^{13}C and ^{23}Na NMR studies of Na_2C_{60} and Na_6C_{60} fullerides

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We report on ^{13}C and ^{23}Na NMR measurements on Na_2C_{60} and Na_6C_{60} compounds. The room-temperature ^{13}C NMR spectra of Na_2C_{60} and Na_6C_{60} samples present a narrow isotropic line at 172 and 176 ppm, respectively. The Na_6C_{60} resonance is shifted 20 ppm more down field than the resonances of A_6C_{60} compounds with heavier alkalis, indicating a partial charge transfer to the threefold degenerate t_{1u} level which is totally filled in the latter compounds. The ^{23}Na NMR spectrum of A_2C_{60} shows one line at 73 ppm and the one of A_6C_{60} presents two lines at 73 and 147 ppm. The intensity ratio of the latter lines is about 2:1. According to previously reported x-ray data we attribute the line at 147 ppm to the Na tetramers in the octahedral sites and the line at 73 ppm to the Na cations in the tetrahedral ones which are singly occupied. [S0163-1829(97)07137-3]

I. INTRODUCTION

Alkali-metal fullerides have attracted large scientific interest due to their remarkable chemical and physical properties. For smaller ions such as Na, the alkali intercalation compounds have a unique characteristic. First, Na_3C_{60} does not superconduct[1,2] and second the small ionic radius permits intercalation of clusters of up to 8–9 Na ions into the octahedral sites, yielding compounds with x up to 11.[3] X-ray analysis indicates that Na fullerides preserve the fcc of the host lattice contrary to the A_xC_{60} $(x \geqslant 4)$ compounds with heavier alkalis, where the alkalis cations expand the fcc structure of the host pristine C_{60} and distort it into a bct or bcc structure with single occupation of both tetrahedral and octahedral sites.[4] In this paper we present clear evidence, using ^{23}Na NMR of the formation of Na tetramers in the octahedral sites and single occupation of tetrahedral ones in Na_6C_{60} compounds. In Na_2C_{60} the single occupation of the tetrahedral sites and the absence of sodium in the octahedral ones is also evidenced. These results are in quite good agreement with x-ray data.[1] Our ^{13}C and ^{23}Na NMR measurements also indicate incomplete charge transfer in Na_6C_{60} compounds, contrary to A_6C_{60} (A=K, Rb, and Cs) fullerides.

II. EXPERIMENT

The Na intercalation into C_{60} using a vapor transport method has been described previously.[3] Briefly, reactions were carried out in evacuated oxygen-free high conductivity copper tubes, which are readily vacuum sealed by swaging. We prepared several samples using predetermined amounts of C_{60} and Na. We used higher annealing temperatures and longer times than usually needed for C_{60} intercalated compounds. Great care was taken to prevent direct contact between molten sodium and C_{60} powder during the doping reaction. We estimated the actual Na concentration in the obtained samples by titration $(x=2,6)$. All samples have been characterized by x-ray diffraction.

NMR spectra were recorded at a ^{13}C frequency of 50.3 MHz (4.7 T field) and a ^{23}Na frequency of 105.8 MHz (9.4 T field) on Bruker ASX 200 and ASX 400 spectrometers. The NMR signal was obtained as the Fourier transform of the free induction decay after a $\pi/2$ rf pulse. All ^{13}C resonances were referenced to tetramethylsilane (TMS) and the ^{23}Na ones to a 0.1 M NaCl solution. We have applied magic angle spinning (MAS) by using a home-built NMR probe head and a specially designed spinner which allows to spin the air sensitive samples in sealed NMR tubes with frequencies up to 3.5 kHz. Approximately 40 mg of each studied compound was filled in the NMR tube.

III. RESULTS AND DISCUSSION

In Fig. 1 we present room-temperature ^{13}C NMR spectra of Na_2C_{60}. The static spectrum shows a line with an axially symmetric shape, indicating that the C_{60} molecules reorient rapidly about a given symmetry axis. The chemical shift tensor components derived from the static spectrum are $\sigma_\perp=176.8$ ppm and $\sigma_\parallel=157.9$ ppm. It was reported earlier that C_{60} molecules in $Na_{1.3}C_{60}$ compound rotate about the [111] axis.[5] We believe this model to apply to Na_2C_{60} because the $Na_{1.3}C_{60}$ corresponds to a mixing of Na_2C_{60} and pure pristine C_{60} as we have checked and as has also been recently reported.[6]

The ^{13}C MAS NMR spectrum shows an isotropic line at 172 ppm and no other signals were observed indicating the absence of other phases in our sample. The isotropic line at 172 ppm is about 28 ppm more paramagnetically shifted than the pristine C_{60} line (143.6 ppm), due to polarization of the

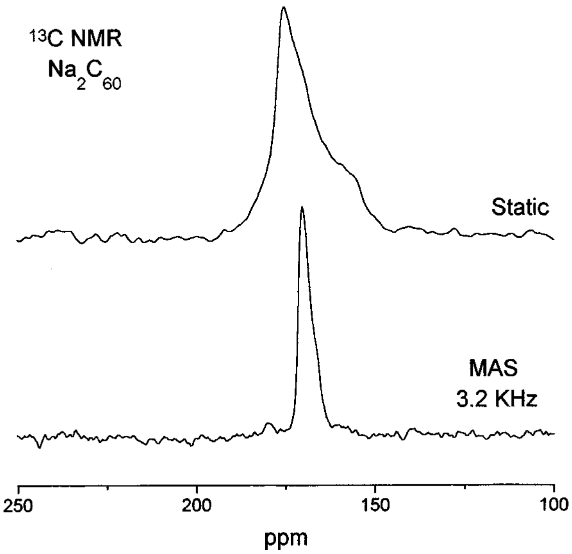

FIG. 1. Room-temperature ^{13}C NMR spectra of Na_2C_{60}: (a) the static spectrum and (b) the MAS NMR spectrum with spinning the sample at 3.2 kHz.

transferred electrons on the carbons. This is in accordance with reported ESR results on Na_2C_{60} which show a significant electrons spin magnetization at room temperature due to a singlet-triplet equilibrium of the spin state of the dianions.[7]

Figure 2 shows ^{13}C NMR spectra of Na_6C_{60} at room temperature; (a) the static spectrum and (b) the MAS spectrum with spinning the sample at 3.2 kHz. The observed powder spectrum presents a chemical anisotropy extent (50 ppm) which is small compared to that of the saturated compounds with heavier alkalis (300 ppm).[8,9] This indicates a significant motional narrowing in the Na_6C_{60}, contrary to the latter compounds where the C_{60} molecules are totally blocked. We calculated chemical shift tensor components of the static Na_6C_{60} spectrum and found $\sigma_{11}=165.1$ ppm, $\sigma_{22}=175.4$ ppm and $\sigma_{33}=185.6$ ppm which indicate an orientationally disordered phase.

The ^{13}C MAS NMR spectrum shows an isotropic line at 176 ppm which is 20 ppm more down field shifted than in A_6C_{60} (A=K, Rb, Cs) compounds.[9] This shift reflects a strong polarization of the transferred electrons and a weaker charge transfer to the C_{60} molecules in Na_6C_{60} in agreement with Raman results which show that the shift of the Ag(2) mode is smaller than that of A_6C_{60} by 5 cm^{-1}.[10,11] According to our ESR data (see the inset of Fig. 2) the thermal spin susceptibility behavior is of Pauli type in the temperature range of 100 to 300 K and also the linewidth shows a linear increase with temperature in the same range. This result seems to indicate that Na_6C_{60} is metallic at least in the investigated temperature range, contrary to the previously reported photoemission data indicating an insulating behavior of this phase.[12] NMR measurements of the thermal relaxation are in progress in order to check this assumption and will be published elsewhere. Also, we think that the observed large paramagnetic shift of the isotropic line of Na_6C_{60} is due to a strong polarization of the conduction electrons on the

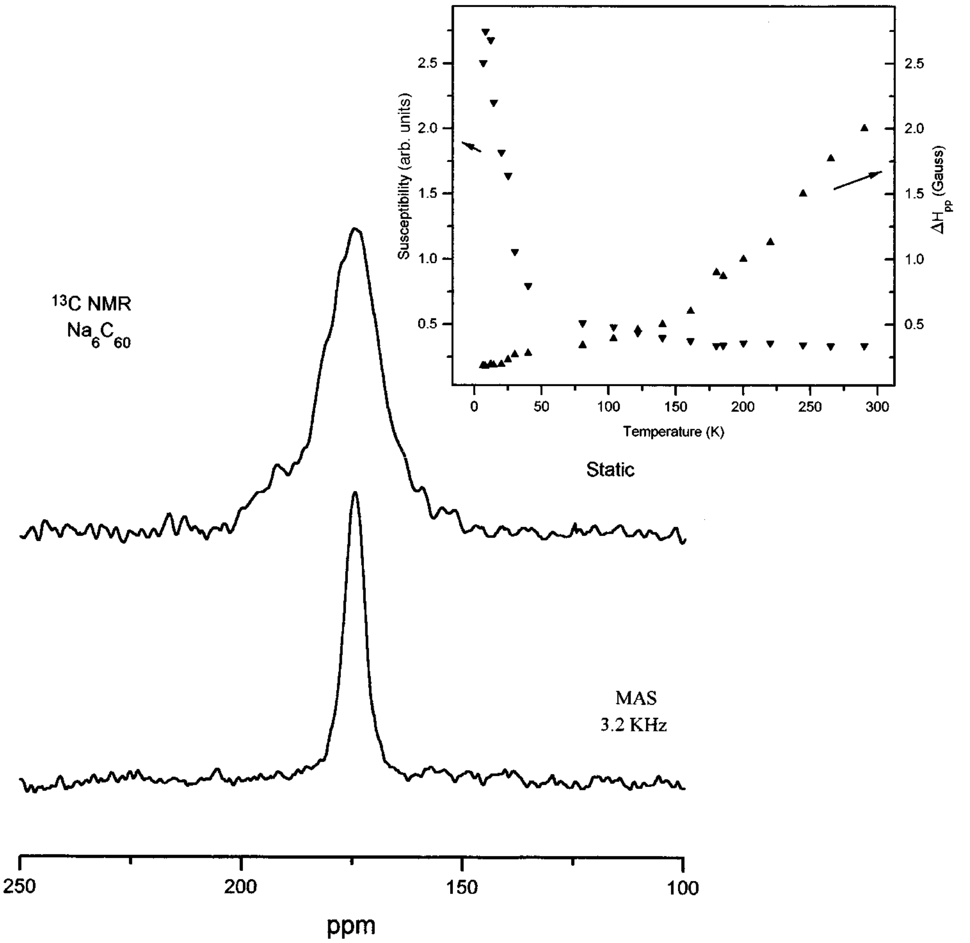

FIG. 2. Room-temperature ^{13}C NMR spectra of Na_6C_{60}: (a) the static spectrum and (b) the MAS NMR spectrum with spinning the sample at 3.2 kHz. The inset shows the temperature variation of the susceptibility and linewidth of the ESR signal of the Na_6C_{60} sample.

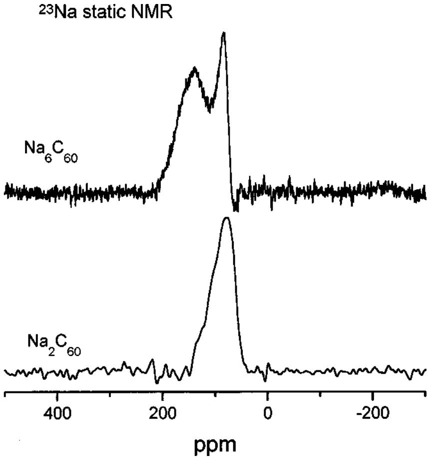

FIG. 3. ^{23}Na static NMR spectra of Na_2C_{60} and Na_6C_{60} compounds obtained at room temperature.

C_{60} molecules. In contrast, as we reported earlier, the observed small shift of the isotropic lines of the A_6C_{60} ($A = $K, Rb, Cs) compounds which is only 13 ppm more paramagnetically shifted than the pristine C_{60} resonance, is rationalized by considering the small energy gap between the filled t_{1u} states, highest occupied molecular orbital (HOMO) and the empty t_{1g} states, lowest unoccupied molecular orbital (LUMO). According to second order perturbation theory a Van Vleck paramagnetic shift should result which depends inversely on the HOMO-LUMO gap.

Figure 3 shows a ^{23}Na static NMR spectra of Na_2C_{60} and Na_6C_{60} at room temperature. In the former spectrum only one line appears at 73 ppm which is significantly shifted from the resonance of NaCl solution used as a standard reference. The latter spectrum shows two lines one at the same position as the Na_2C_{60} resonance and a second line at 147 ppm. This result indicates the presence in the studied compounds structure of two magnetically inequivalent sodium sites. From a deconvolution of the two lines in the Na_6C_{60} spectrum we found that the intensity of the line at 147 ppm is twice that of the one at 73 ppm. According to the x-ray data[1] which suggested a single occupation of the tetrahedral sites and tetramers in the octahedral ones, we attribute the line at 73 ppm to the sodium in the tetrahedral sites which are equivalent in both systems and the one at 147 ppm to the sodium in the octahedral ones. Our results are a good confirmation of the previously reported x-ray data in the studied compounds. As can be seen the observed ^{23}Na resonances are paramagnetically shifted with respect to the used diamagnetic reference, suggesting the presence of residual charge on the sodium in both tetrahedral and octahedral sites in the studied compounds. In the case of tetramers the observed shift which is about 12% of the Knight shift of the sodium ($K = 1230$ ppm) indicating a significant hyperfine coupling of the sodium atoms in the octahedral sites with the residual electrons on the Na clusters or with the polarized electrons on the C_{60} molecules. Our NMR and ESR results indicate that the Na tetramers manifest no quantum size or surface effects as should be expected in the case of small metal particles formation as we showed earlier in the zeolite NaY loaded with sodium.[13] Therefore, we can exclude the presence of small metal aggregates in the octahedral sites and claim that the studied Na tetramers are strongly ionized in good agreement with LDA calculations.[14] However, contrary to the latter calculations our results show lower charge transfer to the C_{60} molecules compared to the saturated fullerides were the alkali atoms are almost totally ionized. Also, ^{23}Na NMR results show clearly that the sodium atoms in the octahedral sites are less ionized than the ones in the tetrahedral sites, leading to a smaller down field shift of the latter atoms.

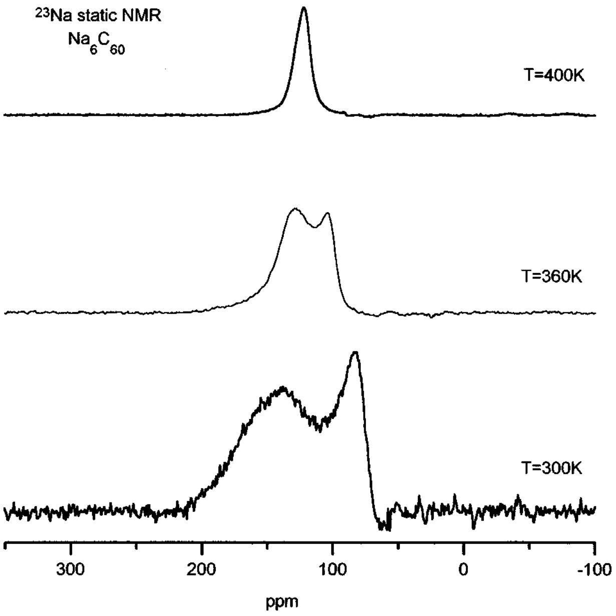

FIG. 4. ^{23}Na static NMR spectra of Na_6C_{60} obtained at (a) 300 K, (b) 360 K, and (c) 400 K.

By heating the Na_6C_{60} sample under vacuum from 300 to 400 K (see Fig. 4), a collapse of the two ^{23}Na NMR lines was observed and only one line appears at 120 ppm at 400 K. The latter line is the average of the two lines observed at ambient indicating an averaging of the inequivalent sites due to a rapid motion of sodium atoms under thermal treatment. The observed behavior is totally reversible.

IV. CONCLUSION

In this paper, we confirm in accordance with previously reported x-ray data the presence of Na tetramers in the octahedral sites in Na_6C_{60} and single occupation of the tetrahedral ones in both studied compounds. We also showed the absence of small metal particles in the former compound. ^{13}C and ^{23}Na NMR results indicate clearly a weaker charge transfer in Na Na_6C_{60} compared to the saturated compounds with heavier alkalis. Work is in progress to investigate the thermal relaxation and the molecular dynamics in these compounds and also the magnetic and electronic properties of Na_xC_{60} compounds with $x > 6$ using NMR and ESR techniques.

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