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THE ONE-CONFIGURATION APPROXIMATION IN THE  
CALCULATION OF THE X-RAY AND ELECTRON SPECTRA  
OF THE TRANSITION ELEMENTS

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The  $L\beta_{2,14}$  and  $L\gamma_{1,9}$  x-ray spectra and electron spectra of the 4d and 4f levels of the atoms of all the rare earth elements in high-spin compounds have been calculated in the isolated-ion model in the one-configuration approximation. The limits of applicability of the one-configuration approximation have been established. Comparison of the calculated and experimental spectra has revealed a number of discrepancies, the nature of which indicates that a many-configuration calculation is necessary.

The characteristics of the x-ray and electron spectra of transition elements in high-spin compounds change considerably on going from one substance to another. Thus their correct interpretation makes it possible to obtain valuable information on the electronic state of the ions of transition elements.

In spite of the fact that the suggestion regarding the anomalous behavior of the characteristics of transition metal spectra associated with the interaction of an internal vacancy with the electrons of unfilled levels was first made in 1927 [1] and confirmed experimentally in a series of papers on the study of the spectra of the elements of the iron group [2] and the rare earth elements [3, 4], there has not up to the present been a single calculation which fully explained all the characteristics of any spectrum. This is due to the fact that the exact calculation of the spectra of the transition metals is extremely tedious. Thus in all work devoted to the theoretical study of these spectra, a number of approximations are made. In practically all studies, the influence of ligands is modeled by the removal of several electrons (the number of which is equal to the formal valence of the transition element in the compound), and the subsequent calculations are carried out in the isolated-ion model. The next approximation which is made in most theoretical work is the assignment of a definite electron configuration to the free ion.

These two approximations reduce considerably the volume of the calculations, but the calculation nevertheless remains fairly tedious. Thus in the first theoretical work devoted to the interpretation of the spectra of the transition metals, a number of additional simplifications were made. Calculations carried out in the "average volume" approximation for most x-ray spectra of elements of the iron group [2] and the rare earth elements (REE) [3] confirmed the suggestion that the extent of the multiplets of the transition elements is due to the interaction of an internal vacancy with the electrons of an incomplete level, and made it possible to explain qualitatively the behavior of certain characteristics of the spectra with change in the atomic number and on going from one compound to another. Many characteristics of the spectra, however, for example the relative intensities of the long-wave and short-wave regions of the spectra, the asymmetry indices in the long-wave part of the multiplet, and the line widths, remained unexplained in this approach.

The next stage in the development of the theory of the spectra of the transition elements was the change to a many-term calculation within the framework of the one-configuration approximation. A number of additional simplifications, which are not fundamental in character but which greatly decrease the volume of the

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calculations, made it possible to calculate in this model most of the x-ray and electron spectra. Calculations of the  $K\alpha_{1,2}$  and  $K\beta_{1\beta'}$  emission spectra [5],  $M_{II,III}$  absorption spectra [6], and electron spectra of the 3p and 3d levels [7] of the elements of the iron group in this approximation with additional allowance for the influence of the ligand field within the framework of crystal field theory, and also calculation of the  $L\alpha_{1,2}$ -,  $L\beta_{1\beta'}$ -,  $L\gamma_{1,9}$ -,  $K\beta_{1\beta'}$  emission spectra [8],  $M_{IV,V}$  [9] and  $N_{IV,V}$  absorption spectra [9-11], and electron spectra of the 4d [7, 8] and 4f [7, 12] levels of the REE explained a number of integral characteristics of the spectra and improved considerably our understanding of the origin of the details of the fine structure.

At the same time, this work [5-12] revealed a number of examples of noncorrespondence between the experimental spectra and the theoretical spectra calculated in the one-electron approximation of the isolated-ion model. The most important of these discrepancies are that the theoretical extent of the multiplet is greater than the experimental, and the widths of the long-wave components of the multiplet are greater than the widths of the short-wave components.

In order to be able to improve the theory, it is necessary to reveal all the noncorrespondence between the calculated structure of the multiplets  $n'l^4l'^4n'l^N$  and the experimental spectra for all possible values of  $N$  ( $n$  and  $l$  are the quantum numbers characterizing the electrons of the incomplete level, and  $n'$  and  $l'$  are the quantum numbers of the internal vacancy). It is first necessary, however, to calculate the spectra of the REE, since the influence of the environment on these will be expected to be least among the transition elements, as a consequence of the shielding of the 4f electrons by the filled 5s and 5p levels, and these spectra may help to reveal inadequacies associated to a large extent with the inaccuracy of the one-configuration approximation. The most complete picture of the inadequacies of the one-configuration approximation may be given by spectra whose structure is determined by configurations with vacancies in the  $N$  level.

The present paper describes the calculation of the structure and form of the spectra of all the REE, due to configurations with a vacancy in the 4d and 4f levels.

## 1. $L\gamma_{1,9}$ AND $L\beta_{2,14}$ X-RAY SPECTRA

The calculation of the energy structure of the configurations  $4d^9 4f^N$ , determining the form of the  $L\gamma_{1,9}$  and  $L\beta_{2,14}$  x-ray spectra and electron spectra of the 4d level, is extremely tedious, so that in the present work it is carried out with several approximations.

Comparison of the calculation of the structure of the configuration  $4d^9 4f^{13}$  ( $^{70}\text{Yb}$ ) with and without allowance for spin-orbital coupling of the 4f electrons, showed that the coupling leads to a change in the structure of the multiplet of the order of 0.5-1.0 eV. Since the spin-orbital coupling parameter  $\zeta_{4f}$  decreases in proportion to  $(Z - \sigma)^4$ , the spin-orbital coupling of the 4f electrons can apparently also be neglected for elements with  $Z < 70$ .

The study carried out for the case of the configurations  $4d^9 4f^7$  ( $^{64}\text{Gd}$ ) and  $4d^9 4f^{11}$  ( $^{68}\text{Er}$ ) showed that neglect of the spin-orbital coupling of the 4d electrons in the calculation of the matrix elements between states derived from excited terms of the configuration  $4f^N$  also leads to changes in the structure of the multiplet of the order of 0.5-1.0 eV.

These approximations make it possible to decrease considerably the volume of the calculations [for example, for  $^{66}\text{Dy}$  ( $4d^9 4f^9$ ) the calculation is reduced by a factor of approximately 50].

The calculation was carried out using the Slater parameters  $F^k$  and  $G^k$ , calculated from the functions in [13] and decreased by a factor of 1.5, and the spin-orbital coupling parameter  $\zeta_{4f}$  from the same paper. The comparison in Table 1 of the experimental and theoretical relative intensities  $I_{\gamma_9}/I_{\gamma_1}$  and  $I_{\beta_{14}}/I_{\beta_2}$ , and also the energy differences between the  $L\gamma_1$  and  $L\beta_2$  lines  $\Delta E_{\beta_2\gamma_1}$ , obtained by decreasing the difference  $E_{\gamma_1} - E_{\beta_2}$  by an amount  $EL_{II} - EL_{III}$ , determined from the difference in the energies of the  $L\alpha_2$  and  $L\beta_1$  lines, shows that the calculation gives the integral characteristics of the spectra satisfactorily. At the same time the data in Table 1 show that the calculated values of  $\Delta E_{\beta_2\gamma_1}$  and  $I_{\gamma_9}/I_{\gamma_1}$  are systematically greater, and the values of  $I_{\beta_{14}}/I_{\beta_2}$  systematically smaller than the experimental values. Additional study showed that considerable improvement in the agreement between these characteristics and experiment is achieved by decreasing the matrix elements of the operator of the spin-orbital coupling of the 4d electrons.

The comparison of the calculated structure and experimental form of the  $L\beta_{2,14}$  and  $L\gamma_{1,9}$  spectra for all the REE, given in Fig. 1, shows another noncorrespondence between theory and experiment. The short-wave range of the spectrum is described effectively, but considerable discrepancies are observed in the long-wave range. For example, the spectra of Tm and Yb do not contain theoretical components under the long-wave

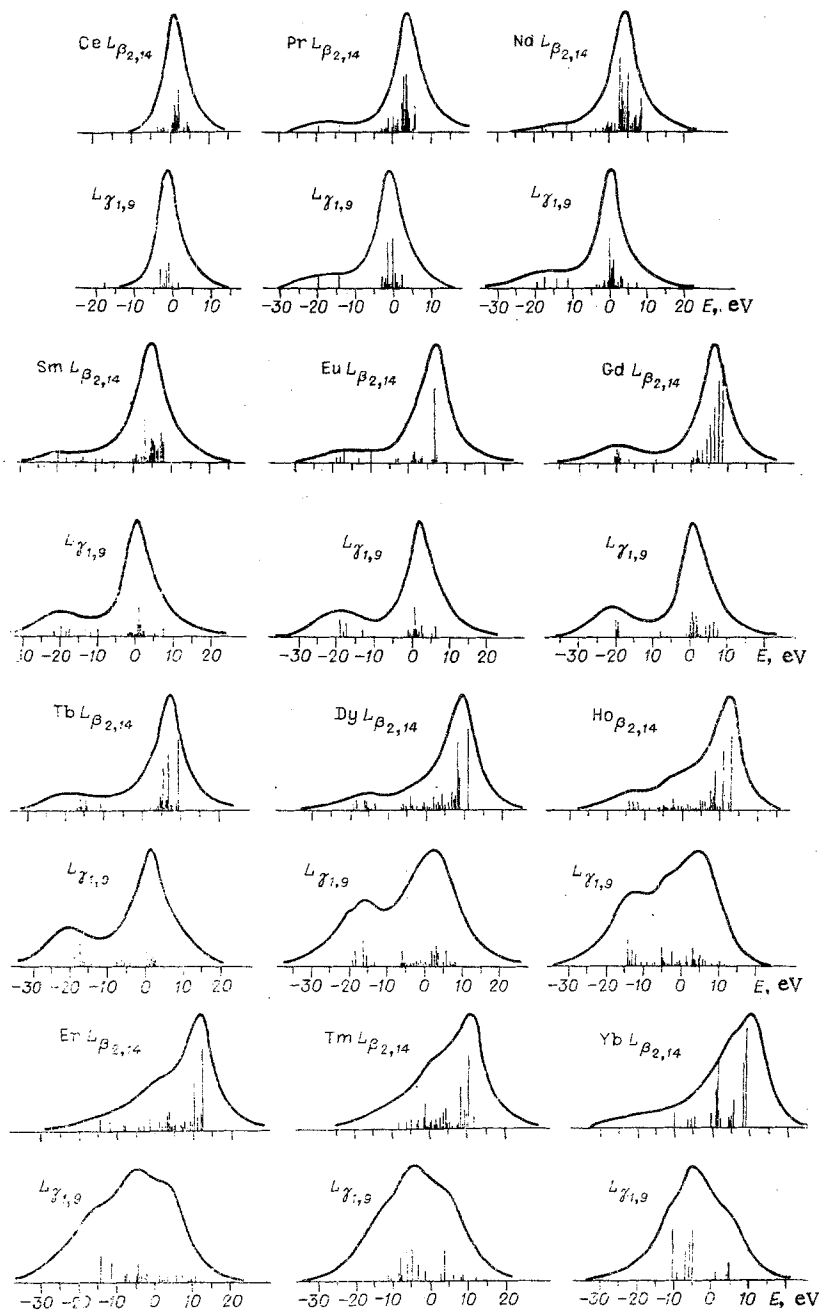


Fig. 1. Comparison of the calculated structure and experimental form of the  $L\beta_{2,14}$  and  $L\gamma_{1,9}$  spectra.

TABLE 1. Comparison of the Experimental and Theoretical Values of  $I\beta_{14}/I\beta_2$ ,  $I\gamma_9/I\gamma_1$ ,  $\Delta E\beta_2\gamma_1$ , and the Widths of the 4d and 4f Levels, Used to Obtain the Form of the Electron Spectra

z	N	$I\beta_{14}/I\beta_2$		$I\gamma_9/I\gamma_1$		$\Delta E\beta_2\gamma_1$ (eV)			Widths (eV)	
		Expt.	Theor.	Expt.	Theor.	1	2	3	4d	4f
58	1	—	0,01	—	0,07	2,0	0,6	2,5	0,8	—
59	2	0,09	0,03	0,12	0,14	2,5	3,3	4,1	0,9	—
60	3	0,06	0,04	0,12	0,14	2,0	1,2	3,0	1,0	0,3
62	5	0,12	0,10	0,30	0,32	0,8	5,7	4,4	1,2	0,5
63	6	0,15	0,12	0,36	0,39	5,0	2,7	5,6	1,2	0,3
64	7	0,22	0,20	0,34	0,36	5,9	5,2	6,2	1,3	0,3
65	8	0,28	0,29	0,39	0,45	5,2	4,7	5,5	1,4	1,1
66	9	0,17	0,14	0,33	0,38	10,5	6,9	6,5	1,5	0,7
67	10	0,14	0,11	0,34	0,37	7,8	9,8	7,5	1,6	1,1
68	11	—	—	—	—	10,9	5,9	16,1	1,8	0,3
69	12	—	—	—	—	14,5	9,9	16,5	1,9	1,1
70	13	—	—	—	—	13,1	76,8	14,3	2,0	0,3

Note. 1. Data obtained with  $E\gamma_1 - E\beta_2$  from [18] and  $EL_{II} - EL_{III}$  from [19]. 2. Data obtained with  $E\gamma_1 - E\beta_2$  and  $EL_{II} - EL_{III}$  from [20]. 3. Values calculated in the present work.

edge, and the origin of the long-wave tail in the spectrum of Er is not explained; it is difficult to imagine that in the spectra of the other elements the widths of the  $L\gamma_9$  and  $L\beta_{14}$  lines can be attributed entirely to an increase in the natural widths of the long-wave components over the short-wave components.

All these discrepancies between theory and experiment make it possible to assume the existence of a large number of levels in the long-wave range of the spectrum, which are not described in the one-configuration approximation and which are therefore genealogically derived from excited configurations. It is to be hoped that allowance for excited configurations will make it possible to improve considerably the agreement between theory and experiment.

In fact, interaction with excited configurations, the levels of which lie in the long-wave range of the spectrum, leads to a displacement of the levels of the configuration  $4d^9 4f^N$ . The long-wave levels of the configuration  $4d^9 4f^N$  are displaced more extensively than the short-wave components, since they lie closer to the levels of the excited configurations, and the displacement is proportional to  $1/\Delta E$ . This leads to a decrease in the extent of the entire structure of the configuration  $4d^9 4f^N$ . Moreover, the admixture of basis states of the configuration  $4d^9 4f^N$  makes possible transitions to levels genealogically related to the excited configurations. The levels which lie close to ( $< 1$  Ry) in terms of lower multiplicity of the configuration  $4d^9 4f^N$  will be revealed in the long-wave range of the  $L\gamma_{1,9}$  and  $L\beta_{2,14}$  spectra as edges and elongated tails and will lead to additional broadening of the  $L\gamma_9$  and  $L\beta_{14}$  lines. Far-lying levels should appear much less strongly in the spectrum, and their recording presents a complex experimental problem.

As configurations which should have the greatest influence on the structure of the long-wave range of the spectrum it is possible to point to the configurations  $4d^9 4f^{N+1} 5p^5$ ,  $4d^9 4f^{N-1} n l$  ( $n = 5 - \infty$ ;  $l = 1, 3, 5, 7$ ), and also those which are associated with the excitation of a 4s or 4p electron. Examples of configurations of the second type are provided by the configurations  $4p^4 4d^9 4f^{N+2}$ ,  $4s^0 4d^9 4f^{N+2}$ .

## 2. ELECTRON SPECTRA OF THE 4d LEVEL

The electron spectra of the 4d level, obtained with high resolution, give more complete information on the details of the fine structure of the configuration  $4d^9 4f^N$  than the  $L\gamma_{1,9}$  and the  $L\beta_{2,14}$  spectra, since when they are obtained there is no distorting influence of the natural width of the 2p level.

The calculation of the structure of the spectra is simplified considerably if it is assumed that the relative values of the ionization cross sections of the levels of the configuration  $n_1 l_1^{N_1-1} n_2 l_2^{N_2}$  in the excitation  $n_1 l_1^{N_1-1} n_2 l_2^{N_2} \rightarrow n_1 l_1^{N_1-1} n_2 l_2^{N_2} e l_3$  are independent of the symmetry of the electron in the continuous spectrum ( $l_3$ ) and are proportional to the sum of the probabilities of the electric dipole transitions into all levels of the configuration  $n_4 l_4^{N_4+1} n_1 l_1^{N_1-1} n_2 l_2^{N_2}$  in the transition  $n_4 l_4^{N_4+1} n_1 l_1^{N_1-1} n_2 l_2^{N_2} \rightarrow n_4 l_4^{N_4+2} n_1 l_1^{N_1-1} n_2 l_2^{N_2}$  (it is assumed that the state of the configuration  $n_1 l_1^{N_1-1} n_2 l_2^{N_2}$  is fixed). Thus the relative values of the ionization cross sections of the levels of the configuration  $4d^9 4f^N (4d^{10} 4f^N \rightarrow 4d^9 4f^N e l)$  are independent of  $l$  and are proportional to the sum of the probabilities of the transitions into the  $L_{II}$  and  $L_{III}$  levels ( $2p^5 4d^{10} 4f^N \rightarrow 2p^6 4d^9 4f^N$ ). This makes it possible not only

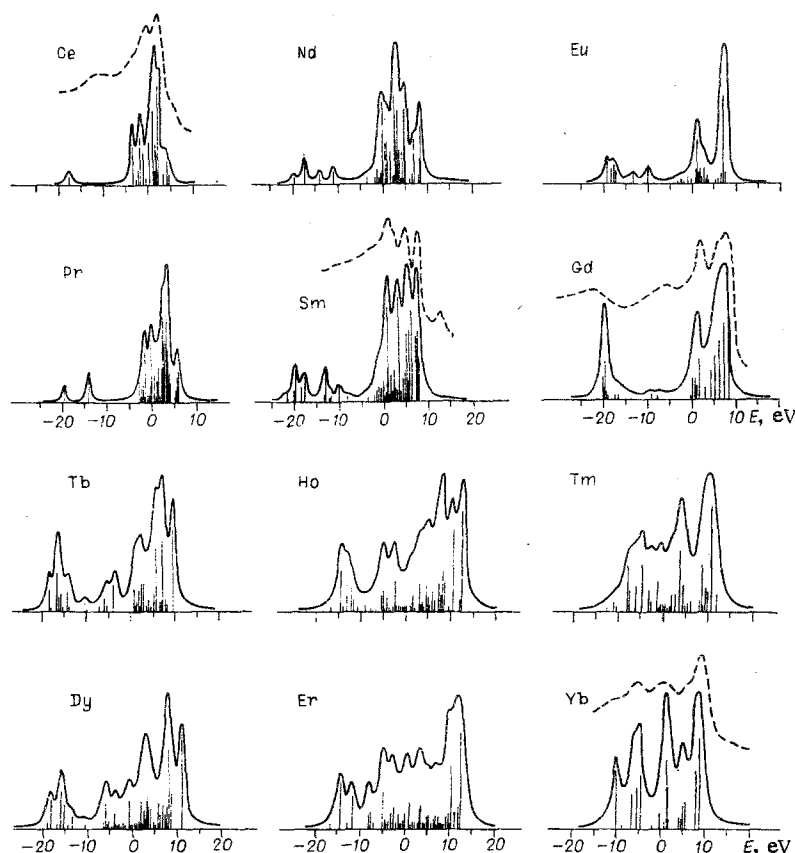


Fig. 2. Comparison of the experimental (dashed line) and theoretical (solid line) electron spectra of the 4d level.

to use the eigenvectors and eigenvalues of the secular equations for the configurations  $4d^9 4f^N$ , obtained in the calculation of the  $L\gamma_{1,3}$  and  $L\beta_{2,14}$  spectra, but also the values of the probabilities of the transitions.

The spectra obtained as a result of the calculation are given in Fig. 2. The components of the multiplets are represented in the form of dispersion curves with a width equal to the width of the components of the pre-threshold region of the  $N_{IV,V}$  absorption spectra [14] (see Table 1), and are summed. For Ce, Sm, Gd, and Yb the broken line gives the experimental data from [15, 16]. Comparison of the experimental and theoretical spectra shows that the calculation gives the basic experimental features satisfactorily. It should be noted, however, that the relative arrangement of the components in the spectra is not obtained sufficiently satisfactorily. The reason for this discrepancy is apparently that it is not a completely correct procedure to decrease the matrix elements by the same factor by changing the radial integrals. Elimination of this unsatisfactory feature is possible only in the many-configuration approximation.

### 3. ELECTRON SPECTRA OF THE 4f LEVEL

In the calculation of the energy structure of the configuration  $4f^{N-1}$ , which determines the form of the electron spectrum of the 4f level, allowance was made for the electrostatic and spin-orbital coupling of the 4f electrons. The number  $N$  of 4f electrons in the rare earth ions is assumed to be the same as that in the calculation of the structure of the  $4d^9 4f^N$  configurations. The electron spectra obtained by diagonalizing the matrices of the secular equation and calculating the ionization cross sections are compared with experiment in Figs. 3-5. It was found that to obtain good agreement between the experimental and theoretical spectra, the parameters  $F^k$  and  $\zeta_{4f}$  obtained for triply charged ions [17] must be increased. This is due to the fact that for the calculation of the electron spectra it is necessary to have the parameters  $F^k$  and  $\zeta_{4f}$  for the quadruply charged ions, and increase in the charge leads to localization of the 4f function and hence to an increase in these parameters.

For Tm and Ho, good agreement between theory and experiment is obtained by increasing  $F^k$  ( $\zeta_{4f}$ ) by factors of 1.09 (1.25) and 1.23 (1.23) respectively. It should be noted that in the spectra of Tb, Dy, and Er,

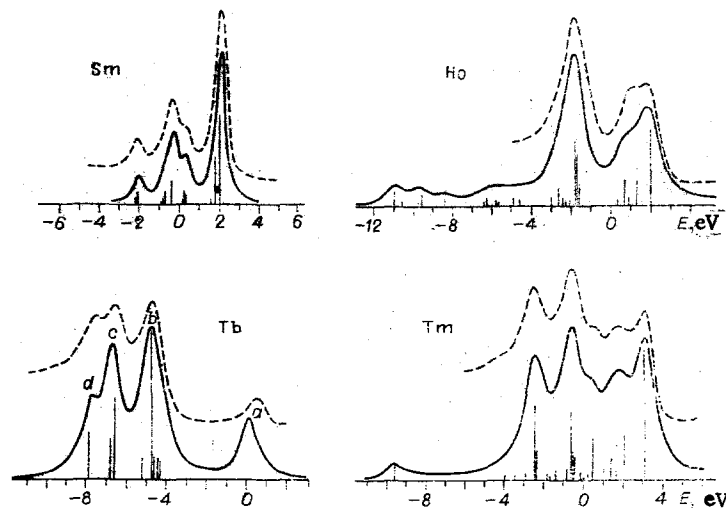


Fig. 3. Comparison of the theoretical (solid line) and experimental (dashed line) forms of the electron spectra of the 4f level of Sm, Tb, Ho, and Tm.

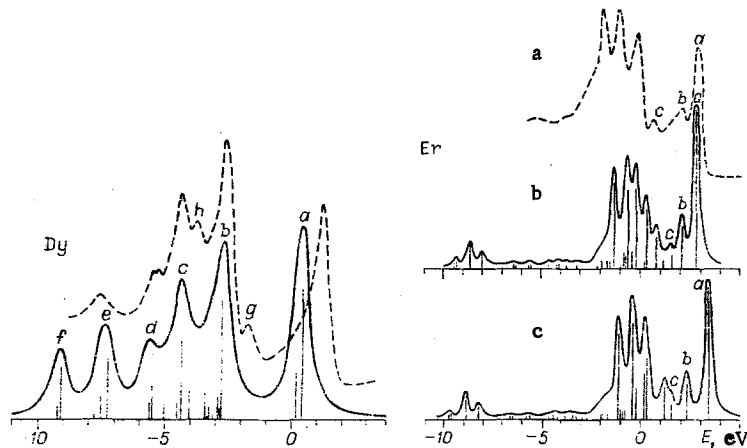


Fig. 4. Comparison of the theoretical (solid line) and experimental (dashed line) forms of the electron spectra of the 4f level of Dy and Er.

none of the values of the parameters  $F^k$  and  $\zeta_{4f}$  make it possible to obtain complete agreement between theory and experiment, so that Figs. 3-5 give the spectra of these elements with the unchanged parameters from [17]. The widths of the dispersion components used in the calculation of the form of the spectra are given in Table 1. For example, in the spectrum of Tb, in order to obtain agreement between the position of the peak b relative to the peak a, it is necessary to take the coefficient of the increase in the parameters  $F^k$  as equal to 1.15, whereas to obtain agreement between the position of the peaks c and d relative to the peak a this factor should be 1.08. Change in the magnitude of  $\zeta_{4f}$  has little influence on the form of the spectrum of Tb, and variation in this quantity does not make it possible to improve the agreement. Similar results were obtained for Dy. The coefficient of increase in the parameters, determined from the condition for obtaining agreement in the positions of the peaks b, c, d, and e relative to the peak a was found to have the values 1.30, 1.23, 1.15, and 1.18, respectively. Moreover, in the calculated spectrum the maxima g and h do not appear with change in the parameters  $F^k$  and  $\zeta_{4f}$ .

In the spectrum of Er, satisfactory agreement is observed between theory and experiment in the high-energy range of the spectrum (compare Figs. 4a and 4b), whereas the low-energy range of the spectrum shows "more relief." By increasing  $\zeta_{4f}$  by a factor of 1.4 it is possible to achieve the formation of three peaks instead of four in the high-energy range (Fig. 4b), but this increases considerably the distance of the peaks b (state  $^5I_7$ ) and c (state  $^5I_6$ ) from the peak a (state  $^5I_3$ ).

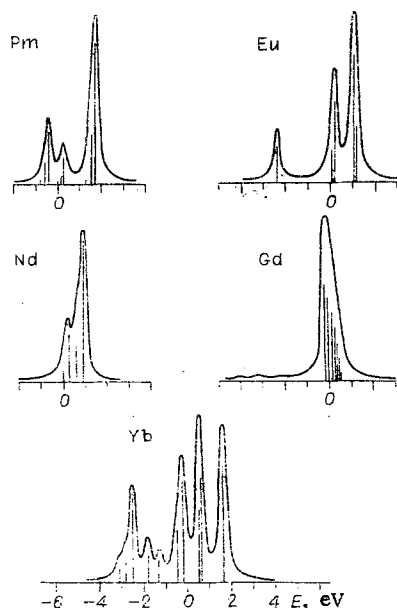


Fig. 5. Theoretical structure and form of the electron spectra of the 4f level of Nd, Pm, Eu, Gd, and Yb.

These discrepancies show that in order to obtain agreement between theory and experiment it is necessary to introduce nonlinear changes in the matrix elements, and indicate again that the factor responsible for the discrepancy is the neglect of states derived from excited configurations, that is, the restricted nature of the one-configuration approximation.

Thus the study of the  $LY_{1,9}$  and  $L\beta_{2,14}$  lines, and also the electron spectra of the 4d and 4f levels, carried out in the present work, confirm the main conclusions of [7, 8, 12] regarding the possibility of explaining the complex form of these spectra on the basis of the structure of the hole configurations  $4d^9 4f^N$  and  $4f^{N-1}$ . At the same time, more detailed comparison of the experimental results and the spectra calculated for all the REE has made it possible to reveal a number of new discrepancies between experiment and the one-configuration theory. The nature of these discrepancies indicates the need for a many-configuration calculation.

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