TWO-PHOTON ABSORPTION IN A CaF$_2$:Ho^{3+} CRYSTAL

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B. V. ERSHOV, Yu. P. PIMENOV, Academician A. M. PROKHOROV,
V. B. FEDOROV

TWO-PHOTON ABSORPTION IN A CaF_2:Ho^{3+} CRYSTAL

The use of lasers as light sources makes it possible to observe effects of multiquantum absorption in matter. Two-photon absorption in ionic crystals was first observed by Kaiser and Garrett ([1]). The authors observed two-quantum absorption of ruby-laser light in a broad (about 5000 cm^{-1}) absorption band of the divalent europium ion Eu^{2+} in a CaF_2 fluorite lattice. Along with this, it is of interest to investigate two-photon absorption for trivalent rare-earth ions Re^{3+}. For Re^{3+} ions, one-quantum electric-dipole transitions in the optical wavelength range are forbidden by parity. The prohibition is removed only by the crystalline field. Therefore the energy levels have a considerably smaller width ($\sim 100 \div 300$ cm^{-1}) than the energy levels of divalent Re^{2+} ions. At the same time, two-photon electric-dipole transitions in the optical range are parity-allowed. Both these circumstances make it possible to hope to detect intense two-photon absorption in crystals doped with trivalent rare-earth ions and make these crystals an interesting object of investigation from the standpoint of solving the problem of the two-photon laser ([2,3]).

As the object of our investigation we chose a fluorite crystal CaF_2 doped with trivalent holmium Ho^{3+}. This crystal had previously been studied at our institute in work ([4]). It was found that the Ho^{3+} ion in the fluorite lattice possesses intense green luminescence in the region 5400–5500 Å. At liquid-nitrogen temperature, induced emission was obtained at a wavelength of 5512 Å.

Experiments on two-photon absorption were carried out according to a scheme analogous to that in work ([1]). Two-photon absorption of the source light caused excitation of one of the energy levels of the Ho^{3+} ion. Then, as a result of nonradiative energy transfer to the $^5S_2$ level, green luminescence arose, which was used to indicate the effect of two-photon absorption.

As light sources we used lasers on ruby (light quantum 14 400 cm^{-1}) and on neodymium glass (quantum 9430 cm^{-1}). Both lasers had resonators made of plane mirrors and operated in a “spiking”regime. The samples studied were cylindrical fluorite crystals CaF_2 doped with trivalent holmium Ho^{3+}. The diameter of the samples was 1 cm, the length 4–5 cm. The holmium concentration was 0.3 wt.%. The sample could be illuminated simultaneously by two lasers. The

Fig. 1. Spectrum of one-quantum absorption of the Ho^{3+} ion in the CaF_2 lattice.

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laser pulses could be delayed relative to one another by up to 10^{-3} sec. The light of the green luminescence excited by the lasers in the CaF_2:Ho^{3+} crystal passed through a monochromator to a receiver consisting of an FEU-14B photomultiplier and an S-29 oscilloscope with a storage device for recording oscillograms. In the course of the experiment, oscillograms of several processes were recorded successively on the S-29 screen and then photographed. The linearity of the receiver was checked. The laser pulses were oscillographed by means of an FSK-G1 photoresistor. The large time constant of the photoresistor ($\sim 2 \cdot 10^{-4}$ sec) did not allow the spiking ···

the character of the generation, but did not distort the shape of the envelope of the generation pulse. During the measurements, the stability of the generation level of the lasers was monitored over a series of successive flashes. This made it possible to compare experiments carried out successively in time.

In the experiments performed, two-photon absorption of neodymium-laser light (9430 cm^{-1}) and ruby-laser light (14400 cm^{-1}) was found, and a two-photon transition with absorption of two different quanta with frequencies 14400 and 9430 cm^{-1} was also found under simultaneous illumination of the specimen by neodymium- and ruby-laser light. The experimental results are presented in Figs. 1 and 2.

Fig. 1. Spectrum of one-quantum absorption of the Ho^{3+} ion in the CaF_2 lattice. $T = 300°K$, specimen length 25.5 mm

Figure 1 shows the spectrum of one-photon absorption of the Ho^{3+} ion in the CaF_2 lattice, recorded in the range from 4100 to 30000 cm^{-1}. The classification of the levels is given in accordance with the review article ([5]). To check the spectrograph scale, the positions of three mercury lines are given. It is evident from Fig. 1 that two-photon absorption of neodymium-laser light occurs in the same band from which green luminescence is observed. However, this is not quite so. According to the level scheme of the Ho^{3+} ion in Fig. 8 of Ref. ([5]), the "green" band is formed by two terms: the metastable level $^5S_2$ and the level $^5F_4$. Comparison of the absorption spectrum of $CaF_2 : Ho^{3+}$ and the luminescence spectrum in the green region at temperature $T = 77°K$, recorded on high-resolution instruments by the authors of Ref. ([4]), makes it possible to indicate approximately the boundary between these terms. This boundary is determined by the short-wavelength edge of the spectrum of green luminescence and is located near 5365 Å (18640 cm^{-1}). Thus, two-photon absorption of neodymium-laser light occurs with excitation of Ho^{3+} atoms to the level $^5F_4$. Green luminescence comes from the level $^5S_2$ and arises as a result of nonra-

Fig. 2

Figure 2: Fig. 2

diative transfer of excitation from the level $^5F_4$ to the level $^5S_2$. In the fluorite lattice (see Fig. 1) these levels overlap. The indicated transition, as well as two other observed two-photon transitions $^5I_8 \rightarrow {}^5G_3$ and $^5I_8 \rightarrow {}^5G_5$, are shown in Fig. 1 by solid arrows.

Figure 2 gives an oscillographic recording of the time dependence of the green luminescence excited by two-photon absorption of laser light. The peaked character of the excitation is not seen in the time dependence of the luminescence intensity, since the spontaneous lifetime at the level $^5S_2$ is large and amounts to (see Fig. 2b) 10^{-3} s.

The oscillogram in Fig. 2a confirms the two-photon nature of the luminescence excitation. When the light flux of the ruby and neodymium lasers incident on the specimen is reduced by a factor of two, the luminescence intensity decreases by a factor of 4. The possibility of a cascade (through an intermediate level) process of excitation of the green glow by neodymium and ruby-

by ruby lasers is ruled out by the absence, in the spectrum in Fig. 1, of suitable levels.

In the oscillogram of Fig. 2b the time delay between the pulses of the ruby and neodymium lasers was chosen so that the maxima of the green luminescence produced by them coincide in time. In this case, when the crystal under study is illuminated simultaneously by both lasers, the intensity of the green luminescence exceeds the sum of the luminescence intensities from the neodymium and ruby lasers operating separately. This increase in intensity occurs as a result of absorption to the level $^5G_5$ of two different light quanta: red light from the ruby laser and infrared light from the neodymium laser.

Oscillograms in Figs. 2b and 2c differ in that in the first case the pulse of the ruby laser is delayed relative to the pulse of the neodymium laser. In the second experiment (Fig. 2c) both lasers operate simultaneously.

Fig. 2. Oscillograms of the green luminescence of a $CaF_2 : Ho^{3+}$ crystal excited by two-photon absorption of light from a ruby laser and from a laser on neodymium glass. Time scale 0.7 msec/cm. Energy in the ruby-laser pulse 7.8 J, in the neodymium-laser pulse 11.3 J.
a –green luminescence under simultaneous illumination of the sample by the light of the ruby and neodymium lasers; the upper curve corresponds to a twofold reduction (by means of colored-glass filters) of the intensity of both lasers;
b –the two upper oscillograms: on the left, the pulse of the laser on neodymium glass; on the right, the pulse of the ruby laser. The three lower oscillograms are the green luminescence from excitation by the ruby laser, by the laser on neodymium glass (middle curve), and from simultaneous excitation by both

lasers (lower curve), the pulses of which are shown above;
c —the same as in case b, but in the absence of a time delay between the pulses of the ruby laser and the laser on neodymium glass; the oscilloscope gain was changed in comparison with trace b.

From the oscillogram of Fig. 2c it is seen that the maximum of the luminescence excited by the light of the neodymium laser lags behind the maximum of the luminescence from the ruby laser by about 10^{-3} sec. Since the shape and duration of the ruby- and neodymium-laser pulses differ little, this lag cannot be attributed to a displacement of the luminescence maximum relative to the maximum of the exciting pulse, which occurs when the duration of the luminescence is comparable with or greater than the duration of the excitation pulse. Thus, the indicated lag can be explained only by a considerable duration of the process of nonradiative energy transfer from the level $^5F_4$, excited by two-photon absorption of the light of the neodymium laser, to the lumi-

luminescent level $^5S_2$. From the oscillogram in Fig. 2b it follows that the characteristic time of this process is approximately 10^{-3} sec.

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P. N. Lebedev Physical Institute
Academy of Sciences of the USSR

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