



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

Vladislav F. Zolin*, Vera I. Tsaryuk, Konstantin P. Zhuravlev, Valentina A. Kudryashova

V.A. Kotelnikov Institute of Radioengineering and Electronics, Russian Academy of Sciences, 1 Vvedenskii sq., Fryazino, Moscow reg. 141190, Russia

ARTICLE INFO

Article history:

Received 15 March 2011

Received in revised form 16 June 2011

Accepted 25 June 2011

Available online 2 July 2011

Keywords:

Eu^{3+}

Ln^{3+}

Crystal field parameters

Luminescence

Carboxylates

X-ray crystal structure

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.

© 2011 Elsevier B.V. All rights reserved.

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, $\text{Cs}_2\text{NaLnCl}_6$, 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

* Corresponding author at: Laboratory of Molecular Electronics, Institute of Radioengineering and Electronics of RAS, 1 Vvedenskii sq., Fryazino, Moscow reg. 141190, Russia. Tel.: +7 4965652577; fax: +7 4957029572.

E-mail address: zolvin@mail.ru (V.F. Zolin).

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 $[\text{Eu}(\text{C}_2\text{H}_5\text{COO})_3 \cdot \text{Phen}]_2$ 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 $\text{EuP}_5\text{O}_{14}$ 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 $^5\text{D}_0$ – $^7\text{F}_4$ transition with the diagram of the Stark splitting ($\text{DSS}[X(J)]$) for $^7\text{F}_4$ 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 $^7\text{F}_4$ state fixed at experimental spectrum. In accordance with [20], the functions $X(J)$ are determined by Eq. (1):

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

where $F_J(4)$ and $F_J(6)$ are scaling coefficients of the CF values depending on J and presented in [20]. For $^7\text{F}_4$ ($J=4$) 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 $\text{DSS}[X(J)]$ 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 $J=3$, $\text{DSS}[X(3)]$ [20] can be also considered here as a tool for determination of $X(3)$ for use in evaluation of the sign of relation of

Download English Version:

<https://daneshyari.com/en/article/27396>

Download Persian Version:

<https://daneshyari.com/article/27396>

[Daneshyari.com](https://daneshyari.com)