On the Interpretation of the level structure of the Ground 3d^5 Manifold of Mn III, Fe IV, Co V and Ni VI

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Abstract. The level structure of the ground 3d^5 configuration of Mn^{2+}, Fe^{3+}, Co^{4+} and Ni^{5+} ions was theoretically interpreted by means of a least-squares fit of the energy parameters to the observed values within the framework of the single-configuration approximation. In the Hamiltonian in addition to real electrostatic, spin-orbit, and spin-spin interactions, electrostatic and spin-orbit interactions correlated by configuration mixing were included. It was shown that the correct positions of almost all the energy levels are determined when the Hamiltonian includes the terms of the lineal (two-body operators) and nonlinear (three-body operators) theory of the configuration interaction. The most correct theoretical description of the experimental spectra was obtained by taking into account relativistic interactions and correlation effects of spin-orbit interactions. Adjustable parameters of the interactions included into the Hamiltonian were found.

1. Introduction
The theory of the energy levels of iron-group and rare-earth paramagnetic ions with open d and f shells is usually developed within the framework of the single-configuration approximation. Furthermore, in most cases, among all the interactions occurring in a free many-electron atom, only the strongest interactions are taken into account, such as the electrostatic repulsion of electrons and the spin-orbit interaction. In this case, consistent quantum-mechanical calculations yield positions of the energy levels that differ from the experimental positions by several tens or, sometimes, hundreds of reciprocal centimeters. Because of this, the energy spectra are very often analyzed using semi empirical methods, with which the best possible agreement between the theory and experiment is achieved by varying the radial integrals considered as free parameters.

Such semi-empirical variants of the theory allow one to leave the framework of the single-configuration approximation and take into account the correlation effects, as well as all relativistic interactions. This is done by replacing the real Hamiltonian matrix with the matrix of some effective energy operator, which, in addition to the known interactions binding the states of the main configuration, includes the contributions of configuration interactions, which leads to the appearance of new two- [1-6] and three-body [7, 8] operators. As a result, the total number of necessary radial parameters...
in the effective Hamiltonian describing the d^n configuration of a free ion becomes equal to 11 and increases to 19 for the f^n configuration.

Nevertheless, the effective Hamiltonian with 19 operators and parameters of a free atom with an open 4f shell is frequently used in practical calculations for interpretation of the observed spectra of rare-earth ions in crystals and allows one to find the positions of theoretical energy levels, which often differ from the experimentally determined levels only by several reciprocal centimeters [9-11]. As for the elements of the iron group, which have an open 3d shell, their optical spectra have never been described using the total effective Hamiltonian with 11 parameters and operators. At best, one uses a free-ion Hamiltonian containing four parameters [12, 13], namely, B and C, characterizing the electrostatic interaction of electrons, 3dζ, representing the spin-orbit interaction, and α, associated with the configuration interaction. The reason for this is that, in addition to narrow lines, the spectra of transition metals in crystals always contain broad bands of electron-vibrational character [14] and, to explain their origin, one has to include into the Hamiltonian terms describing the interactions of an ion with crystal lattice vibrations, which are stronger than the neglected interactions in the free ion. At the same time, the effects of weak (relativistic and configuration) interactions are often observed against the background of broad bands and, moreover, the positions of the bands themselves sometimes cannot be explained without taking into account these interactions. In such cases, it is necessary to use a more precise free-ion Hamiltonian.

In many papers [6, 15-18], the behavior of free ions of the iron group was described with the use of Hamiltonians with more than four parameters. The highest accuracy in interpretation of the optical spectra was reached using a Hamiltonian obtained on the basis of the group-theoretical considerations and containing 17 effective orthogonal operators [19, 20]. However, due to the great number of orthogonal operators, the complexity of their physical interpretation, and the lack of experimental data, the technique of orthogonal operators will hardly find wide use in description of the behavior of impurity ions in crystals in the near future.

In the present study, we propose an interpretation of the level structure of the 3d^5 ground manifold of Mn III, Fe IV, Co V and Ni VI, some of which can serve as dopants to impart important technological properties to various crystals. We will describe theoretically the experimental spectra of such ions [21], using an 11-parameter Hamiltonian in order to determine the role of various interactions and to use the data obtained for the analysis of the optical spectra of these ions in crystals.

2. Hamiltonian of a many-electron atom

To describe the states of the 3d^n configurations, we will write the effective free-ion Hamiltonian in a form similar to that used for rare-earth ions with 4f^n configurations:

\[ H = \sum_{k=0,2,4} F^k f_k + \zeta_{3d} A_{so} + \alpha L(L+1) + \beta G(R_s) + \sum_{k=2,3} T^k t_k + \sum_{k=2,4} M^k m_k + \sum p^k p_k \]  

(1)

The first term in (1) represents the electrostatic repulsion of electrons (\(H_{EL}\)), characterized by the radial Slater integrals \(F^k(3d, 3d)\). The next term is the ordinary spin-orbit interaction of electrons (\(H_{SO}\)), determined by the parameter \(\zeta_{3d}\). Then, we have the terms pertaining to the theory of the linear configuration interaction (CI) (\(H_{L,CI}\)), characterized by the parameters α and β [4]. The operator \(\alpha L(L+1)\), where \(L\) is the angular momentum of the ion, adequately represents the relativistic orbit-orbit interactions as well [22]. The factor \(G(R_s)\) in the term \(\beta G(R_s)\) is the Casimir operator of the \(R_s\) group. The fifth term allows us to take into account the nonlinear CI effects (\(H_{NL,CI}\)) (the effective three-body operators), determined by configurations with single-electron excitations. These interactions are characterized by the parameters \(T^2\) and \(T^3\) [8]. The next term describes the spin-spin (\(H_{SS}\) and spin-other-
orbit \(H_{SO} \) relativistic interactions, determined by the radial Marvin integrals \(M^Q(3d, 3d)\) [23]. The last term in (1) corresponds to the electrostatically correlated spin-orbit interaction of electrons \(H_{ELSO}\) [5, 6], characterized by the parameters \(P^2\) and \(P^4\), which were defined in [19].

The matrix elements of the operators \(A_{SO}\) and \(m_i\), dependent on the angular variables, were calculated by the standard technique of irreducible tensor operators, \(n_j\) symbols, and fractional parentage coefficients. A detailed description of the necessary mathematical apparatus can be found in monographs [24-28]. The electrostatic interaction matrices \(f_k\) and the reduced matrix elements of the double tensor operator \(V^{(11)}\) necessary for \(A_{SO}\) were taken from the tables given in [29]. For the eigenvalues of the Casimir operator of the \(R_5\) group, we used the expression [24]

\[
\langle w_1 w_2 \rangle G(R_3) \langle w_1 w_2 \rangle = \frac{1}{6} \left( w_1(w_1 + 3) + w_2(w_2 + 1) \right),
\]

where \(w_1\) and \(w_2\) are the parameters characterizing the irreducible representations of the \(R_5\) group, which are also given in the tables of [29] for all the states of the configurations under study. The matrix elements of the three-body operators \(t_k\) of the nonlinear CI theory were taken from [8]. The reduced matrix elements of the \(p_k\) operators in \(H_{ELSO}\) were expressed in terms of the matrix elements of the orthogonal operators \(z_i\) introduced in [19]. The total matrix of Hamiltonian (1) was composed using all the states of the 3d\(^5\) configuration present in the scheme of the total angular momentum \(SLJM_f\).

### 3. Interpretation of the optical spectra

To interpretation theoretically the spectra of ions with \(I^n\) configurations, we have used a program (developed by E. N. Irinyakov) for self-consistent comparison of the theoretical \((E^T)\) and experimental \((E^E)\) data for energy levels by minimizing the residual \(F(x_1, \ldots, x_n) = \sum_i W_i (E_i^E - E_i^T)^2\), where \(x_i\) are the variable parameters and \(E_i\) and \(W_i\) are the energy and the weight factor of the \(i\)th level. The program allows one to describe the experimental energy levels most correctly and to find the best set of parameters under the condition of an unambiguous correlation between the theoretical and the experimental energy levels. It is this situation that we consider since, for all the ions the positions of all the 37 energy levels of the ground 3d\(^5\) configuration are found from the analysis of the optical spectra and the energy levels are unambiguously attributed to the suggested Russell-Saunders states.

As an example, table 1 shows the interaction parameters calculated for the ion Ni\(^{5+}\) by four variants (I, II, III, and IV) differing by the number of terms taken into account in Hamiltonian (1). The first column of table 1 lists the parameters used and some characteristics of the calculation accuracy. Here, the Racah parameters \(B\) and \(C\) are related to the Slater integrals \(F^k\) by the formulas \(B = (9F^2 - 5F^4)/441\) and \(C = 5F^4/63\); \(n\) is the number of experimentally measured energy levels (coinciding with the number of levels in the spectrum of the 3d\(^5\) configuration of the Ni\(^{5+}\) ion) and \(m\) is the number of variable parameters necessary for the calculation of the rms error \(\sigma\) for each calculation variant \(\sigma = \sqrt{\sum_{i=1}^{n} (E_i^T - E_i^E)^2 / (n - m)}\); and \(\Delta_m = \max |E_0^E - E_i^E|\) is the absolute value of the maximum deviation of the calculated energy of the level \(E_i^T\) from the experimental energy \(E_i^E\).

It is seen from table 1 that both the rms error \(\sigma\) and the deviation \(\Delta_m\) decrease considerably as the terms \(H_{LCL}, H_{SLCL}, H_{SS}, H_{SO},\) and \(H_{ELSO}\) with the parameters \(\beta, T_2, T_3, M^0, M^2, P^2,\) and \(P^4\) are successively taken into account. From variant I to variant IV, the error \(\sigma\) decreases by a factor of about 3. The first calculation version, which takes into account only the \(H_{EL}\) and \(H_{SO}\) interactions, yields incorrect order for several multiplets. When only one of the \(H_{LCL}\) terms with the parameter \(\alpha\) are taken into account (variant I), the maximum deviation \(\Delta_m\) is observed for the level \(2^2S_{1/2}\); the maximum deviation for
is observed for the lowest levels $^2F_{7/2}$ and $\Delta m$ becomes considerably smaller as we add the term with the parameter $\beta$ (variant II). At the same time the error $\sigma$ decreases approximately 2-fold.

**Table 1.** Numerical values of different sets of adjustable parameters (in cm$^{-1}$) for the 3d$^5$ configuration of the Ni$^{5+}$ ion

| Parameter | I       | II      | III     | IV      |
|-----------|---------|---------|---------|---------|
| $B$       | 1419    | 1419    | 1420    | 1420    |
| $C$       | 5176    | 5215    | 5208    | 5210    |
| $\xi$     | 894     | 901     | 906     | 932     |
| $\alpha$  | 100     | 108     | 109     | 109     |
| $\beta$   | -245    | -222    | -232    |         |
| $T^2$     |         | -7.3    | -7.4    |         |
| $T^3$     |         | 24      | 22      |         |
| $M^6$     |         |         | 3.41    |         |
| $M^2$     |         |         | 3.21    |         |
| $p^2$     |         |         | 65      |         |
| $p^4$     |         |         | 47      |         |
| $m$       | 4       | 5       | 7       | 11      |
| $\sigma$  | 138.9   | 65.6    | 61.4    | 58.1    |
| $\Delta m$| 381 ($^2S_{1/2}$) | 157 ($^2F_{7/2}$) | 122 ($^2F_{7/2}$) | 136 ($^2F_{7/2}$) |

Note: $n$ (I-IV) = 37; $n$ and $m$ are dimensionless integers.

In the calculations by variants I and II, the theory predicts a wrong fine structure of the $^4G$ (the $^4G_{11/2}$, $^4G_{5/2}$, $^4G_{9/2}$ and $^4G_{7/2}$ instead of the $^4G_{5/2}$, $^4G_{7/2}$, $^4G_{11/2}$ and $^4G_{9/2}$) and $^4D$ (the $^4D_{3/2}$ and $^4D_{5/2}$ levels are interchanged) terms. The introduction of the $H_{NLCl}$ operators (variant III) no changes the situation, leading to the incorrect position of the some energy levels but to a small decrease in $\sigma$. The maximum deviation $\Delta m$ in this case is observed also for the $^2F_{7/2}$ level but it becomes considerable less. The improvement of the theoretical description of the experimental spectra is achieved by taking into account the relativistic interactions ($H_{SS}$ and $H_{SOO}$ operators) and the correlation effects of the spin-orbit interaction ($H_{SLO}$ operators). The introduction of these operators leads to correct position of all the energy levels. Table 2 presents the theoretical $E_i^T$ and experimental $E_i^E$ energies of all the levels together with the difference $\Delta_i = E_i^T - E_i^E$, enabling one to see how well the theory agrees with the experiment in the case of variant IV. Table 2 also gives the compositions of the state terms in the wave functions of the given levels. The parameters corresponding to the best theoretical description of the experimental energy levels and the values of $\sigma$ obtained in the calculations by variant IV for all the ions considered are given in table 3. This table also repeats for comparison the parameters for the Ni$^{5+}$ ion. The agreement between the theory and experiment for the other ions of the isoelectronic sequence of the 3d$^5$ configuration is somewhat worse to that obtained for the Ni$^{5+}$ ion (table 2). For all the other ions theory predicts a wrong fine structure of the second and third $^2D$ (numbering of the same name terms in order of increasing of energy) and $^2P$ terms. Moreover for the ions Fe$^{3+}$ and Co$^{4+}$ a wrong fine structure is found for $^4F$ and second $^2G$ terms and for ions Mn$^{2+}$ and Fe$^{11+}$ the $^2I_{11/2}$ and $^2I_{13/2}$ levels and $^2F_{5/2}$ and $^2F_{7/2}$ levels (second $^2F$ term) are interchanged. The largest deviation $\Delta m$ is obtained for the energy level $^2D_{5/2}$ (second term) of Mn$^{2+}$ ion for the energy level $^2D_{3/2}$ (third term) of Fe$^{3+}$ ion and for the energy level $^2F_{7/2}$ (second term) of Co$^{4+}$ ion. The reason of these differences between the theory and the experiments is apparently that the this theory is strictly speaking only applicable to the cases of well isolated ground configurations of equivalent electrons. From the ions considered this situation
Table 2. Energy levels (in cm$^{-1}$) and state compositions (in %) for the 3d$^5$ configuration of the Ni$^{5+}$ ion obtained using the parameters of variant IV

| $J$ | $E^T$ | $E^E$ | $\Delta$ | State compositions |
|-----|-------|-------|----------|-------------------|
| 5/2 | 0.0   | 0.0   | 0.0      | 99.81 $^6S + 0.19 \ ^6P$ |
| 11/2| 41967.4 | 41920.9 | 46.5 | 99.74 $^4G + 0.26 \ ^2H$ |
| 5/2 | 42029.5 | 42003.6 | 25.9 | 99.16 $^4G + 0.73 \ ^2F1 + 0.07 \ ^4F + 0.02 \ ^4D$ |
| 9/2 | 42048.8 | 42023.2 | 25.6 | 99.82 $^4G + 0.11 \ ^2F + 0.07 \ ^2H + 0.01 \ ^4G1$ |
| 7/2 | 42057.3 | 42035.1 | 22.2 | 99.55 $^4G + 0.30 \ ^2F1 + 0.11 \ ^4F + 0.02 \ ^4D$ |
| 5/2 | 45876.6 | 45884.2 | -7.6 | 89.01 $^4P + 9.49 \ ^4P + 0.86 \ ^2D3 + 0.35 \ ^2D1$ |
| 3/2 | 46126.9 | 46104.4 | 22.5 | 99.74 $^4G + 0.26 \ ^2F1 + 0.07 \ ^4F + 0.02 \ ^4D$ |
| 1/2 | 46340.9 | 46324.8 | 16.1 | 99.08 $^4P + 2.80 \ ^2D3 + 0.12 \ ^2S$ |
| 7/2 | 42048.8 | 42023.2 | 25.6 | 99.82 $^4G + 0.11 \ ^2F + 0.07 \ ^2H + 0.01 \ ^4G1$ |
| 5/2 | 45876.6 | 45884.2 | -7.6 | 89.01 $^4P + 9.49 \ ^4P + 0.86 \ ^2D3 + 0.35 \ ^2D1$ |
| 3/2 | 46126.9 | 46104.4 | 22.5 | 99.74 $^4G + 0.26 \ ^2F1 + 0.07 \ ^4F + 0.02 \ ^4D$ |
| 1/2 | 46340.9 | 46324.8 | 16.1 | 99.08 $^4P + 2.80 \ ^2D3 + 0.12 \ ^2S$ |
| 5/2 | 50793.8 | 50777.6 | 16.2 | 99.82 $^4G + 0.26 \ ^2F1 + 0.07 \ ^4F + 0.02 \ ^4D$ |
| 3/2 | 50801.6 | 50780.5 | 21.1 | 99.13 $^4D + 7.88 \ ^4P + 0.19 \ ^2F + 0.07 \ ^2D2$ |
| 11/2| 61182.4 | 61196.0 | -13.6 | 98.24 $^2I + 1.74 \ ^2H + 0.01 \ ^4G$ |
| 13/2| 61296.0 | 61279.5 | -10.5 | 100.00 $^2I$ |
| 5/2 | 64083.2 | 64152.4 | -69.2 | 50.60 $^2D3 + 30.71 \ ^2F1 + 15.81 \ ^2D2 + 1.31 \ ^2F$ |
| 3/2 | 65166.1 | 65173.5 | -7.4 | 95.08 $^2F + 4.61 \ ^2G2 + 0.20 \ ^2H + 0.11 \ ^4G$ |
| 7/2 | 67173.4 | 67085.1 | 88.3 | 95.42 $^2F1 + 2.47 \ ^2F + 1.33 \ ^2G2 + 0.31 \ ^2F2$ |
| 5/2 | 68540.6 | 68444.9 | 95.7 | 51.31 $^2F + 38.29 \ ^2F1 + 7.62 \ ^2D2 + 2.40 \ ^2D1$ |
| 9/2 | 72850.4 | 72908.8 | -58.4 | 74.24 $^2H + 23.57 \ ^2G2 + 2.16 \ ^2F + 0.03 \ ^4G$ |
| 11/2| 73702.9 | 73756.6 | -53.7 | 98.00 $^2H + 1.76 \ ^2I + 0.25 \ ^4G$ |
| 7/2 | 74636.2 | 74627.7 | 8.5 | 97.77 $^2G2 + 0.97 \ ^2F1 + 0.96 \ ^2F + 0.22 \ ^2F2$ |
| 9/2 | 75455.7 | 75441.7 | 14.0 | 71.77 $^2G2 + 25.50 \ ^2H + 2.66 \ ^4F + 0.05 \ ^4G1$ |
| 5/2 | 79438.7 | 79391.4 | 47.3 | 97.87 $^2F2 + 1.09 \ ^2F + 0.66 \ ^2D2 + 0.36 \ ^2F1$ |
| 7/2 | 79472.3 | 79608.3 | -13.6 | 98.09 $^2F2 + 1.46 \ ^2F + 0.18 \ ^2F2 + 0.17 \ ^2F1$ |
| 1/2 | 86469.7 | 86532.1 | -62.4 | 99.75 $^2S + 0.12 \ ^2P + 0.12 \ ^2P$ |
| 3/2 | 96530.6 | 96461.2 | 69.4 | 99.82 $^2D2 + 0.08 \ ^2D + 0.07 \ ^2D1 + 0.03 \ ^2D3$ |
| 5/2 | 96566.2 | 96566.5 | -0.3 | 99.18 $^2D2 + 0.65 \ ^2F2 + 0.12 \ ^2D + 0.03 \ ^2D1$ |
| 9/2 | 107893.6 | 107848.3 | 45.3 | 99.94 $^2G1 + 0.06 \ ^2G2 + 0.01 \ ^4G$ |
| 7/2 | 107905.0 | 107887.0 | 18.0 | 99.73 $^2G1 + 0.18 \ ^2F2 + 0.09 \ ^2G2 + 0.01 \ ^4G$ |
| 3/2 | 129969.2 | 129951.6 | 17.6 | 99.15 $^2P + 0.62 \ ^2D1 + 0.23 \ ^2D3$ |
| 1/2 | 130025.9 | 130025.9 | -17.8 | 99.87 $^2P + 0.12 \ ^2S + 0.01 \ ^4D$ |
| 5/2 | 140880.4 | 140922.2 | -41.8 | 76.64 $^2D1 + 23.30 \ ^2D3 + 0.04 \ ^2D2 + 0.01 \ ^4F$ |
| 3/2 | 140907.7 | 141006.8 | -99.1 | 76.01 $^2D1 + 23.03 \ ^2D2 + 0.84 \ ^4P + 0.10 \ ^2D2$ |

take place only for Ni$^{5+}$ because the energies of levels of its ground configuration stretch for 141006 cm$^{-1}$, but the energies of the levels closest of the excited 3d$^4$4s configuration begin with 307843 cm$^{-1}$. 


For the Co\(^{4+}\) ion the interval between energies of the levels of the ground and first excited 3d\(^4\) 4s configurations is equal to 80410 cm\(^{-1}\) and for the Fe\(^{3+}\) ion it already is equal only 19508 cm\(^{-1}\). However, the levels of the 3d\(^5\) ground configuration of Mn\(^{2+}\) ion, beginning with approximately 62000 cm\(^{-1}\), are strongly overlapped with the levels of the 3d\(^4\) 4s configuration, while the upper 2D\(_{3/2}\) level of ground configuration locate at 89543 cm\(^{-1}\). In this context, the 3d\(^5\) configuration of the Mn\(^{2+}\), Fe\(^{3+}\) and Co\(^{4+}\) ions, apparently, can not be considered as well isolated.

### Table 3. Numerical values of parameters (in cm\(^{-1}\)) for the 3d\(^5\) configuration of the ions Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{4+}\) and Ni\(^{5+}\) obtained in variant IV

| Ion     | B    | C    | \(\xi\) | \(\alpha\) | \(\beta\) | \(T^2\) | \(T^3\) | \(M^0\) | \(M^2\) | \(P^2\) | \(P^4\) | \(\sigma\) |
|---------|------|------|---------|----------|---------|--------|--------|--------|--------|--------|--------|---------|
| Mn\(^{2+}\) | 917  | 3224 | 345     | 65       | 207     | 21     | 17     | 2.72   | 1.22   | 117    | 99     | 77.7    |
| Fe\(^{3+}\) | 1101 | 3946 | 486     | -14     | -14     | 17     | 20     | 3.01   | 1.33   | 96     | 81     | 65.6    |
| Co\(^{4+}\) | 1264 | 4598 | 685     | 96      | -145   | 0.1    | 21     | 3.12   | 2.94   | 70     | 59     | 55.0    |
| Ni\(^{5+}\) | 1420 | 5210 | 932     | 109     | -232   | -7     | 22     | 3.41   | 3.21   | 65     | 47     | 58.1    |

During the calculations within version IV, we found that the iterative procedure with variations in all parameters very rapidly converged to different minima of the merit function values; however, the sets of parameters of magnetic interactions obtained in this case were physically unacceptable. In particular, the Marvin integral \(M^2\) was sometimes larger in magnitude than the integral \(M^0\), or some of these integrals turned out to be negative. At the same time, it is known that all integrals \(M^k\) are positive by definition and, in addition, they should decrease in magnitude with increasing \(k\). Sometimes, on the contrary, the integrals \(M^k\) satisfied the above-mentioned conditions but the parameters \(P^k\), characterizing the \(H_{ELSO}\) interaction, demonstrated anomalous behavior; exactly parameter \(P^4\) was larger in magnitude than the parameter \(P^2\). Physically, since the matrix elements of \(H_{ELSO}\) are products of the matrix elements of \(H_{EL}\) and \(H_{SO}\), the parameters \(P^k\) should behave like analogous Slater integrals \(F^k\), i.e., should be positive and decrease with an increase in \(k\). The existence of many sets of parameters at which approximately identical minimum values of the merit function are obtained apparently indicates that the problem of anomalous behavior parameters \(M^k\) or \(P^k\) is a purely mathematical problem related to the difficulty of searching for a physically acceptable minimum of a function of many variables. In this case, one could try to solve this problem through reasonable choice of the initial values of the parameters and use such an algorithm in iterations that would not allow the program to leave at any price the local minimum of the merit function. We imposed the following condition on the initial parameters \(M^2\) and \(P^4\): their ratios \(M^2/M^0\) and \(P^4/P^2\) should correspond to those obtained in [30] in the interpretation of optical spectra of iron-group ions with 3d\(^3\) and 3d\(^7\) ground configurations. As an algorithm, we used the Fletcher–Powell gradient method [31], which provides the slow but reliable achievement of the nearest minimum. In the initial stage of the calculations, we varied all parameters except for \(M^2\) and \(P^4\) and, after attainment of the intermediate minimum, all the parameters including \(M^2\) and \(P^4\) were varied. The procedure rapidly converged to a new local minimum at the values of the parameters that are listed in table 3.

### 4. Discussion of the results

For most interactions, the parameters given in table 3 in general agree with the data obtained by similar calculations in other studies. It makes no sense to compare our results with the data of these papers in more detail because different authors used different, not our, sets of parameters. However, we may conclude that the use of Hamiltonian (1) allowed us to obtain the most correct semi empirical description of the experimental spectra. Further progress in such studies can be achieved, as was shown in
on the example of the Cr$^{3+}$ and Ni$^{3+}$ ions, only by additionally taking into account the correlation effects of magnetic interactions using the Hamiltonian containing 17 effective orthogonal operators. As follows from Table 3, most of the parameters are positive and monotonically increase with increasing atomic number $Z$ of the element in isoelectronic sequence. The $\beta$ parameter of the linear CI theory and the electrostatically correlated spin-orbit interaction parameters $P_2$ and $P_4$, in contrast, decreases with increasing $Z$. The $\beta$ parameter is positive at the beginning of sequence and then changes its sign.

It should be noted that, in addition to the four calculation variants considered above, we performed calculations in which, along with the parameters of variant III, either the relativistic $H_{SS}$ and $H_{SOO}$ interactions or the correlation $H_{ELSO}$ effects were additionally taken into account. In another variant, we varied all the parameters of variant IV but excluded the $H_{SS}$ interaction from the matrix of Hamiltonian (1). As a result, it was found that the theoretical interpretation of the spectra by the two variants (taking into account either only the parameters $M_0$ and $M_2$ or only $P_2$ and $P_4$) was considerably worse as compared to variant IV. In contrast, the calculation excluding the $H_{SS}$ interaction gives even a slightly better coincidence between the theory and experiment. These calculations show that, for the description of the fine structure of the spectra of iron-group elements to be successful, it is necessary to take into account all the spin-dependent interactions simultaneously. The same conclusion was drawn by the authors of [6] from the analysis of the spectra of doubly ionized atoms of the iron-group elements Me III (Me = Ti, V, Cr, Mn, Fe, Co, and Ni).

5. Conclusions
The energy levels of the ground configuration of free ions Mn$^{2+}$, Fe$^{3+}$, Co$^{4+}$ and Ni$^{5+}$ are satisfactorily interpreted theoretically only if the Hamiltonian contains the two- and three-body operators representing the effects of correlation of the electrostatic interaction of electrons by configuration mixing. The best agreement between the theory and experiment is achieved when all the spin-dependent relativistic interactions and the correlation effects of the spin-orbit interaction are additionally and simultaneously taken into account. The found adjustable parameters of all the interactions monotonically change with the atomic numbers of the elements in the isoelectronic sequence. The current practice of analysis of the behavior of iron-group ions in crystals using a free-ion Hamiltonian that involves terms with only four parameters ($B$, $C$, $\xi$, and $\alpha$) seems to be erroneous since it is incapable of predicting correctly the levels of even a free ion. Such calculations may lead to wrong conclusions concerning the crystal-field effects and the electron-phonon interaction. Most appropriate is, evidently, the method based on the use for a free ion of an 11-parameter Hamiltonian, with the parameters of the weak interactions being fixed while the parameters of the crystal field and strong interactions are varied.

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