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Radiative transitions in solid C_{60} under UV laser and VUV synchrotron radiation

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Photoluminescent properties of pure C_{60} thin solid films have been investigated in the emission range of 1.2–2.4 eV over a wide temperature interval under excitations with 3.7 and 36 eV photons. Dose dependence of the luminescence degradation of C_{60} films under long-time UV and VUV irradiation has been discovered and examined at various ambient conditions. Temperature dependence of luminescence from 10 to 300 K exhibited a step-like peculiarity in the vicinity of the structural phase transition near $T_c \sim 250$ K, and a decrease from 13 to 10 K. Also a C_{60} luminescence in the process of doping by neutral potassium atomic beam «in situ» at 400 K has been examined. The luminescence decay time measurements gave values of 1.2 ± 0.1 ns for a singlet excited state, and ~400 microseconds for a triplet state, the latter decays non-radiatively with a probability of more than 80%. The experimental data obtained lead us to a conclusion that the intrinsic nature of luminescence in solid C_{60}, correlates with the bulk properties which may be attributed, mainly, to self-trapped singlet excitons. The influence of the triplet state was also observable via protection against photopolymerization due to energy transfer from the excited triplet state of C_{60} to intercalated dioxygen.

1. Introduction

The efficient synthesis of pure C_{60} and the discovery of superconductivity in $T \approx 19$–30 K range in alkali metals–C_{60} compounds have stimulated further investigations of the structural and electronic properties of these materials.

The icosahedral C_{60} molecule has a closed cage structure, with the surface consisting of 12 five-membered carbon rings, separated by 20 benzenoid six-membered carbon rings. It possesses the highest symmetry of all the fullerene family, and, hence, the most high stability [1].

The presence of extended valence electron system provides an interesting experimental system for the study of electronic excitations [1]. The C_{60} molecules, forming a solid film, interact with each other by physical Van der Waals forces. Solid C_{60} provides an interesting example of a molecular semiconductor, in which both the intra-molecular and solid state effects are important [2].

The commonly observed wide photoluminescence band, peaked at 1.7 eV, is situated in the region of optical transparency of the crystal.

At present there are two interpretations of photoluminescence in solid C_{60}. The first one relates this phenomenon to defects either on surface, or on grain boundaries, which lead to the local distortion of the symmetrical molecule and to the increase in the radiative $t_{1u} \to h_u$ (LUMO-HOMO) transition probability, which is forbidden by parity for isolated C_{60} [3,4]. This assumption is confirmed experimentally by lower luminescence quantum yield for isolated C_{60} molecules in solutions, than in solids, and by some experimental results [3] that will be considered further.

The second model attributed the luminescence to localization of electronic excitations, self-trapped excitons, on the quasi-two-dimensional surface of the spinning C_{60} molecule [4]. This localization may be provided due to relatively weak π-bonds in the carbon chains of the C_{60} cluster, analogous to π-conjugated polymers [5].

Here we present new experimental data on photoinduced luminescence of solid C_{60}, including emission and absorption spectra, photoluminescence degradation under long-time irradiation, temperature dependence, ambient gas pressure influence on luminescence, photoluminescence quenching under doping «in situ» by neutral potassium atomic beam, and luminescence decay by using time-resolved spectroscopy.

2. Experimental procedure

The details of the experimental technique and sample preparation were reported elsewhere [6,7]. Thin solid 0.6–1 μ films of pure C_{60} on quartz substrate had no detectable C_{70} admixtures, up to the level of 1%.

The investigations of optical properties were carried out at two different experimental set-ups, by using different excitation methods.

1. The ultrahigh-vacuum set-up at the Kurchatov Institute, Moscow, was supplied with a liquid He cryostat, a pulsed N_2-laser (337 nm, 5 ns, 0,5 mJ per pulse, beam spot on the sample ~ 2 mm^2), and a special thermoemission source to produce a K^0 atomic beam [8] for «in situ» doping at 400 K. The detection system, including an analyzing monochromator and a photo-multiplier (PM) tube in a photon counting mode, allowed us to obtain spectra in the range of 1.2–2.4 eV, at temperatures from 80 to 400 K.

Photoluminescence of pure and potassium doped films, absorption spectra, dose dependence of luminescence, luminescence response to ambient gas pressure, and time-decay measurements of the integral intensity in a microsecond and a millisecond time scales were studied here. Simultaneously, sample resistivity measurements were performed in the photoluminescence versus intercalation experiments.

2. The undulator beamline BL3A1 at the synchrotron radiation (SR) source (UVSOR facility, IMS, Okazaki, Japan) was adjusted to the main harmonics with $E = 36 \pm 10$ eV, the photon flux on the sample reaching the value of ~ 10^{14} ph/s·mm^2, under the SR source current of 100 mA, and the beam spot area of about 1 mm^2.

The liquid helium (LHe) flow-type cryostat, supplied with necessary assemblies, provided a good temperature stability of samples in the interval of 10–300 K. The emission spectra were analyzed by HR-320 monochromator with different PM tubes, and registered by an electrometer.

Experiments on luminescence, dose dependence, temperature dependence over a wide temperature range, and decay time measurements were carried out here.

The decay time experiments were performed in the single-bunch mode, when the time interval between bunches was equal to 176 ns, and the bunch length did not exceed the value of 0.5 ns. The experimental technique included a fast discriminator, a Time-Amplitude Converter, a multi-channel analyzer, and a PM tube operating in a photon counting mode. Due to a low quantum yield of the luminescence, $\eta \approx 6 \cdot 10^{-4}$ at 30 K for solid film [9] under ~ 3 eV excitation, and a necessity to obtain enough number of counts per channel for taumetry measurements, we obtained only data on the integral intensity.

3. Results

The luminescence spectrum under the laser 3.7 eV excitation at 80 K is presented in Fig. 1, curve *A*. Besides a broad main peak at 1.67 eV, a vibronic structure of a C_{60} molecule was demonstrated on the low-energy side of the luminescence spectrum: a shoulder at 1.60 eV, a second peak at 1.50 eV, and a shoulder at 1.33 eV. The peculiarities at 1.50 eV and 1.33 eV were attributed to a totally symmetric pentagonal pinch mode, and 1.60 eV shoulder originated from non-totally symmetric modes, as manifestation of the Jahn-Teller effect.

The same vibronic structure was illustrated on the absorption spectrum on the curve *B*, from which one may deduce a band gap value of $E_g = 1.80$ eV. A similar picture has also been reported in Refs. 4, 10. The observed small absorption peak around 2 eV on the curve *B*, i.e., in the same position as in Ref. 9, was attributed to the $h_{1u} \to t_{1u}$, optically forbidden transition, perturbed by the crystalline surrounding. The first allowed $h_u \to t_{1g}$ transition (2.7 eV) was practi-

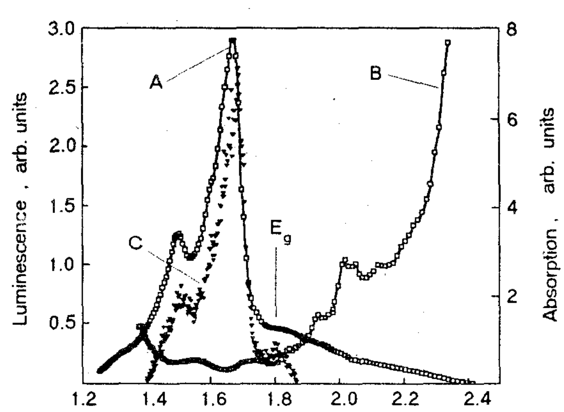

Fig. 1. Absorption (B) spectrum of solid C_{60} film and emission (A) spectrum under 3.7 eV laser excitation at 80 K. The emission (C) spectrum of the same film under 36 eV undulator excitation at 13 K.

cally undetectable for our film thickness, as well as $h_g + g_g \rightarrow t_{2u}$ (3,5 eV), and the other high energy transitions, up to 5.5 eV, reported in [9].

In addition to the luminescence bands mentioned above, we note a high energy broad emission at 1.8–2.4 eV, that has not been reported elsewhere. Its shape correlated with that of our absorption spectrum.

The curve *C* displays a photoluminescence spectrum of the same film under VUV undulator excitation at $E = 36$ eV and $T = 13$ K. The main luminescence bands on the curves *A* and *B* practically coincide, and agree with the results of other works [4,10]. Unfortunately, we could not make a definite conclusion about the presence of the similar band in the 1.8–2.4 eV region in the undulator experiments, due to the presence of the background luminescence.

A photoluminescence intensity degradation during long time irradiation, both by 3.7 eV and 36 eV photon beams, has been observed in all the experiments in ultra-high vacuum conditions. Almost no visual defects were observed under the microscope on the film surface after long-time irradiations. The measurements were made both for the main 1.67 eV emission peak, and for the integral intensity by using filters.

Figure 2 shows the luminescence degradation versus time due to long irradiation for three cases: of the integral spectrum (curve *1*) and of the main 1.67 eV (740 nm) peak (curve *2*) for undulator excitation at 13 K and the main 1.67 eV peak for laser excitation at 80 K (curve *3*).

The curves have the similar shape and can be decomposed on two exponents, «fast» and «slow», with the decay time values, respectively, ≈ 30 and ≈ 600 min for curves *1*, *2*, and ≈ 16 and ≈ 200 min for curve *3*. The curves *1* and *2* for the VUV excitation

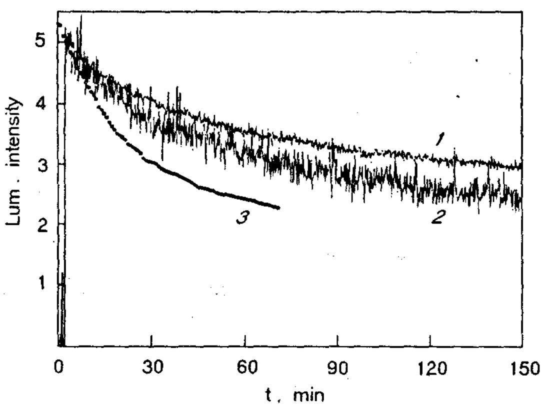

Fig. 2. The photoluminescence intensity degradation of C_{60} film under long time irradiation by the UV and VUV light: curve *1* — for the integral intensity, and curve *2* — for the main 1.67 eV peak under 36 eV excitation at 13 K; curve *3* — for the 1.67 eV main peak, under 3.7 eV excitation at 80 K.

are practically identical, obtained under a fluence of about 50 mJ/cm^2.

The curve *3* was obtained under the laser fluence of about 10 mJ/cm^2.

However, the films irradiated by UV laser excitation under «bad» vacuum conditions, at a residual gas pressure $\approx 10^{-3}$ Torr, displayed neither photoluminescence spectra change, nor any luminescence degradation either at 80 K, or at 300 K. We explain this phenomenon in terms of energy dissipation from excited C_{60} molecules, after $S_1 \rightarrow T_1$ intersystem transition, to the surface layer of adsorbed residual gases.

A similar effect of an energy transfer from the C_{60} excited triplet state to adsorbed molecular oxygen, resulting to a singlet state oxygen production, and $C_{60}O_2$ formation, has been reported in [11]. Those results displayed a small influence of evacuating air in luminescence, as in our case. Our additional photoluminescense measurements also confirmed the presence of the oxygen peak at 1 290 nm, resulting from the energy transfer from excited triplet state of C_{60} to adsorbed molecular oxygen [11]:

$$T_1(C_{60}) + {}^3\Sigma^-(O_2) \rightarrow S_0(C_{60}) + {}^1\Delta_g(O_2) \ .$$

Under «bad» vacuum conditions we did not find a noticeable quenching of photoluminescence due to $C_{60}O_2$ formation, because oxygen was likely adsorbed in the surface layer of C_{60} grain boundaries. The penetration depth of 3.7 eV photons was estimated to be about 0.1 μ, i.e., it, apparently, exceeded the depth of the surface layer with adsorbed O_2, and, therefore, the effect of partial luminescence degradation due to $C_{60}O_2$ admixtures would be miserable.

An experimental study of ambient gas pressure effect on luminescence spectra, carried out at 80 and 300 K, has also shown no observable spectral changes at different pressure values, from UHV up to 1 atm, and for different gases (air, nitrogen, krypton).

On the contrary, an interesting result on the luminescence intensity increase proportionally to a gas pressure in the experimental chamber according to the Langmuir formula has been reported in [3], the results being sensitive to the type of ambient gas. We think that this could depend on the porous structure of those slightly pressed powder samples that could possibly adsorb large amounts of gases, and cause certain photo-physical processes. Luminescence could be connected to gas adsorption at considerable depths comparable with the photon penetration depth, and lowering of the symmetry of the C_{60} molecules. The latter reduced the inhibition of the radiative transitions and enhanced photoluminescence with pressure, as was proposed by the authors.

Figure 3 shows the temperature dependence of the integral luminescence intensity under 36 eV photon

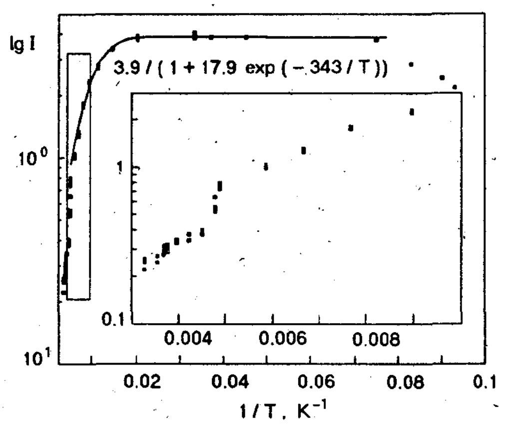

Fig. 3. The temperature dependence of the integral luminescence intensity from 10 to 300 K under 36 eV excitation. The inset shows a jump connected to the structural phase transition at ≈ 250 K.

excitation from 10 up to 300 K. The photon beam was switched on only during the short-time measurements, in order to exclude the influence of radiation dose dependence on photoluminescence. Let's consider a part of the spectrum located at T = 13–250 K. Assuming thermal quenching of photoluminescence, we used the well-known relation [10], assuming radiative and nonradiative decay channels:

$$I(t) = I_0[1 + \tau_0 K_n \exp(-E_a/kT)]^{-1} . \quad (1)$$

In this equation, I_0, τ_0 are the intensity and the decay time at the initial low-temperature region, respectively; E_a and K_n are the activation energy and the rate of the $S_1 \rightarrow T_1$ intersystem crossing, following after $S_0 \rightarrow S_n$ excitation, and subsequent $S_n \rightarrow S_1$ de-

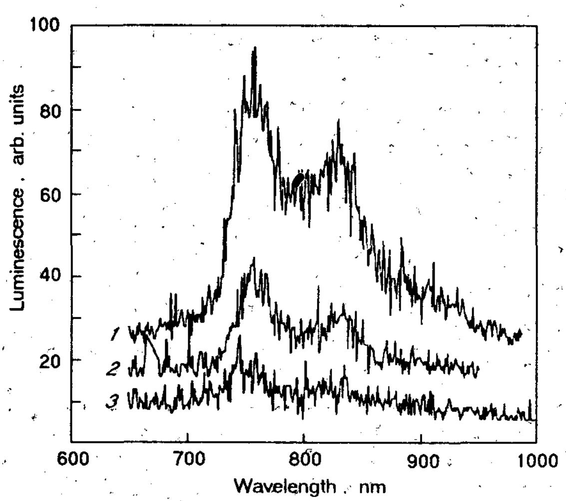

Fig. 4. The luminescence spectra of solid C_{60} film obtained in the process of doping by potassium atomic beam at 400 K. The doping level increases from curve *1* to curve *3* for pure C_{60} at ρ, Ohm·cm: $2.9\cdot10^5$ (*1*); $3.3\cdot10^4$ (*2*); $1.9\cdot10^3$ (*3*).

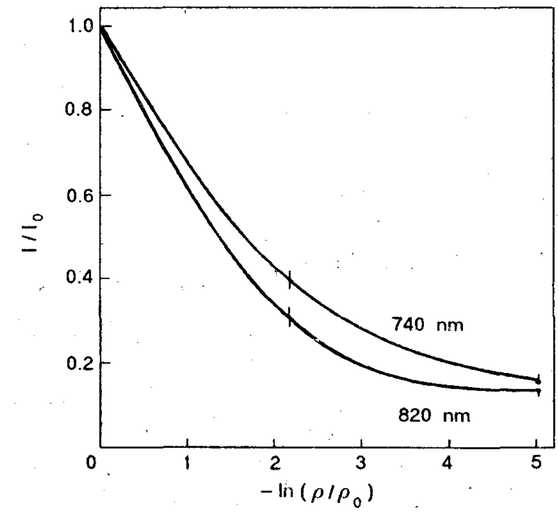

Fig. 5. The main 740 nm peak and the 820 nm peak luminescence versus the logarithmic resistivity for doped curves *2*, *3* in Fig. 4. All points are normalized to those for the undoped curve *1*.

excitation. The approximation of the experimental data by this formula gives the following parameter values: $\tau_0 K_n$ = 17.9 and E_a = 34.3 meV.

The second portion of the temperature dependence curve at 10 K < T < 13 K demonstrates the intensity decrease on further cooling.

The luminescence jump was observed near the temperature of the structural phase transition fcc → sc at ~ 250 K (see the inset in Fig. 3) within the temperature interval of about 10 K.

The luminescence spectra, obtained during the process of doping «in situ» by potassium atomic beam at T = 400 K under laser excitation, are displayed in Fig. 4 for three doping levels: the curve *1* — for pure C_{60}, curves *2*, *3* — for increasing doping levels. Figure 5 shows the main 1.67 eV (740 nm) peak, and the second, 1.50 eV (820 nm), peak luminescence versus resistivity dependences on doping, relative to the undoped C_{60} film (curve *1* in Fig. 4).

These systems gave the following results.

1) The doping procedure neither causes selective quenching of luminescence, nor gives rise to any new luminescence peak.

2) The doping concentration growth leads to a sample resistivity decrease and to a luminescence quenching. The almost full quenching was achieved at the resistivity value of $2\cdot10^3$ Ohm·cm (curve *3*). However, the resistivity versus temperature dependence, measured for this doping concentration (not shown), indicated that the sample was still remaining a semiconductor.

3) The luminescence peak intensity decreased much smaller, than the resistivity (see also Fig. 5): the curve *1* in Fig. 4 differs twofold by intensity from curve 2, while their resistivity differs by 10 times.

4) The cooling of doped samples from 400 to 80 K increased the luminescence, but to a lesser extent than for pure C_{60}, and without any noticeable changes in the spectrum shape (spectra not shown).

Time-resolved experiments on the integral luminescence intensity decay under the VUV undulator excitation ($E = 36$ eV) at $T = 13$ K, after subtracting the background emission, exhibited the presence of a single exponent in the decay curve, with the lifetime $\tau_0 = 1.2 \pm 0.1$ ns. The low quantum yield and the presence of unremovable stray light would not allow us to obtain better statistics for checking up the presence of more long exponents, comparable with the time interval of 176 ns between SR bunches. Of course, we could not measure microsecond or longer decay times here.

Our previous results [6] on laser-induced time-resolved integral luminescence decay curve, obtained with the same C_{60} film at 80 K by using microsecond techniques, indicated the presence of two exponents in the decay curve: 1) The main «fast» component, with the time constant less than 0.4 microsecond (limited by the instrument response time), occupied 80% of the maximum decay curve; 2) and the «slow» component, having ~ 400 microsecond decay time, occupied roughly not more than 20% of the amplitude.

4. Discussion

The electronic structure of solid C_{60} molecular crystal is known to be a semiconductor type, with an energy gap value scattering from 1.5 to 2.4 eV by different measurements [13, 14]. Our estimates in Fig. 1 (curve B) showed the value of $E_g = 1.80$ eV. The recent precise E_g measurements due to the temperature dependent microwave conductivity [14] gave the magnitude of 1.86 ± 0.1 eV for C_{60} and 1.57 ± 0.1 eV for C_{70}. Since the possible contamination by C_{70} in our case was estimated to be below 1%, we relate the absorption in the 1.8–3 eV region to the solid state effects. This assumption can also be confirmed by the results of [1,2], where the absorption in the region above 3 eV for isolated C_{60} molecule and for solid film differ insufficiently, while the absorption below 3 eV has been observed for solid C_{60} only.

The commonly observed wide photoluminescence band is located in the region of optical transparency of a crystal, with the Stokes shift value $E_g - E_0 \approx \approx 0.13$ eV. This confirms the vibronic relaxation of the emission center, if neutral excitations are responsible for luminescence. In addition, this is confirmed by the weakly pronounced vibronic structure of the curve A in Fig. 1. In addition, we propose a high energy wide-band structureless emission at 1.8–2.4 eV to be connected with recombination of holes and electron polarons at the «hot» stage of the relaxation, before self-trapping. This assumption can be confirmed by the experimentally observed transitions in the absorption spectra, such as $H_g + G_g \to T_{2u}$, $H_u \to H_g$, $H_g + G_g \to T_{1u}$, $H_u \to T_{1g}$, with energies from 5.5 to 2.7 eV [9].

The main luminescence peak at 1.67 eV may be attributed to a radiative decay of self-trapped exciton, as it was proposed in [3,4].

Dose dependence of photoluminescence degradation was obtained at two different excitation energies (at 3.7 eV and for 36 eV excitation with the very different optical penetration depth). Both dependences displayed rather similar results (Fig. 2). The process showed an irreversible character, and pointed towards a bulk nature, taking place within the penetration depth of the incident photon beam.

Note that our photoluminescence of polycrystals with worse quality (grain size ≈ 0.01 mm) than the used high quality single crystalline films, gave almost an order of magnitude lesser intensity, and did not exhibit the degradation effect. We consider, that this is due to oxygen diffusion deep into the grain boundaries and adsorption on defect sites of polycrystals, occuring even under evacuation, with subsequent quenching of luminescence by defects and $C_{60}O_2$ formations, as was mentioned above [11]. The pumping energy was transferred to these systems, without near-surface degradation of the samples.

The similar effect of the singlet O_2 photoluminescence intensity decrease in high quality C_{60} single crystals, exposed to O_2, in comparison with powders and polycrystalline films, was reported in [15]. The photoluminescence spectra varied only by intensity, which probably resulted from slower O_2 diffusion in high quality single crystals.

One of the known phenomena allowing the possibility of interpreting the photoluminescence degradation under UV or VUV irradiation may appear to be a photodimerization.

It was reported in [16,17] that a dimerization process may play an effective role in nonradiative transitions. This occurs via a «2 + 2 cycloaddition» photochemical reaction, breaking the double C = C bonds between hexagons in two adjacent excited C_{60} molecules, and reforming these bonds as a four-sided ring, thus changing the Van der Waals-type interactions between C_{60} molecules to the covalent C – C bonds. The photodimerization appeared to occur between one monomer in the first excited triplet state and the second monomer in the ground state. This mechanism could reduce the number of weak π-bonds in double-chains, possibly, responsible for radiative transitions. Therefore, one of the explanations of photoluminescence degradation under UV light may be attributed to the polymerization process.

Though this phenomenon may change the electronic structure, the absorption coefficient of a 36 eV photon remains practically unchanged, and is affected by excitation of the internal electronic shells. Since the photons are absorbed in a more than ≈ 10 nm layer, the long time irradiation decreases the number of double bonds in this layer, and thus eliminates the luminescence centers. As a result, the luminescence degradation occurs.

However, the Raman scattering results [16] indicated to a temperature threshold for the photopolymerizability at $T > T_c \approx 250$ K, when the freely spinning two molecules had a higher possibility of promoting the dimerization process. At 90 K $< T <$ 250 K two of the three rotational degrees of freedom are lost, and the molecules undergo an orientational hopping about the four specific (111) directions. At 90 K the molecules undergo a second transition to a merohedrally disorded glass phase.

It is also known that photoinduced polymerization and oxidation are initiated by excitations of electrons beyond the HOMO-LUMO gap [18], whose possible presence could be noticed due to the structureless 1.8–2.4 eV band of the luminescence spectrum in Fig. 1, curve *A*.

The observations of protection against photopolymerization due to intercalated dioxygen [16,18] also agree with our results on photoluminescence versus dose dependence for solid films upon letting some atmosphere into the experimental chamber, or for evacuated, but worse quality polycrystals, when the luminescence degradation practically disappeared, as has been reported earlier. The observations showed [18], that oxygen is stored in solid C_{60} in a molecular form, without chemical interactions with a C_{60} molecule.

The rate limiting polymerization process was found to be the photoexcitation of the excited singlet state [16], and the rate constant was proportional to the incident light flux. In this case we should have a single exponential photoluminescence decay with dose, or flux. Instead, a decrease in the decay rate with dose has been observed, and this dependence could be composed of two, fast and slow, exponentials, having, ≈ 30 min and the ≈ 600 min lifetimes, respectively. We believe that the fast component could be related to a photodimerization process, and the slow one could be related to an oxygen quenching of the photodimerization process.

In the thermal luminescence quenching equation (1), modeling the main part of the experimental curve in Fig. 3, the rate constant for the intersystem $S_1 \rightarrow T_1$ crossing corresponds to that of nonradiative relaxation K_n. Taking the experimental value for τ_0 and parameters from Eq. (1), one can deduce the value $K_n = 3.8 \cdot 10^{10}\ \mathrm{s}^{-1}$, which is close to the value $K_n = 3 \cdot 10^{10}\ \mathrm{s}^{-1}$ for free C_{60} molecules [19]. It is probably smaller, because we also observed the presence of the radiative channel in $T_1 \rightarrow S_0$ decay.

The photoluminescence decrease at low temperatures, from 13 to 10 K, seems to correlate with the experimentally detected freezing of rotational motion of C_{60} molecules at $T = 4.5$ K on a thin film by STM technique [20], which had been predicted previously in [13]. A similar behavior of luminescence may be attributed to the decrease in the formation of self-trapped excitons due to freezing of rotation of C_{60} molecules at LHe temperature, since, after this, the surface becomes 3-dimensional, instead of quasi-two-dimensional, and the self-trapping process becomes less probable. This effect requires further experimental study.

Freezing of rotation would decrease the polymerization probability at LHe temperature. This question can be roughly considered by comparison of the dose dependence curves *2* and *3* on the Fig. 2, obtained at 13 and 80 K, respectively. The curve *3* posesses fast and slow time constants which are half those for curve *2*. The laser-induced luminescence degradation looks more pronounced at 80 K, though the laser fluence was almost one fifth the undulator one (50 mJ/cm^2). We think the problem requires additional experiments to clarify this question.

The observed step-like jump of luminescence intensity in the region of 200–250 K we connect to the first-order structural phase transition from the fcc Bravais lattice sites structure, occupied by C_{60} molecules ($Fm3$, $a = 13.879$ Å), to the SC structure ($Pa3$, $a = 14.110$ Å) near $T_c \sim 250$ K. The intensity increase on cooling may be attributed to this transition, accompanied by an abrupt orientational ordering reconstruction in solid C_{60} from isotropic molecular rotation above T_c of nearly spherical C_{60} molecules, to uniaxil jump reorientations around the (111) axis between two nearly degenerated orientations separated by 60 degrees below T_c [13], with an activation barrier of 290 meV between them [27]. A corresponding abrupt decrease in the reorientational correlation time from $2 \cdot 10^{-9}$ to $9.2 \cdot 10^{-12}\ \mathrm{s}^{-1}$ may lead to an increase in probability of the relaxation of electronic excitations through rotational modes, thereby, decreasing the luminescence yield. Such a behavior of the luminescence intensity allows to conclude in favor of the intrinsic (bulk) nature of the luminescence in solid C_{60}.

The drop of luminesence can also be described in terms of E_a decrease from 34.3 meV at $T < T_c$ to 17 meV at $T > T_c$, i.e., the activation barrier for the

$S_1 \rightarrow T_1$ intersystem crossing decreases after the phase transition upon heating the sample.

A number of experiments display other peculiarities in the region of this phase transition.

1. A sharp electrical conductivity increase at 251 K was reported for C_{60} single crystal, the temperature range of the change being about 7 K [22]. The authors relate it to a phase transition from the merohedral twinning fcc structure to the orientationally ordered SC. The observed effect could be also interpreted by the disturbance for the free rotating C_{60} molecules by oxygen molecules adsorbed inside solid C_{60} [18].

2. A change of absorption spectra of a C_{60} crystal was observed near 260 K by using photoacoustic spectroscopy [23]. It was related to random rotations of molecules, resulting to the electronic structure changes, becoming similar to that of isolated cluster.

3. A dramatical decrease in the lifetime for singlet O_2 luminescence in solid C_{60} from 20 ms near T_c to 2 ms at 300 K, was reported in [15].

4. The frequency shift and linewidth reduction of Raman and IR bands near T_c in C_{60} single crystals was described in [24].

These peculiarities seem to be a manifestation of the same bulk process occuring near this phase transition.

Interstingly, we obtained a luminescence drop near $T_c \approx 250$ K, but found no peculiarities near the second phase transition at $T \approx 90$ K. The same picture was also observed in [15,24].

The temperature dependences in the other works differ in shape. For example, the curve in [25] displayed a constant decrease in photoluminescence from 28 up to 300 K, without discontinuities. Other authors obtained the maximum emission near 100 K [4,26], i.e., the second phase transition due to freezing of C_{60} molecule rotation, and their curves differ. We think that our temperature dependence was performed with a larger number of points, and under lower incident power than in all these works, which may be important at LHe temperature where quantum effects could be valid.

The luminescence quenching during the potassium intercalation (curves *4*, Fig. 5) occured in the range of two decades of resistivity changes, and photoluminescence signal appeared to be comparable with that of the noise, without any considerable spectral changes. We think these results correlate with those in [27] on optical density versus potassium doping of a thin film, when there was a little change in the shape of the spectra from pure C_{60} to the resistance minimum at K_3C_{60} after five decades of resistance changes.

Our intercalation experiments allowed us to draw some additional conclusions in favor of the nonradiative decay of electronic excitations, especially at the temperature of doping at 400 K. First, the nonproportionality of the luminescence quenching to the number of free carriers (see Fig. 5) indicates possible formation of additional quenching centers, such as K_3C_{60}.

The estimate of K_3C_{60} concentration for the almost quenched luminescence (see the curve *3* in Fig. 4), obtained from the resistivity versus doping level dependence [27], gives the value of $0.7 \cdot 10^{20}$ cm^{-3}, and hence, the distance between centers is about 20–40 Å. The most probable mechanism for luminescence quenching at such small distances may be a resonance energy transfer from the luminescence center, i.e., the exciton, to the quenching center by the Förster–Dexter mechanism [28]. This assumption is confirmed by the observations of $T_{1u} \rightarrow T_{1g}$(1.35 eV) and $H_{1u} \rightarrow T_{1u}$,(2.0 eV) transitions in [9], leading to increased adsorption with potassium doping in K_3C_{60} which is close to the energy band of the radiative transition in our doped C_{60}.

The lifetime of the singlet state lays in the interval from 0.65 ns to below 7 ns [25,29]. The results on C_{60} condensed media gave the value of 1.2 ns at LHe temperature [30], which is in excellent agreement with our singlet lifetime.

The decay time of the triplet state measured by different authors by the optical and EPR technique of C_{60} in solutions, varied from 40 to above 400 μs [31,32]. In polymer solutions the processes of triplet-triplet annihilation and ground state quenching cut short the triplet lifetimes [31,32]. Therefore, we think our triplet state decay time agrees with these results.

Both the singlet, 1.2 ns, and triplet 100–250 μs excited states of C_{60} in polymethyl metachrylate films were found at RT by using picosecond and nanosecond laser flash photolysis techniques [31].

In summary, our singlet and triplet radiative lifetimes agree with those of other works. One could also consider another possible mechanism for localization of excitons due to with a photo-dissociation under intense VUV-UV irradiation [33–35]:

$$C_{60} + \text{photon} \rightarrow C_{58} + C_2 . \qquad (2)$$

This multi-photon induced process may be two-staged, with structural transformation of the C_{60} icosahedral to less stable isomer, and subsequent ejection of the C_2 molecule off the deformed cluster [34,36]. Theoretical predictions gave the activation energy in the range of 11–13 eV, while experimental results displayed almost two-fold smaller values [34,35]. The process was observed in the microsecond time scale following multi-photon absorption under the fluence of 10–100 mJ/cm^2.

We think that in our case this process could occur rather for undulator 30 eV irradiation under the fluence of 50 mJ/cm^2, than for a 3.7 eV laser beam with fluence of 10 mJ/cm^2. But the delayed microsecond character of this two-stepped reaction would not give the possibility of detecting the undulator induced luminescence, if it is connected to radiative decay of excited C_{58} or C_2 molecules.

5. Conclusion

The observed photoluminescence demonstrates direct evidence for the formation of neutral excited states, which have a relatively efficient radiative decay channel at low temperatures. One should note a strong temperature dependence of the photoluminescence, including a peculiarity near the structural phase transition. We consider this to be an indication of the importance of solid-state effects. Temperature growth may lead to increase in the nonradiative decay probability through an incnease in exciton mobility and in the diffusion rate to defect sites. The experimental data allow us to conclude that the observed photoluminescence in solid C_{60} film is intrinsic, because its intensity correlates with the changes in the bulk properties. The wide luminescence band, the Stokes shift, the partial quenching of emission by doped potassium atoms, dose and temperature degradation of luminescence at $T < 13$ K, as well as the nanosecond decay time, indicate its connection, mainly, to self-trapped singlet excitons, with a small admixture of triplet radiative decay. The influence of the triplet state also manifests itself through the observations of protection against photopolymerization due to the energy transfer from excited triplet state of C_{60} to intercalated dioxygen.

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