4. The temperature variation of the magnetic susceptibility of samarium oxalate, for which the effect of the crystalline field should be small, is very close to the theoretical curve for free ions.

5. Energy differences between the first excited state and the ground state were calculated from the magnetic data. The values obtained (250 cm^{-1} for Eu^{+++} and 1020 cm^{-1} for Sm^{+++}) agree quite well with spectroscopic results.

In conclusion, the authors wish to express their deep gratitude to Professor P. G. Strelkov for his constant interest in the work and to Professor I. N. Zaozerskii, who kindly prepared the samples and gave us a number of valuable suggestions.

Translated by M. G. Gibbons
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Methods of Investigating the Width of Raman Lines and Their Application

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The effect of various factors on the observed width of Raman lines was considered, and methods of excluding the effect of these factors on the results of measurements are described. Results are given of measurements of the width of a number of Raman lines using a prism spectrograph with large dispersion. A comparison is made of the data obtained with data found by other methods.

1. STUDIES of the width and the form of Raman lines are of great interest from the viewpoint of obtaining data on intramolecular and intermolecular interactions. The knowledge of the width of these lines is also very important for the correct selection and substantiation of the methods of measuring intensities. However, the width and the form of lines remain (up to the present time) the least investigated parameters in Raman spectra, owing to the fact that their investigation is associated with great experimental difficulties. These difficulties were, apparently, successfully overcome for the first time in the work of Sterin[1], although attempts to carry out such measurements were made many times previously[2,3]. In the work of Sterin two Raman lines were studied with the aid of a Fabry-Perot etalon: the line $\Delta\nu = 992$ cm^{-1} of benzene and $\Delta\nu = 802$ cm^{-1} of cyclohexane. Irrespective of the fact that these belong to the strongest (and narrowest) Raman lines, the interferometric method of measuring proved very difficult. Hence, this method would not be very suitable for the study of weaker lines. Also, additional difficulties arise when it is necessary to study the wider lines, owing to the fact that the dispersion region of the Fabry-Perot interferometer is inadequate. For this reason, we developed indirect methods for the evaluation of the widths of the Raman lines. Such indirect methods are the "photometric" method, based on the study of the dependence of the intensity of lines on the width of slit of the spectrograph[4,5], and the method of the "effective width" of lines, based on a comparison of the integral intensities with the intensities at the maximum of the lines[6,7,8]. These indirect methods are essentially based on the data obtained in the work of

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[1] Kh. E. Sterin, Dissertation, Inst. of Physics, Acad. Sci. USSR, 1949; Izv. Akad. Nauk SSSR, Ser. Fiz. 14, 411 (1950).

[2] P. P. Shorygin, Zh. Fiz. Khim. 15, 1072 (1941).

[3] A. C. Manzies, Proc. Roy. Soc. (London) 172, 89 (1939).

[4] M. M. Sushchinskii, Izv. Akad. Nauk SSSR, Ser. Fiz. 11, 348 (1947).

[5] M. M. Sushchinskii, Trudy Fiz. Inst. Akad. Nauk 5, 185 (1950);

[6] M. M. Sushchinskii, Izv. Akad. Nauk SSSR, Ser. Fiz. 14, 387 (1950).

[7] M. M. Sushchinskii, J. Exper. Theoret. Phys. USSR 22, 765 (1952).

[8] M. M. Sushchinskii, Izv. Akad. Nauk SSSR, Ser. Fiz. 17, 608 (1953).

Sterin[1].

The development of indirect methods does not minimize, of course, the importance of studying the forms and the widths of lines by direct methods, the more so because the indirect methods are not suitable for the study of the line contours. In addition, for the development and substantiation of the above-mentioned indirect methods of evaluating the width of lines, the data of Sterin are not sufficient, since they relate only to a class of the sharpest Raman lines. Therefore, the problem arose of obtaining by direct methods new data on the width and shape of lines of various types. The present work deals with the development of a procedure for measuring the width and the contour of Raman lines with the aid of a spectrograph of medium dispersion. We have also compiled the data of measurements for a number of different types of Raman lines.

2. In the study of spectral lines it is necessary to take into account a number of factors exerting an influence on their observable width and shape. Such distorting factors can be diffraction on the aperture diaphragm of the spectrograph, defects in the optical system, the final value of the width of slit and the resolving capacity of the photolayer. In the case of Raman lines, it is also necessary to take into account the width of the exciting line. The broadening produced by each of the factors enumerated above can be characterized as an "apparatus function," which corresponds to the action of a given factor under the condition of a neglibibly small effect of all the other factors. In order to illustrate the role of each of the distorting factors, we have compiled in Table I an approximate evaluation of the width of the apparatus function corresponding to each of these effects for several types of spectrographs. For the characteristic of diffraction broadening the values of the normal width of slit are given by

$$S_0 = \frac{\lambda f}{d} D,$$

where f is the focal distance, d the effective diameter of the objective of the collimator, D the linear dispersion of the instrument. We have not taken into account the effect of defects in the optical system of the spectrograph, since these are to some degree individual characteristics. For the apparatus function of the photolayer, in agreement with the data of the photoplates used, we assumed a width of the order of 0.015 mm. The value of the width of the exciting line was taken as that of a lamp with cooled electrodes[9] from the measurements with a Fabry-Perot etalon.

TABLE I

Spectrograph	Actual Relative Opening	Magnification	Linear Dispersion*, cm^{-1} mm	S_o, cm^{-1}	Apparatus function of the Photolayer, cm^{-1}	Real Width of Exciting Line, cm^{-1}	Observed Width of Exciting line***, cm^{-1}
ISP-51	1:6	0.9	140	0.36	2.1	0.2	2.5
V-III	1:11	0.7	56	0.21	0.8	0.2	1.0
Diffraction Lattice** . .	1:12	1.0	28	0.14	0.4	0.2	0.7

* All data given are calculated for the line 4358 Å.

** This apparatus will be described in more detail separately.

*** When a narrow slit is used for the photographing of the spectra.

Some idea of the total action of all the distorting factors considered above is given by the observed width of the exciting line. The values

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[9] M. L. Sosinskii, Izv. Akad. Nauk SSSR, Ser. Fiz. 17, 621 (1953).

of this quantity for the three spectrographs we have considered are given in the last column of Table I.

3. It should be kept in mind that the distorting action of each of the factors considered above depends not only on the width and on the shape of the corresponding apparatus functions, but also on the shape of the lines under investigation. Therefore, a separate account of the effect of each of the distorting factors in the study of the width and the shape of Raman lines is associated with considerable difficulties. However, an individual account of these factors is not at all requried: in order to exclude completely the effect of all the distorting factors, and to find the real contour from the observed contour of a Raman line, it is sufficient to have the data on the observed contour of the exciting line. This problem was considered in detail in a previous paper[10]. According to the data of this study, for the real contour of the Raman line φ_k we have:

$$\varphi_{\text{K}}(\lambda) = \frac{1}{2\pi} \int\limits_{-\infty}^{+\infty} \frac{K(u)}{K_{\text{B}}(u)} e^{-i\lambda k}\, du, \tag{1}$$

where

$$K(u) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{+\infty} k(x)\, e^{iux}\, dx;$$

$$K_{\text{B}}(u) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{+\infty} k_{\text{B}}(x)\, e^{iux}\, dx,$$

and $k(x)$ and $k_{\text{B}}(x)$ are the observed contours of the Raman and the exciting line, respectively. It is significant that for the determination of the real contour of the Raman lines it is not required to know the apparatus function of the spectral instrument used and the real contour of the exciting line, the experimental determination of which is associated with great difficulties; however, the observed contours of the Raman line $k(x)$ and the exciting line $k_{\text{B}}(x)$, entering into the expressions for $K(u)$ and $K_{\text{B}}(u)$, can be determined comparatively simply.

Calculations by Eq. (1) can be carried out very easily, when the observed contour of the exciting line is disperse Examples of finding the real contours of the Raman lines of various shape for this case are given in reference 10. If, however, the observed contour of the exciting line $k_{\text{B}}(x)$ is not disperse, then we may consider the dispersed curve $k_{\text{D}}(x)$ as having the same width as the first approximation, and the difference

$$\Delta k_{\text{B}} = k_{\text{B}} - k_{\text{D}} \tag{2}$$

as the correction. Moreover,

$$K_{\text{B}}(u) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{+\infty} [k_{\text{D}}(x) + \Delta k_{\text{B}}(x)]\, e^{iux}\, dx = K_{\text{D}}(u) + \Delta K_{\text{B}}(u), \tag{3}$$

where

$$\Delta K_{\text{B}}(u) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{+\infty} \Delta k_{\text{B}}\, e^{iux}\, dx.$$

Substituting (3) into (1), and assuming approximately that

$$\frac{1}{K_{\text{B}}} \approx \frac{1}{K_{\text{D}}} \left[1 - \frac{\Delta K_{\text{B}}}{K_{\text{D}}}\right],$$

we find:

$$\varphi_{\text{K}}(\lambda) = \frac{1}{2\pi} \int\limits_{-\infty}^{+\infty} \frac{K(u)}{K_{\text{D}}(u)} e^{-i\lambda u}\, du - \frac{1}{2\pi} \int\limits_{-\infty}^{+\infty} \frac{K(u)}{K_{\text{D}}(u)} \frac{\Delta K_{\text{B}}(u)}{K_{\text{D}}(u)} e^{-i\lambda u}\, du. \tag{4}$$

The second term of this expression represents the correction to the contour of the Raman line which should be introduced so as to take into account the deviation of the observed contour of the existing line from the dispersed curve.

Our experiment shows that approximating the observed contour of the exciting line with the dispersed curve gives in practice satisfactory results in the majority of cases. Of the factors which may lead to deviations from the dispersion, the most significant, apparently, is the fairly wide slit width with which, for a number of reasons, it is necessary to photograph Raman spectra. When the same width of slit is used for photographing the exciting line, the latter will be distorted in such a manner that in its observed contour the drop in intensity at the edges will occur faster

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[10] M. M. Sushchinskii, J. Exper. Theoret. Phys. USSR 25, 87 (1953).

than in the dispersed curve of the same width. In this case, instead of calculating the correction by Eq. (4), a faster and more effective solution of the problem of obtaining the real contour of the Raman line from the observed contour may be attained by an initial exclusion of the effect of the width of slit.

Methods for the exclusion of the width of slit are developed in the work of Rayleigh[11], Runge[12], Paschen[13] and others. For our purpose, it is sufficient to use the simplest Rayleigh version which consists in the following: Under conditions of almost incoherent illumination of the spectrograph slit, the observed contour of the spectral line can be expressed in the form

$$f(x)=\frac{1}{2s}\int\limits_{x-s}^{x+s}\psi(\lambda)\,d\lambda, \qquad (5)$$

where $2s$ is the width of the slit, and $\psi(\lambda)$ is the contour of the line at an infinitely narrow slit depending on all the other distorting factors. Approximating the function $\psi(\lambda)$ along the length of the slit by the parabola

$$\psi(\lambda)=a\lambda^2+b\lambda+c, \qquad (6)$$

we obtain:

$$f(x)=\psi(x)+as^2/3. \qquad (7)$$

Assuming that the change in a is small when we substitute $\psi(x)$ by $f(x)$, we find a from the observed distribution; then

$$\psi(x)=f(x)-as^2/3. \qquad (8)$$

Rayleigh proposed the use of a graphic method, instead of the analytical, for the determination of the correction $as^2/3$, which can be reduced to the following: from the points $x - s$ and $x + s$ on the abscissa perpendiculars are extended until they cross the curve $f(x)$; the points of intersection are joined by a chord, and one third of the cut-off ab (Fig. 1) is added (or subtracted) to the ordinates $f(x)$. Carrying out the same operation for a number of points x, it is possible to construct the complete contour of the line corresponding to an infinitely narrow slit (this operation does not take more than 10-15 minutes).

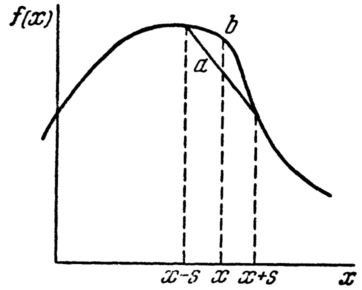

FIG. 1. A graphical method for excluding the effect of the width of slit.

Thus, we can exclude the distortions produced by the extremity of the width of slit in the combination line. In order to take into account the remaining factors, the exciting line is photographed with a slit of not more than 0.2 - 0.3 s_0. Then, the limitations superimposed by the partial incoherence of the illumination are removed, and the distorting effect of the slit is negligibly small, since its width is 10-15 times smaller than the width of the remaining apparatus function. Account of the remaining apparatus distortions (together with the exciting line) is taken by the methods described above.

Thus, the procedure which we are proposing for the investigation of the contours and the width of the Raman lines can be reduced to the following:

a) The photographing of the Raman spectra with the aim of obtaining the highest possible intensity may be carried out with a sufficiently wide slit. The width of slit, however, should not exceed one half of the width of the line studied; under this condition the distortions introduced by the slit are still negligible;

b) When at the width of slit, with which the photographing of the Raman spectra is carried out, the observed contour of the exciting line is found to be dispersed, then to obtain the real contour of the Raman lines from their observed contour can be reduced to the analytical operations described in reference 10. In the simplest case, when the observed contour of the Raman line is also dispersed, then it is only necessary to subtract the observed width of the exciting line from the observed width of the Raman line ; moreover, the real contour of the Raman line remains dispersed;

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[11] Rayleigh, Phil. Mag. 42, 441 (1871).

[12] C. Runge, Z. Math. 42, 205 (1897).

[13] F. Paschen, Wied. Ann. 60, 712 (1897).

c) When the contour of the exciting line differs noticeably at the width of slit used in the photographing of Raman spectra from the dispersed (whereupon the drop in intensity at the edges of the line occurs faster than for a dispersed line of the same width), then the photographing of the exciting line should be carried out at a narrow slit (several times smaller than the normal width of slit). Thus the distorting effect of the slit is removed and the contour of the line should approach that of the dispersed. The distorting effect of the slit on the contour of the Raman line is excluded by the graphic method described above. From the "restored" contour of the Raman line its real contour can be obtained as in step b) (by using the contour of the exciting line photographed with a narrow slit);

d) It may be found that the contour of the exciting line photographed with a narrow slit differs noticeably from the dispersed. In this case the required corrections may be found by Eq. (4).

For the practical application of the methods described in this section it is, of course, necessary to take into account the actual accuracy of measurements. An analysis of the material available at our disposal shows that the corrections for the deviations of the contour lines from the dispersed form are not very significant. With a limited accuracy of measurement, attempts to make the data more precise by introducing such corrections may prove illusory. Thus, in many cases, the introduction of corrections is not justified, and the actual refinement of the data can be carried out by a simple subtraction of the observed widths of the Raman and the exciting lines.

4. Using the methods described, the width of the Raman lines in the spectra of a number of hydrocarbons was measured. The photographing was carried out with a triprism spectrograph V III* (the parameters of the instrument are given in Table I.) The width of slit used in the photographing of the Raman spectra was 0.03 mm, which corresponded to 1 cm^{-1} in the spectrum (the given spectrograph has a magnification of 0.7; the dispersion of the instrument in the region of the line 4358 Å represents 56 cm^{-1} per 1 mm). The photographing of the exciting line (the source --a lamp with cooled electrodes) was carried out also with a slit of 0.03 mm in one series of the experiments, and with a slit of 0.002 mm in the second series. For the exact installation and measurement of the width of slit the diffraction method described in reference 15 was used.

The spectra were photographed on "Zenit 700" plates. The exposure on the average was 7 hours. The photometering was carried out on the microphotometer MF-2 with a 30-fold magnification, at a slit width of the photometer 0.15-0.20 mm.

The observed width of the exciting line in the photographing with a slit width of 0.002 mm was equal to

$$\delta_B = 0.019 \pm 0.003 \text{ mm}$$

or 0.1 ± 0.15 cm^{-1} in the spectrum. The measurements carried out with lines of the iron spectrum, obtained at the same slit width, showed that the width of the apparatus function is maintained over the length of the spectral region in which the Raman lines were located.

When photographing with a width of slit of 0.03 mm, the observed width of the exciting line was equal to 0.028 ±0.003 mm (or 1.6 cm^{-1} in the spectrum). The study of the contours of the exciting line showed that they approximate the dispersed. However, the drop in the intensity when moving away from the maximum of the line occurs somewhat more rapidly than for the dispersed curve. These deviations are more noticeable when the exciting line is photographed at a width of slit of 0.03 mm. Hence, in the refinement of the data of the Raman lines we excluded the effect of the width of slit by the method described in Sec. 3. It was found in practice that the exclusion of the width of slit introduces into the final results a small, but systematic correction amounting to 0.2-0.3 cm^{-1} for narrow lines, and 0.3-0.5 cm^{-1} for wide lines.

The deviations from dispersion of the exciting line, obtained with a narrow slit, give a correction which, when evaluated by formula (4), is found to be within the limits of experimental errors. Therefore, this correction was not taken into account.

The results which we have obtained for a number of Raman lines are given in Table II. The investigation of the line contours showed that,

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* The measurements of the width of Raman lines with the aid of the spectrograph were carried out also by Chulanovskii and co-authors[14]. However, the procedure they used is suitable only for fairly narrow lines.

[14] V. M. Chulanovskii and A. Mironova, Izv. Akad. Nauk SSSR, Ser. Fiz. 12, 560 (1948); V. M. Chulanovskii, M. P. Burgova and A. N. Mironova, Izv. Akad. Nauk SSSR, Ser. Fiz. 14, 406 (1950).

within the limits of experimental errors, they can all be described by the dispersion curve.

TABLE II

Substance	$\Delta\nu$, cm^{-1}	I_∞	δ cm^{-1}	I_0 ISP-51*	δ_{eff} cm^{-1}	δ_{cal} cm^{-1}	I_0 V-III
Toluene	521	210	3.2	100	2.1	2.3	80
	1031	230	2.0	130	1.8	1.8	120
	1211	260	3.4	120	2.2	2.7	100
	1605	310	6.5	85	3.6	7.5	50
Cyclohexane	802	500	2.0	250	2.0	2.0	250
	1029	480	10	105	4.6	11	65
	1267	440	11	90	4.9	12	—
	1445	470	12	85	5.5	14	50
Cyclopentane	889	550	9	150	3.7	8	90
	1031	270	20	44	6.2	16	18
	1449	300	17	42	7.2	19	21
Cyclopentane	900	350	5.2	140	2.5	3.7	—
	1108	460	6.6	130	3.5	7.0	—
	1614	380	3.2	150	2.5	3.7	—
Methylcyclohexane . . .	770	300	3.2	115	2.6	4.0	—

* The data on the intensities at the maximum of the lines (ISP-51), used in the Table, were obtained by taking into account a great many repeated measurements of these values, carried out by Kh. E. Sterin and V. T. Aleksanian at the Commission on Spectroscopy in the Dept. of Physico-Math. Sciences, Academy of Sciences, USSR.

5. The selection of the objects for investigation was determined in this study mainly by the desire to obtain data for lines of diversified width belonging to different classes of hydrocarbons and types of vibrations, so as to obtain material which could be used for a more strict substantiation of the method of the effective width of lines, proposed previously[6-8]. In the method mentioned, the evaluation of the width of lines δ_{eff} was carried out by a comparison of the integral intensities I_∞ with the intensities I_0 at the maximum of the lines

$$\delta_{\mathrm{eff}} = I_\infty / I_0. \qquad (9)$$

When using this method, the required normalization should be based on the data of direct measurements of the width of several lines. Up to the present time such measurements are only those of Sterin relating to two completely symmetrical lines: benzene ($\Delta\nu = 992$) and cyclohexane ($\Delta\nu = 802$), with a width of 1.8 and 1.9 cm^{-1}, respectively. In subsequent investigations it was found that such a normalization cannot be used for lines differing greatly in width, since the ratio of the intensities at the maximum I_0 for lines of different width, generally speaking (see reference 5), does not correspond to the ratio of these values at an infinitely narrow exciting line. But, according to the meaning of Eq. (9), the values of I_0 for the photographic conditions enter into it. Under these conditions the distortions associated with the end width of the exciting line (and apparatus distortions) are completely excluded. When we use values for I_0 not obtained under such "ideal" conditions, the values of δ_{eff} determined by Eq. (9) will have a definite provisory meaning, since they are singularly connected with the real width of lines δ. However, δ_{eff} and δ, generally speaking, no longer coincide.

In order to correlate the values obtained by the method of the effective width of lines (using for I_0 the data of investigation[16]) with the results of the direct measurements of δ, we compared the

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[15] E. Prenss, Spectr. Acta **4**, 412 (1950).

two values for a number of lines. It was found that the relationship between δ_{eff} and δ (at $\delta_{eff} > 2$; the region $\delta_{eff} < 2$ was not investigated in detail) can be expressed by the formula

$$\delta = \alpha(\delta_{eff} - \beta), \qquad (10)$$

where $\alpha = 3.4$; $\beta = 1.4$.

This relationship is shown in Fig. 2, where δ_{eff} is plotted along the abscissa and the values of δ from the data of our measurements along the ordinate (see Table II). In the calculations of δ_{eff} we have used for I_0 the data of reference 16, and for I_∞ the values measured by the photoelectric method, described previously[17]. As is evident, the deviations between the direct and indirect methods of measuring the width of lines with such a recalculation of the values δ_{eff} do not exceed the limits of experimental errors. In the last column of Table II are given the relative intensities of the lines obtained by using a narrow exciting line. One can see that for the wide lines, when using a narrow exciting line, the value of I_0 is actually smaller than the corresponding intensities obtained when using a wide exciting line.

The possibility of obtaining the actual widths of lines (using the graduated graph) from the values of δ_{eff}, found by Eq. (9), also provides the possibility of transferring from the values of I_0, obtained in reference 16 with an instrument of medium dispersion (type ISP-51) and with a fairly wide exciting line (~ 2 cm^{-1}), to such values of I_0 which correspond to "ideal" conditions of photographing. In fact, if we know I_∞ (which can be determined, at least in principle, without great difficulties) and if we know δ_{eff}, then it is possible to find [by Eq. (10)] the actual line widths δ. Then, obviously, the values I_∞/δ will give the intensities I_0 reduced to ideal conditions of photographing.

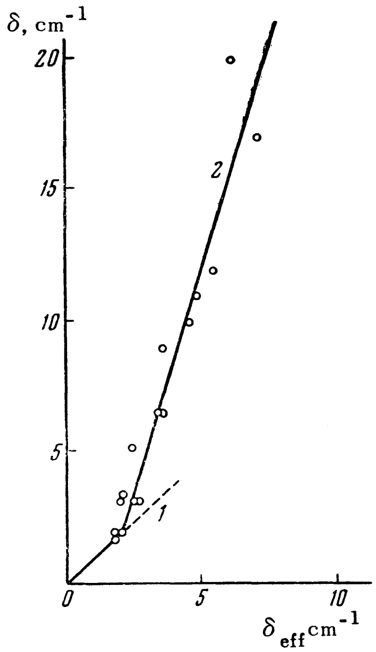

FIG. 2. The dependence of the effective width on the actual width of line. $1 - \delta = \delta_{eff}$ (ideal conditions of photography); $(\delta_{eff} - \beta)$.

It should be noted that all the measurements of I_0 in investigation[16] are expressed in the absolute scale, at the basis of which are placed the data of a number of typical lines for several standard hydrocarbons. To such hydrocarbons belong benzene, cyclohexane, methylcyclohexane, toluene and cyclopentane. Therefore, the finite scale should be based on careful measurements of the intensities of the typical lines of such hydrocarbons. Such measurements were carried out with great care by Kh. E. Sterin and V. T. Aleksanian, to whom we express our thanks for providing these data.

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[16] P. A. Bazhulin et al, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk 1, 14 (1941); 3, 198 (1943); 1, 7 (1946); 6, 480 (1949); 5, 501 (1950). P. A. Bazhulin and Kh. E. Sterin, Izv. Akad. Nauk SSSR, Ser. Fiz. 11, 456 (1947).

[17] M. M. Sushchinskii, J. Exper. Theoret. Phys. USSR 20, 304 (1950).