Crystal field of rare earth impurities in LaF$_3$

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Abstract

The crystal field parameters of 13 trivalent lanthanide ions substituted for La in LaF$_3$ were calculated using the combination of the band structure and Wannier function calculations. Performing an atomic exact diagonalization with thus obtained crystal-field parameters we compute the crystal-field splitting of atomic multiplets. The calculation is compared with the available experimental results and a good agreement is found.

Keywords: crystal field, rare earth, ab initio calculation

1. Introduction

Lanthanum trifluoride doped with the rare-earth (R) ions is commonly used for the optical applications and as a material for electrodes in detectors. During the past decades the optical spectra of all R impurities except Pm in LaF$_3$ were measured and the results analyzed using the semiempirical crystal field models [1, 2]. With the exceptions of the work of Ishii et al. [3] and Brik et al. [4], based on the discrete variational multi-electron method (DV-ME), the ab-initio theory was missing, however. DV-ME method and its results are discussed and compared to the present ones in part 5. The survey of the attempts to calculate the crystal-field parameters (CFP) in the rare-earth compounds may be found in [5, 6].

A new theoretical approach has been recently used to calculate the crystal field parameters of rare-earth in aluminates, gallates, cobaltites and manganites with the orthorhombic perovskite structure [7, 8, 9]. The method uses the density functional theory band structure calculation, followed by a transformation of the Kohn-Sham Hamiltonian to the Wannier basis and an expansion of its local part in the spherical tensor operators. The CFP serve as an input to an atomic exact diagonalization program, which takes into account also the 4f-4f interaction, spin-orbit coupling and the Zeeman interaction. The calculated results agree remarkably well with the experiment: the crystal-field-split multiplet levels within a few meV and magnetic properties are correctly described as well. For any site symmetry the method yields an unambiguous set of CFP. This is important especially if the local symmetry of the R site is low and many CFP are needed to fully characterize the crystal field. Semiempirical methods, as well as the analysis of optical data make usually use of the least squares fitting, a procedure often yielding ambiguous results. With the exception of a single parameter, to be discussed below, the present method is fully ab-initio i.e. the only necessary inputs are the atomic composition and the crystal structure of the compound in question.

In the orthorhombic perovskites, to which the method was already successfully applied [7, 8, 9], the symmetry of the R site is $C_s$ and 15 parameters, 3 real and 6 complex CFP, are necessary. The

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situation of R impurities in LaF$_3$, which is considered here, is similar. The site symmetry of La$^{3+}$ site in LaF$_3$ is $C_2$ and again 15 parameters, 3 real and 6 complex CFP, are necessary.

The paper is organized as follows: the method and the computational details are described in sections 2 and 3, respectively. The calculated energy levels and CFP are presented in section 4. In the same section the theoretical crystal field spectra are compared with the experimental data collected by Carnall et al. [1, 2]. Section 5 contains discussion, followed by the conclusions in section 6.

2. Methods

An effective Hamiltonian operating on the 4$f$ electrons can be written as

$$\hat{H}_{eef} = \hat{H}_A + \hat{H}_Z + \hat{H}_{\text{CF}},$$

(1)

where $\hat{H}_A$ is the spherically symmetric free ion Hamiltonian, $\hat{H}_Z$ corresponds to the Zeeman interaction and $\hat{H}_{\text{CF}}$ is the crystal-field term. In the Wybourne notation $\hat{H}_{\text{CF}}$ has the form

$$\hat{H}_{\text{CF}} = \sum_{k=0}^{k_{\text{max}}} \sum_{q=-k}^{k} B_q^{(k)} \hat{C}_q^{(k)}, \quad \hat{C}_q^{(k)} = \sum_{i,j=1}^{7} [C_q^{(k)}]_{ij} f_i^\dagger f_j,$$

(2)

where $\hat{C}_q^{(k)}$ is a spherical tensor operator of rank $k$ acting on the 4$f$ electrons of the R ion, for which $k_{\text{max}}$ is equal to six. The coefficients $B_q^{(k)}$ are the CFP. Hermiticity of $\hat{H}_{\text{CF}}$ requires that $(B_{-q}^{(k)})^* = (-1)^q B_q^{(k)}$. The operators $f_i^\dagger$ ($f_i$) create and annihilate an electron in an $f$-orbital $i$. The details of $\hat{H}_A$ are given e.g. in Ref. [11].

Calculation of the CFP proceeds in four steps:

1. Standard selfconsistent band calculation with 4$f$ states included in the core. The result of this step is the Kohn-Sham potential, which is subsequently used in the next step. The calculation is non spin-polarized.

2. A Hamiltonian describing R 4$f$ states together with fluorine 2$p$ and 2$s$ states subject to the Kohn-Sham potential from the previous step is diagonalized. To eliminate other valence states an orbital operator which adds a large positive constant to the potential acting on these states is used. Relative position of 4$f$ and fluorine states is adjusted by applying similar operator to the fluorine states, which shifts their potential by the 'hybridization' parameter $-\Delta$ (the only parameter of method).

3. The 4$f$ band states are transformed to Wannier basis using the wien2wannier [12] and wannier90 [13] packages. The result of this step, relevant for CFP calculation is the Hamiltonian $\hat{H}_W$ in the basis of 4$f$ Wannier functions.

4. Local 4$f$ Hamiltonian $\hat{h}_{\text{loc}}$ is obtained as the on-site part $\hat{H}_W$. Finally $\hat{h}_{\text{loc}}$ is expanded in series of spherical tensor operators. The coefficients of expansion are the CFP $B_q^{(k)}$.

To find $B_q^{(k)}$ we made use of the fact that $\hat{C}_q^{(k)}$ form complete orthogonal set of operators in the subspace of 4$f$ states. Then

$$B_q^{(k)} = \frac{1}{n_{k,q}} \sum_{i=1}^{7} \sum_{j=1}^{7} h_{ij}^{\text{loc}} [\hat{C}_q^{(k)}]_{ij},$$

(3)

where $n_{k,q}$ is the normalizing factor:

$$n_{k,q} = \sum_{i=1}^{7} \sum_{j=1}^{7} [\hat{C}_q^{(k)}]_{ij} [C_q^{(k)}]_{ij}.$$

(4)
With the CFP in hand we use a modified ‘lanthanide’ package [14] to solve the eigenvalue problem for Hamiltonian (1) and calculate the splitting of multiplets by the crystal field. Detailed description of the analysis may be found in [7, 8].

2.1. Hybridization parameter

The parameter $\Delta$ appears due to the hybridization between the rare-earth 4$f$ states and the valence states of its ligands. In the 3$d$ metal compounds the hybridization is in most cases a dominating source of the crystal field. For the Co:ZnO system Kuzian et al. [15] successfully reproduced the $g$-factors and the zero-field splitting, by treating the hopping between the cobalt 3$d$ orbitals and the 2$p$ states of the fluorine ligands as a perturbation. Our treatment of the hybridization is analogical to that of Kuzian et al. and is briefly described in Ref. [7]. $\Delta$ can be estimated using a charge transfer energy

$$\Delta \approx E_{\text{tot}}(4f^{n+1}, N_{\text{val}} - 1) - E_{\text{tot}}(4f^n, N_{\text{val}}),$$

where $E_{\text{tot}}(4f^n, N_{\text{val}})$ is the total energy of the ground state of the system ($n_{4f}$ electrons in 4$f$ shell of R ion and $N_{\text{val}}$ electrons in the valence band), while $E_{\text{tot}}(4f^{(n+1)}, N_{\text{val}} - 1)$ corresponds to the excited state in which one of the valence electrons was transferred in the 4$f$ electron shell. The hybridization parameter thus can be calculated by performing two calculations with 4$f$ electrons treated as the core states - the first one with $4f^n, N_{\text{val}}$, the second with $4f^{(n+1)}, N_{\text{val}} - 1$ electron configurations. The results of such a calculation for R:LaF$_3$ system are presented in section 4.

3. Details of calculation

The LaF$_3$ crystallizes in trigonal symmetry ($P\overline{3}c1$ space group) with six La in the hexagonal unit cell [16]. To determine the band structure (steps 1 and 2 in the previous section) the WIEN2k package [17] was used with the exchange-correlation of the generalized-gradient approximation form [18]. For the pure LaF$_3$ compound the experimental crystal structure was taken from [16]. In R:LaF$_3$ one of the six La atoms was replaced by a rare-earth atom and the internal structure was optimized by minimizing the atomic forces. The resulting structure has only the identity and $C_2$ symmetry operations. The unit cell containing 24 atoms is displayed in Fig. 1. The eigenvalue problem was solved in 47 points of the irreducible part of the Brillouin zone and the number of basis functions was $\sim$ 1780 (corresponding to parameter $RK_{\text{max}} = 7$). The calculations were non-spin-polarized. The atomic radii of R and F were 2.4 and 2 a.u., respectively.

The multiplet splitting and magnetism of rare-earth ions depend only weakly on the free ion parameters, though there may be exceptions when the energy difference of the free ion multiplet is small. Carnall et al. [1, 2] analyzed systematically the available absorption and luminescence data of trivalent lanthanide ions doped into LaF$_3$. Using the least squares analysis the free ion parameters were obtained, which we used in Ref. [7, 8, 9], as well as here. In addition 9 real CFP were obtained, corresponding to the $C_{2v}$ symmetry by which the actual $C_2$ symmetry was approximated.

The comparison between experimentally observed and calculated crystal field splittings of the $|L, S, J, M_J\rangle$ multiplets deserves special attention. The experimental data reported by different authors are summarized in [2]. Understandably not all energy levels were detected (for Pm the experimental data are missing altogether). This makes the comparison of theory and experiment complicated as in many cases the missing levels are not unambiguously identified. Moreover, the crystal field could lead to overlap of different $|L, S, J, M_J\rangle$ multiplets. Faced with this situation we characterize the agreement of theory and experiment by the mean square deviation

$$\chi = \left[ \frac{1}{N_{\text{detected}}} \sum_{i=1}^{N_{\text{group}}} \sum_{j=1}^{n_i} (E_{\text{exp}}^{i,j} - E_{\text{calc}}^{i,j})^2 \right]^{1/2},$$

(6)
Figure 1: (Color online) Unit cell of R_{1/6}La_{5/6}F_{3} used in the calculation of CFP. The C_{2} symmetry axis is along the axis a.

Table 1: R:LaF_{3}. \( N_{\text{detected}} \) is number of experimentally detected levels, energies of which are compared with the calculation. \( N_{\text{group}} \) is number of groups (isolated or overlapping multiplets) from which these levels originate. \( N_{\text{total}} \) is total number (detected and undetected) of levels in \( N_{\text{group}} \) groups.

| R   | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|
| \( N_{\text{group}} \) | 2  | 11 | 22 | 15 | 10 | 10 | 11 | 14 | 16 | 17 | 12 | 2  |
| \( N_{\text{detected}} \) | 7  | 75 | 104 | 65 | 31 | 51 | 77 | 137 | 80 | 56 | 6  |
| \( N_{\text{total}} \)   | 7  | 90 | 115 | 68 | 59 | 57 | 99 | 84 | 170 | 84 | 90 | 7  |

where \( N_{\text{group}} \) equals to the number of multiplets with the provision that overlapping multiplets are treated as a single group. \( n_{i} \) is the number of states detected in the \( i \)th group and

\[
N_{\text{detected}} = \sum_{i=1}^{N_{\text{group}}} n_{i}. \tag{7}
\]

The energies \( E_{i,j}^{\text{exp}} \) and \( E_{i,j}^{\text{calc}} \) are the experimental and calculated energies, respectively, of the \( j \)th eigenstate belonging to the \( i \)th group. These energies are taken relative to the lowest energy of the group, which minimizes the influence of the free ion parameters. When some of the eigenstates are not experimentally detected several ways to match \( E_{i,j}^{\text{calc}} \) and \( E_{i,j}^{\text{exp}} \) are possible. We did not attempt to minimize \( \chi \) by probing all such pairings, rather the correspondence used by Carnall et al. \[2\] was adopted. In Table I the numbers of experimental levels, which we below compare with those calculated, are given for each R, except Pm.
Figure 2: (Color online) Comparison of the hybridization parameter $\Delta$ calculated using eq. 5 with the value which minimizes the mean square deviation $\chi$ (eq. 6). The curve in this, as well as in the following figures, serves as a guide for the eyes only.

4. Results

4.1. Energy levels

The atomic program yields energies of all eigenstates arising from the electron configuration $4f^n$ (there are 7 such eigenstates for $n_{4f}$=1 and 13, maximum number 3432 is reached for $n_{4f}$=7, corresponding to Gd$^{3+}$ ion). We calculated the energies as a function of the hybridization parameter $\Delta$, which was varied between 0.1 to 1 Ry with a step 0.1 Ry. By comparison with the experimental data we found that optimal $\Delta$ lies between 0.3 and 0.5 Ry. In Fig. 2 the optimal $\Delta$ is compared to $\Delta$ calculated using (5). The dependence of the mean square deviation $\chi$ (6) on the $\Delta$ is shown in Fig. 3 for all R except Pm. For Nd$^{3+}$ all of the levels corresponding to the ten low lying multiplets were detected and as an example the comparison of theory and experiment is shown in Fig. 4.

4.2. Crystal field parameters

Tables 2, 3 collect the CFP calculated for $\Delta = 0.4$ Ry. They refer to the orthogonal system depicted in Fig. 1 with axis $z$ parallel to the hexagonal axis $c$, $x \parallel a$ and $y \perp a, c$. The dependence of CFP on the hybridization parameter is for $\Delta \geq 0.2$ smooth. For $\Delta < 0.2$ the Wannier functions lose their atomic character and the CFP values become scattered. For different R the character of $B_q^{(k)}(\Delta)$ dependence is similar, which is documented in Figs. 5 and 6 for R = Nd and R = Er, respectively. In these figures the absolute values $|B_q^{(k)}|$ are shown.

It is difficult to compare the calculated CFP with those obtained by Carnall et al. [1] by fitting the optical data. Carnall’s et al. CFP are real because of an assumed, approximate site symmetry. We can compare, however, the values of $B_q^{(0)}$, which are real and, in addition, the quantities $s_k$

$$s_k = \left[\frac{1}{2k+1} \sum_{q=-k}^{k} |B_q^{(k)}|^2 \right]^{1/2},$$

(8)
Figure 3: (Color online) The mean square deviation $\chi$ (eq. 6) as function of the hybridization parameter $\Delta$.

Figure 4: (Color online) Nd:LaF$_3$. Comparison of experimental and calculated crystal field splitting for $\Delta = 0.4$ Ry and ten low lying multiplets. The energy, which was subtracted from the lowest eigenenergies of the four lowest multiplets, is explicitly given in the figure (units of cm$^{-1}$), for six higher lying groups of levels corresponding values are 11592, 12596, 13514, 14834 and 15997 cm$^{-1}$. Experimental data were taken from Ref. [2].
Figure 5: (Color online) Nd:LaF$_3$. Dependence of the absolute value of the CFP on the hybridization parameter $\Delta$.

Figure 6: (Color online) Er:LaF$_3$. Dependence of the absolute value of the CFP on the hybridization parameter $\Delta$. 
Figure 7: (Color online) Parameters $B_{20}$, $B_{40}$, $B_{60}$ as function of the number of $4f$ electrons. Full symbols correspond to results calculated with hybridization parameter $\Delta = 0.4$ Ry. Open symbols were determined using the CFP given by Carnall et al. [1].

Table 2: Real part of the CFP in R:LaF$_3$ (units of cm$^{-1}$). Hybridization parameter $\Delta = 0.4$ Ry.

| $kq$ | Ce  | Pr  | Pm  | Nd  | Sm  | Eu  | Gd  | Tb  | Dy  | Ho  | Er  | Tm  | Yb  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 20  | -268| -274| -257| -241| -254| -260| -255| -248| -261| -340| -347| -343| -333|
| 22  | -52 | -61 | -104| -102| -106| -90 | -101| -79 | -130| -90 | -79 | -76 | -76 |
| 40  | 608 | 527 | 498 | 474 | 437 | 420 | 408 | 395 | 354 | 292 | 273 | 259 | 247 |
| 42  | -344| -306| -285| -271| -259| -247| -240| -229| -222| -214| -204| -195| -185|
| 44  | 37  | 28  | 25  | 10  | 0   | -6  | -12 | -19 | -9  | -16 | -16 | -15 | -14 |
| 60  | 638 | 548 | 516 | 479 | 450 | 420 | 420 | 399 | 390 | 324 | 299 | 282 | 268 |
| 62  | 467 | 408 | 378 | 350 | 333 | 312 | 304 | 286 | 287 | 287 | 270 | 255 | 243 |
| 64  | -340| -291| -267| -236| -222| -207| -197| -189| -181| -176| -165| -156| -148|
| 66  | -640| -550| -494| -452| -421| -398| -384| -363| -335| -325| -308| -293| -277|

which were introduced by Leavitt [10]. The $q$-averages $s_k$ are real and invariant with respect to the rotation of the coordinate system. This comparison is displayed in Figs. 7 and 8 respectively.

5. Discussion

We first discuss the DV_ME method [5] and its application to Pr:LaF$_3$ and Eu:LaF$_3$ as described in [3, 4]. The method calculates the multiplet splitting in two steps. In the first step the density functional theory based calculation is performed for a cluster consisting of the R$^{3+}$ ion and its ligands. The rest of the crystal is taken into account by adding an effective Madelung potential to the Hamiltonian. In the second step the many-electron problem is solved by selecting as a basis the cluster one-electron eigenstates with the dominant $4f$ character. Choice of the ligands to be included in the cluster and the cluster embedding are difficult problems (cf. Ref. [20] and Fig. 1 in [3]). Another problem is connected with the one-electron part of the many-electron Hamiltonian. The on-site interaction of the $4f$ electrons with the potential they create themselves is not accounted
Figure 8: (Color online) Quantity \( s_k \) (see eq. 8) as function of the number of \( 4f \) electrons. Full symbols correspond to results calculated with hybridization parameter \( \Delta = 0.4 \) Ry. Open symbols are the CFP as given by Carnall et al. [1].

Table 3: Imaginary part of the CFP in R:LaF\(_3\). Hybridization parameter \( \Delta = 0.4 \) Ry.

| \( kq \) | Ce | Pr | Pm | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 22 | 125 | 109 | 93 | 75 | 55 | 44 | 33 | 15 | 23 | 24 | 25 | 24 | 21 |
| 42 | -265 | -240 | -220 | -189 | -182 | -168 | -165 | -153 | -172 | -172 | -165 | -158 | -150 |
| 44 | 524 | 470 | 439 | 415 | 398 | 384 | 373 | 358 | 342 | 330 | 314 | 300 | 285 |
| 62 | 1017 | 864 | 771 | 700 | 655 | 612 | 583 | 555 | 520 | 504 | 477 | 451 | 427 |
| 64 | -394 | -336 | -295 | -266 | -246 | -231 | -218 | -207 | -190 | -190 | -182 | -172 | -163 |
| 66 | 641 | 567 | 533 | 495 | 472 | 451 | 439 | 423 | 404 | 384 | 362 | 344 | 326 |
for. This spurious self-interaction is inherent to most of the DFT based methods and it may seriously deform the calculated crystal field. Also the one-electron part, taken from the discrete variational calculation already contains the electron correlation, which is for the second time included in the many-electron Hamiltonian. This are likely to be the reasons why the DV-ME calculated crystal field for Eu:LaF$_3$ is in poor agreement with the experiment (cf. Table 1 in [3]). The agreement is significantly improved only when two semiempirical parameters are introduced. In the present method the self-interaction is avoided by calculating the potential with the 4$f$ states in the core, where they contribute to the spherical part of the potential only (cf. 1st step in section 2) and there is no double counting of the correlation.

The present results show convincingly that the method of CFP calculation, described in section 2, can be successfully used also if the R site has a low symmetry. The mean square deviation $\chi$ shown in Fig. 3 calculated for optimal value of the hybridization parameter is, with exception of Yb, smaller than 30 cm$^{-1}$. We point out that no attempt was done to regroup the experimental results, which would make $\chi$ even smaller. The hybridization of the 4$f$ states with the valence states of the fluorine plays an important role - as documented in Figs. 5 and 6 increase of the hybridization (i.e. reduction of the parameter $\Delta$) changes some of the CFP by as much as 100 %. We note that large value of $\Delta$ corresponds to the vanishing hybridization. The dependence of CFP on $\Delta$ is smooth, allowing thus an interpolation if there is a need.

With increasing number of the 4$f$ electrons the strength of crystal field the CFP of 4th and 6th order decrease, while 2nd order CFP remain almost unchanged (cf. Figs. 7, 8), a similar behavior we found for R$^{3+}$ impurities in the YAlO$_3$ [7]. The values of $s_k$ (see eq. 8) and the $B^{(k)}_0$ compare well with those deduced from the data of Carnall et al. [1] (Figs. 7, 8). The remaining difference may be connected with too high (16.7 %) content of R atoms in the unit cell. To decrease this content would require a supercell with several hundreds atoms, which is beyond our present computational possibilities. Other possible sources of the difference are the replacement of the actual $C_2$ local symmetry by $C_{2v}$ in the Carnall et al. [1] analysis, uncertainty in experimental data (especially in cases of undetected levels) and keeping $\Delta$ fixed at 0.4 Ry.

Previously we treated $\Delta$ as an adjustable parameter [7, 8, 9]. In the present work we have also attempted to calculate $\Delta$ in a straightforward way described in section 2.1. The calculated $\Delta$ and $\Delta$ obtained from the fitting of experiment are in a fair agreement (Fig. 2), indicating thus that the model can be made fully ab-initio.

6. Conclusions

The method to calculate crystal field parameters was successfully applied to rare earth impurities in LaF$_3$, showing its applicability to R on sites with an arbitrary local symmetry. Despite the ionic character of the compound the R(4$f$) - F(2$p$, 2$s$) hybridization plays a significant role. The parameter $\Delta$, which is needed to describe this hybridization, can be calculated independently and the calculated value is in a fair agreement with value which fit the experiment. The method thus has potential to be fully ab-initio i.e. only the atomic composition and the crystal structure are needed to determine the crystal field. This would be particularly useful in systems in which the optical absorption data are scarce or missing and in systems with defects and/or several different R ions. The method has only moderate demands on the computing facility and it is now freely accessible to public [21].

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