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The prediction and discovery of Rayleigh line fine structure

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Abstract. The history of the theoretical prediction and experimental discovery of the Rayleigh line fine structure (which belongs to one of the most important phenomena in optics and physics of condensed matter) is discussed along with the history of first publications concerning this topic.

1. Introduction

The scattering of light has long been studied worldwide, and these studies have given many outstanding results.

Of special interest are studies of the spectra of light scattered in various media. The spectrum of scattered light proved to be associated with physical phenomena that seemed to be unrelated to the light scattering. In this field, many new, unexpected, and spectacular phenomena have been discovered, which are important for physics in general.

No wonder that L I Mandelstam said at one of his remarkable seminars at the Physics Department of Moscow State University on 20 December 1939 [1]: ''The totality of problems related to the scattering of light has been unclear even recently. It is a pity that you are not aware of the entire genesis of this item. We are dealing with the most recent history, and this genesis is still topical. All this happened before my eyes. Undoubtedly, this is one of the most interesting pages in the history of physics''.

These words belong not only to an attentive observer but first of all to an active creator in this and other fields of physics.

He studied, together with G S Landsberg, extremely spectacular phenomena in the spectroscopy of molecular scattering of light, such as combination scattering of light (the Raman effect), predicted and analyzed the fine structure of the Rayleigh line, and investigated selective (resonance) scattering in vapors. Still earlier, Mandelstam elaborated the theory and performed extremely complicated experiments on light scattering by fluctuating 'irregularities of the free surface of a liquid' [1] [2], developed the theory of an optical image and the theory of 'radiation from a light source located very close to the interface of two transparent media', and carried out very sophisticated experiments related to this problem [2].

L I Mandelstam was not only an outstanding theoretician but also a very skilful experimenter and engineer working in a variety of fields of physics. The above-cited statement by Mandelstam was made sixty years ago [1].

At present, many things have been elucidated; however, there are still many unresolved problems, and studies are being continued.

How has the problem of molecular scattering of light appeared and how has it developed and achieved its modern level? These questions represent an interesting, almost detective-like story, which can be outlined here in most general terms.

By molecular scattering of light is commonly meant light scattering by the fluctuations of physical quantities that give rise to optical inhomogeneities. Such a role of fluctuations in the scattering of light was first pointed out by M Smoluchowski [3], who offered a correct physical explanation for the effect of critical opalescence appearing upon phase transitions.

Einstein described the situation in this field in the following way [4]:

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[1] It is interesting to note that after publication of Mandelstam's paper [2] in 1913, A Einstein presented its content at a colloquium. After the seminar, Einstein sent Mandelstam a postcard with the following content (dated 23 July 1913, according to the postmark):

''Dear Mr. Mandelstam,

I just have presented your excellent paper on the surface fluctuations, of which Ehrenfest told me earlier. I regret you were not here.

Best regards, Yours A Einstein''.

(There are many signatures of participants of the seminar on the postcard.)

"If the work required to produce noticeable deviations from the mean density or the mean composition of a mixture in volumes of liquid with linear dimensions of the order of the wavelength is small, then obviously opalescence (the Tyndall effect) should take place.

Smoluchowski showed that this condition is really satisfied near the critical state; however, he did not calculated the amount of light scattered due to opalescence. This deficiency should be remedied below."

In his comprehensive paper [4], Einstein presents a method for calculating density fluctuations in liquids and concentration fluctuations in solutions. The method first applied by Einstein can be employed for calculating any thermodynamic fluctuations and is still being used. In the same paper, Einstein also calculated the intensity of light scattered by fluctuations of 'an almost homogeneous nonabsorbing medium'. The fluctuation was expanded in a three-dimensional trigonometric series, the amplitudes of harmonics being calculated using the Boltzmann principle.

The trigonometric Fourier components of pressure fluctuations, for example, represent acoustic 'waves'; however, in the Einstein theory, these are static terms of the Fourier series, while the expansion itself is no more than a calculation procedure.

Three years earlier, Einstein [5] made a fundamentally new step in a completely different field of physics. Until his work [5], the heat capacity C_V of a solid at constant volume was described by Dulong–Petit's law which was substantiated by the kinetic theory of matter that assumes the uniform energy distribution over the degrees of freedom (kT per each degree of freedom of an oscillator). Such calculations of the heat capacity did not provide good agreement with experiments, especially at low temperatures. Einstein's idea [5] was that the energy $h\nu\left[\exp(h\nu/kT)-1\right]^{-1}$, rather than kT, corresponds to each degree of freedom (where h is the Planck constant, and ν is the frequency of elastic vibrations of particles comprising a solid). The values of C_V predicted by this theory agree much better with the experimental temperature dependence of C_V. However, at low temperatures a better agreement between the theory and experiment was still required. Einstein understood that the use of a single frequency for all oscillators is a simplification [5], but he did not develop this theory further and did not relate the elastic frequencies to the Fourier components introduced in calculations of the intensity of scattered light.

In his theory of the fluctuation roughness of a free liquid surface, Mandelstam expanded the fluctuations in a two-dimensional Fourier series and calculated the scattered light intensity as a reflection from a two-dimensional 'lattice' [2]. However, he also did not mention here the heat capacity of a solid.

The further development of the theory of heat capacity of solids belongs to P Debye. Debye proposed an elegant idea [6]. He treated an amorphous solid as a continuum, whose vibrations can be determined from equations of the theory of elasticity, taking into account the corresponding boundary conditions [7, 8].

The total number of normal vibrational modes with frequencies within the interval from Ω to $\Omega+\mathrm{d}\Omega$ is

$$\mathrm{d}Z(\Omega)=\frac{3\Omega^2\,\mathrm{d}\Omega}{2\pi^2V^3}\,\Phi\,, \tag{1}$$

where V is the mean velocity of elastic waves in an amorphous solid: $3/V^3=2/V_t^3+1/V_l^3$ (here, V_t and V_l are the velocities of the transverse and longitudinal elastic waves, respectively), and Φ is the volume of the body under study.

Although a solid in the Debye theory is assumed continuous [6], the number of point radiators comprising the solid is assumed finite and equal to N, while the number of degrees of freedom is $3N$. As a result, the maximum frequency $\Omega_{\max}$ is not infinite, but is defined by the condition

$$Z(\Omega_{\max})=\int_0^{\Omega_{\max}}\mathrm{d}Z(\Omega)=\Phi\,\frac{\Omega_{\max}^3}{2\pi^2V^3}=3N\,. \tag{2}$$

Assuming that the body consists of point particles and denoting the distance between the particles by d, one should set $\Phi/N=d^3$. Then, one obtains

$$\Omega_{\max}=\left(\frac{3}{4\pi}\right)^{1/3}\frac{2\pi V}{d}\,, \tag{3}$$

$$\Lambda_{\min}=\left(\frac{4\pi}{3}\right)^{1/3}d\,. \tag{4}$$

The estimate yields $\Omega_{\max}\cong 10^{14}$ Hz, and $\Lambda_{\min}\cong 1.5$ A.

The Debye theory predicts the law $C_V\sim T^3$ [6], where T is the absolute temperature. The Debye theory clearly shows that we are dealing with elastic vibrations of a solid, their frequencies covering the range from 0 to $\Omega_{\max}\equiv 2\pi f_{\max}\sim 10^{14}$ Hz and their wave vectors being randomly directed inside the body. The interference of these waves produces the optical inhomogeneities, which we call fluctuations.

2. On the spectrum of molecular scattering of light

Why did Einstein [4] and Mandelstam [2], being engaged in research on light scattering and expanding fluctuations into harmonic components, say nothing about the problem of the heat capacity; and why did Einstein and Debye, being concerned with the problem of the heat capacity and introducing the elastic waves, say nothing about the scattering of light? It is likely that it was not so easy to understand at that already distant time that the Fourier components introduced by Einstein and Mandelstam and the elastic waves used by Debye are the same thing.

It is impossible to say now who was the first to understand that in all the cases considered above we are dealing with thermal elastic waves, but it is reasonable to assume that this idea occurred to one or some of those who were engaged in this problem. If this narrows the scope of the possible physicists, it is easy to make a choice from the physicists mentioned above.

The author of this article well understands that his considerations may be erroneous, but presents them here because they may prove to be correct, being, however, no more than a guess [2].

[2] My guess is possibly confirmed by some general statements made by L I Mandelstam in his *Lectures on Some Problems of Vibration Theory* [1], which he read at the Physics Department of Moscow State University in the year of his death (1944). L I Mandelstam noted that the division of physics into acoustics, optics, etc. was evidently made "in accordance with physical phenomena that we perceive in a similar way". And further on: "The situation with vibrations is fundamentally different: we distinguish them not according to our physical perception but based on the general

L I Mandelstam, who became head of the Chair of Theoretical Physics at the Physics Department of Moscow State University in 1925, set the experimental task to detect a change in the frequency of the scattered light, caused by its modulation by elastic thermal waves.

L I Mandelstam performed experiments devoted to the detection of the predicted effect together with G S Landsberg, who already worked at that time at the Physics Department of Moscow State University (now, M V Lomonosov Moscow State University). It is clear that Mandelstam conceived the idea of modulation of light waves by thermal elastic waves before 1925. But now it is difficult to say exactly when this occurred.

However, there are statements of the persons who were close to L I Mandelstam, such as N D Papaleksi and G S Landsberg. Thus, N D Papaleksi, who wrote the biography of L I Mandelstam in a book *Academician L I Mandelstam* published for his 100th birthday anniversary [9], said the following concerning the question of interest to us: "Contemplating the problems of light scattering, L I Mandelstam concluded as early as 1919–1920 that thermal fluctuations in a homogeneous body containing no impurities will cause not only Rayleigh scattering of light but the spectrum of the scattered light should be changed, although only slightly".

By analyzing the circumstances that led L I Mandelstam to the conclusion that the frequency of light scattered by a condensed medium should change, G S Landsberg [10, 11] refers to the same period of time as Papaleksi: "Generally speaking, fluctuations appear and subside at random. However, the theoretical treatment of these processes allows one to establish some important general properties.

L I Mandelstam performed such a treatment as early as 1918, although the relevant article on the scattering of light by an inhomogeneous medium appeared much later in 1926 [12], when some of the results obtained by L I Mandelstam had already been published by L Brillouin in 1922" [13].

The above-cited statements of Papaleksi and Landsberg refer approximately to the same period of time between 1918 and 1919. At that time, L I Mandelstam had already been discussing the possible changes in the spectrum of scattered light with his colleagues. As far as I can judge, L I Mandelstam could discuss a new physical problem and, possibly, a new physical phenomenon only once it had matured and was clear in his own mind.

The question of how an idea, which leads to new discoveries, comes to the mind of a person is very complicated, and it hardly can be explained at all. In some cases, however, one can guess or, it will be better to say, imagine an acceptable (for oneself) scheme of how the person obtained a correct solution. Now, it is interesting to conjure up how L I Mandelstam [12] and Leon Brillouin [13], mentioned above by G S Landsberg, came to the conclusion and even substantiated it quantitatively that the Rayleigh line should exhibit a fine structure — the phenomenon in the spectrum of scattered light that is called at present Mandelstam–Brillouin scattering.

After defending his master's dissertation on determining the oscillation period of a discharge in a capacitor (Strasbourg, 1902), L I Mandelstam published a comprehensive study "To the theory of a Brown transmitter" [14]. Leaving aside all the complications inherent in the theory of such a complex subject, note only the fundamental feature of any transmitter. In order to transmit any signal, a carrier wave emitted by a transmitter should be modulated either by the acoustic frequencies of voice, music, etc. or in some other way, but it should be necessarily modulated.

Anybody who is working in this field knows that the modulation of the carrier frequency produces additional frequencies (sidebands) in the emission of the transmitter. It is well known at present that the Mandelstam–Brillouin components represent the side frequencies that are caused by the modulation of an electromagnetic wave of scattered light by elastic thermal waves.

However, Mandelstam's paper [14] was published as early as 1904 — too early for stimulating the prediction of fine structure of the Rayleigh line. Einstein published his paper on the theory of heat capacity of solids in 1907 [5]. In this paper, he applied the Planck formula not to photons but to the elastic vibrations and, hence, considered the frequency of elastic vibrations rather than the spectrum of scattered light.

I suppose that Einstein simply did not think about the spectrum of scattered light. In paper [4], he suggested a statistical method for calculating fluctuations and obtained an expression describing the intensity of light scattered by these fluctuations. These results represent the greatest achievement of statistical physics. Note also that Mandelstam [2] calculated the intensity of light scattered by a fluctuationally rough surface using the general principle formulated by Einstein [4]. Moreover, he performed experiments which confirmed the theoretical predictions [2].

The Debye theory of heat capacity of solids [6] already considers elastic thermal waves with a great variety of frequencies, which are limited only by the maximum frequency. However, Debye too did not think about the spectrum of scattered light.

As far as I can judge, only Mandelstam [12] and Brillouin [13] paid attention to the fact that real Debye waves can modulate scattered light and produce 'side frequencies' or the fine-structure splitting of the Rayleigh line.

As I have said above, Mandelstam, who was elaborating the theory of a radio transmitter and many other related problems, could immediately extend, by analogy, the phenomena observed in radiophysics to optics. If it was the case, he envisioned a beautiful picture of the fine structure in the spectrum of light scattered by a medium.

It is for this reason that, when Mandelstam took a chair at the Physics Department of Moscow State University in 1925, he immediately formulated the task of the experimental detection of the fine-structure splitting. And unhurriedly, he published in 1926 the relevant theory in a journal which was not very popular in the West [12]. The problem was formulated in the following way: "This note is devoted to the problem of the time dependence of the Fraunhofer diffraction pattern which appears during propagation of a plane light wave through a slightly optically inhomogeneous medium, when inhomogeneities are caused by propagating elastic perturbations or when a medium consists of various components and its inhomogeneity is caused by variations in

method used for their study and on their common properties, independently of their physical content or, more exactly, independently of the great variety of their physical content. Here, we are dealing with acoustic, electric, and optical phenomena, which are very different to our perception. It is this circumstance that makes the theory of vibrations so significant and interesting. By studying one field, you acquire intuition and knowledge in a quite different field of science. You can draw far-reaching analogies: the dark places, say, in optics are illuminated as if by a searchlight in studies of vibrations in mechanics, etc."

the concentration, which is levelled off due to diffusion, or, finally, when the temperature is not constant and is levelled off due to the thermal conductivity''.

In a brief paper of not six full pages, Mandelstam presents a complete and sufficiently rigorous solution of the problem of the spectrum of molecular light scattering by an isotropic medium, caused by fluctuations in the density (pressure), temperature (entropy), and concentration (in the case of solutions). In this paper, pressure fluctuations were described by the wave equation, while fluctuations in the temperature and concentration were described by the diffusion equation. The intensity of scattered light and its frequency dependence were quantitatively found in each case.

Mandelstam obtained the following expression (in his notation) for the spectrum of light scattered by density (pressure) fluctuations [12]:

$$\frac{\delta\nu}{\nu} = 2\,\frac{a}{c}\sin\frac{\theta}{2}\,. \tag{5}$$

Further, Mandelstam says: ''The light scattered in a direction different from the direction of propagation of the incident monochromatic wave consists of a doublet, the frequency (circular) of each of the doublet components being different from that of the incident wave by $\delta\nu$, and $\delta\nu/\nu$ being dependent only on the ratio a/c and angle θ''. (Here, a is the speed of sound, and θ is the scattering angle.)

He continues, referring to Eqn (5): ''We are obviously dealing with a special type of Doppler principle''. At the end of this sentence there is a footnote, which reads: ''In his paper ([13] — **I F**), Brillouin also considers scattering of light by sound waves. By the way, the Doppler effect is mentioned in this paper''.

Work [13], which has been mentioned above several times, represents a comprehensive and detailed study described on 35 pages and devoted mainly to calculations. It seems to me that this paper was stimulated by Debye's paper [6], who treated the energy of the thermal motion in a continuous body as the energy of elastic waves with various frequencies changing from zero to a limiting frequency which is specified in Eqn (3).

Brillouin himself formulated the problem in the following way: ''In particular, if we assume as will be done below that infinite elastic waves having any frequencies can propagate through a transparent medium in any direction, but light scattered at an angle [3] of θ to the incident beam will be produced only by the elastic wave propagating along the bisectrix of angle θ with the wavelength determined by Eqn (18)''. Formula (18) in Ref. [13] yields the Bragg condition

$$2\Lambda n\sin\frac{\theta}{2} = \lambda\,, \tag{6}$$

where Λ, λ, n are the wavelengths of the elastic wave and light, and the refractive index, respectively.

In brief, the reflection of light from an elastic wave travelling at a velocity of a (from compression or rarefaction) will result in the same change in the frequency due to the Doppler effect as follows from formula (5).

Note that because the number of waves is very large, for any wave with the wave vector q one can always find a wave with the wave vector $-q$ and, therefore, a standing wave will appear, which will modulate the scattered light, the frequency shift caused by the modulation being the same as predicted by formula (5) (as was specially discussed by Landsberg [15]).

The Doppler frequency shift obtained by Brillouin [13] turned out to be the most valuable result of his paper. In addition to the Doppler shift of the scattered light frequency, Brillouin also derived expressions for the scattered light intensity using the Planck quantum radiation formula. Thus, the expressions for the scattered light intensity derived in Ref. [13] can be applied to low temperatures and high frequencies of light (for X-rays), and Brillouin paid special attention to these results and devoted almost his entire paper to their discussion.

Meanwhile, as follows from estimates [8], the Einstein formula for the scattered light intensity and other similar formulas that neglect quantum corrections are valid down to temperatures $T \cong 0.1$ K. Therefore, the quantum corrections may be required only in some exotic cases.

As for the application of formulas from Ref. [13] to the propagation of X-rays, their scattering will hardly depend on fluctuation inhomogeneities. In particular, Debye and Sears [16] wrote the following in this respect: ''He (Brillouin — **I F**) is trying to apply his theoretical calculations to X-ray scattering. Now we know that such an approach is not correct because for such short wavelengths the variations in the electron density caused by the atomic or molecular structure are much more important than thermal fluctuations''.

Therefore, there is no sense in introducing quantum corrections to the expression for the scattered light intensity, which are important at the low temperatures and high frequencies inherent in X-rays.

The prediction of the possibility of observing a doublet in the spectrum of light undergoing molecular scattering is essential. As mentioned above, Mandelstam [12] predicted a doublet in the spectrum of molecular scattering of light, if the reader believes in the fantasy of the author of this paper, by analogy with the radiophysical modulation of the carrier frequency of a transmitter, resulting in the appearance of sidebands.

Concerning the same prediction made by Brillouin, it is interesting to guess what stimulated him to make this prediction. It is natural that we can only talk about the facts lying on the surface that catch the eye.

Leon Brillouin passed away in early October 1969, aged 80, in New York. A Kastler devoted a lecture to his memory under the name ''The life and creative genius of Leon Brillouin'', which was published in Russian in *Uspekhi Fizicheskikh Nauk* [17]. Kastler said in his lecture that after receiving an 'agrégé' degree (which is approximately equivalent to a candidate of science) from École Normal Supérieure in 1912, Brillouin was happy to work for a year in Munich at the Institute of Theoretical Physics headed by A Sommerfeld, where the young M Laue also worked and put forward an excellent idea that if X-rays were short electromagnetic waves, then a crystalline lattice of a solid would serve as a diffraction grating for them and, therefore, the diffraction of X-rays could be observed. This idea attracted the attention of researchers at the Institute of Experimental Physics headed at that time by W Roentgen. Laue's idea was experimentally confirmed at the latter Institute. The atmosphere and wide scope of theoretical and experimental investigations had a profound impact on the further studies of L Brillouin.

Kastler tells the following about the time after Brillouin returned from Munich University: ''When he came back to

[3] In paper [13], the scattering angle is denoted by 2θ.

Paris in June 1913, he began his doctoral study that was called "Theory of solids and quanta". However, these studies were interrupted by the World War I in 1914. He was drafted into the army, where he became a lieutenant of the army radio service and worked with Henry Abraham, Maurice and Louie de Broglie at the laboratory headed by general Ferrier on the improvement of telegraph communication and the construction of resistor-based amplifiers...".

Then, Kastler notes: "After defending his dissertation in 1920, Leon Brillouin read a course of lectures on radiophysics at the Higher Electrical Engineering School for ten years from 1921 to 1931".

From the aforesaid, one can conclude that among the physicists mentioned previously only Mandelstam [14] and Brillouin [17] were engaged in studies of radiophysical problems; and because, as mentioned above, there exists a direct analogy between the modulation of the carrier frequency in a radio transmitter and the modulation of scattered light by elastic thermal waves, it is reasonable to assume that this analogy stimulated their predictions.

It seems that the researchers working in the field of radiophysics, having learned about Debye elastic waves, had to understand at once, and maybe even later, that the Rayleigh line should exhibit a fine structure. Except for Einstein, Mandelstam and Brillouin, molecular scattering of light was studied at that time by Cabannes in France, Hans in Germany, Strutt, Jr. in Great Britain, Raman in India and Wood in USA but, as is known, none of them predicted a fine structure of the Rayleigh line; however, to the best of our knowledge, none of them dealt with radiophysical problems.

It is possible that my hypothesis about the role of the radiophysical analogy is wrong, and this prediction was made simply by accident. It might be. However, it seems to me that an accidental discovery in this case is unlikely.

As for Einstein, it seems that he was able to do anything, but he was preoccupied with other great matters which he managed to realize so brilliantly. After the fundamental paper published in 1910 [4], Einstein did not study the problem of light scattering.

It seems that the situation was quite different in the case concerning Debye, who discovered the elastic thermal or Debye waves existing in any body at nonzero absolute temperature. Debye did not pay attention to the scattering of light by these waves and to their special feature. The Brillouin paper published in 1922 [13] probably stimulated the paper by Debye and Sears [16] on ultrasonic light diffraction.

Debye himself described the situation arisen in the following way [18]: "Some time ago, F W Sears and I managed to show that a liquid through which high-frequency sound waves are propagating strongly scatters the light passing through it. Moreover, the interference phenomena take place in complete analogy with normal grooved diffraction gratings, and the wavelength of the sound wave in the liquid plays the role of the diffraction grating constant".

Lucas and Biguard [19] observed ultrasonic light diffraction simultaneously with Debye and Sears [16], and the detailed theory of this phenomenon was developed by Rytov [20].

It should be emphasized that only the Doppler effect and modulation of the scattered light can cause all the variations and features observed in the spectrum of light undergoing molecular scattering. Modulation plays an important role in many fields of physics and technology and its general theory was elaborated by Rytov [21] and Kharkevich [22]. In the case under study, the modulation of the scattered light was produced by thermal elastic waves of sinusoidal shape with very small amplitude.

The effective amplitude of a thermal elastic wave was estimated in Ref. [23] as

$$A_{\text{eff}} = \left(\frac{kT\,\mathrm{d}\Omega}{\rho\pi^2 V^3}\right)^{1/2}. \tag{7}$$

By equating $\mathrm{d}\Omega$ to the half-width of the Mandelstam–Brillouin scattering line, we obtain, for example, for benzene $A_{\text{eff}} \cong 10^{-11}$ cm.

Notice here that the thermal elastic wave in question essentially differs from an artificial acoustic wave generated, for instance, by a piezoelectric emitter. While the latter decays in time and space during propagation in a medium, the thermal elastic wave decays neither in time nor space [23, 24] and its amplitude remains constant and depends only on the square root of the ratio of the absolute temperature to the cube of the speed of sound (7). This is true both for crystals and liquids.

However, the theory of the phenomenon shows that the speed and absorption coefficient of sound of the corresponding frequency up to $\Omega_{\max}$ can be determined from the width and position of the Mandelstam–Brillouin scattering line components [8, 23, 24].

3. Beginning of experimental studies aimed at discovering the fine structure of the Rayleigh line

In Moscow, L I Mandelstam together with G S Landsberg began experimental investigations of the spectra of scattered light. First of all, it was necessary to build an experimental setup and to choose an appropriate object for studies. The researchers had reasons to begin the study with solids.

The best samples of natural crystals could be found first of all among quartz single crystals. At that time, this was a complicated problem, but I have already written about it several times [25, 26].

Samples of quartz single crystals were chosen and the researchers could begin the work. Landsberg described the situation in this field in his first paper "Molecular scattering of light in solids" [27] in the following way: "However, the scattering of light in solids was poorly studied experimentally. In a short note [28], Strutt describes some observations of light scattering by crystalline quartz and assumes that the observed effect is caused by foreign impurities".

Therefore, when Landsberg began his studies, it was not definitely known whether it is possible to observe molecular scattering of light in crystals at all.

An appropriate experimental setup was built in the shortest time, and the study of light scattering in crystals began to develop very rapidly for that time. Already in 1927, Landsberg published two papers [27, 29] in one of the most popular Western journals, where he proved conclusively that molecular light scattering exists in a quartz crystal and can be studied. He found a criterion for separation of spurious scattering by foreign impurities from molecular light scattering.

These papers proved that it is possible to proceed to the main problem of discovering the fine-structure splitting of the Rayleigh line.

At the same time, Landsberg continued to study scattering of light in quartz (together with K S Vul'fson) [30] and in rock salt (together with S L Mandelstam, Jr.) [31].

It is amazing that so many outstanding discoveries included in the arsenal of modern science, were made in such a small optical laboratory for less than five years.

At first, two people were working at the laboratory: L I Mandelstam, who was head of the chair of theoretical physics and had many other responsibilities, and G S Landsberg, who was engaged at the beginning of their collaboration in a search for crystal quartz samples suitable for studies.

Notice that when L I Mandelstam moved to Moscow and began to work at the Physics Department of Moscow State University, a group of physicists gathered around him. As V A Fabrikant wrote [32], these were " ...both physicists of the elder generation, such as G S Landsberg and I E Tamm, and young people — A A Andronov, A A Vitt, M A Leontovich, and S É Khaĭkin". V A Fabrikant himself got to know G S Landsberg only in 1928, while M A Leontovich was engaged in the study of the Kursk magnetic anomaly in the P P Lazarev Institute between 1920 and 1925 and he began to collaborate with L I Mandelstam and G S Landsberg probably in 1925, being a post-graduate student of L I Mandelstam.

However, M A Leontovich was also obliged to do the job of a laboratory worker. He recalls this period of his work in the laboratory: "I can also recall how we were on duty in turn near a mercury lamp. The photographs were taken using exposures that lasted for several weeks, and it was necessary to come and turn a mercury lamp to adjust it to burn in the proper regime. A cassette should be charged and photographs should be developed in the dark. In this connection, I had awful troubles with G S Landsberg. He was a very delicate person. When he wanted to express his disapproval, he became extremely polite and delicate, and this was worse than the most severe abuse. Once, I incurred such a penalty when I charged a photographic plate for a week's exposure from the wrong side" [33].

Sergeĭ Leonidovich, a son of L I Mandelstam, recalls the same period of time: "I also remember that the spectrum of combination light scattering could be obtained only after very long exposures, and it was necessary to keep a mercury lamp burning during the entire exposure time. My mother did it, in particular, at night. We lived at that time in the Physics Institute of Moscow State University on Mokhovaya street, and the door from our flat could be opened directly to the laboratory where the experiment was performed.

The studies were interrupted by a severe event concerning our family: one of the far relatives of my father, a clerk of a bank, was arrested and sentenced to imprisonment in one of the first processes of that time; and my father, together with the poet O É Mandelstam, who was our far relative, exerted every effort to solicit A Ya Vyshinskiĭ, who was a rector of Moscow State University at that time, to mitigate the destiny of the sentenced man" [34].

These brief excerpts from the memories of that time, which are separated from our time almost by three quarters of a century, testify that although only three persons were engaged in the studies (only one of them being entirely occupied by this problem) they were working with enthusiasm and even the members of their family helped them; while, on the other hand, they knew much sorrow in their lives.

It is well known that the initial search for fine structure of the Rayleigh line resulted in the discovery of combination scattering of light (the Raman effect), which was made a week before the discovery by Ch Raman, but misfortunes postponed the relevant publication [23].

However, after the study of combination light scattering, L I Mandelstam and G S Landsberg again started the experimental study of 'the initial problem', as they called it.

The optical laboratory at the Physics Department of Moscow State University was not only very small but was poorly equipped at that time. They had an old quartz spectrograph ('Fuss'), a Lummer – Gehrcke glass plate, and a mercury lamp. S L Mandelstam [34] recollects that when a foreign colleague asked Landsberg why he used 'the most unsuitable instrument for this purpose', Grigoriĭ Samuilovich answered: "We did not have other instruments". A Lummer – Gehrcke plate also was not suitable for the solution of the problem and it could give only a qualitative answer about variations in the spectrum of scattered light.

There is a note in Landsberg's archives that gives an insight into the experiments with the use of a Lummer – Gehrcke plate. G S Landsberg wrote: "The experiments in this field, which we performed in our laboratory for a long time, have led to some results.

Light scattering in quartz was studied using a Lummer – Gehrcke plate ($5 \times 15 \times 140$ mm) oriented in such a way that the angle $\theta = 90°$.

As a light source, a mercury lamp was used with a voltage 40 V applied to terminals to provide adequate sharpness of the interference pattern.

The intensity of the 4358-A line detected using the glass optics was far greater than that of the other lines, so that there was no need to use optical filters or any other methods for monochromatization.

Although experiments were performed in a completely isolated room without windows and heating at comparatively constant room temperature, nevertheless it was necessary to check that any interference caused by possible variations in the room temperature was absent over quite prolonged exposures (for 6 hours) [4].

To do this, a direct light from the same mercury lamp, whose intensity was reduced with diaphragms and optical filters approximately to that of the light scattered by quartz, was incident on a second Lummer – Gehrcke plate which was similar to the first one.

The sharpness of the interference pattern obtained after the 144 h exposure by the direct light proved to be the same as that of the corresponding pattern obtained during short exposures. Therefore, temperature variations and other factors under our experimental conditions produced no adverse effects.

At the same time, the interference pattern obtained from the scattered light was far less distinct than the interference patterns produced by the direct light and was quite similar to the pattern obtained when a mercury lamp was placed in a magnetic field (Zeeman splitting).

Therefore, without a doubt, the lines of the scattered light are broadened or split. However, our experiments allow us to estimate the magnitude of this broadening (splitting) only quite approximately.

[4] It is likely that here is a slip in writing, and '6 days' should be read instead of '6 hours'.

The distance between the two successive orders in our plate is approximately 0.17 A for $\lambda = 4358$ A, i.e. the noticeable spreading of the interference pattern indicates that the splitting (broadening) of the lines amounts at least to several hundredths of an angstrom''.

Of course, L I Mandelstam and G S Landsberg could not be satisfied with the results they obtained using their equipment, and they applied to Academician D S Rozhdestvenskiĭ, who was a director of the State Optical Institute (GOI) founded by him in Leningrad (St. Petersburg). Among the equipment available at GOI, there was the Michelson echelon which could be used for resolving the fine structure of the Rayleigh line theoretically predicted by formula (5), if it really existed.

G S Landsberg [10] described the situation in the following way: ''Because of the lack of the adequate optical instruments at Moscow State University, L I Mandelstam and G S Landsberg initiated similar studies by E F Gross simultaneously at the State Optical Institute in Leningrad. Gross was also informed that this phenomenon could be tentatively observed in quartz.

At the same time, Gross performed successful experimental studies of the line structure of light scattered by liquids, where, as mentioned above, the line broadening seemed to be more probable''.

We can say quite definitely that studies aimed at the discovery of the fine structure of the Rayleigh line in the spectrum of light scattered by a quartz crystal were consistently pursued in Moscow, using the Lummer–Gehrcke plate, and in Leningrad, using the Michelson echelon. One can assume that both L I Mandelstam and G S Landsberg and Gross devoted initially all their efforts to the discovery of the effect and did not think about the way of a presentation of the discovery, whether it would be made either in Moscow or Leningrad.

It follows from the above statement of G S Landsberg that this phenomenon had been discovered but, so to speak, in different ways. More exactly, the Lummer–Gehrcke plate allowed one to observe only the broadening of the line of scattered light, whereas the Michelson echelon allowed one to distinguish the scattered line broadening from its splitting into components.

We can judge the development of the studies in Moscow and Leningrad and the relations between the researchers during these studies from the data available. There are several letters of E F Gross in the archives of G S Landsberg placed at our disposal by his son Leonid Grigor'evich, as well as a draft of an unpublished brief note about the results of an experimental study by L I Mandelstam and G S Landsberg and some drafts of letters addressed to E G Gross.

In his biographic essay [35] about Gross, Prof. B V Novikov mentions Gross's archives and says that he found nothing in it relevant to the subject of interest for us. In particular, the letters of G S Landsberg to E F Gross were not preserved. Therefore, here we will discuss only the reliable materials from archives and publications.

4. The beginning of parallel studies in Moscow State University and the State Optical Institute aimed at discovering the fine structure of the Rayleigh line

It is impossible to ascertain definitely when L I Mandelstam and G S Landsberg suggested beginning parallel studies in GOI. Also, it is not known by whom, how and where it was decided to develop these studies at GOI. The only unquestionable fact is that L I Mandelstam and G S Landsberg arranged this matter with the director of GOI, Academician D S Rozhdestvenskiĭ. It is also known that Evgeniĭ Fedorovich Gross began to solve this experimental problem.

I should like to think that E F Gross was very lucky. A chance to collaborate with such outstanding physicists as Mandelstam and Landsberg in solving such an important problem for physics does not often fall to a researcher. It follows from the letter of E F Gross to G S Landsberg, dated 11 April 1929, that by then the problem has been already formulated. E F Gross began a search for an appropriate quartz sample. It is likely that Landsberg wanted to come to Leningrad to take part in the first experiments with Gross, as a person much experienced in studies of light scattering by quartz, but the study had not yet started at that time and, therefore, his arrival would be premature. One can assume that Gross began his experimental studies formulated by Mandelstam in April 1929.

In Moscow, G S Landsberg and L I Mandelstam began to solve the same problem at once after they got acquainted, at least, not later than in 1926, because the first paper mentioned above was published in 1927.

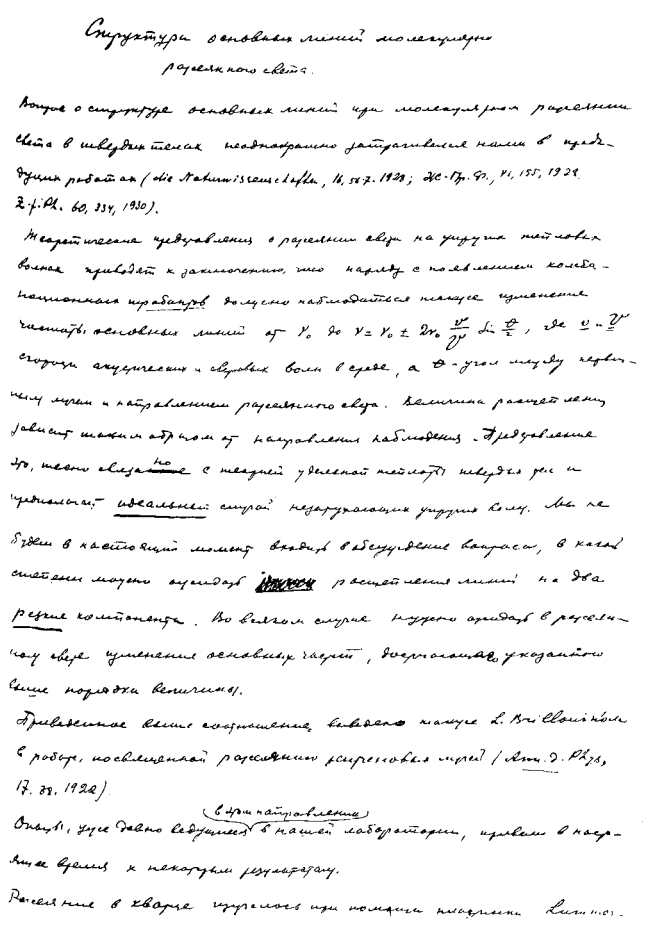
Almost a year passed after the beginning of experimentation by E F Gross. In the archives of G S Landsberg, there is no evidence of how this year passed. However, it follows from the archives and letters from E F Gross that G S Landsberg was in Leningrad in this year. The next letter from E F Gross was dated by 26 March 1930, and here Gross already discusses the question about the publication of his results that confirmed the correctness of the theoretical predictions.

Before proceeding to the discussion of the events developing in time and of the specific results of laborious experimental studies, it is expedient to draw attention to the style of physical studies that L I Mandelstam and G S Landsberg followed in their lives. It is insufficient to say that they were very fastidious or even 'captious' to themselves and other people, whoever they were, when the case in point was the measurement of any quantity or observation of a physical phenomenon. The reliability of the measurements or the observation of the phenomenon should be proved by all possible methods, and only when no doubt remained concerning the validity of the result obtained, this result was accepted and could be discussed; otherwise there was no grounds for discussion.

All this requires the time, and this can be irritating, annoying, etc., but it was the only way they required and not otherwise.

Their attitude to the text of a paper prepared for publication was also distinctive. It goes without saying that the text should be well written. But this was not sufficient. Each phrase should express only the thought the author wanted to express and nothing more. This is difficult to accomplish in some cases, but this was required categorically. A paper containing finished results was not sent for publication at once. It should 'ripen'. Maybe something should be changed, excluded or added. It is possible that the thought which the authors wanted to communicate to a reader should be presented differently, etc. This was their way of working, and they never had to withdraw their results.

It is well known that there exists a completely different style of scientific work, when a researcher immediately publishes some concept or an experimental evidence which



First page of a note written by G S Landsberg probably as a variant of the text intended for publication simultaneously with a paper by E F Gross on the fine structure of scattered line in a quartz crystal (from the archives of G S Landsberg). The complete text is presented on page 98.

appears new to him. If these results are not confirmed in the future, he made a mistake; but if they are, he will be the first who said, found, or established it and, thus, he will have the priority. Such a style of working was absolutely unacceptable to L I Mandelstam and G S Landsberg. Notice here that it seems that the style of working of many researchers is somewhere between these two styles. Some are closer to the first, while the others are closer to the second. All people are different and behave differently.

Let us now turn to the second letter of E F Gross, dated 26 March 1930. He says that he is sending a text of the note describing the results of his experiments, and probably assumes that G S Landsberg and L I Mandelstam have prepared a note on the results of their experiments. Gross writes: *I am sending you quickly the text of my note. The text is written in German, because, although we forgot to arrange with you where we would publish our notes, I think we will publish them in Naturwissenschaften or Zeitschrift für Physik. I am sorry for the delay with the letter.*

As mentioned above, the letters of G S Landsberg were not found in Gross' archives, as Prof. B V Novikov told me; and, therefore, it is difficult to say how the Muscovites responded to the letter of 26 March 1930. However, G S Landsberg always regarded everything with attention, including letters. In the archives of G S Landsberg, rough copies of his letters to E F Gross were preserved, which were written on pieces of paper without the full appeal and date. Of course, these drafts were not intended for publishing, and it is not inconceivable that the content of the letter sent to Gross was somewhat different. I suppose, however, that these rough copies give an idea of the attitude to various aspects of the problem on the part of those involved in its solution.

The content of the draft presented below may be related to the answer to the letter of E F Gross from 26 March 1930, and not only to it. It reads:

Dear Evg. Fedor.!

I am returning, according to your wish, the manuscript of your note.

During this time, I have performed several additional experiments and, after the return of L I (Mandelstam — **I F**), *we discussed all our results and concluded that at present it would be premature to publish them, so we are continuing our work.*

As for the question of your publication and the form of its presentation, we leave it completely to your own judgement.

I also ask you, as I have written already, to exclude the reference to my information on the broadening of the lines, which I have sent to you.

With best regards G.

The date and usual signature of G S Landsberg at the end of this letter (draft) are absent, but it is in his handwriting and it bears traces of his editing, as in the other drafts contained in the archives.

In the next letter from E F Gross written on 3 April 1930, G S Landsberg's letter cited above is mentioned and Gross asks "to exclude from your note any mention about me and the studies performed in the State Optical Institute..."

The further development of the events is partly reflected in the next letters from E F Gross to G S Landsberg. Thus, in the letter from 20 April 1930, E F Gross writes:

Dear Grigoriĭ Samuilovich!

Should we postpone the publication of our experiments with quartz? If you consider this would be premature based on your experiments, we can use my results.

As I have already told you when you were in Leningrad, I think that I should not publish the results of my experiments with quartz alone.

However, it is possible not to publish our papers independently but adopt the second variant, which we discussed with you: to publish the joint note now, and then to publish our papers independently. Initially, we chose the first variant as the most reasonable, but the second variant also has its advantages. Both you and I have studied quartz. Because our studies were initiated by Leonid Isaakovich, it would be reasonable to publish our first paper together. In any case, I suppose we should not risk our work because of the way of its presentation. All this is in fact unessential! It would be a pity if we are late again with publication concerning a phenomenon which has been extensively studied in Russia.

So, this is my proposal: now, we publish jointly the results of our experiments with quartz, and after this publication, each of us may publish independently only his own results (*as you have done already, when you published, together with Leonid Isaakovich, your theoretical considerations concerning the effect in crystals, which we both studied*). *You will publish the results of your further experiments with quartz about which you have told me, and I will publish the results of my experiments with the use of a high-dispersion spectrograph, experiments with liquids, etc.*

Please let me know as soon as possible your opinion about my suggestions.

In the next paper, dated 30 April 1930, E F Gross writes again: *I repeat again that I would not wish to publish alone the results of my experiments with quartz*.

The answer from G S Landsberg has a date. Although it has no signature, the draft is in Landsberg's own handwriting and has many editing corrections. This latter reads:

Moscow, 19/V 1930

Dear Evgeniĭ Fedorovich!

At present, it would be premature to discuss the way of presenting a future publication. Of course, we will inform you about any results we obtain. If these results are contradictory, we will study the reason for it, if they are consistent with each other, we will find a way for our joint publication.

However, I say again that by no means would we like that our doubts postpone your publication, if you consider your results sufficiently convincing.

There is the draft of a letter without date and signature in the archive of G S Landsberg, which could reflect the meaning of the letter sent to E F Gross. I present here the part relevant to the subject discussed:

Dear Evgeniĭ Fedorovich!

As I have already written to you, we do not think that the results of our experiments are sufficiently convincing to be published at present, and we want to elucidate all the doubtful matters. However, it would be a pity to delay the publication of your paper, because you are confident in your results. We think that the effect is well substantiated theoretically, especially now, when it could be a natural supplement to combination scattering of light. Because of this, the positive result of your experiment seems to be quite plausible. However, one should be involved in the experiments oneself in order to consider the results, which are near the detection threshold, sufficiently convincing.

Thus, you should alone decide on the possibility of publication. We think that our participation in your publication is unsuitable, but I repeat that this should not stop you.

G S Landsberg probably sent the next letter to E F Gross once Gross had already sent his results for publication, L I Mandelstam and G S Landsberg being unaware of it.

G S Landsberg writes in this letter:

Dear Evg. Fedor.!

After a series of control experiments, we have obtained results that we consider quite reliable. The photographs we obtained definitely demonstrate line broadening or blurred splitting, which is not smaller than that theoretically expected (ca. 0.17 A).

These results do not contradict yours, although we cannot state that we observed line splitting.

However, the Lummer–Gehrcke plate available to us would allow us to detect only quite sharp splitting.

Splitting accompanied by line broadening would produce a picture similar to a simple broadening covering both lines.

Thus, we suppose that at present we can publish our results simultaneously.

If you consider, as before, the parallel publication desirable, you may send both papers simultaneously to Naturwissenschaften.

Gross sent the reply to Landsberg's letter on 17 June 1930. I present this letter completely.

Dear Grigoriĭ Samuilovich!

Unfortunately, your letter was somewhat late. Just before this, I decided at last to send a short note about my experiments to Zeitschrift für Physik, which was written approximately in the form I have already sent to you.

The complete uncertainty concerning the publication of my experiments, which lasted for 3 months, finally ended my indecision. This was promoted, of course, by your repeated amiable advice not to delay the publication of my note.

Dmitriĭ Sergeevich (Rozhdestvenskiĭ — **I F**), *who met Leonid Isaakovich at the end of May at the session of the Academy of Sciences, also told me that Leonid Isaakovich still prefers to be careful in relation to this problem and does not trust my experiments.*

Meanwhile, having some experience in studies with the use of optical instruments of high resolving power, I knew that in this case it was very difficult to get even the results that I have obtained, and to make them even more convincing is very difficult.

And 3 months is not a short period!

However, because I am more or less confident in my results, after long hesitations I decided at last no longer to delay the publication and to publish a paper at my own risk.

It would be a pity if my work on this problem were to be wasted. (*It seems that for you this question does not matter.*)

Having considered the content of your letter and the text of your note, I doubt that it is expedient for me to take part in a parallel publication. So, I leave completely to your own judgement the question of your publication.

I would also like to attract your attention to the fact that your conclusion about the magnitude of the line broadening is not quite correct in my opinion.

Because the distance between the orders in your plate is ca. 0.165 A, *it seems to me that the disappearance of the interference pattern indicates that the line broadening* (*full width*) *is no less than this value* (*the line half-width is no less than the half distance between the orders*).

The theoretical linewidth (*full width*), *assuming that individual Feinstuctur components are indiscernible, is* ca. 0.35 A, *i.e. it is greater by a factor of two.*

Best regards,

Yours E Gross.

The last notes in the correspondence between G S Landsberg and E F Gross were the following: the note from G S Landsberg, dated 21 June 1930, containing the request to return the manuscript of the paper by Landsberg and Mandelstam, which they probably intended to publish simultaneously with a paper of Gross, and the note from E F Gross, which read:

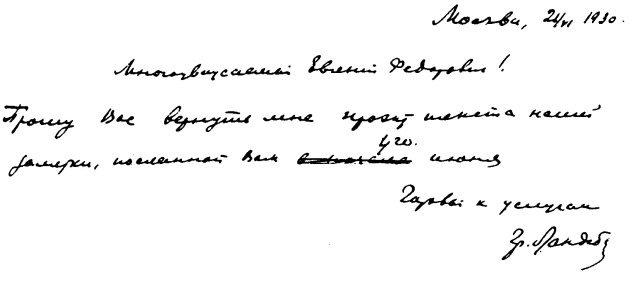
Dear Grigoriĭ Samuilovich!

As you asked, I return the manuscript of your note.

With best regards,

E Gross

Leningrad, 4/VII 1930.



A letter from G S Landsberg to E F Gross with the request to return 'a variant of the text of our note', in which G S Landsberg and L I Mandelstam probably informed E F Gross about the results they wanted to publish. Their note was not published.

Now, it is well known that E F Gross published his note. Below, we present the text of this note. However, the existence of the note by G S Landsberg and L I Mandelstam, where they described the results of their experiments, was unknown because they did not publish it. E F Gross clearly wrote in the letter presented above: *...I doubt that it is expedient for me to take part in a parallel publication*. But it seems unlikely that G S Mandelstam and L I Mandelstam did not publish their experimental results for this reason. Unfortunately, the text of the note that E F Gross returned in July 1930 is not available. However, there is the draft of a text in the archives of G S Landsberg in his own handwriting. We can assume that it is a copy of a variant of the note that was sent to E F Gross.

We will present below the text of this note, which is undoubtedly of interest; the more so, as physicists do not know that G S Landsberg and L I Mandelstam were engaged in an extensive experimental search for the fine structure of the line of light scattered by quartz crystals.

5. Results of the first experiments of G S Landsberg and L I Mandelstam and of E F Gross, described by themselves

The attitude of Landsberg and Mandelstam to the results of their experiments devoted to the search for fine structure in the spectrum of light scattered by quartz, which they performed for many years, was manifested quite definitely. They simply did not publish these results. It seems likely that here again it may be explained by their very high requirements to themselves and their results.

Meanwhile, their note reports quite distinct and definite observations. Because of this, we present below the text of a draft note written by Landsberg, although it cannot be said with confidence that the authors would have approved this step.

In the text of the note presented below, which is in Landsberg's own handwriting, the authors were not named, and it is unknown whether this text was agreed with the co-author or was only prepared for this. There is a date in the text. Its content is as follows:

Structure of the basic lines involved in the molecular light scattering

We have considered the question of the structure of the basic lines of molecular light scattering in solids in several of our previous works [die *Naturwissenschaften* **16** 567 (1928); *Zhurnal Prikladnoĭ Fiziki* **IV** 155 (1929); *Z. Phys.* **60** 344 (1930)].

According to the theoretical concept, the scattering of light by elastic thermal waves should result, along with the appearance of combination satellites, in a change of the frequency of the basic lines from ν_0 to $\nu = \nu_0 \pm 2\nu_0(v/V)\sin(\theta/2)$, where v and V are the velocities of acoustic and light waves in a medium, and θ is the angle between the incident beam and the direction of scattered light. Therefore, the magnitude of the splitting depends on the direction of observation. This concept is closely related to the theory of the specific heat of solids and considers an ideal case of undamped elastic waves. We will not discuss here to what degree the lines can be split into two sharp components. In any case, one should expect a change in the frequencies of the basic lines of the scattered light amounting to the magnitude pointed out above.

The relation presented above was also derived by L Brillouin in his work devoted to the scattering of X-rays [*Ann. d. Phys.* **17** 88 (1922)].

The experiments in this field, which have long been performed in our laboratory, have given some results.

The scattering in quartz was studied using a Lummer – Gehrcke plate ($5 \times 5 \times 140$ mm) which was oriented in such a way that $\theta = 90°$. The scattered light was directed to one part of the L – G plate, while the second part of the plate was illuminated by a direct light which was properly attenuated and directed to the plate using several mirrors. A photograph displays side by side the interference patterns obtained from direct and scattered light.

We used Ilford Monarch photographic plates which were exposed for 6 days. The light scattered by quartz gives no interference pattern, whereas the reference half of the photograph yields distinct lines [5].

The distance between two successive orders for our plate corresponds to 0.165 A (for $\lambda = 4358$ A). Therefore, the disappearance of the interference pattern means that the line broadens no less than by this magnitude, which coincides with the theoretical broadening predicted by the above formula. The photograph of light scattered by the benzene molecules, obtained on the same setup, demonstrates a clear interference pattern, although far less distinct than from the direct light. This agrees with the estimate made by J Cabannes, according to which the line broadening in benzene should be < 0.1 A.

The question of whether we are dealing with broadening of the lines or their splitting cannot be solved conclusively, based on the experiments performed. Because of the insufficient resolving power of our plate, it is impossible to distinguish line splitting (especially, when it is accompanied by some broadening of the components) from line broadening. The report by E F Gross published below favors line splitting. The quantitative estimate of the measured line splitting made by Gross coincides with the theoretical value and does not contradict our observations.

To confirm the correctness of the general concept, it is important to perform experiments on light scattering at other angles θ.

Moscow, 2/V 1930.

The results described in this note, as the authors said, do not answer the question of whether line splitting or broadening was observed. However, it was found in this work that the spectrum of light scattered by quartz differs from the spectrum of the exciting light. Undoubtedly, this was not too little at that time and, which is important, this demonstrated that Landsberg and Mandelstam, having equipment that was inappropriate for the solution of the problem under study (other instruments were unavailable), nevertheless obtained interesting results.

Landsberg and Mandelstam were well aware that their equipment was inappropriate, and it is for this reason that they initiated the study by E F Gross at GOI in Leningrad.

[5] Weak, hardly noticeable maxima on the negative may be related to a faint stray light or the combination satellite corresponding to $\lambda = 21\mu$. This satellite is strong enough (about 25% of the basic line). However, it is quite possible that this satellite is not monochromatic enough in order to give rise to the interference pattern [cf. *Z. Phys.* **2** 58, 250 (1929)].

Gross published his paper [36] on May 1930. The complete text of this paper translated by T E Holtz is presented below.

On variation of the wavelength upon scattering of light by crystals [6]

E F Gross

(Leningrad, 11 June 1930)

It has already been repeatedly pointed out that the molecular scattering of light is related to variations in the density caused by elastic vibrations which, according to Debye [6], are always present in solids. The scattering (reflection) of light by these trains of elastic waves travelling in solids with the speed of sound can be accompanied by a change in the wavelength of the light wave, caused by the change in the amplitude of scattered light with time. As a result, instead of the frequency ν_0 of the incident light, the two changed frequencies

$$\nu = \nu_0 \pm 2\nu_0 \frac{v}{c} \sin \frac{\theta}{2} \qquad (1)$$

should be observed in the scattered radiation, where v and c are the speed of sound and light in a solid, respectively, and θ is the angle between the incident and scattered light beams.

On the request of Professor L Mandelstam, who long ago predicted the fine structure of the scattered light [7], to verify the validity of this theoretical prediction for crystalline quartz, I performed the experiments with the aim of observing this phenomenon and finding the expected line splitting.

The light from a water-cooled mercury arc lamp at $\lambda = 4358$ A was focused by a condenser onto a large piece of very pure quartz.

The light scattered at an angle of 90° was analyzed with the help of a step grating (30 steps). The experiment was severely complicated by the necessity of using very long exposures (about 80 hours) due to a weak intensity of the scattered light. Variations in atmospheric pressure and temperature (despite the fact that the step grating was protected against temperature variations) caused some blurring of the image.

Based on some photographs obtained, I can make certain conclusions which I want to report briefly below.

The lines of light scattered by quartz are broader than the line of the incident light. The spectrum of scattered light looks as if it consists of several lines. One can distinguish individual maxima in the photographs, which are shifted with respect to the wavelength of the incident light.

Some photographs also exhibit the initial line which, however, is weaker than the shifted lines. On other photographs, this line is probably absent. However, one should take into account that it was difficult to completely suppress the extraneous light.

As a whole, there are hints that four lines are present, two of them being more distinct.

As is known, it is impossible to determine the wavelength unambiguously with the help of a step grating. In some orders, the difference of the wavelengths equal to approximately 0.180 A can be obtained for the most distinct maxima, in good agreement with the theoretical value of about 0.187 A. The two other maxima can be interpreted as lines separated by a double distance and can be tentatively assigned to overtones.

It seems likely that these results confirm the existence of the required effect.

At present, the experiments are being repeated using different equipment, and also the dependence of the line splitting on the scattering angle θ is being verified.

The conclusions about the absence of this phenomenon made by Bogros and Rocard [39] on the basis of their experiments seem to be erroneous. Neither upon critical opalescence of a mixture of two liquids, caused by the enhancement in slowly growing variations in the concentration, nor in the critical liquid–vapor state, when the velocity of propagation of the density variation (and, hence, the speed of sound) should be negligible, according to the condition $dP/dV = 0$, can one expect any noticeable splitting of the lines of scattered light.

For this reason, I have not observed the possible splitting or broadening of the lines of scattered light in experiments with an optical glass. According to Raman [41], the enhanced scattering of light in amorphous solids, as in liquids, is caused by local inhomogeneities of the density or concentration, but they should be considered 'immobile' in this case [8].

The experiments will be described in detail elsewhere.

I express my cordial gratitude to the director of the State Optical Institute Professor D Rozhdestvenskiĭ for his great interest in this work, his useful suggestions and constant support of the experiments.

I cordially thank Professor L Mandelstam for his active interest in my experiments and fruitful discussion of their results, which were initiated by him and which seem to confirm his ideas.

Leningrad, the State Optical Institute,

May 1930.

6. Some doubts and perplexities

One should not impose too heavy demands on the first experimental work that confirmed the prediction of a new optical effect, especially now, when almost 70 years have elapsed and this phenomenon is well understood. However, it seems that some perplexities should be stated.

In Mandelstam's paper [12], of which E F Gross was well aware, it was shown that the spectrum of light scattered in any medium should exhibit a central line caused by fluctuations of the entropy or temperature.

As a rule, the quite intense stray light caused by the presence of dislocations and a variety of foreign impurities is added to the central component.

Therefore, it is difficult to understand the statement of Gross [36, 37] that: "The basic line was also observed on most of the photographs, but it always was weaker than the shifted lines. This line was absent on some of the photographs". It

[6] References in the original paper are given in footnotes. In the text presented here, these references are given by the numbers in the general reference list (**I F**).

[7] See, for example, works by L Mandelstam [12], L Mandelstam, G Landsberg and M Leontovich [38], and also L Brillouin [13].

[8] Of course, the light splitting will not appear if the enhancement of scattering in a glass is caused by impurities.

seems that the absence of the central line is a misunderstanding, since nobody ever observed it later.

There is also confusion related to the observation of the shifted lines. Gross wrote: " ...one should take into account that it was difficult to completely suppress the extraneous light. As a whole, there are hints that four lines are present, two of them being more distinct".

In the opinion of Gross, "the two other maxima can be interpreted as lines separated by a double distance and can be tentatively assigned to overtones".

It seems that the overtones would appear only as a result of the acoustic nonlinearity, which is out of the question in this case. The equidistant position of the shifted lines was never observed as well.

In a solid, six shifted lines can be simultaneously observed — two of them caused by the longitudinal elastic wave, and four others caused by two transverse waves (fast and slow). The position of the corresponding lines will not be equidistant but will be determined by the speed of sound. In addition, the central or Rayleigh line will be always observed. Gross's statement that the speed of sound can be zero in the critical region of a solution of two liquids and in the critical liquid – vapor region, resulting in the absence of the line splitting in the spectrum of scattered light, causes perplexity. It follows from Mandelstam's paper [12] known to Gross that the line splitting is related to the adiabatic speed of sound, which does not change drastically in the critical region.

The statement of Gross that [36]: "...I have not observed the possible splitting or broadening of the lines of scattered light in the experiments with an optical glass" also remains unclear. He explains this negative result by the fact that "... the enhanced scattering of light in amorphous solids, as in liquids, is caused by local inhomogeneities of the density or concentration, but they should be considered 'immobile' in this case".

In his later studies [37], Gross observed the fine structure of the Rayleigh line in liquids, and other authors later observed the fine structure of the Rayleigh line in glasses as well. It follows from Mandelstam's paper [12] that the fine structure of the line of scattered light should be observed in any continuous medium.

Gross's remark in his letter to Landsberg, dated 17 June 1930, that "...your conclusion about the magnitude of the line broadening is not quite correct in my opinion" is perplexing. Gross, as Landsberg and Mandelstam did, calculated the line broadening (splitting) using the formulas of Mandelstam [12] and Brillouin [13] for the same quartz single crystal; therefore, the result should be the same.

If, however, Gross cast doubt on the experimental data of Landsberg and Mandelstam, the more so it is unjustified, as Landsberg wrote in his note presented above: "The distance between two successive orders for our plate corresponds to 0.165 A (for $\lambda = 4358$ A). Therefore, the disappearance of the interference pattern means that the line broadens no less than by this magnitude, which coincides with the theoretical broadening predicted by the above formula". This statement is absolutely correct. Here, quantitative measurements are absent. The expression 'no less' has been underlined!

In his paper [40] published ten years later than his first work in this field, Gross demonstrates a clear understanding of specific features of the spectrum of molecular scattering of light considered above. Unfortunately, Gross did not present in his first experimental work [36] the photograph of the spectrum that he obtained and processed. He also did not demonstrate the photographs of the spectra in his subsequent papers on scattering of light in crystals.

Gross says directly in one of his letters that L I Mandelstam does not trust his experiments. Mandelstam and Landsberg refused to publish a paper together with Gross (as Gross suggested) and they even refused a parallel publication (in his last letter, Gross also refused a parallel publication). Thus, although their parallel studies were agreed, there were no agreement on the time and the way of publication. Gross hurried to publish the results, whereas Landsberg and Mandelstam did not, but it seems they prepared a parallel publication, although it is unknown to what degree they could accomplish this.

E F Gross finally refused a parallel publication and published his results independently.

In his letter to Landsberg, dated 17 June 1930, Gross says directly that Dmitriĭ Sergeevich Rozhdestvenskiĭ met and talked with Leonid Isaakovich Mandelstam, who "... still prefers to be careful in relation to this problem and does not trust my experiments".

What does this claim mean? What does "does not trust my experiments" mean? At present, nobody can give an exact answer to this question. However, I can state my opinion on this subject.

Mandelstam's theory [12] predicted that the spectrum of light scattered by quartz should exhibit a triplet consisting of a central line located at the frequency of the exciting light and of the Stokes and anti-Stokes satellites. Brillouin predicted theoretically only the Stokes and anti-Stokes satellites, in the absence of a central line [13].

It seems that Mandelstam could not trust the experiments only for one reason: he did not see the reliably shifted components and was probably surprised by the absence of the central line on some photographs.

L I Mandelstam was an outstanding physicist and a sophisticated experimenter. As far as I can judge, if he did not trust something, this means that he could not make definite conclusions confirming his own theory, based on the results available.

It should be emphasized that Gross himself was probably also not confident in his results because he wrote in the same letter of 17 June 1930: "However, because I am more or less confident in my results..." (see the complete phrase above).

If an experimenter himself is not confident in his results and writes in the letter to his colleague: "I am more or less confident in my results", this may mean for Landsberg and Mandelstam that the result that would convincingly confirm the theory has not been obtained.

There is yet another circumstance that could perplex L I Mandelstam. In his first publication [36], Gross states that he observed four lines, two of them being weaker than the others. And further, he says that the two weaker maxima can be interpreted as the lines shifted by a double distance and as overtones of the first two frequencies (see the text of the first note of Gross, presented above).

Of course, the author of this paper can only guess why L I Mandelstam said to D S Rozhdestvenskiĭ that he does not trust the results of E F Gross.

7. The fine structure of the spectrum of light scattered by liquids

The fine structure of the line of light scattered by liquids was discovered by E F Gross, who observed this phenom-

enon in seven liquids, including aniline, toluene, benzene, water, etc.

While the light scattered by quartz was analyzed with the aim of detecting the fine structure predicted by the theory [12, 13], in the case of liquids, as Gross said [43]: "Soon after the discoveries of the Raman effect, I made an attempt to find out whether the Raman lines caused by the rotation of molecules are present in the spectrum of light scattered by various organic liquids". Therefore, experiments with the use of a high resolving power spectrograph, which were initially aimed at the detection of the rotational spectrum of combination light scattering in liquids, resulted in the discovery of a fine structure of the same nature as in a quartz single crystal.

This was an unexpected discovery of an entirely new phenomenon, which appeared impossible at that time due to the strong damping of high-frequency elastic thermal waves or Debye waves in liquids. Now, this result appears natural and can be easily explained, but at that time it was unusual and even put the kinetic theory of liquids in a different light [46].

The frequency shift caused by modulation of the scattered wave by the elastic thermal wave is described by the expression [12, 13]

$$\frac{\Delta\nu}{\nu} = \pm 2\,\frac{v}{c}\,\sin\frac{\theta}{2}\,. \tag{8}$$

Here, the shifted components are located on both sides of the line of exciting light, where v and c are the speeds of sound and light, respectively.

In his studies of the spectral composition of light scattered by liquids [44, 45], Gross observed some features which were so unusual that it seemed that the theory of the phenomenon should be completely changed.

In the experiment under consideration, Gross [43] observed not one Stokes and one anti-Stokes components but several components on each side of the central component, and for this reason he stated: "For scattering of light by liquids, the equality (8) should be replaced by the equality

$$\nu = \nu_0\left(1 \pm 2n\,\frac{v}{c}\,\sin\frac{\theta}{2}\right), \tag{9}$$

where $n = 0, 1, 2, 3$, and, accordingly, the theory of light scattering by elastic waves should be modified.

The number of components I observed with my instrument was $n \leqslant 3$, however, the components with $n > 3$ may be also observed".

These observations were confirmed in the next paper [45], where Gross also pointed out that the observed lines corresponding to $n = 1$ in formula (9) were more intense than the external components (with $n = 2, 3, \ldots$).

Experiments performed by different authors in various countries, using mainly laser excitation sources, have shown that only one Stokes and one anti-Stokes components were observed in all the liquids studied. These components are well described by formula (8) and are now called the Mandelstam – Brillouin components. It is difficult to say why Gross observed a greater number of components in his works [36, 37, 40, 42 – 45] than their actual number. In our opinion, this is explained by some misalignment of the Michelson echelon, however, other reasons are also possible.

In his work published in 1932 [45], Gross confirmed the validity of his previous observations with the example of two

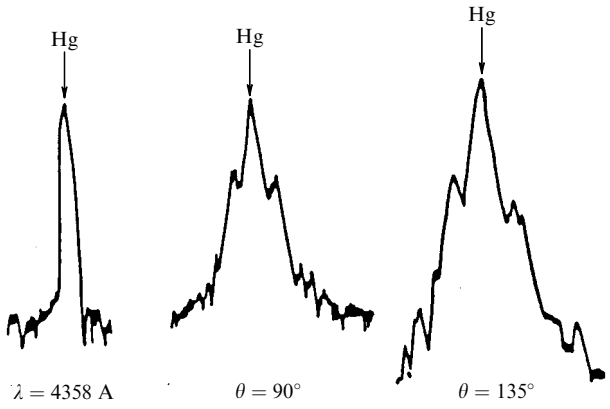


Figure 1. Microphotograms of the spectrum of light scattered by liquid benzene at angles $\theta = 90°$ and 135° upon excitation by a 4358-A line from a mercury lamp (E F Gross [45]).

liquids, carbon disulfide and chlorobenzene, which were not studied earlier. In this paper, Gross for the first time presents microphotographs of the spectrum of light scattered in benzene at different angles upon excitation by a 4358-A line of a mercury lamp (Fig. 1).

For comparison, the spectrum of light scattered by benzene at $\theta = 90°$ upon excitation by a 6328-A line from a Ne – He laser is shown in Fig. 2.

It is difficult to believe that this is the same spectrum of the same liquid. The extremely narrow and intense laser lines have drastically changed the spectroscopic techniques and allowed us to discover many new effects which were earlier inaccessible for study.

New equipment has also allowed us to distinguish reliably the lines inherent in the spectrum, which prove the validity of the theory, from spurious lines.

Let us return to Gross's statement [45]: "The appearance of an unshifted central line which should be absent, according to the Brillouin – Mandelstam theory, can be explained by the superposition of the unresolved shifted lines due to higher-order reflections". It seems that this statement is the result of a misunderstanding, because Mandelstam calculated the time dependence of the intensity of the central (unshifted) line caused by temperature fluctuations in pure liquids or fluctuations of the concentration (composition) in a solution [12]. This dependence is described by formula (12) in Ref. [12].

The Mandelstam – Brillouin components are related to fluctuations in the density, which are determined by pressure fluctuations Δp, while the central or Rayleigh line is related to fluctuations of temperature ΔT or entropy ΔS.

The time dependence of pressure fluctuations is determined by the Navier – Stokes equation.

The Fourier components of pressure fluctuations are actual thermal elastic waves.

Fluctuations of temperature or entropy vary with time exponentially, in accordance with the Fourier equation.

The propagation velocity of thermal elastic waves caused by pressure fluctuations is the speed of sound.

The decay time of fluctuations of temperature or entropy is determined by the thermal diffusivity.

The central component of the spectrum of light scattered by a solution also contains light scattered by fluctuations of the concentration, and the decay time of these fluctuations is determined by the diffusion coefficient.

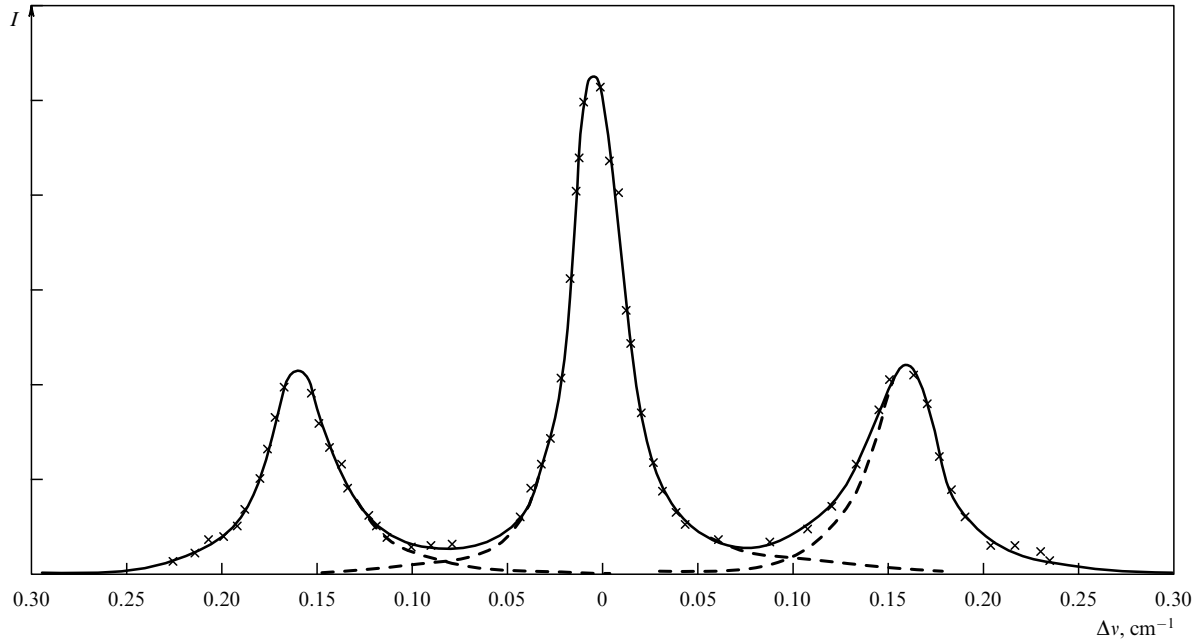


Figure 2. Microphotogram of the spectrum of light scattered by liquid benzene at $\theta = 90^\circ$ upon excitation by a 6328-A line from a Ne – He laser (Mash, Starunov, Tiganov, Fabelinskiĭ [47]).

Thus, the Mandelstam – Brillouin line and the Raman line are formed by different independent fluctuations.

Along with fluctuations of pressure, entropy, and concentration, there also exists the fluctuation of anisotropy (anisotropy is nonthermodynamic quantity), which is represented in the spectrum by a broad band — the Rayleigh line wing.

Modern studies of the spectra of molecular scattering of light are well developed. The spectroscopy of scattered light represents a division of molecular optics, molecular acoustics and, in particular, high-frequency acoustics ($\sim 10^{10}$ Hz), and also a division of molecular physics [8, 15, 16, 23, 24, 47].

The quantitative processing of these spectra allows one to determine, in particular, the speed and absorption of hypersound, the relaxation time of viscosity, and also the relaxation time of anisotropy.

The spectra of molecular scattering of light in gases, plasmas, liquids, solutions, and solids can be efficiently used for obtaining new information.

The content of this paper concerns only the history of the discovery of the Mandelstam – Brillouin components falling within the part of a scattering spectrum.

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