Low-temperature exoemission accompanying phase transitions in fullerite

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Low-temperature (77—570 K) emission of negative charges (exoemission) has been revealed and studied during cooling followed by heating of crystalline C_{60} and the C_{60}—C_{70} binary system. Peaks of emission current appear at the phase transition temperatures. Intense weakly decaying electron emission caused by the relaxation of strained structures containing weakly bound electrons occurs in the C_{60}—C_{70} binary system at 77 K.

Key words: fullerites, low-temperature thermocycling; strained bonds; relaxation; exoemission; structural phase transitions.

Considerable attention is paid to specific features of the structure and dynamics of the lattice and the existence of various phases of crystalline C_{60} in the studies of the physics and chemistry of fullerenes. Since the use of fullerenes is promising in electronics and optoelectronics, study of electronic properties of these compounds and related materials is of interest.[1—3] Fullerenes (fullerites) are strong oxidants due to their electronegativity and ability to form stable C_{60}^- ions, and they can be used for the preparation of many new compounds.

We have found and studied low-temperature emission of electrons and ions (exoemission) from the surface of fullerite samples in the 77—570 K temperature range. The exoemission occurs from the solid surfaces in a wide temperature range (4—700 K) due to mechanical (thermomechanical), radiational, or chemical actions.[4] On heating or cooling, maxima of emission currents are usually observed at temperatures of phase or relaxation transitions.[4—8]

The purpose of this work is the study of processes of orientational structural phase transition (SPT) of the order—disorder type and of electronic phenomena that accompany SPT in fullerite upon temperature cycling by exoemission methods. The high sensitivity of exoemission methods makes it possible to detect all specific features of structural rearrangement related to the appearance of strains and their relaxation during heat compression—expansion processes resulting in the formation and emission of weakly bonded electrons. The results obtained are interpreted from the viewpoint of the physicochemical mechanism of exoemission.[4,5]

Experimental

Samples of C_{60} fullerites of 99.8 % purity and C_{60}—C_{70} (80 : 20) binary system available from the Russian-American Company TERM Ltd. were studied. The composition and purity of fullerites were determined by chromatography and mass spectrometry. Ionic-molecular equilibria in fullerene vapor at 800—900 K and the electron affinity of higher fullerenes have been studied previously for similar samples of this series.[9] The temperature of orientational SPT for a C_{60} sample determined by differential scanning calorimetry (DSC) was 284—286 K.

The exoemission was studied upon cooling to 77 K and subsequent heating to room temperature as well as the emission of negative ions appeared on heating of the sample to $T \leq 650$ K. The exoemission was detected *in vacuo* (~10^{-4} Pa) in a pulse mode by a VEU-6 secondary-electron amplifier with the set of radiometric equipment. The positive potential was fed to the input of a detector, and the negative charge emission was detected. The electric field strength between the sample and the input window of the detector was ~200 V cm^{-1}. The ratio between the amount of electrons and ions in the total negative charge flow was determined by application of transverse magnetic field.

Samples were cooled by liquid nitrogen vapor fed with the controlled velocity from the outside of the sample support in the temperature range from 293 to 77 K in the regime close to linear. A setup for feeding nitrogen vapor was changed by a heater for heating in the 293—650 K temperature range. A thermocouple was mounted outside of a thin support of stainless steel with a sample. The sample was cooled and heated with the same rate, $v \approx 12$ K min^{-1}. The construction of the experimental setup has been described previously.[10]

The procedure of measurements was the following. After evacuation, fullerite was cooled to 77 K with the simultaneous detection of exoemission. The sample was kept for 1 h at the temperature of liquid nitrogen and then heated to room temperature, and the intensity of thermally stimulated emission (TSE) was measured. The described procedure of measuring the intensity of exoemission during one day was one testing cycle. Five cooling—heating testing cycles with the interval of 17 h were performed for each of the samples studied. The sixth testing cycle was carried out after keeping a sample in a vacuum for three weeks, and the results of this cycle allowed one to estimate the effect of prolonged relaxation on electronic phenomena at SPT induced by temperature cycling.

After temperature cycling in the 293—77 K temperature range, the sample was heated in the linear regime accompanied

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 87—94, January, 1996.

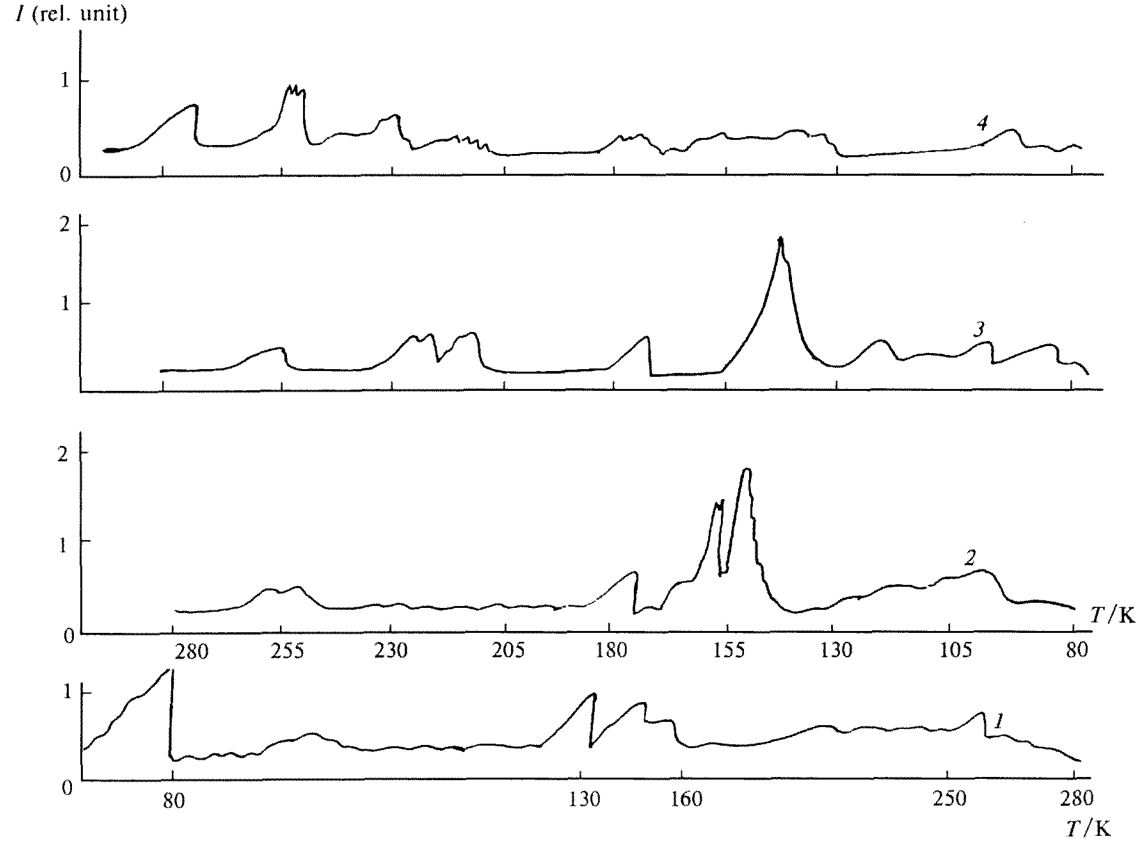

Fig. 1. Temperature dependence of the intensity of emission (*I*) from the C_{60} sample on cooling to 77 K (*1*) in the second cycle and on heating to 293 K (*2—4*) in the first—third testing cycles, respectively.

by the detection of negative charges and determination of the ionic component in the emission current.

The pulse mode of measurements was necessitated by the very low exoemission currents (10^{-17}—10^{-19} A). Almost every elementary act of the physicochemical process that caused charge emission was detected, when the coefficient of charge collection (electrons or ions) was close to unity.[5] Thus, the high sensitivity of exoemission methods made it possible to follow all specific features of the lattice dynamics, orientational transitions of the order—disorder type accompanied by charge emission, at the molecular level.

Results and Discussion

Low-temperature emission from a C_{60} sample. The results of measurements of exoemission current during cooling C_{60} to 77 K followed by heating in the first three testing cycles are presented in Fig. 1. The small peaks of emission current exceeding the background level are mainly observed in the processes of linear heating. During cooling in the second testing cycle (see Fig. 1, curve *1*), an increased emission level is observed in the 250—200 K and 160—130 K temperature ranges and at 77 K. More distinct bursts of the emission current are observed in the process of heating the sample in the 140—160 K temperature range (curves *2* and *3*).

The appearance of the emission peaks in one or another temperature range and their intensity depend on the pre-history of the sample. After certain number of cooling—heating testing cycles for the C_{60} samples, the intensity of the emission peaks reaches some maximum value. For example, in the fourth cycle, the intensity of the peaks on heating in the 150—160 K temperature range by one—two orders of magnitude exceeds their intensity in the first testing cycles (Fig. 2, *a*). The additional doubled emission peak appears in the range of T = 115—120 K, which is by two orders of magnitude higher than those presented in Fig. 1. The intensity of these and other peaks is low in the fifth testing cycle (see Fig. 1, T = 150—160, 230—270, 95, and 170 K).

The analysis of the experimental results shows that the most intense bursts of emission current on heating C_{60} samples from 77 K appear at the SPT temperatures.[1] Under normal conditions, C_{60} molecules form a molecular crystal with the face-centered cubic (FCC) lattice and retain rotational degrees of freedom. The energy of intermolecular interaction corresponding to these degrees of freedom is low, and this phase is always characterized by disorder. The first-order phase transition related to the fixation of orientations of individual clusters is observed at 255—250 K.[11—13] The observed

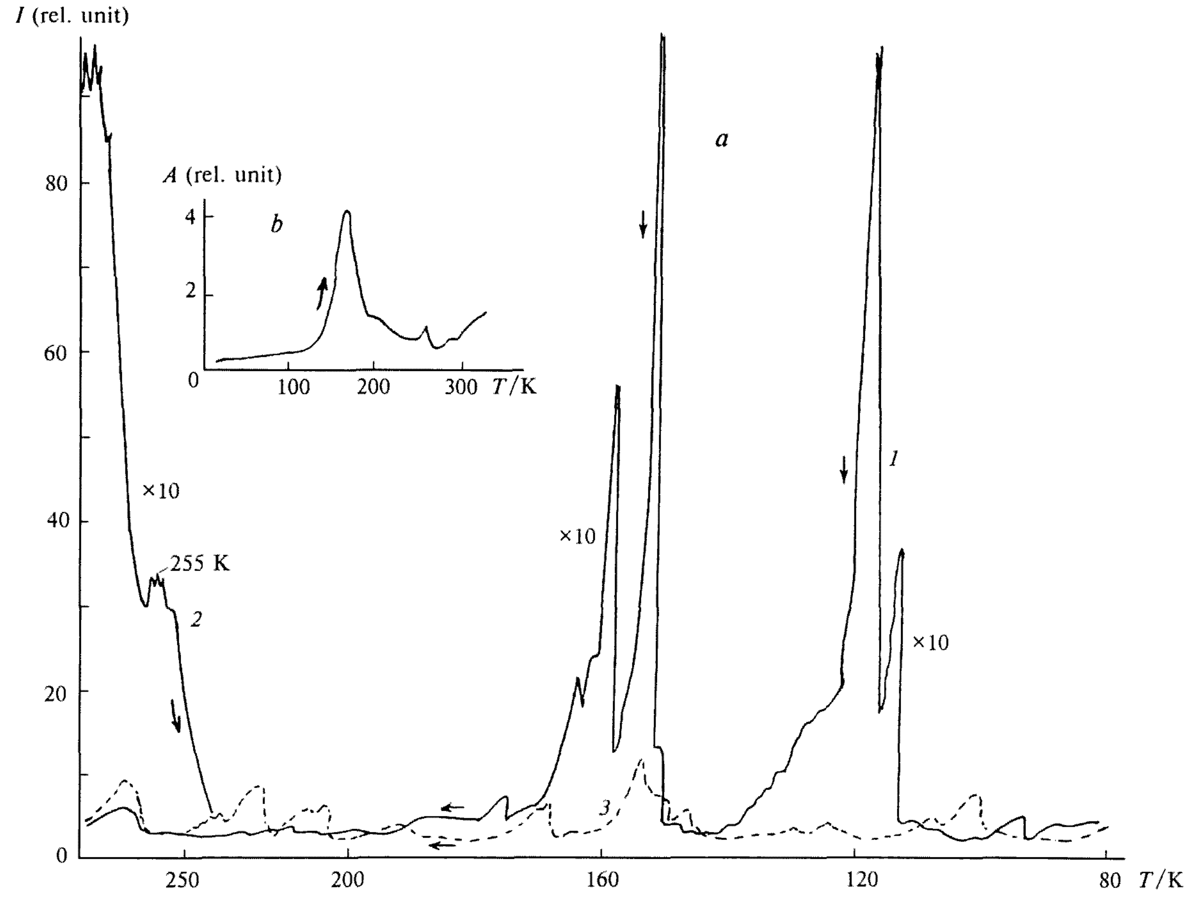

Fig. 2. *a*. Temperature dependence of the intensity of emission (*I*) from the C_{60} sample on heating from 77 to 293 K in the fourth testing cycle (*1*) and on cooling to 77 K (*2*) followed by heating to 293 K (*3*) in the fifth testing cycle. *b*. Temperature dependence of ultrasonic absorption (*A*) for C_{60} (Ref. 13).

shift in T_{max} is attributed to an increase in the heating rate. The anomalies in the heat conductivity[12] and acoustic parameters[13] as well as a decrease in the line width in the Raman spectrum[14] are observed at 250 K. According to the results of measurements of the specific heat conductivity (c_p) of the fullerite single crystal, the orientational transition takes place at 260.4 K on cooling and at 261.5 K on heating. The hysteresis on the temperature curve c_p in the heating—cooling cycles is also observed at $T < 240$ K. The orientational transition to the glassy state is identified at 100 K.[15]

The orientational phase transition, whose equilibrium temperature is equal to 256 K,[16] was determined in C_{60} by the DSC method. The blurred beginning of this transition at 190 K is related to the replacement of the jumpwise rotation of C_{60} molecules by isotropic rotation at ~100 K. When the C_{60} sample is heated from 77 K, only small bursts of emission current (T_{max} = 255 K, see Fig. 1, curve *4*) correspond to this phase transition. A small burst of emission current is also seen at 255 K (see Fig. 2, *a*, curve *2*) upon cooling against the background of the descending curve in the fifth testing cycle.

According to the data of ultrasonic absorption,[13] the SPT accompanied by the strains relaxation with the activation energy equal to 250 MeV (see Fig. 2, *b*) is observed at 160—190 K. There is a good correspondence between T_{max} of ultrasonic absorption and the emission current peaks observed in the 155—160 K temperature range. The sample behaves as a glass-like one in the range of T = 180 K.[13] Small bursts of emission current, which can reflect the beginning of the transition from the glass state to the crystalline one, appear near this temperature (T_{max} = 170 K) in curves *2*—*4* in Fig. 1 and in curves *1* and *2* in Fig. 2. The energy of slow relaxation (in this case, crystallization) is consumed to the release of weakly bonded electrons.

In the low-temperature phase with the primitive cube (PC) lattice ($T < 260$ K), the changes in the photoinduced conductivity with the peak at 150—160 K[17] are observed, which also testifies to structural anomalies or SPT at 155 K. It is assumed that this corresponds to the photoinduced redistribution of recombination centers.

In the fourth cycle of testing the C_{60} sample (see Fig. 2, *a*), intense bursts of emission current are dis-

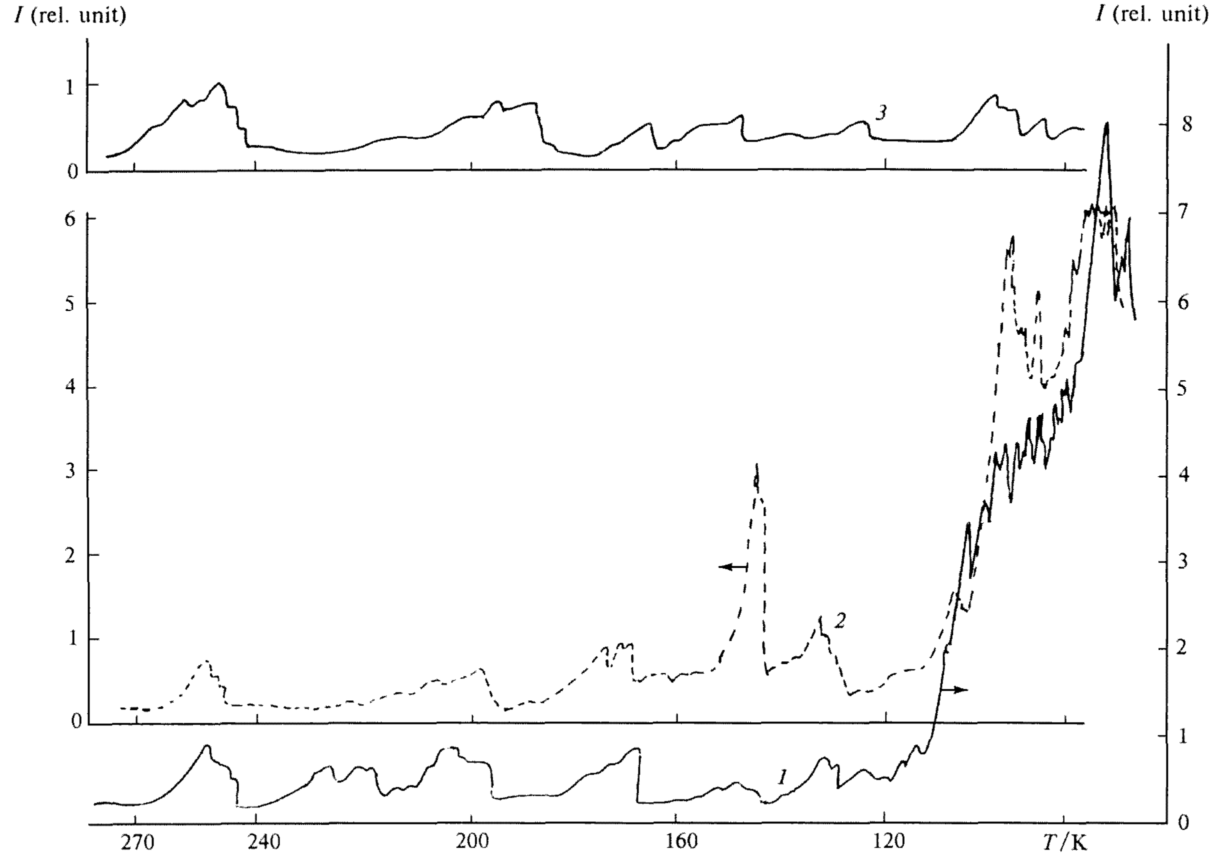

Fig. 3. Temperature dependence of the intensity of emission (*I*) from the sample of the C_{60}—C_{70} binary system on heating from 77 K in the first (*1*), second (*2*), and fifth (*3*) testing cycles.

tinctly manifested in the temperature ranges of the known SPT: on heating (at 155—160 and 270—280 K), characterizing disordering processes, and in the course of the subsequent cooling (at 280 and 255 K). The temperature maximum of the emission at 270—280 K coincides with the phase transition temperature (T_c = 284—286 K) determined for the given sample by the DSC method. The peculiarities of the changes in the form of the NMR signal for C_{60} at ~140 and 233 K have been described previously.[11] The latter temperature differs from that established by X-ray analysis (T = 249 K). Thus, various methods characterize various aspects of orientation SPT of the order—disorder type and provide both different and coincident temperatures of SPT.

It is likely that the peculiarities in the behavior of the heat conductivity of the C_{60} crystal at ~85 K[12] are also related to the strains relaxation. It is assumed that the time of appearance of excitations in response to the heat pulse at this temperature determines the measure of orientational disorder in the fullerite crystal. "Frozen" orientational disorder is retained within the whole temperature range below 85 K. The NMR spectra of fullerite exhibit a narrow signal against the background of the main broad line, which corresponds to rapidly rotating cluster; molecules "jump" between states with various orientations.[12] A small burst of emission current for C_{60} at ~77 K was observed on cooling in the second testing cycle (see Fig. 1, curve *1*). However, the emission current peaks at $T < 80$ K are manifested most distinctly for the C_{60}—C_{70} binary system, in which emission processes that accompany the structural rearrangement are considerably extended in time upon the temperature compression (see below).

The appearance of the most intense emission peak in the fourth testing cycle on heating the C_{60} sample in the 115—120 K temperature range should be especially mentioned. This peak corresponds to the SPT that has not been described in the literature. However, this phase transition can be a precursor of the SPT observed at 140 K by narrowing of NMR lines.[11] Thus, the low-temperature exoemission method makes it possible to detect SPT determined by other methods (T_c = 260, 140—160, and 85 K) as well as additional phase transitions that have not been established previously (T_c = 115—120 K).

Low-temperature emission from a sample of the C_{60}—C_{70} binary system. On cooling a C_{60}—C_{70} mixture, a sharp burst of emission current is observed only at T < 85 K. Unlike the C_{60} sample, for C_{60}—C_{70} the most intense bursts of emission current are observed in the first two testing cycles (Fig. 3, curves *1* and *2*). In addition to small maxima at 250 K related to the known[1] orientational transition in the C_{60} crystal, there are a lot of small

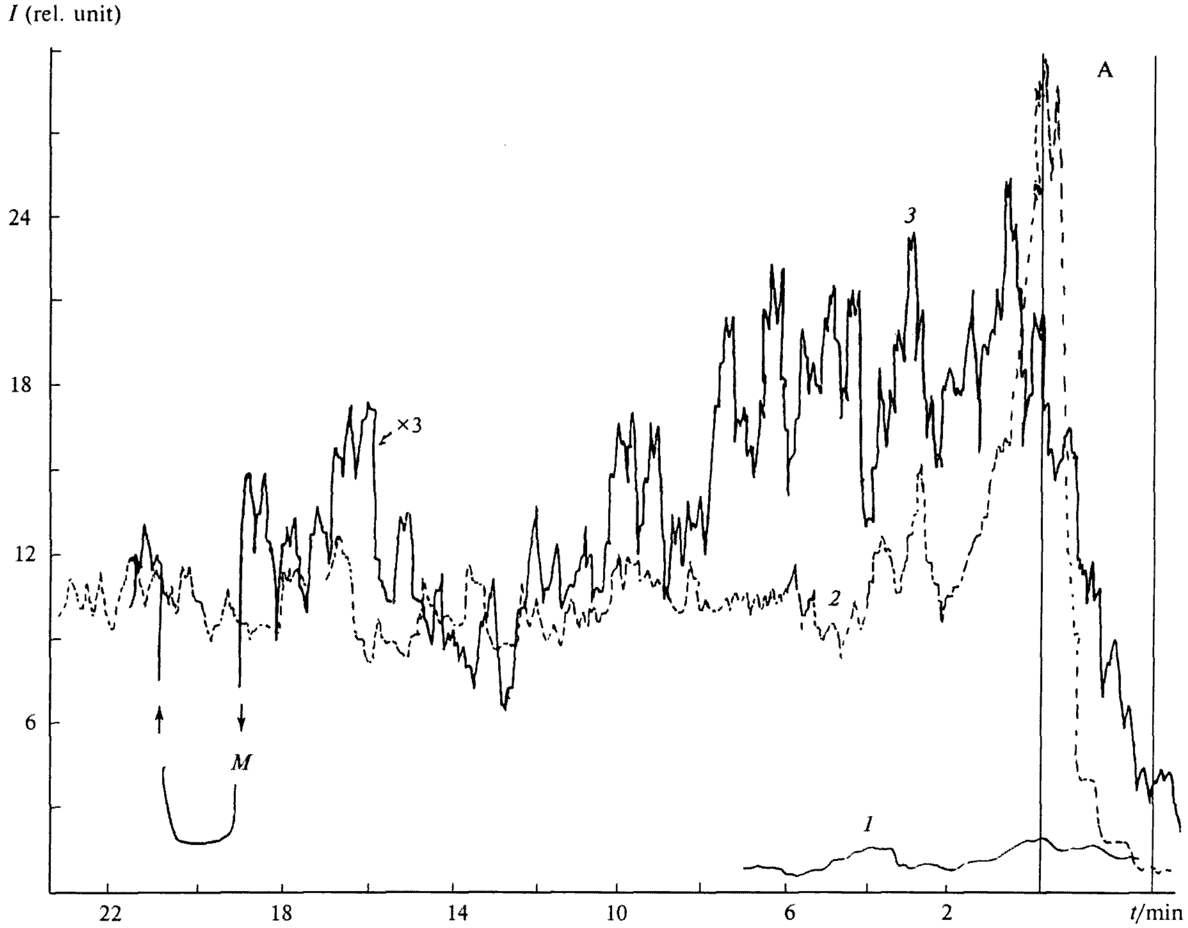

Fig. 4. Change in the intensity of emission (*I*) on cooling near 77 K followed by storage of the C_{60} (*1*) and C_{60}—C_{70} (*2, 3*) samples at this temperature in the first (*1, 2*) and third (*3*) testing cycles. *M* is the application of the electron-deflecting magnetic field. The regions of the curves restricted by the vertical lines (area A) correspond to linear cooling from 85 to 77 K.

intense peaks of emission current in the whole temperature range from 120 to 270 K. This testifies that multiple processes of structural rearrangement accompanied by disturbance of intermolecular bonds and ejection of weakly bonded electrons occur. In the second testing cycle, the emission current burst at 145 K is detected, which is close to that characteristic of C_{60} (see Fig. 1, curve *3*), established previously[11] by NMR spectroscopy.

Especially drastic differences in emission properties of the C_{60}—C_{70} binary system and fullerite C_{60} appear at $T < 120$ K (see Fig. 3, curves *1* and *2*). A decrease in the emission current on heating has a saw-tooth character and is accompanied by fluctuations in intensity. As a results of the thermocycling, when the structural rearrangement caused by the multiple temperature compression—expansion is mainly completed, the described sharp fluctuations of emission current disappear (see Fig. 3, curve *3*). Thus, unlike the results obtained for C_{60}, the number and intensity of emission peaks decrease monotonically as the number of testing cycles for the C_{60}—C_{70} mixture increases. After a prolonged (three weeks) relaxation (storage in a vacuum), no exoemission occurs in the sixth testing cycle neither on cooling nor upon subsequent heating.

The pattern of a sharp increase in emission current on cooling the mixture and the emission kinetics decrease during the storage of the sample at 77 K are presented in Fig. 4. It should be emphasized that emission currents and fluctuation phenomena increase near $T = 77$ K even in the first testing cycle and are observed only for the binary fullerite system. In the process of storage of this sample at 77 K, an increased (by one-two orders of magnitude) level of emission currents is retained for a long time (>30 min). A similar saw-tooth character of exoemission kinetic curves was observed for the low-temperature cycling, resulting in the fatigue rupture of polymeric and other composition and construction materials under the action of thermomechanical loading.[6] These fluctuations of exoemission currents (streamers) are typical of insulators in which charge separation caused by thermochemical loads results in phenomena of microbreakdowns.

The current fluctuations observed testify in favor of the dielectric character of the fullerite surface layer and recombination of oppositely charged microregions that appear in strained structures due to different electron affinities of C_{60} and C_{70} molecules. The processes of orientational disordering resulting in charge separation and formation of oppositely charged regions near adjacent fullerite molecules have been considered previously.[1] The slow relaxation of strains at 77 K results in their recombination and microbreakdowns in the dielectric surface layer. The intense electron emission slowly decaying in time can be due to the distortion of intermolecular bonds. Since symmetry and electron affinities of C_{60} and C_{70} molecules (2.65 and 2.72 eV, respectively) differ substantially, the appearance of microregions with different densities of localized electrons in the binary system (see Figs. 3 and 4) is more probable.

According to the NMR spectroscopy data, the "frozen" orientational disorder is retained in C_{60} fullerite at 85 K, and molecules "jump" rapidly between states with different orientations. It is also mentioned[1] that at $T < 100$ K crystalline fullerite forms one more phase with the face-centered crystal lattice, but the cell constant (24.4 Å) of this phase is twice as high as that for the high-temperature modification, and the basis of the elementary cell consists of eight orientationally nonequivalent molecules. According to our data, in the case of the C_{60}—C_{70} binary system, this phase transition is accompanied by the substantial rearrangement of the electron structure and release of electrons.

In the case of fullerite C_{60}, the sharp bursts of emission current at the SPT temperatures are observed only in the fourth testing cycle. An increase in the emission intensity as a result of thermomechanic loading is explained by the fatigue of the material, weakening and partial decomposition of intermolecular and intramolecular bonds. The activation effect of thermocycling is associated with the structural changes and accumulation of residual strains. Local cleavages of strained bonds are accompanied by the formation of weakly bound electrons, and the restoration of broken bonds accompanied by the energy release causes the charge emission. Similar phenomena of an increase in the emission in first testing cycles were observed for the low-temperature cycling of polymeric materials[6] and high-temperature superconductors.[18]

Unlike C_{60}, it is probable that in the case of the C_{60}—C_{70} binary system the material is decomposed along the weaker intermolecular bonds even in the first testing cycle and does not require preliminary thermomechanical action.

Let us consider the possible mechanism of exoemission in the low-temperature cycling of fullerites on the basis of the known[1—3] views about orientational SPT of the order—disorder type and on the physicochemical mechanism of exoemission.[4,5] The processes of orientational ordering are related to the electron density redistribution. The mobility of structural elements, including localized electrons, increase at the temperature of SPT (T_c). For example, it has been shown[1] that certain changes in the orientation of nonequivalent C_{60} molecules result in the contact of regions of adjacent molecules with maximum and minimum charge densities. Phase transitions affect substantially the transfer of charges localized on the fullerite surface. It has been established[19] that the stepwise increase the mobility of holes occurs below T_c in the range of 250—200 K. It is evident that the recombination of electrons and holes is the most probable near T_c. The energy of recombination of charges and distorted bonds is consumed to the release of localized electrons or weakly bonded ions. SPT can simultaneously result in the change in depths of electron traps, which occurs due to the relaxation of strained structures. The nature of electron traps is presently unclear. According to the physicochemical mechanism of the exoemission,[4] these are an increase in the mobility of charges and release of the relaxation energy (in the recombination of charges and broken bonds), which occur with the maximum probability in structural phase transitions, that are the reasons for the low-temperature emission of electrons and ions (exoemission).

Ion emission from a sample of the C_{60}—C_{70} binary system at high temperatures. After six testing cycles, the C_{60}—C_{70} sample was heated to ~550 K in the same cell used for detecting emission. "Spontaneous" emission of negative charges occurred on heating in the linear regime at 420 K. During the first heating (Fig. 5, curve *1*), the emission was accompanied by a decreased vacuum caused by the removal of residues of a solvent tightly bound to fullerite. The currents of ion emission are low ($\sim 10^{-17}$ A); therefore, the evaporation of fullerite hardly affects the dynamic vacuum (with continuous pumping). The emission intensity passes through a maximum in the range of ~470 K. It is established from the results of application of a transverse magnetic field that only negative ions are emitted at high temperatures in the first and second heating processes. The emission of C_{60}, C_{70}, and other ions in fullerene vapor has been observed previously[9] in the 800—900 K temperature range in the mass-spectrometric Knudsen cell. The high sensitivity of exoemission methods makes it possible to establish that the flow of molecules evaporating from the solid state contains negative ions at considerably lower temperatures. Preliminary low-temperature cycling (thermomechanical loads) can also facilitate a substantial decrease in the temperature of ion emission. The repeated heating (see Fig. 5, curve *2*) results in the bending of the emission intensity followed by its sharp increase, instead of the maximum of the emission intensity at ~470 K (see Fig. 5, curve *1*).

We suppose that the beginning of the emission of negative ions from the sample at $T > 420$ K is a precursor of one of the high-temperature phase transitions in fullerite, when the mobility of structural elements increases substantially. Most likely, this is the phase transition in C_{60} at $T = 557$ K.[20] In the work mentioned,[20] orientational phase transitions for C_{60} were observed at $T_c = 250$ and 557 K. The latter temperature

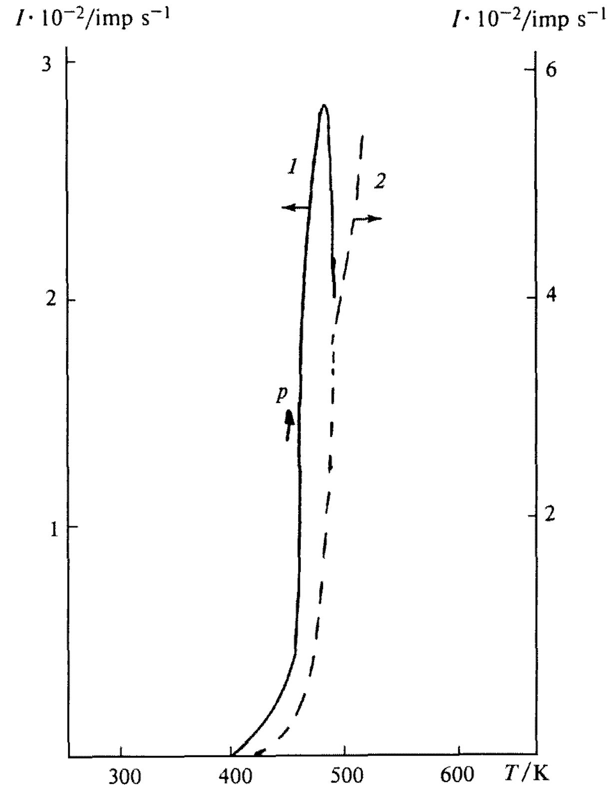

Fig. 5. Temperature dependence of the intensity of emission of negative ions (I) upon heating to 500 K the C_{60}—C_{70} sample that was preliminarily subjected to low-temperature cycling. Curves *1* and *2* are the first and second heatings, respectively; *p* is the increase in pressure in the system.

is close to $T = 530$ K corresponding to a sharp increase in the intensity of the ion current (see Fig. 5, curve *2*). The first-order phase transition has been established[21] for fullerite C_{70} at 280 K (the beginning of rotation of "long" axes, linear expansion by 0.8 % and compression by 0.2 % perpendicular and parallel to *c*-axes, respectively). Phase transitions were also established at 300 K (the beginning of precession of "long" axes) and 360 K (the complete orientation disordering accompanied by the compression of *c*-axes by 6 %). No ion emission was observed in these temperature ranges.[21]

Fullerite is a strong electron acceptor, and phase transitions affect charge transfer processes.[2] The regularities of low-temperature (77—293 K) and high-temperature (>420 K) emission found can be the direct experimental proof of this influence. Charge transfer processes are accompanied by their release from traps, whose depths change due to structural rearrangement in the course of SPT. The study performed shows that the emission current bursts induced by the low-temperature cycling coincide with SPT observed by other methods. According to the physicochemical mechanism of the exoemission,[5] the breakage of strained bonds and their recombination in the course of subsequent relaxation upon orientational disordering can be an energy source for low-temperature emission of electrons and ions in the fullerite samples considered.

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Received January 26, 1995;
in revised form April 28, 1995