TWO-PHOTON EXCITATION OF THE LUMINESCENCE OF URANYL CRYSTALS BY A RUBY LASER

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TWO-PHOTON EXCITATION OF THE LUMINESCENCE OF URANYL CRYSTALS BY A RUBY LASER

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Two-photon excitation of luminescence was first observed in CaF_2:Eu^{2+} crystals by Kaiser and Garrett (^{1}). Subsequently, a series of studies was carried out on a number of semiconductor crystals (^{2}–^{5}). The purpose of these investigations was both to study the nature of two-photon excitation of luminescence and to explore the possibility of obtaining stimulated emission from crystals under powerful optical excitation. By the method of two-photon excitation it is possible to obtain stimulated emission in a shorter-wavelength region of the spectrum than that of the exciting light. A characteristic feature of this process is the excitation of the entire volume of thick samples, since the exciting light is only weakly absorbed.

It is of undoubted interest to extend such studies to a broad class of molecular crystals and, in particular, to crystals of uranyl complexes. Crystals of this class, as is known (^{5}–^{8}), possess an unusually high quantum yield of luminescence under one-photon excitation, and their spectra display a clearly expressed narrow-line vibronic structure. The latter circumstance is especially important to bear in mind in attempts to obtain stimulated emission, since at sufficiently low temperatures the vibrational level to which the laser transition occurs is practically unpopulated, which facilitates the creation of population inversion. An attempt to observe luminescence in a sodium uranyl acetate crystal, $NaUO_2Ac_3$, was made in (^{9}), but without a sufficiently distinct result. In these studies a ruby laser operating in the free-running regime was used, which led to relatively weak excitation. Therefore, to record the luminescence it was necessary to apply a series of exciting pulses, which destroyed the crystal and, apparently, distorted the true luminescence spectrum.

We investigated the luminescence of crystal hydrates of uranyl nitrate, $UO_2(NO_2)_2 \cdot 6H_2O$, uranyl acetate, $UO_2Ac_2 \cdot 2H_2O$, and $CsUO_2(NO_3)_3$, $K_2UO_2(SO_4)_2 \cdot 2H_2O$, and of their frozen solutions in EIA* under excitation by a ruby laser with modulated quality factor. Excitation was carried out in transmission, and the radiation of the crystal was recorded, with the aid of a system of crossed filters and an ISP-51 spectrograph, both photographically and photoelectrically.

The luminescence of single-crystal samples of the indicated compounds with thickness of the order of 2–3 mm was studied. The power density of the exciting light, using a short-focus lens with $f = 50$ mm, reached 80 MW/cm^2. Higher excitation densities led to destruction of the crystals.

Figure 1 presents a photograph of the spectrum of potassium uranyl sulfate crystals, recorded with a single pulse of the exciting light. The first, most intense line, 19,650 cm^{-1}, as is seen from the comparison spectrum, corresponds to the transition from the first excited electronic level to the first vibrational level of the ground state ($0'$—1). The resonance line ($0'$—0-transition), owing to strong reabsorption in the bulk of the sample, is practically not observed in the spectrum. The absence of substantial changes in the intensity distribution in the spectrum leads one to suppose that, under our conditions, no contribution from stimulated emission is observed.

This may be due to a number of reasons, the principal ones being the non-plane-parallel character of the samples studied, as well as insufficient power of the exciting light. Another reason may be nonlinear quenching of the luminescence of uranyl crystals (^{10}), arising at high concentrations of excited molecules.

Indeed, investigation of our samples under one-quantum excitation of "average" light power by means of an IFK-120 lamp showed the presence of nonlinear quenching of luminescence. For example, in potassium uranyl sulfate crystals at $T = 300$°K, when the intensity of the exciting light was changed by a factor of 10, τ of the sample changed from $2.3 \cdot 10^{-4}$ to $1.5 \cdot 10^{-4}$ sec. However, under more powerful laser excitation we did not find any further substantial shortening of τ.

Studies of two-photon excitation of the luminescence of uranyl nitrate and uranyl acetate crystals showed a significantly lower luminescence intensity, which could be recorded only with multiple excitation. The reasons for such a difference are apparently connected with the peculiarities of two-photon excitation or with a difference in the quantum yield of luminescence.

Several reasons can be conceived that lead to the appearance of luminescence of uranyl crystals upon excitation by ruby-laser light.

1. Stepwise excitation through an intermediate level located in the region of 1.78 eV (6943 Å). However, the existence of such an electronic level in uranyl crystals is unknown. One could assume the presence, in this region, of weak triplet absorption in uranyl crystals, which may lead both to stepwise excitation of luminescence and to triplet-triplet annihilation (^{11}).

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* Ether—isopentane—ethanol in a volume ratio of 5 : 5 : 2.

However, our investigation of the two-quantum excitation of frozen solutions of these compounds, where diffusion of triplet molecules is hindered, in the presence and in the absence of oxygen (which quenches the triplet state), showed the presence of diffuse luminescence spectra characteristic of uranyl solutions. These experiments indicate the absence of the hypothetical triplet level.

2. Excitation of the luminescence of uranyl crystals by the second harmonic of the ruby laser. Indeed, for example, uranyl nitrate crystals, by their structure, allow the existence of this process, since they are piezoelectrics and therefore lack a center of inversion. However, we did not succeed in observing any substantial difference in luminescence intensity under two-photon excitation along different crystallographic directions. Moreover, the luminescence observed in solutions also argues against this mechanism, although the possibility of the occurrence of the second harmonic in an isolated molecule is not excluded ([12]).

3. We believe that the luminescence of uranyl crystals and frozen liquids observed by us is connected with the process of two-photon absorption of laser light through a virtual level. It appears promising to carry out similar experiments on specially treated crystals under more powerful excitation, with the aim of obtaining generation in a potassium uranyl sulfate crystal with wavelength $\lambda = 5111$ Å, corresponding to the $0'$—1-transition ($T = 77^{\circ}$K).

It should be noted that generation in uranyl crystals should possess an extraordinary spectral narrowness compared with generation by

Fig. 1. a—luminescence spectrum of $K_2(UO_2)(SO_4)_2 \cdot 2H_2O$ upon excitation by a ruby laser, $T = 77^{\circ}$K; b, c—luminescence spectrum of the same sample at $\lambda_{\text{exc}} = 366$ mμ; $T = 77^{\circ}$K.

Fig. 2. a—generation spectrum of CdS upon excitation by a ruby laser, $T = 77^{\circ}$K; b, c—luminescence spectrum of the same sample at $\lambda_{\text{exc}} = 366$ mμ; $T = 77^{\circ}$K.

semiconductor crystals of the CdS type with optical pumping. Similar experiments carried out by us on these crystals show in the generation spectrum (Fig. 2) relatively broad bands corresponding to the generation of free excitons with the simultaneous creation of longitudinal optical phonons. The width of the spectrum of this generation is determined by the excess of gain over losses:

$$\alpha_y - \alpha_\pi \sim (\nu - \nu_{\text{e}} + \nu_\phi)^{3/2} \left[\varphi(J,T) e^{-E_{\text{kin}}/kT} - n(T)\right],$$

where ν_{e} is the frequency of the exciton transition; ν_ϕ is the frequency of a longitudinal optical phonon; $\varphi(J,T)$ is a certain function of temperature and pumping level; E_{kin} is the kinetic energy of the exciton; $n(T)$ is the mean number of optical phonons.

Analysis of this expression shows that as the pumping intensity is increased, the generation spectrum broadens and the maximum shifts to the short-wavelength side of the spectrum.

In uranyl crystals, owing to the narrowness of the luminescence lines, in contrast to semiconductor crystals one should expect narrow-line generation, especially at helium temperatures.

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Note added in proof. In studying single crystals of $CsUO_2(NO_3)_3$ excited by a ruby laser, along with the luminescence spectrum we have found stimulated combination scattering (SCS). In the SCS spectrum 4 anti-Stokes lines and 2 Stokes lines are observed (the photographic materials used are insensitive to the infrared region of the spectrum). The corresponding vibration $\nu_{\text{SCS}} = 876 \pm 2\ \text{cm}^{-1}$ can be compared with the totally symmetric vibration of the ${UO_2}^{++}$ ion, $\nu_s = 884 \pm 2\ \text{cm}^{-1}$, determined from the electronic-vibrational luminescence spectrum. The clearly manifested difference in the frequencies ν_{SCS} and ν_s is possibly associated with the smallness of the wave vector k for the vibrations participating in SCS, since the latter is observed at small angles to the exciting light.

It should be noted that the SCS arising in $CsUO_2(NO_3)_3$ crystals is a competing process that hinders the occurrence of stimulated-radiation generation on the electronic-vibrational transition.

Note: Figure translations are in progress. See original paper for figures.

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