

THE DEVELOPMENT OF S. I. VAVILOV'S IDEAS IN THE FIELD OF LUMINESCENCE

V. L. LEVSHIN

Usp. Fiz. Nauk 75, 241-250 (October, 1961)

AMONG S. I. Vavilov's many-sided activities, his creative work in the field of photoluminescence played a quite special role. This is the field in which he attained the most significant results, and to which he devoted his attention throughout his life.

S. I. arrived at the decision to devote himself seriously to the problem of luminescence in 1920. This decision arose from his interest in the action of light on matter, an interest which appeared even during his first research as a student (1912-1913) in connection with the photochemical studies of his director P. P. Lazarev. Luminescence, a close relative of photochemistry, is another important type of interaction of light with matter.

By 1920, the spectroscopic characteristics of luminescence had been rather broadly studied by foreign researchers. However, the course which the process takes under various conditions had not yet been studied. At that time, incandescent bodies were practically the only sources of artificial lighting, and the nature of cold light, or luminescence, was still unclear. Luminescence still seemed to be a mysterious process.

As objects of study, S. I. chose the solutions of luminescent dyes.

I recall a conversation with S. I. in the early Twenties on the role which our future studies on luminescence would play. He mentioned that the line of research which we had chosen, the study of the luminescence of solutions, had not been taken up seriously anywhere at that time. The photoluminescence of solutions became S. I.'s fundamental field of study. He advanced the study of these luminescence processes far, discovered their energetics and kinetics, and established important laws.

Upon beginning research in a poorly studied field, S. I. naturally tried to concentrate his interests on phenomena having simple kinetics. He correctly considered that any complications would hinder the elucidation of the course of the fundamental process and its interpretation. This explains why S. I. dealt so cautiously with the luminescence of phosphors, for which it is often completely impossible to isolate the fundamental process. Recognizing the necessity of studying the crystal phosphors owing to their great practical importance, S. I. promoted the development of such studies, formulated certain problems, and supervised certain of the studies, but he did not make the crystal phosphors an object of his own personal research.

As I have stated, the goal at which S. I. aimed was the creation of a quantitative picture of the photolumi-

nescence of solutions. S. I. approached the solution of this complex problem by several pathways, attacking it from several sides as it were. For brevity, we shall deal here only with the three principal approaches.

The first approach was the determination of the value of the energy-transformation coefficient in luminescence processes, and of the factors affecting the efficiency of transformation of the excitation energy.

The second approach was the study of the kinetics of the processes by determining the lifetime and decay laws of the afterglow.

The third approach was the study of the nature of luminescent molecules considered as elementary emitters, and of the kinetics of luminescence, making use of the polarization of the luminescence.

The natural consummation of these studies was the establishment of the relation between the studied phenomena and the creation of a unified theory linking them.

I must give a picture in this report of the developments in the study of luminescence since S. I.'s death, and especially of those fields in which he worked.

* * *

The first problem which S. I. took up in his researches was that of the coefficient of utilization of the absorbed light energy. Very confused notions existed in the early Twenties concerning the magnitude of the coefficient of transformation of the energy of the absorbed light into luminescent light. The generally-accepted view was that the transformation coefficient in the fluorescence of liquids is infinitesimal.

Absolute measurements of weak emission intensities presented great difficulties. S. I. devised a clever method of determining the absolute transformation coefficient from relative measurements by comparing the intensity of the exciting light scattered by a matte surface with that of the fluorescence of the solutions. He found that the most effective fluorescent dye solutions show very high transformation coefficients, reaching 80%. S. I. designated the ratio of the energy of fluorescent light obtained to the energy of the absorbed light as the "fluorescence yield."

The introduction of the concept of fluorescence yield opened the way for quantitative energy calculations. It also became necessary to study the factors affecting the value of the fluorescence yield.

However, before we deal with this question, we shall consider the subsequent development of the concept of fluorescence yield itself. S. I. introduced this concept for fluorescence processes in which the steady state

of luminescence is established instantaneously. In order to extend the concept to long-lived luminescence, it must be made more precise. Here, there are two possible approaches to the measurement of the fluorescence yield.

The first method of measuring the fluorescence yield consists in measuring all the energy absorbed by the unexcited substance, and then, all the radiation emitted by the substance at some time or other for a very long period of time. Then the ratio of the two measured energies is the yield. However, it is not only very inconvenient to measure the energy of emissions which decay very slowly, but in this approach the transformation of energy during the different stages of the emission process takes place under varying conditions, and the yield obtained is only a certain average value.

The second method consists in measuring the energy of the emission and the absorption during one and the same time interval. In this case, when a steady state has been established, the absorbed energy serves to maintain the given state of excitation, and the yield turns out to be a function of this state. When a steady state has not been established, the observed magnitude still has a physical meaning, but doesn't tell us much about how completely the material transforms energy, since it neglects the fraction of the energy being stored up by the material to be emitted later.

Thus, long-lived processes may show a strong dependence of the yield on the conditions of excitation (the intensity and duration of the illumination), which are not significant in short-lived fluorescence processes.

At present we know many substances, especially among the crystal phosphors, in which several mutually-interacting luminescent processes occur simultaneously, but differ essentially in kinetics and often in their emission spectra. In such cases, naturally, the very difficult problem arises of determining the partial yield of each of these emission processes.

Now, as for the conditions influencing the yield, we must first of all consider the dependence of the yield on the wavelength of the exciting light (Fig. 1), which was established by Vavilov. This phenomenon is described by the well-known Vavilov law, which is formulated as follows: "As long as the wavelength of the luminescent light is greater than that of the exciting light, the luminescence yield is proportional to the wavelength. Where the wavelength of the luminescent light becomes shorter than that of the exciting light, a rapid decline in the yield is observed."

The first statement refers to the left-hand linear portion of the experimental curve in Fig. 1, which passes through the origin when extrapolated. It amounts to the constancy in this frequency range of the quantum yield of the luminescence, i.e., the ratio of the number of quanta of luminescence to the number

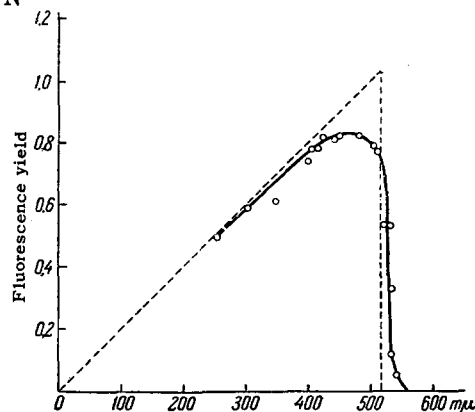


FIG. 1. Dependence of the fluorescence yield of an aqueous solution of fluorescein on the wavelength of the exciting light (S. I. Vavilov). The dotted line indicates the curve which would be observed if Einstein's equivalence law were strictly obeyed.

of absorbed quanta. The second statement indicates that the yield rapidly declines in the anti-Stokes spectral region (the right-hand side of the diagram). In this region, quanta of greater energy are obtained in exchange for the smaller quanta of the exciting light. This additional energy is taken from the vibrational energy of the molecules. If we assume the quantum yield in this region also to be constant, then the energy yield of the luminescence might become greater than unity and the energy of the luminescence would exceed that of the exciting light, being increased at the expense of the thermal energy of the medium. However, experiment shows the truth to be otherwise. The energy yield rapidly falls in this region. Hence, under such conditions of excitation, a greater and greater fraction of the absorbed quanta is transformed into heat.

The question of whether the yield can exceed unity and why the yield declines in the anti-Stokes region was not solved during S. I.'s lifetime. Pertinent studies have been carried out by B. I. Stepanov and his associates V. V. Antonov-Romanovskii, M. A. Alentsev, and M. V. Fock since S. I.'s death. These studies showed that in certain systems under certain conditions it is possible to obtain a yield somewhat greater than unity, and that this does not contradict the second law of thermodynamics. These same studies introduced the concept of negative luminescence, which means a decrease in the emission in some spectral region below the thermal-emission level, owing to the depletion of those relatively low molecular energy levels which serve as the initial levels in the emissive transitions for the given spectral range. This depletion is brought about by the exciting light rays, which raise the electrons from the levels being depleted to higher ones. The equilibrium filling of energy levels is not restored immediately after cessation of the excitation. That is, negative luminescence shows a certain persistence.

The problem of why the yield declines in the anti-Stokes region has also been treated in a number of theoretical and experimental studies in recent years. However, this problem cannot yet be considered as solved.

The luminescence yield is reduced by various quenching processes: by addition of quenching impurities, by increase in the concentration of the luminescent substance, and by the solvent. These types of quenching differ essentially from one another in their kinetics.

In certain cases, the diffusion of the excited molecules into proximity with quenching molecules during the lifetime of the excited state plays an important role. Vavilov studied processes of this type, while B. Ya. Sveshnikov has made later additions to the theory of the diffusion processes. These studies predated comparable foreign studies by more than fifteen years. They are being continued successfully at present under Sveshnikov's direction.

However, diffusional motion is by no means always necessary for the appearance of quenching. In a number of cases quenching occurs to a large extent in solid materials and very viscous solutions in which there is practically no diffusion. In these cases, in order to explain the phenomenon, we must assume that energy transfer occurs from the excited molecules to quenching centers. These centers may be either special impurities, or in some cases may be altered molecules of the luminescent substance itself.

Our studies of recent years have clearly confirmed the association theory of concentration quenching, according to which the quenching centers in concentrated solutions are associated molecules of the luminescent substance, which have lost the ability to luminesce because of their association. The migration of energy to such an aggregate leads to quenching.

Interesting studies of intramolecular energy transfer have been carried out by one of S. I.'s students, A. N. Sevchenko.

* * *

Let us now proceed to the studies involving the second approach. The kinetics of luminescent processes is quite varied. Luminescent molecules can be directly excited and then emit immediately. Emission can occur upon recombination of electrons with ionized centers created by the exciting light. Finally, various metastable states may participate in the process and delay the emission from the excited substance. In all of these cases, the variation in the intensity of the emission after cessation of the excitation may follow various laws and continue for varying times. Thus the importance of studying the laws governing decay and persistence of the emission is obvious.

S. I. supplemented the definition of luminescence given by Wiedemann by introducing criteria for the lifetime. According to Vavilov, luminescence is the

radiation in excess of the thermal radiation possessing a lifetime greater than the period of the characteristic vibrations of the molecules.

The study of decay laws in order to determine the nature of luminescence became highly developed in the Thirties. These studies made it possible to determine the nature of the luminescence of many substances, in particular the uranyl compounds, etc. However, in studying very short-lived luminescence, the researchers encountered great difficulties. A significant advance was the invention of instruments called fluorometers, which make it possible to measure the lifetime of emissions of the order of 10^{-9} seconds. Such fluorometers have been built by L. A. Tumerman, by V. V. Shimanovskii, and by M. D. Galanin. However, the measurements were still not very reliable. Besides, the particular time range from 10^{-5} to 10^{-8} sec was not at all accessible to study.

After S. I.'s death, the problem of refining the apparatus was solved. Much of this was accomplished by S. I.'s students, A. M. Bonch-Bruevich and N. A. Tolstoi. The latter has succeeded in building instruments (ultra-taumeters) which completely cover the formerly inaccessible range of lifetimes from 10^{-5} to 10^{-8} sec. The course of the decay in a number of new classes of compounds has been studied by use of these refined instruments, in particular the rubies and the platinumocyanides.

By using a highly refined fluorometer, A. M. Bonch-Bruevich has solved a problem which had been formulated by S. I. He demonstrated again with greater accuracy that the speed of light is independent of the motion of the source. That is, he confirmed one of the basic postulates of the theory of relativity.

The study of the lifetime of excited states and the decay laws of the afterglow is still one of the most important problems in luminescence, and is being conducted systematically by study of luminescence kinetics. However, the phenomenon can be reduced to elementary processes only in rare cases. Ordinarily, and especially in the crystal phosphors, we observe a combination of many processes which differ in nature. The current problem is to separate the elementary processes and to discover how they influence one another.

I should note that, in our studies on the lifetimes of excited states, S. I. and the present author were the first to observe an appreciable accumulation of molecules in the excited state under powerful excitation. This was manifested by a decrease in the absorption spectrum of the ground state. Such an accumulation is being widely utilized at present for the amplification and generation of light in any required spectral range.

Let us return to the above-mentioned definition of luminescence by Wiedemann and Vavilov, which takes the thermal emission as a base line for emission energy, above which the luminescence is measured. We

note that recent studies of B. I. Stepanov have shown especially clearly that there is a close connection between these two different forms of emission. This connection is manifested in the fact that the form of the luminescence spectrum can be determined from the absorption spectra of luminescent substances and from the spectrum of the thermal emission of a black body.

On the other hand, luminescence processes are so complex that the concept of the lifetime of luminescence is currently being subjected to thorough discussion and refinement, just as the concept of the luminescence yield has been.

An essential characteristic of luminescence is its polarization. The degree of polarization depends on the one hand on the characteristics of the emitters, and on the other hand, on their relative arrangement. Hence, the study of polarization phenomena has created ample possibilities for determining the nature of elementary emitters, for determining their spatial distribution, for studying the motion of the emitters during the lifetime of the excited state, and for detecting and studying the migration of energy between emitters.

As I have stated, S. I. was especially interested in the problem of the nature of elementary emitters. To solve this problem, he developed the method of polarization diagrams. These were curves giving the dependence of the degree of polarization on the azimuth angle of observation and the angle between the electric vector of the exciting light and the plane of observation. These curves show characteristic forms, which are quite different for magnetic and electric dipoles and for quadrupoles (Fig. 2).

The method of polarization diagrams which S. I. proposed has been expanded considerably by the additional calculations of P. P. Feofilov, A. N. Sevchenko, and G. P. Gurinovich. By applying this method, Feo-

filov has determined the nature of certain elementary emitters, namely the rare-earth elements and uranium, existing as impurities in cubic crystals, as well as the orientation of these emitters with respect to the crystallographic axes. The further development of this method will undoubtedly furnish a great amount of information on the nature of elementary emitters.

Undoubtedly, the following phenomena found by Gurinovich and Sevchenko will be very significant in the study of the structure of the electron clouds of molecules: the degree of polarization of the emission differs in different regions of the luminescence spectrum; and the polarization curves showing the dependence of the polarization on the wavelength of the exciting light and on the wavelength of the luminescence are mirror images of one another with respect to the frequency of the electronic transition.

Another important approach in the study of polarization phenomena is to study the depolarization of the emission as a function of the migration of energy between excited molecules.

S. I.'s studies have shown, along with those of A. N. Sevchenko and M. D. Galanin, that depolarization of the luminescence occurs under certain conditions even in solids and in exceedingly viscous solutions in which rotation of the molecules themselves is impossible. S. I. explained this phenomenon as due to transfer of excitation energy from the system of excited molecules to the unexcited molecules. As we shall see below, these phenomena have been subjected over the following years to a further detailed investigation. Figure 3 summarizes the characteristics of the luminescence.

* * *

We have discussed the three fundamental approaches, the three pathways which S. I. took in elucidating the nature and kinetics of the photoluminescence of solutions. These approaches are still being applied in the study of luminescence, with well-known variations and additions.

Upon obtaining these voluminous data, S. I. was the first to correlate them with a unified theory explaining the variation in the luminescence yield, in the lifetime of the emission, and in the depolarization (Fig. 4). He derived this theory on the basis of the hypothesis of an inductive interaction between the excited and the unexcited molecules. The migration of excitation energy to the chaotically oriented unexcited molecules of the luminescent substance must naturally lead to depolarization of the luminescence. If a certain fraction of the transitions results in quenching, the migration must be associated with a decrease in the yield. The occurrence of quenching processes of this type leads to a decrease in the lifetime of the emission.

These conceptions of S. I.'s have been expanded considerably in the later studies of M. D. Galanin, B. Ya. Sveshnikov, et al. In place of the phenomemo-

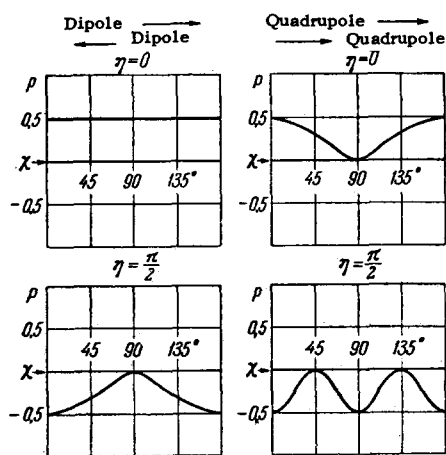


FIG. 2. Polarization diagrams. p is the degree of polarization, η is the angle between the electric vector of the exciting light and the vertical, and χ is the angle between the direction of observation and the direction of the exciting light.

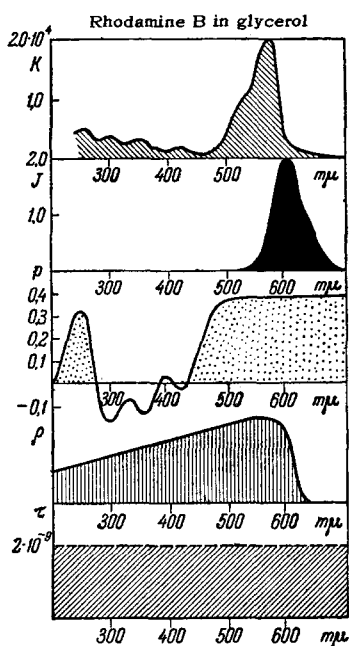


FIG. 3. A chart prepared by S. I. Vavilov to summarize the quantities characterizing the luminescence of glycerol solutions of rhodamine B. From top to bottom: the absorption spectrum; the fluorescence spectrum; the dependence of the limiting degree of polarization on the wavelength of the exciting light; the luminescence yield; and the lifetime of the emission.

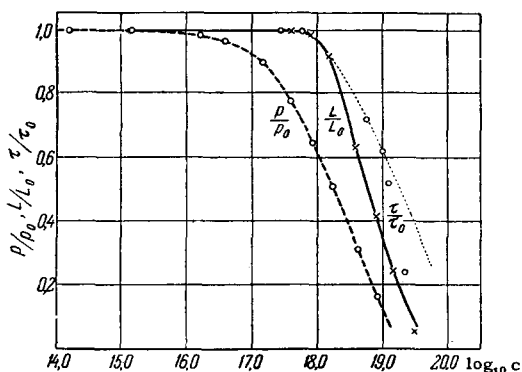


FIG. 4. The concentration-dependence of the degree of polarization p/p_0 , the yield L/L_0 , and the mean lifetime of the excited state τ/τ_0 in solutions of fluorescein in glycerol at room temperature.

logical theory, which starts with the experimental data, but does not take into account the specific properties of the absorbing and emitting oscillators, Galanin has derived a more detailed theory which starts with a definite conception of the electrical nature of the interacting particles. If we take into account the interactions of the oscillators, we can calculate more completely the variations in the lifetime, the yield, and the polarization of the luminescence.

Especially great advances have been made in the theory of depolarization of luminescence due to migration of energy, which has been subjected to detailed

experimental tests in the most recent studies of Sveshnikov and his associates. In agreement with the theory, solutions, which have random orientation of the molecules, exhibit a rapid depolarization of the emission either when the concentration is increased, or when the later stages of the decay of the luminescence are being observed.

N. D. Zhevandrov has discovered a very peculiar effect in molecular crystals. He showed that, owing to the regularity of the crystal structure, migration of energy results here not in depolarization, but in a degree of polarization which is independent of the orientation of the electric vector of the exciting light. The observed constant degree of polarization is governed here by the distribution of the molecular oscillators.

The question of quenching of luminescence is more complex. Quenching processes are varied, and their mechanisms differ. In a number of cases, as Vavilov and Sveshnikov showed, the essential factor is the diffusion of the molecules during the lifetime of the excited state. In other cases in solids and viscous solutions, quenching takes place by resonance transfer of energy. A calculation made by Galanin has shown that the decay of the luminescence in such cases follows a non-exponential law, and the variations in the yield and the lifetime of the luminescence need not be parallel.

Studies carried out in our laboratory have shown that quenching at high concentrations is due mainly to the migration of energy to non-luminescent aggregates, and is complicated considerably by the inactive absorption of the aggregates themselves.

The theoretical studies of A. S. Davydov and the numerous studies conducted in recent years in the Ukrainian Academy of Sciences by A. F. Prikhot'ko and her associates have demonstrated the great importance of energy migration in molecular crystals. Ya. I. Frenkel' has shown that exciton transfer of energy must necessarily occur; this type of energy transfer is continually attracting more interest from experimental and theoretical researchers. E. F. Gross, M. D. Galanin, N. D. Zhevandrov, V. M. Agranovich, A. S. Selivanenko, and many others are working along this line.

Thus, the theory of energy migration has recently been confirmed repeatedly, although the nature of the phenomenon and its kinetics have turned out to be considerably more complex than was reckoned in the original phenomenological theory.

* * *

Up to this point we have been discussing problems regarding the photoluminescence of molecular compounds. Another class of luminescent substances, even more important in practice, is that of the crystal phosphors, which are a particular type of semiconductor. The kinetics of their luminescence is essentially different from that occurring in solutions.

The systematic study of crystal phosphors began in the Soviet Union twelve years later than the study of the luminescence of molecules. Even in these first investigations, some of the problems were also formulated by Vavilov. The studies on crystal phosphors quickly encompassed a broad field.

Although the luminescence of crystal phosphors differs from that of molecules, it also involves as an essential feature the migration transfer of excitation energy. The crystal phosphors also exhibit many types of quenching of luminescence similar to the processes in solution. The emission itself, in arising from special centers, often retains features of the emission spectra of the atoms comprising the centers. Here also, as in the field of molecular luminescence, we may determine the luminescence yield, the lifetime of the emission, and the decay laws. Thus the many-sided experience gained from the studies of S. I. and his associates in the field of molecular luminescence could be applied widely. This experience has aided in understanding the basic features of the complex kinetics of the luminescence of crystal phosphors, as such processes consist in the interaction of a number of separate processes having different lifetimes.

The study of the luminescence of crystal phosphors is now a fundamental branch of the studies on luminescence being carried out in the Soviet Union.

Along with photoluminescence, luminescence under other types of excitation is being studied on a broad front. Especial attention is being devoted to cathodoluminescence, and in many Soviet laboratories electroluminescence is being studied. We should note the studies of V. V. Antonov-Romanovskii, A. M. Bonch-Bruevich, M. V. Fock, A. N. Georgobiani, V. E. Oranovskii, V. N. Favorin, et al. Considerable advances have been made in the study of radioluminescence, which is the emission of scintillations in molecular and ionic crystals due to the action of hard radiation and elementary particles. These processes are being studied by M. D. Galanin, Z. L. Morgenshtern, I. M. Rozman, et al. All of these new approaches have become highly developed during the recent decade and are being successfully studied in the Soviet school of luminescence.

S. I. always attempted to relate his scientific studies to the solution of problems in the national economy and technology.

One of the most important lines of practical research developed under S. I.'s direction was the study of luminescent analysis. Quantitative methods of luminescent analysis were first developed by M. A. Konstantinova in the laboratories of the Institute of Physics of the Academy of Sciences of the U.S.S.R. Various analytical instruments have been designed in the State Optical Institute and other institutions.

Luminescent analysis has continued to develop rapidly during the last decade. Great advances have been made in luminescent defectoscopy, which is applied in the metal-working and vacuum industries

(A. V. Karyakin, V. K. Matveev, et al.). The development of luminescent analysis in biology and medicine is of especial importance. These studies, carried out by E. M. Brumberg, A. V. Karyakin, and M. N. Meïsel', have made great advances. A completely new method of studying the cell plasm has been developed in recent years, making use of its ultraviolet fluorescence. The photography of cells by this luminescence in the ultraviolet luminescent microscope makes it possible to study certain processes taking place in the cell plasm.

Another very important practical application of luminescence is in fluorescent lighting. Vavilov directed the studies on the design of fluorescent lamps, carried out in the Lebedev Institute of Physics of the Academy of Sciences, the State Optical Institute, and the All-Union Electrotechnical Institute. The lamps developed have been put into production. Fluorescent lighting is rapidly spreading now. Streets and commercial buildings are being illuminated by fluorescent lamps. The economy of fluorescent lighting permits the maintenance of a high level of illumination in working areas and facilitates the selection of the most suitable light composition. This results in a considerable increase in labor productivity.

S. I. greatly promoted the development of the luminescent industry. As everyone knows, luminescent screens are a necessary part of television sets, of radar scopes, and image tubes, and are widely used in automatic machinery, in medical practice, and in many other technical applications. On the basis of deep investigations of the emission processes of crystal phosphors, our scientific laboratories now ensure the possibility of obtaining phosphors with any technically-required characteristics, while our industries ensure their production.

The extensive development of studies on luminescence in the Soviet Union in recent years may perhaps be shown especially by some index figures. At each of the two All-Union Conferences on Luminescence held during S. I.'s lifetime in 1944 and 1948, covering all fields of luminescence, fifty to sixty papers were presented. At present, these conferences are being held yearly, are organized about specific subjects, and ordinarily include more than 100 papers each.

Besides the general conferences, major special conferences are being held on narrower subjects, as well as conferences of the individual Republics.

* * *

The studies on luminescence in the Soviet Union are not limited, of course, to those which I have been able to mention in this paper. I must note the highly important contributions in other fields of luminescence introduced by the school of Academician A. N. Terenin, and in particular, by his student B. S. Neporent and his associates.

A feature of the last few years has been the establishment of new large centers: in Tartu on the study of crystal phosphors, headed by F. D. Klement; in Kiev, in the Ukrainian Academy of Sciences and the University, headed by A. F. Prikhot'ko and one of S. I.'s students, A. A. Shishlovskii. A large new center has been established in the Belorussian Academy of Sciences. It is directed by B. I. Stepanov and one of S. I.'s students, A. N. Sevchenko.

Luminescence has interested and attracted a number of major scientists whose interests had previously been in other fields. Among these are É. V. Shpol'skii and E. F. Gross. They and their schools have already enriched the study of luminescence with very important results. We must also note the growth

of theoreticál investigations in the field of luminophor chemistry in which large laboratories are involved.

Luminescence has penetrated to the very furthest reaches of our country. It is being studied in Syktyvkar in the north, in Osh in the south, and in Chita and other numerous cities in Siberia and Central Asia.

Insofar as we may judge from the literature, Soviet physicists have quantitatively and qualitatively made a greater contribution to the development of the study of luminescence than those of any other country.

This is the greatest monument to Sergei Ivanovich Vavilov, the greatest proof of the worth and fruitfulness of his studies.

Translated by M. V. King