Temperature dependence of the ESR line width of C_{60}^- in C_{60} crystals doped with sodium, potassium, zinc, and indium

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The ESR line width of the C_{60}^- anion in samples of fullerides (Na, K, Zn, and In) with low metal content (0.01%) is ~0.1 mT at 77 K and ~1 mT at 300 K. The line shape is fitted better by the Lorentzian function than by the Gaussian function. The spin-lattice relaxation likely makes some contribution to the line width. Time-dependent changes in the ESR spectra were observed: they are related to diffusion of cations to defects of the crystalline lattice.

Key words: fullerene, ESR, relaxation.

We have previously studied the ESR spectra of C_{60} fullerides of metals due to their electric properties.[1—3] The ESR spectra of the C_{60}^- anions obtained by the reduction of fullerene in the liquid phase have been studied.[4—6]

As compared to other paramagnetic C_{60} derivatives, the C_{60}^- anion is characterized by the difference between its *g*-factor and the *g*-factor of a free electron and by a sharp increase in the line width as the temperature increases.[1—6] No similar temperature dependences were observed in ESR spectra of aromatic radical anions close in electronic structure to C_{60}^-. The specific features of C_{60}^- are assumed[6] to be related to the high symmetry of the molecule, the degenerate character of the molecular orbital occupied by an unpaired electron, and the Jahn—Teller effect.

In this work, we studied the temperature dependences of the ESR line widths of C_{60}^- in polycrystalline samples of C_{60} doped with sodium, potassium, zinc, and indium.

Experimental

Doping of C_{60} was carried out in ESR-tubes using C_{60} (3—5 mg) and some excess of metal. Sodium and potassium were in the form of metal mirrors, and zinc and indium were in the form of pieces. The contents of the tube was pumped out (to 10^{-3}—10^{-4} Torr) at 573 K for 2—3 h, then the tube was sealed and placed in a cylindrical furnace. In the case of sodium and potassium, the temperature gradient was established. The temperature in the point of fullerene location was 493 K, while for the metal it was 50° lower. In the case of zinc and indium, the temperature was 773 K, and no gradient was established. Annealing was performed to obtain a uniform metal distribution over the crystals. During annealing, fullerene was in the hot zone, and the metal was at room temperature.

The double resonator of an E-12 spectrometer (Varian) was used for recording the spectra. One resonator contained the sample under study, and the standard sample with the g-factor of 2.0028 was placed in the second resonator. The position of the standard signal in the spectra is marked by the vertical line.

Results and Discussion

The ESR spectrum (Fig. 1) recorded after 10-min sodium doping at 493 K consists of two superimposed

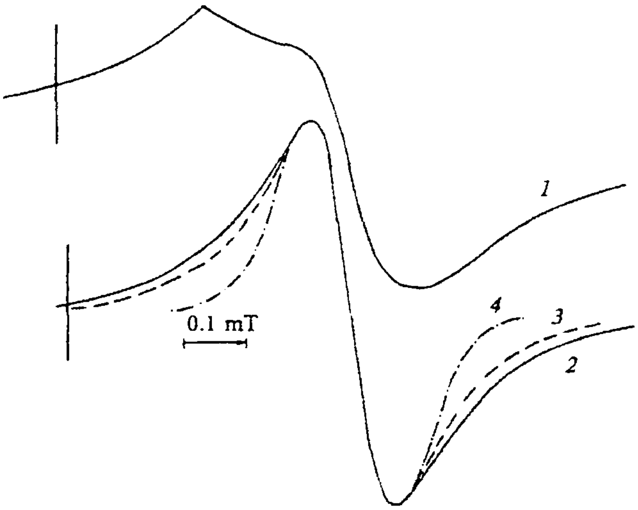

Fig. 1. ESR spectra of $C_{60}^-Na^+$ in C_{60} at 77 K: *1*, after the 10-min reaction of sodium vapor with fullerene; *2*, after 40-min annealing at 493 K; *3* and *4*, Lorentzian and Gaussian shapes of the line plotted using the experimental line width. The vertical line reflects the position of the standard signal in the magnetic field.

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signals: a narrow downfield signal and a broad upfield signal. According to their positions relative to the standard, both of them are assigned to C_{60}^-. It can be assumed that the downfield signal corresponds to the C_{60}^- anions in the surface layers, and the upfield signal can be assigned to those in the crystal bulk. This assumption is confirmed by the fact that 40-min annealing at 493 K results in the disappearance of the downfield signal in the ESR spectrum (see Fig. 1) due to diffusion of the Na^+ cations to the crystal bulk and partially due to the decomposition of $C_{60}^-Na^+$.

Curves *3* and *4* in Fig. 1 are lines with Lorentzian and Gaussian shapes. They were plotted using the experimentally determined line width between points of the maximum slope of ΔH_{pp}.

In the experiment with potassium, the nonuniformity of the sample is manifested in a somewhat different manner. After the reaction at 493 K for 10 min, the spectrum of the reaction mixture at 77 K contains no explicit properties of heterogeneity (Fig. 2, curve *1*). When the temperature increases above 100 K, heterogeneity appears as a distortion of symmetry of the line (Fig. 2, curve *2*). Curves *3* and *4* are the result of the graphic decomposition of spectrum *2*. Lines *1* and *4* have the same *g*-factor, and line *3* is shifted downfield by 0.2 mT. The width of line *3* is 0.15 mT, and that of line *4* is 0.3 mT.

The temperature changes in the spectra are likely related to transitions of the K^+ cations between energetically different sites of their localization in the surface layers. Heterogeneity of the samples can be eliminated by annealing (573 K) for 2 h. The corresponding samples are uniform due to the high temperature and low reaction rates with zinc and indium.

A certain concentration of the paramagnetic material is needed for studying the temperature dependence of the ESR line width of C_{60}^-, because the amplitude decreases more than by an order of magnitude when the temperature increases from 77 K to room temperature. In the case of potassium and sodium, the required amplitude of the C_{60}^- anion is detected already after the 10-min reaction at 493 K.

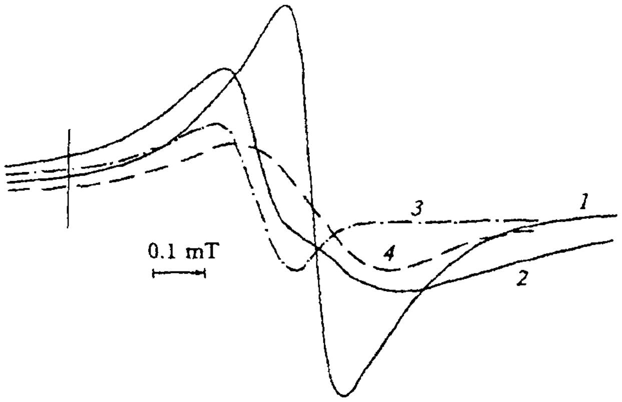

Fig. 2. ESR spectra of $C_{60}^-K^+$ in C_{60}: *1*, at 77 K after the 10-min reaction of potassium vapor with C_{60}; *2*, at 205 K after the 10-min reaction; *3* and *4*, result of the graphic decomposition of spectrum *2*. The vertical line reflects the position of the standard signal in the magnetic field.

In the reactions of C_{60} with zinc and indium at 773 K, multicharged C_{60}^{n-} ions are formed at the initial stage along with C_{60}^-. They decompose during annealing to give higher concentrations of C_{60}^- than the direct reaction of formation.

$$C_{60}^{n-} \rightarrow n\,C_{60}^-$$

The temperature dependences of the line width ΔH_{pp} of C_{60}^- are presented in Fig. 3. The spectra of sodium and potassium fullerides exhibit somewhat greater line width than those in the spectra of zinc and indium derivatives, but the slope angles of the plots in the 77—200 K range are almost identical.

The temperature increase above the point of the phase transition of a simple cubic lattice to a face center cubic lattice (260 K) is accompanied by an increase in the slope angles of the corresponding dependences for $C_{60}^-Na^+$ and $C_{60}^-K^+$.

In the 260—300 K range, the temperature dependence of the line width of $C_{60}^-K^+$ has a hysteretic character. At room temperature, the line width is equal to 1.2 mT, while it is 0.7 mT for the sample at the same (room) temperature, but after cooling and passing through

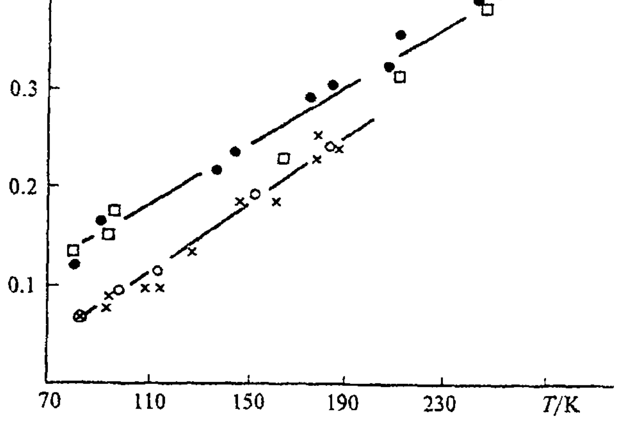

Fig. 3. Temperature dependence of the ESR line width (ΔH_{pp}) of the C_{60}^- anions in fullerides with different cations: *1*, Na^+; *2*, K^+; *3*, Zn^{2+}; and *4*, In^{3+}.

the phase transition. Heating at 573 K for 1 min results in an increase in the line width to 1.2 mT.

The spectra of sodium, potassium, and zinc fullerides depend on the exposure time of the samples (Fig. 4). New lines appearing during exposure are characterized by high values of g-factors and, at first glance, narrower widths compared to those of the initial lines of C_{60}^-. It is difficult to determine exactly the widths of the new lines because of superposition with adjacent lines. In the case of sodium fulleride, two new lines appeared, and in the case of zinc fulleride, one new line (an intermediate line located between those of C_{60}^{n-} and C_{60}^- in a regular lattice) was observed.

Annealing at 573 K for 30 min recovers the initial shapes of the spectra (see Fig. 4, spectrum *3*). The time changes observed are likely related to diffusion of the metal cations to defects of the crystalline lattice. Different types of the defects are described in Ref. 7. This diffusion results in the shift of the paramagnetic center to the defect region of the crystal.

Unlike planar aromatic radical anions, whose electronic structures are described by molecular wave functions that are a superposition of p_z-atomic orbitals, the molecular orbital of the unpaired electron of C_{60}^-, along with p_z-orbitals, contains the contribution of p_x- and p_y-orbitals. This difference results in a situation where the orbital moment is completely suppressed in aromatic radical anions, and for C_{60}^- one should expect a certain contribution of the orbital magnetic moment to the total magnetic moment of the species and the corresponding difference of its g-factor from the g-factor of a free electron.

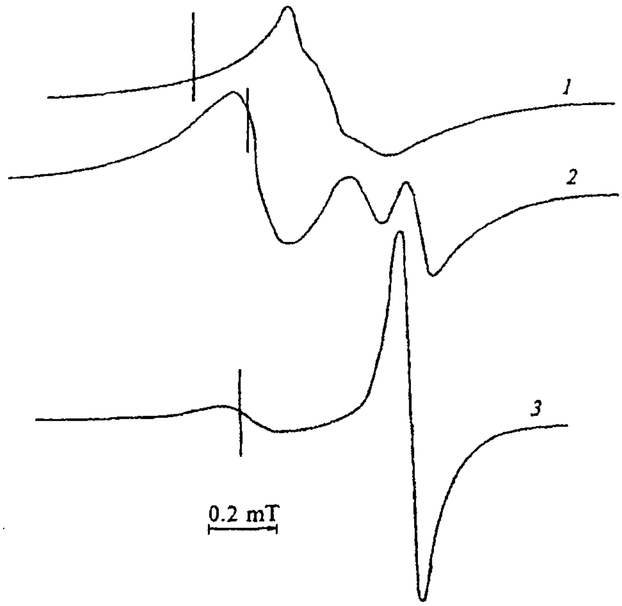

Fig. 4. ESR spectra of $C_{60}^-Na^+$ (*1*) and Zn_xC_{60} (*2*) 2 months after exposure and of Zn_xC_{60} (*3*) after 30-min annealing at 573 K. The vertical line reflects the position of the standard signal in the magnetic field.

Anisotropy of the g-factor was observed at 8 K [5] and 9.5 K [8] in the spectra of C_{60}^-: $g_\parallel > g_\perp$ and $\Delta g = 0.0012$. When the temperature increases to 55 K, anisotropy of the g-factor is averaged.[8]

The anisotropy parameters of the g-factor of C_{60}^- can be qualitatively considered for a hypothetical anion in the P-state in the tetragonal field. The solution of the spin-Hamiltonian results in the following expressions:

$$g_\parallel = g_e,$$

$$g_\perp = g_e - 2\lambda/\delta,$$

where δ is the distance between the energy levels of the p_z- and p_x-, p_y-orbitals.[9] For the C atom, $\lambda = 28\ \mathrm{cm}^{-1}$.[10]

The variation of the measured average value $g_{av} = 1/3(g_\parallel + 2g_\perp)$ can be reasonably related to a change in the δ value. A decrease in symmetry of the metal cation environment in the surface layers or near defects of the crystalline lattice as compared to that in the regular lattice should lead to an increase in the Coulomb interaction between the cation and the C_{60}^- anion. This interaction should result in splitting of the degenerate t_{1u}-level of the unpaired electron and distortion of the spherical symmetry in the spin density distribution. A relation between the δ parameter and the splitting value of the t_{1u}-level can be assumed.

The charge and size of the cation exert a slight (but not contradicting the reasoning presented above) effect on the g-factor value of C_{60}^-: for $C_{60}^-Na^+$, 2.0001; for $C_{60}^-K^+$, 1.9997; and for $Zn^{2+} \cdot 2C_{60}^-$ and $In^{3+} \cdot 3C_{60}^-$, 1.9996.

The change in the line width of C_{60}^- from 0.4 to 4.5 mT in the 80—300 K range has been observed previously.[6] The ESR line width of aromatic radical anions in solution at room temperature is ~0.01 mT.

To reveal the factors determining the ESR line width of C_{60}^- in the fullerene crystal, we analyzed the line shape, which, as follows from Fig. 1, is close to the Lorentzian shape. This shape of the crystalline matrix implies that the role of nonuniform broadening is small. Anisotropy of the g-factor could be the only source of nonuniform broadening for a small concentration of paramagnetic centers and in the absence of the unresolved hyperfine structure. The Lorentzian shape of the line and its small width at 77 K compared to the ($H_\perp - H_\parallel$) value[5,8] imply that anisotropy of the g-factor is averaged in the crystal.

The rotation of the paramagnetic center is the most general mechanism of anisotropy averaging. Highly-symmetrical molecules possess an increased mobility in the solid phase. In this connection, it should be mentioned that the rotation frequency of $C_6H_6^-$ at 77 K is higher than $\gamma_e a_H$, where a_H is the HFC constant (0.375 mT).[11] However, when the orbital of the unpaired electron in $C_6H_6^-$ is degenerate, its g-factor does not substantially differ from 2.0032, and the line width has no sharp temperature dependence. The comparison performed suggests that the nonplanar structure of C_{60}^- is the main reason for its spectral peculiarities.

In addition to the rotational mobility of C_{60}^-, which leads to anisotropy averaging in solid solutions, an additional mechanism is possible in the C_{60} crystal. The mechanism is associated with migration of the unpaired electron between the C_{60} molecules closest to the cation. If anisotropy of the *g*-factor is related to the Coulomb interaction between the cation and anion, this migration will result in a change in the anisotropy axes, *i.e.*, in pseudo-rotation.

The absence of nonuniform broadening means that the line width is determined by the relaxation time t_2:

$$1/t_2 = 1/t_2' + 1/(2t_1),$$

where t_2' is the spin-spin relaxation time, and t_1 is the spin-lattice relaxation time. The t_2' value is related to uniform broadening of the line, and for the majority of radicals $t_1 >> t_2'$.

The study of the dependences of the intensity of the ESR signal of the C_{60}^- anion (Na^+ and K^+ cations) at 77 K on the power of the UHF energy revealed no properties of saturation, whereas the ESR lines of aromatic radical anions are saturated with small powers under these conditions. Thus, for C_{60}^- the inequality $t_1 >> t_2'$ is not evident.

The analysis of our data and low-temperature studies[8] do not allow us to conclude on the influence of the Jahn—Teller effect on the ESR spectra.

The absence of a strong dependence of the ESR spectra of fullerides on the nature of the cation suggests that the temperature effect on t_1 and the line width is mainly related to the crystal dynamics.

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