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Crystal field analysis of energy level structure of LaF_3:Eu^{3+}

M.G. Brik [a,*], I. Tanaka [b], T. Ishii [c], K. Ogasawara [c], A. Nakamura [c], S. Watanabe [c]

[a] *Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4 Takano Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103, Japan*
[b] *Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan*
[c] *School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan*

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Abstract

Crystal field calculations have been performed for the LaF_3:Eu^{3+} crystal. The complete $|JM_j\rangle$ basis was used without any truncation; the energy levels obtained are given an assignment and compared, on one hand, with the experimental results, and, on the other hand, with the results of fully relativistic first-principles calculations for the same crystal.

Keywords: Crystal field theory; Rare-earth ions; Discrete variational multi-electron methods

1. Introduction

The lanthanum trifluoride LaF_3 is a classical host for studying optical properties of the trivalent rare-earth (RE) ions. Since both the growth of the large single crystals and variation of the RE ions concentration cause few problems, extensive spectroscopic data and crystal field (CF) studies for LaF_3:RE^{3+} can be found in the literature [1–10]. The earlier work [11,12] was concerned with the potential application of LaF_3 as a solid-state laser active medium, whereas some of the recent studies [13,14] are focused on possible nano-applications of the title material. The earlier CF analysis [3] assumed D_{3h} symmetry at the La^{3+} position which is substituted by the RE^{3+} ions; later on, lower symmetries such as C_{2v} [6,7,9] or C_2 [10] have been employed for fitting the CF parameters to the experimental spectra.

In the present work we follow the authors of Ref. [9] in using the C_{2v} symmetry (though the actual symmetry at the La^{3+} site is C_2, the C_{2v} symmetry is more tractable for computational purposes). We report on the results of the energy level calculation for the Eu^{3+} ion and use the obtained results as a tool for checking out the validity of the fully relativistic discrete variational multi-electron method (DV-ME) of the multiplets calculation developed in [15] and applied to the RE^{3+} ions in $LiYF_4$ [16] and in a free state [17].

2. Methods of calculation: CF Hamiltonian and the DV-ME method

The optical properties of rare-earth ions with n electrons in the 4f shell are commonly described by the following Hamiltonian [9]:

$$H = H_0 + \sum_{k=0,2,4,6} \mathrm{F}^{\mathrm{k}}(n\mathrm{f}, n\mathrm{f})\mathrm{f}_k + \zeta_{\mathrm{f}} A_{\mathrm{SO}} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{i=2,3,4,6,7,8} t_{\mathrm{i}} T^{\mathrm{i}} + \sum_{h=0,2,4} m_{\mathrm{h}} M^{\mathrm{h}} + \sum_{f=2,4,6} p_{\mathrm{f}} P^{\mathrm{f}} + H_{\mathrm{CF}}. \quad (1)$$

The first term in Eq. (1) H_0 represents the spherical part of a free ion Hamiltonian and can be omitted without any lack of generality. F^k are the Slater parameters and ζ_f is the spin–orbit interaction constant; f_k and A_{SO} are the angular parts of electrostatic and spin–orbit interactions, respectively. The two-body correction terms (including Trees′ correction)

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[*] Corresponding author. Tel.: +81 75 7117708; fax: +81 75 7814757.
E-mail address: brik@fukui.kyoto-u.ac.jp (M.G. Brik).

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are described by the third, fourth, and fifth entries, correspondingly, whereas three-particle interactions (for ions with three or more equivalent 'f' electrons) are represented by the sixth term. Finally, magnetic interactions (spin–spin and spin–other orbit corrections) are described by the terms with operators m_h and p_f. The CF effects (if an ion is embedded into a crystal or glass) give rise to the last term, which will be defined below. The matrix elements of all operators entering Eq. (1) can be found in [18,19].

In the framework of the CF theory, the potential created by the crystal lattice at the position of an impurity ion can be expressed in general case as follows:

$$\begin{aligned} H_\text{CF} = {} & \sum_{k=2,4,6} \sum_{m=1}^{n} B_0^k C_0^k(m) \\ & + \sum_{k=2,4,6} \sum_{q=1}^{k} \sum_{m=1}^{n} [B_q^k (C_q^k(m) + (-1)^q C_{-q}^k(k)) \\ & + B_{-q}^k i (C_{-q}^k(m) - (-1)^q C_q^k(m))]. \end{aligned} \tag{2}$$

Here B_q^k stand for the CF parameters, and $C_q^k(m)$ are the one-electron spherical operators acting on the angular coordinates of the mth electron. Since the direct calculation of the $B_q^k{'}$s implies performing a summation over crystal lattice sites (a rather laborious task, which requires detailed knowledge of the crystal structure), usually the$B_q^k{'}$s are treated as parameters defined from fitting of the calculated splittings to the experimental spectra. Such an approach is widely and commonly used nowadays, though it deals with a large number of parameters to fit (generally speaking, up to more than 20 in case of C_1 symmetry, if no restraint are superimposed on their variation) becoming a rather complicated problem.

The complete set of the free ion and CF parameters for the whole series of the RE ions in LaF_3, which fits the experimental spectra best of all, is given in [9], and we have used them for calculating energy level schemes for all RE ions.

The second method employed in the present paper is the DV-ME method, which is based on the configuration-interaction (CI) calculation program using the four-component fully relativistic molecular spinors obtained by the discrete-variational Dirac–Slater (DV-DS) cluster calculations [15]. In the DV-ME method, a relativistic many-electron Hamiltonian for explicitly treated n electrons is (in atomic units)

$$\begin{aligned} H = {} & \sum_{i=1}^{n} \left[c\boldsymbol{\alpha}\mathbf{p}_i + \boldsymbol{\beta} c^2 - \sum \frac{Z_\nu}{|\mathbf{r}_i - \mathbf{R}_\nu|} + V_0(\mathbf{r}_i) \right] \\ & + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \end{aligned} \tag{3}$$

where $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ are the Dirac matrices, c the velocity of light, $\mathbf{r}_i$, $\mathbf{p}_i$ the position and the momentum operator of the ith electron, Z_ν and $\mathbf{R}_\nu$ the charge and position of the νth nucleus, and $V_0(\mathbf{r}_i)$ the potential from the other electrons [20]. The above Hamiltonian was diagonalized within the subspace spanned by the Slater determinants composed of relativistic 4f and 5d orbitals and the energy level schemes of 4f^n and $4\text{f}^{n-1}5\text{d}^1$ configurations for all trivalent lanthanides in LaF_3 have been obtained. To avoid making the paper too lengthy, we do not give here an exact description of the latter method (it can be found in [15–17] and references therein), but mention here only those essential features which are relevant to the following discussion.

The main advantage of the method is that at the start of a calculation one needs to know only the crystal structure data. The usage of the molecular orbital concept through all calculations ensures taking into account covalency effects. There are no restrictions on the cluster symmetry, and the Hamiltonian (3) can be used for the description of the $4\text{f}^{n-1}5\text{d}^1$ electron configuration as well (the Hamiltonian (1) requires some additional terms in this case, increasing the number of the parameters to fit for these configurations). It is also possible to perform computer simulation of the absorption spectra both for the $4\text{f}^{n-1}5\text{d}^1$and 4f^n electron configurations. Though these merits of the DV-ME method are very attractive, it is not free from some disadvantages. The energy levels in the DV-ME method are somewhat overestimated (by 20–30%) for all RE ions, and the reason for this overestimation is due to underestimation of electron correlations [15]. A posteriori introduction of a scaling factor (which is confined within the interval from 0.7 for Ce^{3+} to 0.9 for Yb^{3+}) significantly improves the correspondence between experimental and theoretical energy level schemes, as will be shown in the next section.

3. Results of calculation and discussion

The results of calculation for both methods are summarized below, in Table 1. Actually, the energy levels were obtained for the whole series of the RE ions in LaF_3, but in the present paper we narrow our consideration and show the results for Eu^{3+} only, since inclusion of other ions will enlarge the size of the paper. For every $^{2S+1}L_J$ manifold the energy levels are grouped in four rows: (1) experimental energy levels (E), if available; (2) theoretical energy levels obtained using the CF Hamiltonian (1) (CF); (3) theoretical energy levels obtained using the DV-ME method (R); (4) the corrected DV-ME results (CR). As is seen from the table, the "E" and "CF" groups are in good agreement with each other, whereas the "R" energy levels are overestimated. To improve the correspondence between the "CR" and "E" (or "CF") groups, we performed an additional analysis of the Stark splittings of the considered levels. Table 2 contains the positions of the barycenters of the $^7\text{F}_J$ ($J = 0$–6) manifolds and their Stark splittings obtained from the experimental data and DV-ME method, as well as their ratios. It is remarkable to note that the ratios of the barycenter energies and Stark splittings (parameters α and β, respectively) are practically the same for all manifolds. This clearly shows that the

Table 1
Energy levels (cm^{-1}) for LaF$_3$:Eu^{3+}: experimental and theoretical

State	Prefix[a]	Experimental results (E) [9] and theoretical (CF calculations (CF), relativistic calculations (R), corrected relativistic (CR) levels (cm^{-1})) calculations													
$^7F_0$		E	0												
		CF	0												
		R	0												
		CR	0												
$^7F_1$		E	313	375	415										
		CF	329	383	423										
		R	313	437	630										
		CR	320	360	422										
$^7F_2$		E	964	–	997	–	098[b]								
		CF	952	983	021[b]	119	127								
		R	063[b]	075	124	429	492								
		CR	960	964	979	073[b]	093								
$^7F_3$	1	E	–	843	867	884	889	908	996						
		CF	846	863	873	900	901	927	017[b]						
		R	968	003[b]	221	245	308	315	650						
		CR	838	847	902	908	923	925	009[b]						
$^7F_4$	2	E	614	788	852	873	894	926	–	047[b]	068				
		CF	600	774	828	902	905	977	993	071[b]	080				
		R	750	306[b]	369	457	571	732	786	131[c]	188				
		CR	602	780	800	828	865	916	934	044[b]	062				
$^7F_5$	3	E	–	–	–	–	–	–	–	–	–	–	–		
		CF	791	812	876	935	999	008[b]	040	059	064	080	112		
		R	525[b]	593	624	004[c]	012	106	210	246	349	393	407		
		CR	797	822	833	970	972	006[b]	044	057	094	110	115		
$^7F_6$	4	E	–	–	–	–	–	–	–	–	–	–	–	–	–
		CF	934	951	012[b]	040	046	047	125	130	132	152	169	177	183
		R	957[b]	049[c]	153	287	298	354	378	401	464	490	532	633	634
		CR	937	971	010[b]	059	063	084	093	101	125	134	150	187	188

[a] These numbers are the leading integers to the entries in each row.
[b] An increase in the prefix of unity for that number and the remaining entries.
[c] An increase in the prefix by two unities for that number and all remaining entries.

overestimation effects contribute in the same manner to all manifolds. Below we suggest an empirical equation, which takes into account the overestimation effects, as follows:

$$E_{\mathrm{CR},i} = \alpha \bar{E}_{\text{DV-ME}} + \beta(\mathrm{E}_{i,\text{DV-ME}} - \bar{E}_{\text{DV-ME}}), \tag{4}$$

where i enumerates different entries in the "R" row, and the sense of other notations is clear from Table 2. We found the "CR" values for each manifold using Eq. (4) to be significantly better that the "R" set and very close to the "E" and "CF" sets. The "quality" of the correspondence is shown by the root-mean-squared (rms) deviation

$$\sigma = \sqrt{\frac{\sum_{i=1}^{m}(E_{i,\mathrm{exp}} - E_{i,\mathrm{calc}})^2}{m}}, \tag{5}$$

where m is the number of the experimental energy levels used in the calculations. For the "CF" set the rms deviation is 20.5 cm^{-1}, for the "CR" set it is just slightly greater, namely,

Table 2
Barycenters of the ^7F_J manifolds and their Stark splittings in LaF$_3$:Eu^{3+} calculated using experimental data (or CF calculations, if no experimental data were reported) and relativistic DV-ME method

State	Barycenter, $\bar{E}$ (cm^{-1})		$\alpha = \frac{\bar{E}_{\mathrm{exp}}}{\bar{E}_{\text{DV-ME}}}$	Stark splitting, ΔE (cm^{-1})		$\beta = \frac{\Delta E_{\mathrm{exp}}}{\Delta E_{\text{DV-ME}}}$
	Exper. (CF)	DV-ME		Exper. (CF)	DV-ME	
$^7F_0$	0	0	–	0	0	–
$^7F_1$	368	460	0.80	102	317	0.32
$^7F_2$	1020	1237	0.82	134	429	0.31
$^7F_3$	1898	2244	0.85	171	682	0.25
$^7F_4$	2883	3588	0.80	454	1438	0.32
$^7F_5$	3980	5042	0.79	321	882	0.36
$^7F_6$	5084	6365	0.80	249	677	0.37

21.6 cm^{-1}. This correspondence serves as a firm justification of the applicability of the DV-ME method to the calculation of the energy levels of the RE elements in crystals, with only two semi-empirical parameters. It should be pointed out here that these parameters are not allowed to vary freely, but are exactly determined (though a posteriori) from the comparison of the experimental and DV-ME results. An essential fact is that the DV-ME method reproduces an exact order of the energy levels (in terms of the C_2 point group irreducible representations) comparing with experimental results, without any energy levels interchange [21]. The DV-ME method is also a powerful tool in computing the absorption spectra of the RE ions, and those ones for the title host are reported in [22]. We also believe that an introduction of the scaling factors α and β into the Hamiltonian (3) will yield in obtaining more precise energy level scheme and absorption bands positions without any analysis after the main calculations are finished. This work concerning the modification of the Hamiltonian (3) is in progress now.

4. Conclusion

An analysis of the energy level structure of LaF_3 doped with RE^{3+} ion is performed using two models: the common CF Hamiltonian for the 4f^n electron configuration and the DV-ME method; the calculations are reported in full details for the LaF_3:Eu^{3+} system. The energy levels obtained from the common CF calculations were used as a test for the DV-ME method. As a result, two scaling factors, describing the overestimation effects in the DV-ME method, were estimated. The subsequent application of these factors in the treatment of the DV-ME results led to a good agreement between the experimental and DV-ME energy levels with the rms deviation 21.6 cm^{-1}.

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