page. If I had shown you their work you would have done it in the same way as they did!”

Alexei Nikolajewich’s “cunning” impressed itself firmly upon my memory. It is quite unnecessary to say how proud I was of his praise. From now on my acquaintance with Alexei Nikolajewich became a firm friendship and he would often invite me to his home and see him. I soon became a frequent and informal visitor, not to his working office, but to his home, his flat in Leningrad or to his country house, and later, during the evacuation, in Kazan, Borovoye, and Moscow. Every time, almost without exception, he had something new and interesting to show me; the manuscript of some work he was preparing for the press, or a criticism of somebody else’s work, the text of a lecture which he was going to give (he always prepared his oral addresses in writing). He usually asked me to give my opinion and never took criticism in bad part, often agreeing with me.

Once, when arguing hotly about something with him I began to prove that he had acted wrongly and did it in a rather harsh manner (I think I called him Lord Plymouth—a term at the time of the notorious commission for non-interference in Spain). For some days I was afraid I had offended him but my fears were soon dispelled. It happened that I was travelling in the same carriage as Alexei Nikolajewich and A. F. Jeoff from Leningrad to Moscow. Alexei Nikolajewich recounted this incident to A. F. Jeoff and, purposely raising his voice that I might hear, with obvious approval added “and Vladimir Alexandrovich knew how to swear!” Then I realized that our dispute had only strengthened our friendship. I think it was on that same visit to Moscow that Alexei Nikolajewich showed me his new work “On the Calculation of Heating of an Oil Cable During a Short-Circuit”. I found some small inaccuracies and pointed out how it might be corrected. Alexei Nikolajewich considered the correction so important that he mentioned it in the publication. Such patience in the face of criticism and readiness to take into account the opinion of a younger colleague (Alexei Nikolajewich was my senior by 25 years) is far from being ordinary amongst all great scholars and is characteristic of Alexei Nikolajewich. Sometimes I would tell Alexei Nikolajewich about my own work which often had very little to do with his field (e.g. atomic physics and the relativity theory), and I was always astonished by the case with which he grasped an idea which was new to him. Alexei Nikolajewich preserved all the freshness of his mind to profound old age.

Alexei Nikolajewich Krylov—that remarkable scholar, patriot and man—will be ever remembered by all those who knew him and his works will stand as an eternal monument to his memory.

V. Fock

SOME REMARKS CONCERNING THE DIFFERENCE BETWEEN LUMINESCENCE AND TEMPERATURE RADIATION. ANTI-STOKES FLUORESCENCE

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It is shown that the second law of thermodynamics cannot determine a limiting value of the yield of anti-Stokes fluorescence, the latter being essentially a noneversible process. Furthermore only the intensity, but not the yield of anti-Stokes fluorescence, is a function of temperature. The relation of fluorescence to the temperature is properly described by the yield when the wave length of the exciting light exceeds that of the peak of the fluorescence band.

1. Anti-Stokes fluorescence with a yield greater than one

A paper which I published under a similar title 10 years ago lately has been subjected to a severe criticism by Vavilov (1). This paper was directed against a statement made by Lenard, according to which the existence of anti-Stokes fluorescence is in contradiction to the second law of thermodynamics, unless it is combined with another effect compensating for the loss of energy in the luminescent system. Vavilov is of the opinion that Lenard was right and that my deductions were completely erroneous. I still feel certain, however, that my point of view was correct and that Vavilov’s arguments do not prove the contrary. Vavilov’s method of invalidating my conclusions is based on the assumption that there can be established a reversible “mental” cycle containing as one step the excitation of anti-Stokes fluorescence, by which the initial state is restored at the end of each cycle and the heat of a reservoir transformed completely into mechanical energy by repeating the cycle. This, of course, would be incompatible with the second law of thermodynamics. It is to be regretted that instead of asserting “that such a cycle can be realized in principle with any approximation”, Vavilov did not try to apply his theoretical considerations to the example of anti-Stokes fluorescence which was fully described in my paper. He would have found that in performing this task he had to violate the very principle he wanted to apply, namely the second law of thermodynamics. It suffices to analyse a single step in his cycle. The exciting radiation impinging on the fluorescent system is supposed to be strictly monochromatic and unidirectional; even in the case of resonance radiation the light is scattered in all directions and its wave length is slightly altered by Doppler effect. With other words: the entropy of the radiation is increased. How is it possible to reverse this radiation “by radiation pressure” entirely into mechanical energy in order to complete the reversible cycle?

The example which I discussed was the emission of the D_1-line by sodium vapour irradiated with light containing only the D_2-line in its spectrum. It seems advantageous to use here an example of somewhat different nature which will be useful also for the discussion of the second part of Vavilov’s paper.

If a diatomic vapour, such as I_2 and N_2, is exposed to strictly monochromatic light, the wave length of the latter can be chosen so that it is absorbed exclusively by molecules of a certain vibrational energy, for instance, with \( v' = 4 \). If the temperature of the vapour is so low that only few molecules are in this high state of oscillation, the incident radiation will be absorbed only slightly by the vapour, but the absorption which does occur will be exclusively to molecules with \( v'' = 4 \) and there will be raised to some vibrational level \( v'' \) of an excited electronic state.
Returning to the ground state they will emit a resonance spectrum containing the four anti-Stokes lines which correspond to the transitions from \(v'\) to \(v'' = 3, 2, 1\) and 0. The spectrum moreover will contain Stokes lines having greater wave lengths than the exciting line. However, the relative intensity of the Stokes lines and the anti-Stokes lines is determined only by the Franck-Condon principle and depends in no way on thermodynamics. There is no law preventing the anti-Stokes lines from having a far greater intensity than the Stokes lines. An example of this kind has been treated theoretically and experimentally by W. G. Brown (2): the resonance spectrum of Na, excited by the cadmium line 5086 Å consists of four anti-Stokes lines and not a single Stokes line of appreciable intensity. This example has the advantage over that described in the earlier paper that the vapour pressure can be so low that no interaction between excited molecules and other molecules can occur. Thus no quenching action can compensate the cooling effect due to the gradual elimination of molecules with the high vibrational energy corresponding to \(v'' = 4\). It has already been mentioned in the earlier paper, that even the existence of a quenching effect would not change anything in the validity of these considerations as long as it was not proved that the loss of energy by anti-Stokes radiation and the gain of energy by quenching are connected by some law.

Vavilov's fundamental error is the assumption that a reversible cycle containing the excitation of photoluminescence can be realized. Photoluminescence is essentially an irreversible process, irrespective of anti-Stokes emission. It entails the irradiation of a system of relatively low internal energy (or of low temperature) with light emitted by a system of high energy (or high temperature, at least high “excitation temperature”). The simplest instance is provided by the resonance radiation of a monoatomic gas. The light source and the “resonance lamp” may be surrounded by an adiabatic reflecting enclosure; the light source is a transparent bulb containing sodium vapour at a high temperature, emitting the D-lines (or in a “mental experiment” one may even be allowed to assume that at the beginning of the experiment all atoms of the source are in the excited state 3P). The resonance lamp is a similar bulb containing the same number of sodium atoms at so low a temperature that no light is emitted. The resonance lamp absorbs all of the radiation which it receives from the source and re-emits it immediately. Some of this secondary radiation is reflected to the source but is only very slightly absorbed because most of the atoms are still in the excited state. This process will continue until equilibrium is established, with both bulbs containing the same number of excited atoms, and it can be reversed as little as the analogous process in which the source and the resonance lamp are replaced by black bodies of high and low temperature respectively.

It need hardly be emphasized that Vavilov's objections to the existence of a fluorescence yield greater than one due to anti-Stokes excitation refer to the energy yield and not to the quantum yield. The latter can, of course, never exceed 100%; an anti-Stokes quantum yield of 100% corresponds, however, to an energy yield greater than one.

2. The alleged temperature dependence of the anti-Stokes yield

After having established the theorem that the energy yield of anti-Stokes fluorescence can never exceed one, Vavilov continues by asserting that this yield must be a function of the temperature and must drop to zero at the absolute zero of temperature. The latter is correct only in so far as \(0/0 = 0\). While the intensity of the anti-Stokes fluorescence decreases with decreasing temperature, this is not true for the yield which is determined by the ratio between the fluorescence intensity and the intensity of the absorbed radiation*.

The impossibility of maintaining Vavilov's view point is obvious in the case of the anti-Stokes fluorescence of a diatomic vapour at low pressure. Since the excited molecules undergo no collisions, anti-Stokes fluorescence is due only to molecules which were in higher vibrational states before the absorption occurred. The number of such molecules decreases with decreasing temperature, and so does the absorption of the incident monochromatic radiation; but all molecules, which do absorb,

* These considerations, as well as the initial part of Vavilov's treatment, do not take into account the possible existence of competing quenching processes; if the efficiency of such processes becomes smaller at low temperatures, the fluorescence yield (Stokes and anti-Stokes) must even increase with decreasing temperature.
emit exactly the same radiation which they would emit at a higher temperature; thus the fluorescence yield remains unaltered.

The conditions are only slightly more complicated, when the fluorescence is excited in a condensed medium, such as a dye solution—the case which is discussed by Vavilov. In this case the excited molecules are in a state of constant exchange of energy with the molecules of the surrounding medium and thermal equilibrium of their vibrational energy is established before the emission occurs. The shape of the absorption and emission band of such a solution is determined by two factors: the probability of transitions from a given vibrational level of one electronic state to the various vibrational levels of the other electronic state, and the equilibrium population of the various vibrational levels. The former again is governed by the Franck-Condon principle and the latter is a function of the temperature. The possible influence of the changing configuration of the surrounding molecules will be discussed later.

At moderate temperatures most molecules are in the lowest vibrational state \( v'' = 0 \), and the peaks of the absorption and fluorescence bands will correspond to transitions from the vibrationless levels of the ground state and the excited states respectively to some vibrational levels \( v' \) and \( v'' \) respectively. The absorption line of greatest wavelength originating from the level \( v'' = 0 \) corresponds to the transition to the excited state with \( v'' = 0 \) (the \( 0-0 \) band in the spectrum of a diatomic vapour). In this excited state the molecules undergo collisions which transfer some of them to higher levels \( v' = 1, 2, 3, \ldots \) so that they are able to emit radiation of wave length shorter than that of the exciting light. This kind of anti-Stokes fluorescence depends on the temperature and vanishes at \( T = 0^\circ \text{K} \), but only because the short wave length tail of the fluorescence band itself vanishes under Stokes excitation as well as under anti-Stokes excitation. This is not the phenomenon discussed by Vavilov, who deals only with anti-Stokes fluorescence excited by light of wave length greater than that of the peak of the fluorescence band.

Although a general rule for the location of the \( 0-0 \) band cannot be stated, this band always will lie somewhere between the peaks of the absorption and the emission bands (Fig. 1). Absorption in the region beyond the peak of the fluorescence band can originate only at higher vibrational levels of the ground state. And from here on the case is identical with that of a diatomic vapour which has been discussed above: only the intensity of the anti-Stokes fluorescence and not its yield decreases with decreasing temperature. The molecules do not remember the process by means of which they have reached the excited state where they acquire thermal equilibrium.

3. The drop in fluorescence yield

It seems to be a well proved fact that the curve representing the fluorescence yield as
a function of the wave length of the exciting light shows a sharp drop at the wave length corresponding to the peak of the fluorescence band*. Since this fact cannot be explained by Vavilov's theory, another interpretation must be found. An interpretation which has been proposed by Jablonski (2) is definitively rejected by Vavilov, and this is the only point in his paper respecting which I agree with him, although not for the same reason.

Jablonski assumes that the drop in the fluorescence yield is due to the superposition of another weak band on the long wave length tail of the normal absorption band and that absorption in this ‘forbidden’ band raises the molecules to a metastable or quasi-stable state from which no normal fluorescence is emitted. It is well known that such states exist in many molecules and that when all competing processes are avoided by adequate experimental conditions a long lasting afterglow is emitted by the molecules in this state. This afterglow is a typical fluorescence of long duration, in F. Perrin's terminology, or a ‘slow fluorescence’ as I proposed to call the phenomenon. Vavilov's first argument against Jablonski's hypothesis is probably correct, since the drop in fluorescence yield has been observed in a few instances (rhodamine solutions) in which a slow fluorescence never could be obtained. Vavilov's second argument, on the other hand, need hardly be refuted; he states that the excitation spectrum of the afterglow ‘is not seldom the same’ as that of the normal fluorescence and that then the forbidden absorption band must coincide with the normal absorption band. As a matter of fact, the slow fluorescence is excited always and exclusively by light absorption in the normal absorption band, and, in so far as dye solutions are concerned, the existence of the forbidden transition has never been observed in the absorption spectrum.

* For a complete bibliography on the subject see Vavilov's paper (1).

The average duration of the slow fluorescence, which is independent of temperature (3), is of the order of a second, and thus the probability of the forbidden transition is about 10⁸ times lower than that of the normal fluorescence. Since, according to Jablonski's own measurements, the drop in the fluorescence yield occurs at a wave length at which the absorption is still about 1% of the peak absorption, it cannot be due to an appreciable degree to the forbidden transition.

In a short discussion of this problem a different interpretation has been pointed out by myself (4). The long wave tail of the absorption band may be caused, in part, by perturbations of the electronic energy states of the absorbing molecules due to the interaction with molecules of the solvent. If these perturbations persist over a sufficient period of time after the absorption has occurred, the probability of the conversion of the absorbed energy into heat is larger for these excited molecules than for others. Hence their fluorescence yield is smaller. The argument that the time of a ‘collision’ is much too short for producing such an effect is not convincing. On the one hand, the so-called cage effect keeps two molecules in close neighbourhood for a much longer time in a condensed system than in the case of a collision in a gas and, on the other hand, it is not possible to evaluate the time which under these conditions is necessary for the dissipation of the absorbed electronic energy.

* Concerning the different behaviour of some other organic compounds compare (4).

REFERENCES
