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Seventy years of combination (Raman) scattering

I L Fabelinskiĭ

Contents

Abstract. The discovery of the combination scattering of light (the Raman effect) is discussed briefly in historical perspective. Landsberg and Mandel'shtam in Moscow observed spectral lines of the new phenomenon for the first time in crystals on February 21, 1928, and published their results on July 13, 1928, while Raman and Krishnan, in Calcutta, observed similar lines in a number of liquids on February 28, 1928, and published their results on April 21, 1928. Landsberg and Mandel'shtam gave the right interpretation of the new phenomenon in their first publication. The reason for the delay of this publication is explained. A brief note is given on the fate of the discovery and of the people who made it. Raman is the only one who was awarded the Nobel Prize for physics in 1930. The list of the 1930 Nobel Prize nominees in physics is presented. Developments in the field of combination scattering are discussed and the role of the phenomenon in applied research and science illustrated.

1. Introduction

Combination scattering of light (the Raman effect), one of the most remarkable discoveries in physics of the XXth century, proved to be an exceedingly effective method of quite diverse studies in physics, chemistry, biology and other sciences.

Combination scattering of light made a great contribution to the study of molecular structures, intermolecular interactions and the time-dependent kinetics of various phenomena, including chemical reactions and eigenfrequencies of individual molecules. The appearance of high-power laser sources allowed the discovery of new phenomena in combination scattering of light, which we shall discuss in more detail below.

Briefly and not rigorously speaking, the phenomenon of combination scattering of light consists in the following.

Imagine a diatomic molecule, for example, a hydrogen molecule with two electrons comprising the electron shell of H_2 molecules. If the selected molecule is conceived as motionless then the light incident on it and described by the well-known expression for the electric field strength $\mathbf{E} = \mathbf{E}_0 \cos(\omega t)$ will build up oscillations of the electron shell in time with its own frequency ω and induce a momentum $\mathbf{P} = \alpha_0 \cos(\omega t)$ (where α_0 is a constant) in the molecule; this momentum will determine the light scattered in all directions with the frequency ω of the exciting light. It is of importance to emphasize that in the case under consideration the frequency of the scattered light is the same as that of the exciting light.

The picture described of the interaction between light and a molecule cannot however be realized in practice. In the real case, the atoms constituting a molecule will 'shake' under the action of thermal motion, and for the induced molecular momentum one should write the expression

$$\mathbf{P}(q\omega) = \alpha(q)\mathbf{E}_0 \cos(\omega t) \,, \tag{1}$$

where q is a generalized coordinate, $\alpha(q)$ is the molecular polarizability in the function of coordinate, which is generally a tensor quantity but is assumed for simplicity to be scalar, and possible molecular rotation is disregarded.

I L Fabelinskiĭ P N Lebedev Physics Institute, Russian Academy of Sciences, Leninskiĭ prosp. 53, 117924 Moscow, Russia
Tel. (7-095) 135 24 11
Fax (7-095) 938 22 51
E-mail: fabelins@sci.lpi.msk.su

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For small displacements of atoms from their equilibrium position and for sinusoidal atomic oscillations in the molecule, the polarizability can be expanded as follows

$$\alpha(q) = \alpha(0) + \frac{\partial\alpha}{\partial q}\, q\cos(\Omega t + \varphi)\,. \tag{2}$$

Here φ is an arbitrary phase, and Ω is the frequency of the oscillations or, as is termed above, of the molecular 'shaking'.

Now substituting (2) into (1), after simple transformations we obtain

$$\mathbf{P} = \alpha(0)\mathbf{E}_0\cos\omega t + \frac{1}{2}\frac{\partial\alpha}{\partial q}\, qE_0\Big\{\cos\big[(\omega+\Omega)t+\varphi\big] + \cos\big[(\omega-\Omega)t-\varphi\big]\Big\}\,. \tag{3}$$

The intensity and the spectral composition of scattered light will be determined by the induced momentum (3), and it is therefore obvious that the lines of frequency ω and two more lines — one of frequency $\omega-\Omega$ (a Stokes line or a 'red' satellite) and the other of frequency $\omega+\Omega$ (an anti-Stokes line or a 'violet' satellite) must be present in the scattered light.

When L I Mandel'shtam and G S Landsberg saw such a spectrum on their negative, they provided the explanation, which is presented above; this explanation was correct and holds up to now.

This explanation can also be extended to a more involved case of a more complex molecule and even of oscillations in crystals.

Now, 70 years after the discovery of this remarkable phenomenon, when it is being used fruitfully in various branches of science and thousands if not tens of thousands of papers have been devoted to it, dozens of thick monographs and reference books have been written, it is pertinent to recall how it all began there, in the places where the phenomenon was discovered — in Russia and India.

We know better of the events that took place in Russia, although those who participated in the work of the laboratory are already dead. The author of the present paper worked for 20 years in the laboratory headed by G S Landsberg, attended L I Mandel'shtam's lectures and seminars and even spoke with him, and had a lot of communications with M A Leontovich, who was then an assistant in the optical laboratory, and with S M Rytov — a post-graduate student of L I Mandel'shtam.

We know less of the studies carried out in India. Our knowledge in this case is limited to an acquaintance with what was published by C V Raman himself and other Indian scientists.

Much has been written of the history of combination scattering of light, and even the present author has specially written of it twice [1, 2]. Interesting materials can also be found in the books of reminiscences about L I Mandel'shtam [3], G S Landsberg [4], and M A Leontovich [5].

On the 70th anniversary of the discovery of this distinguished physical effect it is worth remembering how this discovery was made and what was said about it then.

2. How the combination scattering of light was discovered. The studies in Moscow

In Russia, the studies of light scattering began on the initiative of L I Mandel'shtam who had been invited to the Faculty of Physics of Moscow State University as head of the department of theoretical physics. L I Mandel'shtam accepted the offer and moved to Moscow†. This was in 1925. At that time Landsberg, who became Mandel'shtam's co-worker and friend, had already been working for some time at the physics faculty of Moscow State University. Shortly thereafter Mandel'shtam formulated an experimental problem to reveal the fine structure in the spectrum of light scattered by a solid body, the structure that was induced by modulation with elastic thermal waves. These are the thermal waves whose energy is equal to the kinetic energy of the thermal motion of particles in the medium. The number of such waves is huge, equal to the number of degrees of freedom $3N$ of particles in the sample, and the frequencies of these waves extend from zero to the maximum frequency $v/d \sim 10^{13}$ Hz (here v is the speed of sound, and d is the interparticle distance).

In scattered light, for example, waves appear of a frequency of about $\sim 10^{10}$ Hz, propagating at a scattering angle $\theta \cong 90°$. The separation between the components of the desired fine structure must accordingly be very small. For instance, when scattered light is observed at a right angle to the exciting light beam, the doublet lines must be spaced by approximately 7×10^{-2} A. This is a very small separation, but sufficient to be registered.

L I Mandel'shtam and G S Landsberg undertook the task to reveal the fine structure in the spectrum of scattered light in crystals.

The coefficient of light scattering in quartz single crystal, which can obviously be regarded as the best natural crystal, makes up 10^{-8} relative to exciting light, and therefore any foreign inclusion or cord masks the light of molecular scattering and makes it impossible to observe the scattered light spectrum.

First of all one had to find such a quartz single crystal in which molecular scattering of light could be confidently identified. This burden lay mainly on Landsberg's shoulders.

In those remote years there was no centre where one could come and select the required quartz specimen. At that time, pieces of quartz (rock crystal) were used to make seals with the name, coat of arms or some other signs of an owner. A letter was sealed with molten sealing wax which was pressed with the seal. The quartz would not break or crack at high temperature and a quartz seal was a beautiful thing.

After the revolution of 1917 such seals were no longer necessary, and the most beautiful of them ended up antique shops as trinkets. It was in such antique shops that G S Landsberg used to buy seals and then he brought them to the laboratory. There they were immersed in the solution and in the dark with a strong beam he chose the best portion of the sample to investigate the molecular scattering of light. A photograph of such a seal was presented in my previous papers [1, 2].

Of undoubted interest is what G S Landsberg said about the situation with the research in which he himself was successfully engaged [6].

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† When dismissed from Novorossiĭsk University (Odessa) in 1899 because of the students disturbances, L I Mandel'shtam continued his education in Strasbourg and then worked there at the department headed by C F Braun. In 1915 Mandel'shtam was already working in Petersburg as an engineer. In 1917 he was elected Professor of Physics of Tiflis Polytechnical Institute. From 1918 to 1922 he worked at the Odessa Polytechnical Institute. In 1922 he became an advisor at the Radio laboratory in Moscow. In 1924 he moved to Leningrad together with the Radio laboratory.

From 1925 to his death, Leonid Isaakovich Mandel'shtam worked at the faculty of Physics of Moscow State University and since 1934 also at P N Lebedev Physics Institute of the Russian Academy of Sciences.

"Historically, it turned out like this. When L I Mandel'shtam obtained a chair at Moscow State University in 1925, as the first experimental problem in optics he suggested a study of the fine structure of scattered light in crystals. By 1925 the very fact of molecular scattering in crystalline bodies had not yet been established reliably enough. Hence, it was necessary to begin the investigation of light scattering in crystals from the very beginning. Only after I had solved the basic problem, i.e. established molecular character of the observed scattering and found the criteria for distinguishing between molecular scattering and scattering on random inclusions in a crystal, did it appear possible to proceed in 1927 to the main task".

As follows from what has been said in Section 2, interferometer or grating spectrometer with a high resolution were needed for fulfilment of the 'main task'. Mandel'shtam and Landsberg had however only a poor-quality spectroscope and a Lummer – Gehrcke plate at their disposal.

They did not of course think that it would be so simple to reveal the desired effect with their mediocre spectrograph, but they also had another idea and G S Landsberg [7] spoke about it. Light scattering in quartz was excited by the resonance line of the mercury spectrum $\lambda = 2536.5$ A. If a resonant (selective) filter (a vessel filled with mercury vapors at a heat-controlled pressure) is placed in the path of scattered lines, the scattered lines of unshifted frequency can be totally absorbed and the lines of a changed frequency can be recorded. This can be registered even with a mediocre spectrograph.

The search for suitable quartz samples and their study was completed by G S Landsberg with his disciples K S Wul'fson and S L Mandel'shtam, Jr. in early 1927. The publications appeared in *Zeitschrift für Physik* (see references in [1]). After that Mandel'shtam and Landsberg proceeded to the 'main task' — the search for the variations in the spectrum of scattered light, mentioned above.

Upon long exposures, in the vicinity of different spectral lines they observed additional lines — satellites, which were particularly intense in the vicinity of the resonance line $\lambda\,2536.5$ A. Both Stokes and anti-Stokes components were observed. There were no such lines in the spectrum of exciting light. The spectral displacement of satellites was huge compared to the expected one. The observed phenomenon turned out to be unexpected and surprising. L I Mandel'shtam and G S Landsberg were exceedingly thorough researchers. The observation of satellites required new and extensive investigations because it was necessary to prove that they were not blicks, for instance, or something of the kind, but real lines in the scattered light spectrum.

Various experiments began. In particular, to make sure that the observed satellites were not blicks, a resonant filter was placed on the way of the scattered light to the spectrograph. The exciting line of the spectrum was weakened to the extent that it could not produce blicks, and nevertheless the satellites remained as before.

In the photograph of the spectrum with a 15-hour exposure one can only see a Stokes satellite by the resonance line (see the print from the negative of February 23 – 24, 1928 in Refs [1, 2]).

There exists a correspondence between the honorary member of the USSR Academy of Sciences O D Khvol'son and L I Mandel'shtam concerning the time when the new lines in the spectrum of light scattered in quartz were first observed [1, 2]. One can therefore say with certainty when Mandel'shtam and Landsberg first observed satellites in the spectra obtained.

It is known exactly from the available negative that in the spectrum of scattered light with a 15-hour exposure the resonance line $\lambda\,2536.5$ A showed a Stokes satellite. In the negative there fixed the date '23 – 24/II, 1928' written in Landsberg's hand. This negative was presented in both my publications [1, 2].

While making a detailed acquaintance of all the available materials, I got the impression that they might have seen satellites in the scattered light spectrum in the second half or as the last resort at the end of 1927.

The point is that the appearance of satellites in the scattered light spectrum, which differed in the wavelength by three orders of magnitude from the anticipated value, was so unexpected and surprising that they presumably (in my opinion) first took the satellites — the lines of combination light scattering — for blicks. By this means they began to eliminate the cause of 'blicks' by placing a resonant filter in the path of scattered light to the spectrograph. The creation of the resonant filter in 1927 – 1928 took, of course, much time. But they were exceptionally exacting and grudged neither time nor effort to obtain reliable experimental results.

Here is what they themselves said of the experiment which convinced them that they had observed a new phenomenon [8a]: "The following experiment seems to us to be decisive: between the scattering quartz crystal and the spectrograph slit we placed a quartz vessel which was filled with mercury vapors and totally absorbed light with a wavelength of 2536 A. We did not obtain this line in the spectrogram, but obtained only the satellites."

From the very beginning of their experimental studies Mandel'shtam and Landsberg realized that they were not observing the effect they had initially expected to find. In their first publication [8a] we find the following: "In the investigation of molecular scattering of light in solids, which we undertook to find out whether a change in wavelength occurs that might be expected within the Debye theory of heat capacity, we ran into a new phenomenon which seems to us to be of certain interest. The phenomenon consists in a change of wavelength whose value however has an order of magnitude and origin other than that we expected".

In the same paper we find the correct explanation of the new phenomenon in the language of light quanta: "One of the possible theoretical explanations perhaps consists in the following: upon scattering of light, some natural IR frequencies of quartz can be excited owing to the energy loss by the scattered light. The energy of the scattered quantum and, therefore, its frequency will thus decrease by the magnitude of a proper IR quantum. If we proceed from the frequency which corresponds to the wavelength $\lambda = 20.7$ μm, we have good agreement between the calculated and measured results."

In February, 1928 everything was already clear, and even such cautious physicists as Mandel'shtam and Landsberg who never made haste to push on their publications could safely submit their findings. However, their first publication was submitted to the *Naturwissenschaften* journal only on May 6, 1928 (the journal was issued on July 13, 1928).

The reason for the delay between the discovery of the new phenomenon and the related publication had nothing to do with physics.

The point is that just at that time (on March 15, 1928) L I Gurevich, a relative of L I Mandel'shtam, was arrested, and it turned out that Mandel'shtam was able to sort the matter out and assist in discharging the man from prison more efficiently than anybody else.

The physical research and everything concerning it then stopped, and L I Mandel'shtam had to turn to another field of human activity.

When this legal affair was over, he could continue his work and proceed to the publication of reliable results, but much time had already been lost.

The next extensive paper presenting a detailed investigation of the spectra of combination scattering in quartz and Iceland spar was published in *Z. Phys.* [8b]. This paper already has a contemporary form — it gives a complete picture of the spectra and offers the explanation.

It should be stressed that beginning with their first publication G S Landsberg and L I Mandel'shtam had a quite correct view of the nature of the phenomenon which they had revealed and gave it an adequate quantum and classical description. They did not only understand the origin of the Stokes and anti-Stokes components, but also offered a correct interpretation and even derived a quantitative expression for their intensity, namely,

$$I_{\mathrm{s}} = A\left[1-\exp\left(-\frac{h\nu'}{k_{\mathrm{B}}T}\right)\right]^{-1}, \tag{4}$$

$$I_{\mathrm{as}} = A'\left[1-\exp\left(-\frac{h\nu'}{k_{\mathrm{B}}T}\right)\right]^{-1}\exp\left(-\frac{h\nu'}{k_{\mathrm{B}}T}\right), \tag{5}$$

where $A/A' = \left[(\nu-\nu')/(\nu+\nu')\right]^4$, ν' is the satellite frequency, ν is the exciting light frequency, and k_{B} is the Boltzmann constant, so that

$$\frac{I_{\mathrm{s}}}{I_{\mathrm{as}}} = \frac{A}{A'}\exp\left(\frac{h\nu'}{k_{\mathrm{B}}T}\right). \tag{6}$$

These formulae provided a quantitative expression of what had already been said in words in the first papers [8a], and thus their representations did not differ radically from the modern one.

In the first papers [8a] it was emphasized that the position of the lines of combination light scattering, or satellites, in the spectrum is different for various substances, and therefore they characterize peculiarities of the substance in which the light is scattered.

This important observation proved to be quite correct, and just this feature of the phenomenon made a significant contribution to the determination of molecular structure and to a number of other applications of combination scattering of light.

3. The discovery of Raman scattering of light in Calcutta

In India, the studies of light scattering began before 1925, but one can judge their development only from what the researchers themselves wrote about it and from what their colleagues wrote about the research and researchers, and therefore the description of what happened in Calcutta cannot be complete enough. As far as we can judge, Raman and Krishnan [9 – 12] sought the lines in the spectrum of scattered light of frequency changed owing to the optical analogue of the Compton effect. In his inauguration address Raman [22] expressed his thoughts as follows: he spoke of how Dr. Ramanathan and Mr. Krishnan had investigated 80 different liquids and had found, in their opinion, a faint luminescence in each of them; thereupon he pointed out that "... a powerful impetus to further research was provided when I conceived the idea that the effect was some kind of optical analogue of the X-ray scattering discovered by Professor Compton†, for which he was recently awarded the Nobel Prize for physics. I immediately undertook an experimental reexamination of the phenomenon in collaboration with Mr. Krishnan".

Notice that the Compton wavelength λ_{C} does not depend on the substance, but does depend on the scattering angle θ and the particle mass m. The Compton wavelength for an electron is $\lambda_{\mathrm{C}} = 2.4\times10^{-10}$ cm (2.4×10^{-2} A) and for a proton is $\lambda_{\mathrm{C,p}} = 1.3\times10^{-13}$ cm (1.3×10^{-5} A). For molecules this quantity can be thousands of times smaller.

Such a negligible change of the wavelength in the optical spectrum cannot be so easily registered. Raman may have been ignorant of the theory of Compton effect, while the analogy with the Compton wavelength variation suggested itself.

This is the author's view of the situation and of Raman's idea which he was guided by when he started his experimental research on light scattering in liquids and vapors.

In their first publication [9] dated February 16, 1928 and published in *Nature* on March 31, 1928, C V Raman and K S Krishnan described experiments with the Sun as the source of light, and thus no lines could be observed in the scattered light. But the experimenters applied the method of crossed light filters and obtained results which allowed them to state that they had observed light of a changed frequency.

In their second article [10] Raman and Krishnan stated that along with the solar light they also used the light of a mercury lamp. In the scattered light spectrum they observed discrete lines. This work was dated March 8 and was published in *Nature* on April 21, 1928. As to the spectral lines observed, they said the following: "Preliminary visual observation appears to indicate that the position of the principal modified lines is the same for all substances, though their intensity and the continuous spectrum does vary with the chemical nature of the substance". This erroneous conclusion might have prompted the title of the paper "The Optical Analogue of the Compton Effect". That the position of the satellites was independent of the substance was not confirmed in experiment, but it was alluring to assume that this was so, and moreover Raman and Krishnan believed that the anti-Stokes satellites were due to negative absorption as had been predicted by Einstein.

Indeed, in Ref. [11] Raman and Krishnan wrote of anti-Stokes satellites as follows: "The presence of these lines proves simultaneously the existence in the liquids of molecules residing at the excited energy levels and the fact that the incident radiation induces a return to a lower energy state; in other words, there is a negative absorption of radiation".

They were so convinced of correctness of their conclusions that even the title of the paper [11] in *Nature*, dated May 15, 1928 and published on July 7, 1928, was: "The Negative Absorption of Radiation". A strong desire to take the results of their experiment for the Compton effect on light and then to believe that the anti-Stokes components testified to the existence of negative absorption could only mean that at least

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† The Compton effect can be summarized as follows. In X-ray scattering by free or virtually free electrons, photons of the initial and a lower energy will be present in the scattered light. The increased photon wavelength differs from the initial one by the magnitude of the Compton wavelength $\lambda_{\mathrm{C}} = [h/(cm)](1-\cos\theta)$, where h, m, and c are the Planck constant, the electron mass, and the speed of light, respectively, and θ is the scattering angle.

before May – June of 1928 Raman and Krishnan had not understood the genuine nature of the phenomenon which they had observed in their experiments.

One might think that the paper by Landsberg and Mandel'shtam [8a] dated May 6 and published on July 13, 1928, which reported the discovery of combination scattering of light in quartz and Iceland spar and gave quite a correct account of this phenomenon, should have provided Raman and Krishnan with an insight into the nature of the same phenomenon which they had observed in liquids.

But this did not happen for some reason. The point is that C G Darwin who was present at the 6th Congress of the Association of Russian physicists published his impressions of the Congress in *Nature* in October 1928 [13], which occupied 2/3 of a journal page and were largely concerned with superficial things. Assessing the scientific reports of the Russian researchers, he wrote as follows:

"Perhaps the most interesting works are that of Prof. Ioffe on the reflection of electrons, including an unsuccessful attempt to reveal polarization, and that of Profs. Mandelstam and Landsberg. The latter described how they had independently discovered Raman effect, the scattering of light accompanied by the frequency change. This was predicted some years ago by the Kramers theory of dispersion (and a little earlier by Smekal), and the verification is made by light scattering from a solid or liquid and observing the change of frequency.

This change is a measure of the wavelengths of the infrared absorption by the scattering material, and so, apart from the interest in this phenomenon in itself, the phenomenon promises to be important for the spectroscopy of solids."

Thus, Darwin's notice contains both the correct assessment of the phenomenon discovered by Raman and independently by Landsberg and Mandel'shtam and its correct explanation. The notice by Darwin [13] cited above coincides in contents with the article by Born [14] concerning the same point. Everything seemed to be clear, but as an answer to Darwin, a paper by Raman [15] appeared in *Nature* on January 12, 1929. In the paper there was a strange assertion, namely, that it was ostensibly a well-known fact that the existence of lines with changed wavelengths in the scattered light was established as far back as 1923 in the studies carried out in Calcutta. Then the paper reads: Dr. Ramanathan [16] showed that when violet light passes through thoroughly purified water or alcohol, a notable amount of radiation in the green region of the spectrum is present in the scattered light. Further analysis of the effect in other objects was described by Krishnan [17] and Raman [18].

The above description of the findings produced by Ramanathan and Krishnan clearly shows that it was Stokes luminescence that was observed, and as to the paper by Krishnan [17], it is devoted to a measurement of the degree of depolarization and the intensity of light scattered in 65 liquids with dust thoroughly removed. In some of the liquids fluorescence was observed, and the author of the paper clearly understood that this was fluorescence and not the combination scattering of light described by Darwin [13]. As regards fluorescence, study began not in 1923 in Calcutta but, as indicated by S I Vavilov [19], it was like this: "... the scientific study of luminescence numbers nearly 400 years. Galilei already investigated luminescence".

Exceedingly bewildering is the assertion that the change of frequency in scattered light has been observed beginning from 1923 in works carried out in Calcutta. Does this assertion mean a lack of understanding of the difference between luminescence or fluorescence and combination scattering of light?

Raman's article [15] that appeared in *Nature* in January 1929 was apparently written for the sake of the last passage where he stated: "The Russian physicists, to whose observation about the effect in quartz Prof. Darwin refers, made their first communication on the subject after the publication of the articles in *Nature* of March 31 and April 21.

Their paper appeared in print after sixteen other printed papers on the effect, by various authors, had appeared in recognized in scientific periodicals".

None of these 16 ostensible publications has ever been cited. Neither were they known to Born [14] and Darwin [13] who were obviously better acquainted with the literature than the experimenters; in particular, Darwin pointed out the predictions of the effect by Smekal and Kramers, a fact was unknown to the authors of the discovery.

Raman's articles [15] in *Nature* was evidently not only the act of struggle for priority, but also the claim for exclusiveness of his experiment. He seemed to believe that all the others only repeated it.

This was certainly not so, and the words of Rutherford [20], the then head of the Royal Physical Society, which he spoke after Raman's publication [15], may serve as a confirmation. This is what Rutherford said about the experiments by Raman, Landsberg and Mandel'shtam: "An excellent account of these beautiful experiments was given this year by Raman and Krishnan in our 'Proceedings'. Similar effect was observed by Landsberg and Mandel'shtam in examining the light scattered by common crystals. Such experiments are not easy, for the intensity of scattered light is very small, and long exposures with intense sources of light are necessary to bring out the relatively faint new lines. An examination of the results showed that the changes in frequency of spectral lines depend on characteristic frequencies of the molecule, connected with its vibrational states".

In 1928 – 1930 it was already clear that Raman and Landsberg and Mandel'shtam had discovered one and the same phenomenon at one and the same time and independently of each other. However the question of the interpretation of the nature of the new phenomenon by Raman and Krishnan remains unclear.

It is difficult to say when Raman rejected his erroneous concepts concerning the nature of the phenomenon of combination scattering of light. Neither do we know whether he came to the correct understanding of the nature of the phenomenon by himself or under the influence of other publications and, in particular, the papers by French authors (see references cited in Ref. [1]). On seeing the shifted spectral components, these French authors obviously realized at once that this was combination scattering of light because it was the very phenomenon they had tried to reveal in the gaseous state of a substance, but unfortunately the intensity of the exciting light had been insufficient.

4. When was combination scattering of light discovered? Had it been predicted?

It is not infrequent that a question not yet decided or a phenomenon not yet discovered, which has not attracted attention for a long time, all of a sudden simultaneously becomes the object of investigation of several researchers or even several research groups in quite different places. This was the case with combination scattering of light. We have briefly described, to the best of our knowledge, how the studies went on in Moscow and in Calcutta, and now it is interesting to find out when the new phenomenon was discovered in Moscow and when in Calcutta. This question can be answered by those who, separated by a distance of 7000 km, discovered the same phenomenon at the same time quite independently of each other. O D Khvol'son, obviously when preparing the fourth edition of his book "Contemporary Physics" [21], asked L I Mandel'shtam in a written form: "Could you indicate the time when you first observed the new lines? I am writing an article and it would be very important for me to have this information". (In this book by Khvol'son, Section 3 of Chapter 7 is entitled "The Phenomenon of Raman, Mandel'shtam and Landsberg".)

L I Mandel'shtam answered O D Khvol'son as follows: "We first paid attention to the appearance of the new lines on February 21, 1928. In the negative of February 23 – 24 (a 15-hour exposure) the new lines were already distinctly pronounced". This was a definite and clear answer to the question.

A no less clear answer to the same question can be received from Raman [22] who said in his inauguration address: "The line in the spectrum of the new radiation was first seen on the 28th February, 1928. The observation was given publicity the following day".

At the 6th International Conference on the Raman spectroscopy held in Bangalore (India) in 1978 and devoted to the 50th anniversary of the discovery of this phenomenon, Bhagavantam said: "What was called 'a new radiation' by the researcher himself at the time he discovered it and what has since then come to be known as 'the Raman effect' was first observed by Professor Raman in Calcutta at the laboratory of the Indian Association for the Cultivation of Science at 210, Bow Bazar Street, during the evening hours of February 28, 1928. The first public announcement was made in a Calcutta daily newspaper dated February 29" [22a].

It resembles a phrase of our actors touching upon topical questions: "morning — in the papers, evening — on the stage".

The research style and approach to publication of their results in the case of Landsberg and Mandel'shtam differ so much from those shown by Raman and Krishnan that it is absolutely impossible to compare them.

The first observation of the new phenomenon was made a week earlier by the Russian than by the Indian physicists. But the first report on the new phenomenon was due to Raman and Krishnan (the paper reporting observation of the new lines). It appeared in *Nature* on April 21, 1928, while Landsberg and Mandel'shtam published their results in *Naturwissenschaften* only on July 13, 1928.

Above, we partly explained the reason for the delay in accomplishing the research of the Russian physicists. But even if it had not been for the misfortune, I think the publication of Russian physicists would all the same have appeared later than that of the Indian scientists.

After the paper had already been written, Landsberg and Mandel'shtam discussed it for a long time trying to polish it so that not a single phrase might be misunderstood and that all phrases be unambiguous and express nothing else but the authors' thoughts. Sometimes they put the ready paper aside and then returned to the discussion again. The results of the measurements and observations should have been reliable.

In mid-1928 it was already absolutely clear that the effect of combination light scattering discovered in Russia in quartz and Iceland spar and in India in a number of liquids had one and the same origin. In the summer of 1928, the 6th Congress of the Association of Russian Physicists was held in Russia. This representative congress was attended by many prominent scientists. Twenty one of the four hundred participants were foreign scientists. Among the foreign guests were Born, Brillouin, Darwin, Debye, Dirac, Pohl, Pringsheim, J Franck, and Scheel.

The congress opened in Moscow on August 5, 1928 after which the participants went to Nizhniĭ Novgorod and then by ship down the Volga river. The closing session in Saratov was on August 15, 1928.

The raves about this congress were given by M Born [14] in *Naturwissenschaften* and C Darwin [13] in *Nature*. M Born wrote in his paper: "The phenomenon discovered by Landsberg and Mandel'shtam in crystals is essentially identical to the effect observed by Raman and his colleague Krishnan in liquids. Russian physics can justly take pride in the fact that this important discovery was made by the Moscow researchers independently of the Indians and nearly simultaneously (February 20, 1928). This coincidence is one more demonstration of the international nature of our science which now spans the entire world".

From the above it is clear that the experimental achievements of our physicists did not remain unknown.

The question arises of whether combination scattering of light was an accidental discovery or it was first predicted and then discovered experimentally. Since Landsberg and Mandel'shtam sought for what is now referred to as the Mandel'shtam – Brillouin effect and Raman and Krishnan sought for the optical analogue of the Compton effect, one can say with certainty that they found not at all what they had been seeking, and it is therefore obvious that their discovery of combination scattering of light (the Raman effect) was accidental.

It seems to me that the most important discoveries in the history of physics are largely made incidentally. For example, such a significant discovery as electromagnetic induction was made by Faraday accidentally, and then it determined the level of modern civilization. It concerns, of course, not only this discovery.

One might think that all discoveries can be divided into two groups: accidental and predicted. The situation described above is unusual in that combination scattering of light (CS) does not, strictly speaking, belong to either of these two groups.

The point is that CS was predicted in 1923 by A Smekal [23] who proceeded from the following elementary quantum concepts: if a photon 'lifts' an atom to a higher energy level, the photon expends an energy ΔE, which is equivalent to its frequency lowering by $\Delta E/h$, and therefore apart from the frequency ν there will exist light of frequency $\nu - \Delta E/h$. When an atom transfers its energy ΔE to the photon, the line with frequency $\nu + \Delta E/h$ will be present.

This interesting and significant paper by Smekal so clearly pointed to the possibility of observing additional frequencies in scattered light spectrum that it inspired Kramers and Heisenberg [24] to consider the problem more thoroughly. The paper by Kramers and Heisenberg was submitted to publication on January 5, 1924 and was published in 1925 before the establishment of quantum mechanics.

Kramers and Heisenberg used the correspondence principle which, briefly speaking, suggests that the matter should be considered from a quantum point of view and the radiation field from a purely classical one [24–26]. Using the notation of Ref. [26], the Kramers–Heisenberg formula for the cross section $\mathrm{d}\sigma$ of the ω photon scattering from the electronic system accompanied by the emission of the photon ω' can be represented as follows:

$$\mathrm{d}\sigma = \frac{\omega\omega'^3}{\hbar^2 c^4} \left| \sum_n \left\{ \frac{(d_{2n} l'^*)(d_{n1} l)}{\omega_{n1} - \omega - \mathrm{i}\Omega} + \frac{(d_{2n} l)(d_{n1} l'^*)}{\omega_{n1} + \omega' - \mathrm{i}\Omega} \right\} \right|^2 \mathrm{d}\Omega \,, \quad (7)$$

where $\omega' - \omega = E_1 - E_2$; $h\omega_{n1} = E_n - E_1$; d_{n1} and d_{n2} are quantities proportional to the matrix elements; l, l' are the unit vectors indicative of the directions of oscillator polarization.

The scattered light intensity $\mathrm{d}I \sim \mathrm{d}\sigma$ is proportional to the cross section of the photon scattering.

The paper by Kramers and Heisenberg made it possible not only to state that the Stokes and anti-Stokes satellites were present in the scattered light, but also to calculate their intensity, at least in principle.

Now that the theory of crystal lattice vibrations developed by Born and Karman [27] back in 1912 is included in any course in theoretical physics (see, for instance, Ref. [28]), it appears that if a crystal lattice consists of N particles bound by a quasi-elastic force, two types of dispersion curves (the dependence of the elastic vibration frequency on the wavelength Λ or on the wave number $k = 2\pi/\Lambda$) will exist. The acoustic, or the Debye curve, will consist of three branches — one for a longitudinal wave, and two for transverse elastic waves. Acoustic frequencies may start from zero and extend to the maximum value $f_{\max} = v/d$, where v is the speed of sound and d is the interparticle distance. The other dispersion curve is called the optical or the Born branch. The optical-branch frequencies are high ($\sim 10^{12} - 10^{13}$ Hz).

From what has been said it follows that in their early paper Landsberg and Mandel'shtam sought for the modulation of scattered light by acoustic waves and found the result of modulation of scattered light by optical waves, i.e. combination scattering of light [29].

A natural question arises: Why did they not seek at once the modulation of scattered light by the waves of the Born branch? There is no one now who could answer this question. Of those who took part in the work in Moscow nobody remains alive.

We shall never obtain an exact answer to this question. My opinion, perhaps erroneous, is that Raman, along with Landsberg and Mandel'shtam, were merely unacquainted with the paper by Born and Karman (1912). Neither did they know the papers by Smekal (1923) and Kramers and Heisenberg (1925).

5. On the fate of the discovery and of those who made it

As has been said above, almost all prominent discoveries are made accidentally. The cases are very different. It is most easy to make sure of this by judging from experimental studies. One can see that most often it so happens that what is sought for and what is found are quite different things, and the latter turns out to be more significant than the former. An excellent example is the combination scattering of light which is one of the greatest discoveries in physics of the twentieth century.

Leonid Isaakovich Mandel'shtam (1879–1944)

Now that 70 years have passed since the discovery of this phenomenon, one can outline the fate of the discovery itself and of those who made it.

Landsberg and Mandel'shtam in Russia and Raman in India discovered one and the same phenomenon, and this was already clear in 1928. The fact that Landsberg and Mandel'shtam observed the new phenomenon a week earlier than

Grigoriĭ Samuilovich Landsberg (1890–1957)

Raman and Krishnan and published their report two months and 21 days later may be substantial for establishing the time of publication, but is absolutely immaterial for the estimation of their contribution to science.

The contribution of Landsberg and Mandel'shtam to science is great — they not only discovered the new phenomenon absolutely independently of Raman, but also understood its nature at once and gave a theoretical description which is still valid today.

Meanwhile, Raman was not aware of the nature of the observed phenomenon for a long time and first assumed it to be the optical analogue of the Compton effect [10] and then ascribed the anti-Stokes satellites to the negative absorption of light [11].

The phenomenon of combination scattering of light proved to be exceedingly fruitful. It enriched many branches of physics, chemistry, and biology and played a prominent role in other fields of science and technology. This aspect of the problem will briefly be touched upon below, but we can confidently already conclude that the fate of the discovery in all the above-mentioned fields was significant, and one could hardly wish anything better than that.

The fate of the authors of this discovery was absolutely different in what concerns the discovery of combination scattering of light. To begin with, the phenomenon itself is called the 'Raman effect', although it would be fair to call it 'the effect of Raman, Mandel'shtam and Landsberg', as O D Khvol'son did in his book [21], but this did not happen.

Another difference in their fates was connected with the mistake of the Nobel prize committee which gave the 1930 Prize in physics to Raman alone, although Landsberg and Mandel'shtam had been nominated for the same work, and according to the rules and practice of the Nobel prize committee all three might have been awarded.

Raman's reaction to the news that he had been awarded the Nobel prize was typical of him, as Bhagavantam said in his talk at the 6th International Conference on the Raman Spectroscopy held in Bangalore (India) in 1978 [22a]: "I had the privilege of being one of his active collaborators at the time when he was awarded the Nobel prize for physics and I vividly recall his reactions when I communicated to him the first news of the award after hearing it on telephone from one of the Indian news agencies in Calcutta. He asked if he was the sole awardee or was he to share the bed with foreigners. His emotional exuberance and other such traits often won him the description of a person lacking tact in dealing with the public.

Two months before he knew he was awarded the Nobel prize, he had the supreme audacity of booking his steamer passage to be in time for the ceremony at Stockholm".

I think that as human beings, Landsberg and Mandel'shtam might, of course, have been disappointed at not having received the deserved Nobel Prize together with Raman. But for the 20 years that I worked in Landsberg's laboratory I heard not a single word or a sigh nor saw a motion to express his displeasure or offence concerning the injustice done to him. The same refers to Mandel'shtam.

Recently, in his paper "Why did Soviet scientists not always receive deserved Nobel Prizes?" [30] V L Ginzburg analyzed the case of Landsberg and Mandel'shtam and Raman, as well as a similar case for the chemist V N Ipat'ev. It is not so easy to give an unambiguous answer to the question put in the title of Ref. [30], but I generally share the viewpoint expressed by V L Ginzburg.

The widely spread rumours that the prize was not given to our scientists because the Nobel prize committee did not like the Soviet regime do not withstand criticism and should be ignored in my opinion.

50 years after the Nobel prizes were awarded, the Nobel prize committee published some materials, among which were the following: the members of the Nobel prize committees, authorized for nomination; the census of nominees; the census of nominators and their positions; the list of disallowed nominations and the reason for exclusion, and the list of Nobel prize winners in physics and chemistry for 1900–1937. Such materials were once (and only once) published in 1987 [31].

Since then various tall stories have circulated concerning the received and declined Nobel prizes, it is pertinent to present here exact copies of the lists of the nominees for the 1930 Prize, the list of the nominators and the related characteristics, as well as Tables 6 and 7 containing necessary explanations [31].

The lists of the members of the Nobel prize committees on physics and chemistry are of general interest as well, although they have no immediate relation to the subject of our paper.

The list of nominees for the 1930 Prize in physics is given on pages 120–123 of the book [31].

The title of the list reads: 1930, Census of Physics Nominees; Winner: Raman, C V. In the first column we see the list of the nominees in the alphabetic order. The second column shows the nationality of the nominee (Ge — Germany, Us — the United States of America, Fr — France, Ru — Russia, In — India, and Au — Austria). In the third column named Code, the letter d shows that in the nominator's opinion the Prize should be divided between the nominee and someone else. The letter u indicates that the Prize should be undivided and be given to the nominee alone. The fourth column presents the names of the nominators.

On the bottom of this part of the list, under the title 'Disallowed Nominations', in the first column there stands the name of the rejected nominee, then the country where the nominee works (second column), the symbol explained in Table 7 (third column) and the name of the nominator (fourth column).

The title of the second part of the list reads: 1930, Census of Physics Nominators; Winner: Raman, C V.

The first column gives the names of the nominators in the alphabetic order.

The second column (Auth) indicates to which of the six categories (see Table 6) the nominator belongs.

Table 6 enlists those who was authorized for the nomination of the Nobel prize. Number 13 (in the column Auth of the list of nominators) means that the nominator fits in items 1 and 3 of Table 6.

In the third column (Status) the number stands for the order of the choice — 1, 2, 3. If, for example, Bohr gives 1de to Raman and 1ue/1de to Wood, he recommends that Wood alone should be awarded or the prize should be divided between Wood and Raman.

The last, fourth column includes the names of the nominees.

At the end of the list, under the title 'Disallowed Nominations', in the first column stands the name of the nominator, in the second column stands the symbol explained in Table 7 with the motivation for the exclusion of the candidate for the Nobel prize, in the third column the

1930: CENSUS OF PHYSICS NOMINEES

Winner: Raman, CV

Nominee	Nat'y	Code	Nominator
Born, M	Ge	d	*Pringsheim, P*
Bowen, IS	Us	d	*Millikan, RA*
Bowen, IS	Us	d	*Osborn, HF*
Cotton, A	Fr	u	*Guillaume, CE*
Cotton, A	Fr	u	*Villat, H*
Davisson, CJ	Us	d	*Millikan, RA*
Davisson, CJ	Us	d	*Osborn, HF*
Davisson, CJ	Us	u	*Richardson, OW*
Debye, P	Ge	u	*Walther, A*
Debye, P	Ge	u	*Warburg, E*
Ferrié, GA	Fr	u	*Townsend, JSE*
Gerlach, W	Ge	d	*Campbell, WW*
Heisenberg, W	Ge	d	*Frenkel, Y*
Heisenberg, W	Ge	d	*Nagaoka, H*
Heisenberg, W	Ge	d	*Perrin, J*
Heisenberg, W	Ge	d	*Planck, M*
Heisenberg, W	Ge	d	*Pringsheim, P*
Heisenberg, W	Ge	u	*Svedberg, T*
Hilbert, D	Ge	u	*Hadamard, J*
Landsberg, GS	Ru	d	*Khvol'son, O*
Langevin, P	Fr	d	*Nicolle, C*
Mandel'shtam, L	Ru	u	*Papaleksi, N*
Mandel'shtam, L	Ru	d	*Khvol'son, O*
Paschen, F	Ge	d	*Franck, J*
Raman, CV	In	d	*Bloch, E*
Raman, CV	In	d	*Bohr, N*
Raman, CV	In	u	*Broglie, L de*
Raman, CV	In	u	*Broglie, M de*
Raman, CV	In	d	*Khvol'son, O*
Raman, CV	In	d	*Perrin, J*
Raman, CV	In	u	*Pfeiffer, R*
Raman, CV	In	u	*Rutherford, E*
Raman, CV	In	u	*Stark, J*
Raman, CV	In	u	*Wilson, CTR*
Russell, HN	Us	d	*Osborn, HF*
Saha, M	In	u	*Bose, DM*
Saha, M	In	u	*Mitra, SK*
Schrödinger, E	Au	d	*Campbell, WW*
Schrödinger, E	Au	u	*Cantone, M*
Schrödinger, E	Au	d	*Frenkel, Y*
Schrödinger, E	Au	u	*Krutkov, Y*
Schrödinger, E	Au	u	*Laue, M von*
Schrödinger, E	Au	u	*Mirolubov, N*
Schrödinger, E	Au	d	*Nagaoka, H*
Schrödinger, E	Au	d	*Planck, M*
Schrödinger, E	Au	d	*Plate, L*
Sommerfeld, A	Ge	d	*Franck, J*
Sommerfeld, A	Ge	d	*Millikan, RA*
Sommerfeld, A	Ge	d	*Osborn, HF*
Sommerfeld, A	Ge	d	*Plate, L*
Stern, O	Ge	d	*Campbell, WW*
Stern, O	Ge	d	*Franck, J*
Weiss, P	Fr	u	*Cabrera, B*
Weiss, P	Fr	d	*Gley, E*
Weiss, P	Fr	d	*Nicolle, C*
Wood, RW	Us	d	*Bloch, E*
Wood, RW	Us	d	*Bohr, N*
Wood, RW	Us	d	*Franck, J*
Wood, RW	Us	u	*Rozhdestvenskiy, D*
Disallowed Nominations			
Broglie, M de	Fr	§7B	*Gley, E*

1930: CENSUS OF PHYSICS NOMINATORS

Winner: Raman, CV

Nominator	Auth	Status	Nominee
Bloch, E	5	1d	Raman, CV
Bloch, E	5	1d	Wood, RW
Bohr, N	13	1de	Raman, CV
Bohr, N	13	1ue/1de	Wood, RW
Bose, DM	5	u	Saha, M
Broglie, L de	3	u	Raman, CV
Broglie, M de	6	u	Raman, CV
Cabrera, B	6	u	Weiss, P
Campbell, WW	1	1d	Gerlach, W
Campbell, WW	1	1d	Stern, O
Campbell, WW	1	2u	Schrödinger, E
Cantone, M	5	u	Schrödinger, E
Franck, J	3	1u	Stern, O
Franck, J	3	2d	Paschen, F
Franck, J	3	2d	Sommerfeld, A
Franck, J	3	3u	Wood, RW
Frenkel, Y	5	1d	Heisenberg, W
Frenkel, Y	5	1d	Schrödinger, E
Gley, E	1	1ue	Weiss, P
Guillaume, CE	13	u	Cotton, A
Hadamard, J	1	u	Hilbert, D
Khvol'son, O	6	1d	Raman, CV
Khvol'son, O	6	1d	Landsberg, GS
Khvol'son, O	6	1d	Mandel'shtam, L
Krutkov, Y	5	u	Schrödinger, E
Laue, M von	3	u	Schrödinger, E
Millikan, RA	3	1u	Sommerfeld, A
Millikan, RA	3	2u	Davisson, CJ
Millikan, RA	3	3u	Bowen, IS
Mirolubov, N	5	u	Schrödinger, E
Mitra, SK	5	u	Saha, M
Nagaoka, H	6	1d	Heisenberg, W
Nagaoka, H	6	1d	Schrödinger, E
Nicolle, C	1	1d	Langevin, P
Nicolle, C	1	1d	Weiss, P
Osborn, HF	1	1u	Sommerfeld, A
Osborn, HF	1	2u	Davisson, CJ
Osborn, HF	1	3u	Bowen, IS
Osborn, HF	1	4u	Russell, HN
Papaleksi, N	5	u	Mandel'shtam, L
Perrin, J	13	1de	Heisenberg, W
Perrin, J	13	1ue/1de	Raman, CV
Pfeiffer, R	1	u	Raman, CV
Planck, M	13	1d	Heisenberg, W
Planck, M	13	1d	Schrödinger, E
Plate, L	1	1d	Schrödinger, E
Plate, L	1	1d	Sommerfeld, A
Pringsheim, P	5	1d	Born, M
Pringsheim, P	5	1d	Heisenberg, W
Richardson, OW	3	u	Davisson, CJ
Rozhdestvenskiy, D	5	u	Wood, RW
Rutherford, E	13	u	Raman, CV
Stark, J	3	u	Raman, CV
Svedberg, T	2	u	Heisenberg, W
Townsend, JSE	5	u	Ferrié, GA
Villat, H	5	u	Cotton, A
Walther, A	5	u	Debye, P
Warburg, E	5	u	Debye, P
Wilson, CTR	3	u	Raman, CV
Disallowed Nominations			
Gley, E	§7B	1ue	Broglie. M de

Table 2

Members of the Nobel prize committees

Member	Dates of service	Position
Committee on physics		
Ångström, K	1900–1910	Uppsala University
Arrhenius, A	1900–1927	Stockholm Högskola
Carlheim-Gyllensköld, V	1910–1934	Stockholm Högskola
Granqvist, G	1904–1922	Uppsala University
Gullstrand, A	1911–1929	Uppsala University
Hasselberg, B	1900–1922	Academy of Sciences
Hildebrandsson, H	1900–1910	Uppsala University
Hulthén, E	1929–1962	Stockholm Högskola
Lindh, AE	1935–1960	Uppsala University
Oseen, CW	1923–1944	Uppsala University
Pleijel, H	1928–1947	Royal Inst. of Tech.
Siegbahn, M	1923–1962	Uppsala University
Thalén, R	1900–1903	Uppsala University
Committee on chemistry		
Cleve, PT	1900–1905	Uppsala University
Ekstrand, ÅG	1913–1924	Government service
Euler-Chelpin, H von	1929–1946	Stockholm Högskola
Hammarsten, O	1905–1926	Uppsala University
Holmberg, B	1934–1953	Royal Inst. of Tech.
Klason, P	1900–1925	Royal Inst. of Tech.
Palmaer, W	1926–1942	Royal Inst. of Tech.
Pettersson, O	1900–1912	Stockholm Högskola
Ramberg, L	1927–1940	Uppsala University
Söderbaum, H	1900–1933	Academy of Agriculture
Svedberg, T	1925–1964	Uppsala University
Widman, O	1900–1928	Uppsala University

Table 6

Nominators' authority code

1. Members of the Academy of Sciences
2. Members of the Academy's Nobel committees
3. Previous winners in physics and chemistry
4. Physics and chemistry professors at the Nordic universities listed in the special regulations of 1900
5. Chairholders at invited universities
6. Specially invited individuals

Table 7

Code of excluded nominations

§4	Division proposed contrary to statutes
§7A	Self-nomination
§7B	Received after deadline of February 1
§8A	No specific work mentioned or work not published
§8B	Candidate not mentioned
NP	Candidate received prize during the previous two years
†	Candidate died before February 1 of year of nomination
UA	Proposal from unauthorized nominator
WD	Proposal withdrawn
-P	Outside domain of the physics committee
-C	Outside domain of the chemistry committee

number stands for the order of the choice and then follows the name of the rejected nominee (the fourth column).

The list of the nominees for the 1930 Nobel prize in physics immediately produces a strong impression. The nominees and the nominators represented, in fact, the flower of physics, and not only of 1930.

Among those nominated for the discovery of essentially the same phenomenon were Raman from India and Landsberg and Mandel'shtam from the Soviet Union.

Striking is the number of physicists and the scientific authority of those who proposed Raman. C V Raman was nominated by ten physicists, N Bohr, L de Broglie, J Perrin, E Rutherford, J Stark, and our countryman O Khvol'son among them. L Mandel'shtam was nominated by only two — O Khvol'son and N Papaleksi, and G S Landsberg — by O Khvol'son alone.

The objectivity and the behaviour of Professor Khvol'son, the author of a five-volume course in physics (1923), can be praised very highly. The three others of our countrymen (other than Khvol'son and Papaleksi) made their nominations of worthy candidates for the 1930 Prize, but did not propose Landsberg and Mandel'shtam for their outstanding discovery, while the number of nominees is unrestricted and, for example, N Bohr proposed four candidates for the 1929 Prize.

Regretfully, Landsberg and Mandel'shtam, who deserved the Nobel prize, were nominated by only one and two countrymen, respectively. No one can say that their discovery was unknown. In August of 1928 it was reported at the Sixth Congress of the Association of Russian Physicists, and the Congress was attended by four hundred scientists!

There remains the question why the Russian physicists were not awarded the Nobel prize for physics while the Indian physicist received the prize for exactly the same work done at the same time. It is likely that no definite answer to this question will ever be given.

However, V L Ginzburg [30] is right when he points out the reasons which possibly played the leading part. First of all it was, of course, the indifference of our Russian physicists who had the right to nominate candidates for the prize. Then it is strange that foreign physicists who knew well of the work of Landsberg and Mandel'shtam and had the right to nominate, did not do so. For example, Rutherford, highly praised the discovery of Landsberg and Mandel'shtam in 1929 (see above), but for some reason proposed Raman alone. The Russian academician, professor O D Khvol'son came out with the candidatures of Landsberg, Mandel'shtam and Raman thus showing a good understanding of the essence of the matter and demonstrating the impartiality worthy of a prominent man.

Finally, the list of nominees and nominators appeared in front of the members of the Nobel prize committee on physics and they saw that Raman had been proposed by ten outstanding physicists, while Landsberg — by only one countryman, and although a well-known professor and a distinguished scientist, he could not be compared, for example, with Bohr, Rutherford, and L de Broglie.

Although the Nobel prize committees consist of distinguished independent people, they all are human beings.

Perhaps, if the members of the Nobel prize committee had understood clearly that the discovery of Raman and Landsberg and Mandel'shtam was the discovery of one and the same phenomenon, they would have realized that the nomination of Raman implied also Landsberg and Mandel'shtam.

If it had been as clear at that time as it is now, one may think that the Nobel prize committee would not have made such an unfortunate mistake†.

Landsberg and Mandel'shtam made many outstanding scientific achievements. They were both awarded the highest national prizes. Especially significant were scientific contributions of L I Mandel'shtam who founded a distinguished scientific school of physicists in Russia.

It is strange that combination scattering of light as the discovery of Russian scientists was not marked by an international, national, academic or even institute's prize, and this seems to be shocking!

6. The beginning of a systematic study of the new phenomenon

It seems that it was before the beginning of systematic studies of the new phenomenon — the combination scattering of light — that Born and Darwin in their short notes, as well as Rutherford in his speech predicted a great future to the new phenomenon in various fields of science and particularly in the study of solids. This was partly mentioned above and was presented in more detail in the reviews [1, 2]. Recurring, we shall pay attention to the fact that the new phenomenon attracted the attention of physicists in many countries of the world.

We shall only point out that in our country this work was mainly carried out by G S Landsberg, L I Mandel'shtam and their co-workers and disciples, in particular, M A Leontovich and S L Mandel'shtam, Jr., in India by C Raman, in France by Cabannes, and in the USA by R Wood. Investigations in this direction were also carried out in England and Italy.

The scale of research in the 1920s was negligibly small compared to the scale of scientific research developed nowadays, when the present paper is being written.

And still the interest in the new phenomenon was so great that already in 1928, the year of the discovery, 70 publications were devoted to it, and by the end of the next year they were 200.

The investigations did not stop at that point, but on the contrary progressed more and more rapidly, and towards 1939 there were already 1800 papers in which the combination scattering spectra of 2500 compounds had been examined.

From the very beginning the number of papers was so large and the contents so diverse that in 1931 K Kohlrausch wrote a book containing a review of the papers and in 1938 he published an additional volume entitled "Der Smekal–Raman-Effekt" [32].

In 1934, the review by Placzek appeared [25], which in the Russian translation has the title "Rayleigh Scattering and the Raman Effect" and is devoted to the theory of both types of light scattering.

In 1943, K Kohlrausch [33] published a lengthy book "Ramanspektren" and in 1952 it appeared in Russian translation under the title "The Spectra of Combination Scattering" and had 44 a.u. (1 author unit consists of 40,000 ens). The book is endowed with an extensive and comprehensive introductory article written by G S Landsberg.

In 1949 there appeared a two-volume monograph "Molecular Vibrations" by M V Vol'kenshteĭn, A M El'yashevich, and B I Stepanov [34]. Ten years earlier, in 1939, the book "Spectra of Diatomic Molecules" by G Herzberg [35] was published in the USA and translated into Russian in 1949 (36 a.u.), and the monograph "Infrared and Raman Spectra of Polyatomic Molecules" by the same author appeared in the USA in 1945 and was translated into Russian in 1949. Finally, in 1966 G Herzberg published the book "Electronic Spectra and Electronic Structure of Polyatomic Molecules" (75.62 a.u.) which was translated into Russian in 1969. The same year the book by M M Sushchinskiĭ "Spectra of Combination Scattering from Molecules and Crystals" appeared [36]. We shall also mention the series of books "Light Scattering in Solids" [37]: issue I edited by M Cardona, which was published in Germany in 1975 and in the Russian translation in the Soviet Union in 1979; issue II edited by M Cardona and G Güntherodt [37], published in Germany in 1982 and in the Soviet Union in the Russian translation in 1984; issue III, published in Germany in 1982 and translated into Russian and published in this country in 1985, and, finally, issue IV (1983), whose Russian translation was published here in 1986.

The book "Raman Spectroscopy in Gases and Liquids" edited by A Weber [38] was also translated into Russian and appeared in 1982.

There were also a great many papers, review articles and books devoted to combination scattering of light; the enumeration of all of them would be impossible and unnecessary here and would constitute a voluminous book. The list of books given above is far from a complete survey. In particular, among the books cited there are no bulky proceedings of the conferences devoted to various aspects of combination scattering of light and its applications to the study of various phenomena, molecular structure, and to the solution of analytical and purely applied problems.

Combination scattering of light is of course an exceedingly refined and effective tool for the investigation of the interaction between radiation and matter in the broad sense of this concept.

The present paper does not in the least claim completeness in listing all the research works and applications of CS, but some material points should be indicated.

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† Recently, to the question of Prof. A M Bloch to the Secretary of the Nobel prize committee on physics, Prof. A Barani: "Why were Landsberg and Mandel'shtam not awarded the 1930 Nobel prize in physics together with Raman?", Prof. A Barani answered: "If we go back to the history of the 1930 Nobel prizes in physics, prime attention should be paid to the manner in which the discovery of combination scattering of light was presented. Whereas Raman was prompt and efficient in his concern with the publication of his experimental results, the Soviet physicists did not hurry, and in their first report even cited the papers by Raman. Who will react to the real discoverer in such a situation?" (see the Russian newspaper "Poisk" No. 24, June 6–12, 1998). It is good that at least now the true discoverer is known.

The appearance in the laboratory practice of laser light sources, namely, gas lasers such as Ne–He or Ar^+ with a narrow emission line and directional laser radiation made it possible to examine such minor details of spectral peculiarities that were inaccessible to the experiments using a mercury arc as a source of light. This gave rise to the appearance of a whole branch — high-resolution spectroscopy, and even ultrahigh-resolution spectroscopy [39]. Some researchers have the impression that before the creation of lasers there was no spectroscopy at all. But this is not so. Surprisingly much had been done before the appearance of lasers in 1960. During the 20 years between the discovery of CS and the creation of gas lasers, spectroscopists did not waste time. To make sure of this, it suffices to get acquainted with the books cited above.

Simultaneously with gas lasers, in the same 1960 appeared high-power solid-state lasers whose application led to the discovery of the new phenomena — stimulated combination scattering (SCS) of light and hypercombination scattering of light. The creation of a new method called coherent anti-Stokes Raman scattering (CARS) was also due to the appearance of lasers.

These new nonlinear phenomena which are based on CS will be briefly discussed below.

7. The spectra of combination scattering of light

If a molecule consists of N atoms, it has $3N$ degrees of freedom, and may accordingly generate $3N$ vibrations. Three translational and three rotational degrees of freedom should however be excluded, and then only $3N-6$ degrees of freedom will remain. For example, for a water molecule, when $N=3$, there remain just three degrees of freedom. But everything is not so simple as it may seem at first glance.

The conventional classical view of the nature of CS remains the same as that described by Landsberg and Mandel'shtam and which in the simplest case leads to formulae of the type (3). Atomic vibrations in a molecule deform the electronic shell, which gives rise to modulation of the scattered light and to the appearance of the shifted Stokes and anti-Stokes lines in the spectrum. The number of these lines will not be equal to the number of the degrees of freedom because different atoms vibrating in a molecule may deform the electronic shell in a similar manner, and then in the scattered light there will be a single but degenerate line, and this degeneration may be multiple.

If a molecule possesses some anisotropy, its rotation will also modulate scattered light.

The translational vibrations of a molecule manifest themselves in the form of a vibrational spectrum, and the molecular rotation will appear in the spectrum as a rotational spectrum. Figure 1 presents the scheme of the installation used by Landsberg and Mandel'shtam [7, 8] in their first experiments with light scattering in quartz and Iceland spar.

The vibrational spectrum of CS in crystal quartz is given in Fig. 2 as an example. Scattered light was observed at an angle of 90° and a 110-volt mercury lamp (Hereus) served as the source of light.

The scheme of the installation for observation of scattered light at an angle of 90° remains now practically the same, while the source of light has changed — the mercury arc has been replaced by the laser, and quite a different system is used for spectrum recording.

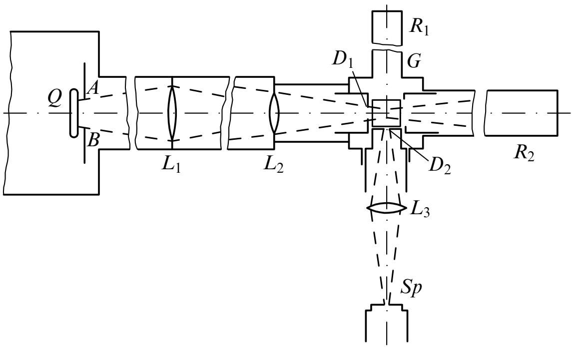

Figure 1. Setup designed by Landsberg and Mandel'shtam during their early works for the investigation of scattered light in crystal quartz and Iceland spar: Q is the source of light; L_1 ($f=450$ mm) and L_2 ($f=250$ mm) are two lenses; AB is a rectangular slit 20×4 mm^2 in size; D_1 and D_2 are diaphragms. The crystal is placed in an opaque chamber G. R_1 and R_2 are packings providing a dark background. L_3 is a lens focusing the scattered light onto the slit of the spectrograph Sp [8].

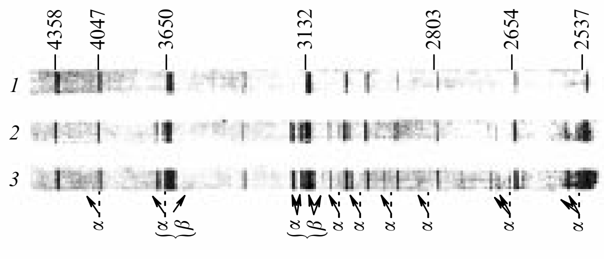

Figure 2. Spectra of light scattered in quartz (double magnification): *1* standard spectrum; *2* and *3* are the spectra of scattered light registered at 20 and 210 °C (the exposure of 105 h); α are red satellites, and β are violet satellites [8].

The scheme of a modern installation is presented in Fig. 3 for comparison with the 70-year-old installation illustrated in Fig. 1. Figure 4 shows the vibration-rotation band spectrum of CS in CO_2.

The spectra of combination scattering appeared to be effective for the study of molecular structure. A CS spectrum for a spectroscopist is nearly the same as a photograph of a building for an architect. A molecule is known to possess a centre, an axis, or a plane of symmetry [2]. Vibrations of various elements may either break or not break its symmetry. If vibrations leave the system in the initial state in all its symmetry elements, such vibrations are totally symmetric. The spectral lines due to such vibrations are most intense.

One can make a general assertion that CS lines appear in the spectrum only if the molecular polarizability α depends on the generalized coordinate q, i.e. the condition $\delta\alpha/\delta q \neq 0$ holds. Such vibrations are called active in CS. When a vibration changes the electric moment of a molecule, but the condition $\delta\alpha/\delta q = 0$ holds, no lines corresponding to this vibration appear in the CS spectrum and a line or a band of infrared absorption occurs.

The selection rules for combination scattering and infrared absorption are well elaborated theoretically, and they can be found in the literature cited. In some cases it is relevant to speak of the characteristic frequencies of such bonds as, for instance, C–H, C–C, N–H, Si–H and others. Lines of combination scattering in the spectrum are characterized by their position or frequency, intensity, width, and

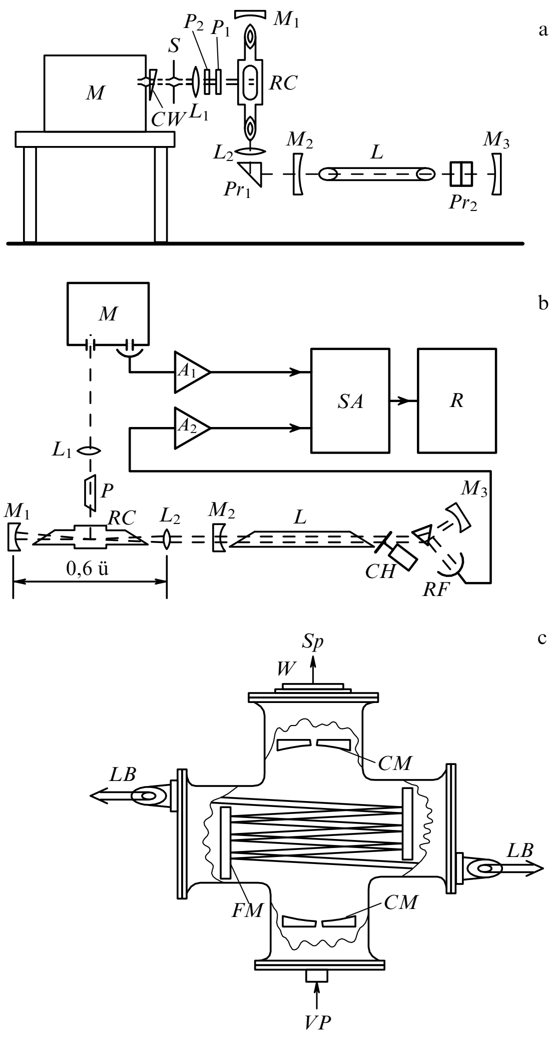

Figure 3. Photoelectric setup with a laser for recording the spectra of combination scattering of light in gases [41] for a vertical (a) and a horizontal (b) cuvette (RC) positions: L is an argon ion laser; M is a monochromator; L_1 and L_2 are lenses; P_1 and P_2 are polarizers. In each of the setups, the cuvette for combination scattering may be positioned either inside or outside the laser cavity (the interior cavity is formed by mirrors M_1 and M_3, and the exterior one by mirrors M_2 and M_3). For operation outside the laser cavity, the mirror M_1 can be so positioned that the laser beam passes through the cuvette many times. The calcite wedge (CW) depolarizes the radiation before it enters the monochromator. The polarization of the laser beam is perpendicular to the plane of the figure (a) or is parallel to it (b): S is a stop; Pr_1, Pr_2 are the reversing prisms; A_1, A_2, SA, R form a recording system; CH is a chopper; RF is a photoelectric cell; P is a prism; (c) multipath cuvette for studying combination scattering of light. The laser beam (LB) comes in and out through the Brewster windows; CM are light-collecting concave spherical mirrors; FM are flat mirrors; W is a transparent window; VP is a vacuum pump, and Sp is a spectrograph.

polarization. An analysis of all these characteristics provides extensive information on the molecular structure and quasi-elastic atomic bonds inside molecules, including the estimation of the modulus of elasticity.

The determination of line widths has given much knowledge about the molecule as a quantum system and made it possible to investigate the vibration-rotation spectra of anisotropic molecules.

The first thorough interferometric determinations of CS line widths were made by Kh E Sterin [42] and the theoretical description of CS line widths is due to I I Sobel'man [43]. The CS lines of a molecule typically change little upon passing over from one aggregate state to another because the intramolecular bonds are much stronger than the intermolecular forces. This important fact allows an experimenter to get information on molecular vibrations more easily than by obtaining spectra in the gaseous phase.

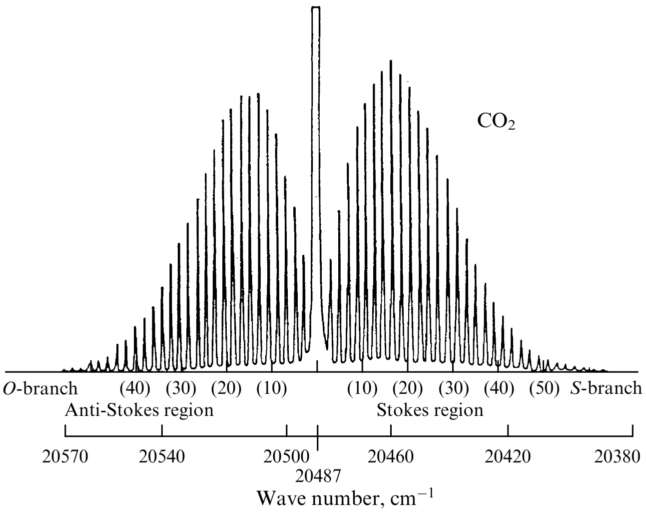

Figure 4. Spectra of Rayleigh scattering (the central line) and of purely rotational combination scattering for a CO$_2$ molecule. The excitation was induced by the $\lambda\,4881$ A line of argon (Ar$^+$) laser radiation [90].

It should however be noted that there are exceptions belonging to the cases of the so-called hydrogen bonds [44], the region of phase transformations [45] and resonance combination scattering of light [38, 46, 47].

8. Resonance phenomena

By resonance phenomena we understand events occurring when the frequencies of two or more processes are coincident or close to each other, or somehow related to each other.

The resonance interaction between radiation and matter provides extensive information both on the matter and the radiation, in particular, such interactions are clearly pronounced in the spectrum of combination scattering of light but not only here.

It is noteworthy that Landsberg and Mandel'shtam were the first to experimentally examine the effect of resonance interaction between scattered light and matter in mercury vapors [48 – 51], and they called this phenomenon 'selective scattering in mercury vapors'.

For the intensity of scattered light in vapors and gases, Rayleigh obtained the well-known formula in which the dependence on the wavelength (frequency) is determined by the Rayleigh law ($I \sim \lambda^{-4}$) and by the quantity $(n^2 - 1)^2$, and, accordingly, $I \sim \lambda^{-4}(n^2 - 1)^2$. Far from the region of the natural frequency of a substance, the scattered light intensity is determined by the dependence on the wavelength primarily through the Rayleigh law. The quantity $(n^2 - 1)^2$ changes very little with varying wavelength.

Landsberg and Mandel'shtam paid attention to the fact that near the absorption line (or band) of a substance the situation radically changes, and then the dependence on the wavelength is primarily determined by the factor $(n^2 - 1)^2$.

The experimental research of Landsberg and Mandel'shtam [48] consisted of delicate and very difficult tests.

The eigenfrequency (the wavelength) of mercury vapors is λ 2537 A. In the experiments described, the vapors were exposed to the light of a condensed spark jumping across rotating zinc electrodes. The intensities of the zinc spectral lines 2502 A and 2558 A were examined. According to the Rayleigh law, the difference in the intensity of these lines is only 9%, whereas the experiment gives a difference by a factor of 20. This result agrees with theoretical evaluations.

At that time such experiments were exceedingly involved and difficult. The details can be found in Refs [48–51]. The same mechanism of resonance scattering underlies other types of scattering as well.

Resonance combination scattering of light was first observed by Shorygin [52] who revealed that the intensities of CS lines in some solutions of organic compounds were "hundreds of thousands of times (!) higher near the absorption band than they were under ordinary conditions of excitation far from resonance".

This very spectacular optical phenomenon was extensively and thoroughly studied from both experimental and theoretical points of view [48–52, 37, 38, 46].

When the combination frequency in a crystal, which corresponds to scattered light modulation by the optical branch, coincides with the frequency of excitation of the medium, then the dispersion curve (the dependence of frequency on the wave number) acquires the form shown in Fig. 5. In the region of such a resonance, mixed vibrations (or polaritons) of the medium and electromagnetic radiation occur. Curve *1* corresponds to the photon branch, and curve *2* to the polariton branch. The dot-and-dash straight line corresponds to the initial optical frequency ω_0. The dashed line describes the photon dispersion [53–56].

In the spectra of combination scattering of molecules or crystals, a characteristic phenomenon called Fermi resonance is observed. Such a resonance occurs when, for example, in the spectrum of combination scattering of a CO_2 molecule the frequency of valence or totally symmetric vibrations ν_1 is almost coincident with the first overtone of deformation vibrations $2\nu_2$ [47, 57–59].

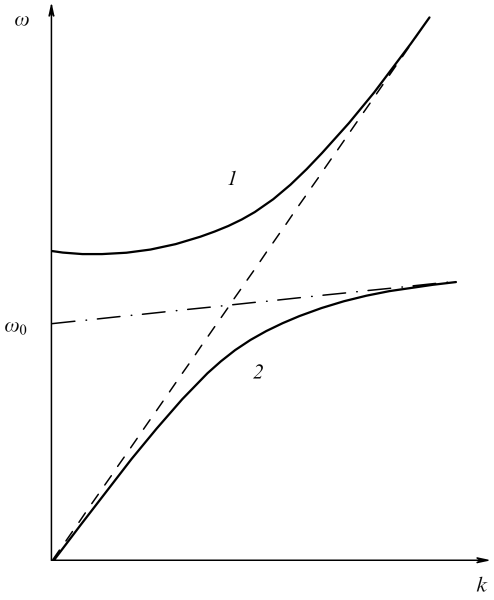

Figure 5. Picture of the formation of photon (*1*) and polariton (*2*) branches (solid curves). The dot-and-dash line shows the original vibration frequency ω_0 of the optical branch of the crystal, and the dashed line illustrates the photon branch, where ω is the frequency, and k is the wave number.

Fermi resonance is also pronounced in polariton spectra [47, 53, 54, 60] (Fig. 6). The Fermi resonance can be described as a result of the interaction of two nonlinearly coupled linear oscillators. The whole range of questions associated with this problem was stated and thoroughly studied by Mandel'shtam [49] and his disciples [61].

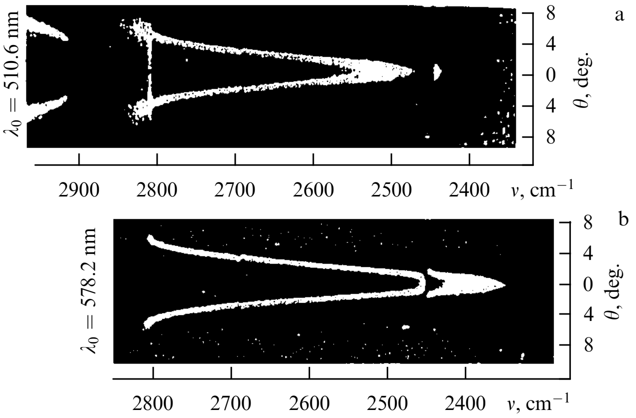

Figure 6. Effect of polariton Fermi resonance in the spectrum of combination scattering from polaritons, observed at small scattering angles θ in ammonium chloride crystals: (a) and (b) correspond to two exciting lines of respectively 510.6 and 578.2 nm of a copper-vapor laser [60].

This kind of resonance phenomenon can be demonstrated on an example of the simplest mechanical model: a spiral swing of length l, characterized by the modulus of elasticity k, with a massive girder or cantilever fixed to one of its ends and a load of mass m to the other. Such a pendulum can perform vertical oscillations of frequency $\omega_1 = \sqrt{k/m}$ and angular oscillations of frequency $\omega_2 = \sqrt{g/l}$, where g is the acceleration of gravity.

One can see that if $\omega_1 = 2\omega_2$, the energy of vertical oscillations of the system is efficiently transferred to angular oscillations and back again.

9. Phase transitions

The CS spectra appeared to be an efficient means for the study of second-order and related phase transitions. Numerous investigations of the behaviour of CS lines in various media, and mainly in crystals are now available.

This fruitful direction of research was initiated by the theoretical papers by V L Ginzburg [45, 54, 62] and further developed by his disciples Levanyuk and Sobyanin [63]. Other theoreticians also joined these studies. A somewhat detailed description of the development of the theory goes beyond the scope of the present paper.

From the above-mentioned phenomenological theory it follows that near the critical point of a crystal the frequency of a CS line will gradually shift towards the frequency of the unshifted line and will finally merge with the exciting light frequency, and the satellite as a shifted line will thus disappear. The disappearance of a CS line implies that some vibrations do not any longer exist in the crystal. The lowering of the soft mode frequency is given as an example in Fig. 7. On the soft mode one can also observe the opalescence effect in the region of a ferroelectric phase transition [62]. An example of such a phenomenon is presented in Fig. 8.

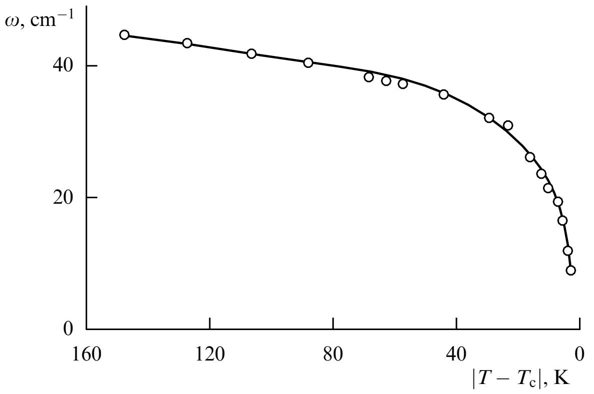

Figure 7. Temperature dependence of the soft mode frequency ω in SbSI [64].

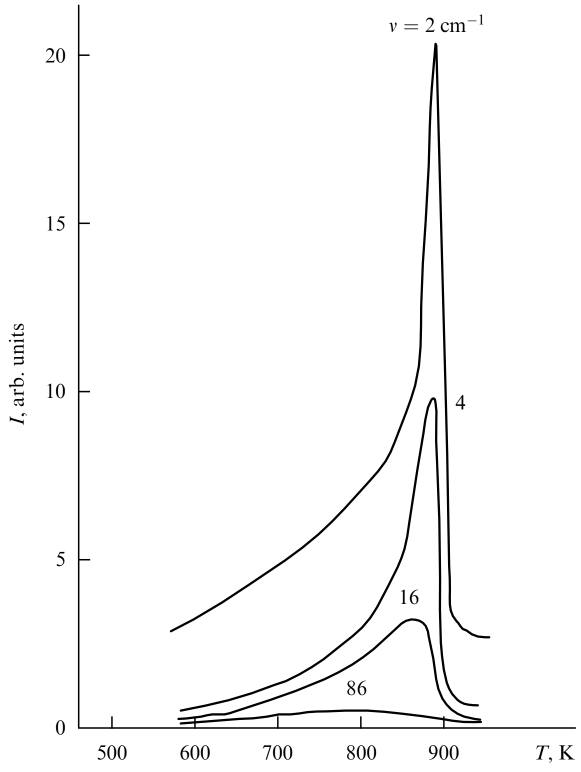

Figure 8. Opalescence effect in the spectrum of combination scattering (soft mode) near the ferroelectric phase transition point (898 K) in a tantalate crystal. The numbers alongside the curves indicate the frequencies for which the temperature dependence of the intensity of combination scattering is determined [60].

It is of particular interest for us to stress here that the first experimental examination of the soft mode in the combination scattering spectrum in a single-crystal quartz is due to Landsberg and Mandel'shtam [65]. In these experiments, in approaching the $\alpha \leftrightarrow \beta$ transition temperature in a crystal quartz, the CS line of 207 cm^{-1} was found to behave 'anomalously'. Far from the transition point, the CS line in quartz is observed as a clearly pronounced spectral line which broadens with increasing temperature and disappears in a β-quartz at a temperature $T > T_c = 846$ K (T_c is the $\alpha \leftrightarrow \beta$ transition point). The authors of this experiment realized that they were observing a very significant phenomenon. They noted that such behaviour of the CS line was indicative of an appreciable change or the disappearance of bonds responsible for the corresponding vibration. This was an adequate understanding of the phenomenon and a deep insight into its essence although the fundamental phenomenological theory appeared only 20 years later [45, 62, 63].

The fact that Landsberg and Mandel'shtam really observed the soft mode effect was confirmed later [66, 67].

10. Stimulated combination scattering of light

With the emergence of high-power solid-state pulsed and quasi-continuous lasers there appeared a vast field of science — nonlinear optics [68 – 71] — and its various branches such as, for example, nonlinear fibre optics [72] and others.

Two years after a solid-state ruby laser of T Maiman was put into operation, namely in 1962, Woodbury and Ng [73] designed a Q-switched ruby laser. The laser was Q-switched by a Kerr cell filled with liquid nitrobenzene. When analyzing the operation of their laser they revealed that along with the laser radiation typical of a ruby laser, radiation appeared at a wavelength lower than the characteristic spectrum by 1345 cm^{-1}. Such radiation was not expected. It turned out that this radiation coincided in frequency with the strongest CS line of nitrobenzene. This was how stimulated combination scattering of light (SCS) was discovered. It is of interest to emphasize that both the thermal CS described above and SCS were discovered accidentally, but both had been theoretically predicted — the former by Smekal [23] and Kramers and Heisenberg [24], and the latter by Placzek [25].

Obviously, it can readily be explained by the fact that the experimenters were not acquainted with the works of the theoreticians. This judgement is however fairly primitive, and actually the situation may have been much more involved, in which case it becomes an interesting subject for a historian of science.

In stimulated scattering there typically occurs one most intense Stokes component of CS, which coincides in frequency with that of thermal scattering. However, anti-Stokes components also appear. At the present time the theory of this phenomenon is well elaborated [68 – 71, 74].

Note that thermal CS generates an incoherent radiation which makes up a $(10^{-7} - 10^{-8})$th part of the exciting light, whereas SCS is a coherent radiation with an intensity of the order of half the exciting light energy or even more.

The shape of the CS line in the SCS spectrum is distorted and is not good for examining molecular structure, but this new typical nonlinear optical phenomenon opens up many other possibilities.

We shall point out here another new nonlinear optical phenomenon. Soon after the appearance of laser sources of light, Maker and Terchune [75] proposed and developed a new powerful method of investigation in spectroscopy of combination scattering. This method is based on the nonlinear interaction of three beams of light with frequencies ω_L, ω_s, and ω_L that are encountered in a medium under investigation.

The frequency difference of two of the three indicated beams is such that $\hbar(\omega_L - \omega_s) \sim \hbar\Omega$, where $\hbar\Omega$ is the energy separation between the ground level E_1 and the first excited level E_2. Owing to the nonlinear interaction of these beams radiation occurs at the frequency $\omega_{as} = 2\omega_L - \omega_s$, which is recorded in experiment. The intensity of such radiation may exceed that of thermal CS by five – ten orders of magnitude.

Along with the energy conservation law, the momentum conservation law must also hold:

$$2\hbar\mathbf{k}_L = \hbar\mathbf{k}_s + \hbar\mathbf{k}_{as} ,$$

where $\mathbf{k}$ are the wave vectors.

Being vector quantities, the momenta must be summed as vectors.

The difference in propagation directions of exciting and scattered beams facilitates the observation, the more so as $\mathbf{k}_L$ and $\mathbf{k}_{as}$ have a strictly definite and different propagation directions and do not scatter in all directions. Since this method analyzes an anti-Stokes CS satellite, it will further on be referred to as coherent anti-Stokes Raman scattering (CARS).

This method offers many opportunities for studying both CS and the various properties and peculiarities of material medium. The CARS method became particularly powerful when tunable lasers became available.

It is also noteworthy that the method does not require any spectral apparatus. The resolution is determined by the sum of the widths of laser beams employed. In modern installations CARS allows a resolution of lines spaced by about $\sim 0.001\ \text{cm}^{-1}$.

The CARS-spectroscopy method plays such an important role that it allows the solution of various problems hardly solvable otherwise. As an example we shall present the solution of two problems using the CARS-spectroscopy method: the study of the nonstationary problem of energy exchange between the vibrational levels of a complex (SF_6) molecule, and the study of excitation propagation (polariton) in a crystal.

The CARS method allows, in particular, research on the type of molecular distribution over the vibration-rotation levels and control of the evolution of this distribution under the action of collisions. The high spectral and temporal resolution of CARS spectroscopy makes it possible to obtain detailed information, inaccessible to other methods, about the distribution function of molecules over vibrational levels, which is formed under the action of an intense laser pulse (for example, in the IR range) and to determine the mode composition of excited vibrational states. Furthermore, the possibility of creating an essentially nonequilibrium distribution of molecules over vibrational levels in a laser field allows determination, using the CARS-spectroscopy method, of the rate and the main channels of vibrational relaxation in collisions with highly excited molecules. The CARS spectra and the distribution functions of molecules, calculated from these spectra, are shown in Fig. 9 [76].

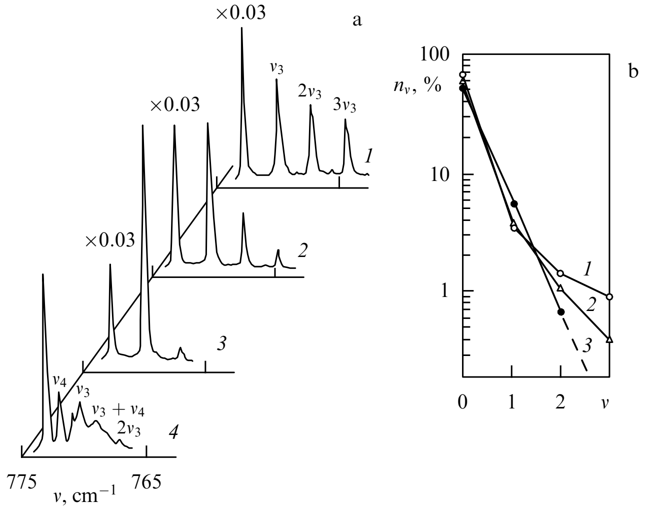

Figure 9. Transformation of CARS spectra of a SF_6 molecule (0.05 Torr) upon collisions with an increasing time lag between excitation and probing: *1* — 50 ns, *2* — 250 ns, *3* — 1 μs, *4* — 10 μs (a), and the population distribution functions of vibrational levels of mode ν_3, reconstructed from spectra *1*, *2*, *3*. The straight line continued with dashes corresponds to the Boltzmann distribution function of energy [76] (b).

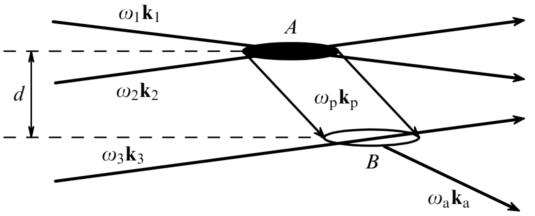

Figure 10. Schematic drawing of the mutual position of the exciting ($\omega_1\mathbf{k}_1$, $\omega_2\mathbf{k}_2$) and the probing ($\omega_3\mathbf{k}_3$) beams in the crystal under study upon CARS from polaritons with separated beams; *A* is the polariton excitation region ($\omega_p\mathbf{k}_p$), and *B* is the probing region [77].

A biharmonic excitation of quasi-particle (exciton) in a BeO crystal by two beams of light of different frequencies and wave vectors ω_1, $\mathbf{k}_1$ and ω_2, $\mathbf{k}_2$ in the region of intersection and nonlinear interaction of the two beams (Fig. 10) generates a polariton in a certain area. In the experiment carried out by Polivanov [77] and Orlov and Polivanov [78], a probing beam could be directed to zone *A*, where a polariton is formed, and outside this region up to zone *B*. The position of the probing beam can be varied, and thus the motion and the evolution of the polariton can be traced out from the CARS spectrum. Figure 11 illustrates such an evolution, and Fig. 12 shows the spatial variation of the CARS signal.

The application of picosecond and subpicosecond lasers will promote experiments with space-time resolution, which will allow dephasings of coherent polaritons and their group velocity to be determined [78 – 82].

11. The use of SCS for attaining low temperatures†

In the refined experimental research undertaken for the purpose of deep substance cooling, SCS radiation was efficiently used to lower substantially or nullify the speed of translational atomic motion. In these experiments [83, 84], in vapors of caesium atoms there propagate two oppositely aligned beams of intense light. The frequency difference of these beams is $\omega_1 - \omega_2$. To an accuracy of a minute detuning δ, this difference is equal to the frequency Ω of transition

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† A brief and simplified version of the talk by V A Alekseev at the session (May 1998) of the Council on Spectroscopy, devoted to the 70th anniversary of the discovery of combination scattering of light.

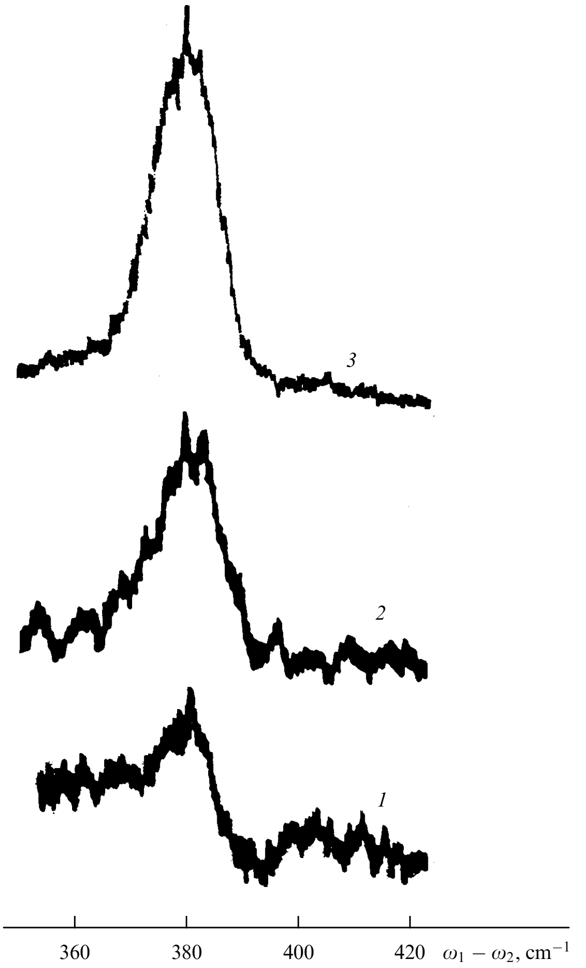

Figure 11. CARS spectra from polaritons in a BeO crystal, obtained at different distances d between the probing beam and the polariton excitation region: *1* — $d=0$, *2* — $d=200$, *3* — $d=400$ μm [78].

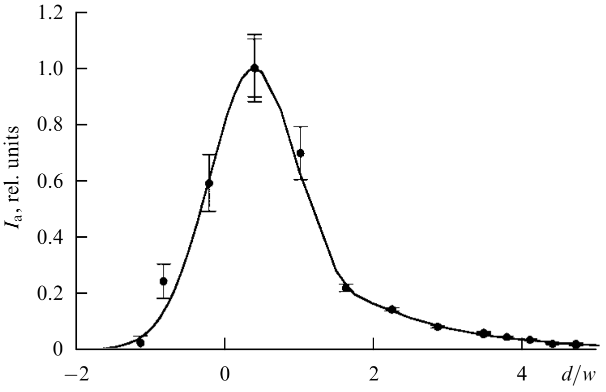

Figure 12. Amplitude of the signal of CARS from polaritons with a frequency of nearly 380 cm^{-1} in a BeO crystal versus the normalized distance between the exciting and probing beams. The points stand for the experiment, and the curve shows the result of the calculation done by fitting the quantities of the relative contribution of direct and cascade processes and the free path lengths of coherent polaritons. Here $w=160$ μm is the radius of the beams incident on the crystal (the distance at which the field amplitude decreases 'e' times compared to the maximum amplitude on the beam axis) [77, 78].

(from level *1* to level *2*) between components of the hyperfine structure of caesium atom (Fig. 13). This transition is accompanied by a variation of atomic velocity.

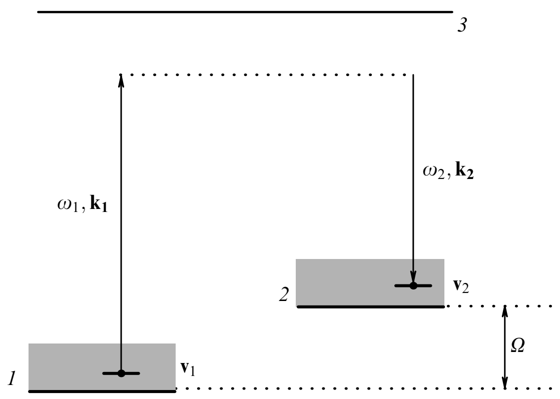

Figure 13. Schematic of the energy levels of a caesium atom.

The laws of conservation of momentum and energy relate the magnitude of the detuning δ to the velocity $\mathbf{v}$ of the atoms involved in the SCS process:

$$(\mathbf{k}_2-\mathbf{k}_1)\mathbf{v}_1+\frac{\hbar}{2m}(\mathbf{k}_2-\mathbf{k}_1)^2=\omega_1-\omega_2-\Omega=\delta\,.$$

Here $\mathbf{k}_1$, $\mathbf{k}_2$ are the wave vectors of the laser beams, $\mathbf{v}_1$ and m are the atomic velocity and mass. The first and second terms in the left-hand side of the above equation are the Doppler shift and the recoil in the course of SCS.

Thus, for each value of the velocity $\mathbf{v}_1$ of atom at level *1* there exists a frequency detuning δ corresponding to leaving level *1* only by atoms of velocity $\mathbf{v}_1$ (see Fig. 13).

It becomes possible to choose the pumping spectrum, so as to completely exclude the participation of zero-velocity atoms in the SCS process. To do so, rectangular laser pulses 30 μs in duration and with appropriately chosen frequencies ω_1 and ω_2 were used. After pulses with frequencies ω_1 and ω_2, another laser emits a pulse with a frequency corresponding to the transition from level *2* to level *3*. The caesium atoms are activated to the excited level *3*, from which they return to the ground level *1* as a result of spontaneous decay.

Next, the wave vectors of the SCS-exciting lasers changed their directions in order that the atoms with oppositely directed velocities should be involved in the process. Thus, it was a cyclic process of transitions *1* → *2*, *2* → *3*, and *3* → *1* with accumulation of zero-velocity atoms at the ground level *1*. Indeed, if after the spontaneous decay *3* → *1* the velocity of the atom is $\mathbf{v}_1\neq 0$, the atom is again involved in the SCS process, but if $\mathbf{v}_1=0$, the atom is excluded from the SCS process and stays at level *1* (see Fig. 13).

The whole cooling process lasted 20 μs within which the preliminarily cooled atoms fell under the gravitational force and flew through the laser beam of 4 mm in diameter.

Since it is only zero-velocity atoms that do not participate in the SCS process, they are concentrated near zero velocities and the longer the process, the more intense their concentration.

The authors [84] reached a temperature of 3 nK $=3\times10^{-9}$ K. This is obviously the lowest temperature yet reached.

SCS played a crucial part in this remarkable experiment.

12. Lasers with high-contrast pulses and high energy and radiation intensity

SCS lasers are well known and successfully applied when it is necessary to transduce laser radiation in frequency, to shorten the laser pulse duration and to obtain some other characteristics of radiation.

Losev and Soskov [86] succeeded, using the SCS process, in very strongly heightening the contrast of a single pulse. In that paper, a ruby laser pulse with λ 693 nm, an energy of 1.5 J and duration of 25 ps generated SCS in liquid SF_6, and then a pulse with λ 1056 nm, an energy of 100 μJ and duration of 0.8 ps was obtained in compressed hydrogen. After amplification, the pulse possessed an energy of 30 mJ. A double transformation by means of SCS and a reliable decoupling between the master oscillator and the amplifying SCS system provided a contrast equal to 10^{12}, which is apparently a record result for laser pulse contrast.

13. High-power SCS laser

Lasers that emit light of intensity of the order of 10^{22} W/cm^2, which would be important for the solution of some fundamental problems, partly discussed by Ginzburg [54], have not yet been created, but a significant step in the creation of lasers with high-energy pulses and a large flux density was taken with the application of stimulated combination scattering of light (the SCS laser).

The joint efforts of Alekseev and Sobel'man [87] (P N Lebedev Physics Institute of the Russian Academy of Sciences) and E M Zemskov [85] (the Research-Industrial Association 'Astrofizika') resulted in the appearance of a pulsed laser radiation of huge energy and high power and having a strict directionality. Such a device has already been discussed on an example of the laboratory model [88, 89].

The SCS laser is organized as follows: two types of lasers are created, namely, (1) a laser, as a source of light for pumping, which emits light of as high an energy as possible; the divergence and other characteristics are not so important, and (2) a laser (SCS laser) operating in this case on generation of light of the first Stokes line of combinationally scattered light (a laser without an inverse medium). An SCS laser must have a high efficiency of transformation of the pumping light into SCS, a high radiation density and a small beam divergence. Since the intensity of stimulated scatterings, including SCS, depends on the pumping light intensity, the pumping can be realized simultaneously by several lasers which need not be phased but should only be synchronized. The SCS laser has another advantage: it allows one to choose different wavelengths of emitted light. The creation of such a superhigh-power SCS laser was confronted with many difficulties which, however, were overcome. We shall point out some of them for the reader to have a vivid picture of an operating SCS laser.

As is well-known, the pumping of an SCS laser can be realized in two ways: longitudinal pumping, when the radiation and the transduced radiation propagate in one direction, and transverse pumping, when the directions of the pumping radiation and of the transduced radiation are perpendicular to each other. The preferential feature of transverse pumping is the spatial separation of the pumping beams and the Stokes radiation, which is of importance in the case of limited light strength of the optical elements of SCS lasers. Transverse pumping has, however, a serious shortfall, i.e. the spatial instability of transduced radiation: with increasing power of the Stokes component the generation is contracted in the operating volume towards the side that faces the pumping. The distribution of the output radiation becomes strongly nonuniform and hardly suitable for practical application. Neither transverse nor longitudinal pumping is suitable for designing SCS lasers, because in this case it is impossible to obtain output radiation with a density exceeding the pumping density.

In view of this, the pumping of a real SCS laser should be realized with a divergent beam only (Fig. 14). Since such a pumping is intermediate between longitudinal and transverse, the summation should also be intermediate between these limiting cases.

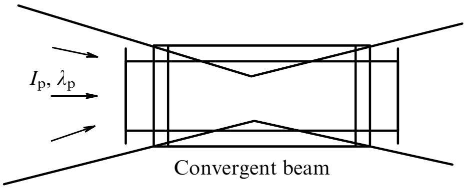

Figure 14. Schematic drawing of the run of convergent beams pumping an SCS laser [85].

For pumping pulses with an energy of tens of kilojoules and a pulse duration of hundreds of microseconds (i.e. for high radiation forces), the classical working substances (nitrobenzene, carbon disulphide, and others) are decomposed because they do not possess high radiation strength. Moreover, for long pumping pulses other nonlinear processes also occur (Mandel'shtam – Brillouin scattering, self-focusing and others) that sharply lower the efficiency of transformation in SCS. Because of this, the working medium of SCS lasers should satisfy a number of strict requirements. First of all, the molecules of the working medium should possess high efficiency in SCS. The second requirement is high radiation strength. This requirement is as a rule satisfied by the simplest molecules and, in particular, nitrogen and oxygen molecules, which meet this condition in full measure. Since these gases are readily liquefied, the most acceptable working media for an SCS laser radiating high-energy light are liquid nitrogen and liquid oxygen.

The magnitude of specific emission of energy at a level of 2 – 5 J/cm^3 is obviously reasonable, and for the conversion of the pumping energy of hundreds of kJ the volume of the working substance (with allowance for the ballast volume) must be 200 – 300 litres (Fig. 15).

The necessity to obtain a divergence of 5×10^{-5} rad requires maintenance of uniform temperature over the entire working volume with a gradient not larger than 0.01 – 0.001 K/m. This is a strict requirement. A method of thermostatic control with a not high expenditure of cryogenic liquids was found and a cryogenic 300-litre chamber with a temperature gradient not exceeding 0.01 K/m was created.

We also note that the energy density of SCS laser radiation of about 2 – 5 J/cm^3 for a pulse duration of 20 μs, with which one has to deal, leads to glass destruction in its volume. The search for a glass with a sufficient radiation strength among the available variety of glasses failed. This

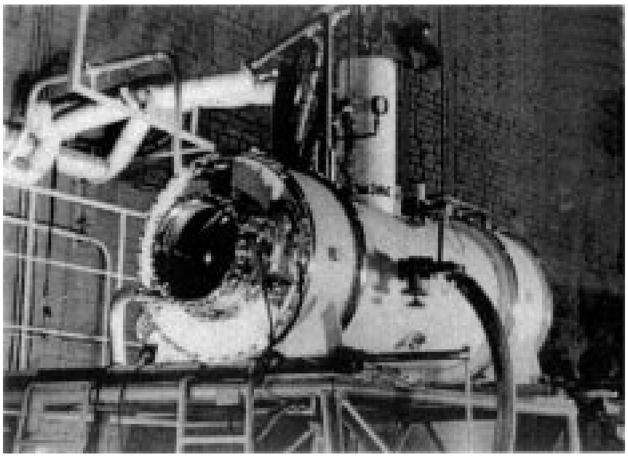

Figure 15. Picture of the 300-litre cryogenic cuvette of an SCS laser. Operating size of the cuvette: length 2000 mm, and diameter 400 mm. External dimensions: length 2700 mm, and diameter 900 mm [85].

difficulty was overcome only by creating a new type of glass with a particularly high radiation strength. The glass is branded as 'CC'.

14. Some characteristics of the SCS laser described above

An SCS laser was pumped by lasers with energy of about 10^5J each. From two to six pumping lasers with a pulse duration from 20 to 150 μs were used in experiments. The efficiency was 41%.

In the experiments described, the specific emission of energy was 6 J/cm^3. The SCS laser radiation intensity amounted to $10^{15} - 10^{16}$ W/(cm^2 sr).

The diameter of the light beam emergent from the SCS laser was 10 – 15 cm, and the light beam divergence was about 10^{-5} rad. Such lasers and modified versions of them will undoubtedly find diverse application.

This short review of the history of the discovery and application of combination scattering of light briefly outlined only a small part of what has been done. Many points have not even been mentioned. For example, nothing has been said about the application of CS to determining the individual composition of hydrocarbons — the problem to which Landsberg and his disciples and colleagues spared no effort and not without success.

The fundamental works on the application of CS to the study of polymers and organic molecules and many other things have not been pointed out, and it was not the author's objective to give a full description of this undoubtedly one of the most important discoveries of our century and its development and application. This is the task of historians of science, and I hope they will accomplish it.

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