Resonant hyper-Raman scattering of light by optical phonons

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We report on the first experimental observation of resonant hyper-Raman scattering of light by optical phonons.

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Hyper-Raman scattering (HRS) of light constitutes a three-photon process in which a quantum of scattered radiation $\hbar\omega_s$ is generated at the expense of two quanta of the exciting radiation $\hbar\omega_l$: $\omega_s = 2\omega_l \pm \omega$, where ω is the frequency of the scattering excitation of a medium (see, for example, the review[1] and references therein). In recent times, HRS has attracted progressively greater attention from researchers. This appears to be associated with the new spectroscopic possibilities of HRS. For example, it is possible to use the latter to study excitations that are inactive in the conventional Raman scattering (RS), as also those that are inactive in both the RS and IR spectra. In particular, HRS facilitates the study of polariton excitation in centrally-symmetrical media.

In this work we report on the first experimental observation of resonant HRS of light by optical phonons. The experimental investigation was carried out using equipment described earlier.[2] The scattering was excited by means of a neodymium-doped

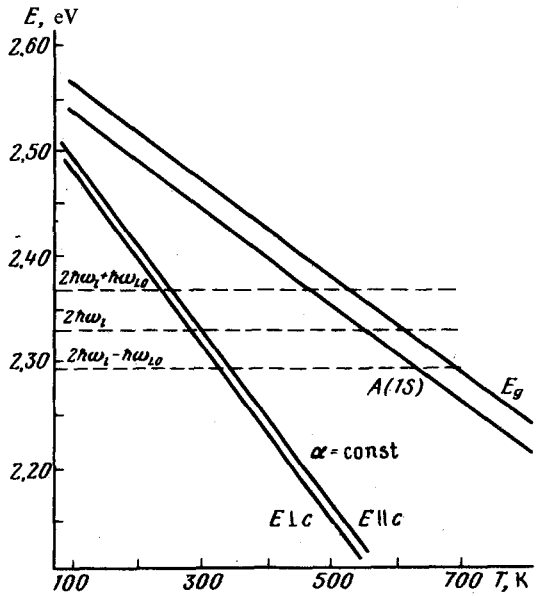

FIG. 1. Temperature functions of forbidden band width E_g, position of A (1s) exciton and constant absorption level $\alpha \approx 1$ cm^{-1} for two different polarizations ($\mathbf{E} \| c$ and $\mathbf{E} \perp c$; c is direction of optical axis) for CdS crystal; $\nu = \omega/2\pi c$.

yttrium aluminum garnet (YAG) laser ($\lambda_l = 1.064$ μm) operating at a single transverse mode in a pulsed Q-switched regime at a pulse repetition frequency of 50 Hz. The scattered light was recorded by means of a FEU-79 gated and cooled photomultiplier operated as a photon counter. Selected by means of a MDR-2 monochromator, HRS was observed at a 90° angle with respect to the direction of propagation of the exciting radiation. As a test object we picked a CdS crystal, since in this case, using a YAG laser to excite HRS, the frequency of scattered light falls in the near-resonant region (edge of absorption of this crystal) and the resonance conditions may be varied by changing the sample temperature, since the width of the forbidden band E_g depends significantly on the crystal temperature. Figure 1 shows the temperature dependence of the width of the forbidden band E_g, location of the exciton A (1s) line,[3] and level of constant absorption $\alpha = \text{const}$ (for two directions of light polarization) of the CdS crystal. The temperature dependence of the constant absorption level $\alpha = \text{const}$ was measured in the same sample as the one used for the HRS investigations. The dashed lines indicate the doubled quantum energy of the pumping laser ($2\hbar\omega_l = 2.33$ eV) and the quantum energy of the Stokes and anti-Stokes components.

The resonant HRS was investigated by way of measuring the integral intensities of both the Stokes and anti-Stokes components of scattering by longitudinal optical phonons of symmetry E_1 ($\nu_{LO} = 307$ cm^{-1}) as a function of CdS crystal temperature for a scattering geometry $x(z,z+x)y$. Figure 2 shows the results of these measurements. The solid curves connect the experimental points.

It can be seen from Fig. 2 that the intensity of both the Stokes and anti-Stokes components increases at first with increasing temperature, whereupon it sharply falls off. This sharp drop is due to absorption of the scattered light in the sample, and the

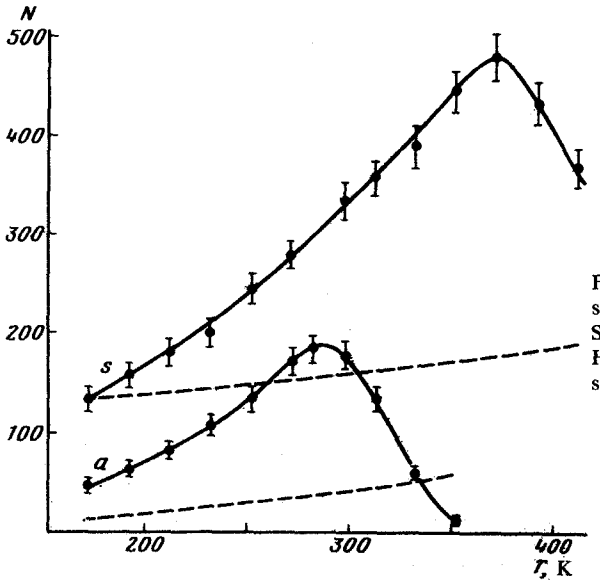

FIG. 2. Temperature functions of integral intensity N (number of photomultiplier counts) of Stokes (s) and anti-Stokes (a) components of HRS by longitudinal optical phonons of E_1 symmetry.

location of the inflection points in the intensity curves of the Stokes and anti-Stokes scattering components agree with the curves in Fig. 1. An increase in the scattering intensity with increasing crystal temperature can be achieved by a temperature dependence of the phonon mode population and the variation of resonant conditions of the scattering process with the temperature. The dashed curves represent the calculated temperature dependence of the scattering intensity, subject only to variations in the phonon mode population. The curves are normalized at a point corresponding to the Stokes component at $T = 173$ K. A comparison of the solid and dashed curves in Fig. 2 shows that the experimentally-observed functions cannot be explained by changes in the phonon mode population only, a fact that attests to the manifestation of resonance effects in HRS. In addition to this, in the case of HRS on equilibrium phonons under the conditions outside the resonance the following relationship should be satisfied between the intensities of the Stokes (s) and anti-Stokes (a) components[2,7]

$$I_a/I_s = [(2\omega_l + \omega)/(2\omega_l - \omega)]^4 \exp(-\hbar\omega/kT). \quad (1)$$

However, it follows from the experimental results (Fig. 2) that the above relationship remains unfulfilled [the scattering intensity in the anti-Stokes region is greater than indicated by Eq. (1)]. This deviation from Eq. (1) may also be explained by the occurrence of resonance effects in the HRS spectra: the anti-Stokes component undergoes a "stronger resonance" than the Stokes component because

$$E_g - \hbar\omega_a < E_g - \hbar\omega_s.$$

We should also note certain special features of the experimental HRS spectrum of the CdS crystal. According to the selection rules and the aforementioned scattering geometry, an HRS spectrum should contain transverse components (TO) of the oscillation $A_1(\nu_{TO}^{A_1} = 234\ \text{cm}^{-1})$ and longitudinal (LO) and transverse (TO) components of

the oscillations E_1 ($\nu_{TO}^{E_1} = 243$ cm^{-1}, $\nu_{LO}^{E_1} = 307$ cm^{-1}). In the resultant spectrum, however, only a single line is seen which corresponds to a longitudinal optical (LO) phonon of E_1 symmetry and a line at an undisplaced frequency (i.e., with $\nu = 0$ cm^{-1}).[1)] We were unable when changing the resonance conditions to detect lines in the HRS spectrum which correspond to transverse optical (TO) phonons (of both the A_1 and E_1 symmetries), although the experimental setup was capable of a reliable detection of the HRS line that was one half the strength of the observed line with $\nu = 307$ cm^{-1}.

It is of interest to compare the obtained results with data relative to manifestation of resonance effects in the conventional Raman scattering (RS) spectra of light for the same crystal. The intensity of RS on longitudinal optical phonons monotonically increases as the quantum energy of exciting photons approaches the forbidden band energy of a crystal, as is the case with the HRS. However, the nature of the intensity of RS on transverse optical phonons is non-monotonic, since it goes through a minimum at $E_g - \hbar\omega_s \sim 0.8$ eV.[5] The absence of the HRS lines due to the transverse phonons is, possibly, also associated with the interference effects of various contributions to the scattering tensor. We were unable to detect in the resonant HRS spectra scattering at double the frequency of the longitudinal optical phonon ($\nu = 2\nu_{LO}$), whereas in the resonant RS spectra the intensity of scattering at this frequency was approximately an order of magnitude higher than the scattering intensity on the longitudinal optical phonons ($\nu = \nu_{LO}$).[6]

In conclusion we should note that a full interpretation of the observed special features of the resonant HRS spectra requires additional experimentation that involves the use of tunable lasers to excite scattering (this will provide a possibility of varying the resonance conditions over a broader range), and the development of a theory of resonant HRS by optical phonons.

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[1)]Discussion of the scattering mechanism at an undisplaced frequency $\nu = 0$ cm^{-1}, and also of possible cascade processes that contribute to the HRS spectrum, is provided in Ref. 4.

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