Hyper-Raman scattering by polaritons in a centrally symmetric $SrTiO_3$ crystal

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The first observation of polaritons in the hyper-Raman scattering is reported. The lower and upper branches of the polaritons in a centrally symmetric $SrTiO_3$ crystal are investigated.

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We have realized experimentally a new type of spectroscopy of volume polaritons—spectroscopy of hyper-Raman scattering by polaritons (HRSP). The HRSP has a number of important advantages compared to the conventional spectroscopy of Raman scattering by polaritons (RSP).[1] One of the main advantages of this method is that it allows investigation of the HRSP in centrally symmetric crystals (CSC), which are inaccessible for RSP. Equally important is the fact that polaritons in the HRSP are observed in the upper branch of the cubic crystals (CSC and nonCSC).[2] Investigation of HRSP in anisotropic crystals has wider possibilities. Finally, the HRSP can be easily observed in CSC at the scattering angle $\theta \approx 0°$, since the frequencies of the pumping ω_i and of the scattered light near $2\omega_i \pm \Omega$ are spectrally strongly dispersed. It is more difficult to observe HRSP in the RSP near $\theta \approx 0°$ because of the light from the strong exciting line ω_i.

In this paper we investigated the HRSP in a centrally symmetric cubic $SrTiO_3$ crystal of O_h^1 symmetry. The vibrational representation of the crystal includes the $3F_{1u}$ and $1F_{2u}$ optical vibrations, from which only the F_{1u} are allowed in the IR spectra, whereas all types of vibrations are active in the HRS.[3] Both types of vibrations are forbidden in the RS.

The HRSP spectra were recorded by using the multichannel photoelectric system.[4] The focused exciting radiation ($\lambda_i = 1060$ nm) was directed along the crystallographic axis of the sample. The cubic symmetry of the crystal allowed us to obtain a high-transmission system of collection of scattered light, which used ring diaphragms.[5] The average radius of the ring determined the scattering angle θ and the width of the ring's slit determined the angle $\Delta\theta$ of collection of the scattered light ($\Delta\theta = 0.5°$). In our experiment the angular resolution of the HRSP spectra was determined primarily by the angle of divergence $\Delta\phi$ of the exciting beam in the crystal ($\Delta\phi = 1°$). The multichannel recording system allowed us to investigate at the same time the part of the spectrum which was equal to 1000 or 2000 cm^{-1}, depending on the dispersion of the spectrograph. The polariton spectra of the upper branch were investigated with a resolution of 30 cm^{-1} and of the other branches with a resolution of 10 cm^{-1}.

The following relations are fulfilled in the Stokes process of HRSP, in which three photons and one polariton with the wave vector $\mathbf{q}$ and frequency Ω participate:

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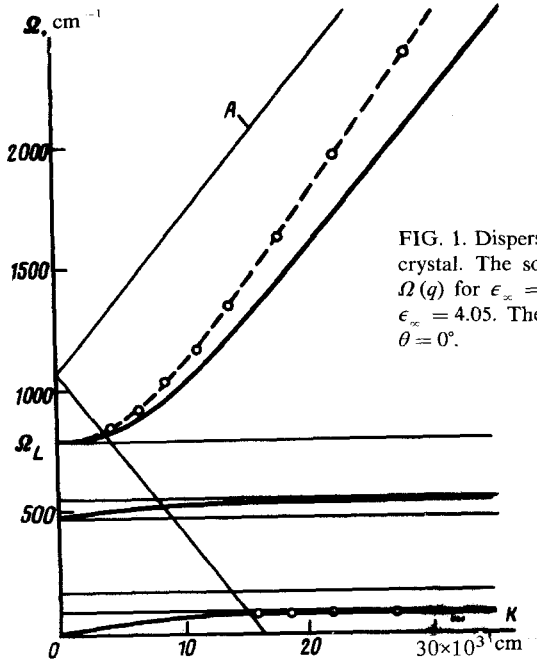

FIG. 1. Dispersion dependences of the polaritons in the $SrTiO_3$ crystal. The solid lines represent the calculated dependences $\Omega(q)$ for $\epsilon_\infty = 5.5$ and the dashed lines denote tne same for $\epsilon_\infty = 4.05$. The line A represents the dependence $q_{\min}(\Omega)$ for $\theta = 0°$.

$$2\omega_i = \omega_s + \Omega \,, \tag{1}$$

$$2\mathbf{k}_i = \mathbf{k}_s + \mathbf{q} \,. \tag{2}$$

Here the subscript i and s refer to the incident and scattered radiation, respectively. The wave vectors $\mathbf{q}$ depend on the scattering angle θ. The relations (1) and (2) make it possible to determine the polariton dispersion $\Omega(q)$ from the experimental dependence $\Omega(\theta)$. On the other hand, it is easy to show that in HRSP, like in RSP, [6] the dispersion dependence of polaritons is described by the relation

$$q^2 = 4\pi^2\Omega^2\epsilon_\infty \prod_{m=1}^{3} \frac{\Omega_{Lm}^2 - \Omega^2}{\Omega_{Tm}^2 - \Omega^2} \,, \tag{3}$$

where ϵ_∞ is the high-frequency dielectric constant and Ω_{Lm} and Ω_{Tm} are the frequencies of the longitudinal and transverse oscillations of the crystal. The wave vector $\mathbf{q}$ and the frequencies in Eq. (3) are given in cm^{-1}. To calculate according to Eq. (3) the dispersion dependences of different polariton branches in the $SrTiO_3$ crystal, which are shown in Fig. 1, we used the values of ϵ_∞, Ω_{Lm}, and Ω_{Tm} from Refs. 3 and 7. The minimum value of $q_{\min}$ obtained in the experiment can be determined from Eq. (2) at $\theta = 0°$:

$$q_{min} = 4\pi\omega_i (n_i - n_s) + 2\pi n_s \Omega, \tag{4}$$

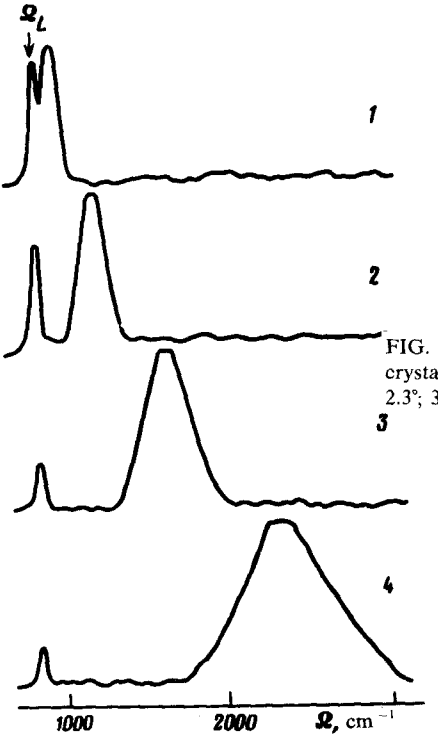

FIG. 2. The HRSP spectra of the upper branch of the $SrTiO_3$ crystal's polaritons for different scattering angles θ: 1, 1.3°; 2, 2.3°; 3, 3.3°; and 4, 4.4°.

where n_i and n_s are the refractive indices, and it depends linearly on the frequency Ω (Fig. 1). The HRSP occurs only on those polaritons whose $\mathbf{q}$ and Ω values satisfy the relations (1)–(3), and hence they lie on the dispersion curves on the right-hand side of the line $q_{\min}(\Omega)$ (Fig. 1). We shall mention two peculiarities of HRSP, which can be expected to occur in the cubic $SrTiO_3$ crystal (Fig. 1). The first one is that the polaritons of almost the entire upper branch, beginning with 825 cm^{-1} and higher, may be active in the HRSP; the second one is that a small shift of the polariton frequencies is expected to occur in the lower branches.

The polariton spectra of the upper branch for some angles θ are shown in Fig. 2. Our spectral frequency range for the instrumental function $\Delta\phi + \Delta\theta$ of the collecting circuit of the scattered light is larger than the natural width of the polariton in the upper branch and increases rapidly with increasing frequency of the polariton. In the HRSP spectrum, therefore, the polariton is also broadened with increasing scattering angle θ (Fig. 2), although the natural width of the polariton in this case decreases in the upper branch. The intensities of the polaritons were adequate only for observation of two branches—the upper and the lower branch. All the experimental values of $\Omega(q)$ are represented by the points in Fig. 1. In the lower branch the frequency of the polaritons decreases from 88 cm^{-1} at $\theta = 90°$ to 75 cm^{-1} at $\theta = 0°$. The polariton is shifted significantly in the upper branch—from $\sim$830 cm^{-1} at $\theta = 0°$ to 2370 cm^{-1} at $\theta = 4.4°$ inside the crystal.

The experimental points in the lower polariton branch lie well on the calculated

curve. The points in the upper branch deviate systematically from the calculated curve in one direction (Fig. 1). Analysis of possible reasons for the deviation showed that the most probable reason may be the incorrect value of $\epsilon_\infty = 5.5$ for $SrTiO_3$ obtained from literature,[7] which was used in calculating the dispersion curves according to Eq. (3). If, however, we take $\epsilon_\infty = 4.1 \pm 0.1$, then the experimental points fit well the calculated upper branch (dashed curve in Fig. 1).

Thus, our experiment demonstrates that polaritons can be investigated successfully by using the HRS method.

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