
FULLERENES AND ATOMIC CLUSTERS

Synthesis and Study of Manganese-Containing Endohedral Fullerenes

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Abstract—Fullerenes containing manganese and iron atoms are synthesized in a high-frequency carbon–helium plasma at atmospheric pressure. The electron paramagnetic resonance (EPR) spectrum of the synthesized compound contains not only lines attributed to iron atoms but also the lines of a manganese ion pair with an additional hyperfine structure. The latter lines are assigned to the endohedral complex $Mn_2@C_n$ ($n > 70$). The possible existence of these structures is evaluated from quantum-chemical calculations of the optimum geometry of the endohedral fullerene $Mn_2@C_{84}$ with C_{2v} symmetry. It is found that the manganese atoms are spaced ~ 2.72 Å apart at the center of the molecule.

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1. INTRODUCTION

Fullerenes have a unique spherical structure consisting of a set of pentagons and hexagons with carbon atoms located at their vertices. If a particular atom is placed inside a fullerene, it can be isolated from the environment. Since the discovery of the technique for synthesizing fullerenes [1], intensive studies have been performed in this field [2–4]. It has turned out that these structures (referred to as endohedral fullerenes) are not simple to fabricate. The collective π system of a fullerene forms a shell that closes empty spaces in hexagons and pentagons almost completely, thus hindering direct incorporation of a guest atom into the fullerene cage. The incorporation of a guest atom into the fullerene cage can be accomplished during formation of a fullerene molecule, through bombardment with accelerated ions, or by opening a fullerene molecule with the use of chemical methods and then by closing this molecule back [4]. The first two methods are the most extensively employed in practice.

The electronic state of the endohedral molecules $La@C_{82}$, $Sc@C_{82}$, and $Y@C_{82}$ was determined from the electron paramagnetic resonance (EPR) spectra and considered in sufficient detail by Bartl et al. [5]. A characteristic feature of the EPR spectra of these molecules is their hyperfine structure associated with the electron–nucleus interaction and the explicitly measured splitting of the electron charges: $La^{3+}@C_{82}^{3-}$, $Sc^{3+}@C_{82}^{3-}$, and $Y^{3+}@C_{82}^{3-}$. It was found that, for these compounds, the hyperfine splitting constant has an anomalously low value ($a_Y = 0.48$ Oe, $a_{La} = 1.25$ Oe, $a_{Sc} = 6.25$ – 18.80 Oe), which corresponds, for example,

in the case of scandium, to approximately 0.6% of the electron density of an unpaired electron in the $4s$ shell [6]. This fact indicates a hyperfine interaction between the atomic nucleus and an electron localized at a distant orbital (the fullerene sphere surrounding the electron).

Basir and Anderson [7] investigated a reaction between manganese ions and fullerene C_{60} . The structure of the reaction products was determined from the destruction products and from the charge transfer. The authors of [7] believed that the manganese ions and fullerenes can form both exohedral and endohedral complexes.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Endohedral fullerenes were synthesized in a plasma-chemical reactor with high-frequency arc vaporization of graphite electrodes [8] containing 0.01% Mn. A finely dispersed carbonyl iron powder was placed in the axial hole of an electrode 2 mm in diameter. The concentration ratio between iron and carbon introduced into the plasma was 1 : 10. Pure fullerenes were removed by extracting benzene from the carbon condensate collected from the walls of the chamber. Then, substances soluble in pyridine were extracted. In both cases, the extraction was performed in a Soxhlet apparatus. In our experiments, we examined a pyridine extract from which the solvent was removed through distillation with a sand bath.

The EPR spectra were recorded on a Bruker E500 spectrometer in the temperature range from 7.5 to 222 K. X-ray powder diffraction analysis was performed on a DRON-4 powder diffractometer. The

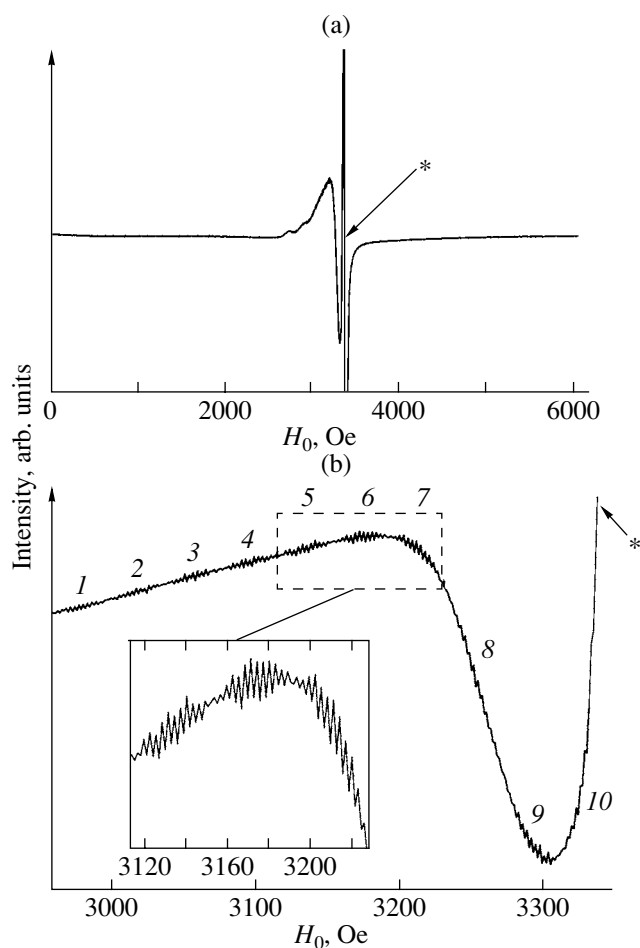


Fig. 1. EPR spectrum measured at a temperature of 7.5 K: (a) the overall spectrum and (b) the spectrum attributed to the Mn^{2+} pair. Asterisks mark the lines assigned to the fullerite radical.

quantum-chemical calculations were carried out using the pseudopotential method within the framework of the density functional theory with the VASP program package [9, 10].

3. RESULTS AND DISCUSSION

The EPR spectrum of the compound under investigation in the temperature range 40–293 K exhibits a signal from a fullerite radical and a number of lines corresponding to different states of iron (Fig. 1). A decrease in the temperature is accompanied by the appearance of an unusual EPR spectrum consisting of a set of structured lines. This spectrum is characterized by the best-resolved and most intense lines at temperatures in the range from 7.5 to 19.5 K (Fig. 1). The intensity of these lines is approximately one order of magnitude less than that of the principal signal.

As can be seen from Fig. 1b, the EPR spectrum contains groups of lines with an 11-component structure at 40- to 35-Oe intervals. The distance between the lines

of this structure is equal to 2.93 Oe. The intensities of the lines are distributed according to a binomial law. It can also be seen from this figure that, in the structure of the groups, the intensities have a nearly binomial distribution.

The most intense line in the EPR spectrum is observed in the magnetic field $H_0 = 3175$ Oe (Fig. 1b, line 6), which corresponds to the factor $g = 2.11$. In the direction of a decrease in the magnetic field to $H_0 = 2993$ Oe, we can distinguish five groups of “principal” lines (1–5) with a decreasing intensity and three lines (7–9) with a similar behavior in the direction of an increase in the magnetic field to $H_0 = 3328$ Oe. Component 11 of the structure is overlapped by the more intense line attributed to the fullerite radical. In magnetic fields weaker and stronger than those corresponding to the given group of lines, the EPR spectrum also contains similar lines; however, they are weaker and less resolved.

It is obvious that the observed EPR spectrum has a hyperfine structure with a splitting constant $A = 40$ Oe and an additional hyperfine structure with a splitting constant $a = 3$ Oe. Judging from the number of components and the hyperfine splitting constant, lines 1–9 can be assigned to an isolated pair of exchange-coupled Mn^{2+} ions [11]. The additional hyperfine structure lines of the manganese ion pair are associated with the nuclear spin of the two manganese atoms. However, in this case, the electron–nucleus interaction is approximately ten times weaker than that manifesting itself in the hyperfine structure of the manganese ion pair. One possible reason for the observed EPR spectrum could be the endohedral incorporation of the exchange-coupled Mn^{2+} ions. The analysis of the intensity of the EPR spectrum suggests that the content of endohedral manganese compounds is very low. Most probably, the atoms are located inside the C_{84} molecules or other higher fullerenes that are capable of containing two guest atoms. The additional hyperfine structure of the EPR spectrum can be attributed to an unpaired electron that is extended over the fullerene cage and interacts with the total nuclear spin of the manganese ion pair ($I_{\text{tot}} = 10$). In contrast to the results obtained by Bartl et al. [5] and Kato et al. [6], the presence of the EPR spectrum of a manganese ion pair with a characteristic hyperfine structure in our case indicates that the valence of the manganese ions is close to 2+. The additional hyperfine structure suggests an incomplete compensation of the spin magnetic moments of the four electrons transferred to the fullerene cage.

The position of the components of the hyperfine structure lines and their behavior with variations in the temperature (an increase in the intensity with decreasing temperature) indicate a transition in one of the low-lying energy levels (Fig. 2). Judging from the g factor, this transition can be associated with a transition inside the spin multiplet of the manganese ion pair with $S = 1$ [12], taking into account the absence of other line pack-

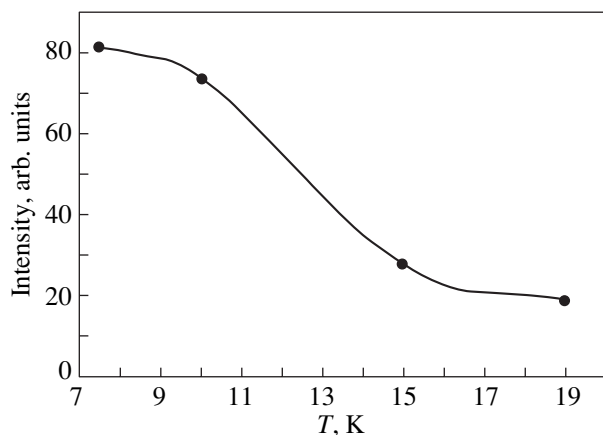


Fig. 2. The temperature dependence of the intensity of line group 6 (Fig. 1b).

ets in the spectrum and assuming antiferromagnetic exchange between the manganese ions. This assumption is justified because direct exchange between the manganese ions does not exclude the possibility of indirect exchange associated with the fullerene shell. The absence of an EPR spectrum of the manganese ion pair in weak magnetic fields characteristic of the state with $S = 1$ [12] can be explained by the small initial level splitting due to the high symmetry of the environment of the pair and the absence of dipole–dipole interaction when the pair is in the endohedral state.

According to the x-ray powder diffraction data, the compound under investigation does not have a crystal structure. This excludes the presence of regularly arranged lattice holes that can contain manganese ion pairs. The well-resolved EPR spectrum indicates that the obtained configuration is highly homogeneous, which, in turn, serves as an additional argument in support of their endohedral location. It should be noted that this is the first time the EPR spectra of endohedral complexes in solids were observed with such a high resolution.

In order to evaluate the possibility of forming endohedral manganese structures, we carried out quantum-chemical calculations of their optimum geometry. Fullerene C_{84} was chosen as a reference molecule, because its content is usually predominant among the higher fullerenes [13]. In this case, we calculated the optimum molecular geometry of an isomer with C_{2v} symmetry. The calculations demonstrated that the endohedral compound $Mn_2@C_{84}$ has a stable structure with the manganese ion pair located at the center of the molecule (Fig. 3). The distance between the metal atoms is approximately equal to 2.72 Å. This compound has a structure similar to the structure of the endohedral compound $Sc_2@C_{84}$ synthesized by Nagase and Kobayashi [14].

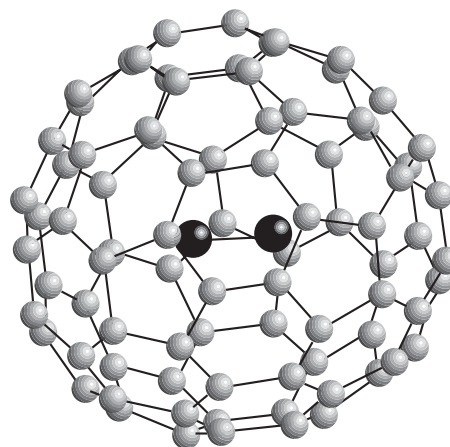


Fig. 3. Structure of the $Mn_2@C_{84}$ molecule.

4. CONCLUSIONS

Thus, endohedral fullerenes containing manganese ion pairs were synthesized through high-frequency arc vaporization of an iron powder and graphite electrodes with 0.01% Mn.

The EPR spectrum measured for a polycrystalline material containing endohedral fullerenes exhibits lines of exchange-coupled Mn^{2+} ions with an additional hyperfine structure.

Taking into account that endohedral complexes with manganese have not been synthesized to date and that the concentration of electrons in the plasma substantially affects the assembly of molecules [15], we assume that it is these iron clusters that change their electronic configuration and thus create conditions favorable for the formation of endohedral fullerenes with manganese.

In a subsequent work, we plan to calculate the distribution of the electron density and to evaluate the type of interaction of manganese ions.

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