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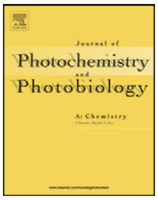

A way of lowering the uncertainty in values of crystal field parameters derived from the spectra of Ln^{3+} ions in cubic field with rhombic distortions

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ABSTRACT

Potentialities of increasing the reliability of crystal field parameters (CFPs) obtained from an analysis of Stark splitting of *J*-states of spin–orbital multiplets $^{2S+1}L_J$ of the Ln^{3+} ions in cubic crystal field with rhombic distortions via a reduction of the region of their final fitting are examined. Suggested method of lowering the uncertainty of the CFP consists in determination of the relation of general cubic CFP of the fourth and sixth ranks (B_4 and B_6) by comparison of a fragment of the experimental Ln^{3+} spectrum with well known picture of dependences of Stark splitting of *J*-states on the relation mentioned. These dependences were calculated many years ago and published as a set of diagrams by K. Lea, M. Leask, W. Wolf, J. Phys. Chem. Solids, 23 (1962) 1381. Cubic parameters derived from the relation determined can be used for a narrowing of the fitting region for the rest of CFP. The method described is applied to the luminescence spectra of dimeric europium carboxylates with heterocyclic diimines. To justify application of this method to the spectra of Eu^{3+} ions in crystal field of cubic symmetry with rhombic distortions it was shown that the influence of the second rank components of the crystal field on the relative Stark splitting of *J*-states of europium ions is minimal for $J = 3, 4$. In some cases, this peculiarity provides an approach of Stark splitting of the levels with $J = 4$ in spectra of compounds with rhombic distortions of cubic crystal field to the image of the splitting at an effective field of cubic symmetry. It was demonstrated that for europium complexes under consideration the relation of the general CFP $B_4/B_6 > 119$. Consequently, the CFPs of the sixth rank are very small and the region of fitting of the rest of CFP can be appreciably reduced.

1. Introduction

Fast development of methods of obtaining and processing the single-crystal X-ray diffraction data on crystal structures was accompanied by a plenty of carelessly conducted spectroscopic investigations of lanthanide coordination compounds that led to imbalance of joint understanding of the results of these studies. One should expect that success of the X-ray studies would facilitate a progress of spectroscopic methods of combined investigations, but in reality it has led to stagnation of spectroscopy, superficial interpretation of the results of spectroscopic part of the studies and to emergence of a lot of “spam” in items of combined papers dealing with optical spectroscopy. Unfortunately, it is one of the most probable negative consequences of scientific progress the community was many times warned about by futurologists [1]. It was ever said that when the results calculated were not analyzed properly the consequences may be much more disastrous than in cases of the lack of such calculations. This point can be abundantly illustrated by uncountable number of publications of modern combined papers on the structure and spectra of lanthanide (mostly of europium or terbium) compounds. An extremely low resolution of luminescence spectra can be taken as common feature of these deficient publications. In these cases the results of analysis of optical spectra are just demonstrating the presence of specific lanthanide ions in the samples and nothing else. As these spectra cannot be used for obtaining the data on Stark splitting of *J*-states of spin–orbital multiplets $^{2S+1}L_J$ of the Ln^{3+} ions, they are not sufficient even for demonstration of an intrinsic relation of both parts of combined investigations. At the same time, some publications of the last years, for example, the most recent of them [2,3] on analysis of the crystal field (CF) and the crystal field parameters (CFPs) for lanthanide compounds with a various symmetry of Ln^{3+} surroundings can serve as exclusions from deficient studies mentioned above. In particular, authors of these papers over many years had worked on systematic description of spectroscopic properties of elpasolites, $Cs_2NaLnCl_6$, and other compounds with cubic symmetry of CF. In this case, one needs only two cubic (or “general”) CFP for description of Stark splitting of *J*-states of the Ln^{3+} ions: of the fourth rank, B_4, and the

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sixth rank, B_6, or their relation. In cases of lowering the CF symmetry, there is a chance to use the relation of cubic CFP decreasing the uncertainty of the set of the residual CFP describing Stark splitting of *J*-states. However, this opportunity depending on the values of non-cubic components of CF, first of all, on the components of CF of the second rank was often overlooked in spectroscopic studies of the last half of the twentieth century. The work presented here is undertaken for determination of the ratio of cubic or general CFP for the series of lanthanide luminescent materials, namely, ternary dimeric europium aliphatic and aromatic carboxylates with heterocyclic diimines (1,10-phenanthroline (Phen) and 2,2′-bipyridine (Bpy)) with CF declining from cubic symmetry [4–6]. It should be regarded as the way of balancing the results of X-ray and optical investigations of complex compounds of the kind.

A spectacular property of crystal structures of these compounds consists in close relation of configurations of coordination sphere of Ln^{3+} ion, which are quasi-independent on the architecture of carboxylate ligands. Taking, for example, the europium propionate with phenanthroline one can find out from the X-ray structural data that corresponding crystals are built of centrosymmetric dimers $[Eu(C_2H_5COO)_3{\cdot}Phen]_2$ with the center of symmetry situated strictly between two Eu^{3+} ions [4]. Six propionate anions of the dimer form three pairs of equivalent anions. Coordination function of carboxylic groups of the first pair is cyclic, the function of the second pair of carboxylates is bridging, and the function of the third pair is bridging-cyclic. So, the coordination polyhedron of Eu^{3+} ion is formed by seven oxygen atoms of carboxylate anions and two nitrogen atoms of phenanthroline (C.N. = 9). The polyhedron can be regarded as a distorted one-capped tetragonal antiprism or a three-capped trigonal prism.

In process of analysis of the Stark splitting of *J*-states of spin–orbital multiplets it will be shown here that for the series of dimeric lanthanide carboxylates with heterocyclic diimines the cubic crystal field components of the sixth rank are especially small in comparison to the components of the fourth rank. That substantially lowers the variation region and evaluation uncertainty in process of fitting the adjustable CFP.

2. Experimental

The syntheses of europium compounds studied in this work as well as the methods of obtaining of their luminescence spectra were described in Refs. [4,5].

3. General procedure of calculations of CFP. Using the diagrams of Stark splitting of Ln^{3+} *J*-states for determination of CFP of the fourth and sixth ranks

After classic work [7] on systematization and description of the spectra of lanthanide ions under influence of CF, the task of evaluation and determination of CFP has been solved many times. In studies of nuclear magnetic resonance and optical spectra of lanthanide ions, where electrostatic repulsion of electrons and spin–orbital interaction were stronger than interaction with ligands, it was solved in the second order of perturbation theory by method of Tesseral harmonics (equivalent operators) [8,9] or by more general methods of spherical harmonics and tensor operators [10,11]. Those three methods are differing by the way of expansion of the CF operator in series of harmonics enumerated, whose matrix elements should be calculated for determination of matrix elements of CF operator. Tesseral harmonics, we will use later in implicit form, speaking of determination of CFP, are described by operators of Cartesian space coordinates that could be substituted by equivalent operators of angular moments with well known matrix elements (here is the method of equivalent operators [8,9]) that are, after all, used for computing of matrix elements of CF operators. In the special case of studies of low-energy *J*-term (or states) of the lowest spin–orbital multiplet this problem can be divided in two steps. The first step consists in the measurements and interpretation of Stark splitting of *J*-states of experimental spectra in the CF of definite symmetry. If in course of interpretation of experimental spectra one could not determine the representations of all possible Stark components of *J*-states in the CF (it can be conditioned, for example, by low signal to noise ratio as it occurs in studies of EuP_5O_{14} polarized spectra in [12]), one still can find positions of unknown Stark components using the invariants of the crystal field theory, that are known functions of CFP and Stark splitting of *J*-states [13,14], or examining approximations such as statistic evaluation of the location of center of gravity for *J*-state (or mean energy of the components of Stark splitting of *J*-state) [15,16]. The second step consists in the determination of CFP by an adjustment of calculated values of Stark splitting of *J*-states to the experimental ones minimizing the root mean square (RMS) difference between them at variation of CFP in the region of adjustment. If this region is unrestricted, the multivaluedness of solution of problem of obtaining CFP will be too high for further use of the results of such fitting. It is evident that the determination of CFP by the adjustment of experimental and calculated values of the splitting mentioned above is a reverse problem related to the class of incorrect problems [17]. The number of solutions of these problems depends on preliminary conditions and restrictions by the frame of model used, for example, such as a choice of direction of the quantization axis [13,14,18]. The details of elaboration of different methods of calculation of CFP and the tables of numeric coefficients used for transfer between the sets of CFP obtained by these methods can be found in Refs. [10,11,13,18,19]. The conditions and restrictions assumed give some ways to decrease the multivaluedness of solutions of the problem of CFP determination. The number of these solutions can be restricted by a stepwise (multi-step) evaluation of CFP. In particular, one can first of all evaluate the CFP of the second rank from energies and representations of Stark components of the states with low *J*. For example, this can be done for the state with *J* = 1. Then, when it is possible, some of the CFP of the fourth rank can be determined using known values of Stark splitting and representations of the states with *J* = 2. In cases of crystals of cubic symmetry, Stark splitting of the states with higher values of total angular momentum (in particular, with *J* = 4, 3) can be evaluated with use of diagrams of Stark splitting of *J*-states in model CF of cubic symmetry for all possible relations of the general cubic CFP (B_4 and B_6) [20]. We suggest to determine the relation of cubic CFP by means of comparison of a fragment of the luminescence spectrum of europium compound of cubic symmetry in the region of $^5D_0$-$^7F_4$ transition with the diagram of the Stark splitting (DSS[*X*(4)]) for $^7F_4$ state of Eu^{3+} (*J* = 4) taken from [20], Fig. 1, without new computing. The comparison can give the abscissa *X*(4) of the diagram which corresponds to the best simulation of Stark splitting of $^7F_4$ state fixed at experimental spectrum. In accordance with [20], the functions *X*(*J*) are determined by Eq. (1):

$$\frac{X(J)}{(1-|X(J)|)} = \frac{F_J(4)B_4}{F_J(6)B_6}, \tag{1}$$

where $F_J(4)$ and $F_J(6)$ are scaling coefficients of the CF values depending on *J* and presented in [20]. For $^7F_4$ (*J* = 4) the values of $F_4(4)$ and $F_4(6)$ are equal to 60 and 1260, respectively, $B_4/B_6 = 21[X(4)/(1-|X(4)|)]$. Choice of the function *X*(*J*) instead of the relation B_4/B_6 as abscissa of the diagram DSS[*X*(*J*)] permits to the authors of [20] to concentrate the results of variation of the relation B_4/B_6 situated in the interminable interval from minus infinity to plus infinity, within the finite interval $[-1,1]$. Correspondent diagram for *J* = 3, DSS[*X*(3)] [20] can be also considered here as a tool for determination of *X*(3) for use in evaluation of the sign of relation of

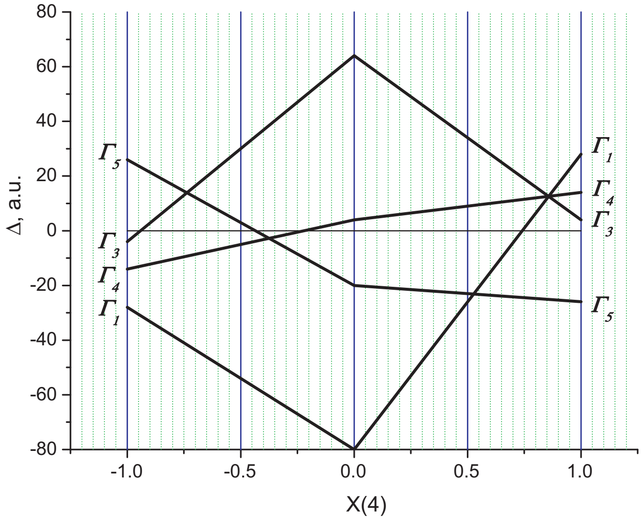

Fig. 1. The diagram of Stark splitting of $^7F_4$ state of Eu^{3+} ion in cubic crystal field DSS[$X(4)$] for all possible relations of CFP of the fourth and sixth ranks. Δ is deviation of Stark components of $^7F_4$ state from its "center of gravity", i.e. from mean value of the energy of these components. Γ_1, Γ_3, Γ_4, and Γ_5 are singlet, doublet, and two triplet representations, respectively [20].

cubic CFP. For calculation of the relation of the CFP of the fourth and sixth ranks by Eq. (1) we should use the value of optimal $X(4)$ giving the best accordance between the spectrum investigated, Fig. 2a, and the succession of points of the plots of the diagram in Fig. 1, having abscissa $X(4)$ In conclusion, the CFP should be refined in process of fitting of correspondent calculated spectra to the experimental data to include the influence of the effects like JJ'-interaction, shifting Stark components with the same representations, etc. [19]. Now, instead of unlimited scope of the region of fitting CFP one may take as the limits of the region of fitting the values comparable with cubic CFP.

4. Results and discussion

4.1. Evaluation of the relation of CFP of the fourth and sixth ranks in real crystals using a model CF of cubic symmetry

In cases of real europium compounds with a low-symmetric environment of Eu^{3+} ion one can also use the cubic model of crystal field for obtaining the relation of CFP of the fourth and six ranks. In that case, one also should compare the experimental arrangements of Stark components of $^5D_0$-$^7F_4$ transition of Eu^{3+} in the spectrum of compound investigated with DSS[$X(4)$]. That allows to find the value of $X(4)$ giving the best agreement between the set of points Δ on the plots (Fig. 1) and the positions of lines in experimental spectra, Fig. 2 b-e, paying at first no attention to residual splitting of lines due to distortions of cubic symmetry. The values of the relation B_4/B_6 obtained from Eq. (1), which correspond to $X(4)$ found from comparison, are shown at the right side of the spectra in Fig. 2. The comparison described is possible, when the crystal field components of the second rank are the only cause of deviation of crystal field from cubic symmetry, and when the influence of these components on Stark splitting of the states with $J = 3$ or 4 is comparatively small. In course of investigations of large number of experimental spectra of europium compounds it is possible to find the most obvious cases of various dependence of the relative Stark splitting on J including the cases of very small influence of the CF components of the second rank on Stark splitting of the states with $J = 3$ or 4 by a primitive screening (and that was done many times in the last fifty years, that had passed since appearance of paper [20]).

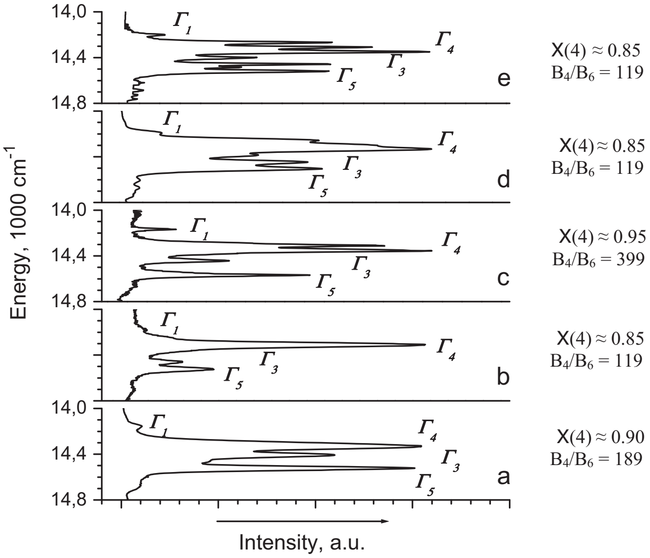

Fig. 2. Experimental Stark splitting of $^5D_0$-$^7F_4$ transition in the Eu^{3+} luminescence spectra (77 K) of dimeric europium carboxylates with 1,10-phenanthroline and 2,2′-bipyridine: propionate $Eu(C_2H_5COO)_3{\cdot}Phen$ (a), 2-nitrobenzoates $Eu(2\text{-}NO_2\text{–}C_6H_4COO)_3{\cdot}Bpy$ (b) and $Eu(2\text{-}NO_2\text{–}C_6H_4COO)_3{\cdot}Phen$ (c), and benzoate $Eu(C_6H_5COO)_3{\cdot}Phen$ (d and e). The spectra "a", "b" and "d" were recorded with ~20 cm^{-1} resolution, the spectra "c" and "e" were obtained with ~10 cm^{-1} resolution. The energy regions for all spectra are the same. Labels of y-axis for "b" and "d" spectra are omitted.

4.2. Effect of apparent increase in effective symmetry of CF for $J = 3, 4$ states of Eu^{3+} ions in crystals with distorted cubic symmetry

For direct demonstration of comparatively small contribution of CF components of the second rank to the splitting of the states with $J = 3$, 4 we calculated the relative RMS deviation of Stark components of J-states from mean energy of these components, or, in other words, from "the centers of gravity" of J-states or from the energies of these states of Eu^{3+} ions in CF of spherical symmetry [2,3,10] under the influence of "probing" CFPs of different ranks and arbitrary fixed values. These calculations were made for components of ^7F_J (the lowest spin–orbital multiplet of Eu^{3+} ion) using sets of "arbitrary" fixed values of probing CFP like 20.0 cm^{-1} for axial CFP describing the CFP of the second rank, and the fixed values 5.0 and 25.0 cm^{-1} as well as 2.5 and −52.5 cm^{-1} for pairs of "cubic" CFP, describing the cubic CFP of the fourth and sixth ranks, respectively. These values of CFP were used in calculations of Stark splitting of J-states of Eu^{3+} ions in the point charge model of Stevens method of equivalent operators [8,9]. Chosen in that way axial CFP B_{20}, B_{40}, and B_{60} in Stevens notation [8,9] are equal to 20.0, 5.0, and 2.5 cm^{-1}. To obtain fixed values of cubic Stevens CFP of the fourth and sixth ranks we should add to the axial B_{40}, and B_{60} two non-axial CFP, B_{44} and B_{64}, equal to B_{40}, and B_{60} multiplied by factors 5 and −21 and equal to 25 and −52.5 cm^{-1}, respectively [8,9]. We can find by the Tables of correspondence of different methods of description of CFP [13,18,19] that in Wybourne description of CF [10,11] these axial CFPs correspond to 40.0 cm^{-1}. Instead of this group of probing CFP one can use any other group of arbitrary fixed CFP obtained by multiplication (or division) of values of all the members of the first group by the same numerical factor, so the set of {5.0, 1.25 and 6.25, 0.625 and −13.125 cm^{-1}} gives the same picture of the relative RMS deviations as the set {20, . . ., −52.5 cm^{-1}} described here. After calculations of the relative RMS deviations from "the centers of gravity" of J-states with those two sets we obtain quite the same dependences that are presented in Fig. 3. For obtaining Stark splitting of the states of ^7F_J multiplet of Eu^{3+} we had written a program of calculation of this splitting for Eu^{3+} luminescence

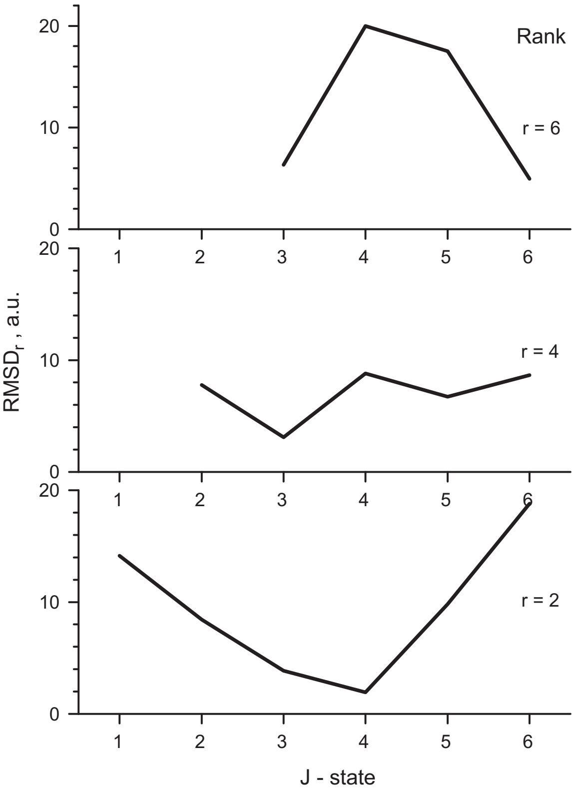

Fig. 3. Dependence of the relative root mean square deviations of Stark splitting components, RMSD$_r$, for J-states of Eu^{3+} ^7F_J multiplet on J for different ranks r ($r = 2$, 4, 6) of arbitrary fixed CFP for cubic crystal field with rhombic distortions.

centers with the C_{2v} point group symmetry in Stevens formalism [8,9], analogous to the program used by Brecher [12]. His data on CFP and on the structure of Eu^{3+} spectra in EuP_5O_{14} were used as references for the check-up of our program. Then, the Stark splitting of J-states of Eu^{3+} was successively calculated for fixed values of B_{20}; B_{40} with B_{44}; and B_{60} with B_{64}, that were described above. The resulting Stark sublevels of the states with $J = 1, 2, \ldots, 6$ were used for evaluation of RMS deviations of Stark components from positions of J states of the Eu^{3+} ion in CF of spherical symmetry. The obtained relative dependencies of RMS deviations, RMSD$_r$, of Stark splitting on J for different ranks, r ($r = 2$, 4, 6) of fixed CFP are presented as plots in Fig. 3. A small value of RMSD$_2$ for $J = 3, 4$ means “an apparent increase” in the effective symmetry of CF for these states. This “seeming effect” should be observed in the spectra recorded with medium resolution even in cases of comparatively high values of crystal field components of the second rank. That effect can help to find the representations of the experimental quasi-degenerate components of the state with $J = 4$ in the model CF of cubic symmetry (Fig. 2) via comparison with the DSS[X(4)] (Fig. 1), as it was described above.

At that stage, using an apparent increase in the effective symmetry of CF one can narrow the region of verification of calculated CFP confining the process of final adjustment of calculated and experimental data on the splitting of J-states to the vicinity of “the points X of maximal similarity” of the model and experimental spectra. The fact that the relative influence of crystal field components of different ranks on Stark splitting is a function of J was ignored by experimenters for about fifty years gone after syntheses and luminescence studies of the lanthanide β-diketonates, carboxylates, and nitrates with heterocyclic diimines, one of the first of them being the nitrates study [21]. That had lead to unnecessary broadening of the regions of the RMS fitting of Stark splitting calculated with the set of CFP evaluated from experimental spectra of the lanthanide ions, for example, in [16], increasing the uncertainty of solutions. The removal of that drawback can result in better understanding of the origin of Stark splitting components in Ln^{3+} spectra.

4.3. Application of cubic model of CF to analysis of luminescence spectra of Eu^{3+} ion

Using DSS[X(J)] for the state with $J = 4$ in CF of cubic symmetry (Fig. 1) and experimental picture of the Stark splitting of $^5D_0$-$^7F_4$ transitions of Eu^{3+} ion for four europium carboxylates (Fig. 2) one can determine the most probable value of X(4) for each of these compounds. Comparison of the fine structure of the spectra presented in Fig. 2 allows attributing the four representations Γ_1, Γ_4, Γ_3 and Γ_5 possible in model of cubic symmetry to certain Stark components. Taking in mind the distribution of intensity in $^5D_0$-$^7F_4$ transition one can see here two Stark components with comparatively high intensity corresponding to transitions from the singlet state Γ_1 ($^5D_0$) to triplets Γ_4 and Γ_5 and two components having lower intensity related to transitions to the doublet Γ_3 and the singlet Γ_1. The determined succession of representations corresponds to an arrangement of Stark components in the region $X(4) > 0.85$ in Fig. 1 being to the right of the singular point, in which three of four components of $^7F_4$ state are degenerate, and to the values of relation $B_4/B_6 > 119$. It means that for complexes under consideration CF component of the sixth rank defined by parameter B_6 is relatively small. So, at the final fitting stage of calculations of CFP with the minimization of RMS deviations of Stark components the Stevens CFP of the sixth rank, B_{60} and B_{64}, should be confined within the intervals narrower than $\pm(1/119)B_4$ and $-(\pm 21/119)B_4$, respectively. All CFP should be modified at this stage of calculations. The variation of CFP of the second and fourth ranks should be included in the final fitting.

At an appreciable deviation of CF from cubic symmetry, it is possible to evaluate the splitting of the states degenerated in the cubic model of crystal field at comparison of the various spectra, in particular, presented in Fig. 2. More wide picture of evolution of Stark splitting of $^7F_4$ state can be observed for series of ternary europium aliphatic and aromatic carboxylates, whose spectra recorded at $\sim$10 cm^{-1} resolution are shown in Fig. 5 of Ref. [4]. Slight changes of $^5D_0$-$^7F_4$ transition in the spectra of aliphatic carboxylates being in an agreement with small differences in distortions of the Eu^{3+} coordination polyhedron [4] witness about an invariability of CFP of the fourth and sixth ranks for compounds indicated. Therefore, changes of $^5D_0$-$^7F_2$ transition in the group of aliphatic carboxylates should be mainly connected with a different contribution of CFP of the second rank. More significant changes of $^5D_0$-$^7F_4$ transition observed at examination of the spectra of ternary europium aromatic carboxylates having voluminous benzoate and naphthoate ligands are in agreement with strong distortions of the Eu^{3+} coordination polyhedron [4,5,22]. The last can be explained by steric influence of the ligands on the crystal lattice packing. Changes of $^5D_0$-$^7F_2$ transition in this group of compounds should be connected with contributions of CFP of the second and fourth ranks.

Another interesting singular point on the diagram in Fig. 1 lies at $X(4) = -0.38$ and corresponds to degeneration of two triplets (Γ_4, Γ_5). Judging from the spectra of europium isonicotinates [23] and the spectra of some europium aromatic dicarboxylates, this opportunity can be also realized by the Nature.

The diagram for $^7F_3$ state DSS[X(3)] is much simpler than the DSS[X(4)], as $^5D_0$-$^7F_3$ transition ($\Delta J = 3$) is much more forbidden than $^5D_0$-$^7F_2$ and $^5D_0$-$^7F_4$ transitions of Eu^{3+}. One can observe there only two or three weak bands in most of the spectra of europium compounds instead of seven maximally possible Stark components. Some data on Stark splitting of the $^7F_3$ level can be obtained in studies of much more allowed $^5D_1$-$^7F_3$ transition of Eu^{3+} ion ($\Delta J = 2$)

or $^5D_4$-$^7F_3$ transition of Tb^{3+} ion ($\Delta J = 1$). But, in the former case, obtaining clear data is complicated by a quenching of $^5D_1$ state of Eu^{3+} ion, in the latter case, by complex structure of Stark splitting. The maximal possible number of components of the $^5D_4$-$^7F_3$ transition is equal to 63, see Figs. 1 and 2 in Ref. [24]. However, in cases of comparatively strong cubic crystal field a succession of the singlet and triplet components of the $^7F_3$ state could be obtained and used for determination of the sign of $X(3)$ in the problem of evaluation of the relation of CFP of the fourth and sixth ranks. Some data on positions of solitary high-frequency groups ($\Gamma_5^{(2)}$, Γ_3 at low X and Γ_1, Γ_4, and $\Gamma_5^{(2)}$ at high X) of $^7F_6$ state mixed with the components of $^5D_4$ state as well as analogous data on $\Gamma_4^{(1)}$ component of $^7F_5$ state could be obtained from the luminescence spectra of the Tb^{3+} ion in CF model of cubic symmetry, see the DSS[$X(J)$] for $J = 6$ and 5 in [20]. These data could be useful for evaluation of $X(J)$ in the spectra of terbium compounds.

5. Conclusions

By means of calculations of the relative RMS deviations of Stark splitting of *J*-terms of spin–orbital multiplets from the center of gravity of the terms in the spectra of europium coordination compounds under influence of the probing CFP of fixed value and different ranks (2, 4, and 6) it was shown that the CFP of the second rank have the lowest influence on Stark splitting of the states of Ln^{3+} ions with $J = 3, 4$. It can be due to the difference in geometry of interacting electronic orbitals of the ligands with 4f-electronic orbitals of the Eu^{3+} ion in coordination compounds. That simple fact is a consequence of the ligand field theory concerning the dependence of the interaction of the ligands with the central Eu^{3+} ions of the complex compound on the structure of coordination center. Non-monotonic RMS dependence of Stark splitting components on *J* at the fixed values of CFP demonstrates that of all factors influencing that dependence the most essential are the angle coordinates of the ligands as their variations can give the most sensitive non-monotonic changes for interaction Eu^{3+}-ligand. In practice, this effect in some cases provides an approach of the experimental picture of Stark splitting of $^7F_4$ state of Eu^{3+} ion to the model image of this splitting in crystal field of cubic symmetry. That gives opportunity for the experimental evaluation of the relation of the CFP of fourth and sixth ranks. This relation can be used for increasing a reliability of interpretation of the spectra of europium and terbium compounds via lowering of the region of variation of adjustable parameters at the last stage of determination of the CFP set.

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