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NMR evidence for sp^3 carbon in the low-temperature phase of Li_xC_{60}

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Li_xC_{60} compounds with x between 6 and 15 are investigated using static and magic-angle spinning ^{13}C nuclear magnetic resonance spectroscopy. The ^{13}C data show evidence for sp^3 bonding among C_{60} molecules. The relative intensities of the sp^3 sites suggest a C_{60} polymerization and support the prediction of a lattice distortion in the Li_xC_{60} low-temperature phase. The ^{13}C chemical shift data indicate an incomplete charge transfer from the Li metal to C_{60}.

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It has recently been shown that C_{60} can be intercalated with Li, forming stable Li_xC_{60} phases with $6 \leqslant x \leqslant 24$.[1] Intercalation of fullerene with small radius alkali metals (i.e., Li or Na) has attracted considerable interest due to the massive doping levels achieved, leading to differences in geometrical and electronic structure with respect to the large radius alkali-metal fullerides (i.e., A_xC_{60} with $A = $K, Rb, Cs and $1 \leqslant x \leqslant 6$).[1–8] In the case of Li_xC_{60} with $x \geqslant 12$, two stable phases have been described based on synchrotron x-ray diffraction.[1] Above 550 K, $Li_{12}C_{60}$ forms an fcc structure (lattice constant $a_{\mathrm{cubic}} = 14.09$ Å) with all Li atoms/ions clustering in the octahedral void of the cubic close-packed C_{60} lattice. Below ~550 K, $Li_{12}C_{60}$ distorts to body centered tetragonal (bct). Virtually identical x-ray diffractograms were found for the Li_xC_{60} compounds with $12 \leqslant x \leqslant 24$, whereas for $x = 6,10$ lower than tetragonal symmetry with possible disorder in the low-temperature phase has been suggested.

Although some basic structural features, as the existence of a cubic high-T phase with Li clustering and lattice distortion below ~550 K, are evidenced by x-ray and quasielastic and inelastic neutron scattering,[1,7] many questions regarding the C_{60} dynamics, chemical structure of the C_{60} packing, and charge transfer with the possibility of covalent Li-C_{60} bonding remain. In this contribution we want to address these points using ^{13}C NMR as a probe for detecting the local C_{60} molecular environment in the low-temperature phase of Li_xC_{60} with $6 \leqslant x \leqslant 15$.

The Li_xC_{60} samples with $x = 6$, 12, and 15 were prepared by thermal decomposition of LiN_3. Stoichiometric amounts of C_{60} (purity >99.5%, Southern Chemicals) and isotopically enriched $^7LiN_3$ (99.7%) were mixed and pelletized. ^7Li intercalation was achieved by heating the C_{60}-LiN_3 mixture (5 K/h) at a pressure of 0.013 mPa in the temperature range $420\,K < T < 480\,K$. Subsequently, the LiN_3 decomposition process was controlled by monitoring the pressure of the nitrogen produced as a function of the pellet temperature. The ~20-mg powder samples were annealed at 580 K (6 h) to improve the crystallinity and homogeneity and then sealed in quartz tubes at ~100 Pa He pressure. The accuracy of the stoichiometric compositions was estimated as $\Delta x = 0.05$.

Figure 1 shows experimental ^{13}C NMR spectra of the low-T phase of Li_xC_{60} under static [Fig. 1(a)] and magic-angle spinning (MAS) [Fig. 1(b)] conditions at 300 K. Experiments were performed with a home-built NMR spectrometer operating at a ^{13}C Larmor precession frequency of 55.31 MHz (5.17-T field) and equipped with either a home-built static probe or a 6-mm MAS probe (Chemagnetics). The spectra were obtained from free-induction-decay (FID) signals following a $\pi/2$ pulse. Background signals from the probe and receiver recovery effects were reduced by applying a π pulse 60 μs before alternate $\pi/2$ pulse signal acquisitions and alternately adding and subtracting the FID signals. In the MAS experiments, the ^{13}C background signal was further checked by running identical measurements without the sample present. We discuss the results for Li_6C_{60} and $Li_{15}C_{60}$, which represent the two extremes of the investigated stoichiometric range. The intermediate case of $Li_{12}C_{60}$ gives qualitatively the same ^{13}C results as $Li_{15}C_{60}$.

Both static spectra share similar features. The line shapes show the signature of an inhomogeneously broadened shift-anisotropy powder pattern, typical for static fullerene sp^2 carbons, superimposed with two sharper features at 155 and 59 ppm. This is indicative of the absence of rotation for the majority of the C_{60} molecules in the low-T phase. In fact, the spectra are well reproduced with the approximation of an average shift tensor with the parameters ($\delta_{\mathrm{iso}} = 153\,\mathrm{ppm}$, $\delta_{\mathrm{aniso}} = 111\,\mathrm{ppm}$, $\eta = 0.28$), i.e., δ_{aniso} and η values equivalent to those of pristine C_{60},[9] together with additional Gaussian contributions at 155 ppm (motionally averaged C_{60}^{n-} line, *vide infra*) and at 59 ppm (see also Table I). The latter resonance can be attributed to sp^3-hybridized carbon atoms [$30 \leqslant \delta_{\mathrm{iso}}(sp^3) \leqslant 80\,\mathrm{ppm}$].[10] These resonances are known to have shift anisotropies smaller than 30 ppm (Ref. 10) and are therefore seen as relatively sharp features in the spectra.[11] The findings indicate that the rotation of the majority of the C_{60} molecules is blocked due to covalent bonding, possibly in a polymer configuration. The C_{60}-C_{60} bonding reaction seems also to be reversible, as it was shown by inelastic neutron scattering measurements that in the low-T phase the typical librational and molecular C_{60} modes are severely broadened or missing altogether, whereas upon crossing the phase transition at ~550 K the C_{60} molecules freely rotate in the high-T phase.[7]

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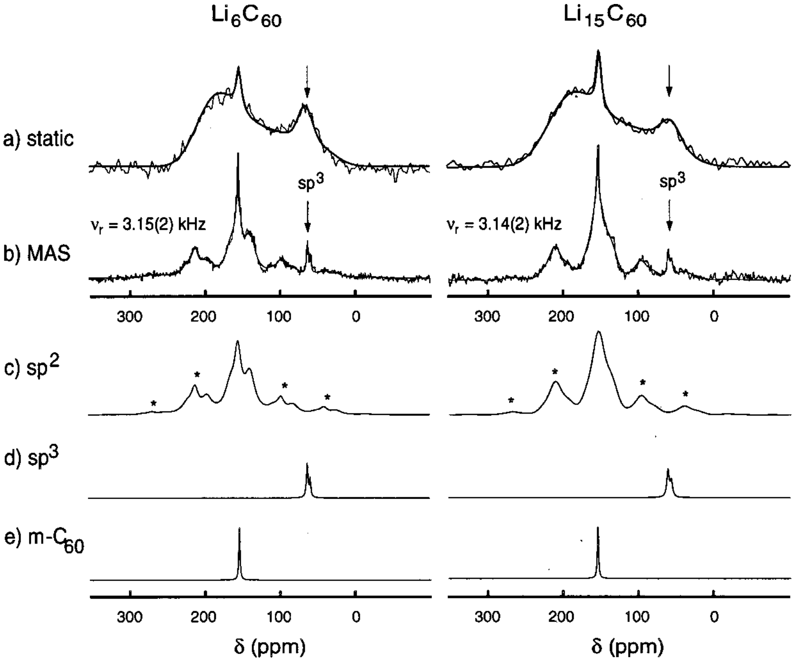

FIG. 1. (a) Static ^{13}C NMR spectra of Li_xC_{60} at 300 K with best fits as described in the main text and Table I. The repetition time between successive experiments was $\tau_r = 10$ s, 10 000 scans (3.5-μs $\pi/2$ pulse). (b) ^{13}C magic-angle spinning spectra of Li_xC_{60} at 300 K with best fits as described in the main text and Table I. $\tau_r = 10$ s, 30 000 scans (4-μs $\pi/2$ pulse). The rotation frequencies are indicated in the figure. (c)–(e) Decomposition of the fits in (b) in their various contributions: (c) sp^2 carbon atoms; spinning sidebands are marked with asterisks. (d) sp^3 carbon atoms; Lorentzian lines. (e) m-C_{60}; mobile C_{60} (Lorentzian lines). The various spectral parameters are summarized in Table I. The chemical shifts are referenced with respect to tetramethylsilane (TMS).

In order to further support these resonance assignments we performed MAS measurements. The experimental spectra with best fits are shown in Fig. 1(b). In addition, the decomposition in the various fitted contributions is displayed in Figs. 1(c)–(e) (compare also with Table I). The dominant feature of the spectra is the sp^2 carbon contribution with isotropic shifts in the range of 140–165 ppm. In both cases a minimum of three components with intensity ratios of 1:1:0.6 (Li_6C_{60}) and 1:1:0.8 ($Li_{15}C_{60}$) (with increasing shift) are necessary to describe the sp^2 line shapes. This might be related to the presence of C_{60} sp^3 bondings and/or a slight deformation of the C_{60} molecule spherical shape leading to inequivalent sp^2 sites. The large linewidths (12–20 ppm) must be attributed in part to structural disorder. In both cases the sideband distribution [as emphasized by asterisks in Fig. 1(c)] corroborates the existence of large sp^2 shift anisotropies. The relative intensities can be well described with spectral parameters analogous to those of pristine C_{60}, however, with an average isotropic downfield shift due to the charged molecules in the Li-doped phases. In fact, no additional resonance line shifts or changes in resonance frequencies or broadenings of the ^{13}C spectra were observed as a function of temperature in the range of 130–300 K. This indicates that the ^{13}C shift values in Table I are indeed determined by the chemical shift and not by additional Knight shift contributions, which are quite susceptible to temperature variations (given by a temperature dependence of the electron spin susceptibility χ_s). We therefore suspect that the relatively short ^{13}C relaxation times $[T_1(Li_6C_{60}) = 0.8(1)\ s, T_1(Li_{15}C_{60}) = 0.9(2)\ s$ at 300 K] (Ref. 12) are due to paramagnetic species, localized, for example, on the Li clusters or possibly also in interstitial electronic trapping sites.[5,6]

TABLE I. ^{13}C 1D line-shape parameters for Li_xC_{60}, 300 K.

	Li_6C_{60}	$Li_{15}C_{60}$
MAS data		
$\delta_{iso}(sp^2)$ (ppm)	[141, 156, 165](2)	[140, 155, 163](3)
$\delta_{aniso}(sp^2)$ (ppm)	111	111
$\eta(sp^2)$	0.28	0.28
σ_{sp^2} (ppm)[a]	16(5), 12(3), 16(7)	19(4), 11(3), 20(5)
$\delta_{iso}(sp^3)$ (ppm)[b]	[59, 63](1)	[59, 62](1)
σ_{sp^3} (ppm)[b]	3(1), 2(1)	4(1), 4(1)
$\delta_{iso}(m\text{-}C_{60})$ (ppm)[b]	155(1)	155(1)
$\sigma_{m\text{-}C_{60}}$ (ppm)[b]	2(1)	2(1)
$f = I_{sp^3}/I_{sp^2}$	0.05(2)	0.06(2)
Static data		
$\delta_{iso}(sp^2)$ (ppm)	154	152
$\delta_{aniso}(sp^2)$ (ppm)	111	111
$\eta(sp^2)$	0.28	0.28
σ_{sp^2} (ppm)[a]	15(5)	30(5)
$\delta_{iso}(sp^3)$ (ppm)[c]	59(3)	59(3)
σ_{sp^3} (ppm)[c]	20(2)	25(5)
$\delta_{iso}(m\text{-}C_{60})$ (ppm)[c]	155	155
$\sigma_{m\text{-}C_{60}}$ (ppm)[c]	4(1)	4(1)
$f = I_{sp^3}/I_{sp^2}$	0.09(3)	0.07(3)

[a] Gaussian broadening.
[b] Lorentzian line.
[c] Gaussian line.
[d] Number in parenthesis represents the error of the last digit.

Both samples show an additional sharp sp^2 resonance at 155 ppm (~3% of the total intensity) that can be attributed to charged but unbound (freely rotating) C_{60} molecules (m-C_{60}). This fraction reflects a certain degree of phase inhomogeneity and was probably not detected by the x-ray measurements. The m-C_{60} line can be assigned to nonpolymerized ''tetragonal'' C_{60} or to a remainder of the high-T cubic phase. The shift values of the sp^3 bonding sites agree well with the values in the static spectra. At least two peaks are resolved for Li_6C_{60} and $Li_{15}C_{60}$. The average chemical shift values are between the values found for sp^3 carbons in high-pressure polymerized rhombohedral or tetragonal C_{60} (~74 ppm) (Refs. 13, and 14) and polymerized AC_{60} (A = Rb,Cs) (~36 ppm).[15,16] No sidebands were detected for the sp^3 lines corroborating the weak chemical shift anisotropy already inferred from the static data.

From the intensity ratio $f = I_{sp^3}/I_{sp^2}$ (see Table I) one can estimate the number of sp^3 carbons per C_{60} molecule $[n_{sp^3} = 60/(1+f^{-1})]$. For this analysis, the m-C_{60} contribution was subtracted from the total intensity. We obtain an average number of $n_{sp^3} = 4(1)$ for both $Li_{15}C_{60}$ and Li_6C_{60}. No effect on the peak intensities in the spectra of Fig. 1 was found at longer pulse repetition times (up to 30 s). Therefore, we do not expect systematic errors in n_{sp^3} caused by incomplete relaxation during $\tau_r = 10\,\mathrm{s}$.

With the result of an average of four sp^3 carbons per C_{60} a variety of bonding configurations are conceivable: (i) two $[2+2]$ cycloadditions for each C_{60}, which keep the total number of bonding electrons constant, or (ii) four bonds per C_{60} molecule to different neighbors where for each sp^3 bond one electron is released per C_{60}. Both, polymerization and dimerization of C_{60} molecules involving $[2+2]$ cycloadditions or single sp^3 bonding have been reported in the literature.[17–29] Considering the constraint, imposed by the synchrotron x-ray data, of a tetragonal lattice distortion in the low-T phase, two extremes in a continuum of possible arrangements can be envisioned: (1) a ''random network polymerization'' in the *a-b* plane involving two $[2+2]$ cycloadditions per C_{60}, or (2) a full polymerization of the C_{60} molecules along both (a,b) axes with four bonds per C_{60} [see Figs. 2(a) and 2(b)]. Both configurations would explain the substantial local structural disorder evidenced by the ^{13}C data (which could be due to C_{60} orientational disorder and/or deformation of the C_{60} spherical shape). Local structural disorder is also supported by the fact that at least two (slightly shifted) sp^3 sites are found. This could be due to slightly different C_{60} bonding types (bond angles and length) or crystallographically different sp^3 sites.

In the case of Li_6C_{60}, a formation of a one-dimensional (1D) $[2+2]$ cycloaddition $(C_{60})_p^{n-}$ polymerization[19] [Fig. 2(c)] or a lower symmetry 2D C_{60} polymerization[20] [Fig. 2(d)] can also be envisaged. Such bonding arrangements are compatible with the present NMR results; however, they would imply a lowering of the tetragonal symmetry (e.g., orthorhombic or monoclinic lattice distortions) and are therefore not supported by the x-ray data for the Li_xC_{60} phases with $x \geqslant 12$.

An additional important feature concerns the charge transfer in the low-temperature Li_xC_{60} phase. Negligible paramagnetic shifts of the ^{13}C lines are observed, which suggest a polyfulleride singlet state. Based on the empirical rule that the chemical shift of negatively charged sp^2 C_{60} carbons increases at ~2 ppm per charge[30] we can infer an average of five- to sixfold negatively charged C_{60} molecules/monomers, i.e., a virtually full occupation of the t_{1u}-derived molecular states (note that for the non-polymerized m-C_{60} $\delta_{\mathrm{iso}} = 155\,\mathrm{ppm}$). An uptake of ~6 electrons per C_{60} is also corroborated by infrared and Raman spectroscopy on $Li_{15}C_{60}$.[31] Based on semi-empirical calculations in Ref. 29 this large charge transfer would also suggest a C_{60} polymerization with single bonds rather than $[2+2]$ cycloadditions.

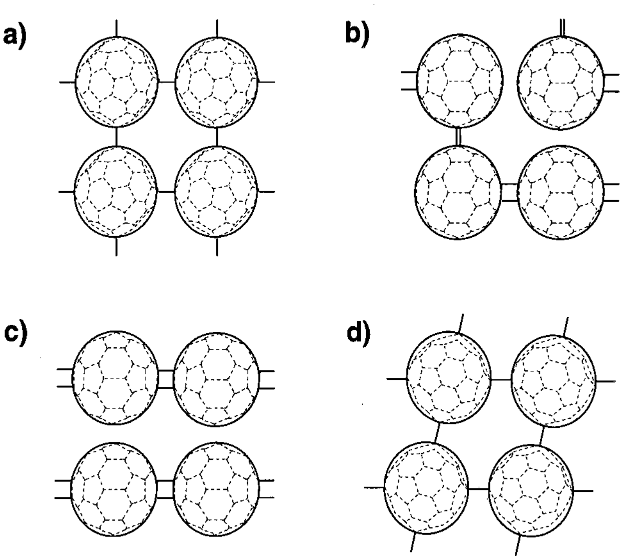

FIG. 2. (a) and (b) Schematic representation of extreme C_{60} bonding arrangements compatible with the sp^3 site intensity extracted from the present NMR data and the constraint of a tetragonal lattice distortion obtained from synchrotron x-ray data in the low-T Li_xC_{60} phase (projected to the *a-b* plane). Both configurations (single bond between C_{60} and $[2+2]$ cycloadditions implying two bonds between C_{60}) could lead to considerable orientational disorder and/or deformation of the C_{60} spherical shape. (c) Schematic drawing of the $[2+2]$ cycloaddition $(C_{60})_p^{n-}$ polymerization along one axis and (d) 2D lower-symmetry C_{60} polymerization with four sp^3 bonds per C_{60}. Both configurations are compatible with the present NMR data but would lower the tetragonal symmetry. Configurations (b)–(d) have been reported in the literature (Refs. 17–20). For simplicity, the C_{60} molecules are orientationally ordered in these schematic diagrams.

The ^{13}C NMR data do not support the presence of Li-C_{60} bonds with strong covalent character as was suggested by x-ray studies.[1] In fact, no $^7\mathrm{Li} \rightarrow {}^{13}\mathrm{C}$ cross-polarization transfer could be observed for contact times up to 20 ms at 300 K. This indicates that ^{7}Li-^{13}C dipolar interactions are averaged almost to zero by the translational mobility of Li and that there are no ^{7}Li-^{13}C J couplings present which would indicate covalent bonds. Moreover, ^{7}Li NMR data at 300 K give clear evidence for motional narrowing due to rapid (local) Li diffusion processes and Li nuclei in ionic states $[\delta_{\mathrm{iso}}(^7\mathrm{Li}) \leqslant 7\,\mathrm{ppm}, \sigma(^7\mathrm{Li})$ (Refs. 1 and 32)]. The onset of motional narrowing occurs around 150 K where a Li jump correlation time of $\tau_c \sim 40\,\mu\mathrm{s}$ can be inferred.[32]

The combined ^{13}C and ^{7}Li shift data indicate an incomplete charge transfer from the lithium atoms to C_{60}, possibly also for $x = 6$, and could be interpreted as indication for the formation of interstitial electronic states that trap part of the excess electrons. Such a behavior has been suggested, based on *ab initio* calculations, to be a general feature of heavily doped C_{60} intercalation compounds.[6] Although it has been found that such electron trapping states are neither C_{60} nor alkali-metal derived[6] it can be argued that the interstitial electron density would still affect the carbon sp^2 chemical shift. Future calculations of the ^{13}C chemical shielding parameters using *ab initio* and density-functional methods[33–35] will help in further elucidating our experimental observations.

In summary, ^{13}C NMR data in the low-temperature phase of Li_xC_{60} with $x=6-15$ reveal the presence of sp^3 hybridized carbon atoms and give evidence of a C_{60} polymerization which explains the lattice distortion in the low-T phase. 1D as well as 2D static ^{13}C exchange spectra at 300 K (data not shown) indicate the rotational blocking of the C_{60} molecules up to an experimental time scale of 0.5 s. The combined ^{13}C and ^{7}Li shift data suggest an incomplete charge transfer from the metal atoms to the C_{60} molecules.

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