Parametric spectroscopy of Raman scattering light in crystals

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Parametric spectroscopy of Raman scattering of light is proposed and realized. In this method the scattered radiation interacts twice with the scattering-inducing pump and is subjected to parametric transformation with increase of frequency, and is only then detected and analyzed. Among the demonstrated advantages of this procedure are the ease of registration of forward scattering, observation of Raman scattering excited in the IR band in crystals that are opaque to visible light, and others.

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We have realized experimentally a new variant of spectroscopy of Raman scattering (RS) of light, namely parametric RS spectroscopy (PRSS). The gist of the method is that the laser pump ω_1 that excites the RS in the crystal ($\omega_1 = \omega_s + \omega_p$) is used again for parametric conversion (PC) that raises the frequency ω_s of the scattered Stokes radiation via generation at the sum frequency $\omega_a = \omega_1 + \omega_s$ in the same crystal or in another one placed in tandem. If one crystal is used, it must be non-centrosymmetric, to ensure (in the dipole approximation) quadratic nonlinearity of the polarization; in addition, the crystal must be sufficiently transparent to the region of the frequencies ω_a. In our experiments we used $LiIO_3$, $LiNbO_3$, KDP, and GaSe crystals. If a separate crystal is used for the PC, then the PRSS procedures can be used, naturally, also to investigate RS in non-centrosymmetric media, since the nature of the converted signal is of no significance in the case of PC with increase of frequency.[1,2]

The PRSS procedure can be shown to have a number of advantages that make it of practical value. One of the principal ones is connected with registration of scattering that is quasicollinear with the pump, i.e., RS in the region of extremely small scattering angles $\theta \approx 0°$. This small region frequently contains important spectroscopic information. This is the situation, for example, in RS by polaritons.[3] The investigation of the region of extremely small θ is made, however, extremely difficult by the pump illumination, so that in most earlier experiments this range was in fact not registered. In the PRSS method, on the other hand, in view of the frequency-conversion spatial selectivity due to phase synchronism, there is no analogous synchronous conversion of the pump (i.e., generation of the $2\omega_1$ harmonic) at that crystal geometry which ensures synchronous generation of the sum frequency ω_a. Therefore the registration of the scattered radiation in the region of extremely small θ is no longer difficult after the parametric conversion.

Another advantage is the appreciable ease of registration of the RS excited in the IR band, particularly the possibility of photography of this scattering. Observation of RS excited by an IR wave ω_1 yields important information on the corresponding nonlinear polarizabilities in the IR band on the RS cross sections, and others. Finally,

RS excited in the IR band affords a possibility of finding the polariton branches in crystals that are opaque to visible light and therefore preclude the traditional use of cw visible-light lasers such as argon lasers. We have registered, for the first time ever, polariton and the LO-phonon RS using excitation with an LTI-7 laser at $\lambda_1 = 1.064$ μm.

Figure 1 shows a diagram of our experimental setup. The emission of the pump-laser *1* (frequency regime with $f = 12.5$ Hz, peak power ~ 1 MW), passing through filter *2* (IKS-7) and reflected from the rotary mirror *3*, entered the nonlinear crystal *4* at an angle ϕ to the optical axis *C*. At the given value of ϕ, the radiation scattered at a definite angle θ is synchronously mixed with the pump, as a result of which a sum frequency ω_a is generated. The result then passed through the entrance slit of monochromator *9* and was detected by photomultiplier *10* whose signal was fed to oscilloscope *11*. Figures 5 and 6 cut off the pump radiation and the non-synchronous second harmonic; the diaphragm *7* fixed the scattering angle; the focusing was by lens *8*. The absolute threshold sensitivity of our installation is $\sim 3 \times 10^{-12}$ W.

The right-hand side of Fig. 1 shows the relative arrangement of the wave vectors

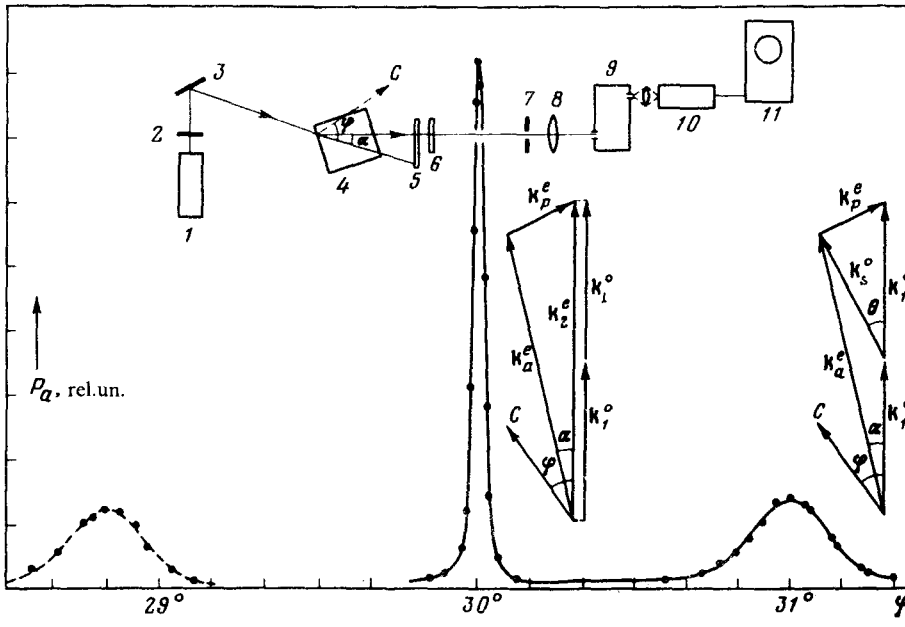

FIG. 1.

of the interacting waves; α is the observed scattering angle, i.e., the angle between the vectors $\mathbf{k}_1$ and $\mathbf{k}_a$. The angles ϕ and α could be varied independently by rotating the crystal and the mirror *3*, but α and θ were uniquely related. Figure 1 shows also the dependence of the intensity of the output signal at the frequency ω_a (in relative units) on the angle ϕ at a fixed $\alpha = 2°$ ($\theta \approx 4°$) for polariton scattering in $LiIO_3$ (solid curve). The maximum at the center at $\phi \approx 30°$ corresponds to the crystal position at which a second harmonic is synchronously generated ($oo \rightarrow e$ interaction mode); this harmonic then undergoes polariton RS ($2\omega_1 = \omega_a' + \omega_p'$, $\omega_p' = 780$ cm^{-1}, $\lambda_a = 0.5550$ μm). Its

angular dimensions determine the angle width 5′ of the synchronism for the frequency-doubling process. At 31°, a new maximum appears, corresponding to the two-stage process of interest to us and on which the PRSS is based: $\omega_1 = \omega_s + \omega_p (o \rightarrow o + e)$ and then $\omega_1 + \omega_s = \omega_a (o + o \rightarrow e)$; $\omega_p = 780\ \text{cm}^{-1}$; $\lambda_a = 0.5550\ \mu\text{m}$. Its height is lower, since the RS cross section is $\sigma(\omega_1) < \sigma(2\omega_1)$. The observed positions of both maxima coincide with the calculated ones.

The RS excited by the $2\omega_1$ wave as a result of illumination by the $2\omega_1$ pump could be observed only in the region $\alpha > 2°$ ($\omega_p > 550\ \text{cm}^{-1}$). At the same time, the PRSS signal could be observed without difficulty for all α. The dashed curve in Fig. 1 shows the PRSS at $\alpha = 0$ ($\omega_p = 673\ \text{cm}^{-1}$ and $\lambda_a = 0.5515\ \mu\text{m}$).

By way of illustration, Fig. 2 shows, in the coordinates α and ω_p (on the left), the

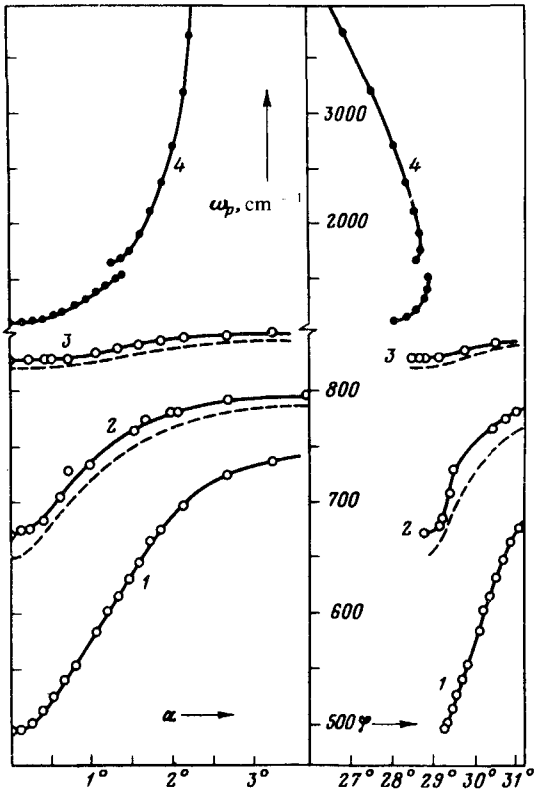

FIG. 2.

dispersion curves of $LiIO_3$ obtained by the PRSS method. Curves 1 and 4 correspond to the processes $e \rightarrow o + e$ (scattering stage) and $o + o \rightarrow e$ (parametric conversion stage), while curves 2 and 3 correspond to the processes $o \rightarrow o + e$ and $o + o \rightarrow e$. Curves 1 and 2 correspond to anisotropic e-polaritons in the bands of polar oscillations of type A and E (795 and 769 cm^{-1}); curve 3 corresponds to the anisotropic longitudinal phonon that is produced when longitudinal phonons of type A (817 cm^{-1}) and E (848 cm^{-1}) are mixed; curve 4 is the upper polariton branch (the break due to the two-particle-state band is seen). The dashed curves (in cases 2 and 3) were calculated.

The results agree well with the previously known ones,[4] a fact that can be regarded as justifying the PRSS procedure. In the right-hand side of Fig. 2 are shown the measured (solid) and our calculated (dashed) curves of the synchronous-addition angle ϕ against ω_p. Similar results were obtained for $LiNbO_3$ and KDP.

A comparison of the RS signals in response to excitations by the waves $2\omega_1$ and PRSS makes it possible to connect the effective quadratic nonlinear polarizabilities $\chi_s = \chi_s(\omega_s, \omega_p)$ and $\chi_\sigma = \chi_\sigma(\omega_a', \omega_p)$, which are responsible for the polariton RS of the ω_1 and $2\omega_1$ waves. Far from the mechanical phonon resonances, the intensity ratio p of these signals, which is equal to the ratio of the maxima on the curves of the type shown in Fig. 1, is $p = (\omega_s \chi_s / \omega_1 \chi_\sigma)^2$ and can be measured without difficulty. Thus, at $\omega_p = 780\ \text{cm}^{-1}$ we have $p = 0.85$ (accurate to 30%) and $\chi_s/\chi_\sigma = 0.45 \pm 15\%$.

Finally, Fig. 3 shows a section, obtained by the PRSS method, of an upper *o*-

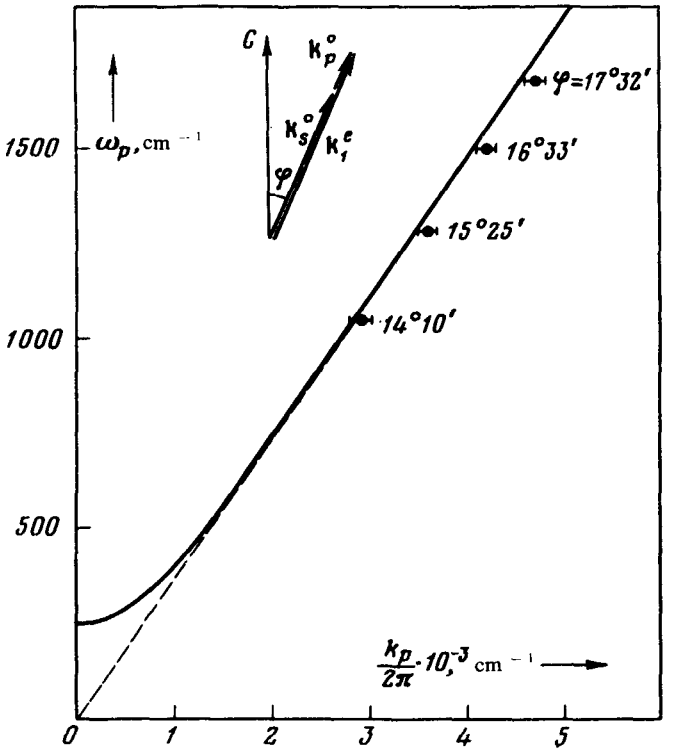

FIG. 3.

polariton branch of a GaSe crystal (solid curve–calculation on the basis of data of Refs. 5 and 6). The latter is opaque in the region $\lambda \leqslant 0.65\ \mu$m, so that the PC of obtaining the RS was produced in an adjacent $LiIO_3$ crystal. In this case $\alpha = 0$ and the RS was retuned by rotating the crystal in accordance with Refs. 7 and 8. The polariton RS in a crystal which is opaque in the visible region of the spectrum was obtained by us for the first time ever, and this was made possible by the PRSS procedure.

In our opinion, the proposed procedure adds to the capabilities of RS spectroscopy of scattering media.

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