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Crystal-field and superposition model analysis of R^{3+}:BaY_2F_8 (R = Er, Dy, Nd)

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Abstract. The experimental values of the energy levels of Er^{3+}, Dy^{3+}, and Nd^{3+} in BaY_2F_8 were fitted to a single-ion Hamiltonian containing free-ion and crystal-field interactions. The crystal-field parameters so evaluated were then analyzed by using Newman's Superposition Model. The agreement between the two sets of parameters is good, provided a possible distortion of the F^- polyhedron around the rare-earth site is taken into account. The effects of a possible displacement of the rare-earth ion substituting for Y^{3+} are also evaluated.

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1 Introduction

Yttrium fluorides single crystals doped with trivalent rare-earth (RE) ions are good candidates as active materials for new generation lasers in the 2–4 μm wavelength range. In fact, they are characterized by rather low phonon energies, in comparison with those of the more widely used YAG. Since the RE substitution occurs at the unique Y^{3+} site, charge compensation is not required, therefore the dopant level can be widely varied.

From a theoretical point of view a calculation of the energy levels of the $4f^N$ configurations in solids based on the single-ion model usually yields good results. In this framework, the RE Hamiltonian can be written as

$$H = H_{FI} + H_{CF} \tag{1}$$

where H_{FI} is the free-ion part of the total Hamiltonian H, while H_{CF} describes the crystal-field interaction. Both H_{FI} and H_{CF} contain a certain number of parameters which are usually determined by fitting the experimental energy levels to the Hamiltonian (1). Notably, the free-ion parameters are characteristic of the considered RE ion, and they usually do not change significantly if the same ion is embedded in different hosts. On the contrary the crystal-field (CF) parameters A_k^q (defined in Sect. 2) depend on the charges and positions of the ions around the RE site, and not on the RE itself. Despite that, an *ab initio* calculation of the CF parameters is often hard, and semiphenomenological models have to be applied. During the last decades, Newman's Superposition Model (SPM) [1–4] has been successfully used in many circumstances [5–7] to analyze crystal-field effects on lanthanide and actinide ions.

In the present work high-resolution FTIR spectroscopy was applied to study the monoclinic Dy-doped and Er-doped BaY_2F_8 single crystals, and to measure and analyze the absorption spectra related to RE transitions. These experimental data, together with similar literature data for Nd, were fitted to a single-ion Hamiltonian. The obtained CF parameters were then analyzed in terms of the SPM, also considering possible small distortions of the RE ligand (F^- ions) cage [6]. The effects of a RE-ion displacement on the CF parameters are then discussed.

2 Single-ion fitting of energy levels

The experimental energy levels of R^{3+}:BaY_2F_8 (R=Dy,Er) were determined by applying the high-resolution (0.02 cm^{-1}) optical absorption spectroscopy in the temperature range 9–300 K. The Dy-doped (4.4% m.f.) and Er-doped (0.5% m.f.) BaY_2F_8 single crystals were grown by means of the Czochralsky method at the Physics Department of the University of Pisa (Italy). These relatively low RE concentrations were chosen in order to avoid the additional lines due to the presence of Er clusters which appear in the spectra of highly doped samples [8]. The optical measurements were performed by means of a Bomem DA8 Fourier Transform spectrometer in the spectral range 3000–20000 cm^{-1}. The experimentally detected transitions were then analyzed in order to obtain the energy level scheme for

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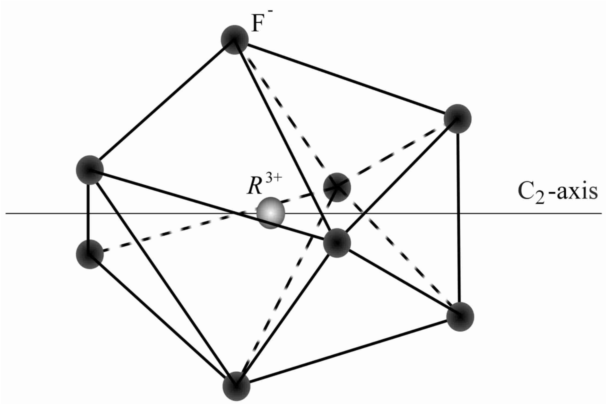

Fig. 1. Structure of a RF$_8$ polyhedron in R^{3+}: BaY$_2$F$_8$. The picture highlights the local C_2 symmetry of the R^{3+} site.

the two considered RE ions. A detailed discussion of the experimental results will be given elsewhere.

The Hamiltonian which was used to calculate the energy levels has the form displayed in equation (1). According to [9], the atomic part is written as

$$H_{FI} = E_{av} + \sum_k F^k \hat{f}_k + \zeta \hat{H}_{S.O.} + \alpha \hat{L}(\hat{L}+1) + \beta \hat{G}(G_2) + \gamma \hat{G}(R_7) + \sum_i T^i \hat{t}_i + \sum_j M^j \hat{m}_j + \sum_k P^k \hat{p}_k \quad (2)$$

where $k = 2, 4, 6$; $i = 2, 3, 4, 6, 7, 8$; $j = 0, 2, 4$. This model free-ion Hamiltonian accounts for two-body electrostatic repulsion (F^k), two- and three-body configuration interactions (α, β, γ and T^i, respectively), spin-orbit coupling (ζ), spin-other-orbit interactions (M^j) and electrostatically correlated spin-orbit interactions (P^k). A detailed description of the various operators and parameters is available in the literature [10]. The CF Hamiltonian [11] is written as

$$H_{CF} = \sum_k \sum_q B_k^q \hat{C}_k^q. \quad (3)$$

The tensor operators $\hat{C}_k^q$ are defined in [12]. In this framework, the CF parameters B_k^q are expressed according to Wybourne normalization; in the following, the parameters A_k^q, according to Stevens normalization, will be used. The two sets of parameters are equivalent, being related by means of the simple expression

$$B_k^q = A_k^q \left\langle r^k \right\rangle N_k^q \quad (4)$$

where N_k^q are constant real numbers [13]. Accurate values of $\langle r^k \rangle$ for various $4f^N$ configurations are given in [14].

A description of the crystal structure of BaY$_2$F$_8$ can be found in [15]. Figure 1 presents in detail the structure of an RF$_8$ polyhedron: since the R^{3+} ion occupies a site of C_2 local symmetry, fourteen non-zero CF parameters appear in equation (3). In this work odd-q parameters were used rather than negative-q, *i.e.* the y-axis was chosen as the C_2-axis. As a consequence, the CF Hamiltonian has the form:

$$H_{CF} = \sum_{k=2,4,6} \sum_{q=0}^{k} A_k^q \left\langle r^k \right\rangle N_k^q \left(\hat{C}_k^{-q} + (-1)^q \hat{C}_k^q \right) \quad (5)$$

and $A_2^1 = 0$ if the orientation of the axes is fixed in a particular reference frame (by rotating the system of an angle ϕ around the y-axis) [16].

Table 1. Free-ion parameters for R^{3+}: BaY$_2$F$_8$. All values are in cm^{-1}. The values which appear in brackets were not allowed to vary in the fitting.

Parameter	Er^{3+}:BaY$_2$F$_8$	Dy^{3+}:BaY$_2$F$_8$	Nd^{3+}:BaY$_2$F$_8$
E_{av}	35648 ± 6	55680 ± 50	24335 ± 50
F^2	96354 ± 56	90000 ± 150	[72625]
F^4	68601 ± 77	65060 ± 220	[53086]
F^6	53204 ± 82	48267 ± 180	[35425]
ζ	2362 ± 1	1911 ± 1	[880]
α	[17.79]	16 ± 1	[17.2]
β	[−582]	[−633]	[−513]
γ	[1800]	[1790]	[1291]
T^2	[400]	[329]	[154]
T^3	[43]	[36]	[42]
T^4	[73]	[127]	[47]
T^6	[−271]	[−314]	[−286]
T^7	[308]	[404]	[246]
T^8	[299]	[315]	[249]
M^0	[3.86]	[3.39]	[2.43]
M^2	[2.16]	[1.90]	[1.36]
M^4	[1.20]	[1.05]	[0.88]
P^2	[594]	[719]	[286]
P^4	[297]	[359]	[215]
P^6	[59.4]	[71.9]	[143]

The single-ion parameters for Dy^{3+} and Er^{3+} in BaY$_2$F$_8$ were determined by fitting all the experimental energy levels below 20 000 cm^{-1}. The procedure used for the calculations is essentially that described in [9]. The free-ion parameters for R^{3+}: LaF$_3$ [9] were tentatively used as starting values, and a few of them were allowed to vary during the fitting procedure. In the case of Nd^{3+} the experimental energy levels were taken from [17]. These data had already been fitted with a single-ion Hamiltonian of C_{2v} symmetry [18], which involves only nine CF parameters. The energy levels below 13 000 cm^{-1} were reanalyzed considering a single-ion Hamiltonian of the true C_2 symmetry: the free-ion parameters were all taken from [18] and kept fixed, while the fourteen CF parameters were freely varied. It should be stressed that such an assumption led to a fair improvement of the fit quality ($\sigma \simeq 12$ cm^{-1}).

The three sets of parameters corresponding to the three examined RE dopants are listed in Table 1 (free ion) and Table 2 (crystal field): the parameters which are listed in brackets were not allowed to vary during the fitting. Table 3 shows the comparison between the experimental and

Table 2. The CF parameters for R^{3+}: BaY_2F_8 obtained by fitting the experimental energy levels are compared with those calculated within the SPM. All values are in cm^{-1}.

Parameter	Er^{3+} fitting	Er^{3+} S.M.	Dy^{3+} fitting	Dy^{3+} S.M.	Nd^{3+} fitting	Nd^{3+} S.M.
A_2^0	-318 ± 20	-316	-320 ± 6	-318	-278 ± 19	-280
A_2^2	100 ± 88	94	-18 ± 30	-12	-129 ± 62	-140
A_4^0	-141 ± 13	-131	-131 ± 4	-124	-48 ± 5	-51
A_4^1	-310 ± 240	-381	-336 ± 58	-405	92 ± 60	-200
A_4^2	-69 ± 62	136	31 ± 43	110	16 ± 60	32
A_4^3	-10 ± 280	236	250 ± 110	198	-710 ± 130	61
A_4^4	336 ± 64	328	306 ± 17	321	170 ± 40	140
A_6^0	6.1 ± 2.2	7.1	6.7 ± 0.4	6.6	3.25 ± 0.40	3.8
A_6^1	43 ± 30	45	30 ± 8	45	10 ± 8	31
A_6^2	7 ± 10	-2.1	5 ± 6	2.3	0.39 ± 3.5	5.8
A_6^3	22 ± 32	1.35	3.7 ± 8.0	0.75	20 ± 16	0.10
A_6^4	56 ± 12	50	50 ± 3	47	42 ± 3	29
A_6^5	256 ± 40	210	211 ± 16	202	133 ± 34	128
A_6^6	48 ± 17	6.1	16 ± 5	7.5	-5.5 ± 5.0	6.4

Table 3. Experimental and calculated energy levels for Dy^{3+}: BaY_2F_8. All values are in cm^{-1}.

Attribution	Experiment	Calculation
$^6H_{15/2}$	0	-2.8
	7.5	8.1
	49.1	51.5
	70.4	70.7
	110.8	112.1
	200	207.2
	220	233.2
	585	570.5
$^6H_{13/2}$	3515.7	3513.8
	3531.1	3532.4
	3554.3	3554.2
	3578.0	3576.1
	3632.9	3631.1
	3680.0	3675.5
	3832.4	3836.3
$^6H_{11/2}$	5851.7	5839.1
	5854.7	5848.2
	5893.7	5892.6
	5950.7	5960.0
	6015.0	6018.1
	6046.0	6041.2
$^6H_{9/2} + ^6F_{11/2}$	7604.9	7603.0
	7645.2	7643.6
	7685.5	7683.9
	7703.0	7702.9
	7773.0	7767.3
	7798.0	7806.4
$^6H_{9/2} + ^6F_{11/2}$	7842.0	7846.1
	7854.5	7855.3
	7909.0	7915.0
	8018.7	8018.7
	8072.0	8073.9
$^6H_{7/2} + ^6F_{9/2}$	8960.0	8953.1
	9002.5	9006.9
	9083.0	9088.2
	9177.7	9174.4
	9184.0	9176.7
	9222.0	9224.6
	9267.0	9268.1
	9303.8	9305.5
	9425.4	9430.1
$^6H_{5/2}$	10166.7	10159.7
	10210.9	10208.5
	10426.2	10438.8
$^6F_{7/2}$	10995.8	11007.0
	11088.7	11087.7
	11128.7	11114.7
	11163.8	11151.4
$^6F_{5/2}$	12422.8	12430.7
	12452.5	12457.4
	12541.5	12532.9
$^6F_{3/2}$	13268.4	13266.9
	13276.6	13281.2
$^6F_{1/2}$	13817.5	13821.2

calculated energy levels of Dy^{3+}: BaY_2F_8, which appear to be quite satisfactory.

3 Superposition-model analysis

The main assumptions of the SPM are that: 1) the CF potential at the RE site can be written as the sum of individual contributions from the ligands, and 2) these single-ion contributions are cylindrically symmetric [3]. In this framework, the CF parameters which appear in H_{CF} can be expressed as

$$A_k^q = \sum_\ell \bar{A}_k\left(R_\ell\right) K_k^q\left(\theta_\ell, \varphi_\ell\right) \tag{6}$$

where K_k^q are the coordination factor defined in [1] and ℓ labels the ligands. The distance (R_ℓ) dependence of the intrinsic parameters is usually assumed to follow the power law

$$\bar{A}_k\left(R_\ell\right) = \bar{A}_k\left(R_0\right)\left(\frac{R_0}{R_\ell}\right)^{t_k} \tag{7}$$

where R_0 is an arbitrarily fixed standard ligand distance [3].

The calculations were performed considering the single-ion contributions for the eight F^- nearest neighbours to the RE. The ligand positions were determined from X-ray diffraction measurements performed on BaY_2F_8 and refined in the assumption that the RE ion lies in a site of C_2 point symmetry [15]. R_0 was tentatively fixed at 2.275 Å (*i.e.* the average Y^{3+}-F^- distance). A satisfactory agreement could not be obtained under these assumptions. In fact, a significant uncertainty in the determination of the CF parameters in the frame of the SPM is expected, caused by the local distortions due to the substitution of the RE paramagnetic ion into a diamagnetic host crystal [3]. As a model distortion, in addition to a possible isotropic expansion of the F^- polyhedron around the RE sites, a variation of the position of the four F^- ions placed near the xz plane was considered (Fig. 2), by introducing a compression factor c for the distances between the central RE ion and the involved ligands. This simple model was preferred to more complex hypotheses because the F^- polyhedron is allowed to change significantly both its size and its shape, without adding a large number of extra parameters. In addition, the considered distortion does not break the C_2 symmetry for the RE site: the choice was made since the experimental energy levels appear to be quite well reproduced by a C_2 single-ion Hamiltonian, without the need of any additional degree of freedom (see Sect. 2). The isotropic expansion does not change the ratios between different CF parameters, so its effect involves only a reduction of the intrinsic parameters $\bar{A}_k$ and there is no need to add new parameters. However, this kind of distortion alone cannot improve the agreement. On the contrary, the anisotropic compression, described by the factor c, significantly affects the above ratios: in such a way, a good agreement with the CF parameters of the C_2 symmetry single-ion Hamiltonian is obtained.

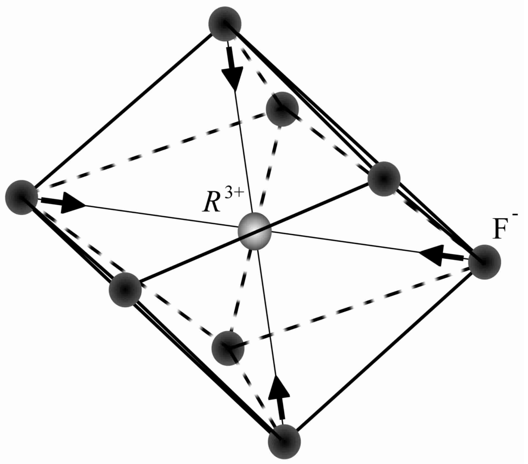

Fig. 2. The model anisotropic distortion of the RF_8 polyhedron (projected on the xz plane). The arrows indicate the four involved F^- atoms. The C_2-axis is perpendicular to the considered plane.

Table 4. SPM parameters for R^{3+}: BaY_2F_8.

S.M. Parameter	Er^{3+}	Dy^{3+}	Nd^{3+}
$\bar{A}_2$	720 ± 10 cm^{-1}	720 ± 10 cm^{-1}	630 ± 20 cm^{-1}
$\bar{A}_4$	48 ± 2 cm^{-1}	48 ± 2 cm^{-1}	22 ± 1 cm^{-1}
$\bar{A}_6$	3.8 ± 0.3 cm^{-1}	3.8 ± 0.3 cm^{-1}	2.5 ± 0.1 cm^{-1}
t_2	5.0 ± 0.5	5.0 ± 0.5	5.0 ± 0.5
t_4	6.0 ± 0.5	6.0 ± 0.5	6.0 ± 0.5
t_6	10.0 ± 0.5	10.0 ± 0.5	10.0 ± 0.5
c	0.980 ± 0.001	0.988 ± 0.001	1.000 ± 0.001
R_0	2.275 Å	2.275 Å	2.275 Å

The values of the fourteen CF parameters determined in Section 2 were fitted with the parameters $\bar{A}_2(R_0)$, $\bar{A}_4(R_0)$, $\bar{A}_6(R_0)$, t_2, t_4, t_6, and c. It must be stressed that, in this framework, the angle ϕ is not an independent parameter: for each ligand ℓ it is $K_2^1(\ell) = 6x_\ell z_\ell / R_\ell^2$, then ϕ is determined by solving the equation

$$\sum_\ell \frac{(x_\ell \cos\phi - z_\ell \sin\phi)(z_\ell \cos\phi + x_\ell \sin\phi)}{R_\ell^{2+t_2}} = 0. \tag{8}$$

The CF parameters for the three examined compounds calculated within the SPM are listed in Table 2, and compared with those obtained from the fitting. The sets of parameters used are given in Table 4. The use of non-integer t_2, t_4 and t_6 did not significantly improve the calculated SPM parameters, and in particular could not lead in any case to satisfactory results in absence of the anisotropic compression c. The same is true for the attempts to vary the value of R_0. The intrinsic parameters and exponents evaluated in the present work for the R^{3+} - F^- pair substantially agree with previous results of other authors for RE ions in LaF_3. Yeung and Newman [19] examined the case R = Er with a method based on the analysis of spectral moments, giving the values $\bar{A}_2 \simeq 340$ cm^{-1}, $\bar{A}_4 \simeq 58$ cm^{-1}, and $\bar{A}_6 \simeq 4$ cm^{-1} for $R_0 = 2.42$ Å. It should be remarked that this method

Table 5. Comparison between the fitted values of the CF parameters for R^{3+}: BaY_2F_8 and their possible calculated range, considering an off-center position for the RE ion. All values are in cm^{-1}. The top and the bottom halves of the table list respectively the parameters with small and large uncertainty.

Parameter	Er^{3+} fitting	Er^{3+} SPM	Dy^{3+} fitting	Dy^{3+} SPM	Nd^{3+} fitting	Nd^{3+} SPM
A_2^0	-318 ± 20	-315 ± 15	-320 ± 6	-316 ± 15	-278 ± 19	277 ± 12
A_4^0	-141 ± 13	-129 ± 9	-131 ± 4	-121 ± 10	-48 ± 5	-51 ± 4
A_4^4	336 ± 64	335 ± 35	306 ± 17	329 ± 35	170 ± 40	146 ± 17
A_6^0	6.1 ± 2.2	6.9 ± 1.1	6.7 ± 0.4	6.4 ± 1.2	3.25 ± 0.40	3.6 ± 0.8
A_6^4	56 ± 12	49 ± 1	50 ± 3	46 ± 1	42 ± 3	28 ± 1
A_6^5	256 ± 40	215 ± 30	211 ± 16	205 ± 25	133 ± 34	129 ± 14
A_2^2	100 ± 88	94 ± 60	-18 ± 30	-12 ± 60	-129 ± 62	-140 ± 50
A_4^1	-310 ± 240	-370 ± 130	-336 ± 58	-410 ± 125	92 ± 60	-207 ± 50
A_4^2	-69 ± 62	110 ± 80	31 ± 43	90 ± 80	16 ± 60	23 ± 39
A_4^3	-10 ± 280	190 ± 310	250 ± 110	155 ± 290	-710 ± 130	40 ± 120
A_6^1	43 ± 30	45 ± 12	30 ± 8	46 ± 10	10 ± 8	30 ± 5
A_6^2	7 ± 10	0 ± 6	5 ± 6	4 ± 6	0.39 ± 3.5	7 ± 4
A_6^3	22 ± 32	0 ± 7	3.7 ± 8.0	0 ± 6	20 ± 16	-1 ± 3
A_6^6	48 ± 17	8 ± 4	16 ± 5	9 ± 3	-5.5 ± 5.0	7 ± 2

leaves the power law exponents undetermined, but it was guessed [3] that $3 < t_2 < 5$. Yeung and Reid [20] fitted the fourth- and sixth-order C_2 parameters for $R = \mathrm{Pr}$, obtaining $\bar{A}_4 \approx 23$ cm^{-1}, $\bar{A}_6 \approx 1.7$ cm^{-1}, $t_4 = 6.1 \pm 1.3$, and $t_6 = 8.7 \pm 1.1$ for $R_0 = 2.436$ Å: it must be noticed that these authors were not able to fit the second order parameters satisfactorily, probably because of the nonnegligible effect of the next-nearest neighbors. This might explain why Yeung and Newman obtained a value for $\bar{A}_2$ which is about one half of that reported in the present work.

The present results, related to BaY_2F_8, stress that a small change of the anisotropic compression factor c is enough to reproduce very well the CF parameters for R = Dy, Er by using the same $\bar{A}_k$ and t_k for the two dopants. In the case of Nd, satisfactory results are obtained without any anisotropic distortion but with somewhat smaller intrinsic parameters $\bar{A}_k$. This might be an indirect confirmation that an isotropic expansion of the F^- polyhedron actually takes place in the case of Nd^{3+}, whose ionic radius is about 10% larger than that of Y^{3+} (while Er^{3+} and Dy^{3+} have almost the same ionic radius as Y^{3+}).

As it was shown above, SPM calculations reproduce most of the fitted values of the CF parameters for R^{3+}:BaY_2F_8. Moreover, the values of the intrinsic parameters and exponents agree with those reported in the literature. However, a careful inspection of Table 2 shows that some fitting parameters appear with a large standard deviation (in a few cases larger than the parameter itself), and that the calculated values of a few parameters lie outside the error bars as obtained by the fitting. An interpretation of such a behaviour was attempted by introducing a displacement of the RE ion with respect to the Y^{3+} ion which it substitutes for. Again, it was chosen to maintain the C_2 site symmetry, so the RE is allowed to shift along the y-axis only. Let Δ be the difference between the y coordinate of the R^{3+} and that of the original Y^{3+} ion.

The analysis was performed using the values for the SPM parameters given in Table 4. Table 5 reports the possible range for all the CF parameters calculated supposing $|\Delta| < 0.05$ Å, along with their standard deviations as determined by the fitting. The parameters which are listed in the top half of Table 5 have a small calculated range: in fact, it was found out that they are almost independent of Δ in the range $|\Delta| < 0.2$ Å. It also appears that they were determined by the fitting procedure with a relatively small standard deviation, and that their calculated values agree with those determined by the fitting. On the other hand, it was found that the parameters which show a large standard deviation are strongly dependent on Δ (bottom half of Tab. 5), and that most of them are allowed to take values within the fitting range if $|\Delta| < 0.1$ Å. Although a quantitative estimate of Δ is not possible because of the uncertainties of the fitting parameters, this finding is in line with a possible off-center position for the RE ion relatively to the original Y^{3+} site.

4 Conclusions

The experimental energy levels for three different trivalent RE dopants in BaY_2F_8 were fitted to a single-ion Hamiltonian of C_2 symmetry. SPM calculations showed a good agreement with the CF parameters obtained from the fitting: moreover, the three sets of SPM parameters are very similar and reasonably agree with the literature parameters for the R^{3+} - F^- pair in other host crystals. In order to get these results a distortion of the YF_8 polyhedron when Y^{3+} is substituted with the RE ion was taken into account, and its magnitude was quantitatively estimated within the SPM. The same model suggests a relation between a possible off-center position for the R^{3+} ion and the large uncertainty of some fitting parameters.

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