

# Multiphonon resonant hyper-Raman scattering

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Multiphonon resonant hyper-Raman scattering of light by longitudinal optical phonons has been detected for the first time in a CdS crystal. The behavior of the scattering cross sections with increasing number of excited phonons is of an alternating nature, and it is directly the opposite of that in the case of resonant Raman scattering. The difference is attributed to different sequences of intermediate states in the cases of multiphonon Raman and hyper-Raman scattering.

The scattering of light near the fundamental absorption edge of a crystal has attracted considerable research interest, since such studies can provide important information on the nature and mechanisms of the electron-phonon interaction. The resonant increase in intensity adds substantially to the experimental possibilities. A huge amount of experimental and theoretical material has now been accumulated on resonant Raman scattering (RS<sup>1</sup>, for example). Another interesting topic is resonant hyper-Raman or two-photon Raman scattering (HRS), which is a process of higher order in the expansion of the polarization of the medium in powers of the electric field. In hyper-Raman scattering, two photons of frequency  $\omega_l$  are absorbed simultaneously, and one scattered photon of frequency  $\omega_s$  is created. The crystal goes from its ground state into an excited state, and one or more phonons are created in the process (these are the cases of single-phonon and multiphonon scattering, respectively<sup>2-4</sup>). Since the elementary event of hyper-Raman scattering involves more photons than are involved in ordinary Raman scattering, there are changes in selection rules and in the role of the intermediate states. As a result, new features appear in the resonant-scattering spectra. Several papers have reported the detection of single-phonon resonant hyper-Raman scattering in crystals.<sup>5-10</sup> Our purposes in the present study were to observe multiphonon resonant hyper-Raman scattering and to identify features which distinguish it from the familiar spectra of resonant Raman scattering.

The experiments used a single-channel computer-controlled spectrometer. The HRS spectra were excited by an LTI-502 periodic-pulse, single-mode Nd:YAG laser (wavelength  $\lambda = 1.064 \mu\text{m}$ , repetition frequency from 5 to 20 kHz at a pulse length of 300 ns and an average power up to 6 W). The laser beam was focused into the sample by a lens with a focal length of 40 cm; the power density in the beam caustic ranged up to  $5 \text{ MW/cm}^2$ . The scattered light was analyzed by a JOBIN YVON THR-1000 single monochromator with a focal length of 1 m, an aperture ratio of 1/10, a linear dispersion  $\approx 5 \text{ \AA/mm}$ , and a diffraction grating with 1800 lines/mm. The scattered light was detected by an FÉU-106 photomultiplier cooled to  $-30^\circ\text{C}$ . The photomultiplier operated in the photon-counting regime with strobing. The cooling and strobing of the photomultiplier kept the thermal noise of the electronic system

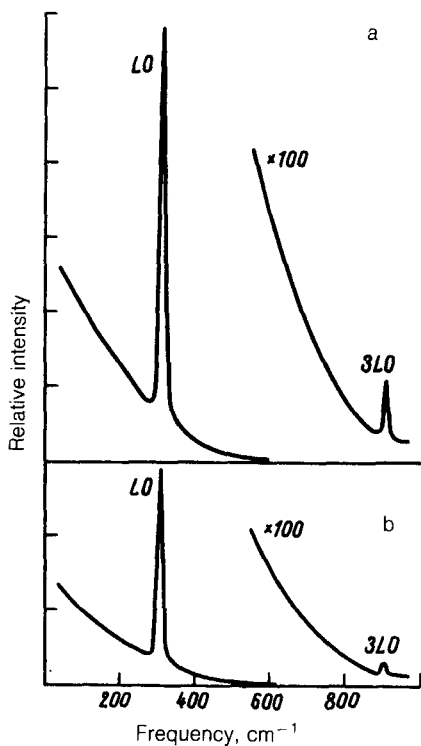


FIG. 1. Spectra of resonant hyper-Raman scattering in CdS recorded at two repetition frequencies of the exciting light pulses: *a*—10 kHz; *b*—20 kHz.

below 1–2 counts per  $10^4$  laser pulses. The multiple scanning, the storage of the scattering spectra, and a preliminary mathematical analysis of these spectra were carried out with the help of an Apple personal computer and software developed especially for HRS experiments.

The CdS crystal was selected as test sample, since its band gap,  $E_g = 2.53$  eV,<sup>11</sup> is approximately twice the photon energy of the Nd:YAG laser, and previous experiments<sup>5</sup> under these conditions have revealed a resonant HRS by longitudinal optical phonons  $\omega_{LO}$ . Furthermore, the resonant RS spectra of CdS have been studied in detail both experimentally and theoretically.<sup>1,12</sup>

The major goal in the planning of the experiment was to detect signals corresponding to Stokes scattering with frequency shifts  $2\omega_{LO}$  and  $3\omega_{LO}$ . Figure 1 shows HRS spectra found from a CdS crystal at room temperature in the  $z(x + x, x)y$  scattering geometry. In this geometry, the incident and scattered waves propagate along the  $z$  and  $y$  axes, respectively, and are polarized along the  $x$  axis<sup>1)</sup> (Fig. 2). The  $\omega_{LO}$  line was detected in two scanning cycles with a buildup time of 5 s per point. The buildup time was increased by a factor of 30 for observation of the signals at  $2\omega_{LO}$  and  $3\omega_{LO}$  (60 per point; 5 scanning cycles). In the resulting spectra we can clearly see (along with  $\omega_{LO}$ ) the  $3\omega_{LO}$  line, but the  $2\omega_{LO}$  line could not be seen under these conditions. We were also unable to observe HRS by transverse phonons. This result is

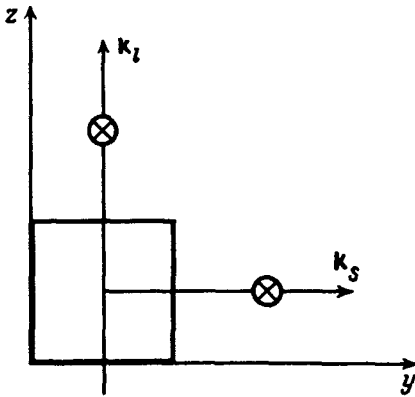


FIG. 2. The scattering geometry. Here  $k_i$  and  $k_s$  are the wave vectors of the exciting light and the scattered light. The polarization of both the exciting light and the scattered light is along the  $x$  axis, *i.e.*, perpendicular to the plane of the figure.

evidence of a Fröhlich mechanism for the interaction in the case of resonant scattering in the CdS crystal.

Spectra *a* and *b* in Fig. 1 were excited by light with pulse repetition frequencies of 10 and 20 kHz, respectively. Doubling the frequency doubles the increase in the average power of the light but does not change the peak power. In spectrum *b*, the amplitude of the  $\omega_{LO}$  line is higher by a factor of about 2, and the amplitude of the  $3\omega_{LO}$  line by a factor of nearly 5, than for spectrum *a*. The intensity ratio of these lines,  $I_{LO}/I_{3LO}$ , varied from 1600 (spectrum *a*) to 700 (spectrum *b*). We believe that the differences observed in the spectra are due to a warming of the crystal in the caustic as a result of the increase in the average power of the exciting light. The warming of the crystal narrows the band gap and thus alters the resonance conditions for the HRS. Estimates based on the temperature dependence of the spectra of HRS by polaritons<sup>14</sup> show that the temperature in the caustic rises by about 20°C under these conditions.

The results of this experiment are unambiguous evidence of an alternation of the intensities of the overtones of the longitudinal optical phonon during multiphonon resonant HRS. Only the lines corresponding to scattering by phonons of odd order ( $LO$  and  $3LO$ ) are observed in the spectra. On the other hand, numerous studies<sup>1,12</sup> of resonant scattering of light in semiconductor crystals have demonstrated that the situation in the spectra of the resonant RS in CdS is directly the opposite: Phonons of even order ( $2LO$ ,  $4LO$ ,  $6LO$ , etc.) are predominant in the scattering.

The theory of resonant RS scattering derived in Ref. 12 provides a qualitative explanation of the differences in the behavior of the intensities of the multiphonon-scattering lines in the resonant spectra of RS and HRS. According to that theory, the irregular nature of the intensities in the RS spectra stems from a difference in the behavior of the scattering cross sections of even and odd orders: For the cross sections of even order, one can construct a chain of intermediate states of alternating parity ( $s$ - $p$ - $s$ ,  $s$ - $p$ - $s$ - $p$ - $s$ , etc.), while for processes of odd order the chain must include at least one matrix element between states of identical parity ( $s$ - $p$ - $s$ - $s$ ,  $s$ - $s$ - $p$ - $s$ ,  $s$ - $p$ - $p$ - $s$ , etc.). The reason is that the first and last states must be  $s$ -states. A factor  $M^2 \ll 1$  accordingly appears in the chain for an odd order. This factor corresponds to

the matrix element for a transition between states of identical parity. This circumstance explains the alternation of intensities in RS spectra which had been observed previously.<sup>12</sup>

Taking a similar approach to analyze the HRS spectra, we find a chain of intermediate states of alternating parity for processes of odd order ( $p$ - $s$ ,  $p$ - $s$ - $p$ - $s$ , etc.). The matrix element between states of identical parity now arises in processes of even order, since the first state for the electron-phonon matrix element in the case of HRS must be two-photon-allowed, i.e., a  $p$ -state. This circumstance explains the alternation of line intensities in the HRS spectra which we observed. A quantitative description of this effect will require the derivation of a theory for resonant HRS in semiconductors.

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<sup>1</sup>In the CdS crystal, which does not have a symmetry center, there is the possibility in principle that the second harmonic of the exciting light will be generated, and that RS will follow. However, second-harmonic generation is forbidden in the scattering geometry specified, so ordinary RS due to this generation is not manifested in the HRS spectra. This question was studied previously<sup>13</sup> for the case of the CdS crystal.

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