Self-excited oscillations of the exciton density and temperature in an impurity molecular crystal

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A model in which self-excited oscillations in the exciton-impurity system of a molecular crystal have been observed for the first time is proposed. This model has been tested experimentally.

In the present letter we will analyze a molecular crystal in which there are exciton capture centers. At low exciton densities the quantum yield of the exciton luminescence is approximately equal to unity and the principal mechanism by which energy is transferred from excitons to the lattice is the bimolecular annihilation. Exposure of a

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crystal to light causes the free excitons and excitons trapped in it to be distributed in a stable manner. A fluctuational increase in the temperature of the crystal causes the excitons to be ejected from the capture centers into the band and the bimolecular quenching rate to rise, further increasing the temperature. At certain values of the external parameters (pumping, temperature of the heat sink) the steady state may therefore become unstable and self-oscillations of the temperature and exciton density will occur in the system. In semiconductor crystals self-oscillations in an electron-exciton system were detected in another mechanism: in double light pumping and microwave pumping.[1]

The behavior of an exciton system of a thin molecular crystal, in which an external source accounts for a uniform exciton distribution in the volume is described by the equations

$$dn/dt = K - n/\tau - \gamma n^2 - 1/2\,\gamma_a n n^+ - \gamma_3 n n^- + \gamma_3 n^+ N e^{-\epsilon_l/T}, \tag{1}$$

$$dn^+/dt = -n^+/\tau_l - 1/2\,\gamma_a n n^+ + \gamma_3 n n^- - \gamma_3 n^+ N e^{-\epsilon_l/T}, \tag{2}$$

$$\alpha T^3 \frac{dT}{dt} = \epsilon_1 \gamma n^2 + \epsilon_2 \gamma_a n n^+ - \beta(T - T_i), \tag{3}$$

where K is the exciton production rate, n is the density of free excitons, n^+ is the density of trapped excitons, n^- is the number of trapping centers which are not occupied by excitons ($n^+ + n^- = n_1$ is the total concentration of trapping centers), γ is the constant of the annihilation of two free excitons, γ_a is the constant of the annihilation of a bound exciton and a free exciton, γ_3 is the constant of the trapping of an exciton at a trapping center, τ and τ_l are the lifetimes of respectively a free exciton and a bound exciton, ϵ_1 and ϵ_2 are the energies liberated as a result of the annihilation of two free excitons and a free exciton and bound exciton (in the case of small capture centers we have $\epsilon_1 \sim \epsilon_2$), ϵ_l is the depth of a trapping center, αT^3 is the heat capacity of the crystal, β is the coefficient of the heat transfer between the crystal and the heat sink, T_i is the temperature of the heat sink, and N is the number of molecules per unit volume of the crystal.

The singularities of the system (1)–(3) in the plane of the external parameters K and T_i are classified in Fig. 1 for a molecular crystal with the parameters characteristic of triplet excitons. In region 1 there is one unstable singularity (a focus or a nodal point). Self-oscillations are expected to occur in this region. In region 2 there are three singularities, two of which are stable. A bistable behavior of the system is expected to occur here. In region 3 one of the three singularities is stable.

The results of calculations show that the region in which oscillations occur expands with an increase in the parameters β and τ. An increase in the depth of a capture center, ϵ_l, causes the maximum temperature at which self-oscillations occur to increase, but the region in which they occur decreases. The frequency of the self-oscillations increases with increasing pumping.

For our experiments we chose a system of triplet excitons in deuterobenzophenone-d_{10} crystals with an admixture of benzophenone-h_{10}, which forms triplet capture

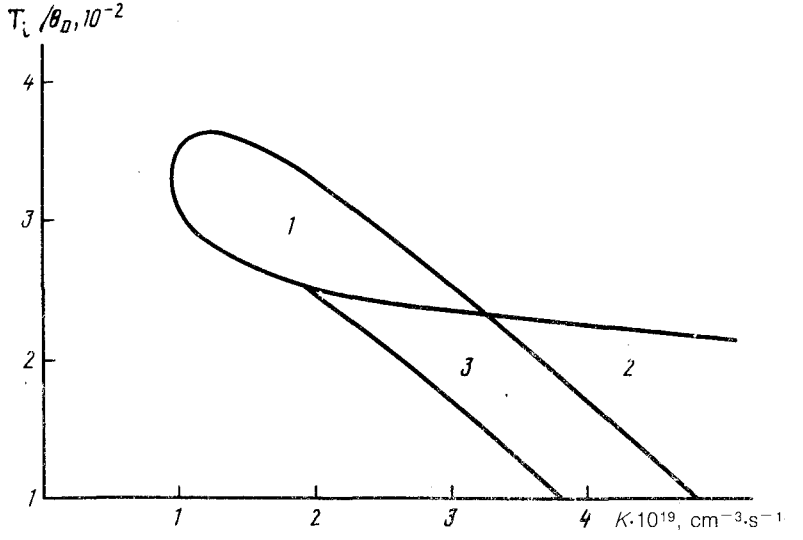

FIG. 1. The results of calculation of the region in which self-oscillations and bistability occur, plotted as a function of the pumping intensity and the heat-sink temperature. The following parameters were used in the calculations: $\tau = 2\times10^{-3}$ s^{-12}; $\tau_t/\tau = 5$; $\gamma = \gamma_a = \gamma_3 = 5\times10^{-13}$ cm^3/s; $\epsilon_t = 34$ cm^{-1}; $\epsilon_1 = \epsilon_2 = 22\,550$ cm^{-1}; $\alpha = 114$ erg/K^4 cm^3; $N = 4\times10^{21}$ cm^{-3}; the concentration of trapping centers is 5%, $\beta = 2\times10^{23}$ cm^{-3} s^{-1}.

centers of depth 34 cm^{-1}. The crystal is inserted into a helium cryostat with a temperature of the working volume in the range from 2.4 K to 4.2 K. The triplet excitons are excited by a high-pressure mercury-vapor lamp ($\lambda = 365$ nm) according to the scheme $S_0 \rightarrow S_1 \rightarrow T_1$. We measured the intensity of the integrated (with respect to the spectrum) phosphorescence of the crystal. The fraction of free excitons in it did not exceed 10^{-2}; the remaining part consisted of excitons trapped by isotopic trapping centers.

In the first series of experiments the sample was immersed in liquid helium. If the thickness of the sample containing the isotopic impurity is less than 0.1 mm, the phosphorescence intensity in the case of steady pumping undergoes periodic oscillations with a frequency of several hertz (Fig. 2). Oscillations set in when the pumping exceeds the threshold value (about 0.5 W/cm^2). With an increase in the pumping level, the oscillation frequency increases (the inset in Fig. 2), causing the periodicity of oscillations to be disrupted.

The following factors can be used as evidence showing that the model proposed above can be used to explain the observed oscillations: 1) The absence of self-oscillations in thick samples and in crystals without small trapping centers for triplet excitions; 2) the manifestation of oscillations in the form of dips in the phosphorescence intensity; 3) threshold nature of the onset of oscillations; 4) increase in the oscillation frequency with increasing pumping level; 5) the approximate equality of theoretical and experimental values of the frequencies ($\nu_{\text{theor}} = 10$–20 Hz, $\nu_{\text{exp}} = 4$–8 Hz). (It is now difficult to compare the frequencies exactly because of the absence of reliable data

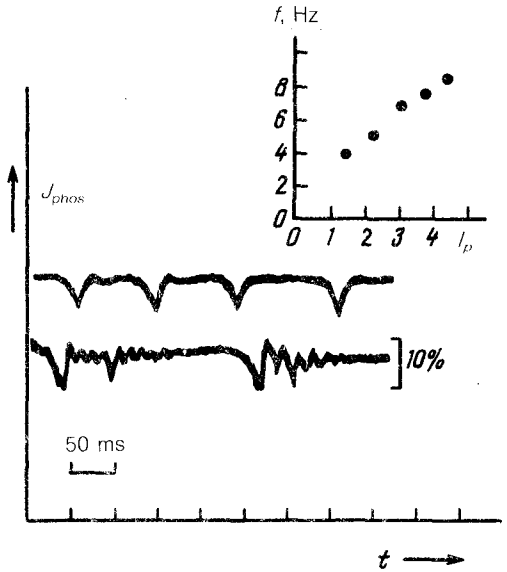

FIG. 2. Fluctuations in the intensity of phosphorescence of a deuterobenzophenone-d_{10} crystal in the case of steady pumping. Each sample contains 5% benzophenone-h_{10} impurity. The samples differ in shape.

on several parameters of the crystal, in particular, the parameter β.) These factors show that our explanation is better than other possible explanations which involve, for example, the regulation of the removal of heat from the crystal as a result of the formation of a gas film between the crystal and the liquid. Observations with a 20× magnification showed that there is no correlation between the oscillations and the

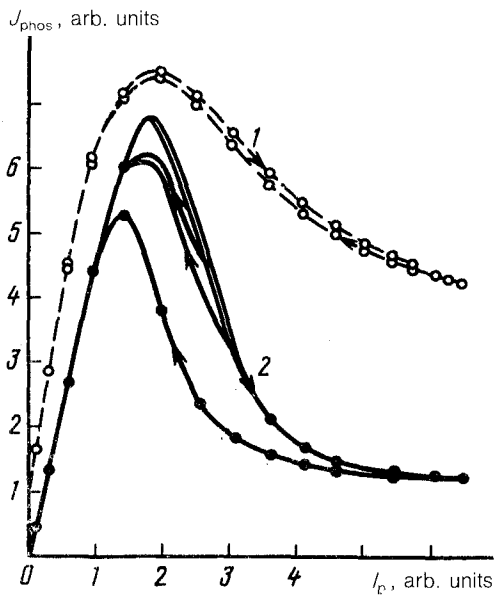

FIG. 3. Intensity of phosphorescence of a deuterobenzophenone crystal with 1% benzophenone impurity versus the pumping intensity at two temperatures of the heat sink: 1—4.20 K; 2—2.43 K.

nucleation of bubbles in helium boiling. The oscillations persist even when the flow of gas from the cryostat is cut off, causing the boiling to stop.

In the second series of experiments the crystal is placed in a gas above the liquid helium. The heat transfer from the crystal to the heat sink occurs slower in this case. Under a wide range of experimental conditions the dependence of the phosphorescence intensity J_{phos} on pumping I_p is found to be hysteretic in nature (Fig. 3), with the hysteresis loop expanding with decreasing temperature T_i. The hysteresis vanishes in a benzophenone sample with natural trapping centers which are not sensitive to the crystal temperature when it approaches 4.2 K. The hysteresis loop is situated on the downward slope of the $J_{\text{phos}}(I_p)$ curve in the region of pronounced nonlinearity.

The appearance of hysteresis can be attributed to the bistability of the system under consideration. There are, however, noticeable differences between the behavior of the $J_{\text{phos}}(I_p)$ curve obtained by us and the prediction of the model: Instead of a bistable loop, which is characterized for each I_p by no more than two stable states, we see a ferromagnetic hysteresis whose width of the loop decreases with decreasing pumping range. The upper branch of the loop is not completely stable: In it the signal contains an additional noise component (in Fig. 3 this situation is represented as a broadening of the corresponding part of curve 2). The particular features of the experimental curve probably stem from the nonuniformity of the optical pumping.

[1]B. M. Ashkinadze and A. V. Subashiev, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 284 (1987) [JETP Lett. **46**, 357 (1987)].

Translated by S. J. Amoretty