

A Study of the Synthesis Products of Fullerenes with Nickel and Cobalt

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Abstract—Qualitative analysis of the products of plasmachemical synthesis of fullerenes with metallic nickel and cobalt has been carried out using electron paramagnetic resonance (EPR) and electron microscopy. These studies show that the synthesis products are mainly fullerenes, metallic nanoparticles coated with an insulating layer, and isolated atomic clusters. © 2001 MAIK “Nauka/Interperiodica”.

INTRODUCTION

In studies of fullerenes, great attention is now paid to their derivatives (heterofullerenes, endohedral complexes, metallofullerenes) [1, 2], because distortions of the symmetry of fullerenes produce new physical and chemical properties [1, 3, 4]. However, obtaining these unique materials in quantities sufficient for analysis is still a complicated task. We have undertaken an attempt to synthesize metallofullerenes containing nickel and cobalt.

MATERIALS AND METHODS

Earlier we described a plasmachemical reactor for the synthesis of fullerenes in a carbon plasma jet produced by an arc discharge between graphite electrodes at frequencies in the kilohertz range [5, 6].

In [7], a technique of synthesizing iron-containing fullerene complexes was described. The central electrode has an axial hole that was filled with carbonyl iron. In the present study, a similar technique was used, except that the hole in the central electrode was filled with nickel or cobalt. Carbon condensate was deposited on the chamber walls during synthesis, and the fullerenes extracted from this with benzol and the growth on the outer electrode (thermolysis residue [6]) were investigated by electron paramagnetic resonance using Se/X-2544 and RE1308 spectrometers in the temperature range 77 to 500 K and by electron microscopy in a JEM-100C electron microscope with an EM-ASID-4 scanning attachment and image processing equipment.

RESULTS AND DISCUSSION

1. In electron microscopic studies of the carbon condensate, particles of nickel coated with a non-conducting material (both groups of particles and isolated particles of sizes 10^3 to 10^4 nm) have been detected

(Fig. 1). The fact that the particles were nonconducting has been established by an indirect method. The particles were placed under a microscope on a conducting (metallic) surface and irradiated with an electron beam. As a charge accumulated on the particles, a discharge via the substrate occurred. The discharge of the particles was accompanied by visually-detected radiation.

2. EPR spectroscopy detected a magnetic resonance of the metallic particles in the soot and the thermolysis residue (Fig. 2): $\Delta H^{\text{Ni}} = 80$ mT, $g^{\text{Ni}} = 2.20$ and $\Delta H^{\text{Co}} = 150$ mT, $g^{\text{Co}} = 2.23$. Similar results ($\Delta H^{\text{Ni}} = 100$ mT, $g^{\text{Ni}} = 2.22$ and $\Delta H^{\text{Co}} = 90$ mT, $g^{\text{Co}} = 2.23$) were obtained earlier by Bagguley [8] in experiments on the ferromagnetic resonance of metallic particles synthesized by the aerosol method in an RF arc discharge in a hydrogen atmosphere at 1 atm pressure with subsequent spinning in paraffin. The diameter of the particles was assumed to be 5–10 nm. It is known for single-domain particles of a monocrystalline metal in the absence of the skin effect that $\Delta H^{\text{Co}} = 11$ mT and $\Delta H^{\text{Ni}} = 12$ mT [9]. The large width of the electron paramagnetic resonance line in our experiments (Figs. 2a, 2b) is explained by the fact that the particles of nickel and cobalt in the soot have sizes amounting to a few millimeters. The g -factor values coincide with the data in [8].

Lines of EPR spectrum of the fullerene extract (Fig. 3) grouped by the types of their variation with temperature

Line No.	g	ΔH , mT
1	2.001	0.1
2	2.15	40
3'	2.6	15
3''	3.6	15
3'''	3.98	13
4	7.7	13

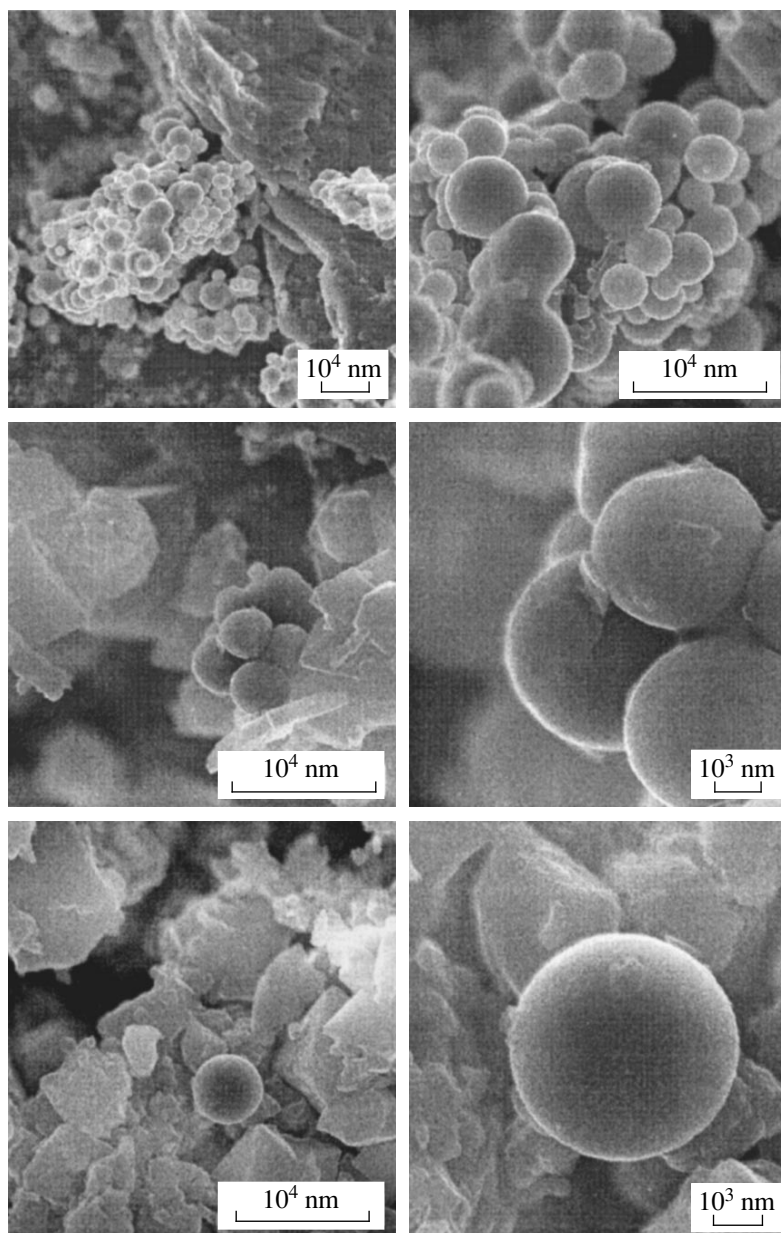


Fig. 1. Nickel particles in a fullerene-containing soot.

Line 1 for $g = 2.001$, as well as a narrower line 2 for $g \sim 2.15$ (Fig. 2), are observed not only in the spectrum of the nickel-containing soot but also in the thermolysis residue and in the fullerene extract, and are discussed below.

3. In the fullerene extract, the content of nickel according to the analysis of the X-ray luminescence data was 0.02%. Lines in the EPR spectra of the extract fall into four groups according to their temperature behavior (see table).

A narrow line 1 (Fig. 3a) for $g = 2.001$ usually observed in the spectra of solid fullerene mixtures [10]

is due to a $C_{60(70)}$ radical. Its shift with temperature, typical of a paramagnetic center, can be seen in Fig. 4 (1).

At $T = 293$ K, parameters of line 2 are $g = 2.15$ and $\Delta H = 40$ mT (Fig. 3 (2)). Raising the temperature to 510 K causes gradual narrowing of this line down to 10 mT, an increase in its intensity and a shift to higher fields ($g = 2.08$). At temperatures below 293 K, the line first broadens to 70 mT (at $T = 250$ K) and then splits into two narrower components (at $T = 230$ K). At still lower temperatures, three lines are seen in the spectrum, having effective g -factor values of 2.06, 2.12, and 2.27, and the line width ~ 20 mT. At 77 K, the spectrum consists of a single asymmetric line 4 (Fig. 3b).

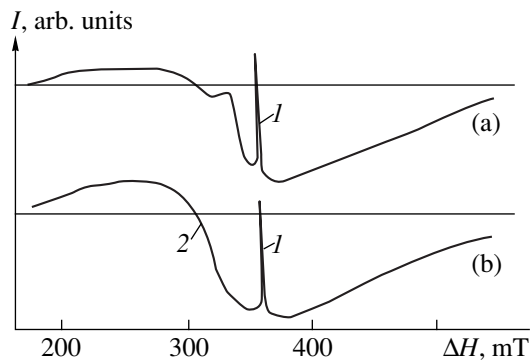


Fig. 2. Ferromagnetic resonance of Ni-containing soot (a) and Co-containing soot (b).

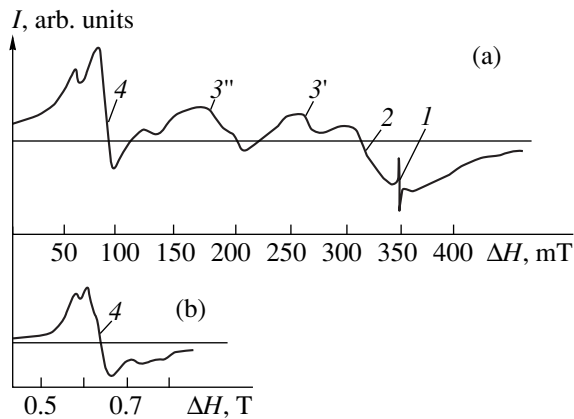


Fig. 3. Magnetic resonance spectra of Ni-containing fullerene extract at frequencies (a) 9 and (b) 35 GHz at 293 K; (a): $g = 2.001$ (1), 2.15 (2), 2.6 (3'), 3.6 (3''), and 7.7 (4).

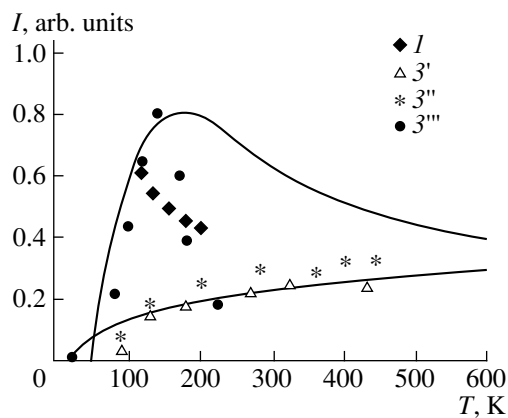


Fig. 4. Temperature variation of the EPR lines with $g = 2.001$ (1), 2.6 (3'), 3.6 (3''), and 3.98 (3'''). Solid line—calculation.

The observed spectrum is possibly associated with fine (~ 10 nm in diameter) crystalline particles of nickel that have anisotropic magnetic properties. Taking this into account, the temperature variation of the line width

(which decreases with increasing temperature) can be explained by movement of the particles, which causes averaging of the anisotropy produced by internal fields. This mechanism was proposed by Kittel [11]. In this case, the width of the resonant line is calculated by the random walk method using the formula

$$\Delta H = \gamma^2 [\Delta H(0)^2 \tau(T)], \quad (1)$$

where $\tau(T)$ is a temperature-dependent mean time between two consecutive changes of the field direction and $\Delta H(0)$ is the line width at $T = 0$ K.

Substituting in (1) the values of $\Delta H(T)$ obtained in our experiment and $\Delta H(0)$ for the fine nickel particles [9, 12], we get $\tau(510 \text{ K}) = 0.9 \times 10^{-11} \text{ s}$, which is much less than the Larmor precession period of the magnetization vector in the field 0.3 T ($1.05 \times 10^{-10} \text{ s}$). Despite the approximate nature of the estimation, this mechanism can explain the narrowing of the line with increasing temperature by averaging of the magnetic anisotropy due to movement of the particles.

As the temperature is lowered from 286 to 77 K, the intensities of the EPR lines corresponding to $g = 2.6$ (curve 3'), 3.6 (curve 3''), and 3.98 (curve 3''') vary as shown in Fig. 4. The line for $g = 3.98$ (3''') becomes noticeable at 230 K and reaches a maximum at 140 K, at which temperature the intensities of the other two lines decrease appreciably. This behavior is possible in dimer or tetramer clusters with antiferromagnetic exchange interaction between the atoms [13]. In Fig. 4, a temperature dependence is shown that has been obtained from a calculation in terms of a dimer cluster model in the Heisenberg–Dirac–van Vleck approximation for homonuclear systems. In this model, the energy levels of a system of two multielectron atoms are represented by a Heisenberg Hamiltonian for the exchange interaction (\hat{H})

$$\hat{H} = -2J\hat{S}_1\hat{S}_2, \quad (2)$$

where S_1 and S_2 are total spins of the atoms.

Energy eigenvalues are determined by a semiempirical parameter of the exchange coupling of atoms (J) and the total spin of the system ($S = S_1 + S_2$), which is obtained from the usual rule for the summation of moments. For a pair of Ni^{+1} ions ($s = 1$), the total spin can take values of $S = 0, 1, 2$. The energy corresponding to each state is

$$E_S = J[S(S+1) - S_1(S_1+1) - S_2(S_2+1)]. \quad (3)$$

The rate of the resonant intralevel transitions for a level with spin S is given by the formula

$$I_S = \frac{\exp[-E_S/(KT)]}{\sum_S (2S+1) \exp[-E_S/(KT)]}, \quad (4)$$

where K is the Boltzmann constant and T is the temperature.

Proceeding from this, curves have been calculated for dimer clusters with spin $s_{1,2} = 1$. Coincidence of the calculated and experimental results suggests that the lines with the effective g -factor values 2.6, 3.6, and 3.98 correspond to dimer formations of nickel with exchange coupling constants on the order of 147 cm^{-1} . Positions of the lines are indicative of a splitting of the energy levels within the multiplets. The observed transitions with $g = 2.6$ and $g = 3.6$ take place within the total spin state with $S = 2$, which is the upper energy level of the cluster. The line $g = 3.98$ is due to transitions within state $S = 1$, which is lower in energy by $\Delta E = 2|J|$. In the low-temperature range, all transitions follow the same relationship. The decrease of the line intensity with increasing temperature for the lower transition cannot be described in terms of the Heisenberg–Dirac–van Vleck approximation; the complex couplings formed are outside the scope of this model.

Models of a dimer cluster containing a fullerene can be constructed using the data given in [14], where systems of C_{60} and C_{70} molecules and C_{70}^{4-} cations have been considered. Two Ni^{2+} ions attach to the fullerene molecule due to a donor-acceptor bond between electrons of the 4*S*-shell and the π system of the fullerene. This bond is activated by the electrostatic interaction between the charge of a C_{70}^{4-} anion and the total charge of the nickel pair $2Ni^{2+}$. Magnetic coupling between nickel ions arises as a result of polarization of the fullerene shell. Another possible candidate for the intermediate atom in this cluster model might be carbon.

The low-field resonant transition ($g \sim 7.7$) is represented by a line characteristic of spectra from anisotropic powders. At 35 GHz, the line position shifts to higher fields ($g = 4$) and the line width increases to $\Delta H = 60 \text{ mT}$. The intensity and width of the line does not change at temperatures down to 77 K. These observations indicate that this line can be related to atomic clusters of asymmetric type as well. A change taking place with an increase in the energy of ultrahigh frequency quanta [13] suggests that the exchange interaction in this cluster has both isotropic and anisotropic components. The isotropic exchange in this cluster is probably much less strong than in a dimer and the temperature dependence should be observable at temperatures below 77 K.

4. Spectra of the fullerenes extracted from soot and containing cobalt are an asymmetric line (Fig. 5a) with the following effective parameters: $g \sim 2.4$ and $\Delta H = 56 \text{ mT}$. With decreasing temperature, the line width increases, but at 104 K, it shrinks to 36 mT and the effective g -factor drops to $g \sim 2.1$. At 77 K, the spectrum is a symmetric line (Fig. 5b). We attribute this spectrum to fine-grained cobalt particles isolated from one another by fullerene molecules. The spectrum at 77 K can be interpreted as due to modifications of the

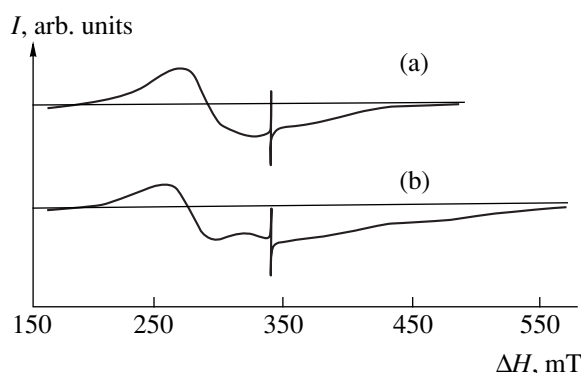


Fig. 5. Magnetic resonance spectra of the Co-containing fullerene extract from soot at (a) room temperature and (b) $T = 77 \text{ K}$.

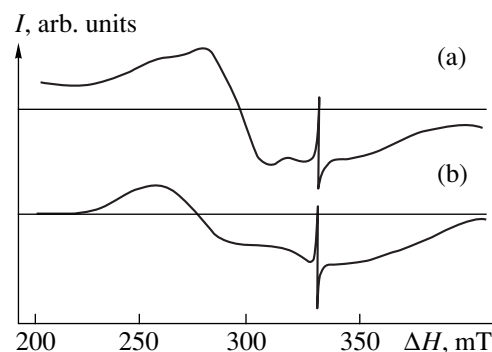


Fig. 6. Magnetic resonance spectra of the Ni-containing fullerene extract cooled in a magnetic field $H =$ (a) 0 and (b) 0.5 T.

cobalt crystals with face-centered cubic and hexagonal close-packed lattices [12].

5. An interesting feature of the obtained materials is their behavior in a magnetic field at 77 K. Spectra of the samples containing cobalt, as well as of those with nickel cooled in a magnetic field of 500 mT differ by the shift of the resonant line to lower fields. The results for nickel are shown in Fig. 6b. Similar effects are observed in spin glasses [15]. In our case, this might be an indication of a coupling between separate magnetic particles.

CONCLUSION

As demonstrated by electron microscopy, in the synthesis of fullerenes with nickel, the latter is found in the form of particles coated with a layer of nonconducting substance. EPR analysis of the fullerene-containing soot with cobalt and nickel indicates the presence (apart from fullerenes) of large-sized particles (10^3 to 10^4 nm), which exhibit skin effect and a domain structure without magnetic anisotropy, and some finer particles ($\sim 10 \text{ nm}$). In the fullerene extract, the ratio of coarse and fine particles changes in favor of the latter. Clusters of several (from two to four) atoms can also be

observed via an intermediate nonmagnetic atom or molecule, possibly that of fullerene. The behavior of the fullerene extracts with cobalt and nickel in a magnetic field at 77 K bears resemblance to that of spin glasses.

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