# Active spectroscopy of noncentrosymmetric crystals under conditions of double $\omega$-$k$ resonance

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A new modification is investigated of spectroscopy of three-wave mixing of the type $2\omega_1-\omega_2\to\omega_a$, wherein wave-resonance (synchronism) conditions are realized for second-harmonic generation in addition to the conditions of Raman frequency resonance. The possibility of measuring the magnitudes and signs of the resonant and nonresonant cubic nonlinearities of a crystal is demonstrated with lithium-formiate as an example.

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The capabilities of the spectroscopy of nonlinear optical mixing of three waves at frequencies $\omega_1$, $\omega_2$, and $\omega_3$, wherein a signal at a frequency $\omega_a=\omega_1-\omega_2+\omega_3$ is analyzed under conditions of interference between two resonant contributions, were demonstrated earlier with double Raman,[1] Raman, and single-photon[2] or two-photon[3] electronic resonances. The conditions for double optical frequency resonance were realized by a proper choice of the frequencies $\omega_1$, $\omega_2$, $\omega_3$.[4] The present paper analyzes a new modification of three-wave mixing spectroscopy (of the type $2\omega_1-\omega_2\to\omega_a$), which is possible in crystals without a symmetry center. If, besides the conditions of Raman frequency resonance $\omega_1-\omega_2\approx\Omega$, where $\Omega$ is the frequency of the Raman-active phonon ($\omega$ resonance), there are also satisfied the conditions of wave resonance ("synchronism") for the generation of the second harmonic $\Delta\mathbf{k}_m=2\mathbf{k}_1-\mathbf{k}_m=0$, where $-\mathbf{k}_1$ and $\mathbf{k}_m$ are the wave vectors of the radiation at the frequencies $\omega_1$ and $\omega_m=2\omega_1$ respectively ($k$ resonance), then, as a result of the coherence of the process, one observes in the spectrum of the signal of frequency $\omega$ not simple addition of the resonant contributions, but the result of interference between them.[5] This makes it possible, using the spectra obtained in $\omega$ and $k$ spaces under conditions of double

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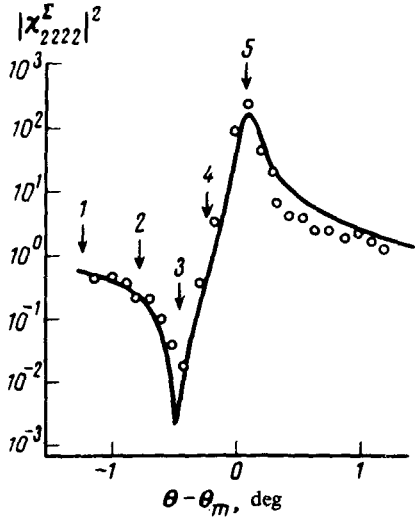


FIG. 1. Dependence of the intensity of the signal at the frequency $\omega_a$ on the angle $\theta$ ($k$ spectrum), obtained at $\omega_1-\omega_2\neq\Omega$. Circles—experimental data, solid curve—result of calculation. The arrows mark the values of those angles at which the $\omega$ spectra were obtained (see Fig. 2).

resonance, to determine the signs and to measure the magnitudes of both the resonant and nonresonant cubic nonlinear susceptibility from the known value of the quadratic nonlinearity.

Under conditions of double $\omega-k$ resonance, two mechanisms contribute to the formation of the signal at the frequency $\omega_a$: a) direct four-photon mixing, due to cubic nonlinear susceptibility; b) successive three-photon (cascade) processes due to quadratic nonlinearity.[5] The process a) is described within the framework of the theory of active Raman-scattering spectroscopy.[6] The contribution due to the processes b) can be determined by solving (in the approximation wherein the pump fields at the frequencies $\omega_1$ and $\omega_2$ are given) the abbreviated equations for the field amplitudes at the frequencies $\omega_m$ and $\omega_a$, obtained on the basis of the standard noninear-optics procedure.[7] Under the condition $\Delta\mathbf{k}\equiv 2\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_a=0$, the effective cubic nonlinearity of the medium can be represented in the form

$$\chi^{\Sigma}_{ijkl} = \chi^{NR}_{ijkl} + \chi^{R}_{ijkl} + \chi^{K}_{ijkl}\,. \tag{1}$$

Here $\chi^{NR}_{ijkl}$ is the nonresonant electronic cubic susceptibility of the crystal; $\chi^{R}_{ijkl}$ is the resonant contribution due to the combination resonance, which for a solitary optical phonon with half-width $\Gamma$ at the frequency $\Omega$ is given by[6]

$$\chi^{R}_{ijkl} = \bar{\chi}^{R}_{ijkl}(-i-\Delta)^{-1}, \tag{2}$$

$$\Delta = (\omega_1-\omega_2-\Omega)/\Gamma, \quad \bar{\chi}^{R} = \frac{N}{2M}(2\Gamma\Omega)^{-1}\left(\frac{\partial\alpha_{ij}}{\partial Q}\right)_0\left(\frac{\partial\alpha_{kl}}{\partial Q}\right)_0,$$

where $M$ is the reduced mass of the unit cell and $(\partial\alpha/\partial Q)_0$ is the Raman-scattering tensor, $N$ is the number of unit cells per unit volume of the crystal. The contribution of the cascade processes to the intensity of the investigated signal is described in (1) by a fourth-rank tensor given by the expression

$$\chi^K_{ijkl} = \bar{\chi}^K 2(i\tau + e^{-i\tau} - 1)(i\tau^2)^{-1}, \tag{3}$$

$$\bar{\chi}^K = \frac{L\pi\omega_m^2}{k_m c^2} \chi^{(2)}_{ijp} \chi^{(2)}_{pkl}$$

where $\tau=\Delta k_m L$, $L$ is the crystal length, and $\chi^{(2)}_{ijk}$ is the tensor of the quadratic nonlinear susceptibility of the crystal.

The experiment was performed in a lithium-formiate crystal with the second harmonic ($\lambda_1=0.53\,\mu$m) of a $Q$-switched yttrium-aluminum garnet laser operating in the $TEM_{00}$ mode, with a repetition frequency 10 Hz mixed with the emission of a tunable dye laser ($\lambda_2=0.56-0.62\,\mu$m) with a generation line width up to 1 cm$^{-1}$. The interacting waves propagated in the $XZ$ plane of the crystal. The radiation with wavelength $\lambda_1$ and wave vector $\mathbf{k}_1$ propagated at an angle $\theta$ to the $x$ axis and was polarized along the $y$ axis [ordinary (0) wave]. The wave vector $\mathbf{k}_2$ of the dye laser, polarized as the ordinary wave, made an angle $\phi$ with the direction of the vector $\mathbf{k}_1$. The angle $\phi$ was chosen to satisfy the phase-locking condition $\Delta\mathbf{k}=2\mathbf{k}_1^0-\mathbf{k}_2^0-\mathbf{k}_a^0=0$ for the four-

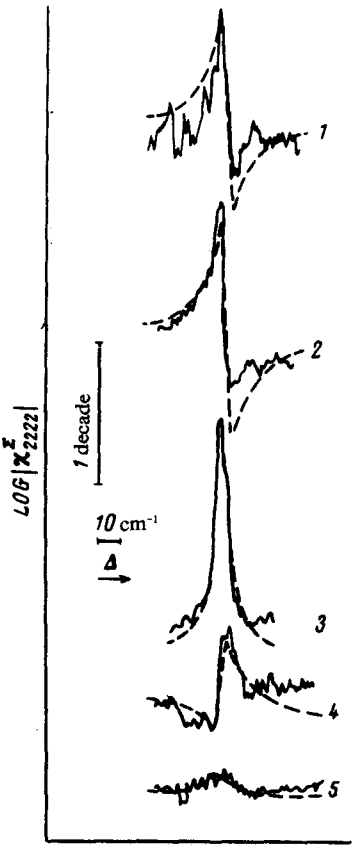


FIG. 2. $\omega$ spectra obtained by varying $\Delta=(\omega_1-\omega_2)/2\pi c$ near the frequency $\Omega=1070$ cm$^{-1}$ Raman-active vibration of lithium formiate. The numbers denote the spectra obtained at the different angles $\theta$ marked by the arrows in Fig. 1. Solid lines—experiment, dashed—results of calculation.

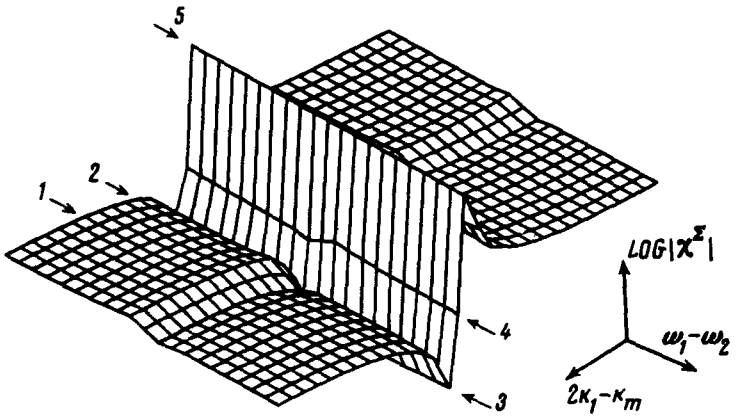


FIG. 3. Calculated dependence of the anti-Stokes signal on the frequency and wave detunings, as obtained from relations (1)–(3) on the basis of the measured values of $\chi^{NR}$ and $\bar{\chi}^{R}$.

photon interaction 000–0. For the chosen mixing geometry, the wave-resonance condition $2\mathbf{k}_1=\mathbf{k}_m$ is satisfied when the angle $\theta$ varies near $\theta_m\approx 39.5°$. The contribution to the intensity of the signal at the frequency $\omega_a$ is the result of two three-photon processes in the 00–$e$ and $e$0–0 interaction. We note that in this case, satisfaction of the phase-locking condition for the four-photon interaction is independent of the angle $\theta$. Consequently, by tuning the dye-laser frequency and by varying the angle $\theta$ it is possible to choose independently the conditions for the resonance in the $\omega$ and $k$ spaces.

To analyze the regularities of the active spectroscopy under conditions of double $\omega$–$k$ resonance, we obtained the dependences of the intensity of the signal $\omega_a$ on the frequency $\omega_2$ ($\omega$ spectrum) and on the angle $\theta$ ($k$ spectrum). The plot of Fig. 1 was obtained at $\omega_1-\omega_2\neq\Omega$, i.e., for "single" $k$ resonance. Figure 2 shows the spectra obtained in $\omega$ space at different values of the wave mismatch $\Delta k_m$, and demonstrate the influence of the interference of different contributions under conditions of double $\omega$–$k$ resonance. The experimentally obtained spectra were compared with the calculated relations obtained from (1)–(3). We note that since the sign of $\bar{\chi}^{k}_{ijkl}$ in (3) is independent of the sign of the quadratic nonlinear susceptibility, the position of the "dip" in the $\omega$ and $k$ spectra makes it possible to determine the sign of the resonant and nonresonant cubic nonlinear susceptibility. In addition, the shapes of the spectra depend substantially on the ratio of the quantities $\chi^{NR}\bar{\chi}^{R}$ and $\bar{\chi}^{K}$. Consequently, from the spectra obtained under the conditions of double $\omega$–$k$ resonance, knowing one of these quantities, we can determine the two others. The unknown quantity $\tau$ is determined here (in the same experiment) from the angle width of the synchronism for second-harmonic generation. The value of the half-width $\Gamma$ of the Raman-scattering line is determined from the $\omega$ spectrum obtained under conditions of "compensation" for the nonresonant background (curve 3 of Fig. 2). The quantity $\chi^{(2)}$ is obtained with sufficient accuracy by measuring the second-harmonic generation, and is most frequently known,[8] so it is most convenient to calibrate against it the unknown values of the resonant and nonresonant cubic nonlinearities.

Measurement of $\chi^{NR}$ and of $\overline{\chi}^{R}$ is carried out in two stages: $\chi^{NR}$ is determined from $\chi^{(2)}$ of the $k$ spectrum, and knowing $\chi^{NR}$ we determine $\overline{\chi}^{R}$ from the $\omega$ spectrum. The measurement procedure is analogous to that described in[9].

The measurements performed from the spectra obtained in the lithium formiate crystal yielded the following values for the components of the tensor (with $d_{24}=2.98\times10^{-9}$ cgs esu taken from[10]) of the resonant and nonresonant cubic nonlinearity near the $\Omega=1070$ cm$^{-1}$ line[1)], namely $\overline{\chi}^{R}_{2222}=+1.1\times10^{-12}$ cgs esu and $\chi^{NR}_{2222}=+5.5\times10^{-13}$ cgs esu.

Using in (1)–(3) the values of $\chi^{NR}$ and $\overline{\chi}^{R}$ obtained in this manner, we calculated the theoretical $\omega$ and $k$ spectra (Figs. 1 and 2) and plotted the dependence of the signal on $\omega$ and $k$ in $\omega$–$k$ space (Fig. 3).

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[1)]We note that according to[11] this line manifests itself weakly in IR spectra. Consequently, the parametric processes connected with excitation of the anomalous longitudinal wave[12] can be neglected.

[1]Haim Lotem, R.T. Lynch, Jr., and N. Bloembergen, Phys. Rev. A **14**, 1748 (1976).
[2]A.F. Bunkin, S.G. Ivanov, and N.I. Koroteev, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 468 (1976) [JETP Lett. **24**, 429 (1976)].
[3]S.D. Kramer and N. Bloembergen, Phys. Rev. B. **14**, 4654 (1976).
[4]R.T. Lynch, Jr., S.D. Kramer, Haim Lotem, and N. Bloembergen, Opt. Commun. **16**, 372 (1976).
[5]V.L. Strizhevskiĭ and Yu.N. Yashkir, Kvantovaya Elektron. (Moscow) **2**, 995 (1975) [Sov. J. Quantum Electron. **5**, 541 (1975)]; Yu.N. Polivanov and A.T. Sukhodol'skiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 240 (1977) [JETP Lett. **25**, 221 (1977)].
[6]S.A. Akhmanov and N.I. Koroteev, Zh. Eksp. Teor. Fiz. **67**, 1306 (1974) [Sov. Phys. JETP **40**, 650 (1975)].
[7]S.A. Akhmanov and R.V. Khokhlov, Problemy nelineĭnoĭ optiki (Problems of Nonlinear Optics), VINITI, Akad. Nauk SSSR, 1964.
[8]F. Zernike and J.E. Midwinter, Applied Nonlinear Optics, Wiley 1973.
[9]M.D. Levenson, C. Flytsanis, and N. Bloembergen, Phys. Rev. B **6**, 3962 (1972).
[10]S. Singh, W.A. Bonner, J.R. Potopowicz, and L.G. Van Uirert, Appl. Phys. Lett. **17**, 292 (1970).
[11]R. Vierne and M. Cadene, Ferroelectrics **5**, 256 (1973).
[12]V.L. Strizhevskiĭ, Zh. Eksp. Teor. Fiz. **62**, 1446 (1972) [Sov. Phys. JETP **35**, 760 (1972)].