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STUDY OF THE FINE STRUCTURE OF THE LINES OF SCATTERED LIGHT AND THE PROPAGATION OF HYPERSOUND

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IT was my good fortune over a period of many years to attend the lectures and seminars of Leonid Isaakovich Mandel'shtam. In the beginning of 1944, he lectured on certain problems of the theory of vibrations.[1] In describing the essential quality which is found in the theory of vibrations, and which at the same time is general for all other branches of physics, he said figuratively that each part of physics, optics, acoustics, mechanics, etc. speaks in its own "national" language. But there is an "international" language in physics, and that is the theory of vibrations.

If one uses such a linguistic terminology, then we can say that L. I. was a polyglot; he understood the languages of all branches of physics. An especially fine knowledge of the "international" language permitted L. I. to see phenomena as others did not see them, and to find the connection between phenomena that appeared unrelated to others. I shall not take it on myself to discuss which of L. I.'s discoveries or investigations played the decisive role, but I think that in this region of which I shall speak today, his knowledge of the "international" language played not a small part.

Mandel'shtam witnessed the birth of molecular scattering of light and his contribution to this subject was very great.

Fifty four years ago, Einstein [2] calculated the intensity of light scattered by density fluctuations, expanding the density fluctuations in a Fourier series of spatially periodic functions. At almost the same time, Debye [3] generalized Einstein's theory of specific heats of solids by expressing the kinetic energy of the thermal motion in terms of the energy of elastic waves. Neither Einstein nor Debye thought that they were talking about the same thing.

Mandel'shtam foresaw the future clearly and showed that the Einstein "formal waves," from which the light scattering occurs, are also the Debye waves, whose energy determines the specific heat of the solid.[1-4] Thus, he found a simple relation between the specific heat of the solid and light scattering, although it appeared that these phenomena have nothing in common with each other.

Along with this, L. I. stated a new viewpoint on light scattering. From this point of view, the scattered light is the diffraction of light by elastic thermal waves, or by hypersound, as we now say.

Figure 1, which has already become classical, illustrates the essentials of the phenomenon. The excited light is propagated in the direction shown by the wave vector **k**, while the elastic and the scattered waves are propagated in the direction of the wave vectors $\pm$ **q** and **k′**, respectively.

The maximum intensity of the scattered (diffracted) light will be observed, as is well known, in the directions satisfying the condition

$$\mathbf{k}' - \mathbf{k} = \pm \mathbf{q}. \tag{1}$$

Setting $|\mathbf{k}'| \approx |\mathbf{k}|$, we get

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

where n is the index of refraction, Λ and λ are the lengths of the elastic and light waves, respectively, θ is the scattering angle. This latter expression allows us to estimate the frequency of the elastic waves which determine the scattering at the various angles:

$$f = 2n \sin\frac{\theta}{2} \cdot \frac{V}{\lambda}, \tag{2}$$

where V is the speed of the corresponding elastic wave.

When $\theta = 90°$ and $\lambda = 4358$ Å, we get $f \sim 7 \times 10^9$ for liquids, while for crystals, in which the sound velocity is much greater than in liquids, the frequency is higher. For example, for sapphire, $f = 5 \times 10^{10}$ cps under these conditions.

In addition to the diffraction of light by an elastic wave, L. I. saw in light scattering another phenomenon, which, in the international language of vibration theory, is known as modulation. The problem is that of the modulation of light as the result of a time-dependent change in the density of the material in an elastic standing wave.

In this case of modulation, a doublet with frequen-

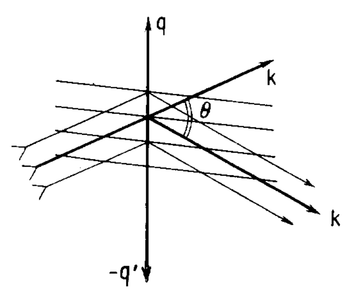

FIG. 1. Diffraction of light by a thermal elastic wave.

cies $\nu \pm f$ appears in the spectrum of scattered light. The relative change in the frequency of the doublet lines, taking (2) into account, will be

$$\pm \frac{f}{\nu} = \frac{\Delta\nu}{\nu} = 2n\frac{V}{c}\sin\frac{\theta}{2}. \tag{3}$$

In the first published work on the subject, L. I. turned his attention to the fact that an unshifted line should also be observed in addition to the displaced lines in the spectrum of scattered light. He looked into the nature of this central line and in essence gave an estimate of its half-width. Thus a triplet should be observed in the liquid.*

The picture of this phenomenon was clear to Mandel'shtam as early as 1918, but he did not rush into publication, and when his extremely thorough paper on its cause appeared in 1926,[5] Brillouin had by that time already obtained part of his results independently and had published them. Therefore, the shifted fine-structure components are now called the Mandel'shtam-Brillouin components.

Following his transfer to the physics faculty of Moscow State University as an experimental investigator in optics, he formulated the problem of the discovery of the fine structure lines of scattered light predicted by him. He undertook this investigation together with G. S. Landsberg.

In 1928 he found the shifted components in the spectrum of scattered light (satellites); the shift was so great that it was impossible to explain it as the modulation of scattered light by an elastic thermal wave. This was the discovery of a new phenomenon, called by its authors combination light scattering. It was immediately described correctly by him as the result of the modulation of the scattered light due to the periodic deformation of the electron shell of the molecule, taking place under the action of the thermal vibrations of the atoms in the molecules.†

The discovery of combination light (Raman) scattering created a new trend in physics; many monographs and many thousand original researches have been devoted to it.

With the appearance of powerful lasers, generation of light in the combination scattering lines has been observed, and today it is possible to transform about 30% of the energy of an initial beam of light into the combination scattering line. It is quite possible that this subtle phenomenon, which serves so effectively the investigation of the structure of molecular and intermolecular interaction, will in addition become a fundamental new technical instrument—a light frequency transformer. Only after the fundamental laws of combination scattering were made clear did Mandel'shtam and Landsberg turn to the study of the fine structure of the scattering line. This phenomenon was discovered in 1930, and Tamm has already discussed this in detail.

When the fine structure of the scattering line was discovered in such liquids as carbon bisulfide, benzene, and carbon tetrachloride, L. I. and his student M. A. Leontovich saw that the very fact of the existence of the Mandel'shtam-Brillouin components in such media confronted the classical theory of sound propagation in condensed media with an insurmountable difficulty.

The problem is the following.

If the hypersound responsible for the formation of the Mandel'shtam-Brillouin components is damped, then the width of these components will be finite, and the half width of each component will be

$$\delta\nu_{\text{M.-B.}} = \alpha V, \tag{4}$$

where α is the amplitude damping coefficient of the hypersound and V is the speed of the hypersound.

Classical hydrodynamics leads to the well known expression for the absorption coefficient

$$\alpha = \alpha_\eta + \alpha_{\eta'} = \frac{\Omega^2}{2V_0^3\varrho}\left(\frac{4}{3}\eta + \eta'\right) \tag{5}$$

($\Omega = 2\pi f$, η and η' are the shear and bulk viscosity coefficients).

If the measured values at the ultrasonic frequencies of 10^6–10^8 cps are extrapolated according to the quadratic law (5) to frequencies $\sim 7 \times 10^9$ cps, and then the resultant values are substituted in (4), we find that $\delta\nu_{M-B} \gg \Delta\nu$, that is, the half-width of the Mandel'shtam-Brillouin component is greater than the distance between the maximum intensity of this component and the maximum of the intensity of the central component. Under such conditions, the discrete structure of the scattering line should not be visible. However, it is very clearly observed.

This fundamental difficulty of the classical theory of sound propagation in condensed systems appeared impossible to resolve within the framework of the theory described above. Mandel'shtam and Leontovich[7] then created a relaxation theory of sound propagation in condensed systems. This theory, not only gave a natural explanation for the existence of a discrete fine structure of the line of scattered light in such liquids as benzene, carbon bisulfide, etc. but is now the basis of molecular acoustics and hyperacoustics.

According to this theory, when account is taken of relaxation of the bulk viscosity coefficient η' alone*, the absorption coefficient (5) is expressed in the following fashion:

*In a solid amorphous body, five components should be observed as a consequence of the existence of longitudinal and transverse waves. In the most general crystalline case, twenty-five components are possible.

†For additional details on the discovery of combination light scattering, see the initial note of I. E. Tamm (on pp. 633-36).

*A relaxation theory[7] was developed by M. A. Isakovich[8] for the case of a relaxation of the shear viscosity coefficient.

$$\alpha_{\eta'} = \frac{\Omega^2\tau (V_\infty^2 - V_0^2)}{2V_0^3 (1+\Omega^2\tau^2)}, \tag{6}$$

where τ is the relaxation time of η', and V_∞ is the speed of sound at infinite frequency. It follows from (6) that at very high frequencies, when $\Omega\tau \gg 1$, one can neglect unity in the denominator of (6) and then

$$\alpha_{\eta'} = \frac{V_\infty^2 - V_0^2}{2V_0^3\tau},$$

that is, it does not depend on the frequency at all. At low frequencies, where one can neglect the value of $\Omega^2\tau^2$ relative to unity,

$$\alpha_{\eta'} = \Omega^2\tau \frac{V_\infty^2 - V_0^2}{2V_0^3},$$

and then the absorption is proportional to the square of the frequency, as follows also from the classical formula (5).

Thus the relaxation theory predicts that $\alpha_{\eta'}$, which also constitutes the principal part of absorption in benzene, carbon bisulfide, and other liquids with large bulk viscosity coefficients, cannot reach at high frequencies $\sim 7 \times 10^9$ cps such a value that $\delta\nu_{M-B} > \Delta\nu$, but the condition $\delta\nu_{M-B} \ll \Delta\nu$ remains satisfied. This is why discrete Mandel'shtam-Brillouin components are observed. On the other hand, relaxation theory requires that the dispersion of sound velocity should be observed. In this case the dispersion should be positive (in Eq. (6), $(V_\infty^2 - V_0^2)/V_0^3 > 0$), and its value can be expressed by the following relation:

$$\frac{\Delta V}{V} = \frac{V}{\Omega^2\tau}(\alpha - \alpha_\eta), \tag{7}$$

where α lies in the ultrasonic frequency region, while α_η is computed from (5). Here it is assumed that $V_\infty \sim V_0$ for $\eta' = 0$, that is, the dispersion is not large. If there is no dispersion of the sound velocity, then Eq. (6) gives $\alpha_{\eta'} = 0$ and relaxation theory cannot explain anything.

At the Physics Institute of the Academy of Sciences, in the laboratory named for G. S. Landsberg, the author and his co-workers succeeded in discovering a significant positive dispersion of the sound velocity in benzene, carbon tetrachloride, carbon bisulfide, and several other liquids. The amount of the dispersion was shown to be of the order of 10–15%.[4,9]

In very viscous liquids, on going from liquid to a glass-like state, it was possible to establish a significant dispersion of the sound velocity; this dispersion amounted to about 70%. Relaxation theory helped select in suitable fashion the appropriate objects of investigation in our experiments. Thus, everything pointed to the fact that the relaxation theory should be correct, but until the last few years, it was not possible to verify it by a direct experiment for liquids with a large bulk viscosity.

From Eq. (7) for $\Delta V/V$, one can obtain τ and compute $\alpha_{\eta'}$ from (6) for frequencies $\sim 10^{10}$ cps. But up to now it has not been possible for anyone to measure $\alpha_{\eta'}$ at such a frequency. We were not able to do this so long as we used the rather broad exciting lines of the mercury spectrum. We were able to measure α at a frequency of $\sim 10^{10}$ cps when together with D. I. Mash and V. S. Starunov,[10] we used a neon-helium gas laser as our light source or excitation of the scattering.

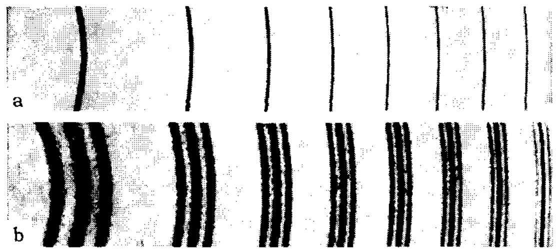

FIG. 2. Interference spectrum of the fine structure of the scattering lines in benzene at room temperature, excited by the line 6328 Å of stimulated emission from an Ne- He gas laser. (a) Spectrum of the exciting line; (b) Spectrum of the fine structure of the scattered lines. The two spectra are reproduced with somewhat different magnifications.

As an example, Fig. 2 shows a photograph of the fine structure of the scattering line in benzene, obtained in the excitation of stimulated emission at 6328 Å. From such a spectra one can easily find the distribution of the intensity in the fine-structure components and determine their shape and half-width. One can measure the integral intensities of the components and verify the Landau-Placzek relation. However, the limited size of this paper does not permit us to dwell on these interesting results.

Measurement of the half-width of the Mandel'shtam-Brillouin component makes it possible to find the absorption from (4). Moreover, by measuring V_∞ and V_0, one can determine τ from Eqs. (6) and (7) of relaxation theory. Values of τ are given in the Table, computed from the dispersion (6) and from the absorption of hypersound (7). Comparison of the results of calculation shows that the simplest variant of the theory with a single relaxation time gives an excellent quantitative description of the cases under consideration. Even we can point out cases in which the dependence of the absorption on the frequency

Relaxation time τ, $\times 10^{10}$ sec, of bulk viscosity coefficient found from the measurement of sound velocity dispersion and absorption of hypersound

Substance	From absorption (Eq. 6)	From dispersion (Eq. 7)
Benzene	2.2	2.4
Carbon tetrachloride	0.75	0.78
Carbon bisulfide	22	20

cannot be described by the formulas of relaxation theory with a single relaxation time but requires a whole spectrum of relaxation times or, more generally, cannot be described in terms of the existing relaxation theory. Careful investigations of these cases still lie ahead. Great complications arise in the explanation of propagation of sound and hypersound in media with large values of the shear viscosity. For these cases, the fundamental measurements have been made in the ultrasonic region of frequencies. Hypersonic measurements here refer only to the measurement of the velocity of hypersound.[9] But even here, it is possible to find the fundamental direction of constantly observed regularities.

Use of a laser as a source of light for the investigation of the width of the Mandel'shtam-Brillouin components in viscous liquids and glasses undoubtedly gives a great deal of new information on the absorption of hypersound in these media.

It follows from what has been pointed out above that Mandel'shtam and Leontovich have created a whole new scientific trend in optics, acoustics, and physics generally. The development of this trend cannot be considered to be finished.

During the last several months, the studies of the Mandel'shtam-Brillouin components have acquired a special interest from another point of view: the excitation of the scattered light by a gigantic pulse from a ruby laser has revealed a whole new aspect of the phenomenon. The intensity of the light of the gigantic pulse is so large that nonlinear effects become important in the medium in which this pulse is focused; in particular, they lead to the generation of light at the frequency of the Mandel'shtam-Brillouin components.

The results of the first experiments of such a type were published in May, 1964 by Chiao, Townes, and Stoicheff [11], who observed the generation of the acoustic components of Mandel'shtam-Brillouin in quartz and sapphire. In their apparatus, the power of the gigantic light pulse of the ruby laser was about 50 MW and of duration of about 3×10^{-8} sec.

The generation of light at the Stokes and anti-Stokes Mandel'shtam-Brillouin components was observed in liquids by Brewer and Rickhoff.[12]

In order to obtain even an approximate and purely qualitative representation of the mechanism leading to the generation of the anti-Stokes Mandel'shtam-Brillouin components, we consider a rough model of the interaction of light with a material medium by means of electrostriction.

As is well known, electric fields, when applied to a material medium produce electrostriction in it—a change in the volume of the medium. The relative volume change of the medium as a consequence of electrostriction is expressed by the relation

$$\frac{\Delta V}{V} = \frac{1}{8\pi}\beta_s\left(\varrho\frac{\partial\varepsilon}{\partial\varrho}\right)_s E^2, \tag{8}$$

where β_S is the adiabatic value of the compressibility, while ρ and ϵ are the density and optical dielectric constant of the medium, respectively; the index s means that the adiabatic value of the derivative is taken. The excess pressure, as is easily seen from (8) and the definition of β_S, will be expressed in the form

$$|\Delta p| = \frac{1}{8\pi}\left(\varrho\frac{\partial\varepsilon}{\partial\varrho}\right)_s E^2. \tag{9}$$

In Eq. (9), E is the sum of all the electric fields inside the dielectric. Let a certain volume be illuminated by the laser beam, the electric field of the light wave of which is $E_0\cos(\omega_0 t - \mathbf{k}\cdot\mathbf{r})$, while the field of the electric wave of the Stokes Mandel'shtam-Brillouin is equal to $E_1\cos[(\omega_0 - \Omega)t - \mathbf{k}'\cdot\mathbf{r}]$. Substituting the sum of these fields in (9), we find that $|\Delta p|$ consists of several high frequency components of which the component corresponding to the lowest frequency will be expressed in the following fashion:

$$\Delta p|_\Omega = E_0E_1\cos[\Omega t - (\mathbf{k}' - \mathbf{k})\,\mathbf{r}]. \tag{10}$$

It is seen from the latter expression that the striction forces create a hypersonic wave whose frequency coincides with the frequency of the thermal hypersonic wave which generates the Stokes Mandel'shtam-Brillouin component. It is seen from (10) that the wave $|\Delta p|_\Omega$ coincides in frequency and direction with the initial hypersonic wave produced by the Stokes Mandel'shtam-Brillouin component.

Thus a situation arises in which the energy of the light wave of the gigantic pulse is transferred to the energy of the hypersonic wave and to the energy of the optical Stokes Mandel'shtam-Brillouin component. The more intense Mandel'shtam-Brillouin component, together with the initial light wave, creates a still-more intense hypersonic wave, etc. Thus the process has the characteristic of parametric resonance. Parametric resonance, parametric excitation and amplification, and general questions of the behavior of systems with periodically changing parameters have been successfully investigated by Mandel'shtam[13] and his students A. A Andronov, A. A. Vitt, G. S. Gorelik, M. A. Leontovich and S. É. Khaĭkin.[14]

Turning to the problem of the stimulated Mandel'shtam-Brillouin scattering, it should be noted that if there is sufficient energy in the initial light flux which causes the scattering, so that generation takes place at the frequency of the Mandel'shtam-Brillouin components, then such a generation does take place. Moreover, generation of hypersound takes place at the frequency Ω. Consequently, in the case under consideration, the gigantic pulse simultaneously creates two new generators.

Even in the very first experiments [11] it was noted that the power of the hypersonic wave of corresponding frequency becomes equal to 1 kW. If one compares the energy of the sound waves, then the generation as the result of parametric resonance creates a hypersonic wave with an energy 16 times larger than the energy of the Debye thermal wave at room temperature.

Here we have considered in purely qualitative fashion a greatly simplified picture of the origin of the generation of the Mandel'shtam-Brillouin component. A rigorous consideration of the problem requires the simultaneous solution of Maxwell's equations and the equations of hydrodynamics for liquids (and also the equations of elasticity theory for solids) with account of the nonlinearity of the system brought about by the intense light wave. Such a solution describes interesting features of the phenomenon which we shall not touch on here*.

In this paper we have only wanted to point out how the phenomena predicted and found by Mandel'shtam and his students and co-workers initiated large scale theoretical and experimental investigations which marked out new and still developing trends in physics.

The best memorial to a real scientist departing from life is a rich natural life of the scientific directions which he began. Not all, even the very great scientists, have such a memorial, but such is the case of Leonid Isaakovich Mandel'shtam.

*Detailed reviews of the theoretical and experimental side of the problem will appear shortly in Uspekhi.

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