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Fe CLUSTERS IN Fe INTERCALATED FULLERITE

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The local structure around Fe ions in the $C_{60}Fe_2$ fullerites before and after heat treatment in temperature of 850 K was investigated by means of Fe *K* edge X-ray absorption near edge structure and extended X-ray absorption near edge structure methods. The X-ray absorption measurements were performed at liquid nitrogen temperature using synchrotron radiation in transmission mode. The X-ray absorption near edge structure and extended X-ray absorption near edge structure studies showed that the heat treatment of the $C_{60}Fe_2$ fullerite at temperature 850 K causing an irreversible transition from monoclinic to fcc structure is accompanied with changes in the state of Fe ions, part of them forms clusters in bcc structure, while others turn to Fe^{3+} ions bonded to fullerenes.

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The development of fullerene chemistry and technology, and resulting possibility of chemical modifications create new research and applications perspectives. Some investigations of the structure, metal-fullerene bonding and interaction between Fe and C_{60} [1-6] have been reported.

An original method of preparation of $C_{60}Fe_2$ fullerite by decomposition of ferrocene in solid fullerite has been elaborated by Byszewski et al. [3]. Recently, we have reported some results of X-ray absorption studies of monoclinic $C_{60}Fe_2$ fullerite, which have shown that the local structure around Fe ion in the monoclinic $C_{60}Fe_2$ fullerite is almost identical to that of ferrocene and that neither a remarkable amount of Fe metallic clusters nor oxidized iron particles were present in the monoclinic $C_{60}Fe_2$ sample [8].

The aim of our studies is to reveal the changes in local structure of Fe ions sites in $C_{60}Fe_2$ fullerite due to heat treatment at temperature 850 K, accompanied with the irreversible transition of monoclinic structure to fcc structure [6]. We carried out the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements for the $C_{60}Fe_2$ fullerites and few other Fe compounds by using synchrotron radiation.

The monoclinic $C_{60}Fe_2$ fullerite was 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 [3,6]. The fcc $C_{60}Fe_2$ fullerite was obtained from monoclinic $C_{60}Fe_2$ fullerite by heat treatment in the range 720–850 K [3,4,6]. This irreversible exothermic transition was examined by the differential scanning calorimetry (DSC) method. The Mössbauer spectroscopy proved that during high temperature treatment part of iron atoms adopt Fe^{3+} ionization state in the fcc $C_{60}Fe_2$ fullerite [7], therefore two possible sites in the reconstructed fcc lattice were suggested: either Fe ion bound to C_{60} or Fe ion inside the C_{60} cage [6].

The experiment was performed at the station XAS1 of the synchrotron radiation laboratory LURE in Orsay. The absorption spectra for the monoclinic and fcc $C_{60}Fe_2$ fullerites, Fe_2O_3 and Fe metal were recorded in transmission mode at liquid nitrogen temperature at the Fe K absorption edge. After one year, the EXAFS measurements were repeated for the same samples and no significant changes were observed, which was an evidence of stability of investigated fullerite compounds.

The absorption spectra were normalized to the absorption at the photon energy 7175 eV, which is far from the absorption edge. The XANES spectra of the monoclinic and fcc $C_{60}Fe_2$ fullerites, Fe metal and Fe_2O_3 are shown in Fig. 1. The beginning of the absorption edges for the monoclinic $C_{60}Fe_2$ fullerite and

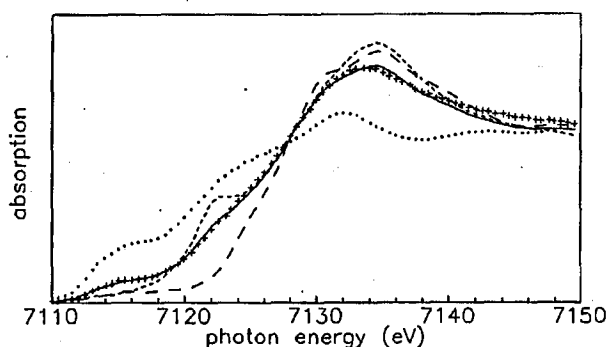


Fig. 1. Fe K edge absorption spectra (XANES) of Fe metal (dots), monoclinic $C_{60}Fe_2$ fullerite (small dashes), fcc $C_{60}Fe_2$ fullerite (crosses), Fe_2O_3 (long dashes) and fitted curve (solid line), as described in the text.

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 Fe_2O_3 , it is the classical chemical shift due to the trivalent state of iron. The observed chemical shift value for Fe K absorption edge of the monoclinic $C_{60}Fe_2$ sample reveals the presence of bivalent iron in that compound. The shape of the XANES spectrum for the fcc $C_{60}Fe_2$ fullerite is distinguished from that for the monoclinic $C_{60}Fe_2$ fullerite. Namely, the pre-edge structure appears at the energy about 7114 eV, which is characteristic of metallic Fe. Additionally, the maximum at 7134 eV are considerably smeared due to the contribution of metallic Fe. Moreover, the shoulder at 7122 eV is almost completely smeared.

We tried to analyse the shape of the absorption edge for investigated fcc $C_{60}Fe_2$ fullerite in the range up to 7140 eV as a weight sum of the normalized Fe absorption edges for model materials containing Fe neutral atoms (Fe foil), Fe^{2+}

ions (monoclinic $C_{60}Fe_2$ fullerite) and Fe^{3+} ions (Fe_2O_3). The best fit (a solid line in Fig. 1) was achieved for the following partial contributions of all three valencies: 24% Fe neutral atoms, 40% Fe^{2+} ions and 36% Fe^{3+} ions.

The Fe K EXAFS spectra of the monoclinic and fcc $C_{60}Fe_2$ fullerites, Fe metal and Fe_2O_3 were analysed in a standard way. The Fourier transform (FT) moduli for $C_{60}Fe_2$ fullerites and Fe metal are shown in Fig. 2, where the FT curve for Fe metal was reduced by a factor of 0.24 in comparison to other curves. The highest peaks in the range of 1–3 Å represent the nearest neighbours of the Fe ion in the samples studied. The FT double peak in the range of 1–3 Å for fcc $C_{60}Fe_2$ fullerite in Fig. 2 is the evidence of the presence of different nearest neighbours shells Fe–C and Fe–Fe. In addition, three peaks in the range of 3.3–5.8 Å for fcc $C_{60}Fe_2$ fullerite are almost identical to Fe metallic ones. The FT results show without doubt that in the fcc $C_{60}Fe_2$ fullerite small clusters of bcc Fe are present. It can be estimated from Fig. 2 that the size of Fe clusters reaches 8 Å.

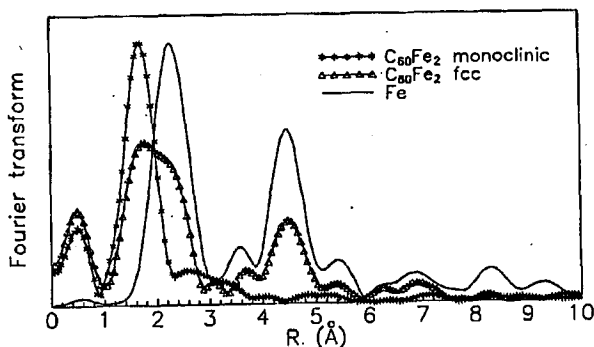


Fig. 2. Fourier transform moduli (in arbitrary units) of Fe K EXAFS for the monoclinic $C_{60}Fe_2$ fullerite (stars), fcc $C_{60}Fe_2$ fullerite (triangles) and Fe metal (solid line).

The Fourier backtransforms were calculated in ranges of 0.98–2.21 Å for monoclinic $C_{60}Fe_2$ fullerite and of 0.98–3.01 Å for both Fe metal and fcc $C_{60}Fe_2$ fullerite. The computer fittings of the theoretical EXAFS models to Fourier backtransforms were performed for monoclinic $C_{60}Fe_2$ fullerite and Fe metal, as known materials. In the case of the fcc $C_{60}Fe_2$ fullerite the best fit was achieved for a three shells model. The 1st shell of 7.74 carbon atoms was found at an average distance of $R = 2.04$ Å with the Debye–Waller factor σ equal to 0.089, which is high in comparison to the value $\sigma = 0.05$ for the monoclinic $C_{60}Fe_2$ fullerite. It should be pointed out that a high value of the Debye–Waller factor has to be related to a big static disorder in the 1st shell. It was found from the fit that the 2nd shell at $R = 2.51$ Å and the 3rd shell at $R = 2.90$ Å contain 1.09 and 0.41 iron atoms, respectively. From the above data we can estimate that at least 10% of total iron in the fcc $C_{60}Fe_2$ fullerite enters Fe clusters.

In summary, the Fe K edge XANES spectra being sensitive to the local chemical state around Fe ions have shown that Fe neutral atoms, Fe^{2+} and Fe^{3+} ions appear in the $C_{60}Fe_2$ fullerite after heat treatment. Additionally, the EXAFS study has proved the presence of small Fe clusters in this form of fullerite. From

the EXAFS spectra one cannot extract the bonding nature of the Fe^{3+} ions in the fcc C_{60}Fe_2 fullerite, however it cannot be excluded that Fe^{3+} ions are located inside C_{60} cages.

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