Observation of nonresonant six-photon processes in a calcite crystal

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Nonresonant six-photon processes have been registered for the first time in the optical band. We measured the effective nonlinear susceptibility of fifth order in a calcite crystal. The sixth-rank tensor component is $\chi^{(5)}_{zyyyyy} \approx 10^{-27}$ cgs esu. We discuss the behavior of the higher nonlinear susceptibilities $\chi^{(n)}$. Data are presented, which show that the decrease of $\chi^{(n)}$ with increasing n is faster the larger n.

1. The aim of the present article is to describe the results of experiments in which nonresonant six-photon processes (connected with the number $\mathbf{P}^{(5)} = \chi^{(5)}\mathbf{E}^5$ in the expansion of the polarization in the field) were registered for the first time and the corresponding susceptibility $\chi^{(5)}$ was measured.

The measurements were made with a $CaCO_3$ crystal, the large birefringence of which has made it possible to obtain synchronous generation of the fifth harmonic of a neodymium-glass laser. We registered in the experiment the fifth harmonic for three different synchronism directions. The value obtained for the component χ_{zyyyyy} was $\approx 10^{-27}$ cgs esu. The measurements were performed at an energy conversion efficiency 10^{-6}. The results (see also the experimental data of [1] and the calculations in [2]) show that the decrease of $\chi^{(n)}$ with increasing n is faster the larger n.

2. Measurement of the higher nonlinearities of condensed media, atoms, and molecules is of considerable interest for the understanding of the physics of nonlinear susceptibility (see [1–3]), and in some cases also for applications.[4] It should be noted that whereas for many media that have no inversion center the resonant and nonresonant susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$, and even $\chi^{(4)}$, have already been measured, the experimental data published to date on media with inversion centers pertain to the lower nonlinear susceptibility $\chi^{(3)}$ for such media. The only exception is,[3] where an estimate was made of the resonant susceptibility $\chi^{(5)}$ responsible for the coherent anharmonic Raman scattering in the H_2 molecule.

3. The object of investigation was chosen to be the crystal $CaCO_3$. Calcite has an inversion center and therefore measurement of $\chi^{(5)}$ is of particular interest here. The large birefringence of calcite and the suitable transparency region make it possible to obtain in it synchronous generation of the fifth harmonic ($\lambda = 0.212$ μ) of a neodymium laser.

4. The experimental setup is shown in Fig. 1. The laser operated in the regime of self-locked longitudinal modes; the lower transverse model was used. The energy of the pulse train was 0.2 J. We used two quartz-crystal prisms to separate the harmonic signal.

The signal from the photomultiplier was amplified and fed to an analog-digital converter. The system operated in the regime in which one-electron pulses were registered.

A calcite crystal 6 mm thick was cut in such a way that the normal to its working surface made an angle

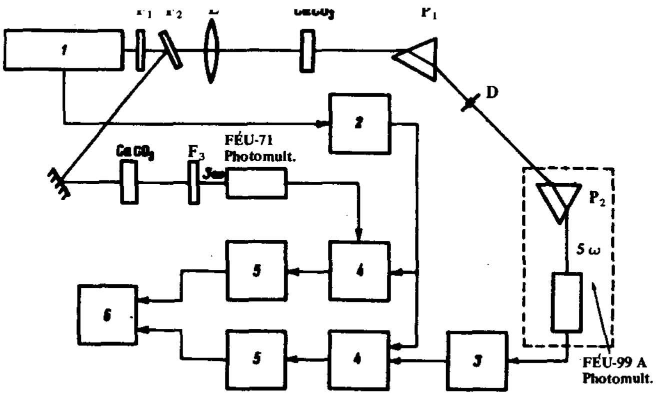

FIG. 1. Experimental setup for the generation of the fifth harmonic: 1) Laser; F_1, F_2, and F_3—filters; L—lens; P_1 and P_2—prisms; D—diaphragm. 2) Strobing-pulse shaper, 3) Amplifier. 4) Amplitude-time converter block. 5) Counter. 6) Printout unit.

$\theta = 55°$ with the Z axis and an angle $\phi = 0°$ with the axis perpendicular to the crystallographic reflection plane. The crystal absorption coefficient at $\lambda = 0.212\ \mu$ was 2.5 cm^{-1}. We used weak focusing of the beam. (We note that the conditions for optimal generation of higher harmonics in strongly-focused beams differ significantly from the optimal-focusing conditions known for the second harmonic.)

5. Fifth-harmonic generation can be either the result of a "direct" six-photon process on fifth-order nonlinearities, or the result of cascade processes on a cubic nonlinearity. The dispersion properties of the calcite crystal admit of phase matching for the following experimentally-investigated processes:

$$\gamma_e(5\omega) = 5\gamma_o(\omega); \qquad k_5^e = 5k_1^o, \tag{I}$$

$$\gamma_e(5\omega) = \gamma_o(3\omega) + \gamma_o(\omega) + \gamma_e(\omega); \quad k_5^e = k_3^o + k_1^o + k_1^e, \tag{II}$$

$$\gamma_e(5\omega) = \gamma_o(3\omega) + 2\gamma_o(\omega); \qquad k_5^e = k_3^o + 2k_1^o. \tag{III}$$

Here k_1, k_3 and k_5 are the wave numbers of the corresponding harmonics, and the subscripts o and e pertain respectively to the ordinary and extraordinary waves. In all cases, only the fundamental-harmonic radiation was incident on the entrance face of the crystal; the third harmonic was produced in processes (II) and (III) in the crystal itself.

The calculated values of the synchronism angles for the aforementioned interactions were $\theta_I = 55°6'$, $\theta_{II} = 52°44'$ and $\theta_{III} = 48°5'$, and agreed within $\pm 5'$ with the experimentally observed angles. The experimental dependence of the fifth-harmonic intensity I_s on the angle θ for the interaction (I) is shown in Fig. 2. The angular width of the synchronism was $\Delta\theta_e \approx 3'$, almost six times larger than the calculated value for plane monochromatic waves, $\Delta\theta_t = 30''$. The reason for the discrepancy is the influence of the finite width of the spectrum of the picosecond pulses ($\Delta\nu = 6$ cm^{-1}).

The fifth-harmonic signal at the maximum of the synchronism curve corresponded to 100 photoelectrons in 200 laser flashes. On the edges of the synchronism curve, we registered after 200 flashes 20 photoelectrons as a result of optical illumination. The photomultiplier darkness noise yielded one photoelectron in the same number of flashes.

The measured ratios of the fifth-harmonic intensities at the maxima of the synchronism curves is given by

$$I_5(\theta_I)/I_5(\theta_{III}) = 2.0 \pm 0.8; \tag{1}$$

$$I_5(\theta_{III})/I_5(\theta_{II}) = 0.2 \pm 0.1. \tag{2}$$

6. The obtained data can be used directly to estimate $\chi^{(5)}$; under the conditions of our experiment we have

$$I_5(\theta_i)/I_5(\theta_j) = [\chi^{(5)}_{eff}(\theta_i)/\chi^{(5)}_{eff}(\theta_j)]^2.$$

All the remaining geometrical and dispersion factors are the same for the investigated interactions within the limits of the measurement accuracy. Using the connection obtained in [5] between the components of the cubic nonlinear susceptibility of calcite, we obtain for the effective susceptibilities $\chi^{(5)}_{eff}$ measured in our experiments the following formulas:

$$\chi^{(5)}_{eff}(\theta_I) = [\chi^{(5)}_{zyyyyy} - 195 C_{11}C_{32}] \sin\theta_I \tag{3}$$

(interference with the direct process is produced by the synchronous cascade process, each of the stages of which is not synchronous)

$$\chi^{(5)}_{eff}(\theta_{II}) = 450\, C_{11}C_{32}, \tag{4}$$

$$\chi^{(5)}_{eff}(\theta_{III}) = 210\, C_{11}C_{32} \sin\theta_{III}, \tag{5}$$

where C_{11} and C_{32} are the components of the cubic-susceptibility tensor.

We note first that the calculated value of the intensity ratio $I_5(\theta_{III})/I_5(\theta_{II}) = 0.15$ agrees well with the experimental value $- 0.20 \pm 0.1$ (see (2)).

In accordance with (1), (3), and (5), we have

$$\chi^{(5)}_{eff}(\theta_I) = (250 \pm 50)\, C_{11} \cdot C_{32}.$$

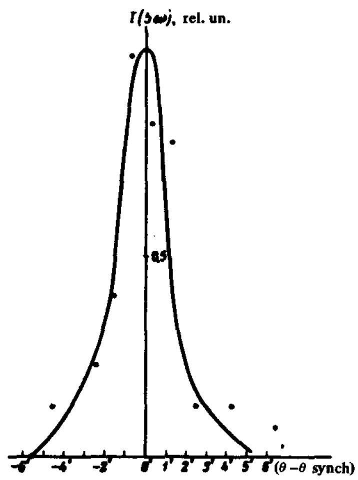

FIG. 2. Angular dependence of the intensity of the fifth harmonic near the direction of the synchronous interaction $K_5^e = 5K_1^o$ in a $CaCO_3$ crystal.

Using the values $C_{11} = 1.8 \times 10^{-14}$ cgs esu[6] and $C_{32} = 4 \times 10^{-16}$ cgs esu,[5] we obtain $\chi_{eff}^{(5)}(\theta_I) = 1.8 \times 10^{-27}$ cgs esu. For the component χ_{zyyyyy} we obtain accordingly $\chi_{zyyyyy} = (85 \pm 55)C_{11}C_{32}$, if $\chi_{zyyyyy}C_{32} < 0$ and $\chi_{zyyyyy} = (475 \pm 55)C_{11}C_{32}$ if $\chi_{zyyyyy}C_{32} > 0$. Substituting the absolute values for C_{11} and C_{32} we obtain the mean values $\chi_{zyyyyy} = 0.6 \times 10^{-27}$ cgs esu for the first case and $\chi_{zyyyyy} = 3.4 \times 10^{-27}$ cgs esu for the second.

7. Our results (together with the data of [1,2]) allow us to draw certain conclusions concerning the dependence of the optical nonlinear susceptibilities $\chi^{(n)}$ on n. According to [7–9], $\chi^{(3)}/\chi^{(2)} = 10^{-5}$ cgs esu for the crystal SiO_2, GaAs, and $LiNbO^3$. The experimental data of that reference as well as of [1], and the calculations of [2], show that the decrease of $\chi^{(n)}$ with increasing n is faster the larger n. Indeed, for $CaCO_3$ we have $\chi^{(5)}/\chi^{(3)} = 10^{-12}$ cgs esu. According to the data of [1], for the LFM crystal we have $\chi^{(4)}/\chi^{(2)} = 0.7 \times 10^{-12}$ cgs esu and $\chi^{(4)}/\chi^{(3)} = 10^{-7}$. For a more detailed discussion of this question, we need of course, additional experimental material.

8. We note in conclusion that the possibilities of measuring higher nonlinearities by the method of synchronous generation of harmonics in the visible band are limited. There are crystals suitable for the generation of the higher harmonics of a CO_2 laser (in particular, $CdGeAs_2$—see [2]). Difficulties are raised here, however, in the registration of weak IR signals. It is therefore of interest to measure higher nonlinearities in systems operating in reflection with media having large nonlinearities.

In particular, the apparatus described above makes it possible to measure, in reflection, the values of $\chi^{(4)}$ and $\chi^{(5)}$ of Si, Te, and Ge crystals.

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