

TWO-QUANTUM COOPERATIVE FREQUENCY CONVERSION OF WEAK LIGHT FLUXES

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The efficiency (η) of two-quantum converters of long-wave radiation into short-wave radiation, based on cooperative processes (Fig. 1), is in the general case a function of the intensity of the converted radiation. This is connected with the superlinear dependence of the intensity of the anti-Stokes luminescence (I_{coop}) on the intensity of the converted radiation (E). We have shown earlier [1] that in some cases the superlinear dependence $I_{\text{coop}}(E)$ degenerates into a linear one. The conditions for the linearization ($I_{\text{coop}} = \alpha E - B$) for all the processes shown in Fig. 1 are of the form

$$w_2^+ \gg r_2^{-1} \text{ and } \gamma \gg w_2^-, \quad (1)$$

where γ is the rate of the relaxation that takes the system out of resonance; the physical meaning of the rates w_2^+ , w_2^- , and r_2^{-1} differs somewhat for each of the processes and is clear from Fig. 1.

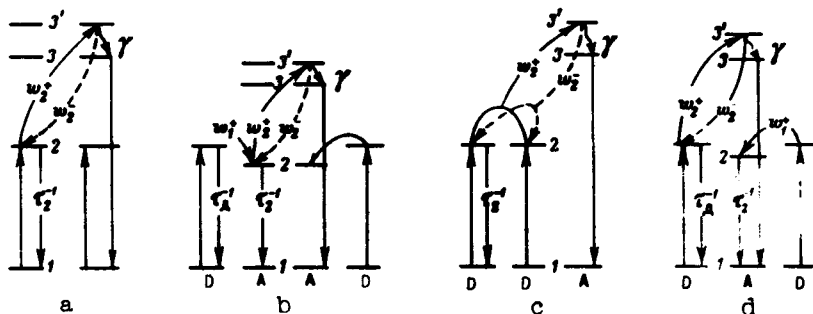
When conditions (1) are satisfied for systems operating in accordance with the mechanisms 1a and 1c, the quantum efficiency (η_{qu}) of population of the high-energy 3 can be close to 0.5, and the energy efficiency of the converter (η_{en}) without allowance for losses to relaxation $3' - 3$ is close to unity. An analogous consequence for systems operating in accordance with the schemes 1b and 1d is obtained when the set of conditions (1) is satisfied together with the condition

$$w_1^+ \gg r_0^{-1}. \quad (2)$$

The physical meaning of these conditions is quite simple: for effective operation of the converter it is necessary that the relaxation of all the intermediate states participating in the process proceed via the radiative state 3. The best known of the cooperative converter systems are crystals activated by one or two sorts of triply-charged rare-earth ions [2, 3].

In crystals with one activator, operating in accordance with the scheme 1a at low flux densities of the converted radiation, we have $I_{\text{coop}} \sim E^2$, indicating a rather low conversion efficiency under these conditions. Only an increase of the intensity of the converted radiation to values exceeding 2 W/cm² leads, as was demonstrated by one of us [4], to the realization of a practically ideal converter of infrared radiation ($\lambda \approx 0.98 \mu$) into visible radiation (0.55 μ) in BaF₂:Er³⁺ crystals. Theoretical estimates [5] have shown that the

Fig. 1. Mechanisms of cooperative two-quantum "upward" frequency conversion: a - energy summation, b - sensitized energy summation, c - cooperative sensitization, d - successive sensitization.



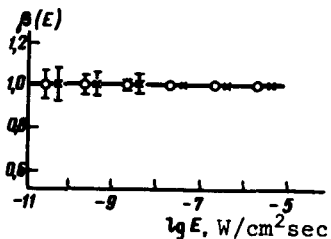


Fig. 2. Plot of $\beta(E)$ for Stokes (circles) and anti-Stokes excitation (crosses): $T = 4.2^\circ\text{K}$. Film KN-4S.

experimental value of w_2^+ obtained in these experiments is close to optimal for similar systems.

The realization of effective converters based on crystals with two sorts of rare-earth ions, operating in accordance with schemes 1b and 1c, requires satisfaction of the aggregate of conditions (1) and (2). Whereas (1) can be satisfied as before by increasing the intensity of the converted radiation, to satisfy (2) it is necessary to produce a unique heterogeneity that leads to effective draining of the excitation energy through the ion-donor system (D) to the ion-acceptors (A). The presently available data on the rates of the elementary processes responsible for the conversion efficiency in these systems [3] give no grounds whatever for hoping to realize on

their basis effective frequency converters for radiation whose density is appreciably lower than 1 W/cm^2 .

Less known but much more promising for the conversion of low-power fluxes are the essentially heterogeneous crystal-phosphor + dye systems [1]. The energy donors in these systems are the strongly-absorbing molecules of the dye absorbed on the surface of the crystal, and the energy acceptors are the electronic states of the crystal.

It was concluded in [1] on the basis of the closeness of the exponents of the power-law dependences of the edge-luminescence intensity of AgHal + dye systems on the intensity of the Stokes and anti-Stokes excitation, that the indicated systems are effective radiation converters at the excitation densities used in the experiments ($\sim 10^{-5} \text{ W/cm}^2$). The essential nonlinearity of the edge luminescence at 77°K , due to the recombination character of the glow and to the emission action of the exciting light, which is particularly strong in the case of anti-Stokes excitation, have not made it possible, however, to assess the efficiency of the process of cooperative summation of energy at low intensities. A natural way of suppressing such nonlinearities due to the semi-conducting processes in crystal phosphors in the region of their temperature quenching may be a lowering of the sample temperature. Our investigations of the efficiency of conversion of long-wave radiation into short-wave radiation by means of commercial photographic materials at 4.2°K have shown that the latter are effective converters starting with an intensity of at least $2 \times 10^{-11} \text{ W/cm}^2$.

The samples were the photographic films KN-3, KN-4S, Foto-250, and VCh, which were not subjected to prior illumination. Modulated (25 Hz) radiation of an incandescent lamp was passed through a DFS-12 monochromator and through additional light filters and was incident on an object placed in a helium cryostat. The luminescence of the sample was separated with the aid of light filters (SZS-22 and ZS-9) and was registered with a photomultiplier (FEU-79).

Figure 2 shows by way of an example plots of the luminescence intensity of the film KN-4S ($\lambda_{\text{max}} = 540 \text{ nm}$) against the intensity of the Stokes (365 nm) and anti-Stokes (680 nm) excitation in the range from 10^{-11} to 10^{-5} W/cm^2 in coordinates $\beta(E)$ and $\log E$, where $\beta(E)$ is the exponent in the relation $I = E^{\beta(E)}$.

As seen from Fig. 2, both relations are linear in the entire investigated interval of excitation intensity, thus indicating that a converter with $\eta_{\text{qu}} \approx 0.5$ has been realized at subnanowatt intensities of the converted

radiation. It is interesting to note that to obtain a photographic density I in the investigated films at these intensities it is necessary to use exposure times longer than 10^4 sec¹).

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ELECTRON PARAMAGNETIC RESONANCE OF NICKEL IN SYNTHETIC DIAMOND

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Synthetic diamonds obtained in nickel-containing systems exhibit at $T < 150^\circ\text{K}$ an isotropic ($g = 2.032 \pm 0.001$) electron paramagnetic resonance (EPR) spectrum from one line (in addition to the triplet due to the disperse paramagnetic nitrogen [1]). Two hypotheses were advanced earlier [2 - 4] concerning the nature of this line. Loubser and Ryneveld [2], and we [3, 4] proposed that the observed spectrum is due to nickel Ni^{1+} with configuration $3d^9$ and effective spin $S = 1/2$, or to Ni^{1-} with configuration $3d^8$ and a bound hole in the valence shell, similar to nickel in germanium [5], with the same effective spin $S = 1/2$. Bratashevskii et al. [6] connected the given line with the interstitial carbon atom (a system with $S = 1$ and $L = 1$ is not a "good" quantum number, owing to the weak spin-orbit coupling).

We have already written [4] that the anisotropy of the spectrum is evidence of a manifestation of the Jahn-Teller effect, similar to that occurring for the EPR spectrum of nickel in germanium [5]. In diamond, however, unlike in germanium, where an anisotropy of the g -tensor is observed already at $T \leq 20.4^\circ\text{K}$, the spectrum remains almost isotropic down to $T = 4.2^\circ\text{K}$. Introduction of donor impurities (phosphorus, nitrogen) into diamond, other conditions being equal, leads to a decrease of the intensity of the EPR lines of nickel. This is connected with the fact that the latter form two acceptor levels, so that the intensity of the EPR signal is directly proportional to the filling of the lower level and inversely proportional to the filling of the upper level [4, 5].

However, all the data presented so far on the nature of the isotropic line $g = 2.032$ in diamond were indirect [1 - 4], since the content of the Ni^{61} isotope in natural compounds is 1.2%. We therefore have grown, by the usual

¹)The significance of the results to the theory of the sensitization of the photographic process and physical simulation of the main photosynthesis reaction - the photolysis of water - will be discussed elsewhere.