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2008 New J. Phys. 10 033021

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The structural and electronic evolution of Li$_4$C$_{60}$ through the polymer–monomer transformation

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New Journal of Physics 10 (2008) 033021 (17pp)
Received 24 August 2007
Published 12 March 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/3/033021

Abstract. In this paper, we combine synchrotron powder x-ray diffraction, $^7$Li nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) experiments to study the structural evolution of Li$_4$C$_{60}$ and how its electronic ground state depends on the crystal symmetry. The compound in the two-dimensional polymer phase with mixed interfullerene bonding motifs is a band gap insulator. EPR, however, reveals the presence of intrinsic centers originating from broken C$_{60}$–C$_{60}$ bonds and local Li off-stoichiometry that create states in the band gap and account for the complex temperature dependence of the spin susceptibility as well as the residual temperature dependence of the $^7$Li NMR shift. At low temperatures, the Li$^+$ ions are statically disordered on the $^7$Li NMR timescale. The observed $^7$Li NMR line narrowing at $T > 200$ K is ascribed to the Li$^+$ diffusion dynamics and above room temperature the polymer phase is already a good ionic conductor. Heating the sample to temperatures above $\sim 470$ K results in gradual depolymerization to the metallic monomer fcc high temperature structure. The transformation is first order and polymer as well as monomer phases coexist over a broad temperature interval (130 K).
1. Introduction

Ever since the discovery of the one-dimensional (1D) polymer phase in RbC$_{60}$ [1], bonding of fullerenes has attracted enormous attention. The prime interest in fullerene-bridged arrays comes from their reduced dimensionality and often accompanying electronic and magnetic instabilities. There are two ways to form a bond between the two neighboring C$_{60}$ molecules. The predominant mechanism involves a $[2 + 2]$ cycloaddition reaction where carbon atoms from different molecules form a four-member ring [2]. Such a mechanism is a driving mechanism for the C$_{60}$ polymerization in photopolymerized C$_{60}$, in pressure-induced polymer phases as well as in most of the A$_1$C$_{60}$ polymer structures (here A = K, Rb, Cs). Another structural motif has been discovered in Na$_2$RbC$_{60}$ [3]–[5] where the C$_{60}$–C$_{60}$ bonding relies on a single C–C covalent bond [6].

Doping of C$_{60}$ with Li does not necessarily lead to the same effects as doping with other alkali metals [7]–[11]. The small ionic radius of the Li$^+$ ion makes a big difference from the structural point of view and very often one even encounters an incomplete charge transfer to C$_{60}$. To investigate these effects, we have recently focused on Li$_4$C$_{60}$ phases. Initial reports [7, 12] suggested that Li$_4$C$_{60}$ forms a 2D polymer tetragonal structure with $[2 + 2]$ cycloaddition bonds bridging the C$_{60}$ molecules in two orthogonal directions. However, recent high-resolution synchrotron x-ray diffraction (XRD) studies lead to a surprising conclusion: Li$_4$C$_{60}$ at room temperature indeed forms a 2D polymer network, but the C$_{60}$–C$_{60}$ bonding encounters $[2 + 2]$ cycloaddition along one direction and a single C–C bond along the perpendicular direction [13]. This structure thus involves both bonding motifs and is unique among all known fullerene structures. $^{13}$C nuclear magnetic resonance (NMR) and Raman spectroscopy suggested that the polymeric phase is a diamagnetic insulator [14]. A high temperature treatment leads to a depolymerization and results in the high temperature monomer face-centered-cubic (fcc) structure [15]. Combined Raman, X-band electron paramagnetic resonance (EPR), $^{13}$C NMR and $^7$Li NMR measurements proved the metallic ground state of the high temperature phase. This positions Li$_4$C$_{60}$ as the only metallic fulleride system with four electrons donated to C$_{60}$ ($n = 4$) adopting an fcc structure.

Solution of the room temperature monoclinic polymer and the high temperature fcc monomer structures of Li$_4$C$_{60}$ opened important questions related to the electronic ground state of both phases. Moreover in Li$_4$C$_{60}$ we thus have a unique chance to investigate and discuss the...
role of structural anisotropy and low symmetry on the electronic ground state as we can access both high symmetry fcc structure as well as the low symmetry monoclinic polymer structure in the same run. In order to understand how and why the monoclinic polymer structure transforms into a cubic monomer structure as well as how this affects the electronic properties, we present here a systematic structural (XRD) investigation correlated with the study of the electronic ground state deduced from EPR and $^7$Li NMR.

2. Experimental details

Powder of Li$_4$C$_{60}$ was prepared, as previously reported [13, 15] either by the reaction of Li vapors with C$_{60}$ or by the thermal decomposition of LiN$_3$. The samples prepared by both methods showed the same structure. NMR experiments were performed with a commercial spectrometer (Apollo, Tecmag) equipped with a home-built solid-state probe and a home-built oven for high temperature measurements. The magnetic field was 6.34 T.

Powder XRD measurements were performed on the ID31 beamline at the ESRF Synchrotron Facility (Grenoble). The samples were sealed in 0.5 mm quartz capillaries in Ar atmosphere; the heating treatment was performed with a hot-air blower (Cyberstar, France).

X-band continuous wave (cw) EPR measurements were performed on Bruker E580 spectrometer using a Varian TE102 dual cavity and an Oxford Cryogenics continuous flow E900 cryostat. For all the techniques the temperature stability was better than $\pm 0.2$ K over the entire temperature range. A home-built high temperature unit was used in EPR experiments above room temperature. Cw EPR measurements were performed at small microwave powers (at low temperatures $P_{MW} = 0.01$ mW), small modulation field ($B_{mod} = 0.1$ G) and low modulation frequency $v_{mod} = 10$ kHz. For EPR and NMR experiments, samples were sealed in standard EPR quartz tubes with reduced He atmosphere for a better thermal contact.

As prepared Li$_4$C$_{60}$ powders were systematically investigated by EPR both on heating as well as on cooling under the following temperature protocols: on heating from room temperature to 620 K spectra were taken in approximately 10 K steps. At each set temperature we waited for 300 s to allow for thermalization of the sample. The same procedure was followed on cooling. In thermal cycling tests this temperature protocol was then repeated several times. Since the same cryostat cannot also be used for low temperature experiments, we had to transfer the samples to another measurement system for these investigations. Low temperature measurements on as prepared as well as on thermally cycled Li$_4$C$_{60}$ powders were taken on cooling in $\Delta T = 5$ K steps and with a 600 s waiting time at the set temperature.

3. Results and discussion

3.1. XRD

Our XRD studies on the structural properties of Li$_4$C$_{60}$ have shown that at room temperature it adopts a monoclinic layered polymeric structure (space group $I2/m$) where each C$_{60}$ unit bonds to its four nearest neighbors in the layers using both the [2 + 2] cycloadDITION and the single C–C bridging motifs, thereby giving rise to two types of differently bonded chains running perpendicular to each other [13, 14]. However, at 773 K Li$_4$C$_{60}$ adopts a fcc structure with typical non-bonding interfullerene distances in excess of $\sim 3$ Å and full 3D character [15]. In order to clarify the nature of the polymer to monomer transition, we followed the evolution
of the structural parameters by temperature dependent synchrotron x-ray powder diffraction measurements. Data were collected between room temperature and 473 K in 50 K steps. Above 473 K, where the coexistence of phases has been found, we collected the data every 20 K up to 623 K. Extraction of reliable lattice constants was performed using the LeBail method in the $2\theta$ range 4–30° (at 293 K: lattice constants, $a = 9.3372(4)$ Å; $b = 9.0433(4)$ Å; $c = 15.0288(6)$ Å; $\beta = 91.002(3)^\circ$; agreement factors, $R_{wp} = 4.56\%$ and $R_{exp} = 2.41\%$). The evolution of the diffraction profiles on warming shows that the polymeric structure is robust up to 423 K, remaining monoclinic with the lattice parameters showing an anisotropic rate of expansion. While the $a$ and $b$ lattice constants show almost negligible changes, the $c$ parameter displays a larger thermal expansivity ($14.4(4)$ ppm K$^{-1}$). This can be understood considering the 2D nature of the polymeric phase in the $ab$ basal plane. A further increase in temperature initiates a drastic change. At 473 K, new peaks of weak intensity appear which index on a fcc unit cell clearly indicating the onset of a structural phase transition (figure 1). These peaks grow significantly in intensity as the temperature is further increased with the concomitant gradual disappearance of the monoclinic Bragg reflections. Inspection of the diffraction profile at 623 K (figure 1 right panel) revealed only the presence of the cubic phase with a unit cell parameter $a = 14.2356(6)$ Å (agreement factors, $R_{wp} = 5.35\%$, $R_{exp} = 2.97\%$).

Figure 1. Left panel: final observed (open circles) and calculated (solid line) synchrotron x-ray powder diffraction profile of Li$_4$C$_{60}$ at 623 K in the range 4–30° ($\lambda = 0.8507$ Å). The lower lines show the difference profiles and the vertical marks indicate the positions of the observed reflections. Right panel: selected regions of the diffraction profiles of Li$_4$C$_{60}$, showing the temperature evolution of the monoclinic (10-1), (101), (011), (002) and (110) Bragg reflections which eventually disappear at high temperature with the concomitant appearance of the (111) cubic Bragg reflection. The shoulder indicated with an asterisk (*) is associated with hexagonal stacking faults and was excluded from the structural refinements.
The temperature dependence of the lattice constants and unit cell volume of Li$_4$C$_{60}$ extracted from the LeBail refinements is shown in figure 2. The transformation of the polymer into a monomer structure is clearly a first-order phase transition as evidenced by the broad temperature range (130 K) of phase coexistence (figure 3). The depolymerization is accompanied by a large volume enhancement ($\delta V / V \sim 5.6\%$). A drastic increase in the linear thermal expansivity coefficient, $d \ln V / dT$ for the cubic phase is also observed ($2.71(2) \times 10^{-5}$ and $4.31(2) \times 10^{-5}$ Å$^3$ K$^{-1}$ for the polymer and monomer phases, respectively), consistent with the absence of interfullerene bonds and in agreement with the values encountered in other monomeric cubic alkali fullerides (cf $3.63(3) \times 10^{-5}$ Å$^3$ K$^{-1}$ for Li$_4$CsC$_{60}$ [16]). A comparison with other polymeric fullerides reveals that the volume enhancement upon depolymerization in Na$_2$RbC$_{60}$ is 2.8% [17] and in Na$_2$CsC$_{60}$ (which polymerizes under high pressure) is 2.9% [18]. Our value is bigger but this is explained if one considers that the Li$_4$C$_{60}$ polymeric phase is very compact and it is a 2D polymer and not 1D like the other two examples.
3.2. $^7$Li NMR

We now focus on the behavior of Li$^+$ ions in the polymeric phase and especially during the structural transformations. To get deeper insight we decided to measure the $^7$Li NMR line shape and its longitudinal relaxation rate $1/T_1$. At low temperatures a $I = 3/2$ quadrupolar powder pattern is clearly evident (figure 4), with an asymmetry as high as 96 kHz at 5 K. The structure of the broad baseline corresponding to the quadrupole split outer transitions speaks for the presence of more than one component. In other words, it suggests that the structurally inequivalent Li ions are affected by the different electric field gradients. Inequivalent lithium ions can be, according to our XRD work, assigned to the two lithium atoms that are located in the pseudotetrahedral and to the other two in the two sites symmetrically displaced around the pseudoctahedral site [14]. The detailed analysis of this broad component with different tensor parameters, and its theoretical simulation together with fitting of model parameters will be the subject of a detailed future work.

On warming, we find at around $\sim$200 K a $^7$Li NMR lineshape transition. The lineshape at higher temperatures gradually turns into a single narrow peak superimposed on a featureless basis which eventually disappears at high temperatures. For instance, the 400 K $^7$Li NMR spectrum (figure 4) is composed of a single narrow (690 Hz full width at a half maximum (FWHM)) peak at the LiCl resonance frequency. In order to clearly demonstrate the lineshape transformation, we also plot in the inset to figure 4 the temperature dependence of the width of the quadrupolar broad component of the line. It reduces from 55 kHz at 160 K to 30 kHz at room temperature. The observation of a single featureless peak may at first glance be surprising especially when compared with the expected two inequivalent Li positions mentioned above. We also stress at this point that XRD results did not suggest any structural change in this temperature range. On the other hand, the observed line narrowing may be associated with the onset of fast Li ions diffusion dynamics, i.e. Li$^+$ ions are for $T < 200$ K statically disordered on the $^7$Li NMR timescale, while for $T > 200$ K their disorder becomes dynamic. The presence of a sharp structureless Lorentzian $^7$Li NMR line above room temperature suggests a high mobility of Li$^+$ ions, and therefore suggests that the polymer phase is a good ionic conductor. This result is,
Figure 4. $^7$Li NMR spectra of Li$_4$C$_{60}$ polymer at low temperatures. Inset: temperature dependence of the width of the quadrupolar broad component of the line; the line narrowing observed above 200 K is attributed to the onset of Li ions diffusional dynamics. Above 300 K the intensity of this component vanishes.

however, not in contradiction with the Fourier analysis of the diffraction patterns, which clearly revealed well localized electron densities in the lattice. Namely, if the Li$^+$ motion is through a jump diffusion, the Chudley–Elliott analysis [19] of the (self)correlation functions still predicts well localized peaks in the Fourier map [20]. The same model successfully describes the Li$^+$ diffusion in other ionic conductors [21, 22].

Temperature activated Li$^+$ dynamics in the polymer phase is evident also from the spin-lattice relaxation time measurements. In the temperature range around 200 K the longitudinal relaxation curves change (inset to figure 5) from the high-temperature single-exponential (i.e. $M_z = M_\infty (1 - r \exp[-\tau/T_1])$) to a low-temperature bi-exponential recovery (i.e. $M_z = M_a (1 - r_1 \exp[-W_1 \tau] - r_2 \exp[-W_2 \tau])$, as expected for quadrupolar relaxation [22] (formerly mistaken as an increase in a single-exponential $T_1$ [23]). The two relaxation rates $W_1$ and $W_2$ strongly increase with increasing temperature and nearly coincide at about 220 K (figure 5). Above $\sim 220$ K where the relaxation curves change to mono-exponential form, also the temperature dependence of the relaxation rate $1/T_1$ changes and becomes much less pronounced. The activation energy for the Li-ion hopping diffusion is estimated to be $E_a = 60$ meV. At this point it may be instructive to compare this activation energy to the activation energy in Li intercalated graphite. In stage-1 intercalated graphite the reported activation energies vary considerably from $E_a = 1$ eV [24] to $E_a = 600$ meV [25] or even to $E_a = 180$ meV in KC$_8$ [26]. The diffusion process in this case proceeds via Li$^+$ ion jumping between graphite potential sites separated by saddle point energy between C–C bonds. The differences in the surface curvature between flat graphite and curved C$_{60}$ change the Li$^+$ ion...
Figure 5. Temperature dependence of the relaxation rates in the Li$_4$C$_{60}$ polymer phase. At low temperatures the magnetization curves are typically bi-exponential described by two relaxation rates $W_1$ and $W_2$, while at temperatures above 200 K single-exponential curves better fit the relaxation rate $1/T_1$. In the inset, we compare the relaxation curves measured at 200 and 280 K.

potential surface and may also account for the considerably smaller activation energy in the Li$_4$C$_{60}$ sample.

Let us focus our attention now on the high temperature behavior. As with increasing temperature the structure evolves from the polymer to the monomer state (see figure 3), the position of the narrow NMR line observed above room temperature becomes strongly temperature dependent. On heating a positive shift of the line is measured (figure 6) over entire temperature range. Deep in the polymer phase the shift with respect to LiCl reference is very small, i.e. a few ppm in agreement with the diamagnetic insulating ground state of the polymer phase. At around 450 K, where XRD indicates the first appearance of the monomeric phase, the rate of the change of shift (i.e. $d
u_C/dT$) suddenly changes taking steeper temperature dependence (figure 6). At 660 K, the shift amounts to already 30 ppm. Since the typical isotropic chemical shift range for the $^7$Li nucleus does not exceed a few ppm, this fact can be reasonably attributed to the onset of a Knight shift associated with the interaction of $^7$Li nuclei with the conduction electrons in a metal. A thermal hysteresis, seen in XRD experiments [27] and characteristic of the first-order transformation from polymer to monomer Li$_4$C$_{60}$ phase, is also reflected in the temperature dependence of the shift measured on cooling. The characteristic change in the $d
u_C/dT$ is now seen at much lower temperature, i.e. at around 420 K. Interestingly, we notice that we still find only a single $^7$Li NMR peak in the temperature range where the coexistence of two phases has been noticed by XRD. This is despite the fact that Li$^+$ ions occupy very different sites in the fcc and polymeric phase [15]. A rapid Li$^+$ ion diffusion facilitated by a small activation energy barrier is effective in mediating quadrupolar interaction above 350 K while homonuclear dipolar broadening prevents the observation of the double peak structure of the resonance below 630 K. Therefore, a single $^7$Li NMR line is observed within the region of phase coexistence. $^{13}$C NMR could possibly provide an alternative probe for the high temperature phase co-existence, but the low sensitivity of $^{13}$C NMR probe prohibits us from monitoring the process directly by NMR.
Figure 6. Frequency shift of the $^7$Li NMR central peak in Li$_4$C$_{60}$ on heating the polymer phase from room temperature (circles) with subsequent cooling of the monomer phase (diamonds).

After cooling back to room temperature, the frequency shift does not reproduce the same value measured for the starting polymer phase. This in general agrees with the hysteretical behavior observed by diffraction in the same temperature range. Diffraction clearly shows that on cooling from the high temperature cubic monomer phase, a complete repolymerization is never observed. For the sake of completeness, we notice that also a smaller second peak, whose origin is still not completely understood, gradually emerges at the side of the main peak at high temperature, as outlined in [15]. Its position roughly follows the same behavior of the main peak in the temperature range 550–660 K where they coexist in the $^7$Li spectrum.

3.3. EPR

Let us now investigate how the electronic properties as seen by EPR follow the structural and Li ion dynamics changes seen by XRD and $^7$Li NMR. The low temperature ($T = 8$ K) X-band EPR signal (see the inset to figure 7(b)) is slightly anisotropic. The temperature dependence of the EPR spin susceptibility obtained by a double integration of the spectra and the linewidth as its FWHM of the integrated spectra are shown in figure 7. The temperature dependence of the EPR spin susceptibility (figure 7(a)) shows a complex behavior and it is not easy to fit its temperature dependence. An empirical approach with a Curie–Weiss type plus temperature independent (Pauli for instance) contribution is not completely satisfactory over the entire temperature range with the polymer structure. We stress at this point that at room temperature the EPR spin susceptibility approaches the value $\chi_{\text{EPR}} = 2.4(4) \times 10^{-5}$ emu mol$^{-1}$. This value is at least an order of magnitude smaller than what is anticipated for a metallic state. It is also two orders of magnitude smaller than the spin susceptibility that would be expected if $S = 1/2$ were localized on each C$_{60}$ unit. This comparison, therefore, suggests that the measured EPR signal probably comes from diluted intrinsic defects in the polymeric structure.
Figure 7. Low temperature (2D polymer phase) dependence of the X-band EPR spin susceptibility (a) and FWHM obtained after integration of the spectra (b). In the inset to (a) we show the temperature dependence of the \(g\)-factor and in the inset to (b) a typical X-band EPR lineshape measured at 8 K.

More firm evidence for the non-metallic ground state of the \(\text{Li}_4\text{C}_{60}\) polymer phase comes from the temperature dependence of the EPR linewidth (figure 7(b)). A very narrow EPR signal has been found in virgin polymer \(\text{Li}_4\text{C}_{60}\) samples and for instance the EPR linewidth measured at \(T = 4\) K is only about 3 G. The EPR linewidth typically decreases with increasing temperature, just the opposite to what is expected for a metallic fulleride. Namely, due to the Elliot relaxation mechanism [28] in all known metallic \(\text{C}_{60}\) compounds the EPR signal linewidth has a positive slope [29, 30].

Interestingly, we also find a bump in the temperature dependence of the EPR linewidth between 150 and 200 K, which also correlates with the gradual change in the \(g\)-factor (inset to figure 7(a)). In the same temperature interval the low-temperature EPR signal asymmetry disappears and the room temperature X-band EPR signal has a nearly perfect Lorentzian lineshape. Since \(^7\text{Li}\) NMR demonstrates that the \(\text{Li}^+\) dynamics changes in the same temperature range, we suggest that the two processes are strongly linked. To address the details of the EPR lineshape evolution, we also performed Q-band EPR lineshape measurements between
Figure 8. Temperature dependence of the splitting of the Q-band ($\nu_L = 34.9$ GHz) EPR spectra. In the inset, we show Q-band EPR spectra measured at two selected temperatures ($T = 290$ and $230$ K) to demonstrate the splitting of the lines.

We can at this point make a partial summary for the polymer phase: the observed temperature dependence of the EPR lineshape, spin susceptibility and linewidth in the polymer $\text{Li}_4\text{C}_{60}$ phase all suggest its non-metallic ground state. In fact, from the small magnitude of the EPR susceptibility one can even suggest that $\text{Li}_4\text{C}_{60}$ is a band gap insulator. The defect states are localized at low temperatures and become progressively more and more delocalized above $200$ K, where the $\text{Li}^+$ diffusive dynamics also sets in on the magnetic resonance timescale. From this one may suggest that the origin of the EPR signal in the polymeric phase is not only the $\text{C}_{60}-\text{C}_{60}$ broken bonds but also local Li off-stoichiometry.

Upon heating the sample above room temperature towards the depolymerization regime, we start to observe dramatic changes in the EPR signal. While the room temperature polymer X-band EPR lineshape is nearly perfectly Lorentzian (and very close to a single Lorentzian also in Q-band EPR experiments) we start to detect the gradual growth of the asymmetry with increasing temperature (figure 9). The asymmetry ratio $A/B$ defined as a ratio between the height of the two peaks in the spectrum (see the inset to figure 9) increases from 1 (i.e. Lorentzian lineshape) to nearly 1.6. In fact, at the highest temperatures, i.e. at temperatures above $540$ K, the lineshape already resembles Dyson lineshape typical of metallic systems [31] and frequently encountered in other metallic fullerene samples [32, 33]. The EPR signal we are observing at high temperatures is thus, in fact, a conducting electron spin resonance.
conclusion is in complete agreement with our recent report on the recovery of metallicity in fcc Li$_4$C$_{60}$ [15]. We note that the lineshape changes take place exactly in the same temperature interval where the XRD results suggested the gradual transformation from the polymer to cubic fcc structure occurs (figure 3) so we associate these changes with the transformation from the insulating diamagnetic polymer phase to the metallic cubic phase. The thermal hysteresis in the asymmetry ratio also nicely coincides with the thermal hysteresis seen in XRD and $^7$Li NMR measurements.

Let us now investigate the thermal polymer/monomer transformation more in detail. In figure 10, we show the temperature dependence of the EPR parameters associated with the EPR signal at high temperatures taken during the first and fifth high-temperature cycle. We first comment on the temperature dependence of the EPR spin susceptibility (figure 10(a)). The increase in the EPR spin susceptibility with increasing temperature suggests the gradual formation of EPR active centers due to the breaking of C$_{60}$–C$_{60}$ bonds. The EPR spin susceptibility in the cubic phase ultimately reaches $\chi_S = 1.8(2) \times 10^{-4} \text{emu mol}^{-1}$. On cooling from the highest temperatures the EPR spin susceptibility is nearly temperature independent down to $\sim 425$ K (figure 10(a)), as one would expect for the metallic Pauli-like spin susceptibility. High-temperature EPR spin susceptibility is thus again fully consistent with the metallic ground state of the monomer fcc phase of Li$_4$C$_{60}$. Taking the measured spin susceptibility and then calculating the associated density of states at the Fermi level, we estimate it to be $N(E_F) = 5–8 \text{states eV}^{-1}$. We stress that this value is comparable but still slightly lower than the values determined in other metallic alkali-doped fullerenes [29]. The reduction in the density of states might arise from the strong correlation effects suggesting that the Li$_4$C$_{60}$ is in its cubic phase in the vicinity of the metal–insulator border.

A very similar conclusion can be drawn from the peak-to-peak EPR linewidth ($\Delta H_{pp}$) temperature dependence (figure 10(b)). The EPR linewidth during the first cycle increases with increasing temperature above 400 K, i.e. in the temperature range where the changes in the
Figure 10. Temperature dependence of the (a) EPR spin susceptibility and (b) peak-to-peak linewidth measured at high temperatures during successive thermal cycles. Solid symbols stand for warming while open symbols represent cooling data during the first temperature cycle (circles) and fifth temperature, respectively (squares). See text for details.

EPR linewidths have also been noticed. The high-temperature value of the linewidth depends on the number of high-temperature thermal cycles. For instance, during the fifth thermal cycle it reaches the value of about 18(1) G at 621 K (not much difference with respect to the fourth cycle). This suggests that heating the sample to 620 K—the highest temperature accessible with our EPR experimental equipment, is not sufficient for a complete polymer–monomer transformation and several high temperature cycles are needed to greatly increase the cubic fraction. We stress that $T = 620$ K is just around the temperature interval where according to XRD a nearly complete polymer–monomer transformation should occur (figure 3). The temperature dependence of the EPR linewidth in the cubic phase is very typical for metallic fullerides: the slope of the EPR linewidth versus temperature curve is positive and nearly linear. In other alkali metal doped $\text{C}_{60}$ fullerides this has been interpreted by a spin-phonon scattering via spin–orbit interaction—a mechanism proposed by Elliot [28].

A high temperature cycling also throws additional light on the origin of the EPR signal in the polymer phase. As prepared $\text{Li}_4\text{C}_{60}$ polymer shows at room temperature an extremely narrow
X-band EPR signal (\(\Delta H_{pp} = 0.27(3)\) G) and the calibrated EPR signal intensity corresponds to the spin susceptibility 0.24(4) \times 10^{-4}\text{ emu mol}^{-1}. Thermal cycling results in the broadening and the increase of the intensity of the room temperature EPR signal. The increase in the \(\chi_S\) with the number of thermal cycles is due to poorer crystal (re)polymerization during the cooling proving that the signal is indeed related to the defect formation. We also stress that such a narrow room temperature EPR signal is not very common in fullerides. At the same time we remind the reader that the linewidth depends on the thermal history (figure 10(b)) and since the linewidth roughly scales with the spin susceptibility this implies that the EPR linewidth is also controlled by the concentration of defects. For a magnetically diluted system, where the leading mechanism of the broadening of the EPR is the dipolar interaction, the linewidth is directly proportional to the concentration of the magnetic centers [34] and for polymeric \(\text{Li}_4\text{C}_{60}\) we derive \(\Delta B = c \times 150\) G. Here, \(c\) is the concentration of the paramagnetic centers. If the linewidth of the EPR signal is 0.27 G, this would then suggest that one out of 550 \(\text{C}_{60}\) molecules could be defective.

### 3.4. Discussion

Combined XRD, \(^7\text{Li}\) NMR and EPR measurements unambiguously proved that the polymer phase is a band gap insulator (semiconductor). This important conclusion is in full agreement with our previous work [14]. It is, however, not easy to understand why polymeric \(\text{Li}_4\text{C}_{60}\) would not be a metal. Recent DFT calculations of the electronic structure in fact suggested that all Li-related bands are high in energy [35], and therefore a full charge transfer is predicted with a metallic band structure. In fact, the complete charge transfer in the high temperature cubic metallic phase is consistent with the Raman Ag(2) mode shift analysis [15]. On the contrary in the polymer phase, hints of the incomplete charge transfer came from previous Raman measurements [14] and electron spectroscopy measurements [36]. We stress at this point that a partial charge transfer from Li to \(\text{C}_{60}\) has already been observed in other lithium-based fullerides like \(\text{Li}_3\text{CsC}_{60}\) [37]. \(\text{Li}_4\text{C}_{60}\) emerges as a unique system that provides an insight into the way the alkali metal ions interact with \(\text{C}_{60}\). The size of the \(^7\text{Li}\) NMR shift in the polymeric phase suggests that the degree of mixing of Li s orbital with the \(\text{C}_{60}\) t\(_{1u}\) orbital is rather small in agreement with DFT calculations [35]. Also, low-temperature X-band and Q-band EPR provide not only evidence for the low temperature charge localization in the 2D polymeric phase, but also on the coexistence of two different paramagnetic centers. It is believed that the approaching of a Li ion to \(\text{C}_{60}\) localizes part of the donated electron wavefunction in the space between the two species. Splitting of the pseudo-octahedral site might be an indication of a similar mechanism in our case. The residual temperature dependence of the \(^7\text{Li}\) NMR shift and the complex temperature dependence of the EPR spin susceptibility suggest some charge delocalization for \(T > 200\) K. The transition is not sharp as expected for a usual metal–insulator transition and may be correlated with the enhanced \(\text{Li}^+\) ion dynamics and the disappearance of the fine splitting between different paramagnetic sites in this temperature range. Dramatic changes in the temperature dependence of the \(^7\text{Li}\) NMR shift and the accompanying changes in the high temperature EPR lineshape prove the transition to a metallic state upon de-polymerization. The high temperature cubic metallic phase is also characterized by very small Pauli susceptibility. All these results point to the fact that the interaction of Li with the t\(_{1u}\) electrons is nevertheless important in \(\text{Li}_4\text{C}_{60}\) and should not be neglected.

Despite the polymer’s band gap insulating state, there are still diluted intrinsic electronic states, which are created by broken \(\text{C}_{60}\text{–C}_{60}\) bonds and/or local Li off-stoichiometry. Strong
hints for their presence and assignment come mainly from the high temperature EPR cycling experiments. Probably these structural defects create donor states in the band gap that can donate charges to the polymeric conduction band. The observed complex temperature dependence of the spin susceptibility (figure 7) is probably a result of the temperature dependent concentrations of the localized defect states and the electrons at the bottom of the conduction t_{1u} band, i.e. \( \chi_{\text{EPR}} = \chi_P + \chi_{\text{CW}} \). Here, the Pauli susceptibility \( \chi_P = \mu_0 \mu_B^2 N(E_F) \) becomes temperature dependent due to the temperature dependence of the density of states at the Fermi level \( N(E_F) \). At the same time, due to the temperature dependence of the concentration of neutral donor states \( n_0^d \) also the Curie susceptibility

\[
\chi_{\text{CW}} = \frac{n_0^d g^2 \mu_B^2 S(S+1)}{3k_B T}
\]

should show a complex dependence. If the donor levels are located at \( E_d = 30 \text{ meV} \) below the parabolic conduction band one can indeed explain the observed temperature dependence of the EPR spin susceptibility and residual dependence of the \(^7\text{Li} \) NMR shift in the polymeric phase.

Our \(^7\text{Li} \) NMR data above room temperature but still in the polymer phase clearly indicate high \( \text{Li}^+ \) mobility as a jump diffusion process. \( \text{Li}^+ \) hopping freezes out on the \(^7\text{Li} \) NMR timescale around 200 K. It is intriguing to notice that changes in the \(^7\text{Li} \) dynamics are also detected in the EPR. The fact that above \(~200\) K the lineshape anisotropy in the EPR spectra is averaged out suggests that in this temperature range also the electron dynamics changes, i.e. at low temperatures the states are well localized, while becoming more delocalized above 200 K. This may on one hand directly reflect the temperature evolution of the concentrations of electrons at the bottom of the conduction band and in the donor state, respectively, or alternatively the fact that the diffusive \( \text{Li}^+ \) Coulomb field ‘drags’ the defect \( C_{60} \) states contributing to the EPR signal. To decide which of the two possibilities is correct, we have to wait for additional experimental work.

4. Conclusions

Combined temperature dependent XRD, \(^7\text{Li} \) NMR and X-band EPR measurements are consistent with the band gap insulating polymeric phase, which at around 423–473 K starts to transform into the high temperature metallic fcc phase. EPR finds paramagnetic centers that in the polymer phase belong to defects, such as broken \( C_{60} - C_{60} \) bonds or local \( \text{Li} \) off-stoichiometry. These defects can be viewed also as donor states in the band gap that can donate to the polymeric conduction band and explain the complex temperature dependence of the spin susceptibility and the residual temperature dependence of the \(^7\text{Li} \) NMR shift. Lithium ions are statically disordered at their crystallographic positions at low temperatures. Upon heating over \(~200\) K, the \( \text{Li}^+ \) hopping rate increases. At temperatures at and above room temperature the polymer phase of \( \text{Li}_4C_{60} \) is probably already a good ionic conductor.

Acknowledgments

We acknowledge financial support from the EC-NEST project ‘Ferrocarbon’. SM and DA acknowledge financial support from the Royal Society through the joint project ‘Crystal and electronic structure of alkali doped polymerised \( C_{60} \) networks’.

New Journal of Physics 10 (2008) 033021 (http://www.njp.org/)
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