

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/223163020>

Conductance and EPR study of the endohedral fullerene Li@C₆₀

ARTICLE *in* SOLID STATE COMMUNICATIONS · FEBRUARY 2005

Impact Factor: 1.9 · DOI: 10.1016/j.ssc.2004.12.014

CITATIONS

20

READS

64

6 AUTHORS, INCLUDING:



Vladimir Popok

Aalborg University

132 PUBLICATIONS 1,196 CITATIONS

SEE PROFILE



Martin Jönsson-Niedziolka

Polish Academy of Sciences

51 PUBLICATIONS 518 CITATIONS

SEE PROFILE



Andreas Lassesson

Lund University

34 PUBLICATIONS 352 CITATIONS

SEE PROFILE



E. E. B. Campbell

The University of Edinburgh

322 PUBLICATIONS 7,415 CITATIONS

SEE PROFILE

Conductance and EPR study of the endohedral fullerene Li@C₆₀

V.N. Popok^{a,*}, I.I. Azarko^b, A.V. Gromov^a, M. Jönsson^a, A. Lassesson^c,
E.E.B. Campbell^a

^aDepartment of Physics, Göteborg University, Fysikgrand 3, 41296 Göteborg, Sweden

^bPhysics Faculty, Belarusian State University, F. Skorina Avenue 4, 220050 Minsk, Belarus

^cDepartment of Physics, Ernst-Moritz-Arndt-University Greifswald, 17491 Greifswald, Germany

Received 15 November 2004; accepted 13 December 2004 by C.N.R. Rao

Available online 18 December 2004

Abstract

Thin films and bulk samples of endohedral fullerenes Li@C₆₀ are studied using current–voltage (*I*–*V*) measurements and electron paramagnetic resonance (EPR). Electrical measurements show a linear behaviour for the *I*–*V* curves and give an average resistivity of ca. 1.5 kΩcm for thin Li@C₆₀ films deposited in vacuum, four orders of magnitude lower than C₆₀ samples. A drastic effect on the conductance, lowering it to the values typical for C₆₀, is observed when the Li@C₆₀ samples are exposed to ambient atmosphere. No additional paramagnetic centres (PCs) are found for the Li@C₆₀ compared to C₆₀ that can be related to the formation of dimers or trimers of the endohedral fullerene molecules. However, the presence of the Li atoms in the fullerene cages contributes to a change of the spin–spin and spin–lattice relaxation times. The spin–lattice relaxation time becomes four orders of magnitude longer compared to the spin–spin relaxation time.

© 2004 Elsevier Ltd. All rights reserved.

PACS: 61.48.+c; 72.80.Rj; 76.30.Lh

Keywords: A. Fullerene; D. Electronic transport; E. Electron paramagnetic resonance

1. Introduction

Fullerenes have been known since the middle of the 1980s [1]. Very soon after the discovery of fullerenes, endohedral metallofullerenes, fullerenes with encapsulated metal atoms, were obtained [2–4]. By doping the fullerenes with internal atoms the electronic properties of the molecules can be changed while keeping the carbon cage intact. Therefore, an intensive study of endohedral metallofullerenes has been carried out in order to understand their structure and properties as well as to approach practical applications in various fields. The major aspects of endohedral metallofullerene research have recently been

comprehensively reviewed by Shinohara and co-authors [5, 6]. However, alkali–metal doped endohedral fullerenes have not been extensively investigated so far. Methods that can give more information about the electronic structure are, for example, EPR and electrical conductance measurements. Here, we apply these techniques to the study of endohedral Li@C₆₀.

A perfect C₆₀ molecule has no unpaired electron spins and is diamagnetic. However, an EPR signal can be observed from a nominally neutral C₆₀ due to defects in the fullerene structure. Two single lines are very often observed [7,8]. The signal with a *g*-value close to 2.0023 was attributed to a hole-type excitation or the positive radical ion C₆₀⁺. The EPR line with a *g*-value close to 2.0000 is ascribed to the negative ion C₆₀[−]. In both cases the lines are narrow, the line-width (ΔH) is less than 2 G in room temperature measurements, which means that the hole and

* Corresponding author. Tel.: +46 31 7723435; fax: +46 31 7723496.

E-mail address: popok@fy.chalmers.se (V.N. Popok).

electron are delocalised on all carbon atoms of the molecule. It is also very well known that C_{60} in the pure solid form is a semiconductor with a resistivity of 10^6 – 10^8 Ωcm for the oxygen-free state [9–11]. The resistivity rises by a few orders of magnitude when the fullerene is exposed to air [11, 12].

Most EPR investigations of endohedral fullerenes deal with those molecules encapsulating elements of the 3d group of the periodic table, namely Sc, Y, La and other lanthanides, see for example the review article [5], or those with nitrogen isotopes [13]. The spectra show a number of lines, which are the result of the hyperfine coupling of the unpaired electron with the nuclear spin. Due to the difference in nuclear spin the spectra corresponding to the diverse metals have a different number of lines with various parameters. However, EPR data for alkali-metal doped endofullerenes have not been reported yet. Electron transport properties of endohedral metallofullerenes are just starting to be studied. Recent investigations show that the resistivity of a thin La@C_{82} film deposited in vacuum is of the order of 10^2 Ωcm [14]. The same order of resistivity is found for La@C_{82} and Y@C_{82} heat-treated in vacuum [15].

In this paper we report results of electrical and EPR measurements of an endohedral metallofullerene belonging to the ‘family’ of alkali-metal doped fullerenes, Li@C_{60} .

2. Experimental

Li@C_{60} was synthesised using low-energy (30 eV) Li^+ ion implantation into a fullerene film. The method has been described elsewhere [16]. This method typically gives about 10% yield of the endohedral fullerenes. Fractions corresponding to Li@C_{60} were chromatographically isolated as described earlier [17] and used for sample preparation.

Samples for the electrical conductance measurements were prepared as thin films evaporated in a vacuum of $(4\text{--}7) \times 10^{-8}$ Torr on silicon chips with four cross-configured

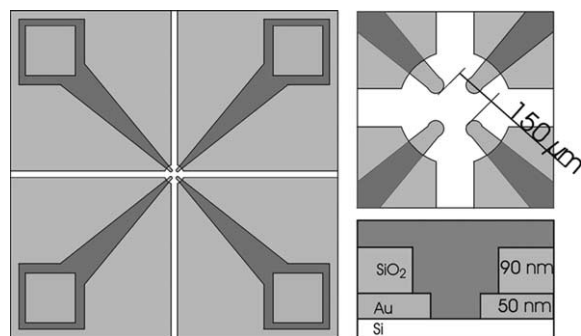


Fig. 1. Configuration of the chip for electrical measurements. Dimensions are 7×7 mm². Chip is covered by SiO_2 layer excepting the windows in the centre (circle) and in the corners (squares). Enlarged central part is in the right top corner; cross-sectional view of this part is in the right bottom corner.

gold electrodes separated by a $150 \mu\text{m}$ -wide gap in the centre of the chip (Fig. 1). A small aperture (diameter of 1 mm) in a mica mask was used to ensure that the film was deposited homogeneously as a circular spot covering the gap and the ends of the electrodes. The standard 4-probe Van-der-Pauw method was applied for I – V measurements in situ and in an air environment at room temperature using a Hewlett Packard 4156B precision analyser. The thickness of the deposited Li@C_{60} films was estimated by a profilometer and found to be 50–80 nm.

Samples for the EPR measurements were prepared as bulk in quartz ampoules and as thin films deposited on teflon substrates by evaporation of the bulk endofullerene at 775 K in a vacuum of $(1\text{--}5) \times 10^{-7}$ Torr. The samples were studied ex situ at room temperature and 77 K using an X-band (9.3 GHz) EPR spectrometer Varian E112. Basic standards of Mn^{2+} in MgO and DPPH were employed for an identification of the EPR spectral parameters.

For comparison, both I – V and EPR measurements were also performed on C_{60} samples prepared in a similar way to Li@C_{60} .

3. Results and discussion

Measured I – V dependences for the C_{60} are presented in Fig. 2. The in situ measurements on C_{60} deposited in vacuum give a resistivity of ca. 50 $\text{M}\Omega\text{cm}$ which is in good agreement with literature values [9–11]. After 5 min exposure to air at ambient pressure and temperature the resistivity increases by a factor of 10. This is in agreement with studies showing the dependence of the conductance on the extent of oxygen diffusion into the fullerene films [11, 12]. Each I – V dependence in Fig. 2 consists of two curves corresponding to the measurements at increasing and decreasing voltage. The hysteresis-like behaviour is caused by charging effects that become pronounced in the case of

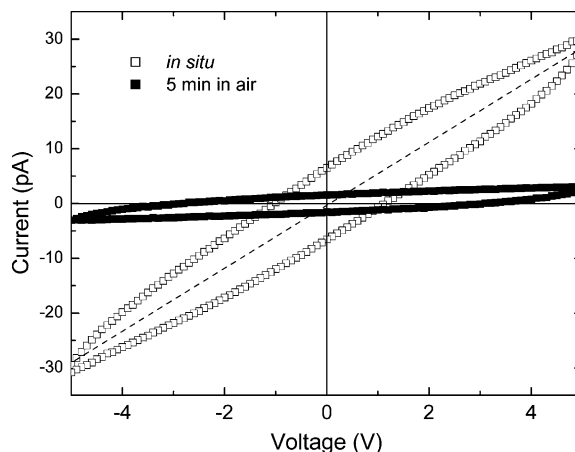


Fig. 2. I – V dependences for C_{60} measured in situ after deposition in vacuum and after 5 min exposure to air.

very low measured currents (pA level) but are eliminated for higher currents (tens of nA). The I - V dependences can be averaged to form a straight line (dashed in Fig. 2) exhibiting ohmic behaviour.

The measurements made in situ after the Li@C₆₀ deposition yield a resistivity of 1.5 kΩcm. This is over four orders of magnitude lower than for the C₆₀. The I - V curves corresponding to this case are presented in Fig. 3. Although the purified Li@C₆₀ consists of the dimer and/or trimer compounds [17], the relatively weak inter-cage bonds are broken on evaporation [18] and the deposited material probably consists predominantly of monomers. It can be expected that the encapsulated Li atom transfers an electron to the fullerene cage leading to an increase of the conductance compared to empty C₆₀, as observed. Further detailed study is needed to estimate the charge transport mechanism and type of conductance.

On exposure to air, conductance of the Li@C₆₀ film is affected much more than the C₆₀ film. After 2 min exposure the resistivity of the endohedral fullerene increases to 4 MΩcm and after 1 h the resistivity is comparable to that of C₆₀. The significant decrease in conductance can be attributed to the much higher reactivity of the Li-containing fullerene cages and the much stronger effect of charge transfer reactions with oxygen. It is also possible that the monomer molecules begin to oligomerise thus also affecting the conductance. The oxidation effecting the conductance was also earlier observed for the La@C₈₂ endofullerene [14,19]. In that case, the resistivity of film immediately after deposition in vacuum was lower (300 Ωcm) and it took a longer time, a few days, until the resistivity rose up to a value comparable to that of C₆₀.

In the case of C₆₀, a single EPR line with a g -value of 2.0025 ± 0.0005 is observed. The ΔH is found to be 1.2–1.5 G for measurements both at 77 and 300 K. This line corresponds to the C₆₀⁺ cation according to the data reported elsewhere [7]. The concentration of paramagnetic centres

(N_{PC}) was on the order of 10^{17} spin/g that corresponds approximately to 1 paramagnetic defect for 5 thousand fullerene molecules. The dependence of the EPR signal intensity (peak to peak amplitude of the first-derivative line) on the microwave power is presented in Fig. 4. The signal increases monotonically with the power. This case corresponds to the situation when a spin–lattice relaxation time (T_1) and spin–spin relaxation time (T_2) have the same order of magnitude which is calculated to be $\sim 10^{-8}$ s.

The Li@C₆₀ samples prepared both as bulk in ampoules and as films deposited in vacuum show EPR spectra similar to those obtained for the C₆₀. All spectra contain a singlet with $g = 2.0025 \pm 0.0005$. There are no additional EPR signals found for the Li@C₆₀ neither at room temperature nor 77 K. However, compared to the C₆₀ the EPR line of the Li@C₆₀ samples is broader, $\Delta H = 2.5$ – 3.1 G, and N_{PC} is lower by one order of magnitude, 10^{16} spin/g. Note that in all measurements the endohedral fullerenes material was exposed to atmosphere before the EPR studies were carried out.

For the bulk Li@C₆₀ samples heated at 775 K, an additional signal with a g -value lower than 2.0025 is observed (Fig. 5). From modelling of the line structure $g \approx 2.0004 \pm 0.0005$ is obtained for the new signal. This can be evidence of appearance of the C₆₀⁻ PCs that typically have the g -value close to that measured [8]. One can suggest that the new PCs are originated by heating-induced electron transfer between the neutral molecules yielding the C₆₀⁻ centres. This assumption is supported by the increase in N_{PC} corresponding to the C₆₀⁺ ($g = 2.0025$) from 10^{16} to 10^{17} spin/g.

Despite no difference found in the g -values of the Li@C₆₀ lines compared to those typical for C₆₀, there is a difference in the saturation effect. One can see in Fig. 4, that the EPR signal of the endohedral fullerene reaches a maximum at 1 mW. Using the obtained dependencies of the

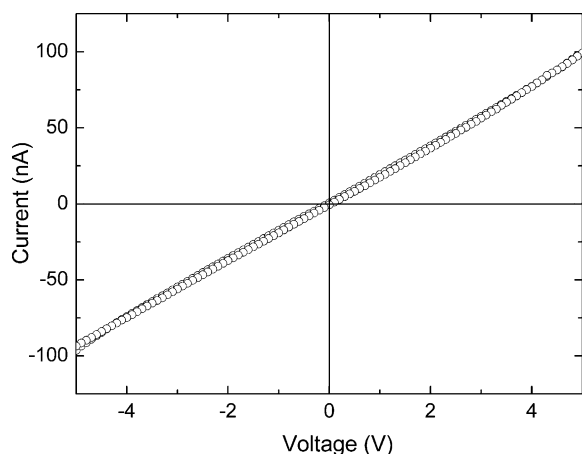


Fig. 3. I - V dependences for Li@C₆₀ measured in situ after deposition in vacuum.

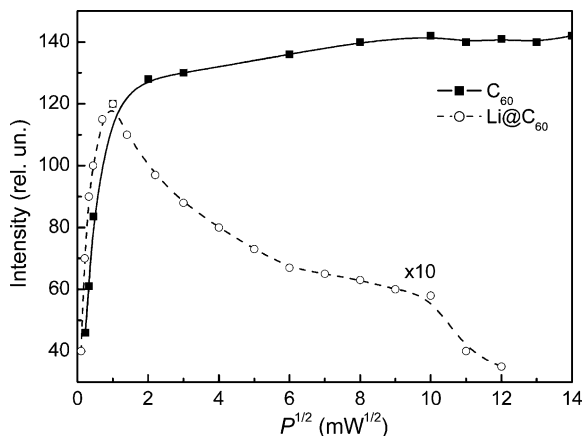


Fig. 4. Dependence of the EPR signal intensity on square root of microwave power for C₆₀ and Li@C₆₀ measured at room temperature.

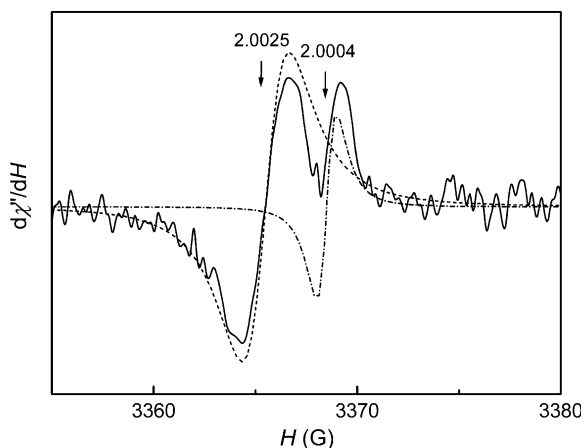


Fig. 5. The experimental EPR spectrum of a Li@C₆₀ sample after heating at 775 K (solid line) and simulated ones for $g=2.0025$ and 2.0004 (dash and dash-dot lines, correspondingly).

EPR parameters on microwave power and the method suggested elsewhere [20] T_1 and T_2 can be calculated. The calculation shows a small decrease in the electron exchange interaction time for the Li@C₆₀ compared to the C₆₀, $T_2 = 2.0 \times 10^{-8}$ and 6×10^{-8} s, correspondingly. The spin–lattice relaxation time $T_1 = 3.2 \times 10^{-4}$ s is found to be ca. four orders of magnitude longer than T_2 for the Li@C₆₀ and C₆₀ as well as than T_1 for C₆₀.

Before discussing the observed paramagnetic properties of the Li@C₆₀ one should note that theoretically the coupling of the Li nuclear spin (which is equal to 3/2) with the electron spin should lead to a quartet of closely spaced lines in an EPR spectrum for the free Li atom. Such spectra were observed earlier for lithium atoms in an argon matrix [21]. However, there are no additional lines observed in the Li@C₆₀ spectra compared to those typical for C₆₀. A Li atom embedded in the fullerene cage does not create any new PC. Recently, it was shown that the chromatographically isolated Li@C₆₀ used for the measurements is present as dimer or trimer compounds [17]. Hence, one can suggest that the Li valence electron forms a bond by coupling with an electron of a neighbouring molecule that eliminates the possibility of an additional PC. The obtained rise of T_1 for the Li@C₆₀ can be interpreted by the lowering of the symmetry of the fullerene cage upon incorporation of the Li ion causing an electrostatic interaction with the charged C₆₀ sphere [22] or by the formation of a double-bond with a neighbouring molecule.

4. Conclusion

Electrical conductance and electron paramagnetism of Li@C₆₀ samples prepared either as bulk material in quartz ampoules or as thin films deposited in high vacuum have been studied. In situ electrical measurements of the Li@C₆₀

deposited in vacuum give a resistivity of ca. 1.5 kΩcm that is a few orders of magnitude lower than for C₆₀. An immediate dramatic increase of the resistivity is found on exposure of the samples to air at ambient pressure and temperature that indicates the much stronger reactivity of the endohedral fullerene with oxygen compared to ordinary fullerenes. It is also possible that the monomer molecules formed on evaporation begin to oligomerise. Further work is needed to elucidate the mechanisms involved in charge transport.

It is found that there are no new signals in the EPR spectra of the Li@C₆₀ compared to C₆₀. It is suggested that the valence electrons of the Li atoms contribute to formation of double-bonds between the fullerene molecules yielding small oligomers that explains the absence of additional paramagnetic centres for Li@C₆₀. However, the encapsulated Li atoms lower the symmetry of the C₆₀ cages leading to an increase of the spin–lattice relaxation time.

Acknowledgements

The authors are grateful to The Swedish Research Council (VR) for financial support.

References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature* 318 (1985) 162.
- [2] J.R. Heath, S.C. O'Brien, Q. Zhang, Y. Liu, R.F. Curl, F.K. Tittel, R.E. Smalley, *J. Am. Chem. Soc.* 107 (1985) 7779.
- [3] Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford, R.E. Smalley, *J. Phys. Chem.* 95 (1991) 7564.
- [4] R.D. Johnson, M.S. de Vries, J.R. Salem, D.S. Bethunde, C.S. Yannoni, *Nature* 355 (1992) 239.
- [5] H. Shinohara, *Rep. Prog. Phys.* 63 (2000) 843.
- [6] Ch.R. Wang, Ch.L. Bai, H. Shinohara, *Mater. Res. Soc. Symp. Proc.* 775 (2003) P10.3.1.
- [7] S.G. Kukolich, D.R. Huffman, *Chem. Phys. Lett.* 182 (1991) 263.
- [8] J. Stankowski, P. Byszewski, W. Kempinski, Z. Trybula, T. Zuk, *Phys. Status Solidi B* 178 (1993) 221.
- [9] T. Arai, Y. Murakami, H. Suematsu, K. Kikuchi, Y. Achiba, I. Ikemoto, *Solid State Commun.* 84 (1992) 827.
- [10] C. Wen, J. Li, K. Kitazawa, T. Aida, I. Honma, H. Komiyama, Y. Yamada, *Appl. Phys. Lett.* 61 (1992) 2162.
- [11] A. Hamed, Y.Y. Sun, Y.K. Tao, R.L. Meng, P.H. Hor, *Phys. Rev. B* 47 (1993) 10873.
- [12] B. Pevzner, A.F. Hebard, M.S. Dresselhaus, *Phys. Rev. B* 55 (1997) 16439.
- [13] A. Weidinger, M. Waiblinger, B. Pietzak, T. Almeida Murphy, *Appl. Phys. A* 66 (1998) 287.
- [14] V. Popok, A. Lassesson, M. Jönsson, A. Gromov, A. Taninaka, H. Shinohara, E.E.B. Campbell, D.M. Guldi, P.V. Kamat,

- F. D'Souza (Eds). Fullerenes and Nanotubes: The Building Blocks of Next Generation Nanodevices, Electrochem. Soc., 2003 Proc. V 2003–15, pp. 560–563.
- [15] I.E. Kareev, V.P. Bubnov, E.E. Laukhina, V.K. Koltover, E.B. Yagubskii, *Carbon* 41 (2003) 1375.
- [16] R. Tellgman, N. Krawez, S.-H. Lin, I.V. Hertel, E.E.B. Campbell, *Nature* 382 (1996) 407.
- [17] A. Gromov, D. Ostrovskii, A. Lassesson, M. Jönsson, E. Campbell, *J. Phys. Chem. B* 107 (2003) 11290.
- [18] K. Komatsu, G.-W. Wang, Y. Murata, T. Tanaka, K. Fujiwara, *J. Org. Chem.* 63 (1998) 9358.
- [19] A. Lassesson, A. Gromov, M. Jönsson, A. Taninaka, H. Shinohara, E.E.B. Campbell, *Int. J. Mass Spectrom.* 228 (2003) 913.
- [20] I.I. Azarko, PhD Thesis, Belarusian State University, 1997.
- [21] P.F. Meier, R.H. Hauge, J.L. Margrave, *J. Am. Chem. Soc.* 100 (1978) 2108.
- [22] S.A. Varganov, P.V. Avramov, S.G. Ovchinnikov, *Phys. Solid State* 42 (2000) 388.