
FULLERENES AND ATOMIC CLUSTERS

Synthesis and Investigation of Iron Fullerene Clusters

N. V. Bulina^a, É. A. Petrakovskaya^a, A. V. Marachevsky^a, I. S. Lityaeva^b,
I. V. Osipova^b, G. A. Glushchenko^a, W. Krätschmer^c, and G. N. Churilov^a

^a *Kirensky Institute of Physics, Siberian Division of the Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia*

e-mail: churilov@iph.krasn.ru

^b *Krasnoyarsk State Technical University, Krasnoyarsk, 660074 Russia*

^c *Max-Planck Institute for Nuclear Physics, Heidelberg, D-62029 Germany*

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Abstract—Iron fullerene clusters are prepared by plasma chemical synthesis and investigated using electron magnetic resonance. It is shown that these clusters can be prepared both by plasma chemical synthesis of fullerenes with iron and by mixing of a fullerene solution with a powder of iron nanoparticles coated with carbon shells. A liquid chromatographic technique is proposed for separating iron fullerene clusters.

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1. INTRODUCTION

Nanosized and nanostructured materials exhibit unique mechanical, physical, and chemical properties [1, 2]. The importance of these materials to high technologies cannot be overestimated. Investigations into the properties and structure of nanomaterials have made it possible to solve important problems in the electronics industry, power engineering, aircraft industry, mechanical engineering, chemistry, biology, and medicine [3]. However, solving practical problems directly depends on the level of fundamental knowledge attained. The experimental data available in the literature on nanomaterials are not sufficient either to construct an adequate theory or even to elaborate basic principles. Even the terminology used for describing nanomaterials cannot be considered to be well established. Some researchers have preferred the term “nanoparticles” [4], whereas others have accepted the term “clusters” [5]. In this paper, we will stick to the term “clusters,” because, in our opinion, it is more appropriate for small-sized particles (less than 10^2 nm) formed during synthesis rather than upon the grinding of massive objects.

One of the fundamental problems concerns the dependence of the properties of clusters on their size. As a rule, the main difficulties encountered in solving this problem arise in the processes of extracting and separating clusters of different sizes into groups of clusters of the same size and even greater difficulties are associated with the stabilization of these clusters [2, 6].

Repeated syntheses of fullerene derivatives with metals have revealed that, apart from fullerenes, metallic particles are also extracted. Examinations of the samples with an electron microscope have demon-

strated that these particles are coated with nonconducting carbon shells [7].

Fullerenes have relatively large molecular sizes (0.7–1.0 nm) and a common π -system involving a great number of electrons responsible for the high polarizability of the fullerene molecule. This should result in van der Waals interactions of the fullerenes with one another and with other clusters or molecules. In our experiments, we used this property of fullerenes for extracting and separating iron clusters.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

For a comparative analysis, we synthesized a series of iron-containing fullerene samples. The addition reaction was carried out using two methods: (i) plasma chemical synthesis (the *A* method) and (ii) a simple mixing of two components (the *B* method).

2.1. Preparation of the $(\text{C}_{60} + \text{Fe})^A$ Sample by the *A* Method

An iron powder was sputtered in a fullerene radio-frequency (44 kHz) alternating-current arc at atmospheric pressure [8]. The discharge was generated between an outer electrode fabricated in the form of a graphite sleeve and an inner electrode in the form of a graphite rod with an axial bore filled with a powder of carbonyl iron (special-purity grade) having a particle size of up to 70 μm . The evaporated carbon and iron were condensed on the walls of the arc chamber in the form of a fullerene-containing soot condensate. This condensate was collected and poured with benzene in

order to separate a fullerene mixture. The product was filtered through an FS-III paper filter. Then, the solvent was evaporated under standard conditions to the point of formation of a powder, i.e., the $(\text{Ful} + \text{Fe})^A$ sample.

2.2. Preparation of the $(\text{C}_{60} + \text{Fe})^A$, $(\text{C}_{70} + \text{Fe})^A$, and $(\text{HFul} + \text{Fe})^A$ Samples by the A Method

The $(\text{Ful} + \text{Fe})^A$ sample was separated into three fractions with the use of liquid column chromatography on an Al_2O_3 LSL₂₅₄5/40 chromatographic sorbent. Particles of this sorbent were coated with a carbon layer during plasma treatment [9]. The first fraction, i.e., the $(\text{C}_{60} + \text{Fe})^A$ sample, was eluted with the use of a 50% mixture of benzene and *n*-hexane, whereas the second [the $(\text{C}_{70} + \text{Fe})^A$ sample] and third [the $(\text{HFul} + \text{Fe})^A$ sample] fractions were eluted with benzene. The solvent was evaporated from the prepared solutions under standard conditions.

2.3. Preparation of the $(\text{Ful} + \text{Fe})^B$ Sample by the B Method

A carbon graphite rod with an axial bore filled with a carbonyl iron powder was sputtered under conditions where fullerenes could not be formed even in minor amounts. We used a radio-frequency (kilohertz) arc discharge between the central electrode (graphite rod) and an outer electrode (inductor) in a helium flow [10]. The powder of carbon and iron thus prepared was poured with a solution of pure (metal-free) fullerenes dissolved in benzene. The solution was thoroughly stirred, filtered, and evaporated.

2.4. Preparation of the $(\text{C}_{60} + \text{Fe})^B$ and $(\text{C}_{70} + \text{Fe})^B$ Samples by the B Method

These samples were prepared according to the same procedure as the $(\text{Ful} + \text{Fe})^B$ sample, but with the fullerenes C_{60} (99.98%) and C_{70} (99.5%), respectively, instead of a fullerene mixture.

The structure and composition of the samples were investigated using x-ray powder diffraction (DRON-4 diffractometer), electron magnetic resonance (SE/X-2544 and R 1308 spectrometers), fluorescence spectrum analysis (SPARK-1 spectrometer), UV-visible spectroscopy (Uvikon 943 spectrophotometer, 200–700 nm), and mass spectroscopy (Bruker BIFLEX time-of-flight mass spectrometer).

3. RESULTS AND DISCUSSION

3.1. The A Method

The x-ray powder diffraction analysis revealed that the soot collected from the walls of the arc chamber after sputtering the iron powder in the fullerene arc contains ~10% body-centered cubic iron in the form of crystallites of a size less than 1 μm . According to elec-

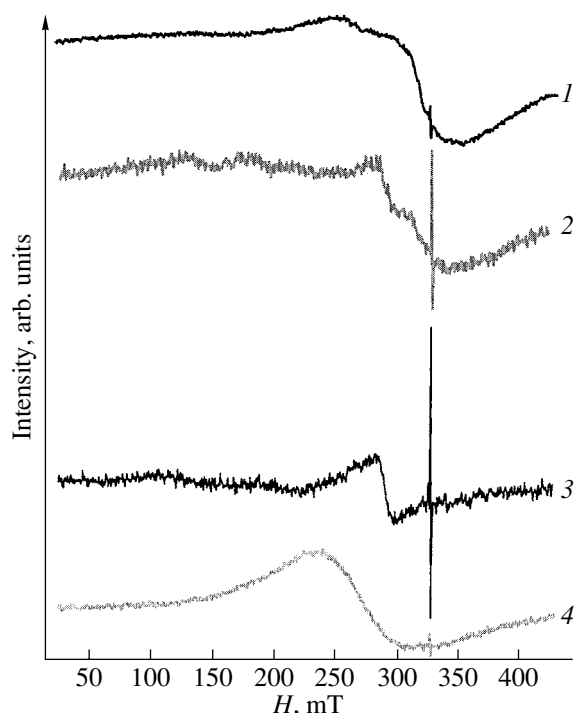


Fig. 1. Electron magnetic resonance spectra measured in the X band for iron-containing fullerenes prepared according to the A method: (1) $(\text{Ful} + \text{Fe})^A$, (2) $(\text{C}_{60} + \text{Fe})^A$, (3) $(\text{C}_{70} + \text{Fe})^A$, and (4) $(\text{HFul} + \text{Fe})^A$.

tron microscopy, metallic particles with an average size of 10 nm are embedded in carbon soot particles.

The fluorescence spectrum analysis showed that the $(\text{Ful} + \text{Fe})^A$ sample contains 0.12% iron. No fullerene derivatives were identified in the mass spectrum of the sample.

The electron magnetic resonance investigation revealed a narrow line attributed to fullerene radicals with $g = 2.001$ [11] and lines assigned to both iron oxide clusters and isolated iron clusters (see Fig. 1, table) in the initial fullerene mixture $(\text{Ful} + \text{Fe})^A$, as well as in the chromatographic separation products $(\text{C}_{60} + \text{Fe})^A$, $(\text{C}_{70} + \text{Fe})^A$, and $(\text{HFul} + \text{Fe})^A$. Analysis of the electron magnetic resonance spectra of the samples prepared using the chromatographic method clearly indicates that these samples contain isolated clusters of different types observed in the initial sample $(\text{Ful} + \text{Fe})^A$. Individual fullerene components involve different

Parameters of the electron magnetic resonance lines for the samples prepared according to the A method

Samples	Effective g factor	Linewidth ΔH , mT
$(\text{Ful} + \text{Fe})^A$	2.4; 2.24; ~2.1	83; 26; ~10
$(\text{C}_{60} + \text{Fe})^A$	2.24; ~2.10	26; ~10
$(\text{C}_{70} + \text{Fe})^A$	2.24	26
$(\text{HFul} + \text{Fe})^A$	2.40	83

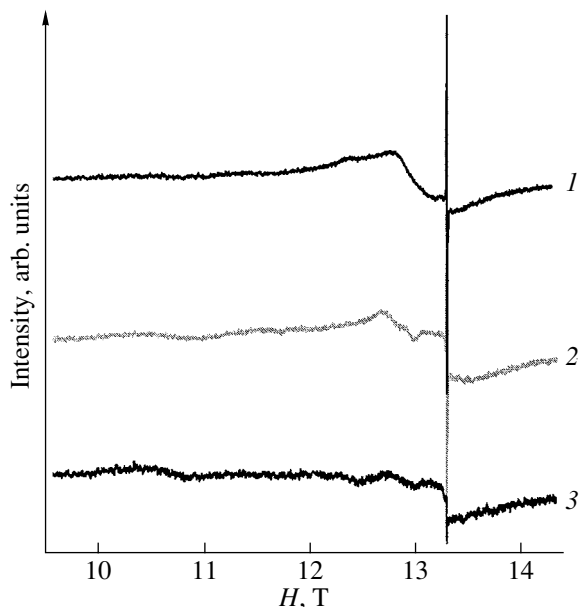


Fig. 2. Electron magnetic resonance spectra measured in the Q band for iron-containing fullerenes prepared according to the B method: (1) $(\text{Ful} + \text{Fe})^B$, (2) $(\text{C}_{60} + \text{Fe})^B$, and (3) $(\text{C}_{70} + \text{Fe})^B$.

nanoparticles whose sizes do not exceed 10 nm. In the $(\text{C}_{70} + \text{Fe})^A$ sample, we revealed only one type of clusters that was also observed in the $(\text{C}_{60} + \text{Fe})^A$ sample (see table). The electron magnetic resonance spectrum of the $(\text{HFul} + \text{Fe})^A$ sample exhibits a broad line attributed to clusters of considerably larger size (10–50 nm).

We assume that all the samples studied contain clusters of the $n\text{C}_x \cdot m\text{Fe}_y\text{O}_z$ type (where $n > 1$; $m > 1$; $x > 60$; $y = 1, 2, 3$; and $z = 0, 3, 4$). The fullerene molecules are most likely bound to the clusters of iron oxide and pure iron through van der Waals interactions, because the electronic spectra do not exhibit shifts or new absorption bands.

It can be seen from the electron magnetic resonance spectra that the intensity of the line attributed to the carbon radicals depends on the intensity of the lines assigned to the clusters: the higher the iron content, the lower the intensity of the line corresponding to the carbon radicals. This supports the assumption that the iron atoms are magnetically coupled through the fullerene molecule, which was also noted by Zybov et al. [12].

3.2. The B Method

The iron–carbon powder prepared by sputtering carbonyl iron in the carbon–helium plasma does not contain fractions soluble in benzene. However, after mixing of this powder with a solution of pure fullerenes dissolved in benzene, the benzene solution contains both fullerenes and iron: in this case, the fullerene extract contains 0.1% Fe [the $(\text{Ful} + \text{Fe})^B$ sample].

As in the case of the samples prepared by the A method, the electron magnetic resonance spectra of the $(\text{Ful} + \text{Fe})^B$, $(\text{C}_{60} + \text{Fe})^B$, and $(\text{C}_{70} + \text{Fe})^B$ samples exhibit lines indicating the presence of iron clusters and a narrow line corresponding to the fullerene radicals (Fig. 2).

The mixing of fullerenes with the initial iron carbonyl powder does not lead to similar results. The fullerene extract in this case does not contain iron. This suggests that the fullerene molecules are attached to the iron clusters owing to the carbon shells coating them.

4. CONCLUSIONS

The results of our investigations have demonstrated that, in a benzene solution, the fullerenes and iron nanoparticles coated with carbon shells form clusters of the $n\text{C}_x \cdot m\text{Fe}_y\text{O}_z$ type (where $n > 1$; $m > 1$; $x > 60$; $y = 1, 2, 3$; and $z = 0, 3, 4$). The size of the clusters lies in the range from 1 to 10^2 nm. These nanostructures are formed both in the case of a plasma chemical reaction involving addition of the fullerene to iron and upon a simple mixing of two components, namely, a fullerene solution and a powder of iron nanoparticles coated with carbon shells.

It is demonstrated for the first time that chromatographic separation of a fullerene mixture containing iron clusters makes it possible to isolate individual fullerenes containing a particular type of clusters.

In the future, a more detailed investigation of the synthesized compounds will be performed with the aim of determining their structure and stability.

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