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Metal-to-insulator evolution in $(NH_3)_xNaK_2C_{60}$: An NMR study

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A singular evolution toward an insulating phase, shown by ^{23}Na and ^{13}C NMR, has been observed in the superconducting fullerides $(NH_3)_xNaK_2C_{60}$ for $x>1$. Unlike most common cases, this insulating phase is nonmagnetic and ^{13}C spin lattice relaxation shows the presence of a spin gap. These two features suggest that a charge disproportion from C_{60}^{3-} to C_{60}^{2-} and C_{60}^{4-} can drive the system from the metallic to the insulating state. The restoring of the Na^+ cation in the center of the octahedral interstice in the insulating phase, as indicated by ^{23}Na and ^{2}H line shape analysis, confutes the current belief that the cation off-centering is effective in quenching the superconductivity.

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I. INTRODUCTION

Soon after the discovery of fullerene it was found that compounds of the A_3C_{60} family, obtained by insertion of alkali metals (A) in the C_{60} lattice, exhibited superconducting behavior with high critical temperatures T_c (up to ~ 30 K). A regular increase in transition temperatures was observed as the cation radius and lattice parameter increased, a trend considered nowadays as a textbook example of the success of standard BCS theory. Indeed, according to this theory, T_c is strongly dependent upon the density of states at the Fermi level $\rho(E_F)$, a quantity which, as a rule, increases with the band narrowing caused by lattice expansion. This mechanism for increasing T_c proved rather successful, so attempts to find alternative ‘‘lattice expanders’’ soon followed, thus suggesting the neutral molecule of ammonia as a good candidate.

A well-known example is given by Na_2CsC_{60}.[1] After ammoniation, it becomes $(NH_3)_4Na_2CsC_{60}$, with an increase in transition temperature from 10.5 K to 29.6 K. In general, a further narrowing of the band is expected to enhance the electron correlation, which eventually induces a Mott-Hubbard transition to an insulating magnetic phase.[2] This is just the case of K_3C_{60}, K_2RbC_{60}, and Rb_3C_{60}, which after ammoniation[3–6] become insulating and antiferromagnetic. In particular the superconductivity (SC) of $NH_3K_3C_{60}$ is recovered after application of external pressure.[7]

An exception to this simple picture is given by the $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ compounds. Here the progressive *increase* of ammonia concentration x yields an *increase* in lattice parameter and an unexpected *decrease* of T_c.[8] This anomalous behavior was originally attributed to the octahedral cation off-centering.[8] Indeed, in these systems the NH_3-Na groups occupy the large octahedral (O) sites of the fcc lattice and the breaking of the cubic symmetry of the crystal field could lift the degeneracy of the C_{60} t_{1u} lowest unoccupied molecular orbital (LUMO), thus inducing a bandwidth increase and a corresponding decrease in $\rho(E_F)$. In a recent work[9] we have found that in $(NH_3)_xNaK_2C_{60}$ with $0.5<x<0.9$ the $\rho(E_F)$, as extracted from Pauli spin susceptibility, actually increases on increasing x and the lattice parameter, thus resulting in being *inversely correlated* with T_c (anti-Migdal behavior). Accordingly, the superconducting critical parameters of the same system (upper and lower critical fields H_{c2}, H_{c1}, and London penetration depth λ) (Ref. 10), are significantly different from those of other superconducting fullerides and do not seem to fit the Ginzburg-Landau theory predictions.

These facts clearly suggest that the role of ammonia in the superconducting phase of $(NH_3)_xNaK_2C_{60}(x<1)$ is quite different from that in the other fullerides, with the detailed properties of its SC state also altered, showing features which are reminiscent of those of polaronic systems.[10]

It is therefore necessary to investigate the properties of $(NH_3)_xNaK_2C_{60}$ when larger concentrations of ammonia are present and thus answer the questions of whether or not the system evolves into an insulating phase, as the T_c vs. a behavior would suggest, and, if so, whether the Na off-centering has any role in the process.

This is the purpose of the present work in which we report the evolution of the $(NH_3)_xNaK_2C_{60}$ system as the doping increases beyond $x=1$. In what follows, a detailed NMR study of ^{13}C (spin lattice relaxation and line shape) and ^{23}Na (line shift) provide evidence for the formation of an insulating phase which segregates and increases in fraction as the ammonia concentration is increased. The electronic and structural properties of this new phase, in which the Na^+ ions recover the octahedral centered position, are also investigated by ^{23}Na and ^{2}H line shape analysis.

II. SAMPLE PREPARATION AND CHARACTERIZATION

The $(NH_3)_xNaK_2C_{60}$ samples were prepared following the procedure outlined in Ref. 8. However, to achieve higher x values, the final vacuum drying from the ammonia solution was performed at lower temperatures (down to $-23\,^{\circ}$C). The accurate ammonia concentration x was extracted from the hydrogen NMR line intensity. This procedure, besides being quite reliable, was consistent also with volumetric methods which, on the other hand, require the destruction of the sample.

Laboratory x-ray powder diffraction confirms the known[8] fcc structure for the compounds with $x<1$ and, on the other hand, it does not show any change in the structure on increasing ammonia doping, apart from a slight increase in lattice parameter (a) from 14.39 Å for $x=0.9$ to 14.44 Å for $x=2$.

Superconducting quantum interference device (SQUID) magnetometry shows a progressive decrease in T_c from 15 K to 9.5 K for ammonia doping in the $0.5<x<1$ range. Above $x=1$ (corresponding to the lowest transition temperature 9.5 K) up to $x=2$, no further decrease in T_c takes place, but instead a *progressive decrease of the shielding fraction was observed*, consistent with the gradual formation of a nonsuperconducting phase. No magnetism was detected in this range.

As mentioned in the Introduction, a similar behavior has been already observed in K_3C_{60}, K_2RbC_{60}, and Rb_3C_{60} which, upon ammoniation, show a Mott transition to an insulating magnetic phase.[3–6] In our case, however, the *absence* of magnetism and the modest lattice expansion suggest that other factors may play a role in suppressing the (super)conducting state.

III. ^{23}Na NMR

Nuclear magnetic resonance has proved a valuable tool for the study of the electronic properties of fullerides since the early time of their discovery.[11,12] Its usefulness mainly arises from the sizable hyperfine interaction of conduction electrons both with carbon and alkali nuclei. In addition, microscopic structural information can be obtained also from the nuclear quadrupole interactions with electric field gradients (EFG's). The latter interaction, however, affects only the resonance of nuclear species with spin $I>1/2$, so the possible candidates in our case are Na and K. We focused our attention on the ^{23}Na nucleus because, thanks to its octahedral position, (i) a large hyperfine interaction with conduction electrons is expected[13] and (ii) its off-centered position implies the presence of a considerable electric field gradient on it.

Figure 1 shows the ^{23}Na NMR spectra taken at RT in samples with different ammonia contents in an external field of 6.88 T; the measured resonances comprise all the three transitions, ^{23}Na being an $I=3/2$ nucleus (see further).

Let us first consider the *shifts* of the lines with respect to a reference NaCl acqueous solution. We notice that, as long as the samples are superconducting, we measure a large paramagnetic shift (165 ppm), which is attributed to the spin polarization of the conduction electrons (Knight shift). The shift and shape of the resonance are consistent with an isotropic (Fermi) hyperfine interaction as expected by the closed-shell electronic structure of the ion. The metallic character of the samples with $x<1$ is not a surprise (this phase having been extensively investigated in previous works[8–10]). However, upon increasing the ammonia nominal concentration above $x=1$, a peak at the reference ^{23}NaCl resonance frequency progressively appears and it becomes the dominant one near $x=2$, representative of the ^{23}Na behavior in an insulating phase.

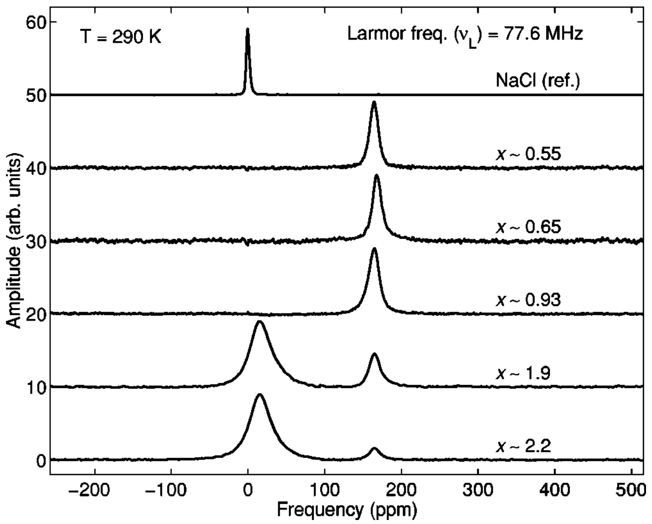

FIG. 1. ^{23}Na NMR spectra of $(NH_3)_xNaK_2C_{60}$ at room temperature (RT). The sizable Knight shift ($\sim$165 ppm) observed for $x<1$ disappears for $x\sim 2$, indicating a transition to an insulating phase.

The residual paramagnetic shift, which is evident in the $x>1$ spectra of Fig. 1, could in principle suggest that the observed 150 ppm shift may be attributed to a (big) change in the hyperfine interaction with conduction electrons from the $x<1$ phase to the $x=2$ phase and not to a localization of the carriers induced by the development of an insulating phase. However, the same displacement of the ^{23}Na line was observed also in superconducting samples ($x<1$) which were exposed to a weakly oxidizing atmosphere (O_2 $\sim$1000 ppm). This treatment suppressed the (super)conductivity of the sample without perturbing its structure (no change in the diffraction pattern). This observation supports therefore the suggestion that the disappearance of the paramagnetic shift is indicative of an insulating phase and the residual shift can be attributed to a chemical shift component. As we will see below, also ^{13}C NMR results will further confirm this issue.

It is important to notice that this system shows two different regimes with respect to ammonia doping: (i) in the range $0.5<x<1$ it behaves as a homogeneous solid solution, irrespective of the intrinsic disorder due to the noninteger stoichiometry; this is guaranteed by the fact that differently doped systems behave like homogeneous superconductors with a well-defined, x-dependent transition temperature; (ii) above $x=1$ the observation of two coexisting phases (one superconducting and the other insulating) indicates, on the other hand, that the separation of the two differently doped phases is energetically favorable with respect to the formation of a solid solution. The transition temperature of the residual superconducting phase, observed for $x>1$, identifies its stoichiometry as $x=1$, while its disappearance as x approaches 2 suggests the emergence of an insulating phase with $x=2$.

Laboratory x-ray powder diffraction shows only cubic reflections in the whole range $0.5<x<2$, while a further increase of ammonia doping (above $x\simeq 2$) results in the ap-

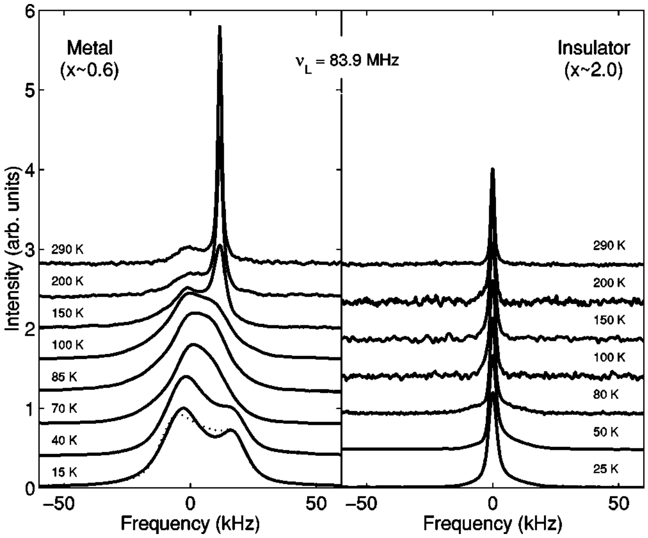

FIG. 2. Temperature dependence of the ^{23}Na line shape for metallic (left) and insulating (right) $(NH_3)_xNaK_2C_{60}$ samples. The large quadrupolar broadening observed in the metallic phase ($\nu_Q \sim 2$ MHz as estimated from the fit of the second-order powder line shape at low temperature) is dramatically reduced (~ 1000 times) in the insulating phase.

pearance of tetragonal reflections, which indicate the formation of a different, ammonia richer phase. To avoid contamination with this other (also insulating) phase, we performed our measurements on the sample with $x = 1.9$. We would like to stress that the presence of a minority superconducting phase, evident also from Fig. 1 (and probably due to ammonia deintercalation during the preparation and manipulation of the samples), does not affect the results obtained in this work, since any possible contribution coming from this phase in the measured spectra has been properly identified and taken into account.

As mentioned before, the quadrupolar interaction of the Na nuclei with the electric field gradient is expected to considerably broaden or split the observed spectra, so that a comparison of the resonance *linewidths* and *structure* turns out to be very illuminating for the identification of Na$^+$ ion sites in the two phases. With reference to the left side of Fig. 2, when $x < 1$ the width at 290 K is surprisingly small, if we recall that Na$^+$ ions are assumed to occupy off-center positions in the octahedral interstices, where the local electric field gradients are quite large. Even if we assume that the observed line corresponds to the central $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition, the expected second-order quadrupolar broadening would be much greater than the observed one.[14] We attribute the observation of a narrow line to a rotational narrowing process. Indeed, thanks to the traceless nature of the quadrupolar interaction, an isotropic and fast rotational motion would be effective in averaging it out. The broadening of the line will be, in this case, restored only by freezing the rotational dynamics upon lowering the sample temperature. The temperature dependence of the ^{23}Na resonance line in the two cases $x = 0.6$ and $x = 2$ (superconducting and insulating phase respectively) is shown in Fig. 2.

In the *metallic phase* the expected broadening is progressively reached on lowering the temperature. At the base temperature ($T = 15$ K), only the $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition (affected only at second order by the quadrupolar interaction[14]) survives, while the other two ($-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ and $\frac{1}{2} \leftrightarrow \frac{3}{2}$, directly affected by the quadrupolar interaction) have moved too far in frequency to be observed. Further evidence supports this interpretation: (i) the different lengths of the 90° pulse at high and low temperatures: a 50% reduction is found in the latter case, where only the central transition is observed;[14] (ii) the line shape at low temperature can be fitted quite well using a second-order quadrupolar broadening, as shown in the lowest spectrum of Fig. 2. A careful modeling of the observed line shape at different applied fields[15] yields an estimate of 2.19 Å for the off-centering along the [111] direction of the Na$^+$ ion, in complete agreement with recent diffraction studies.[16]

All these findings confirm that a motional narrowing process, rather effective in averaging to zero the traceless quadrupolar interaction, takes place at high temperatures. The small bump observed at reference frequency in the room-temperature spectrum is assigned instead to the central transition of the remaining $(1-x)$ fraction of Na$^+$ ions, located in tetrahedral positions. It appears unshifted due to the smaller hyperfine interaction of these ions,[13] whereas its rather large frequency spread could arise from the static quadrupolar interaction (even at room temperature) of the tetrahedral Na$^+$ ions with the EFG created by the neighboring C_{60} units.

Let us now turn to the *insulating phase* (shown in the right side of Fig. 2). In this case the ^{23}Na resonance line is both unshifted and unbroadened at all the investigated temperatures (only at ~ 25 K a small broadening appears, probably due to the slowing down of the lattice vibrational dynamics and of C_{60} rotation). If a quadrupolar interaction were present, it would be small and it would induce a weak second-order broadening of the central $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ line, in addition to possible satellite transitions. To ascertain such quadrupolar effects, the detection bandwidth was extended to ± 500 kHz (a sufficient upper limit, considering the observed peak width). However, no satellites were detected, so we conclude that the narrow resonance is due to a vanishing quadrupolar interaction which merges all transitions in a single resonance line.

To further support this conclusion we performed also an accurate measurement of the 90° pulse length, which would be reduced by a factor $\frac{1}{2}$, if only the central transition were irradiated. The pulse length and power for optimal excitation were found to be the same as in NaCl solution, where a single line comprises all the transitions. Moreover, we checked if this condition was still valid when the power was reduced and the pulse length extended, such as to irradiate only a narrow band around the peak. Since no reduction of the effective 90° pulse length, with respect to the NaCl solution, was noticed, we confirm that the observed resonance comprises all the transitions, thus indicating a vanishing quadrupolar interaction.

The absence of any measurable electric field gradient, in spite of the large ^{23}Na quadrupole moment ($Q_{Na} \simeq 0.11 \times 10^{-28}$ m^2), is exactly what we expect in the center of an

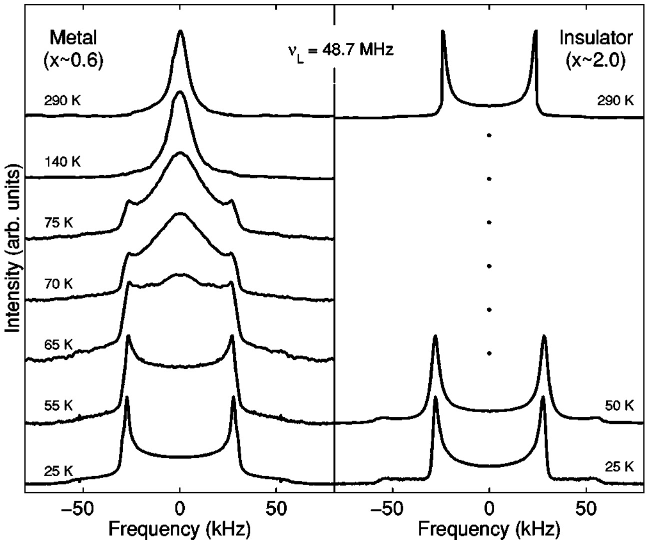

FIG. 3. ^{2}H NMR spectra show typical Pake doublets at low temperatures both in the metallic and insulating samples. The gradual motional narrowing as the temperature rises, observed in the metallic sample, does not occur in the insulating one because of the hampered NH_3 rotation in it.

environment with cubic symmetry.

In conclusion we find that (a) unlike the superconducting phase, in the insulating one the Na^+ cation is located in the center of the octahedral site and (b) the fcc structure evidenced by diffraction is confirmed.

These findings rise some doubts on the current belief, which associates the decrease in T_c to the cation off-centering.[8] In fact, according to that hypothesis, we would still find a superconducting phase at $x=2$ with a sizable increase in T_c instead of the observed insulator.

IV. ^{2}H NMR

As a further test and for a better understanding of the motional narrowing mechanism evidenced by ^{23}Na NMR, we extended our investigation to samples prepared using deuterated ammonia, which allow us to carry out ^{2}H NMR. Deuterium resonance ($I_{^2\mathrm{H}}=1$) is dominated by the quadrupolar interaction with the electric field gradient which, in this case, originates from the σ bond with the nitrogen.[17] Thus, the powder line shape expected for a uniform distribution of ammonia orientations is the typical Pake doublet[18] shown in the lower part of Fig. 3. The expected width of 245 kHz (defined as the distance between singularities) is, however, reduced by the uniaxial rotation of ammonia around its ternary axis,[17] a mechanism we have found to be effective down to 1.6 K. This dynamics is known[17] to produce an overall reduction of the linewidth by a factor of $\sim$4.5 without affecting the spectrum shape. On the other hand, the reorientation of the ternary axis itself can be quite efficient in averaging out the residual traceless quadrupolar interaction, thus making the powder pattern collapse into a single line, as shown in the upper part of Fig. 3 for $x=0.6$ (superconducting phase), while no narrowing was observed for $x=2$ (insulating phase).

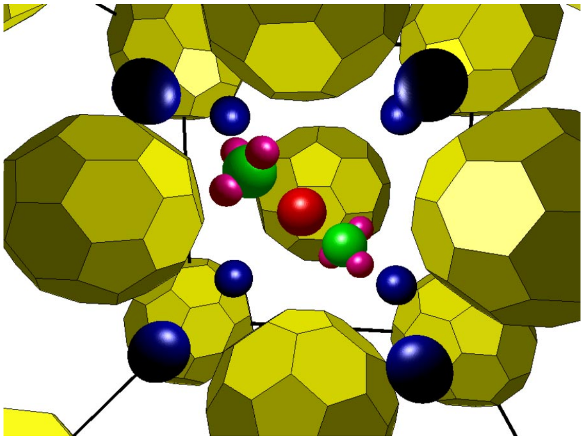

FIG. 4. Pictorial view of the $(NH_3)_2NaK_2C_{60}$ structure as inferred from NMR and x-ray measurements. For $x=2$ the Na^+ ion is "sandwiched" between two ammonia molecules at the center of the octahedral interstice.

These results can be rationalized as follows: in the superconducting phase at high temperatures the NH_3-Na clusters rotate around the center of the octahedron, thus averaging to zero the quadrupolar interactions of both ^{23}Na and ^{2}H. Upon cooling down from RT this dynamics slows down and the situation appears static at $T\sim55$ K on the NMR time scale; i.e., the correlation times are expected to be larger than 0.2 ms. The presence of two ammonia molecules in the insulator ($x=2$ case) inhibits these rotations, which appear to be frozen already at RT.

Since the ^{23}Na NMR suggests that the Na^+ ion is restored in the center of the octahedral site, we can envisage the structure of the insulating phase as that represented in Fig. 4. In spite of the very modest lattice expansion, the O site can still easily host the NH_3-Na-NH_3 cluster. By comparison with $(NH_3)_4Na_2CsC_{60}$ (Ref. 1) and by assuming the same Na-N distance (2.5 Å), only a 1.5% reduction (from 2.29 to 2.26 Å) of the closest H-C distance takes place.

V. ^{13}C NMR

The lack of a magnetic response in the insulating phase, as evidenced by SQUID measurements, suggests that this phase does not arise from a classical Mott transition as the one observed, for example, in $NH_3K_3C_{60}$ (Ref. 19) [where an antiferromagnetic phase exists below $T_N=40$ K (Ref. 3)]. To tackle this problem and to confirm the previous findings we consider a third nuclear probe available in our system: the ^{13}C nucleus, whose spin-lattice relaxation time (T_1) both in the superconducting and in the insulating phase can yield information on electron spin and/or density fluctuations. Figure 5 shows the spin-lattice relaxation rate $1/T_1$ as a function of temperature. While a linear behavior is observed in the $x<1$ phase, as expected on the basis of the Korringa relation for metals,[18] the $x\sim2$ phase follows an activated law, as shown in the fit of Fig. 5, where $E_{\mathrm{act}}=71\pm5$ meV. The disappearance of the Korringa behavior in this latter phase and its lower relaxation rate at low temperatures ($0.1\ \mathrm{s}^{-1}$ for $x\sim2$ at 45 K to be compared with $0.55\ \mathrm{s}^{-1}$ for $x\sim0.9$) both

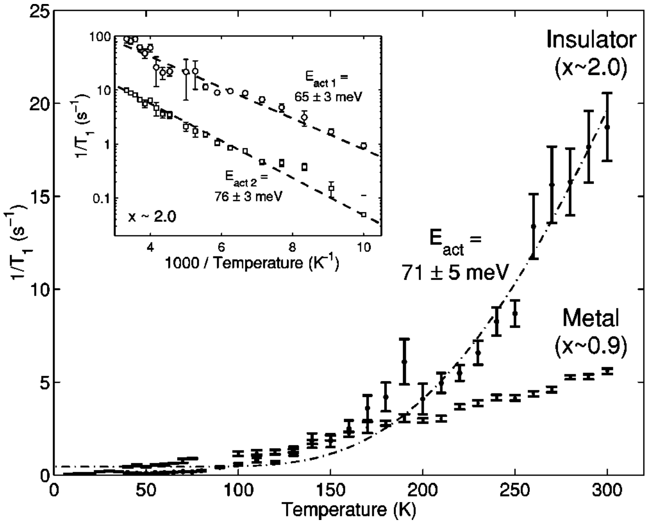

FIG. 5. ^{13}C NMR $1/T_1$ vs temperature dependence in insulating and metallic $(NH_3)_xNaK_2C_{60}$. Whereas the latter follows a linear Korringa law, the insulator shows two thermally activated exponential relaxations, as reported in the inset. The fit with a single relaxation shown in the main figure (dotted line) is characterized by an average $E_{act} = 71 \pm 5$ meV spin gap.

indicate the absence of interactions with conduction electrons in the relaxation process, thus further confirming its insulating nature. By a comparison of these results with the ^{13}C relaxation data in similar insulating systems (i.e., Na_2C_{60} and K_4C_{60}) (Ref. 20), we attribute the activated behavior to the interaction with a thermally excited triplet state. The reorientational dynamics of C_{60} can also contribute, through the modulation of the chemical shift anisotropy (CSA), to the relaxation of carbon nuclei, but the evaluation of this term[20,21] and the comparison with other known cases [for example, Na_2C_{60} (Ref. 22)] show that the expected contribution is restricted to a bump in $1/T_1$ located around $T = 180$ K, visible also in our case. The interaction with excited electrons is therefore the only responsible for the observed activated behavior of the relaxation, thus suggesting the presence of an electron energy gap.

Moreover, a careful analysis of the recovery curves shows a *double exponential behavior* (the amplitude of the differently relaxing components being almost equal), which is more pronounced in the high-temperature region (100–300 K). Although a nonexponential relaxation could be ascribed also to the inequivalence of different carbons in the fcc lattice or to fluctuations of anisotropic interactions (i.e., CSA or Knight shift) (Ref. 23), in both these cases the effect would be more pronounced at low temperatures. Since the opposite is observed, the double-exponential relaxation is more likely due to the presence of two classes of nonequivalent carbon nuclei, both relaxing through activated electronic spin-triplet states. In this case we expect different relaxation rates throughout the temperature range. The double-exponential recovery thus indicates the presence of two spin gaps with different activation energies. The inset of Fig. 5 shows the temperature behavior of the two components in the recovery curve. Fitting the data with the function $1/T_1 = Ae^{-E_a/k_B T} + \text{const}$ yields, respectively, $A_1 = 914 \pm 84$ s^{-1}, $E_{a1} = 65 \pm 3$ meV and $A_2 = 185 \pm 11$ s^{-1}, $E_{a2} = 76 \pm 3$ meV.

The presence of a singlet-triplet gap,[20] like the one observed here, is typical of Jahn-Teller- (JT-) distorted $C_{60}^{(2,4)-}$. This, together with the lack of magnetism and the presence of two different energy gaps, indicates that a quasistatic charge unbalance or, in chemical language, a disproportion as $C_{60}^{3-} \rightarrow C_{60}^{2-} + C_{60}^{4-}$ could take place in our system. The different pre-exponential factors could account for two different hyperfine interactions of the paramagnetic electrons with the ^{13}C nuclei. Their ratio ($A_1/A_2 \sim 5$) is close to the value (~ 4) reported for Na_2C_{60} and K_4C_{60} (Ref. 20). The two activation energies, on the other hand, are quite close, in agreement with theoretical predictions.[24] It is interesting to note that recent studies by Brouet *et al.*, also based on NMR relaxation measurements, report the observation of a similar JT-induced spin gap not only in $C_{60}^{(2,4)-}$ systems,[20] but even in conducting CsC_{60} (Ref. 25) and superconducting Na_2CsC_{60} and Rb_3C_{60} (Ref. 26), in which the presence of C_{60} anions with even charges is explained as the result of fast dynamical charge disproportions or fluctuations. If we suppose that the same effect could be present in the metallic phase of $(NH_3)_xNaK_2C_{60}$ (although it could not be observed in relaxation time measurements for other reasons[26]), the known anomalies of this superconductor and the observed evolution to the insulating phase could be the effect of the slowing down and, eventually, of a freezing of these charge fluctuations.

The ^{13}C spectra taken at low temperature ($T = 20$ K), where narrowing due to molecular reorientational dynamics is ineffective, show in both cases Gaussian line shapes. They are roughly centered at 200 ppm with respect to TMS (tetramethylsilane) and have different full width at half maximum (FWHM) values: 118 ppm for $x \simeq 0.9$ and 177 ppm for $x \simeq 2.0$. Both the linewidths and their positions fully agree with previous observations: those for $x \simeq 0.9$ doping conform to the values found in other superconducting fullerides,[27] whereas the values for $x \sim 2$ doping agree with those measured in the C_{60}^{2-} and C_{60}^{4-} insulating systems.[22,28] The linewidth observed in the metallic phase, smaller than that in the insulator, can be attributed to the different sign of the CSA with respect to the Knight shift anisotropy, yielding a line narrowing once the two tensors are added. These observations are also consistent with the insulating nature of the $x = 2.0$ phase.

VI. CONCLUSIONS

In conclusion we have shown that $(NH_3)_xNaK_2C_{60}$ for $x > 1$ evolves toward a rather singular insulating phase which, unlike other known cases, does not show any magnetic order. Moreover, this phase is hardly imputable to a lattice expansion but, more likely, it originates from a charge disproportion among C_{60} anions, evidenced by the presence of a spin gap. According to theoretical analysis,[29] in odd-electron systems the JT effect adds to the Coulomb repulsion to localize electrons in a nonmagnetic ground state, while the opposite happens in even-electron systems. The related gain in energy could drive our system to favor a JT-induced transition towards the insulating state rather than following the conventional Mott-Hubbard route. This system would represent the first example of a JT-induced metal-to-insulator transition in superconducting fullerides.

Similar charge instabilities could also be at the origin of the anomalous T_c versus lattice parameter observed in the (super)conducting phase of our system. This suggestion is supported by the recent observation of a similar spin gap in the conducting CsC_{60} (Ref. 25) and superconducting Na_2CsC_{60} and Rb_3C_{60} (Ref. 26), where a fast dynamical disproportion might be detectable already in the metallic phase.

Fundamental questions remain, however, open to deeper theoretical and experimental investigations, regarding the compatibility between the charge disproportion mechanism on one side and the nonconventional BCS nature of the superconducting condensate on the other.

This nonconventional behavior is clearly evidenced in the superconducting phase of the systems studied in the present work and confirmed also by recent experiments involving the density of states at the Fermi level[9] or the critical magnetic fields and the field penetration depth.[10]

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