# Nonlinear optical phenomena of fullerites

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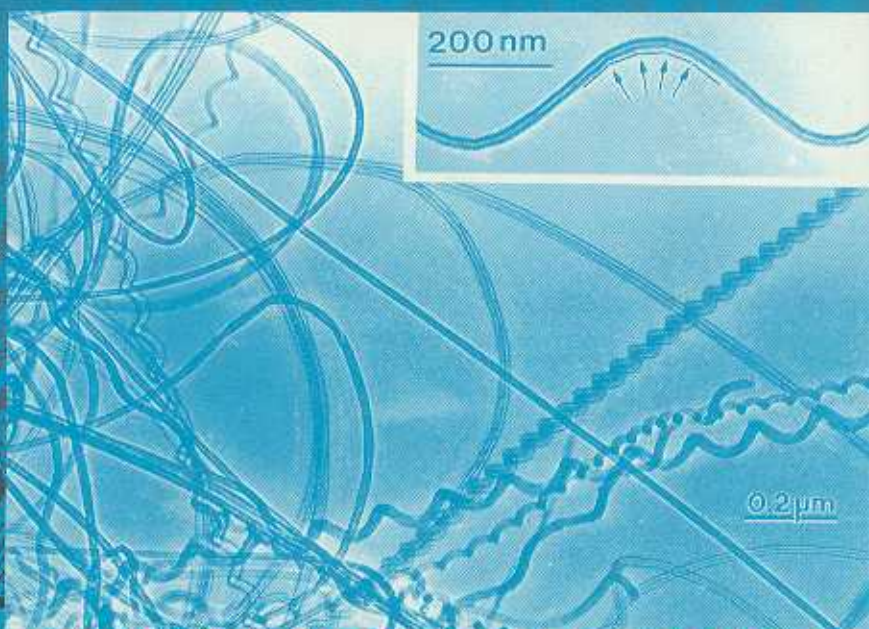National Academy of Sciences of Ukraine V. E…
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200 nm

0.2μm

0.2μm

# NONLINEAR OPTICAL PHENOMENA OF FULLERITES

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## Abstract

A nature of an intensive luminescence of fullerites caused by the creation of Frenkel's excitons is explained.

During the last years a number of papers [1-5] has appeared, in which the fullerites were investigated in the presence of an intensive electromagnetic field. Detailed experiments, carried out by the authors of Refs. [1,2], have shown that when exciting the crystals by weak fields there appears the luminescence band spreading according to a superlinear law with increasing density of the exciting radiation while the maximum shifts to the low frequency region.

The explanation of these facts given in Refs. [1,2], is based upon the technique developed for indirect band semiconductors (Ge, Si) [6], in which the luminescence of similar type was accounted for by the decay of excitons into e-h pairs and their condensation into the electron-hole liquid under the sufficiently large intensities of excitation. Such processes occur when the concentration of excitons, $N_{ex}$, satisfies the relation $N_{ex}a_{ex}^3 \leq 1$. For an exciton radius of $a_{ex} \sim 50 - 100 \AA$, typical for semiconductors, $N_{ex} \sim 10^{17} pairs/cm^3$. In this case, intensities of exciting radiation spread over the range from hundreds $KV/cm^2$ to $MV/cm^2$ [7].

The analysis of experimental results for fullerites has led the authors of Refs. [1,2] to the conclusion that using the same method as for indirect semiconductors one get very small radius of excitons, $a_{ex} = 3.5 \AA$, arising from the excitations in fullerites, i.e it has the same length as the fullerene molecule has. In other words, the excitons in fullerites are the Frenkel's excitons. The following estimations have been obtained in Refs. [1,2]: the critical (Mott's) exciton density should be $\sim 1.4 \cdot 10^{20} cm^{-3}$, while molecular density should be $\sim 3.6 \cdot 10^{20} cm^{-3}$. About 40% of molecules get excited, which is very surprising because the Mott's condensation takes place if the density of exciting radiation does not exceed hundreds of $V/cm^2$. By this reason, in Refs.[1,2] it was emphasised that the "semiconductor" model was used only qualitatively.

In our opinion such anomalous valyes are obtained because for the explanation of peculiarities in the emission spectra of a system of Frenkel excitons with a small

radius ($a_{ex} \approx 3.5 \AA$), the approach developed for a system of Wannier excitons having the radius of about a few tens of the lattice constant, was used.

In our short report we give the new results dealing with the contribution of high-order nonlinearities in the presence of absorption (and luminescence) in the exciton system in an intensive electromagnetic field.

The calculation of nonlinear susceptibility was carried out by using the Hamiltonian [7]

$$H = \sum_q \Omega_q a_q^+ a_q + \sum_k \Omega_k b_k^+ b_k + g \int P_o(x) P_o(x) P_o(x) P_o(x) d^3r - \int P_o(x) E_o(x) d^3r \quad (1)$$

$$x = (\vec{r}, t),$$

where $a_q^+$, $a_q$ and $b_k^+$, $b_k$ are the creation and annihilation Bose operators of excitons and phonons, respectively; $\Omega_q$, $q$ and $\Omega_k$, $k$ are the frequencies and the wave vectors of corresponding equations; $g$ is the exciton-exciton interactioin constant; $P_o(x)$ and $E_o(x)$ are the operators of the exciton and the phonon field, respectively [7].

The expression for nonlinear susceptibility obtained by using the nonequilibrium Keldysh diagram method [8], is expressed in terms of the Fourier component of the retarded Green function as follows

$$\chi(k\omega) = -G_E^R(k)[1 - \frac{g}{2} N(E) G_E^R(k)]^{-1}, \quad k = (\vec{k}, \omega), \quad (2)$$

where $G_E^R(k)$ is the retarded Green function of excitons, $N(E)$ is the function of exciton states density and the index $E$ indicates that both quantities are calculated in the presence of a strong electromagnetic field. The crystal nonlinear susceptibility $\chi(k, \omega)$ is expressed through the crystal parameters and the free photon density $N_k$. The function $N(E)$ is determined from the nonlinear integral equation

$$N(E) = i \int d^4k \frac{1}{2} (G_E^{+-}(k) + G_E^{-+}(k)) \left\{ [1 - \frac{1}{2} g N(E) G_E^R(k)]^2 \right\}^{-1}. \quad (3)$$

The self-energy part, $\Sigma_E^R(k)$ in the second-order approximation in the exciton-exciton interaction constant, $g$, can be given in a simple form

$$\Sigma_E^R(k) = \frac{3}{2} \left( \frac{g}{2} \right)^2 \int d^4q d^4q_1 d^4q_2 \left[ G_E^{-+}(q_2) + G_E^{+-}(q_2) \right] \delta(k - q - q_1 - q_2), \quad (4)$$

where $G_E^{+-}(k)$, $G_E^{-+}(k)$ are two of four Green functions introduced by Keldysh [8], proportional, in our case, to the density of field photons, $N_k$, and, hence, to the density of the exciting radiation intensity. This equation describes the lowest order term of the exciton-exciton scattering. The maximum of the band of exciton absorption decreases, becomes asymmetric, and at some threshold value of phonon density in a crystal near the red frequency edge of the exciton band, the region of amplification responsible for the intensive luminescence can appear. As the phonon density increases, the

amplification coefficient grows, i. e., the intensity of emission from the crystal becomes greater.

In Fig. 1 and in its inset the changes in the exciton spectra in the red frequency region with respect to $\omega_{ex}$ are shown (in Fig.1 we take $\omega_{ex}(k = 0) = 1$). As was noted above, the calculation of the nonlinear susceptibility, $\chi(k, \omega)$, the self-energetic part of Green function $\Sigma(k, \omega)$, defining the processes of absorption (and amplification), and the function $N(E)$ has been carried out in the lowest order in the exciton-exciton interaction constant, $g(\approx (gN_k)^2)$. The shape of the amplification band $(k(\omega) < 0)$ shown in Fig.1 correlates well enough with the one shown in Refs. [1,2] for small excitations $(\leq 30W/sm^3)$. But for sufficiently large exciting intensities $(\geq KW/sm^3)$ the luminescence band [1,2] becomes structural and shifts to the red frequency edge of the spectra.

Apparently, this experimental situation takes place at large values of the parameter $gN_k \approx 1$, when in theoretical calculations we cannot restrict ourselves by lowest order terms in series expansion of the pertubative theory. It is necessary to take into account the contribution of the terms of higher orders, i. e., to consider multiple quantum transitions. For large values of $g$ (which corresponds to a number of organic compounds) the intensive emmision from the fullerites, similar in nature to such nonlinear effects as the e-h condensation in semiconductors or the optical bistability, can occur under rather low intensities of incident radiation.

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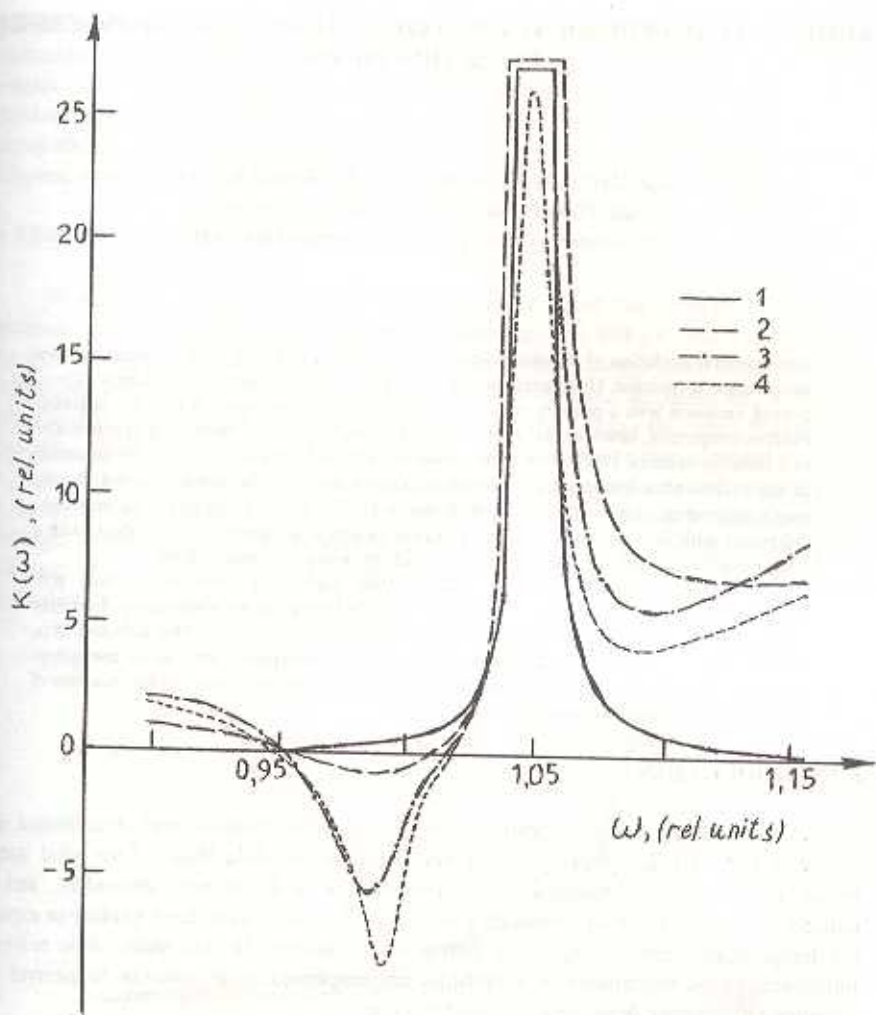8. L.V.Keldysh, Zh.Eksp.Teor.Fiz. **47** (1964) 1515.

Fig.1 The dependence of the exciton band shape on the intensity of exciting density $N_k = N_o$ (rel. units) and the emergence of a region with "negative absorption" Curve 1 - $N_o = 10$; curve 2 - $N_o = 1000$; curve 3 - $N_o = 3000$; curve 4 - $N_o = 5000$.