# Luminescence of NaCl under intense excitation of excitons by a vacuum-ultraviolet $H_2$ laser

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We report, for the first time, the use of a vacuum-ultraviolet $H_2$ laser ($\lambda = 1610$ Å) for resonant excitation of excitons of high density ($\sim 10^{19}$ cm$^{-3}$) in NaCl, as well as observation of a photoluminescence band with a maximum at $5.23 \pm 0.03$ eV, which is ascribed to radiative annihilation of an autolocalized biexciton.

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1. The development of a vacuum-ultraviolet $H_2$ laser suitable for use in physical experiments[1] offers a possibility of intense resonant excitation of lines in broad-band materials, and in particular alkali-halide crystals. We have investigated the luminescence of NaCl crystals, for which the $H_2$ laser radiation falls in the absorption band of the lower exciton level $1S_{3/2}$.

2. The NaCl crystals were excited with an $H_2$ laser whose spectrum consisted of ~10 closely lying lines in the region of 7.7 eV (1610 Å), the laser pulse energy was ~10 μJ, its duration 0.5 nsec, its repetition frequency 10 Hz, and the beam divergence 1°. The laser radiation was focused on an area measuring $0.5 \times 4$ mm on the polished surface of a NaCl crystal cooled with liquid nitrogen. The luminescence of the crystal was registered in the wavelength region ~2000 Å with a VMS-1 monochromator and a photomultiplier, with a time resolution 40 nsec. The luminescence quantum yield was estimated by comparing the NaCl luminescence intensity with that of ZnS crystals having a known quantum yield. Luminescence with a quantum yield less than 0.1% could not be registered because of the background. The crystal temperature was measured with a calibrated thermocouple fastened to the crystal. We used crystals having no noticeable absorption bands in the region 2000—3000 Å.

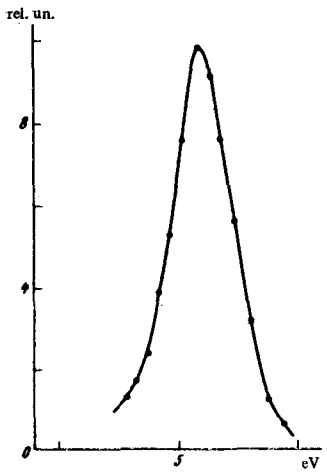


FIG. 1. Luminescence spectrum of NaCl crystal ($T = 100$ °K) following excitation with $H_2$ laser radiation at $h\nu = 7.7$ eV ($\lambda = 1610$ Å).

3. Laser excitation produced in the luminescence spectrum of NaCl at 100 °K a band with a maximum in the region of $5.23 \pm 0.03$ eV (2360 Å), an approximate quantum yield 0.2, and a spectral width 0.53 eV (250 Å) (Fig. 1). The luminescence duration of this band did not exceed the resolution time (40 nsec). No other luminescence band with a quantum yield larger than 0.5% was observed. With increasing temperature, starting with $T = 150$ °K, an abrupt decrease of the luminescence intensity was observed (Fig. 2). At room temperature, weak luminescence is observed in the region of 2.8 eV (4400 Å), with a quantum yield ~0.3%.

4. The observed 5.23-eV luminescence band does not agree with any of the luminescence bands of NaCl at low excitation intensities, and can be ascribed to radiative annihilation of molecular complexes that are autolocalized by excitons and are produced when the excitons collide with one another. At a low excitation intensity the NaCl luminescence spectrum consists of two bands, a σ band at 5.47 eV with a short de-excitation time $\tau = 5 \times 10^{-9}$ sec, and a π band at 3.47 eV with a de-excitation time $\tau = 3 \times 10^{-4}$ sec[2,3]; these bands are connected with radiative annihilation of autolocalized excitons of type σ and π. Figure 3 shows the luminescence scheme and the level structure of the autolocalized excitons in NaCl, calculated on the basis of the model previously employed[4] to explain the mechanism of the luminescence of crystalline xenon. The appearance, at high excitation intensity, of one rather than two bands,

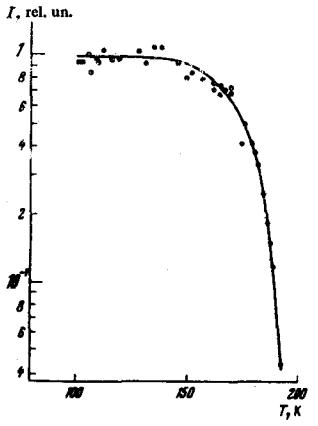


FIG. 2. Temperature dependence of the NaCl luminescence intensity in the 5.23 eV band.

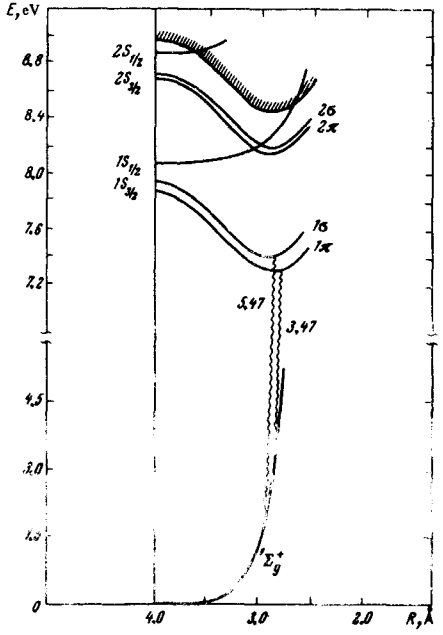


FIG. 3. Structure of the potential curves of autolocalized excitons and luminescence scheme in NaCl.

with a short de-excitation time and shifted 0.24 eV towards the long-wave side of the emission band of the 1σ autolocalized exciton, can be attributed to the formation of autolocalized biexcitons, the energy level of which lies below the energy levels of the 1π and 1σ excitons. According to[5], the biexciton binding energy, in the limit of a small ratio of the effective mass of the electron to the mass of the hole, is $G_B = 0.298 G_{ex}$, where $G_{ex}$ is the exciton binding energy, and amounts to $G_B \approx 0.3$ eV for NaCl, which greatly exceeds the distance between the energy levels of the 1π and 1σ excitons (~ 0.04 eV), and is close to the observed 0.24-eV shift.

We note that the 5.23-eV luminescence band observed by us coincides within the limits of errors with the 5.26-eV luminescence band observed in[6] in NaCl crystals intensely excited by a beam of fast electrons. The shorter luminescence de-excitation time in comparison with the known de-excitation times of the σ and π bands of the autolocalized excitons, observed in[6], agrees with our interpreation that the 5.23-eV band is of biexciton origin, since the binding of an exciton into a biexciton greatly increases the probability of its radiative recombination.[7]

Autolocalized biexcitons can be produced in collisions between a free and an autolocalized exciton or between two free excitons, followed by autolocalization of the exciton. This process should lead to a change in the edge-luminescence spectrum[8] at high exciton densities. The emission of autolocalized excitons and biexcitons in alkali-halide crystals can be used also to obtain lasing in the ultraviolet region of the spectrum. We note that in the described method of resonant excitation of excitons in NaCl with an $H_2$ laser, where the density of the free excitons reaches $5 \times 10^{19}$ cm$^{-3}$, induced emission of ~ 6.9-eV quanta is possible in inelastic collisions of free excitons with one another, accompanied by ionization of one of the excitons.


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