Pergamon

ORIENTATIONAL PHASE TRANSITION IN Na_xC_{60} ($x \leq 2$): ^{13}C NMR STUDY

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Two major fractions, Na_2C_{60} and C_{60}, are shown to contribute into the ^{13}C nuclear magnetic resonance (NMR) spectra of the low-x Na_xC_{60} ($x \leq 2$). The temperature dependencies of the ^{13}C NMR line shape and spin-lattice relaxation rate $(T_1)^{-1}$ show that Na_2C_{60} undergoes phase transition from the low-temperature orientationally ordered sc structure into the high-temperature orientationally disordered one at about 330 K. Exact temperature of the phase transition of 339 K is found by the differential scanning calorimetry (DSC) experiment.

1. Introduction

Considerable interest to sodium containing fullerides is motivated by a number of unique characteristics. For example, Na_3C_{60} is non-superconducting,[1,2] and ternary Na_2MC_{60} (where M=K, Rb, and Cs) demonstrate superconductivity with anomalously low superconducting transition temperatures.[2] A maximal number of the intercalated Na atoms was remarkably increased up to 10 in the host of C_{60} remaining a face centered cubic (fcc) structure.[3] Phase diagram of the Na_xC_{60} distinguishes from the K, Rb or Cs intercalation fullerides and is still ambiguous. Four discrete Na_xC_{60} with x=2,3,6, and 10 have been identified.[1,3,4] A new single phase $Na_{1.3}C_{60}$ has recently been reported by Yildirim et al.[5] who also suggested a solid-solution behavior for $1<x<3$. Absence of superconductivity shows importance of the electronic properties of Na_xC_{60}. Particularly, the data on the electronic state of Na_2C_{60} are contradictory. Benning et

al.,[6] Seta and Evangelisti[7] claimed that Na_2C_{60} is insulating, Gu et al.[8] suggested that it is semiconducting, while Wertheim et al.[9] concluded that the phase of the same composition Na_2C_{60} is metallic in the bulk and insulating in the surface. Regarding molecular dynamic in Na intercalation fullerides, small ionic radius of Na comparing with K, Rb, or Cs, brings about different orientationally transition behavior. A phase transition from orientationaly disordered fcc phase at high temperatures to ordered sc one below 325 K higher than 260 K of the fcc→ sc transition in pristine solid C_{60}[10] has been found in $Na_{1.3}C_{60}$.[5] The fcc→sc transitions at 299-313 K have been found also in Na_2MC_{60}.[11]

In this communication, we concentrate on the low-x Na_xC_{60} ($x \leq 2$). By analysis of the ^{13}C nuclear magnetic resonance (NMR) line shape and spin-lattice relaxation rate $(T_1)^{-1}$ we show a phase transition at 330 K. Transition near this temperature is confirmed in differential scanning calorimetry (DSC) experiment.

2. Experimental

C_{60} (of 99.9% purity; natural abundance of ^{13}C isotopes) and NaN_3 (of >99% purity) were used as purchased, respectively, from Material and Electrochemical

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Research Corporation (Arizona, USA) and from Merck. Na$_x$C$_{60}^*$ of nominal x=1 and x=2 were prepared by the thermal decomposition of NaN$_3$[12,13] in dynamic vacuum in stainless steel vessel doubly sealed into pyrex tube.[3] Samples was annealed at 350 °C for 2 weeks after reaction. NMR measurements have been performed at ^{13}C frequency (125.7 MHz) on a Bruker MSL 500 spectrometer (11.7 Tesla). The temperature (T-) dependences were measured using about 200 mg of powder sample sealed in pyrex tube. Room temperature (RT) ^{13}C magic angle spinning (MAS) spectra were taken using 100 mg of powder sample placed into the rotor under argon atmosphere. The applied rf pulse width was 6 µs. A ^{13}C shift of tetramethylsilane (TMS) was used as a reference. ^{13}C nuclear spin-lattice relaxation times T_1 were measured with the inversion-recovery technique using pulse sequence π-τ-π/2. The DSC measurements were performed on the TA Instruments 910 Differential Scanning Calorimeter with the heating rate 10 K/min. The sample was placed into a special sample holder under argon atmosphere in the glove box. The holder was exposed to ambient atmosphere only for a short time necessary to press-in and transport it into the calorimeter, the step which we could not avoid.

3. Results and Discussion

We start with the phase diagram derived from NMR experiment, since the question either the low-x Na$_x$C$_{60}$ makes solid solution or separates into discret phases is still worth. The ^{13}C NMR spectra of the x=1 and x=2 samples taken at different T are presented in Figs. 1 and 2. The spectra indicated that the system essentially separated into undoped C$_{60}$ (143 ppm) and Na intercalation phases characterized by broader resonance in the low fields. The isotropic shift of the broad signal of the doped phase was found in the RT ^{13}C MAS NMR to be 170.4±0.1 ppm (the bottom spectra in Figs.1,2). We assign the peak at 170.4 ppm in MAS spectra to Na$_2$C$_{60}$.[4] Along with a major line at 170.4 ppm, MAS spectra showed a few minor peaks with a very weak intensities, sequentially, at 172.5±0.2 ppm in both samples, and at 175.5±0.3 ppm in the later one only (Fig.1,2). We attribute these minor peaks to negligibly small fractions of the other Na$_x$C$_{60}$ ($x \neq 2$) and will not discuss them here. Mixture of discrete phases in the low-x Na$_x$C$_{60}$ instead of solid-solution behavior have been reported elsewhere.[6-8] For example, along with C$_{60}$, Benning et al.[6] found only Na$_2$C$_{60}$ in the x=0.1 and x=1.9 samples, Seta and Evangelisti[7] reported mixture of Na$_2$C$_{60}$
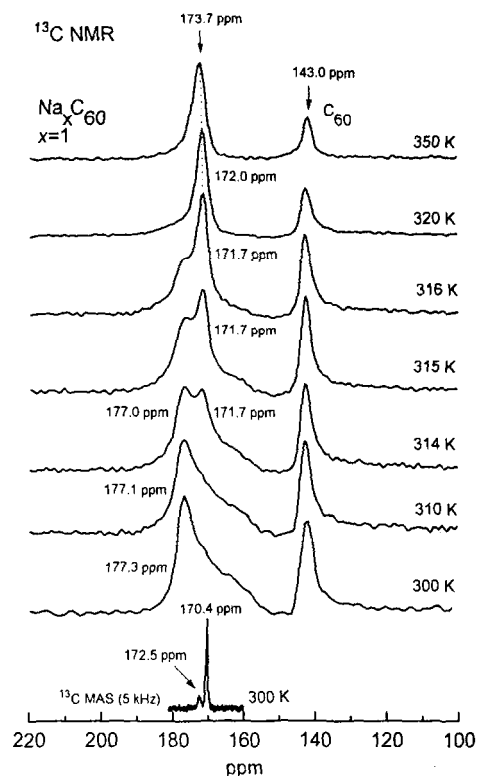

Fig. 1. ^{13}C NMR spectra of the x=1 Na$_x$C$_{60}$ sample at indicated temperatures. Bottom spectrum is ^{13}C MAS NMR spectrum. Shifts are in ppm with respect to TMS. Dotted line shows slight change in the shift at high T.

and Na$_6$C$_{60}$ in the x=1.2 and x=2.6 samples, Gu et al.[8] found only Na$_2$C$_{60}$ in the x=0.9 sample and a mixture of Na$_2$C$_{60}$ and Na$_6$C$_{60}$ in the x=2.3 sample. Hence, for our samples, observed separation into two major fractions, C$_{60}$ and Na$_2$C$_{60}$ was in agreement with Refs.6-8.

The lineshape of the resonance in ^{13}C NMR spectra associated with the doped phase (Figs.1,2) changed dramatically with T indicating phase transition. Above 330 K, the signal had isotropic lineshape and linewidth comparable with that in undoped C$_{60}$ (Fig.1). The shifts in both samples slightly decreased with T, from 173.7 ppm (350 K) to 171.7 ppm (316 K) in the x=1 sample (Fig.1) and from 174.5 ppm (350 K) to 172.0 ppm (315 K) in the x=2 sample (Fig.2). At the same time, constant shift of 143.0 ppm was observed for undoped C$_{60}$. Below 330 K, the resonance gradually broadened and finally transformed at 310 K into the powder pattern typical for the axially symmetric shift tensor when molecule rotates about one of the given axises.[14] An estimate using an isotropic shift
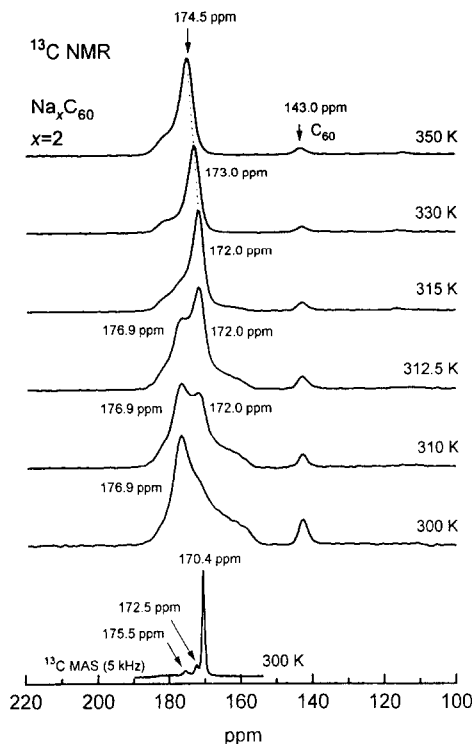
Fig. 2. ^{13}C NMR spectra of the x=2 Na$_x$C$_{60}$ sample at indicated temperatures. Bottom spectrum is ^{13}C MAS NMR spectrum. Shifts are in ppm with respect to TMS. Dotted line shows slight change in the shift at high T.

Fig. 3. The temperature dependence of the ^{13}C spin-lattice relaxation rate $(T_1)^{-1}$ for the x=1 sample. Arrows show transition points for fractions of C$_{60}$ and Na$_2$C$_{60}$.

170.4 ppm derived from the MAS measurement gives $\sigma_{//}$=157.4 ppm and $\sigma_\perp$=176.9 ppm. The shape of broad line did not change thereafter, and no other transformation associating with doped phase was found at lower T.

T-dependences of the ^{13}C nuclear spin-lattice relaxation rates $(T_1)^{-1}$ for x=1 sample are presented in Fig. 3. The recovery curves of the doped phase were meausred on the corresponding signal position of the Fourier transformed spectrum obtained from the free induction decay at the relaxation delay time 2 s. The T_1 measurement for undoped C$_{60}$, in turn, done on the 143 ppm signal position at a very long relaxation delay time 180 s. Data points in both cases have been fitted by single-exponential function in the form $M(t)= M_0[1-2exp(-t/T_1)]$ over the range from 220 K to 360 K (in an assumption that M_0=1). The feature at 330 K in the T-dependence of $(T_1)^{-1}$ of the doped phase (Fig.3) coincides with the lineshape transformation occured at the same T (Fig. 1). One may neglect a contribution of the fraction responsible for the minor peak in the MAS spectra, since the magnetization
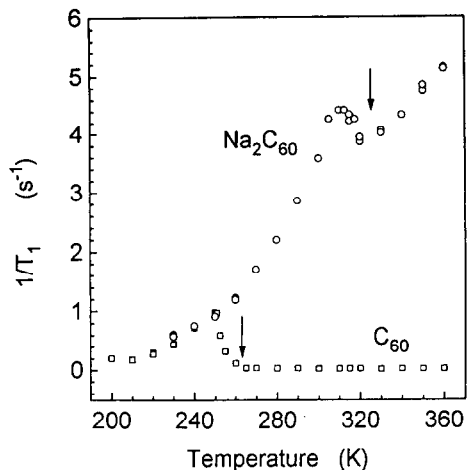
recovery curves at different T were reliably fitted by single-exponential function and due to a very weak intensity of the peak itself. Farthermore, the very fact that the T-dependence of $(T_1)^{-1}$ for the C$_{60}$ signal demonstrated clear transition at 260 K, while for Na$_2$C$_{60}$ did not, and vice versa, transition at 330 K was inherent in the latter phase (Fig. 3), was a direct proof that two nuclear spin systems, of C$_{60}$ and Na$_2$C$_{60}$, were decoupled. Very similar T-dependence of the $(T_1)^{-1}$ with an extremum near 330 K was demonstrated by the x=2 sample as well. The lineshape transformation (Figs.1,2) and extremum in T-dependence of the $(T_1)^{-1}$ at about 330 K were resulted by transition in Na$_2$C$_{60}$, namely. Correspondingly, two transitions, at low and high T, were detected by DSC method. Typical endotherm obtained from x=1 sample is presented in Fig. 4. Peak at 261 K (ΔH=4.8$\pm$0.2 J/g) can be immediately attributed to the undoped C$_{60}$, while peak at 339 K (ΔH=4.8$\pm$0.2 J/g) is from Na$_2$C$_{60}$ which undoubtedly confirms existance of the phase transition in the doped phase within the same temperature range as seen in NMR experiment. Thus, results presented show that Na$_2$C$_{60}$ posseses the high- and low-temperature phases exhibiting different corresponding NMR lineshapes.

In pristine solid C$_{60}$, spin-lattice relaxation mechanism is provided by the chemical shift anisotropy (CSA) combined with molecular rotation.[15,16] For alkali metal fullerides, electron-nuclear interactions contribute into the relaxation mechanisms along with the molecular motion term.[17] In general, $(T_1)^{-1}$ can be given in simple form
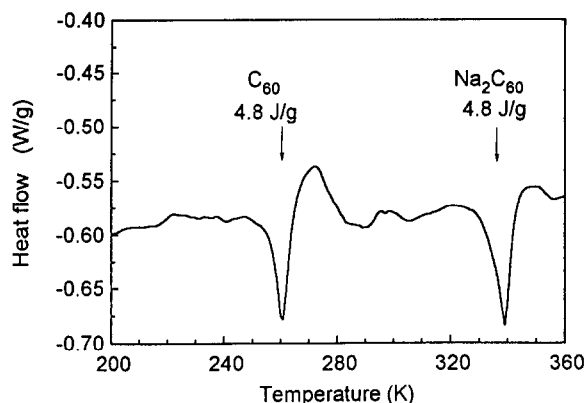
Fig. 4. The endothermic DSC peaks for the $x=1$ sample indicating phase transitions, correspondingly, in undoped C_{60} (261 K) and Na_2C_{60} (339 K).

$$(T_1)^{-1} = (T_1)_{ENI}^{-1} + 2\gamma_n^2\delta B_{loc}^2\tau_c(1+\omega^2\tau_c^2)^{-1},$$ where γ_n is the ^{13}C gyromagnetic ratio, τ_c is rotational correlation time, $\omega=\gamma_nB_0$ is the angular Larmor frequency, δB_{loc} is the local field at the nuclear site. The second term here represents molecular motion. The T-dependent τ_c is usually expressed in the Arrhenius form $\tau_c=\tau_0\exp(T_0/T)$. The former term is a relaxation due to the electron-nuclear interaction (ENI), which can involve the contact and dipolar hyperfine couplings.[17] For pure contact coupling in metals, the rate is given by Korringa relation

$$(T_1)_{ENI}^{-1} = 4\pi k\hbar^{-1}(\gamma_n/\gamma_e)^2K^2T,$$ where $\hbar$ is Planck's constant, k is the Boltzmann constant, γ_e is electronic gyromagnetic ratio, and K is the Knight shift. If one try to fit the T-dependence of $(T_1)^{-1}$ of Fig.3 using general equation, then one can find that the term $(T_1)_{ENI}^{-1}$ by a factor of about 4 smaller than, for example, an anologous contribution found for K_3C_{60}.[18] That can be qualitatively explained by small degree of the electron-nuclear contact coupling due to decreased electron transfer in Na_2C_{60} in comparison with K_3C_{60}. That the ENI take place in this case beyond doubt since T_1 in Na_2C_{60} was much shorter than in the fraction of undoped C_{60} (at 300 K, 0.28 s versus 33.1 s, respectively), and the samples had strong electron spin resonance signals. Qualitative analysis also showed that the equation for $(T_1)^{-1}$ presented above is no longer valid in this situation, and a new term responsible for the rotational motion in the high-T phase should be added. The T-range extended only up to 360 K in this experiment did not allow us to modify the equation and fit

properly experimental $(T_1)^{-1}$ data to evaluate τ_0 and T_0 above and below transition point. The principal values of the shift tensor (which can be derived from the spectra at very low T when motion frozen) and dependence of $(T_1)^{-1}$ on the magnetic field which usually used for the fitting were also unknown. These measurements are in progress. However, regarding the high-T phase, one can note that almost equal linewidths of resonances of Na_2C_{60} and undoped C_{60} in the static ^{13}C NMR spectra, for example, respectively 4.1 ± 0.2 ppm and 2.9 ± 0.2 ppm at 350 K (Fig.1), brings about conclusion that at high T the C_{60} molecules in Na_2C_{60} reorientate in the same manner as in an orientationally disordered fcc lattice of solid C_{60}. Therefore, the rotational correlation time in Na_2C_{60} should be very close to that of pure C_{60} reported elsewhere. Regarding the low-T phase of Na_2C_{60}, sufficiently broad line extends over the range of about 20 ppm (Figs.1,2). It is, however, much narrow than that of the frozen solid C_{60} where the resonance extends over the range of about 200 ppm.[15] An order difference in the linewidth is merely related to the reorientational motion of C_{60} molecule. It has been shown previously in x-ray experiment, that orientationally ordered sc Na_xC_{60} possesses $Pa\bar{3}$ space group.[5] The $Pa\bar{3}$ structure was reported to be stable in the $1<x\leq2$ compounds up to 325 K above which the structure changes into a fcc. Such stability of sc structure in comparison with K and Rb intercalation C_{60} is associated with small ionic radius of Na^+ of 0.98 Å bringing about decreasing of the short range repulsive force between Na^+ and C_{60}. In this situation the Na-C_{60} Coulomb interactions in combination with C_{60}-C_{60} interaction become crucial.[5] It has been shown that C_{60} molecules in Na_2C_{60} rotate about [111] axis at setting angle $\phi=22.24°$.[5] An axially symmetric ^{13}C NMR lineshape of Na_2C_{60} below transition (Figs.1,2) is in a good agreement with the proposed reorientation of C_{60} molecule about one of the four possible [111] directions. Thus, we conclude that a transition seen in DSC and from the ^{13}C NMR lineshape (Figs.1,2) and $(T_1)^{-1}$ (Fig.3) is a phase transition in Na_2C_{60} from the high-T orientationally disordered phase into the low-T orientationally ordered sc one.

In conclusion, we show that Na_xC_{60} with nominal $x=1$ and $x=2$ comprises two main components, Na_2C_{60} and the remain undoped C_{60}. With temperature increase, Na_2C_{60} transforms at 339 K from orientationally ordered sc structure into orientationally disordered one. This value is close to the sc→fcc phase transition temperature of 325 K for $Na_{1.3}C_{60}$.[5]

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