

SHORT
COMMUNICATIONS

Superparamagnetism of Magnetite Particles in C₆₀ Fullerite Powder

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Abstract—A new magnetic material, C₆₀ fullerite powder doped by magnetite (Fe₃O₄) nanoparticles, is obtained by heating a mixture of fullerite and iron(III) acetylacetonate. It is shown that the material offers superparamagnetic properties. Surface bonding between the nanoparticles and the fullerite is established. © 2005 Pleiades Publishing, Inc.

The physical properties of nanocomposites and, hence, their functionality depend on the size of the nanoparticles and the properties of the matrix. A challenging problem in this field is preparing nanoparticles of a given composition by one-stage synthesis. Fullerite seems to be an appropriate matrix for magnetic nanocomposites, which are today viewed as very promising. In this work, we study the resonance and magnetic properties of C₆₀ fullerite powder with Fe₃O₄ magnetite nanoinclusions. The material is prepared by the chemical reaction between C₆₀ and volatile iron triacetylacetonate Fe(acac)₃ (Fe(acac)₃ = Fe(CH₃COCHCOCH₃)₃), during which the magnetite nanoparticles enter the magnetically neutral but chemically active matrix.

The samples of magnetic materials MC₆₀ and M*C₆₀ (M stands for magnetite) were prepared by the original method [1], according to which a solid mixture Fe(acac)₃ : C₆₀ = 1 : 2 is heated to 300°C until the burning of Fe(acac)₃ is seen visually. Then, the process goes in air spontaneously without heating (MC₆₀ samples). When M*C₆₀ samples were synthesized, the crucible with the reagents was cooled by water of temperature 10–15°C.

The heating process was studied by the method of differential thermal analysis (DTA). It was found that, in the presence of C₆₀, Fe(acac)₃ decomposes with the formation of Fe(acac)₂ and the radical (acac) followed by pyrolysis of Fe(acac)₂ without substantial gas evolution from C₆₀. The weight loss meets the conversion of Fe(acac)₃ to Fe₃O₄.

The state of the iron was determined with Mössbauer measurements using a ⁵⁷Co(Cr) source. The electron magnetic resonance (EMR) spectra were taken with an SE/X-2544 electron paramagnetic resonance X-ray spectrometer equipped with a thermal liquid-nitrogen trap. The spectra were characterized by effective (peak-to-peak) resonance linewidth ΔH , which was

found from the derivative of the absorption line, and position H_0 of the peak, which is found by integrating the derivative. Magnetic measurements were made with a SQUID magnetometer. The X-ray fluorescence spectrum taken from the C₆₀ fullerite synthesized by Eletskiĭ exhibits a standard set of peaks typical of the face-centered cubic lattice of C₆₀ at 300 K. For this fullerite, the electron paramagnetic resonance (EPR) of the radical is characterized by parameters $g = 2.0017$ and $\Delta H = 0.08$ mT. In the X-ray spectra taken from the products of the C₆₀–Fe(acac)₃ reaction, the reflections due to C₆₀ persist.

Early Mössbauer measurements revealed magnetite particles in the material synthesized [2–4]. The parameters of the Mössbauer spectrum taken from the MC₆₀ sample are listed in the table. The parameters of the hyperfine structure were obtained by fitting the model spectrum to the experimental one under the assumption that the absorption line is of Lorentz shape. Three distinct nonequivalent positions of the iron were distinguished in the spectrum that are represented by the sextet, doublet, and singlet. As judged from the hyperfine field on the nucleus and the isomer shift value, the sextet can be assigned to defects in the magnetite, whose sublattice remained unresolved because of the poor statistics of the spectrum. The particle size did not exceed 18 nm [3].

The isomer shift of the doublet is typical of trivalent iron oxide, which can be assumed to consist of finer, ≈ 13 nm, superparamagnetic magnetite particles. The isomer shift of the singlet is typical of iron-based alloys, including iron–carbon alloys [2]. In this case, the iron may cover the magnetite particle surface and chemically bonded to the fullerite.

Figure 1a shows the temperature dependences of magnetization for the composite samples cooled in a magnetic field of 20 mT (field cooling, FC) and in the absence of the field (zero-field cooling, ZFC). The

Mössbauer data for MC₆₀

| Sextet | δ , mm/s | H , 10 ⁵ A/m | ϵ , mm/s | FWHM, mm/s | S |
|--------|-----------------|---------------------------|-------------------|-------------|------------|
| 1 | 0.45 ± 0.05 | 490 ± 10 | 0.33 ± 0.08 | 1.66 ± 0.08 | 0.45 ± 0.1 |
| 2 | 0.36 ± 0.05 | 0 | 0.79 ± 0.08 | 0.58 ± 0.08 | 0.41 ± 0.1 |
| 3 | 0.08 ± 0.05 | 0 | 0 | 1.72 ± 0.1 | 0.13 ± 0.1 |

Notes: δ , the isomer chemical shift relative to α -Fe; ϵ , the quadrupole splitting; H , the hyperfine field on the iron nucleus; and S , the fraction of iron-occupied sites.

curves are typical of superparamagnets. In the M*_{C₆₀} sample, the magnetization decreases with increasing temperature by roughly one order of magnitude, the difference in the FC and ZFC curves persisting throughout the temperature range (Fig. 1a shows only the behavior of the magnetization under the FC conditions). Based on the data of DTA and quantitative analysis (the latter show that both the iron and the fullerite do not diminish in weight upon temperature synthesis), we calculated the magnetization per gram of iron. In the MC₆₀ sample at 300 K, this value equals 17.6 emu/g, which correlates with the data for magnetite particles in the carbon matrix, 19–45 emu/g [4].

The EMR spectra taken in the temperature range 80–500 K are presented in Fig. 2. The spectrum for M*_{C₆₀} contains the line of the C₆₀ radical. In the MC₆₀ sample, this line is resolved only in a narrow magnetic field range and is highly broadened, indicating that the magnetization grows. The absorption line intensity for M*_{C₆₀} is roughly one order of magnitude lower than

for MC₆₀, which is also consistent with the magnetization data.

The temperature dependence of the EMR spectra (Fig. 3) is typical of iron oxides in the superparamagnetic state [5–7]. It is known that, because of the first-order phase transition in the temperature range 250–256 K, the C₆₀ fullerite lattice becomes primitive cubic. At these temperatures, the resonance characteristics of the material exhibit a specific feature: the slope of the temperature curves for the EMR linewidth and resonance field changes (Fig. 3a). Such a run confirms the presence of particle–fullerite bonding.

As the temperature grows, the EMR line narrows, which is associated with the averaging effect of magnetization thermal fluctuations. According to the calculation made in [5], the EMR linewidth broadening factor for like particles is proportional to the ratio of their volumes. The experimental spectra show both broad and narrow absorption lines, which differ in position in the magnetic field (this fact is more pronounced for M*_{C₆₀}, Fig. 2b). Presumably, there exists a statistical double-

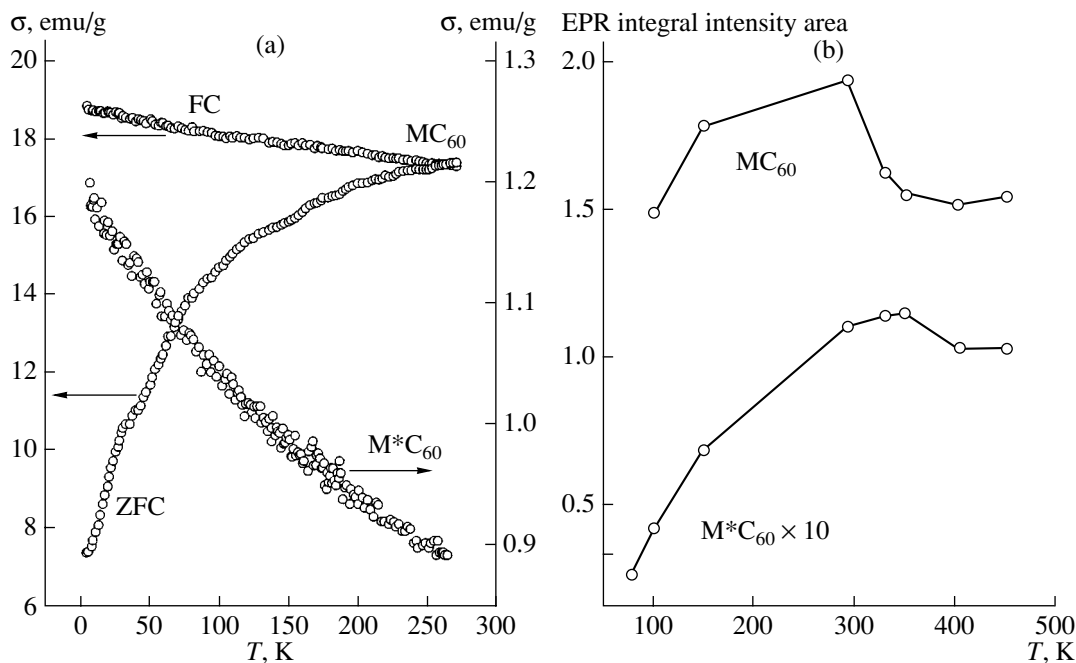


Fig. 1. Temperature dependence of the magnetization.

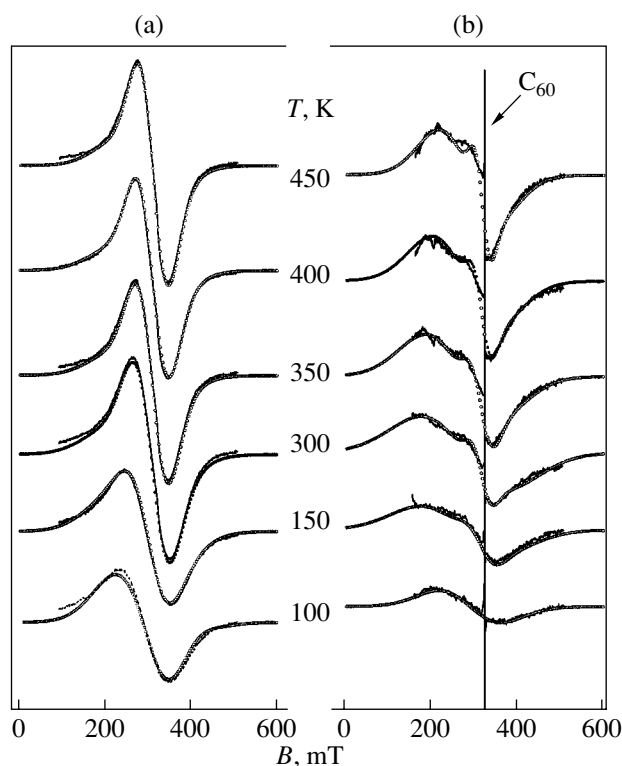


Fig. 2. Temperature dependence of the EMR spectra for (a) MC_{60} and (b) M^*C_{60} . The symbol “○” refers to the computer simulation of the spectrum by using two Gaussian curves. The EPR spectrum of the C_{60} radical is shown by the arrow.

hump particle size distribution similar to that found in [6]. The same takes place in the Mössbauer spectra. Computer-aided simulation of the EMR spectra by using two Gaussian resonance lines gave the best fit to the experimental data (Fig. 2). Such a shape is likely to reflect a considerable influence of nonuniform magnetic anisotropy in the magnetite nanoparticles embedded in the fullerite. This adversely affects the resolution of the Mössbauer spectra. Throughout the temperature range, the value of ΔH_1 of the broader spectral component for the MC_{60} sample is less than ΔH_1^* for M^*C_{60} and resonance fields obey the inequality $H_1 > H_1^*$. For the narrower components, conversely, $\Delta H_2 > \Delta H_2^*$ and $H_2 > H_2^*$. Therefore, the doublet in the spectra for M^*C_{60} is better resolved. The temperature dependences of the parameters of the resonance lines simulated are shown in Fig. 3 for MC_{60} . For MC_{60} at 300 K, the linewidths and their associated resonance fields are $\Delta H_1 = 81.6$ mT, $H_1 = 310.4$ mT and $\Delta H_2 = 151.5$ mT, $H_2 = 281.7$ mT. For M^*C_{60} , $\Delta H_1^* = 59$ mT, $H_1^* = 316$ mT and $\Delta H_2^* = 224$ mT, $H_2^* = 265$ mT. For sized magnetite particles, the EMR linewidths at 300 K are given in [8]. Comparing those values and ours, we obtained two characteristic linear sizes of magnetite particles in

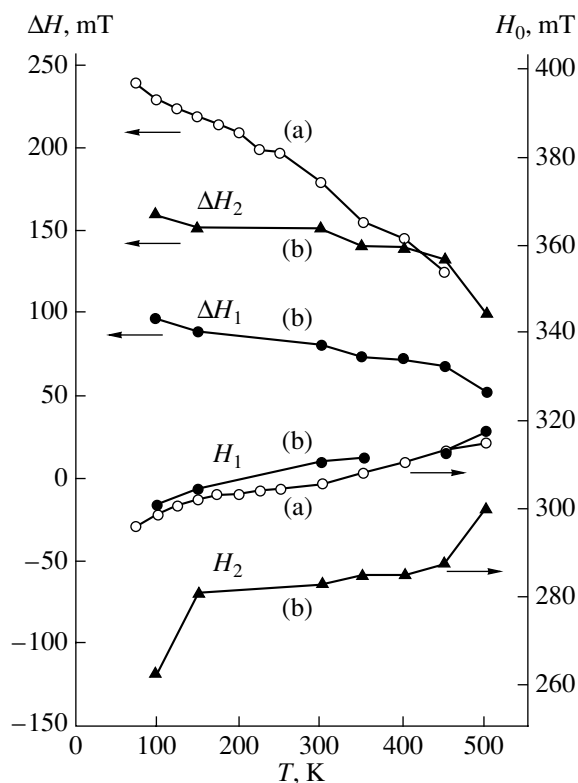


Fig. 3. Temperature dependence of the EMR spectrum parameters for MC_{60} : (a) experimental and (b) simulated spectra.

MC_{60} : 9 and 15 nm. These sizes are comparable to those estimated from the Mössbauer data. In M^*C_{60} , the magnetite particles sizes are 6 and 21 nm.

The difference in particle size between MC_{60} and M^*C_{60} reflects the different synthesis conditions. In the latter case, the process allowed for heat removal. This decreased the rates of vaporization and decomposition of $Fe(acac)_3$ with the formation of the radical. As a result, some iron complexes might stay in the molten state. Apparently, coarser particles are synthesized under such conditions. The decrease in the magnetization and the coarsening of the particles may be attributed to the agglomeration of nanocrystallites and a decrease in their density, as well as to their adsorption on the surface due to the organic products of ligand decomposition. Fine particles form during the gas-phase decomposition of $Fe(acac)_3$ on the surface of the melt. In the case of M^*C_{60} , they became still finer, because vaporization is less vigorous under such conditions.

The temperature run of the magnetization for MC_{60} and the dependence of the magnetization on the cooling conditions lead us to assume that the magnetization in the nanoparticles is suppressed. Because of the particle size distribution, the process covers a wide temperature range. The resonance methods strengthen this assump-

tion. Figure 1b shows the temperature dependences of the integral intensity of the EMP spectra. Its value varies in proportion to the magnetization of the material. According to the general concept [9], the run of these curves clearly indicates magnetization suppression in MC_{60} and in M^*C_{60} . In the latter case, the suppression is observed at a higher temperature, because here coarse particles grow.

In summary, a new magnetic composite (Fe_3O_4 nanoparticles in C_{60} fullerite powder) offers superparamagnetic properties. The suppression of the nanoparticle magnetization starts near room temperature. The magnetic resonant properties of the nanoparticles are sensitive to structural changes in the fullerite. The effects observed are of applied interest.

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