

## $C_{60}FeC_{60}$ COMPLEXES IN Fe INTERCALATED FULLERITE STUDIED BY X-RAY ABSORPTION

E. SOBCZAK<sup>a</sup>, A. TRAVERSE<sup>b</sup>, R. NIETUBYĆ<sup>a</sup>, Y. SWILEM<sup>a</sup>, P. BYSZEWSKI<sup>a,c</sup>  
AND D. ŻYMIERSKA<sup>a</sup>

<sup>a</sup>Institute of Physics, Polish Academy of Sciences  
Al. Lotników 32/46, 02-668 Warsaw, Poland

<sup>b</sup>LURE, Centre Universitaire Paris-Sud, 91405 Orsay Cedex, France

<sup>c</sup>Institute of Vacuum Technology, Długa 44/50, 00-241 Warsaw, Poland

The aim of Fe *K* edge XANES and EXAFS studies is to reveal the local structure around Fe ions in  $C_{60}Fe_x$  intercalated fullerites. The measurements are performed in transmission mode at LN<sub>2</sub> temperature for  $C_{60}Fe_x$  powder samples and other materials: ferrocene  $Fe(C_5H_5)_2$ , Fe metal foil and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The main result is that the XAFS spectra of the  $C_{60}Fe_2$  intercalate is almost identical to that of ferrocene and very different from  $\alpha$ -Fe and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The results support opinion that in the  $C_{60}Fe_x$  intercalates the ferrocene-like bonds in complexes  $C_{60}FeC_{60}$  are formed. Additionally, the XAFS spectra showed that neither remarkable amount of Fe metallic clusters nor oxidized iron particles are present in the  $C_{60}Fe_x$  sample.

PACS numbers: 71.20.Tx, 61.48.+c, 61.10.Ht

Fullerenes were discovered in 1985 [1] and produced in macroscopic scale in 1990 [2], and have already had an enormous impact on research in physics and chemistry. Fullerenes have been intensively investigated, e.g., studies of their crystal structure [3, 4], its stability [5] and their electronic structure [6] have been performed. For example, it has been established that doping with alkali metals can increase the electrical conductivity of solid fullerenes from a very poor conductor with a band gap 1.9 eV to superconducting systems.

All stable fullerenes show three common features: isolated pentagones, large  $\pi$ -bonding delocalization energies and low steric strain. A molecule  $C_{60}$  consists of twelve pentagonal and twenty hexagonal rings covering the surface of a sphere. All sixty atoms in  $C_{60}$  complex are equivalent.

The molecule of fullerene, e.g.,  $C_{60}$ , may play a role of an "artificial atom". These artificial atoms can be used together with ordinary atoms to construct new materials. The  $C_{60}$  has the high symmetry of icosahedral point group which gives high degeneracy up to fivefold one to the electron states. The fivefold degeneracy is characteristic of the *d* states, therefore the transition metals  $M = Fe, Co, Ni$

are good candidates for new magnetic materials  $C_{60}M_x$  with magnetic ions at the interstitial sites. Up to now, some studies of the Fe intercalated  $C_{60}Fe_x$  have been made [7–11], but a question under consideration about the way of intercalation of Fe ions is still open.

The extended X-ray absorption fine structure (EXAFS) is well known and widely used method for determination of the nearest neighbor distances around the atom of which the absorption edge is studied. This method is suitable for both the crystalline and the amorphous materials. The X-ray absorption near edge structure (XANES) gives information on the coordination, local symmetry and metal–ligand covalency, which affect the edge structure and position, e.g., the position of the *K*-absorption discontinuity and the shift of the XANES in ferrous and ferric compounds are a function of the valence state [12].

We chose the XANES and EXAFS methods for studies of local atomic surroundings around Fe atoms in a new fullerite  $C_{60}Fe_x$  prepared by doping the fullerene by iron. The  $C_{60}Fe_x$  intercalate is prepared in the powder form by the decomposition of ferrocene  $Fe(C_5H_5)_2$  molecules in solid fullerite at temperatures ranging from 570 K to 640 K [10]. In order to remove residuals of nonreactive ferrocene, after the reaction the samples were annealed in vacuum at temperature 600 K, which is above the decomposition temperature of  $C_{60}[Fe(C_5H_5)_2]_2$ . The nature of the reaction is probably a substitution of ligands in ferrocene by fullerenes. The  $C_{60}Fe_x$  intercalate has the monoclinic structure with lattice parameters  $a = 24.3 \text{ \AA}$ ,  $b = 12.6 \text{ \AA}$ ,  $c = 17.1 \text{ \AA}$  and  $\beta = 97^\circ$ . In such a lattice  $C_{60}$  form distorted closed packed hexagonal planes. It is supposed that the ferrocene-like bonds in complexes  $C_{60}FeC_{60}$  are formed between Fe ions and carbon pentagons (see Fig. 1).

It is well known that in ferrocene  $Fe(C_5H_5)_2$ , the Fe(II) ions are placed in between the cyclopentadienyl rings [13] with bond distances Fe–C ranging from 2.010 Å to 2.070 Å (mean value 2.045 Å) and C–C bond distances ranging from 1.352 Å to 1.476 Å (mean value 1.403 Å). In ferrocene all electrons are paired in molecular orbitals, therefore ferrocene is diamagnetic. In the fullerene  $C_{60}$  molecule the C–C distances are equal to 1.445 Å in a pentagon and to 1.400 Å in a hexagon.

The experiment was performed at the station XAS1 of the synchrotron radiation laboratory LURE in Orsay. The Si channel-cut monochromator and (331) reflection was used. The absorption spectra for the  $C_{60}Fe_x$ ,  $Fe(C_5H_5)_2$ ,  $\alpha\text{-Fe}_2O_3$  powders and Fe metallic foil were recorded in transmission mode at liquid nitrogen temperature at the Fe *K* absorption edge in the photon energy range from 7080 to 7200 eV with 0.2 eV steps in the case of XANES, and from 7030 to 8100 eV with 2 eV steps in the case of EXAFS spectra.

The photon energy scale is calibrated in such a way that the *K* absorption edge for Fe metal is placed at the photon energy 7112.5 eV. The spectra were normalized at the photon energy 7175 eV. The XANES spectra of the  $C_{60}Fe_x$  intercalate, iron metal and  $\alpha\text{-Fe}_2O_3$  are very different, while the spectra of  $C_{60}Fe_x$  intercalate and ferrocene are almost identical (see Fig. 2). The absorption edges for the  $C_{60}Fe_x$  intercalate and  $\alpha\text{-Fe}_2O_3$  are shifted to higher energy in comparison to that for Fe metal by 6 eV and 9 eV, respectively. In the case of  $\alpha\text{-Fe}_2O_3$ , that is the classical chemical shift due to the trivalent state of iron. The observed chemical

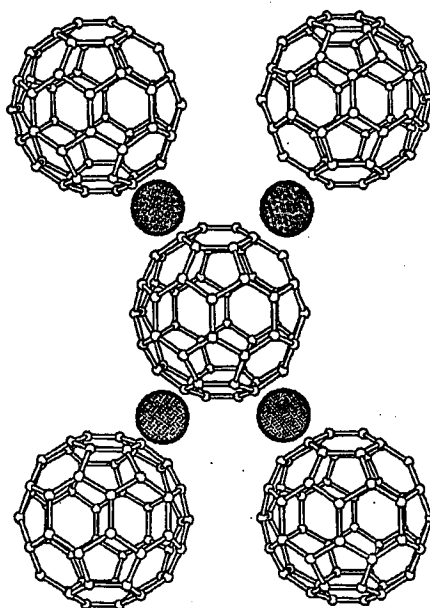


Fig. 1. The bridge bonding structure of C<sub>60</sub>Fe<sub>2</sub> in the (100) plane. Grey circles represent Fe ions.

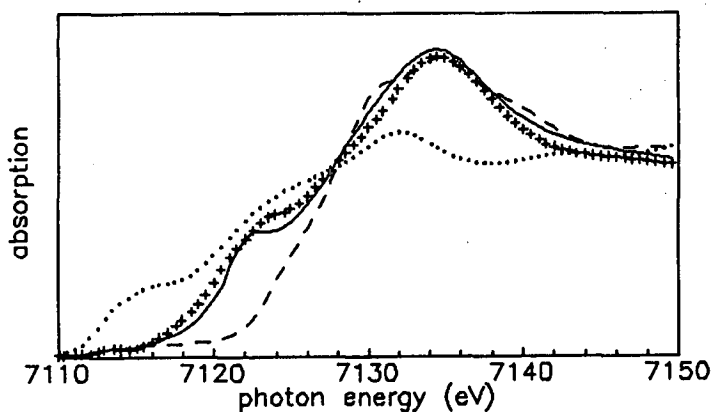


Fig. 2. The Fe *K*-edge XANES spectra of the C<sub>60</sub>Fe<sub>*x*</sub> intercalate (solid line), ferrocene (crosses),  $\alpha$ -Fe (points) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (dashes).

shift for Fe *K* absorption edge of the C<sub>60</sub>Fe<sub>*x*</sub> sample and ferrocene reveals the presence of Fe<sup>2+</sup> in that compound.

The Fe *K* edge XANES spectra of the C<sub>60</sub>Fe<sub>*x*</sub> intercalate and ferrocene Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> are almost identical, therefore we can conclude that the valency of Fe ion and nearest surroundings around Fe ion are similar in both samples. Our results are in a good agreement with the Mössbauer studies [11], which indicated

that the iron ion in the  $C_{60}Fe_x$  is in the state  $Fe^{2+}$  with quadrupole splitting similar to that of ferrocene. The absorption edge for the  $C_{60}Fe_x$  sample is more sharp than that for ferrocene, it means that electron unoccupied bands are narrower in the  $C_{60}Fe_x$  sample than in ferrocene. We believe that it is due to high symmetry of carbon pentagons in fullerene  $C_{60}$  molecule in comparison to the distorted cyclopentadienyl rings in ferrocene.

The Fe  $K$  edge EXAFS spectra of the  $C_{60}Fe_x$  intercalate and ferrocene  $Fe(C_5H_5)_2$  show sine-like oscillation with amplitude strongly damped with increase in momentum  $k$ , which is characteristic of carbon scatters. The Fourier transform (FT) was calculated for three weighting factors  $k^1$ ,  $k^2$  and  $k^3$  and no differences was found in moduli of Fourier transforms. This was an evidence that Fe-Fe neighbors do not exist in the  $C_{60}Fe_x$  intercalate and ferrocene  $Fe(C_5H_5)_2$ . The Fourier transforms for the  $C_{60}Fe_x$  sample and ferrocene are shown in Fig. 3. The main peak represents the nearest carbon neighbors around the Fe ion. Next carbon shells are visible in the FT of  $C_{60}Fe_x$  sample in contrast to that for ferrocene.

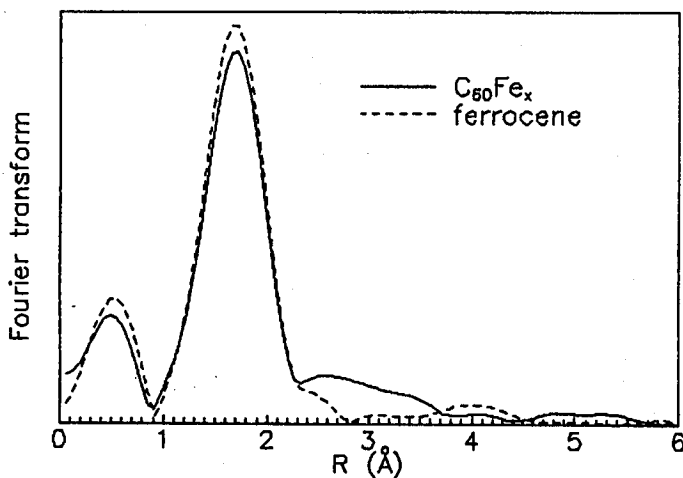


Fig. 3. Fourier transforms of EXAFS for  $C_{60}Fe_x$  intercalate (solid line) and ferrocene (dashes).

In summary, the Fe  $K$ -edge XANES spectra being sensitive to the chemical state of Fe ions have confirmed that in the  $C_{60}Fe_x$  intercalate only ions  $Fe^{2+}$  exist. From the EXAFS analysis we derived that the distances Fe-C for the first atomic shells are identical in the  $C_{60}Fe_x$  intercalate and in ferrocene. Additionally, the XANES and EXAFS spectra showed that neither remarkable amount of Fe metallic clusters nor oxidized iron particles are present in the  $C_{60}Fe_x$  sample. We also observed that the  $C_{60}Fe_x$  intercalate sample remained stable after one year which passed after first series of XAFS experiments.

### Acknowledgments

The authors are very grateful to Dr. D. Bonnin for the computer program for EXAFS analysis. This study was partly supported by the Committee for Scientific Research, Poland (grant No. 7T08A00308).

### References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature* **318**, 162 (1985).
- [2] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, *Nature* **347**, 354 (1990).
- [3] W.I.F. David, R.M. Ibberson, J.C. Matthewman, K. Prassides, T.J.S. Dennis, J.P. Hare, H.W. Kroto, R. Taylor, D.R.M. Walton, *Nature* **353**, 147 (1991).
- [4] P.A. Heiney, J.E. Fischer, A.R. McGhie, W.J. Romanow, A.M. Denenstein, J.P. McCauley, Jr, A.B. Smith III, D.E. Cox, *Phys. Rev. Lett.* **66**, 2911 (1991).
- [5] P.W. Fowler, D.E. Manolopoulos, *Nature* **355**, 428 (1992).
- [6] S. Saito, A. Oshiyama, Y. Miyamoto, N. Hamada, S. Sawada, *Nanotechnology* **3**, 167 (1992).
- [7] Y. Saito, T. Yoshikawa, M. Okuda, N. Fujimoto, K. Sumiyama, K. Suzuki, A. Kasuya, Y. Nishina, *J. Phys. Chem. Solids* **54**, 1849 (1994).
- [8] M.W. Ruckmann, B. Xia, D. Shih, *Phys. Rev. B* **50**, 17682 (1994).
- [9] M. Biermann, B. Kessler, S. Krummacher, W. Eberhardt, *Solid State Commun.* **95**, 1 (1995).
- [10] P. Byszewski, R. Diduszko, E. Kowalska, in: *Proc. 185 Meeting of the Electrochemical Society on Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Eds. K.M. Kadish, R.S. Ruoff, Proc. Vol. 94-24, The Electrochemical Society, Pennington 1994, p. 1392.
- [11] P. Byszewski, Z. Kucharski, J. Suwalski, in: *Int. Winterschool on Electronic Properties of Novel Materials "Progress in Fullerene Research"*, Eds. H. Kuzmany, J. Fink, M. Mehring, S. Roth, World Scientific, Singapore 1994, p. 82.
- [12] D. Le Calonnec, J. Dürr, B. Hannoyer, M. Lenglet, G. Calas, J. Petiau, in: *EXAFS and Near Edge Structure*, Eds. A. Bianconi, L. Incoccia, S. Stipcich, Springer-Verlag, Berlin 1983, p. 210.
- [13] J.D. Dunitz, L.E. Orgel, A. Rich, *Acta Crystallogr.* **9**, 373 (1955).