### From the Editor

A joint symposium of the International Commission on Spectroscopy with the Commission on Spectroscopy of the U.S.S.R. Academy of Sciences was held during the time of the International Astronomical Congress in Moscow, August 12-15, 1958. Many papers were delivered at this symposium, including reviews by S. É. Frish and B. S. Neporent, of the work done on atomic and molecular spectroscopy in the U.S.S.R. These papers are published in the present issue of "Uspekhi."

The Twelfth Spectroscopy Congress, devoted to applications of spectroscopy, was held in Moscow on November 19-26, 1958. Nearly 1500 members of the scientific research institutes, higher institutions of learning, and plant laboratories were in attendance. Many review papers were delivered at the plenary sessions of the Congress and, in addition, many lectures were read to the participants. These papers and some of the lectures are published in the present issue of the journal in a somewhat modified form. Although the papers are in the nature of surveys they do not pretend to cover all the existing literature, and reflect to a considerable extent the activities and interests of the authors.

## WORK ON ATOMIC SPECTROSCOPY IN THE U.S.S.R.*

### S. É. FRISH

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IT is impossible to give in a brief survey anything approaching an exhaustive description of recent U.S.S.R. research in atomic spectroscopy. We therefore dwell only on certain investigations that illustrate the most characteristic trends. These trends are: the study of elementary processes of excitation and emission of spectral lines, the determination of nuclear moments by methods of optical spectroscopy, the study of processes in glowing gases and vapors, the use of the wavelengths of light for measurement purposes, and the application of atomic spectroscopy to analytical problems.

Among the elementary processes that determine the emission of spectral lines, the first to

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be investigated have been the probabilities of transitions, which, as is known, are connected with the oscillator strengths, f. The latter can be determined most accurately by the interferometric "hook method" developed as early as in 1912 by D. S. Rozhdestvenskiĭ,[1] a professor at what was then the St. Petersburg University. In this method a simple measurement of the distance between the "hooks" on the spectrogram yields the value of Nf, the product of the concentration of the absorbing atoms and the oscillator strength.

In his first investigations Rozhdestvenskiĭ used the "hook method" to determine the oscillator strengths of doublets of alkali metals. He subsequently developed experimental apparatus with which he was able, using King's high-temperature electric vacuum furnace, to observe "hooks" in the spectra of vapors of elements with high melting points.[2] With the aid of this apparatus, N. P. Penkin, Yu. I. Ostrovskiĭ, and others made many

measurements of absolute and relative oscillator strengths for lines of many elements (Cr, Ni, Fe, Co, V, Ti, Mn, and others[3]). The relative values of the oscillator strengths were recently determined by observation of the anomalous dispersion in a dc arc discharge by E. I. Nikonova and V. K. Prokof'ev for multiplets of the neutral atoms of Al, Te, Mn, Mo and for ions of Ba, Ca, Sr.[4]

G. P. Startsev developed and tested a new version of the "hook method," based on the use of a three-beam interferometer.[5] Yu. I. Ostrovskiĭ, N. P. Penkin, and L. N. Shabanova proposed to determine the absolute oscillator strengths by combining measurement of the anomalous dispersion with measurement of the equivalent line width.[6] A. L. Osherovich worked on a determination of the absolute value of the damping time for helium by the method of delayed coincidences.[7]

The results of measurements made by the method of anomalous dispersion, on alkali metals and several other elements are in good agreement with the quantum-mechanical calculations of V. A. Fock and his associates. Later M. I. Petrashen' and I. V. Abarenkov developed a simplified semi-empirical method of calculating the transition probabilities.[8] It is important to note that the results of the theoretical calculations are in good agreement with the experimental data only if all types of interactions inside the atom are taken into account, including exchange and polarization forces. As a rule, the semi-classical calculation methods are not confirmed. Thus, carried out by the "hook-method" measurements by V. K. Prokof'ev on sodium and G. S. Kvater on thallium do not confirm the Thomas-Kuhn sum rule.[9] V. A. Fock has shown theoretically that such a discrepancy between experimental data and the sum rule is due to the interaction between the electrons contained in the electron shell of the atom.[10] Recently L. A. Vaĭnshteĭn used electronic computers[11] to calculate the oscillator strengths for many atoms in the single-electron approximation.

The second of the elementary atomic constants, which determines the excitation of the spectral lines, and which is measured in many investigations, is the effective cross section of an atom to exciting collisions with electrons. As is known, it has been assumed that the excitation function of an atomic energy level is directly related to the type of the optical excitation function of the spectral line due to this level. I. P. Zapesochnyĭ and S. É. Frish[12] have shown that this is not true by measuring (with a photomultiplier) the intensities of mercury lines excited by electron impact.

The excitation functions of most mercury lines have each several closely-spaced maxima, which went unnoted in earlier investigations. These secondary maxima are for the most part due to cascade transitions. The true excitation functions of most energy levels of mercury have one sharp maximum each, located near the excitation potential. In certain cases one observes a second smeared-out maximum, located at a higher potential. The presence of other maxima was observed also in the excitation functions of helium.[13] The results obtained for mercury were later confirmed by measurements made by the Dutch physicists Smith and Jongerius.[14]

G. G. Dolgov investigated experimentally the polarizations of the lines of helium, neon, and argon atoms excited with electrons near the excitation threshold.[15]

G. F. Drukarev set up an integro-differential equation for the effective cross section of an atom for collisions with slow electrons, taking exchange forces into account.[16] The role of exchange forces was found to be considerable, and all the earlier calculations for collisions with slow electrons, which did not allow for the exchange forces, were found to be too rough. V. I. Ochkur used the Drukarev method to calculate (with a computer) the effective cross sections of the S and P states of hydrogen. In the case of S states the excitation functions were shown to have a second smeared-out maximum.[17] G. G. Dolgov and L. A. Vaĭnshteĭn calculated, also with a computer, the effective excitation cross sections of many states of helium atoms in the strong-coupling approximation. The partial cross sections were shown to be large near the threshold for collisions with electrons at $l > 0$.[18]

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Mention must be made of the theoretical calculations of the energies of the stationary states of atoms. V. A. Fock gave a method for calculating the exchange forces in atoms and developed an approximate method of calculating the energies of the stationary states, well known as the Fock-Hartree method.[19] The methods developed by Fock were extended and applied by a group of his associates (M. G. Veselov, M. I. Petrashen', and others) to alkali and alkali-earth atoms and to the calculation of atomic probabilities.[20] At the present time approximate methods of calculating atomic properties are extensively employed in many scientific centers of the U.S.S.R., including the Academy of Sciences of the Lithuanian S.S.R., where, under the leadership of A. P. Yutsis, the

energy levels of a large number of various atoms are being calculated.[21]

Electronic computers are used in many calculations. For example, Yu. N. Demkov and his associates calculated, with an electronic computer, the upper and lower limits of the ground-state energy of the helium atom in the nonrelativistic approximation.[22]

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A separate branch in the study of atomic constants is the investigation of nuclear moments by the methods of optical spectroscopy. As early as in 1928, A. N. Terenin and L. N. Dobretsov, simultaneously with Schuler in Germany but independently of him, observed a hyperfine structure in the sodium D lines. Somewhat later, E. F. Gross and A. N. Filippov observed analogous structures in cesium lines.[23] This was followed by many determinations by Soviet physicists of nuclear spin and quadrupole moments by methods of optical spectroscopy. F. M. Gerasimov and S. É. Frish have established that the presence of the nuclear moment manifests itself on the Zeeman effect even in strong magnetic fields, on the order of 20,000 oersteds and more.[24]

Recent investigations are devoted principally to the determination of the moments of the heaviest elements and to the isotopic shift in their spectra. N. I. Kaliteevskiĭ, M. P. Chaĭka, A. R. Striganov and others determined the spin and quadrupole moments of the isotopes of uranium and plutonium and investigated the isotopic shifts of their lines.[25] The hyperfine structure and isotopic shifts were also studied in the spectra of Ce, Pr, Ho, and Dy.[26] The possible role of octupole moments was investigated. Work was done to improve the methods of observing the hyperfine structure; a procedure was developed for automatic registration of the hyperfine components of the spectral lines. Work was also done to increase the aperture ratio and resolving power of the interferometric apparatus by using multiple-layer and dielectric coatings.[27] Sources have been developed with an atomic beam that insures sufficient high line intensity with small broadening.[28]

Yu. P. Dontsov and A. R. Striganov have investigated the mercury green line emitted by a source containing mercury produced by neutron bombardment of gold. Apart from the mercury $Hg^{198}$ line, a weak line belonging to mercury $Hg^{199}$ was observed. The cross section for capture of thermal neutrons by the gold isotope $Hg^{198}$ was determined[29] from the ratio of the intensities of these lines and from the magnitude of the neutron current.

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The processes in glowing gases and vapors were investigated to a considerable extent by Rozhdestvenskii's "hook method." This method, as already mentioned, yields the product Nf. Thus, if f is known, the atom concentration N in a glowing gas can be determined. G. S. Kvater, who investigated the anomalous dispersion in thallium vapor, has shown directly that the concentration of the atoms at the metastable level of thallium in heated vapor satisfies the Boltzmann law.[30] Later S. É. Frish, N. P. Penkin, and A. M. Shukhtin have confirmed that the distribution of atoms over the levels in thermal glow also satisfies the Boltzmann law. Finally, the "hook method" has been used to verify that the ion concentration in a gas heated to a high temperature agrees with the Saha formula.[31]

Further application of the "hook method" has made it possible to study gases in a state far from thermodynamic equilibrium, when the statistical laws are no longer satisfied. The first to use the "hook method" to determine the concentration of excited atoms in a glowing gas was the German physicist Ladenburg,[32] who with Rozhdestvenskii's permission copied his interference apparatus exactly. However, Ladenburg's works were carried out without a parallel determination of the electrical characteristics of the discharge, thus reducing the value of his results. Later on, N. P. Penkin and Yu. M. Kagan, using simultaneous measurement of the anomalous dispersion by the "hook method" and of the electric characteristics of the discharge by the Langmuir probe method, were able to obtain more reliable results. They measured the concentration of the excited atoms in a discharge in mercury vapor, in inert gases, and in mixtures of mercury vapor with inert gases.[33] Deviations from equilibrium distributions were observed, and, the conditions under which equilibrium distribution is approached were investigated. The theoretical violations of thermodynamic equilibrium, caused by the emission of radiation and the limits of applicability of Kirchhoff's law were considered by L. M. Biberman, S. L. Mandel'shtam, and N. K. Sukhodrev.[34]

Gases in electric discharges (gas-discharge plasma) were investigated in the U.S.S.R. not only by the methods of anomalous dispersion, but also by the methods of emission and absorption spectroscopy. The first investigations in this field were made by V. A. Fabrikant and a group

of his associates.[35] By measuring simultaneously the intensities of the emission lines and the extent of reabsorption, and also by performing probe measurements, Fabrikant showed that at low pressures and small current densities the observed intensities of the resonance lines were in good agreement with the intensities calculated from the electron concentration and the electron temperature.

The role of radiation transfer in three-dimensional sources of light was investigated in detail by L. M. Biberman,[36] who developed a theory of diffusion of resonant radiation, taking into account the effect of the change of the photon frequency during its absorption and subsequent emission. This work was carried out independently of and simultaneously with analogous work by Holstein and Zanstra.[37] Along with obtaining a numerical solution of the stationary integral equation, Biberman developed also a simplified method of calculating the diffusion of radiation, a method with which, in particular, he analyzed the important practical case of the glow of a cylindrical volume.[38] The results of the calculations were compared with the experimental data on discharge in low-pressure mercury vapor and in a mixture of mercury vapor with argon.[39]

S. É. Frish and Yu. M. Kagan investigated by spectroscopic methods the motion of positive ions in the positive column of a gas discharge.[40] From the Doppler shifts of the ion lines, observed with the aid of a Fabry-Perot interferometer, they determined the transport velocity of the ions, and found it to be of the same order of magnitude as their thermal velocities. They simultaneously explained the important role of the radial fields in the cylindrical discharge tube. It was made clear that the width of the spectral line of the ion was greater when observed across the tube than when observed along it. Yu. M. Kagan and V. P. Perel' also considered theoretically the problem of the motion of ions in a positive discharge column.[41]

Many investigations were devoted to experimental and theoretical research on the widths of spectral lines. N. N. Sobolev and his associates studied the contours of the lines in a dc arc and explained the role of impact broadening.[42] I. I. Sobel'man and L. A. Vaĭnshteĭn considered the limitations of the impact and statistical theories of line broadening.[43] A rigorous theory was developed for impact broadening due to collisions with electrons, along with a theory of quadrupole broadening. M. A. Mazing and S. L. Mandel'shtam investigated experimentally the broadening of

spectral lines in weakly and strongly ionized plasma and have measured the simultaneous line shifts.[44] It was ascertained that, unlike the ordinary stationary theory, the new nonstationary theory of line broadening gives a non-monotonic dependence of the width on the electron temperature. Another new result of the nonstationary theory was that the ratio of the line width to its shift was found to depend on the nature of the spectral terms.

The influence of reabsorption on the contour of the spectral line was investigated by L. M. Biberman. He indicated the possibility of measuring Nf by determining the line broadening due to reabsorption.[45]

S. L. Mandel'shtam and a large group of his associates investigated the spark discharge from the point of view of understanding the mechanism of excitation of the lines of multiply-ionized atoms.[46] A new hydrodynamic spark theory was created. The spark channel is considered as an explosion due to the abrupt release of a large amount of energy. A radially-expanding shock wave is formed, which ionizes the gas and carries it along with it. For an experimental investigation of the spark, apparatus was developed capable of obtaining interference patterns of the spark-discharge channel. The interference patterns permitted observations of the shock wave, the envelope of the channel, and the channel itself, and also measurement of the temperature at various points of its glow during various instants of time. There is time for an equilibrium particle distribution, obeying the Kirchhoff and Saha laws, to be established in the plasma of the spark channel. The temperature in the spark channel reaches 40,000 or 50,000°.

To investigate nonstationary processes in plasma, A. M. Shukhtin and V. S. Egorov also developed apparatus with which to photograph the "hooks" in the Rozhdestvenskiĭ method within a time interval on the order of a microsecond.[47] A special electronic attachment synchronizes the photograph with a definite stage in the development of the investigated nonstationary process.

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Much work was done in the Soviet Union on the comparison of the length of the standard meter with the wavelength of light. This work was started more than thirty years ago at the initiative of D. S. Rozhdestvenskiĭ. The work began with an investigation of the red line of cadmium ($\lambda$ 6438 A) to ascertain its suitability as a primary standard or the necessity of replacing it with another line.

M. F. Romanova and A. A. Ferkhmin, in an investigation of the red line of cadmium excited in a hollow cathode, observed four components in this line, three of which were approximately of the same brightness and spaced 0.004 A apart, while the fourth, very weak one was 0.009 A away from the three others.[48] Later on, N. R. Batarchukova developed an interference monochromator to separate one hyperfine component from the green line of natural mercury, and investigated single-isotope light sources.[49]

A new method for comparing the length of the standard meter with the wavelength of the red line of cadmium was proposed by A. A. Lebedev and M. F. Romanova, and was implemented in the Scientific Research Measurement Institute by a group headed by M. F. Romanova.[50] A tubular standard 1005 mm long, in which a meter stick was placed, was used. The length of the tubular standard was compared by interference with the length of a small tubular standard, one-ninth as long. The length of this small standard in wavelengths of the red line of cadmium was directly determined by interference. The measurements were made both with the tubular standards evacuated and in air. The meter stick was compared with the No. 28 platinum-iridium standard meter. The following value was obtained for the wavelength of the red line of natural cadmium in air

$$\lambda_n = 0.64384687 \cdot 10^{-6} \ \text{m}.$$

the mean squared error is estimated to be 0.0004 A.

The value obtained for pure $Cd^{114}$ was

$$\lambda_n = 0.64384678 \cdot 10^{-6} \ \text{m}.$$

with a mean squared error of 0.0001 A.

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Spectral-analysis research is under the jurisdiction of another Commission, but I take the liberty of dwelling briefly on Soviet research in spectral analysis, which is normally not segregated from the other investigations. In this connection, work is done in the U.S.S.R. not only on the introduction of various spectral-analysis procedures, but also on the investigation of the physical processes that underlie spectral-analysis methods.

Systematic work on the physical principles of emission spectrum analysis started as early as in 1936 under the leadership of G. S. Landsberg. The purpose of this research was to study the factors that influence the intensities of the spectral lines in the principal light sources used in spectral analysis (flame, arc, and spark). S. L. Mandel'shtam and a group of his associates investigated experimentally and theoretically the line intensities in thermal excitation, in the presence of an electric field that causes ion drift.[51] The intensity of each line was found to pass through a maximum as the temperature was varied. This phenomenon is analogous to the change in the line intensity in star spectra, a phenomenon that serves as a basis of star classification. The line intensities were investigated and the concentration of the atoms in the flame was determined by interference methods. The dependence of the line intensity on the concentration of the atoms was investigated and the "growth curve" theory used in astrophysics proved to be applicable.

The mechanism of evaporation of solid electrodes in an arc was investigated by V. K. Prokof'ev, S. L. Mandel'shtam, and many others.[52] E. I. Nikonova and V. K. Prokof'ev investigated, by the method of anomalous dispersion, the radial distribution of atoms of metals in a dc arc flame, and found that the concentration has a minimum on the axis of the arc. They also investigated the glow of a spark. They established the explosive character of the processes on the electrodes, leading to the formation of the flame, and found the electrode vapors to have a high temperature in the flame, up to 30,000°.[53]

From among the practical methods of spectral analysis, one must single out the simplified visual methods developed as early as in the thirties for semi-quantitative analysis with the aid of styloscopes and stylometers. Owing to their simplicity, these methods are still used in plant practice. At the present time photoelectric instruments are being introduced for quantitative spectral analysis.

Among the more specialized methods of emission spectral analysis, we can mention the evaporation method, developed simultaneously in two different versions by S. L. Mandel'shtam and A. N. Zaïdel and their groups.[54] This method is intended for the detection of small impurities of more volatile elements in heavy metals. It insures high sensitivity, to $10^{-5}\%$. The method consists essentially of separating the analyzed impurities by evaporation from the principal element of the sample, and then subjecting these impurities to spectral analysis.

Many investigations were devoted to methods of spectroscopic determination of gases in metals. O. B. Fal'kova and S. L. Mandel'shtam developed a method for determining nitrogen and oxygen in metals by means of spark excitation in an inert gas atmosphere. The determination of gases in metals

was also subject of many investigations by N. S. Sventitskiĭ.[55] A. N. Zaĭdel developed an original method of spectral analysis of hydrogen in metals, based on balancing the hydrogen dissolved in the analyzed sample by a known amount of deuterium and a subsequent spectral analysis of the hydrogen-deuterium mixture.[56] In addition, Zaĭdel and his associates recently developed a method of quantitative spectral analysis of elements for isotopic composition.[57]

O. P. Bochkova, S. É. Frish, and E. Ya. Shreĭder developed a method for the spectral analysis of gas mixtures.[58] The gas is excited in a quartz capillary by high frequency discharge between external electrodes. By suitable choice of the diameter of the capillary and the gas pressure it is possible to attain sufficiently high sensitivity in the analysis of the gas for both difficultly-excited and readily-excited components. A simplified procedure (without a spectrograph) was developed for the analysis of argon and other inert gases for purity. A procedure was also developed for the analysis of micro-amounts of gases.

The Soviet industry produces all the apparatus necessary for spectral analysis, and this apparatus is described in the appropriate publications.[59] A group of workers headed by F. M. Gerasimov has organized the manufacture of plane and curved diffraction gratings, intended for operation over the entire range of wavelengths, from soft x-rays to the deep infrared with a wavelength of 600 – 700 $\mu$.[60] By suitably slanting the working faces, up to 85% of the reflected light can be concentrated in the maximum.

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