of  $1/T_1 T$  is uniquely fixed by its value at low temperature. The best fits displayed in Fig. 2 with the parameters given in Table I show an excellent agreement in the case of  $\text{Rb}_3\text{C}_{60}$  but is poorer for  $\text{Na}_2\text{CsC}_{60}$ . In this latter compound, it seems that a different regime is relevant for high temperatures, which will be discussed in the following section. Even below 300 K, the increase of  $1/T_1 T$  cannot be ascribed to a single gap value. Similar problems were encountered in the case of  $\text{Na}_2\text{C}_{60}$ , which led us to suggest in paper I that the equilibrium between different JTDs could be modified by changes in the details of the structure as a function of temperature.

To check the consistency of our analysis, the triplet relaxation time  $\tau_{st}$  should be compared to the lifetime  $\tau_p$  of the  $\text{C}_{60}^{2n-}$ . This latter time can only be longer than the average time spent by one electron in the vicinity of a  $\text{C}_{60}$  ball  $\tau_m$ . A lower bound for  $\tau_m$  can be estimated by the time required for an electron to travel at the Fermi velocity from one ball to the other,  $\tau_m = a/v_f \approx \hbar n(E_f)$ . This is calculated in Table I and the comparison with  $\tau_{st}$  deduced from the fits shows that they have a similar order of magnitude at room temperature, so that this analysis is consistent. We note that we have used here the susceptibility given by Eq. (4), although one could assume that only a fraction of it, corresponding to the actual concentration of  $\text{C}_{60}^{2n-}$  in  $\text{A}_3\text{C}_{60}$ , should be used. This would give slightly longer value for  $\tau_{st}$ .

Therefore, this model gives an overall satisfying description of the relaxation behavior in these compounds. The short values found here for  $\tau_m$  and  $\tau_{st}$ , however, show that these phenomena are essentially simultaneous and that this treatment is an oversimplification of the reality. The correlation

TABLE I. Parameters used in the fits shown on Figs. 2 and 3 based on Eq. (2)–(4).  $\chi_m$  is deduced from  $n(E_f)$  and Eq. (1) assuming a hyperfine coupling  $A = 4 \times 10^{-20}$  erg. The absolute values of  $\tau_{st}$  should only be taken as an order of magnitude because it is somewhat model dependent but the qualitative variation between different compounds is meaningful, as well as the condition  $\tau_{st} \leq \tau_m$ , which legitimates the use of this model for the metals.

	$\text{Rb}_4\text{C}_{60}$			$\text{Na}_2\text{C}_{60}$	$\text{Na}_2\text{CsC}_{60}$	$\text{Rb}_3\text{C}_{60}$
	1 bar	8 kbars	12 kbars			
$\chi_m$ ( $10^{-4}$ emu/mol)	1	3.1	3.7	1.3	3.1	4.7
$\Delta$ (meV)	90	80	100	125	85	75
$\tau_m = \hbar n(E_f)$ ( $10^{-15}$ s)		6	7.2		6	9
$\tau_{st}(300 \text{ K})$ ( $10^{-15}$ s)	35.3	3.7	2.6	21	3.7	1.6

between the molecular and metallic term is probably more intricate. We have assumed that the JTD  $C_{60}^{2-}$  can be considered as an isolated molecular entity, even if it is restricted to a limited time scale. The fact that the gap value is not fixed, but tends to decrease with increasing  $n(E_f)$  in compounds with identical structures like  $Na_2C_{60}$  and  $Na_2CsC_{60}$ , shows explicitly that there is a further correlation between the two terms.  $\Delta$  is not purely a molecular value and a more sophisticated description, introducing, for example, a screening of the  $C_{60}^{2n-}$  by conduction electrons, would be required to describe completely this behavior.

In addition, we have mainly tried to explain so far the increase of  $1/T_1T$ , which roughly takes place between 200 and 300 K. At higher temperatures, Eq. (3) predicts a decrease of the lifetime of the triplet states as  $1/T$ . This could change the balance between the two relaxation channels as a function of temperature. The simple estimate that we have used for  $\tau_m$  is also likely to break down at high temperature because it requires that the mean free path for the electronic motion  $l$  is longer than  $a$ . On the contrary, it is known that very small values for the mean free path are deduced from resistivity measurements for fullerides at high temperature, such as 1–2 Å at 500 K in  $Rb_3C_{60}$ .<sup>26</sup> Therefore, we could expect complications at high temperature, which might reveal, on the other hand, valuable information on the charge transport in these materials and we turn to this topic in the following section.

### III. ARE “METALLIC FULLERIDES” METALLIC UP TO HIGH TEMPERATURES?

Some anomalies in the high-temperature behavior of fullerides have been noticed for a long time. In  $Rb_3C_{60}$ , the photoemission spectra at high temperature does not display a clear Fermi edge.<sup>27</sup> In  $Na_2CsC_{60}$ , optical conductivity measurements indicate a disappearance of the Drude-like peak above 300 K.<sup>28</sup> All this motivates us to investigate the high-temperature region in greater detail and we indeed report here two cases,  $Na_2CsC_{60}$  and  $CsC_{60}$ , where the high-temperature behaviors are far from that of a simple metal and are even suggestive of a localization of the charge carriers. For all the data reported here, we have checked that the behavior is fully reversible with temperature, ensuring that there is no deterioration of the sample quality and/or stoichiometry.

#### A. $Na_2CsC_{60}$

##### 1. Progressive localization of the charge carriers inferred from $1/T_1$ behavior

Figure 2 shows that  $1/T_1T$  decreases regularly from 300 to 700 K in the fcc phase of  $Na_2CsC_{60}$ . This is anomalous as among the two terms identified in the relaxation so far, the metallic and the singlet-triplet components, the first one is expected to yield a constant value and the second one, an increase of  $1/T_1T$  or a slight decrease depending on the precise value of the gap (see the fits of Fig. 2). In  $Rb_3C_{60}$ , there might be a similar anomaly above 500 K, where  $1/T_1T$  is somewhat lower than the fitted curve, but this cannot be

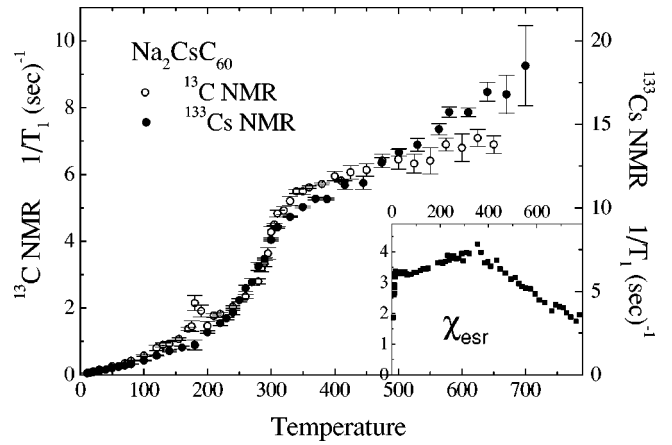


FIG. 4.  $1/T_1$  for  $^{13}C$  and  $^{133}Cs$  in  $Na_2CsC_{60}$  as a function of temperature. For  $^{133}Cs$ , the recovery curves are exponential through the whole temperature range. Inset: ESR susceptibility as a function of temperature measured on a sample from the same batch.

concluded unambiguously within experimental accuracy, and in the following we focus on  $Na_2CsC_{60}$ .

As the use of  $1/T_1T$  might introduce an artificial bias by emphasizing the metallic component, we have replotted on Fig. 4,  $1/T_1$  for  $^{13}C$  NMR, together with the result from  $^{133}Cs$  NMR, which displays essentially the same temperature dependence, except for the molecular motion peak. The interpretation of these data is not straightforward as we do not know how to separate the metallic term from the singlet-triplet (ST) component. Within the metallic framework of the Korringa law, a decrease of  $1/T_1T$  would be assigned to a reduction in the density of states signaling the onset of a broad metal to insulator transition. If it is a change in the singlet-triplet component, it could be due to modifications of the apparent value of the gap as was observed in  $Na_2C_{60}$ . To find a way out of this problem, a comparison with the ESR susceptibility shown in the inset of Fig. 4 is helpful. In the susceptibility, both the metallic and singlet-triplet terms are also present but with different ratios as they are not weighted by the lifetime of the excitations, like  $1/T_1$  is.  $\chi$  is dominated at low  $T$  by a constant Pauli component and then increases up to 350 K, in our opinion mainly as a result of singlet-triplet excitations. Like  $1/T_1T$ , it is clearly anomalous above room temperature, where it starts decreasing sharply. This is very different from the behavior of  $\chi$  in  $Na_2C_{60}$ , where it keeps increasing at high temperature, which tells us that a modification of the ST component alone cannot account for this result. Above 350 K, we observe a strong divergence in behavior between  $\chi$  and  $1/T_1$ ,  $\chi$  falls far below the metallic value, whereas  $1/T_1T$  is still far above. This can only be understood if *the lifetime of the excitations diverges above room temperature*. This reminds us of a situation observed at the transition between solid and liquid in  $X_2Te_3$  ( $X = In, Ga, Sb$ ).<sup>29</sup> Upon melting, the increasing disorder induces a progressive localization of the charge carriers that leads to a decrease of the Pauli susceptibility, due to the reduction of the carrier density. At the same time,  $1/T_1T$  is found to increase, as the lifetimes of the excitations increases rapidly. To account for this effect,  $n(E_f)$  (Ref. 2) in Eq. (2) has been

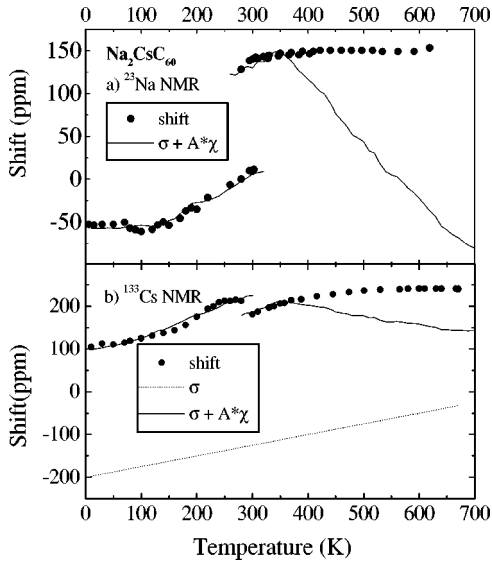


FIG. 5. Shift for  $^{23}\text{Na}$  (a) and  $^{133}\text{Cs}$  (b) in  $\text{Na}_2\text{CsC}_{60}$ . The discontinuity at 300 K is due to the structural transition from the orientationally ordered sc phase ( $T < 300$  K) to the fcc one.  $^{23}\text{Na}$  ( $^{133}\text{Cs}$ ) shifts are measured with respect to a diluted NaCl (CsCl) solution. The lines are comparison with the behavior of the susceptibility assuming values of hyperfine shift and chemical reference discussed in the text.

replaced, by the authors of Ref 29, by  $n(E_f)\tau_m/\hbar$ , where  $\tau_m$  is now free to deviate from the metallic value  $\hbar n(E_f)$ . In our case, both  $\tau_m$  and/or  $\tau_{st}$  could be responsible for the increase of  $1/T_1T$ . However, in both cases, we can conclude that there is a *progressive localization of charge carriers*.

## 2. Nature of the localized charge carriers inferred from the static NMR alkali spectra

If the localization process went as far as to correspond to a static charge separation, we could expect to observe changes in the NMR spectra as a result of inequivalent alkali sites neighboring a different number of  $\text{C}_{60}^{2n-}$ . This is the case in CQ  $\text{CsC}_{60}$  where a splitting of the Cs spectrum is observed at low temperature, corresponding to the localization of 10%  $\text{C}_{60}^{2-}$ , as discussed in detail in paper II. In  $\text{Na}_2\text{CsC}_{60}$ , static charge separation can be ruled out because  $^{133}\text{Cs}$  and  $^{23}\text{Na}$  spectra consist of one featureless narrow line (with the exception of the Na  $T$  line). This is consistent with the value given previously for  $\tau_{st}$ , which is much shorter than the NMR time scale (a few millisecond corresponding to the inverse width of the spectrum), so that a motional narrowing of the spectra should still take place even if  $\tau_{st}$  increases by many orders of magnitude.

There are, however, clear anomalies in the alkali NMR which are revealed when comparing the shifts  $K$  for  $^{133}\text{Cs}$  and  $^{23}\text{Na}$  lines, presented in Fig. 5, together with the electron-spin resonance (ESR) susceptibility. A simple scaling between  $K$  and  $\chi$  is expected,  $K = \sigma + A\chi$ , where  $A$  is the hyperfine coupling and  $\sigma$  is a reference chemical shift. In Fig. 5, it can be seen that both nuclei sense an increase of the susceptibility between 150 K and 300 K, but they do not reproduce similarly the decrease seen by ESR above 300 K.

This also suggests, although in a puzzling way, that the properties of the material are changing above room temperature. Let us now discuss quantitatively the behavior of the shift for the two nuclei.

a.  $^{23}\text{Na}$  NMR. In the sc phase, we can scale the  $^{23}\text{Na}$  shift and the susceptibility, as shown by the line of Fig. 5(a) by using  $\sigma = -300$  ppm and  $A = 4500$  Oe/ $\mu_B$ . This can be compared to values found in paper I for the isostructural  $\text{Na}_2\text{C}_{60}$ ,  $\sigma = -65$  ppm and  $A = 2300$  Oe/ $\mu_B$ . The difference for  $\sigma$  is quite large and not expected, as  $\sigma$  essentially depends on the diamagnetism of the  $\text{Na}^+$  filled orbitals. To avoid this problem, it might be more realistic to assume that the hyperfine coupling to the metallic component is *smaller* than that to localized excitations, maybe because Na moves a little bit towards the  $\text{C}_{60}^{2-}$  or  $\text{C}_{60}^{4-}$ , which increases the hyperfine coupling for this term. This automatically gives a value of  $\sigma$  closer to that of  $\text{Na}_2\text{C}_{60}$ , as the shift is dominated at low  $T$  by the metallic term.

Through the sc-fcc transition at 310 K, we have observed in  $\text{Na}_2\text{C}_{60}$  an increase by 30% of the hyperfine coupling, probably associated to the change of structural environment of Na (see paper I). This is also clearly present in  $\text{Na}_2\text{CsC}_{60}$ . As a guide to the eye, we have plotted the variation of  $K$  that would be expected for  $^{23}\text{Na}$  NMR from that of  $\chi$  assuming no change for  $\sigma$  and a continuous value for  $\chi$ . This only emphasizes what was immediately clear,  $K$  does not follow the static susceptibility at high temperature, it is nearly constant, while  $\chi$  drops by a factor 2. Relying on the previous findings (i) the characteristic lifetime of the localized excitations starts to increase above 300 K and (ii) the hyperfine coupling to the localized excitations is particularly strong, we would like to conclude that the reason for the different behavior of  $K$  and  $\chi$  at high temperature is due to an *increase of the hyperfine coupling associated with the progressive localization of the carriers*. Indeed, we know from CQ  $\text{CsC}_{60}$ , studied in paper II, that the coupling can be very strong with localized singlets in a metallic environment. This enhancement disappears if all the balls are equivalent and bear a singlet, like in  $\text{Na}_2\text{C}_{60}$ , because Na has no reason to move towards a particular ball.

b.  $^{133}\text{Cs}$  NMR. The  $^{133}\text{Cs}$  shift presents a similar behavior but it displays a significant temperature variation below 100 K, which does not appear in the ESR data. Such a linear temperature dependence of the shift has already been observed in the NMR of various alkalis in fullerenes.<sup>30-32</sup> Its origin is not well understood, but as it is not related to the electronic susceptibility,<sup>30</sup> it is probably of orbital origin and we will include this linear variation in the chemical shift  $\sigma$ . Choosing  $\sigma = -200 + 0.25T$ , as indicated in Fig. 5 by the dotted line, allows to extract an additional increase, clearly present between 150 K and 300 K, which scales with the susceptibility, with  $A = 5000$  Oe/ $\mu_B$ . As done for  $^{23}\text{Na}$ , we then extrapolate the variation of  $K$  at high temperatures assuming that  $\sigma$  and  $\chi$  do not change, which requires here a reduction of  $A$  in the fcc phase to 4500 Oe/ $\mu_B$ .<sup>33</sup> Here again, there is a significant difference between  $K$  and  $\chi$ , although less dramatic than for Na. We also observe that the scaling between  $K$  and  $\chi$  is not lost at the structural transition

but at somewhat higher temperatures  $T \approx 400$  K, making it unlikely that the structural transition is directly responsible for the change of the electronic properties of  $\text{Na}_2\text{CsC}_{60}$ . If the divergence between  $K$  and  $\chi$  is to be attributed again to an increase of the hyperfine coupling, this yields  $A = 6000 \text{ Oe}/\mu_B$  at 650 K. Such an increase should also enhance  $1/T_1$ , proportional to  $A^2$ , by a factor 1.5. In Fig. 4, we see that  $1/T_1$  indeed increases a little bit more rapidly for  $^{133}\text{Cs}$  than for  $^{13}\text{C}$ . As  $^{13}\text{C}$  cannot move, its hyperfine coupling can be used as a reference for the “unenhanced” value of  $1/T_1$ . The relative increase of  $1/T_1$  of  $^{133}\text{Cs}$  indeed reaches 1.5 at 700 K, which supports the idea of an increase of  $A$  for  $^{133}\text{Cs}$ .<sup>34</sup>

In summary, many anomalies appear above 400 K in  $\text{Na}_2\text{CsC}_{60}$ , which gives evidence for a change in the electronic properties. Although, the data are conflicting at first sight, because different probes measure apparently different behaviors, we propose that this can be understood assuming that we enter an intermediate regime between metallic and localized behavior. In this regime,  $1/T_1$  is dominated by the increase of the residence time of the charge carriers on a specific  $\text{C}_{60}$  ball, which also modifies the alkali hyperfine couplings. We cannot decide unambiguously whether the charge carriers are localized as  $\text{C}_{60}^{3-}$  or  $\text{C}_{60}^{2n-}$ . Both are consistent with the  $1/T_1$  measurements. The change in the alkali hyperfine coupling somewhat favors  $\text{C}_{60}^{2n-}$ , as we could expect a larger motion of the alkali towards the differently charged  $\text{C}_{60}$ . The idea that a motion of the alkali ions, especially of the light Na ion, is playing an important role in the high-temperature properties of this phase was already suggested in Ref. 28. However, the appearance of a localized charge could be sufficient to trigger such a motion and modify the alkali hyperfine coupling regardless of the charge value.

Because we have detected in the previous part of this paper an important role of JTDs in the metallic phase, it seems reasonable to associate the progressive localization at high temperatures with a conflict between the stabilization of JTDs and the delocalization of the charge carriers. We can, for example, speculate that the population of many different Jahn-Teller distorted states at high temperatures introduces disorder in the electronic system, which hinders the electronic motion. These electrons could then be localized as  $\text{C}_{60}^{3-}$  or  $\text{C}_{60}^{2n-}$  depending on the precise balance between Coulomb repulsion and Jahn-Teller attraction. More importantly, this behavior reveals conversely that a cooperation is required between JTDs and electronic motion to produce the metallic state.

### B. The high-temperature cubic phase of $\text{CsC}_{60}$

Another very anomalous phase is that of  $\text{CsC}_{60}$  at high temperature. It appears to have a Curie-like susceptibility,<sup>35</sup> the  $^{133}\text{Cs}$  NMR shift also follows a Curie law within experimental accuracy and  $1/T_1$  is nearly constant as expected for a paramagnetic insulator.<sup>13</sup> All of this was taken as evidence for electronic localization. We have checked that this behavior extends up to 700 K for the  $^{133}\text{Cs}$  NMR shift (see Fig. 6)

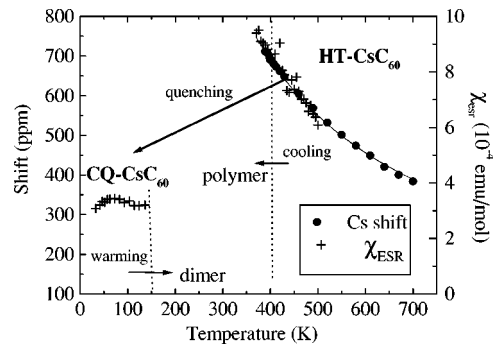


FIG. 6.  $^{133}\text{Cs}$  NMR shift in the high-temperature cubic phase of  $\text{CsC}_{60}$  (black points), the line is a fit to a Curie law. There are two cubic phases in  $\text{CsC}_{60}$ , a cubic quenched (CQ) metastable phase for  $T < 130$  K, and a high-temperature one ( $T > 380$  K). In these two phases, crosses show the behavior of the ESR susceptibility to illustrate the change in electronic properties.

and  $^{13}\text{C}$  NMR  $1/T_1$  (see Fig. 7, actually  $T_1^{-1}$  is not really constant but decreases by 25% from 400 K to 700 K).

Below 350 K, a structural transition takes place to a polymerized phase with very different properties. However, the cubic phase can be studied at low temperatures (below 130 K) by quenching the high-temperature phase *and it seems to be metallic* (see paper II). The variations of the susceptibility in the two phases are reported in Fig. 6 to illustrate this point. The difference is very puzzling, as the structure is the same except for the  $\text{C}_{60}$  orientational order (the CQ phase of  $\text{CsC}_{60}$  is sc,<sup>36</sup> while the high-temperature phase is fcc). If this structural transition were to play a major role in the conductivity, one would rather expect the high-temperature phase to be metallic as  $\text{A}_3\text{C}_{60}$ , contrary to the above indications. The distinct behavior of the two phases raises the question of the ground-state electronic properties of singly charged  $t_{1u}$  orbitals. However, comparing the two  $\text{CsC}_{60}$  phases with  $\text{Na}_2\text{CsC}_{60}$  allows now to trace a connection between these phases.

$\text{Na}_2\text{CsC}_{60}$  also resembles a good metal at low temperature and, for some properties, particularly the ESR “Curie-like”

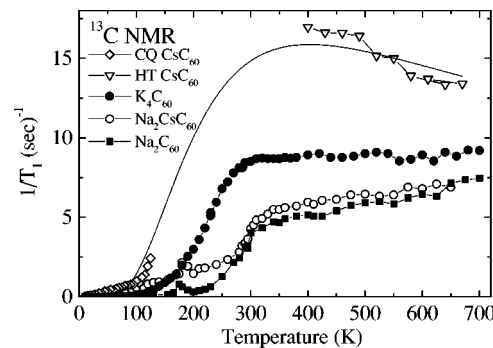


FIG. 7. Comparison of  $^{13}\text{C}$  NMR  $1/T_1$  in different fullerides showing a similar increase up to 300 K that we attribute to singlet-triplet excitations. The line connecting the cubic quenched (CQ) phase of  $\text{CsC}_{60}$  and the high-temperature (HT) one is a fit to Eq. (2) given in the text.

susceptibility, an insulator above 300 K. We have seen through this paper that including singlet-triplet excitations of JTD balls offers a convincing way to explain this behavior, and the same could be true for  $\text{CsC}_{60}$ . The underlying similarity is perhaps best illustrated by looking at the temperature dependence of  $1/T_1$  for  $^{13}\text{C}$  in various phases, as we do in Fig. 7. In this context, it is tempting to interpret the gap between the values of  $1/T_1$  in the CQ phase and those of the high-temperature phase by an increase due to a singlet-triplet component. In CQ  $\text{CsC}_{60}$ , just before the transition to the dimer phase, we do observe an increase of  $1/T_1$ , which might correspond to such a component. Adjusting a fit to Eq. (2) to these points and the high-temperature value gives the line sketched in Fig. 7. This yields a smaller gap  $\Delta = 50$  meV than for the other compounds, but this is consistent with the fact that  $1/T_1$  decreases at high temperatures. Indeed, Fig. 7 shows a systematic relation between the value of the gap and the behavior at high temperature: the lower the gap, the higher  $1/T_1$  and the smaller (eventually negative) the slope of its variation at high temperature. Qualitatively, this is not surprising as, with a small gap, the susceptibility is dominated at high temperature by the Curie law for the triplet states [see Eq. (4)].

Putting these data together then gives a fairly good understanding of the  $\text{CsC}_{60}$  system. We know from the study of CQ  $\text{CsC}_{60}$  in paper II that JTD  $\text{C}_{60}^{2-}$  are formed at low temperatures but, presumably because there is no symmetric JTD for neutral  $\text{C}_{60}$ , they get localized on a small fraction of the  $\text{C}_{60}$  balls, contrary to  $\text{C}_{60}^{2n-}$  in superconductors. The singlets start to move as the temperature increases and the lifetime of a  $\text{C}_{60}^{2-}$  in the metal decreases exponentially. We can speculate that, if the cubic phase of  $\text{CsC}_{60}$  was stable, its properties would evolve gradually towards an almost insulating state at high temperatures, which is the one observed above 400 K.

#### IV. CONCLUSION

To summarize, we have argued that the deviation of the NMR  $1/T_1T$  from the canonical “metallic” Korringa law observed in many  $A_3\text{C}_{60}$  systems can be convincingly attributed to molecular excitations. We propose that the dominant excitations are singlet-triplet transitions of pairs of electrons stabilized by Jahn-Teller distortions on short time scales. By comparing two superconducting metals with very different density of states, we rationalize the coexistence between molecular and metallic excitations, with a phenomenological model connecting the characteristic spin lifetime  $\tau_{st}$  of the triplet state to  $n(E_f)$ . The molecular excitations are harder to detect for metallic compounds with higher density of states, where  $\tau_{st}$  is reduced, and this explains why they have not been clearly identified up to now. In the most heavily studied compounds such as  $\text{K}_3\text{C}_{60}$  and  $\text{Rb}_3\text{C}_{60}$ , the molecular excitations are masked by the metallic term. The conclusion of this study suggests that *the metallic character of the fullerenes with an odd number of electrons is driven by the formation of these pairs of electrons.*

We have then presented data at high temperatures that show a clear evolution of the behavior of the electronic prop-

erties in at least two compounds  $\text{Na}_2\text{CsC}_{60}$  and  $\text{CsC}_{60}$ . In the first case, we interpret the breakdown of the scaling between various quantities at about 400 K as the onset of a progressive localization of the charge carriers. We suggest that this localization is due to a change of the status of JTDs in the metal as the temperature increases. We cannot determine unambiguously whether the charges are localized as  $\text{C}_{60}^{2n-}$  or  $\text{C}_{60}^{3-}$ . A similar, probably slightly more efficient, localization takes place in  $\text{CsC}_{60}$ . Although this phase was already believed to be insulating, seeing this as a metal to insulator transition allows us to connect its properties to those of the low-temperature metallic phase. This adds greatly to the understanding of these systems, as all metallic phases can now be described within the same framework. JTDs appear as a key ingredient in this behavior, which makes it likely that the difference between even and odd stoichiometries, and insulating and metallic stoichiometries, is due to the sensitivity of Jahn-Teller distortions to the parity of the  $\text{C}_{60}$  charge. As recalled in Fig. 1, JTDs are always a little bit more stable for even parity.

This work also raises questions on the nature of charge transport in  $A_3\text{C}_{60}$ . What would be the consequence of the enhanced lifetime of JTDs  $\text{C}_{60}^{2-}$  and  $\text{C}_{60}^{4-}$ ? The role that we assigned here to JTDs is an example of how electronic properties are coupled to phonons and could be a first step towards the concept of polarons. However, we do not know how fast the JTD can adjust itself to a change of the charge of the molecule, produced by jumps of electrons from one ball to the other. The idea of a polaron would imply that one electron moves with a given JTD. In the case of fullerenes, we could as well assume that a JTD is fixed for a given molecule, regardless of its charge, which only increases the lifetime of favorable JTD  $\text{C}_{60}^{n-}$  configurations (namely,  $n$  even). The lack of experimental knowledge about the time scale for the JTD, relatively to the motion of electrons, makes it difficult to discriminate between these possibilities. Nevertheless, some correlation between them is required to establish a coherent bandlike charge transport. This could be destroyed with increasing temperature, resulting in a hoppinglike process, which might be what we witness in  $\text{Na}_2\text{CsC}_{60}$ . This bears interesting similarities to the metal to insulator transition observed at high temperature in manganites with ferromagnetic metallic ground states. In these systems also strong electronic correlations are coexisting with the possibility of JTD of the doubly degenerate  $e_g$  orbitals. It has been proposed that the occurrence of JTDs at high temperatures, which forbids hopping in this case, adds to the double exchange mechanism to trigger a transition to the high-temperature insulating phase.<sup>37</sup> A good understanding of this behavior in fullerenes could then also shed light on the physics of other correlated materials.

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