Stimulated Raman scattering in suspension of submicron diamond particles

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Abstract. We report on the first experimental observation of stimulated Raman scattering (SRS), stimulated low-frequency Raman scattering and multiphoton excited negatively-charged single nitrogen-vacancy (NV-) centers luminescence in ethanol suspension of submicron diamond particles obtained at high pressures and temperatures (HPHT). The Stokes and anti-Stokes SRS components with a frequency shift of 1332 cm\(^{-1}\), corresponding to the fundamental optical mode of diamond crystal were observed. The spectral characteristics and energy thresholds of the studied processes were determined.

1. Introduction

Raman scattering in diamond for the first time was registered in 1930 [1]. This research has not lost relevance nowadays due to the possibility of using diamond as an active medium for Raman converters. Stimulated Raman scattering in natural diamond was observed in the 1960’s [2, 3].

Group-theoretical analysis in the long-wavelength approximation showed that in Raman scattering (RS) spectra of diamond there is one triple degenerate fundamental \(F_{2g}\) symmetry mode. Its frequency shift is 1332 cm\(^{-1}\), which corresponds to the vibrations of two interpenetrating cubic diamond sublattices.

Diamond has unique physical properties: a large Raman gain coefficient, large Raman shift (1332 cm\(^{-1}\)), the highest thermal conductivity of any known materials, low thermal expansion coefficient and transparency between \(\lambda = 230\) nm and \(\lambda = 2500\) nm. These properties cause interest in diamond as an effective medium for SRS generation. Despite a long period of research on diamond as a Raman laser material, its real use began relatively recently and is associated with progress in the development of diamond synthesis with a high optical quality. The use of diamond made it possible to obtain a record output power of a Raman laser in pulsed and continuous modes [4, 5]. High order Stokes and anti-Stokes components generation was realized in diamond, synthesized by chemical vapor deposition (CVD). The conversion efficiency of 45% of energy from the pumping Nd\(^{3+}\):Y\(_3\)Al\(_5\)O\(_{12}\) laser radiation to all Stokes and anti-Stokes components was achieved [6].
Despite the great progress in the study of SRS in solid samples, the realization of the SRS in a system of randomly distributed submicron particles of an active substance is of great interest. Multiple light scattering effectively increase the interaction length and this can lead to compensation for losses due to sample heterogeneity. In the beginning of the sixties [7] stimulated Raman scattering was registered in highly inhomogeneous systems - fine powders. SRS process in fine powders can be described nearly in the same way as a process of random lasing [8, 9].

Nanoscale diamond particles were first synthesized by detonation in 1963 in the USSR [10]. Since then, nanodiamonds have attracted increasing attention around the world. This is facilitated by the continuous process of improving the technology of synthesis and purification of samples. A significant role is played by lowering the cost of production of nanodiamonds. Currently, there is a fairly large number of methods for the synthesis of nanoscale diamonds except detonation: chemical vapor deposition (CVD) [11], high pressure high temperature annealing (HPHT) [12], laser ablation [13], ultrasonic cavitation [14].

The aim of this work was an experimental demonstration of the possibility of using a suspension of diamond nanoparticles as an active medium. We registered spontaneous Raman scattering in nanodiamonds powder and oil-based paste and stimulated scattering in the ethanol suspension of the same diamond nanoparticles. Together with SRS simulated low-frequency Raman scattering in the same samples was studied. This kind of scattering is caused by the laser light interaction with acoustic vibrations of nanoparticles. Its frequency shift corresponds to the eigenvibrations frequencies of nanoparticles, lying in gigahertz range and depending on the nanoparticle size and elastic properties. Thus, SLFRS may be registered only in highly monodispersed media.

2. Samples
Submicron diamond particles used in the experiments have been obtained by synthesis at high pressures and temperatures (HPHT). They have been studied in the following forms: diamond powder, diamond oil-based paste and suspension of diamond submicron particles in ethanol. Suspension of diamond submicron particles was more optically homogeneous compared to diamond particles powder and diamond oil-based paste. The transmission of a cell with diamond particles ethanol suspension 1 cm long is 50%. Radius distribution of diamond particles in ethanol suspension obtained by dynamic light scattering is presented in figure 1.

![Figure 1. Distribution of hydrodynamic radius of diamond nanoparticles in ethanol.](image)

Diamond particles radius obtained by this method is 250 nm.

3. Experimental
Spontaneous Raman (RS) spectra of diamond particles (HPHT) powder and diamond oil-based paste with a 10% mass fraction of diamond with radius of 0.25 μm were excited by cw laser with a generation wavelength $\lambda_0 = 785$ nm and a power of 100 mW. The spectrometer resolution was 1 cm$^{-1}$. 
The normalized spectrum of spontaneous RS of diamond oil-based paste is shown in figure 2. Note that the Raman spectrum of submicron diamond particles looks similar.

![Figure 2. Spontaneous RS spectrum of diamond paste.](image)

The RS spectra of this sample were recorded for 100–400 s exposition and contain only a high-intensity diamond line with a frequency shift \( \nu = 1332 \text{ cm}^{-1} \) (half-width \( \Delta \nu = 3 \text{ cm}^{-1} \)).

To study the stimulated Raman scattering, we used ethanol suspension of submicron diamond particles, on which spontaneous Raman scattering spectra were obtained. Submicron particles of diamonds have radius 250 nm, and they tend to aggregate, forming larger stable aggregates. Disaggregation was carried out by ultrasonic treatment before each spectral measurement.

SRS in submicron diamond particles was excited by the nanosecond pulses of Q-switched ruby laser (\( \lambda = 694.3 \text{ nm}, E_{\text{max}} = 0.4 \text{ J}, \tau_p \approx 20 \text{ ns}, \Delta \nu = 0.015 \text{ cm}^{-1}, \text{divergence} \ 3.5 \cdot 10^{-4} \text{ rad} \)). Exciting light beam was focused at the sample by a lens with focal length 5 cm. The concentration of the submicron diamond particles was \( 10^{11} \text{ cm}^{-3} \). The length of the cell was 1 cm. Experimental setup is shown in figure 3.

![Figure 3. Experimental setup for SRS observing: 1 – ruby laser; 2 – glass plate; 3 – system for laser pulse characteristics measurements; 4 – lens; 5 – quartz cell with a sample; 6 - spectrometer connected to PC.](image)
Energies of the laser pulse and scattered radiation were measured simultaneously. Figure 4 shows SRS spectrum propagating in forward direction. The wavelength of Stokes component was 765 nm and anti-Stokes was 635.5 nm.

As may be seen, the spectrum contains Stokes and anti-Stokes components at 1332 cm\textsuperscript{-1}, which corresponds to the F\textsubscript{2g} symmetry line of the diamond crystal. The maximum conversion efficiency was 7 percent. The experimental threshold (I\textsubscript{th}) for given experimental conditions was estimated to be 0.75 GW/cm\textsuperscript{2}. Taking into consideration the relation I\textsubscript{th}gl = 30, where g – Raman gain and l – length of the active medium, one can get g = 40 cm/GW. This value coincides well with the value which one can find in [15].

Under these experimental conditions, using the experimental setup shown in figure 3, when the threshold value of 0.9 GW/cm\textsuperscript{2} is exceeded, the shape of the spectrum in the region of the SRS anti-Stokes component varies significantly being more complicated. Additional spectral components appearing in the spectrum can be attributed to the multiphoton-excited negatively-charged single nitrogen-vacancy (NV-) centers luminescence. The process of multiphoton excitation of luminescence of different types in the system of diamond nanoparticles was considered in [16]. The diamond luminescence caused by NV - defects is usually characterized by zero phonon line (ZPL) at 638 nm which is accompanied by vibronic side bands at lower frequencies [17].

A distinctive feature of these results is that due to the wavelength of excitation the spectral position of the ZPL and the anti-Stokes Raman component coincide. It leads to a significant increase in intensity in the anti-Stokes region of the spectrum (figure 5).
SRS conversion restriction is associated with a competing process with the SRS, namely, the stimulated low frequency Raman scattering (SLFRS). SLFRS is a stimulated analogue of spontaneous low-frequency Raman scattering caused by the interaction of the electromagnetic radiation with acoustic vibrations of nano- or submicron particles [18]. SLFRS frequency shift is defined by the morphology of the system used, first of all by the average size and elastic characteristics of the particles and the matrix in which they are located and typically lies in gigahertz range.

For SLFRS investigations experimental setup shown in figure 6 was used.

![Experimental setup for SLFRS observing](image)

**Figure 6.** Experimental setup for SLFRS observing: 1 – ruby laser; 2 – glass plates; 3 – system for laser pulse characteristics measurements; 4 – lens; 5 – quartz cell with the sample; 6 – Fabri-Perot interferometers; 7– cameras, registering SLFRS spectra.

SLFRS was excited by 20 ns pulses of the ruby laser (1) in the ethanol suspension of the same nanoscale diamond particles, which were used in the investigations of spontaneous and stimulated Raman scattering. The nanodiamonds had size 250 nm. Exciting light was focused into the quartz cell (5) with nanodiamonds suspension by the lens (4) with focus 5 cm. For simultaneous registration of the SLFRS spectral components, propagating in forward and backward directions, Fabri-Perot interferometers with different ranges of dispersion from 0.167 cm\(^{-1}\) to 16.7 cm\(^{-1}\) (5 - 500 GHz) were used. When the pump intensity reached a threshold value, SLFRS was excited in the studied system. When the exciting light intensity was under the threshold, only one system of rings, corresponding to the pump light, was observed at the exit of Fabri-Perot interferometer. SLFRS excitation led to the appearance of the additional rings system. Pictures, obtained with the help of the interferometers, were registered by the cameras (7) and processed with the special program. Spectrum of the SLFRS first Stokes component in forward direction is presented in figure 7. Analogous spectrum was observed for SLFRS in backward direction. The SLFRS threshold for scattering propagating in backward and forward directions was about 1 GW cm\(^{-2}\). Note that a further increase in the conversion efficiency of the pump wave into the SLFRS wave was limited by optical breakdown, the threshold of which under the present experimental conditions was 1.5 GW/cm\(^2\).
Simultaneously with spectral measurements the conversion efficiency of the exciting light into SLFRS was measured. The maximum conversion efficiency was 40 per cent. The experimental frequency shift was 45 GHz (1.5 cm⁻¹). The frequency shift was the same for SLFRS propagating in forward and backward directions.

Note that the scattering divergence was comparable with the divergence of laser radiation and the spectral width of the scattered light was of the order of 0.2 cm⁻¹.

4. Conclusion
We experimentally showed that a suspension of nano or submicron particles (in our experimental case, submicron particles of diamond) can be used as a Raman active medium. We registered spontaneous Raman scattering (RS) in nanodiamonds powder and oil-based paste. Stimulated Raman scattering (SRS) and stimulated low-frequency Raman scattering (SLFRS) have been studied in the ethanol suspension of the same nanoparticles. First Stokes Raman component with frequency shift 1332 cm⁻¹, corresponding to the vibrations of two interpenetrating cubic diamond sublattices, was registered both in RS and SRS spectra. In SRS spectrum we also registered anti-Stokes component. Increasing exciting light intensity led to the appearance of complicated structure of the anti-Stokes component, which can be explained by multiphoton-excited diamond luminescence caused by NV – defects. This effect was experimentally realized under conditions of coincidence of its spectral position with the position of the anti-stokes component of SRS. A significant influence on the efficiency of the SRS conversion is exerted by SLFRS, which greatly limits SRS conversion efficiency. Thresholds of all studied effects have been determined.

Acknowledgments
This work was supported by Russian Foundation for Basic Research (Grants 18-02-00181, 18-32-00259, 19-02-00750-a, 19-02-00440-a) and China Scholarship Council.

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