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Abstract. A method for crystal-field energy level analysis was proposed which used the group chain scheme introduced by Butler. The ratios of crystal-field parameter calculated by a simple point charge model was used as a constraint condition, which turned out to be the same or essentially the same as those obtained by a superposition model or other models and the absolute values of these ratios can be seen as a measure of the degree of symmetry distortion of the system. As an example, the situation of D_3 symmetry was studied. By using this fitting technique to obtain values for the parameters, only one minimum was found for each of the cases studied. The eigenfunctions obtained have obvious symmetry properties and the low-symmetry distortion of the system can easily be seen from the ratios C_μ^k/C_0^k. Therefore, the crystal-field analysis is not only a formalism but also a real physical insight. The crystal field for Nd^{3+}:$YAl_3(BO_3)_4$ and $NdAl_3(BO_3)_4$ crystals was analysed in detail.

1. Introduction

Crystal-field theory has been widely used in energy level analysis of laser crystals doped with rare-earth and transition-metal ions, as well as in various problems in the fields of physics and chemistry nowadays, and a large number of papers have been published [1–9]. Nevertheless, the way in which the least-squares fitting should be carried out unambiguously is still a problem, especially for situations in which the active ions are in low-symmetry sites. Many minima exist which are indistinguishable from each other. All of them can have a small RMS deviation but they do not all correspond to physical reality and it is difficult to determine which solution is the best only by the fitting of energy level data. One way to overcome this difficulty is to introduce a theoretical model and to select the best set which agrees well with the model. A variety of theoretical models have been proposed [10–19] and some of them were used to assess the reliability of the fitting. However, it must be admitted that no special model can represent singly the crystal-field effect because there are so many kinds of mechanism contributing to the crystal-field effect [10]. In fact, the agreement between theoretical calculation results and the data obtained by energy level fitting is still very unsatisfactory. On the other hand, a set of 'crystal-field invariants' has been proposed and it is believed that they can be used to check the final results [20–22]. It is noteworthy that the crystal-field invariant can always be satisfied by the crystal-field parameters obtained by least-squares fitting of the crystal-field energy levels provided that the RMS deviations of the fitting are sufficiently small. Therefore, it must be said that the crystal invariant cannot be used as an independent criterion to check the validity of final

results. It is suggested in this paper that to utilize fully the symmetry distortion degree of the system, which can be seen clearly from the ratios of crystal-field parameters belonging to the same k-value in the group chain scheme [23] as the constraint condition in the fitting could be a good way to deal with the problem concerned. It turns out that the degree of low-symmetry distortion of the system can be estimated by the simple point-charge (PC) model, or more exactly that the initial values of these ratios can be estimated by the simple PC model. This method was used to study the situations in laser crystals of Nd^{3+}:$YAl_3(BO_3)_4$ (NYAB) and $NdAl_3(BO_3)_4$ (NAB) in which Nd^{3+} ions occupy D_3 symmetry sites.

2. Theoretical formulation of the method

Suppose that the active Nd^{3+} ions occupy the positions belonging to point group G; then the crystal-field Hamiltonian H_{cf} is invariant under the action of any elements of G, i.e. it transforms as O(G) (in Butler's [23] notation). For the situations studied, G=D_3. Consider the group chain $SO_3 \supset O \supset D_3$, H_{cf} can be expressed as

$$H_{cf} = \sum_{k,\mu} C^k_{\mu O} b^k_{\mu O} \tag{1}$$

where $b^k_{\mu O}$ are the basic functions of the group chain $SO_3 \supset O \supset D_3$ and are identical with $|k\mu O\rangle$ in [23], and $C^k_{\mu O}$ are the expansion coefficients of H_{cf} according to these bases. Because all these functions belong to the O representation, the index O can be omitted in equation (1); then

$$H_{cf} = \sum_{k,\mu} C^k_{\mu} b^k_{\mu} \tag{2}$$

where b^k_{μ} can be found from [23, ch 16], which has been expressed as linear combination of spherical harmonics $|kq\rangle$. In order to compare this with the Hamiltonian of traditional crystal-field theory, $|kq\rangle$ should be expressed as C_{kq} by

$$|kq\rangle = N_k C_{kq} \tag{3}$$

where $N_2 = (\frac{3}{2})^{1/2}$, $N_4 = (\frac{1}{2})(\frac{35}{2})^{1/2}$, $N_6 = (\frac{3}{2})(\frac{7}{2})^{1/2}$. On the other hand, H_{cf} can be expressed as

$$H_{cf} = \sum_{k,q} B_{kq} C_{kq}. \tag{4}$$

In the case of the point group D_3, the detailed crystal-field Hamiltonian will be

$$H_{cf} = C^2_{\tilde{1}} b^2_{\tilde{1}} + C^4_0 b^4_0 + C^4_{\tilde{1}} b^4_{\tilde{1}} + C^6_0 b^6_0 + C^6_{\tilde{1}_0} b^6_{\tilde{1}_0} + C^6_{\tilde{1}_1} b^6_{\tilde{1}_1} \tag{5}$$

in the group chain scheme. It can also be expressed as

$$H_{cf} = B_{20} C_{20} + B_{40} C_{40} + B_{43} C_{43} + B_{60} C_{60} + B_{63} C_{63} + B_{66} C_{66} \tag{6}$$

where B_{43} and B_{63} have been made real by a rotation about the Z axis. It can be easily shown that the relationship between the crystal-field parameters of two different schemes will be

$$B_{20} = -(\tfrac{2}{3})^{1/2} C_1^2$$
$$B_{40} = 2(\tfrac{2}{35})^{1/2}[(-\tfrac{1}{3})(\tfrac{7}{3})^{1/2} C_0^4 - (\tfrac{2}{3})(\tfrac{5}{3})^{1/2} C_1^4]$$
$$B_{43} = 2(\tfrac{2}{35})^{1/2}[(-\tfrac{1}{3})(\tfrac{10}{3})^{1/2} C_0^4 + (\tfrac{1}{3})(\tfrac{7}{6})^{1/2} C_1^4]$$
$$B_{60} = 4(\tfrac{1}{231})^{1/2}[(-\tfrac{4}{9})(2)^{1/2} C_0^6 + (\tfrac{7}{9}) C_{1_1}^6]$$
$$B_{63} = 4(\tfrac{1}{231})^{1/2}[(\tfrac{1}{9})(\tfrac{35}{3})^{1/2} C_0^6 + (\tfrac{11}{42})^{1/2} C_{1_0}^6 + (\tfrac{4}{9})(\tfrac{10}{21})^{1/2} C_{1_1}^6]$$
$$B_{66} = 4(\tfrac{1}{231})^{1/2}[(-\tfrac{1}{9})(\tfrac{77}{6})^{1/2} C_0^6 + (\tfrac{5}{21})^{1/2} C_{1_0}^6 - (\tfrac{4}{9})(\tfrac{11}{21})^{1/2} C_{1_1}^6].$$

(7)

Conversely

$$C_1^2 = -(\tfrac{3}{2})^{1/2} B_{20}$$
$$C_0^4 = (\tfrac{1}{2})(\tfrac{35}{2})^{1/2}[(-\tfrac{1}{9})(21)^{1/2} B_{40} - (\tfrac{2}{9})(30)^{1/2} B_{43}]$$
$$C_1^4 = (\tfrac{1}{2})(\tfrac{35}{2})^{1/2}[(-\tfrac{2}{9})(15)^{1/2} B_{40} + (\tfrac{1}{9})(42)^{1/2} B_{43}]$$
$$C_0^6 = (\tfrac{1}{4})(231)^{1/2}[(-\tfrac{4}{9})(2)^{1/2} B_{60} + (\tfrac{2}{27})(105)^{1/2} B_{63} - (\tfrac{1}{27})(462)^{1/2} B_{66}]$$
$$C_{1_0}^6 = (\tfrac{1}{4})(231)^{1/2}[(\tfrac{1}{21})(462)^{1/2} B_{63} + 2(\tfrac{5}{21})^{1/2} B_{66}]$$
$$C_{1_1}^6 = (\tfrac{1}{4})(231)^{1/2}[(\tfrac{7}{9}) B_{60} + (\tfrac{8}{189})(210)^{1/2} B_{63} - (\tfrac{8}{189})(231)^{1/2} B_{66}].$$

(8)

Newman and Ng [20] mentioned that the ratios of the phenomenological parameters were very similar to those calculated by a simple PC electrostatic model for the nearest-neighbour ions, and the calculations of Ellis and Newman [24, 25] showed that the ratio $A_6^6\langle r^6\rangle / A_6^0\langle r^6\rangle$ calculated for the dominant overlap and covalent contributions in the complex $(\mathrm{PrCl_9})^{6-}$ is in fact exactly the same as the electrostatic ratio; its reciprocal was used to determine crystal-field parameters in rare-earth trichlorides [26]. We would like to point out that it is possible to use the superposition model to demonstrate the consistent behaviour of these ratios. According to the superposition model [20], we have the following equations:

$$A_k^q\langle r^k\rangle = \sum_L A_k(R_L) K_{kq}(\theta_L, \phi_L)$$

(9)

and

$$A_k(R) = A_k(R_0)(R_0/R)^{t_k}$$

(10)

where K_{kq} is the geometrical factor given in [20, table 2], t_k is the power-law exponent which depends on the mechanisms involved. In the situations studied (i.e. the D_3 site symmetry), all the R_L-values are equal; then

$$\frac{A_k^{q'}}{A_k^q} = \sum_L K_{kq'}(\theta_L, \phi_L) \bigg/ \sum_L K_{kq}(\theta_L, \phi_L).$$

(11)

It is independent of the t_k-value. This means that the ratios $A_k^{q'}/A_k^q$ (and therefore $B_{kq'}/B_{kq}$) calculated by the simple PC mechanism is the same as those obtained by other mechanisms involved in crystal-field interaction. Even some R_L do not equal each other; the ratios of the crystal-field parameters calculated from the resultant contribution of all the different mechanisms (corresponding to different t_k-values) will be essentially the same as those calculated from only a single t_k-value corresponding to the simple PC mechanism. The calculated result for Nd^{3+}:YAG is shown in table 1; the related structure data were taken from [27]. Obviously, the ratios for the composite effect are essentially the same as those due to only simple PC interaction.

Table 1. Comparison of the ratios of the crystal-field parameters of Nd^{3+}:YAG obtained by the composite superposition model (contributions from a series of t_k-values) and by the single superposition model (contributions from t_k-values corresponding to a simple PC mechanism). The structure data of Nd^{3+}:YAG is taken from [27]. In the calculation using the composite model, t_k-values from $t_k = 5$ to $t_k = 11$ and from $t_k = 7$ to $t_k = 13$ were taken into account for $k = 4$ and $k = 6$, respectively.

	B_{42}/B_{40}	B_{44}/B_{40}	B_{62}/B_{60}	B_{64}/B_{60}	B_{66}/B_{60}
Single	0.19	−0.45	1.96	1.36	−0.14
Composite	0.25	−0.48	1.90	1.35	−0.16

The crystal-field parameter ratios in the traditional crystal field scheme were defined as

$$P_1 = B_{43}/B_{40} \qquad P_2 = B_{63}/B_{60} \qquad P_3 = B_{66}/B_{60}. \tag{12}$$

The corresponding ratios in the group chain scheme were

$$r_1 = C_{\bar{1}}^4/C_0^4 \qquad r_2 = C_{\bar{1}_0}^6/C_0^6 \qquad r_3 = C_{\bar{1}_1}^6/C_0^6. \tag{13}$$

Then the relationships between these two sets become

$$P_1 = [(10)^{1/2} - (\tfrac{7}{2})^{1/2}r_1]/[(7)^{1/2} + 2(5)^{1/2}r_1]$$
$$P_2 = [(-\tfrac{1}{4})(\tfrac{35}{6})^{1/2} - (\tfrac{9}{8})(\tfrac{11}{21})^{1/2}r_2 - (\tfrac{5}{21})^{1/2}r_3]/[1 - (\tfrac{7}{4})(\tfrac{1}{2})^{1/2}r_3] \tag{14}$$
$$P_3 = [(\tfrac{1}{8})(\tfrac{77}{3})^{1/2} - (\tfrac{9}{4})(\tfrac{5}{42})^{1/2}r_2 + (\tfrac{11}{42})^{1/2}r_3]/[1 - (\tfrac{7}{4})(\tfrac{1}{2})^{1/2}r_3]$$

and

$$r_1 = [(\tfrac{10}{7})^{1/2} - p_1]/[(\tfrac{1}{2})^{1/2} + 2(\tfrac{5}{7})^{1/2}p_1]$$
$$r_2 = [(\tfrac{9}{14})(\tfrac{22}{5})^{1/2}p_2 + (\tfrac{9}{7})p_3]/[-(\tfrac{24}{35})^{1/2} + p_2 - (\tfrac{11}{10})^{1/2}p_3] \tag{15}$$
$$r_3 = [-(\tfrac{21}{8})(\tfrac{7}{30})^{1/2} - p_2 + (\tfrac{11}{10})^{1/2}p_3]/[(\tfrac{21}{10})(\tfrac{5}{21})^{1/2} - (\tfrac{7}{4})(\tfrac{1}{2})^{1/2}p_2 + (\tfrac{7}{8})(\tfrac{11}{5})^{1/2}p_3].$$

It is apparent that in the group chain scheme the ratios r_1, r_2 and r_3 should all be zero when the site symmetry is cubic and the gradual distortion from cubic symmetry should correspond to a continued increase in $|r_1|$-, $|r_2|$- and $|r_3|$-values irrespective of the kinds of mechanism that contribute to the crystal field. The data published by Faucher and Caro [28] are very interesting and can be used as an example to explain the fact that the ratios calculated by the simple PC model certainly can represent the degree of symmetry distortion.

The corresponding relation between the degree of distortion and the magnitudes of r_1, r_2 and r_3 can be seen clearly from the results shown in table 2 which were calculated from the data given in [28]. On the other hand, we use a simple structure model to explain this relation in the case of the D_3 point group. The Nd^{3+} ion is sited in the middle between two ligand triangles (figure 1); when these two triangles have a relative rotation and deviate from cubic symmetry, the absolute values of r_i ($i = 1, 2, 3$) will gradually increase. This relation is shown in figure 2. All these analyses and calculations suggest that the better procedure for crystal-field energy level fitting is first to keep the crystal-field parameters ratios the same as those calculated by the simple PC model to reach the minimum and then to adjust the values of these ratios to reduce the RMS deviation further. The eigenfunctions of crystal-field states of each term $^{2S+1}L_J$ are expressed as a linear combination of Butler's group chain basis functions as listed in the appendix. All the coefficients in these combinations can be obtained by the fitting. Because Butler's basis functions belong to definitive irreducible representations of O and D_3 groups, the symmetry properties of the eigenfunctions obtained are obvious and will facilitate the study of the selection rule of the transitions between them. In the following section we shall use this method to analyse the crystal-field energy levels for the laser crystals of NAB and NYAB.
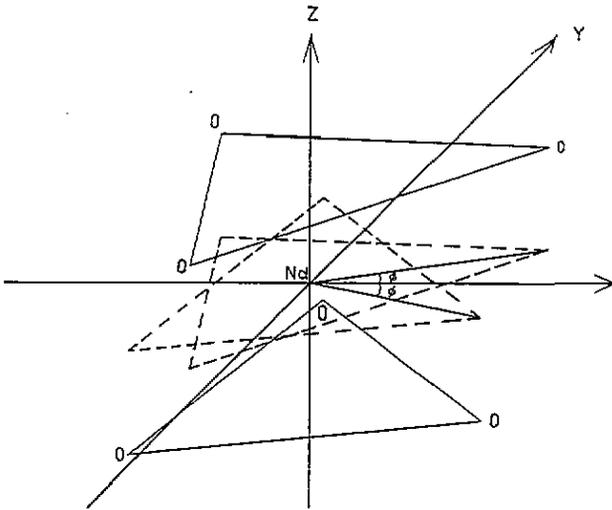

Figure 1. The local structure of NdO_6 and coordinate system for the crystal field analysed in this paper.

Table 2. Variation in the crystal-field parameter ratios of Eu^{3+}:$LaAlO_3$ in the group chain scheme versus temperature; when the temperature increases to 500 K, the point symmetry of the Eu^{3+} site progressively approaches O_h [28].

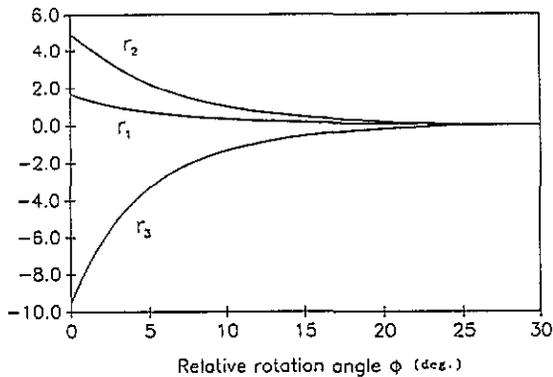| Temperature (K)	$C_{\bar{1}}^4/C_0^4$	$C_{\bar{1}_0}^6/C_0^6$	$C_{\bar{1}_1}^6/C_0^6$
72	0.1452	−0.1072	0.0116
300	0.1041	−0.0670	0.0011
500	0.0345	−0.0334	0.0023

Figure 2. Variation in the calculated crystal-field parameter ratios r_i ($i = 1, 2, 3$) with relative rotation angle between the two ligand triangles, when the Nd^{3+} point symmetry changes from $O \rightarrow D_3 \rightarrow D_{3h}$ corresponding to the relative rotation angle ϕ decreasing from $30° \rightarrow 0°$.

3. Crystal-field energy level analysis of the $NdAl_3(BO_3)_4$ and $Nd^{3+}:YAl_3(BO_3)_4$ crystals

The NAB crystal is a high-neodymium-concentration laser crystal with a low threshold, high gain and good physical and chemical properties [29], and the NYAB crystal has been developed as an ideal self-frequency-doubling laser crystal which can generate its fundamental laser light into second harmonics efficiently by itself [30]. Both NAB and NYAB crystals have structures belonging to the space group R_{32} [31,32]. The structure concerned is composed of two sets of isolated BO_3 triangles—one perpendicular and the other nearly so to the C axis. The Nd^{3+} ions in the NAB and NYAB crystals occupy the centres of the triangle prisms formed by two oxygen triangles which have relative rotation angles of 15.352° and 17.047°, respectively (see figure 1); each oxygen belongs to one BO_3 group. Other structural data are shown in table 3. The fluorescent spectra of these two crystals have been measured by other workers [33, 34] as well as by ourselves. The energy levels of the $^4F_{3/2}$, $^4I_{13/2}$, $^4I_{11/2}$ and $^4I_{9/2}$ terms were assigned according to these data and are given in tables 4–6. The matrix elements of the crystal-field Hamiltonian in the group chain scheme were calculated by means of the Wigner–Eckart theorem and the factorization lemma of the $3jm$ factors, and the results are listed in the appendix. As usually adopted in this field, the intermediate coupling has been taken into account using the reduced matrix elements $\langle f^n SLJ \| U_k \| f^n SL'J' \rangle$ in the intermediate-coupling approximation [35]; in other words, the $^{2S+1}L_J$ states used here are not the pure LS states but the intermediate-coupling states. Before the fitting, a PC calculation of the ratios of B_{kq} have been performed and the corresponding ratios in the group chain scheme were calculated from equations (12) and (15); the results obtained are shown in table 7, and the superposition PC model ratios were *directly calculated from equation (11) and transformed to the B_{kq} ratios using equation (2.9)* and [20, table 1]. In our calculation, by using these ratios as constraint conditions in the fitting, only one minimum was obtained, irrespective of the initial values adopted. Further work on the fitting requires adjustment of the ratios to minimize the RMS deviation of the energy levels. In table 7, comparisons of the initial and final ratios are given and the corresponding crystal-field parameters B_{kq} and C_μ^k are shown in tables 8 and 9. Finally, the experimental and calculated energy levels are compared in tables 4–6. Comparing the results obtained in this paper with those previously published by us [36, 37], obviously, one can see that the RMS deviations were decreased by the new method, although the

amount of calculation work is reduced. If the contribution of the two-electron crystal-field interaction is included, the agreement between the experimental energy levels and the calculated eigenvalues can be improved considerably. As pointed out by Judd [38], a phenomenological method to handle this contribution is to replace the matrix element $\langle f^n SL \| U_k \| f^n SL' \rangle$ by $\langle f^n SL \| U_k \| f^n SL' \rangle + C_k [S(S+1)/(2S+1)]^{1/2} \langle f^n SL \| V_k \| f^n SL' \rangle$; C_k $(k = 2, 4, 6)$ are three new parameters. Nevertheless, in doing this, the ratios of the crystal-field parameters C_μ^k / C_0^k (B_{kq}/B_{k0}) should not be changed, because the additional factor introduced is independent of the irreducible representation index μ (or q). Therefore, the method adopted in this paper is still valid.

Table 3. The O^{2-} coordinate data for the local NdO_6 structure in NAB and NYAB crystals, expressed as (R, θ, ϕ). The sites of $O(i)$ $(i = 1, 2, 3, 4, 5, 6)$ and the coordinate system are shown in figure 1.

	NAB	NYAB
O(1)	(2.3717, 56.32°, 7.68°)	(2.3215, 54.47°, 8.52°)
O(2)	(2.3717, 56.32°, 127.68°)	(2.3215, 54.47°, 128.52°)
O(3)	(2.3717, 56.32°, 247.68°)	(2.3215, 54.47°, 247.52°)
O(4)	(2.3717, 123.68°, −7.68°)	(2.3215, 125.53°, −8.52°)
O(5)	(2.3717, 123.68°, 112.32°)	(2.3215, 125.53°, 111.48°)
O(6)	(2.3717, 123.68°, 232.32°)	(2.3215, 125.53°, 231.48°)

Table 4. Comparison of the observed and calculated Stark splittings from the centre of gravity of the $^4F_{3/2}$, $^4I_{11/2}$ and $^4I_{9/2}$ manifolds of Nd^{3+} in the NAB crystal at 77 K.

Multiplet	Observed splitting (cm^{-1})	Calculated splitting (cm^{-1})	Δ (cm^{-1})
$^4F_{3/2}$	33.5	47.7	14.2
	−33.5	−47.7	−14.2
$^4I_{11/2}$	104.3	91.1	−13.2
	81.3	46.9	−34.4
	−26.7	−6.2	20.5
	−35.7	−15.3	20.4
	−54.7	−47.8	6.9
	−68.7	−68.7	0.0
$^4I_{9/2}$	155.4	162.3	6.9
	106.4	89.2	−17.2
	−21.6	3.1	24.7
	−110.6	−110.9	−0.3
	−129.6	−143.8	−14.2
RMS			23.3

4. Conclusion

The crystal-field energy level fitting has been performed for two Nd^{3+}-doped systems; both have D_3 point-group symmetry. A constant ratio of crystal-field parameters was used

Table 5. Comparison of the observed and calculated Stark splittings from the centre of gravity of the $^4F_{3/2}$, $^4I_{13/2}$, $^4I_{11/2}$ and $^4I_{9/2}$ manifolds of Nd^{3+} in NYAB at 77 K.

Multiplet	Observed splitting (cm^{-1})	Calculated splitting (cm^{-1})	Δ (cm^{-1})
$^4F_{3/2}$	24.5	17.3	−7.2
	−24.5	−17.3	7.2
$^4I_{13/2}$	105.9	123.6	17.7
	94.9	88.7	−6.2
	72.9	64.7	−8.2
	−47.1	−34.1	13.0
	−59.1	−51.9	7.2
	−78.1	−68.1	10.0
	−89.1	−122.8	−33.7
$^4I_{11/2}$	106.3	89.4	−16.9
	69.3	56.9	−12.4
	58.3	51.8	−6.5
	−63.7	−45.6	18.1
	−77.7	−55.2	22.5
	−92.7	−97.3	−4.6
$^4I_{9/2}$	141.8	170.3	28.5
	141.8	110.8	−31.0
	−24.2	−17.2	7.0
	−77.2	−96.0	−18.8
	−182.2	−167.9	14.3
RMS			20.2

as the constraint conditions in the fitting. It should be emphasized that, without these constraints, different sets of initial values always result in quite different minima; some of them cannot even reach any minimum but, if the fitting is under the constraints, all the different sets of initial values will result in exactly the same minimum. In the group chain scheme, it can be seen that the constraint conditions of essentially constant ratios of crystal-field parameters is actually a condition of the degree of low-symmetry distortion so that, for different mechanisms of crystal-field interactions, these ratios are essentially the same. The validity of using this condition is due to the importance of symmetry information in determining the physical effect and the fact that the symmetry rule is a universal rule which should be obeyed by every kind of physical process. In the current literature on crystal-field theory, the properties of the site symmetry of active ions has been used to determine which terms should be presented in the Hamiltonian H_{cf}, but the symmetry information has not been further utilized. However, for systems with the same kind of point group, their low-symmetry distortions may be different. It is just the degree of low-symmetry distortion which determines the relative magnitudes of the crystal-field parameters. The superposition model was applied to show that the ratios of crystal-field parameters obtained by the simple PC effect are the same or essentially the same as those determined from the composite effect consisting of a series of t_k-values; this gives us confidence to use the ratios of the crystal-field parameters obtained by the simple PC model as constraint conditions in the fitting.

In the detailed results of NYAB and NAB crystal-field energy level analysis, three points should be mentioned. Firstly, it should be noted that the Stark splitting of NYAB at room

Table 6. Comparison of the observed and calculated Stark splittings from the centre of gravity of the $^4F_{3/2}$, $^4I_{13/2}$, $^4I_{11/2}$ and $^4I_{9/2}$ manifolds of Nd^{3+} in the NYAB crystal at 300 K.

Multiplet	Observed splitting (cm^{-1})	Calculated splitting (cm^{-1})	Δ (cm^{-1})
$^4F_{3/2}$	21.0	17.8	−3.2
	−21.0	−17.8	3.2
$^4I_{13/2}$	115.6	136.6	21.0
	100.6	96.4	−4.2
	70.6	73.0	2.4
	−49.4	−40.3	9.1
	−71.4	−61.3	10.1
	−77.4	−73.0	4.4
	−88.4	−131.4	−43.0
$^4I_{11/2}$	105.3	97.6	−7.7
	64.3	62.9	−1.4
	58.3	57.6	−0.7
	−49.7	−53.7	−4.0
	−79.7	−60.3	19.4
	−98.7	−104.2	−5.5
$^4I_{9/2}$	164.6	184.0	19.4
	164.6	127.6	−37.0
	−8.4	−17.3	−8.9
	−117.4	−115.1	2.3
	−203.4	−179.2	24.2
RMS			19.7

Table 7. The parameters p_i and r_i ($i = 1, 2, 3$) in NAB and NYAB crystals.

		p_1	p_2	p_3	r_1	r_2	r_3
NAB	Calculated	0.507	−0.117	−0.413	0.440	1.348	−2.506
	Experimental (77 K)	0.546	−0.067	−0.389	0.399	1.212	−2.667
NYAB	Calculated	0.509	−0.289	−0.404	0.437	1.307	−1.634
	Experimental (77 K)	0.570	−0.352	−0.408	0.374	1.327	−1.443
	Experimental (300 K)	0.574	−0.428	−0.429	0.370	1.398	−1.292

Table 8. Crystal-field parameters B_{kq} for NAB and NYAB crystals.

	B_{20}	B_{40}	B_{43}	B_{60}	B_{63}	B_{66}
NAB	513.7	−217.4	−118.6	257.9	−17.4	−100.3
NYAB (77 K)	−186.2	623.5	355.5	−210.1	73.9	85.6
NYAB (300 K)	−191.9	681.1	391.1	−222.3	95.1	95.2

temperature is larger than at 77 K; this is contrary to the situation in the Eu^{3+}:$LaAlO_3$ crystal. Secondly, the absolute values of r_1, r_2 and r_3 for the NYAB crystal are smaller than those of the NAB crystal (table 7); it demonstrates that the distortion from cubic symmetry in the NYAB crystal is lower than in NAB crystal, which agrees well with the structure information obtained from x-ray analysis [31, 32]. Finally, the eigenfunctions for the crystal-

Table 9. Crystal-field parameters C_μ^k for NAB and NYAB crystals.

	$C_{\tilde{1}}^2$	C_0^4	$C_{\tilde{1}}^4$	C_0^6	$C_{\tilde{1}_0}^6$	$C_{\tilde{1}_1}^6$
NAB (77 K)	−629	534	213	−363	−439	967
NYAB (77 K)	228	−1569	−587	456	605	−658
NYAB (300 K)	235	−1721	−637	517	723	−668

field states of the $^4F_{3/2}$ and $^4I_{11/2}$ terms in the NAB crystal obtained by our method can be employed to explain the laser polarization direction of the NAB minilaser used by Winzer *et al* [33]. Otherwise, the eigenfunctions obtained by us without the PC-modelled crystal-field parameter ratio constraints give the incorrect answer for the polarization behaviour, although these minima all have the same small RMS deviations. Therefore, it is obvious that the method of essential constant ratios of the crystal-field parameters is a good way to reach the global minimum, although not as many energy levels have been calculated in this paper as in many other papers; at the same time, the two-electron effect and J mixing effect were neglected. The group chain scheme of the crystal-field theory adopted has a series of advantages such as the fact that the symmetry properties of the irreducible subspaces and eigenstates can be obtained directly using simple group theory. On the other hand, the most important advantage is that the crystal-field parameter ratios C_μ^k / C_0^k obtained can be seen directly to correspond to the degree of low-symmetry distortion departure from cubic symmetry. After information on the low-symmetry distortion has been taken into account, the crystal-field calculations are not only a formalism but also a real physical insight.

Finally, we would like to point out that this method can also be applied to other kinds of point group, especially the lower-symmetry cases such as the D_2, C_5 and C_2 point groups. In the situations of transition ions, this method can also be used.

Acknowledgment

Appendix

The irreducible representations of group O and D_3 considered in this paper are labelled using the Butler [23] notation. The correspondence between the labels used by Butler, Bethe and Mulliken is as follows:

	Mulliken:	A_1	A_2	E	T_1	T_2	E′	E″	U′
O	Bethe:	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8
	Butler:	0	$\tilde{0}$	2	1	$\tilde{1}$	$\frac{1}{2}$	$\frac{\tilde{1}}{2}$	$\frac{3}{2}$

	Mulliken:	A_1	A_2	E	E′	E″	
D_3	Bethe:	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6
	Butler:	0	$\tilde{0}$	1	$\frac{1}{2}$	$\frac{3}{2}$	$-\frac{3}{2}$.

On the basis of the group–subgroup chain $SO_3 \supset O \supset D_3$, some of the wavefunctions of the $4f^3$ configuraiton in Nd^{3+} at the D_3 symmetry position are expressed as linear

combinations of Butler's group chain basic function $|^{2S+1}L_J\mu\nu\rangle$, where μ and ν are the irreducible representations of O and D_3 respectively:

$$|^4F_{3/2}\rangle \rightarrow |^4F_{3/2}\tfrac{3}{2}\tfrac{1}{2}\rangle + |^4F_{3/2}\tfrac{3}{2}\tfrac{3}{2}\rangle + |^4F_{3/2}\tfrac{3}{2} - \tfrac{3}{2}\rangle$$

$$|^4I_{13/2}\rangle \rightarrow |^4I_{13/2}\tfrac{1}{2}\tfrac{1}{2}\rangle + |^4I_{13/2}\tfrac{3}{2_0}\tfrac{1}{2}\rangle + |^4I_{13/2}\tfrac{3}{2_0}\tfrac{3}{2}\rangle + |^4I_{13/2}\tfrac{3}{2_0} - \tfrac{3}{2}\rangle + |^4I_{13/2}\tfrac{3}{2_1}\tfrac{1}{2}\rangle$$

$$+ |^4I_{13/2}\tfrac{3}{2_1}\tfrac{3}{2}\rangle + |^4I_{13/2}\tfrac{3}{2_1} - \tfrac{3}{2}\rangle + |^4I_{13/2}\tfrac{\bar{1}}{2_0}\tfrac{1}{2}\rangle + |^4I_{13/2}\tfrac{\bar{1}}{2_1}\tfrac{1}{2}\rangle$$

$$|^4I_{11/2}\rangle \rightarrow |^4I_{11/2}\tfrac{1}{2}\tfrac{1}{2}\rangle + |^4I_{11/2}\tfrac{3}{2_0}\tfrac{1}{2}\rangle + |^4I_{11/2}\tfrac{3}{2_0}\tfrac{3}{2}\rangle + |^4I_{11/2}\tfrac{3}{2_0} - \tfrac{3}{2}\rangle + |^4I_{11/2}\tfrac{3}{2_1}\tfrac{1}{2}\rangle$$

$$+ |^4I_{11/2}\tfrac{3}{2_1}\tfrac{3}{2}\rangle + |^4I_{11/2}\tfrac{3}{2_1} - \tfrac{3}{2}\rangle + |^4I_{11/2}\tfrac{\bar{1}}{2}\tfrac{1}{2}\rangle$$

$$|^4I_{9/2}\rangle \rightarrow |^4I_{9/2}\tfrac{1}{2}\tfrac{1}{2}\rangle + |^4I_{9/2}\tfrac{3}{2_0}\tfrac{1}{2}\rangle + |^4I_{9/2}\tfrac{3}{2_0}\tfrac{3}{2}\rangle + |^4I_{9/2}\tfrac{3}{2_0} - \tfrac{3}{2}\rangle + |^4I_{9/2}\tfrac{3}{2_1}\tfrac{1}{2}\rangle$$

$$+ |^4I_{9/2}\tfrac{3}{2_1}\tfrac{3}{2}\rangle + |^4I_{9/2}\tfrac{3}{2_1} - \tfrac{3}{2}\rangle.$$

By means of the Wigner–Eckart theorem, we can obtain the matrix elements of the crystal-field Hamiltonian in the D_3 point-group symmetry. All the matrix elements listed below are represented as $\langle\mu\nu|H_{cf}|\mu'\nu'\rangle$ simply.

$J = \tfrac{3}{2}$:

	$\lvert\tfrac{3}{2}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2}\tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2} - \tfrac{3}{2}\rangle$
$\langle\tfrac{3}{2}\tfrac{1}{2}\rvert$	H_{11}	0	0
$\langle\tfrac{3}{2}\tfrac{3}{2}\rvert$	0	$-H_{11}$	0
$\langle\tfrac{3}{2} - \tfrac{3}{2}\rvert$	0	0	$-H_{11}$

$$H_{11} = (\tfrac{1}{2})(\tfrac{1}{5})^{1/2}C_2U^{(2)}C_{\bar{1}}^2$$

$J = \tfrac{13}{2}$:

	$\lvert\tfrac{1}{2}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2_0}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2_1}\tfrac{1}{2}\rangle$	$\lvert\tfrac{\bar{1}}{2_0}\tfrac{1}{2}\rangle$	$\lvert\tfrac{\bar{1}}{2_1}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2_0}\tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2_1}\tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2_0} - \tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2_1} - \tfrac{3}{2}\rangle$
$\langle\tfrac{1}{2}\tfrac{1}{2}\rvert$	H_{11}	H_{12}	H_{13}	H_{14}	H_{15}				
$\langle\tfrac{3}{2_0}\tfrac{1}{2}\rvert$	H_{12}	H_{22}	H_{23}	H_{24}	H_{25}				
$\langle\tfrac{3}{2_1}\tfrac{1}{2}\rvert$	H_{13}	H_{23}	H_{33}	H_{34}	H_{35}				
$\langle\tfrac{\bar{1}}{2_0}\tfrac{1}{2}\rvert$	H_{14}	H_{24}	H_{34}	H_{44}	H_{45}				
$\langle\tfrac{\bar{1}}{2_1}\tfrac{1}{2}\rvert$	H_{15}	H_{25}	H_{35}	H_{45}	H_{55}				
$\langle\tfrac{3}{2_0}\tfrac{3}{2}\rvert$						H_{66}	H_{67}		
$\langle\tfrac{3}{2_1}\tfrac{3}{2}\rvert$						H_{67}^*	H_{77}		
$\langle\tfrac{3}{2_0} - \tfrac{3}{2}\rvert$								H_{65}	H_{57}^*
$\langle\tfrac{3}{2_1} - \tfrac{3}{2}\rvert$								H_{67}	H_{77}

$$H_{11} = -(\tfrac{9}{2})(\tfrac{3}{4862})^{1/2}C_4U^{(4)}C_0^4 - 4(\tfrac{5}{646646})^{1/2}C_6U^{(6)}C_0^6$$

$$H_{12} = -(\tfrac{3}{14})(\tfrac{11}{65})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 - (\tfrac{1}{28})(\tfrac{85}{39})^{1/2}C_4U^{(4)}C_{\bar{1}}^4 + 2(\tfrac{11}{8398})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$

$$- 4(\tfrac{1}{41990})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{13} = (\tfrac{11}{7})(\tfrac{1}{390})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 - (\tfrac{1}{14})(\tfrac{5}{4862})^{1/2}C_4U^{(4)}C_{\bar{1}}^4 - (\tfrac{1}{2})(\tfrac{1}{12597})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$

$$-4(\tfrac{17}{40755})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{14} = (\tfrac{1}{14})(\tfrac{33}{78})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{1}{7})(\tfrac{17}{78})^{1/2}C_4U^{(4)}C_{\bar{1}}^4 + (\tfrac{1}{2})(\tfrac{1}{4199})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{15} = -(\tfrac{2}{7})(\tfrac{1}{15})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{2}{7})(\tfrac{5}{187})^{1/2}C_4U^{(4)}C_{\bar{1}}^4 + (\tfrac{1}{1938})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$
$$+ 16(\tfrac{1}{106590})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{22} = -(\tfrac{4}{7})(\tfrac{1}{910})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{1}{7})(\tfrac{33}{442})^{1/2}C_4U^{(4)}C_0^4 - (\tfrac{2}{7})(\tfrac{110}{4641})^{1/2}C_4U^{(4)}C_{\bar{1}}^4$$
$$-3(\tfrac{22}{146965})^{1/2}C_6U^{(6)}C_0^6 - (\tfrac{66}{7})(\tfrac{1}{29393})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6 + (\tfrac{61}{14})(\tfrac{11}{146965})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{23} = (\tfrac{1}{14})(\tfrac{55}{273})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{55}{42})(\tfrac{1}{221})^{1/2}C_4U^{(4)}C_0^4 + (\tfrac{1}{7})(\tfrac{5}{1547})^{1/2}C_4U^{(4)}C_{\bar{1}}^4$$
$$+ (\tfrac{11}{2})(\tfrac{3}{146965})^{1/2}C_6U^{(6)}C_0^6 - (\tfrac{5}{14})(\tfrac{22}{88179})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$
$$- (\tfrac{71}{7})(\tfrac{2}{440895})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{24} = (\tfrac{9}{14})(\tfrac{1}{91})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{1}{28})(\tfrac{143}{357})^{1/2}C_4U^{(4)}C_{\bar{1}}^4 + (\tfrac{44}{7})(\tfrac{5}{58786})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$
$$- (\tfrac{4}{7})(\tfrac{11}{58786})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{25} = -(\tfrac{2}{7})(\tfrac{11}{210})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 - (\tfrac{1}{21})(\tfrac{5}{238})^{1/2}C_4U^{(4)}C_{\bar{1}}^4 - (\tfrac{11}{14})(\tfrac{11}{6783})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$
$$- (\tfrac{4}{7})(\tfrac{17}{1995})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{33} = -(\tfrac{27}{14})(\tfrac{1}{910})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 - (\tfrac{37}{42})(\tfrac{1}{14586})^{1/2}C_4U^{(4)}C_0^4 - (\tfrac{29}{21})(\tfrac{5}{102102})^{1/2}C_4U^{(4)}C_{\bar{1}}^4$$
$$+41(\tfrac{2}{1616615})^{1/2}C_6U^{(6)}C_0^6 + (\tfrac{66}{7})(\tfrac{1}{29393})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6 - (\tfrac{5}{14})(\tfrac{95}{17017})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{34} = -(\tfrac{3}{7})(\tfrac{11}{546})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 - (\tfrac{113}{42})(\tfrac{1}{3094})^{1/2}C_4U^{(4)}C_{\bar{1}}^4 - (\tfrac{27}{14})(\tfrac{55}{88179})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$
$$- (\tfrac{60}{7})(\tfrac{1}{88179})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{35} = -(\tfrac{3}{7})(\tfrac{1}{35})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{89}{42})(\tfrac{5}{3927})^{1/2}C_4U^{(4)}C_{\bar{1}}^4 - (\tfrac{6}{7})(\tfrac{1}{4522})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$
$$- (\tfrac{2}{7})(\tfrac{95}{2618})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{44} = (\tfrac{3}{14})(\tfrac{33}{442})^{1/2}C_4U^{(4)}C_0^4 - 4(\tfrac{55}{58786})^{1/2}C_6U^{(6)}C_0^6$$

$$H_{45} = (\tfrac{2}{21})(\tfrac{5}{17})^{1/2}C_4U^{(4)}C_0^4 + (\tfrac{1}{2})(\tfrac{3}{2261})^{1/2}C_6U^{(6)}C_0^6$$

$$H_{55} = -(\tfrac{2}{21})(\tfrac{13}{1122})^{1/2}C_4U^{(4)}C_0^4 + 16(\tfrac{13}{248710})^{1/2}C_6U^{(6)}C_0^6$$

$$H_{66} = (\tfrac{2}{7})(\tfrac{2}{455})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{1}{14})(\tfrac{66}{221})^{1/2}C_4U^{(4)}C_0^4 + (\tfrac{2}{7})(\tfrac{110}{4641})^{1/2}C_4U^{(4)}C_{\bar{1}}^4$$
$$-3(\tfrac{22}{146965})^{1/2}C_6U^{(6)}C_0^6 + (\tfrac{66}{7})(\tfrac{1}{29393})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6 - (\tfrac{61}{14})(\tfrac{11}{146965})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{67} = -(\tfrac{1}{14})(\tfrac{55}{273})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{55}{42})(\tfrac{1}{221})^{1/2}C_4U^{(4)}C_0^4 - (\tfrac{1}{7})(\tfrac{5}{1547})^{1/2}C_4U^{(4)}C_{\bar{1}}^4$$
$$+ (\tfrac{11}{2})(\tfrac{3}{146965})^{1/2}C_6U^{(6)}C_0^6 + (\tfrac{5}{14})(\tfrac{22}{88179})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$

$$+ (\tfrac{71}{7})(\tfrac{2}{440895})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1} + i[-(\tfrac{11}{2730})^{1/2}C_2U^{(2)}C^2_{\bar{1}} + (\tfrac{1}{6})(\tfrac{65}{238})^{1/2}C_4U^{(4)}C^4_{\bar{1}}$$

$$- 2(\tfrac{11}{88179})^{1/2}C_6U^{(6)}C^6_{\bar{1}_0} + 2(\tfrac{1}{440895})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1}]$$

$$H_{77} = (\tfrac{27}{14})(\tfrac{1}{910})^{1/2}C_2U^{(2)}C^2_{\bar{1}} - (\tfrac{37}{42})(\tfrac{1}{14586})^{1/2}C_4U^{(4)}C^4_0 + (\tfrac{29}{42})(\tfrac{10}{51051})^{1/2}C_4U^{(4)}C^4_{\bar{1}}$$

$$+ 41(\tfrac{2}{1616615})^{1/2}C_6U^{(6)}C^6_0 - (\tfrac{66}{7})(\tfrac{1}{29393})^{1/2}C_6U^{(6)}C^6_{\bar{1}_0}$$

$$+ (\tfrac{5}{14})(\tfrac{95}{17017})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1}$$

$J = \tfrac{11}{2}$:

	$\lvert\tfrac{1}{2}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2_0}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2_1}\tfrac{1}{2}\rangle$	$\lvert\tfrac{\bar{1}}{2}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2_0}\tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2_1}\tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2_0}-\tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2_1}-\tfrac{3}{2}\rangle$
$\langle\tfrac{1}{2}\tfrac{1}{2}\rvert$	H_{11}	H_{12}	H_{13}	H_{14}				
$\langle\tfrac{3}{2_0}\tfrac{1}{2}\rvert$	H_{12}	H_{22}	H_{23}	H_{24}				
$\langle\tfrac{3}{2_1}\tfrac{1}{2}\rvert$	H_{13}	H_{23}	H_{33}	H_{34}				
$\langle\tfrac{\bar{1}}{2}\tfrac{1}{2}\rvert$	H_{14}	H_{24}	H_{34}	H_{44}				
$\langle\tfrac{3}{2_0}\tfrac{3}{2}\rvert$					H_{55}	H_{56}		
$\langle\tfrac{3}{2_1}\tfrac{3}{2}\rvert$					H^*_{56}	H_{66}		
$\langle\tfrac{3}{2_0}-\tfrac{3}{2}\rvert$							H_{55}	H^*_{56}
$\langle\tfrac{3}{2_1}-\tfrac{3}{2}\rvert$							H_{56}	H_{66}

$$H_{11} = -(\tfrac{7}{2})(\tfrac{1}{858})^{1/2}C_4U^{(4)}C^4_0 - (\tfrac{1}{7293})^{1/2}C_6U^{(6)}C^6_0$$

$$H_{12} = -(\tfrac{4}{11})(\tfrac{5}{39})^{1/2}C_2U^{(2)}C^2_{\bar{1}} - (\tfrac{3}{22})(\tfrac{5}{78})^{1/2}C_4U^{(4)}C^4_{\bar{1}} + (\tfrac{55}{9282})^{1/2}C_6U^{(6)}C^6_{\bar{1}_0}$$

$$+ (\tfrac{59}{11})(\tfrac{1}{9282})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1}$$

$$H_{13} = -(\tfrac{4}{11})(\tfrac{1}{78})^{1/2}C_2U^{(2)}C^2_{\bar{1}} + (\tfrac{17}{33})(\tfrac{1}{39})^{1/2}C_4U^{(4)}C^4_{\bar{1}} - (\tfrac{3}{4})(\tfrac{11}{4641})^{1/2}C_6U^{(6)}C^6_{\bar{1}_0}$$

$$+ (\tfrac{76}{33})(\tfrac{5}{4641})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1}$$

$$H_{14} = (\tfrac{1}{2})(\tfrac{1}{39})^{1/2}C_2U^{(2)}C^2_{\bar{1}} + (\tfrac{1}{3})(\tfrac{1}{78})^{1/2}C_4U^{(4)}C^4_{\bar{1}} + (\tfrac{1}{6})(\tfrac{35}{1326})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1}$$

$$H_{22} = -(\tfrac{41}{22})(\tfrac{5}{3003})^{1/2}C_2U^{(2)}C^2_{\bar{1}} - (\tfrac{47}{22})(\tfrac{1}{858})^{1/2}C_4U^{(4)}C^4_0 - (\tfrac{9}{22})(\tfrac{10}{3003})^{1/2}C_4U^{(4)}C^4_{\bar{1}}$$

$$- (\tfrac{2}{11})(\tfrac{1}{7293})^{1/2}C_6U^{(6)}C^6_0 - (\tfrac{2}{11})(\tfrac{10}{663})^{1/2}C_6U^{(6)}C^6_{\bar{1}_0} + (\tfrac{43}{22})(\tfrac{1}{14586})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1}$$

$$H_{23} = (\tfrac{20}{11})(\tfrac{2}{3003})^{1/2}C_2U^{(2)}C^2_{\bar{1}} - (\tfrac{4}{11})(\tfrac{5}{429})^{1/2}C_4U^{(4)}C^4_0 - (\tfrac{107}{33})(\tfrac{1}{3003})^{1/2}C_4U^{(4)}C^4_{\bar{1}}$$

$$+ (\tfrac{21}{22})(\tfrac{15}{4862})^{1/2}C_6U^{(6)}C^6_0 + (\tfrac{9}{11})(\tfrac{1}{663})^{1/2}C_6U^{(6)}C^6_{\bar{1}_0} - (\tfrac{4}{33})(\tfrac{5}{7293})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1}$$

$$H_{24} = 4(\tfrac{1}{3003})^{1/2}C_2U^{(2)}C^2_{\bar{1}} + (\tfrac{37}{6})(\tfrac{1}{6006})^{1/2}C_4U^{(4)}C^4_{\bar{1}} + 3(\tfrac{1}{1326})^{1/2}C_6U^{(6)}C^6_{\bar{1}_0}$$

$$+ (\tfrac{1}{3})(\tfrac{5}{14586})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1}$$

$$H_{33} = (\tfrac{23}{22})(\tfrac{7}{2145})^{1/2}C_2U^{(2)}C^2_{\bar{1}} + (\tfrac{49}{33})(\tfrac{2}{429})^{1/2}C_4U^{(4)}C^4_0 - (\tfrac{2}{33})(\tfrac{70}{429})^{1/2}C_4U^{(4)}C^4_{\bar{1}}$$

$$+ (\tfrac{4}{11})(\tfrac{17}{429})^{1/2}C_6U^{(6)}C^6_0 + (\tfrac{2}{11})(\tfrac{10}{663})^{1/2}C_6U^{(6)}C^6_{\bar{1}_0} + (\tfrac{47}{11})(\tfrac{2}{7293})^{1/2}C_6U^{(6)}C^6_{\bar{1}_1}$$

$$H_{34} = 4(\tfrac{1}{30030})^{1/2} C_2 U^{(2)} C_{\bar{1}}^2 - (\tfrac{2}{3})(\tfrac{5}{3003})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4 - (\tfrac{1}{4})(\tfrac{5}{663})^{1/2} C_6 U^{(6)} C_{\bar{1}_0}^6$$
$$+ 2(\tfrac{1}{7293})^{1/2} C_6 U^{(6)} C_{\bar{1}_1}^6$$

$$H_{44} = (\tfrac{1}{6})(\tfrac{11}{78})^{1/2} C_4 U^{(4)} C_0^4 - (\tfrac{11}{663})^{1/2} C_6 U^{(6)} C_0^6$$

$$H_{55} = (\tfrac{41}{22})(\tfrac{5}{3003})^{1/2} C_2 U^{(2)} C_{\bar{1}}^2 - (\tfrac{47}{22})(\tfrac{1}{858})^{1/2} C_4 U^{(4)} C_0^4 + (\tfrac{9}{22})(\tfrac{10}{3033})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4$$
$$- (\tfrac{2}{11})(\tfrac{1}{7293})^{1/2} C_6 U^{(6)} C_0^6 + (\tfrac{2}{11})(\tfrac{10}{663})^{1/2} C_6 U^{(6)} C_{\bar{1}_0}^6 - (\tfrac{43}{22})(\tfrac{1}{14586})^{1/2} C_6 U^{(6)} C_{\bar{1}_1}^6$$

$$H_{56} = -(\tfrac{20}{11})(\tfrac{2}{3003})^{1/2} C_2 U^{(2)} C_{\bar{1}}^2 - (\tfrac{4}{11})(\tfrac{5}{429})^{1/2} C_4 U^{(4)} C_0^4 + (\tfrac{107}{33})(\tfrac{1}{3003})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4$$
$$+ (\tfrac{21}{22})(\tfrac{15}{4862})^{1/2} C_6 U^{(6)} C_0^6 - (\tfrac{9}{11})(\tfrac{1}{663})^{1/2} C_6 U^{(6)} C_{\bar{1}_0}^6 + (\tfrac{4}{33})(\tfrac{5}{7293})^{1/2} C_6 U^{(6)} C_{\bar{1}_1}^6$$
$$+ \mathrm{i}[-4(\tfrac{1}{3003})^{1/2} C_2 U^{(2)} C_{\bar{1}}^2 + (\tfrac{1}{3})(\tfrac{13}{462})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4 + (\tfrac{3}{2})(\tfrac{1}{1326})^{1/2} C_6 U^{(6)} C_{\bar{1}_0}^6$$
$$- (\tfrac{10}{3})(\tfrac{5}{14586})^{1/2} C_6 U^{(6)} C_{\bar{1}_1}^6]$$

$$H_{66} = -(\tfrac{23}{22})(\tfrac{7}{2145})^{1/2} C_2 U^{(2)} C_{\bar{1}}^2 + (\tfrac{49}{33})(\tfrac{2}{429})^{1/2} C_4 U^{(4)} C_0^4 + (\tfrac{2}{33})(\tfrac{70}{429})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4$$
$$+ (\tfrac{4}{11})(\tfrac{17}{429})^{1/2} C_6 U^{(6)} C_0^6 - (\tfrac{2}{11})(\tfrac{10}{663})^{1/2} C_6 U^{(6)} C_{\bar{1}_0}^6 - (\tfrac{47}{11})(\tfrac{2}{7293})^{1/2} C_6 U^{(6)} C_{\bar{1}_1}^6$$

$J = \tfrac{9}{2}$:

	$\lvert\tfrac{1}{2}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2_0}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2_1}\tfrac{1}{2}\rangle$	$\lvert\tfrac{3}{2_0}\tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2_1}\tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2_0}-\tfrac{3}{2}\rangle$	$\lvert\tfrac{3}{2_1}-\tfrac{3}{2}\rangle$
$\langle\tfrac{1}{2}\tfrac{1}{2}\rvert$	H_{11}	H_{12}	H_{13}				
$\langle\tfrac{3}{2_0}\tfrac{1}{2}\rvert$	H_{12}	H_{22}	H_{23}				
$\langle\tfrac{3}{2_1}\tfrac{1}{2}\rvert$	H_{13}	H_{23}	H_{33}				
$\langle\tfrac{3}{2_0}\tfrac{3}{2}\rvert$				H_{44}	H_{45}		
$\langle\tfrac{3}{2_1}\tfrac{3}{2}\rvert$				H_{45}^*	H_{55}		
$\langle\tfrac{3}{2_0}-\tfrac{3}{2}\rvert$						H_{44}	H_{45}^*
$\langle\tfrac{3}{2_1}-\tfrac{3}{2}\rvert$						H_{45}	H_{44}

$$H_{11} = (\tfrac{7}{3})(\tfrac{7}{2145})^{1/2} C_4 U^{(4)} C_0^4 + 8(\tfrac{1}{4290})^{1/2} C_6 U^{(6)} C_0^6$$

$$H_{12} = -(\tfrac{1}{3})(\tfrac{1}{11})^{1/2} C_2 U^{(2)} C_{\bar{1}}^2 + (\tfrac{19}{6})(\tfrac{1}{715})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4 - (\tfrac{1}{3})(\tfrac{1}{65})^{1/2} C_6 U^{(6)} C_{\bar{1}_0}^6$$
$$- (\tfrac{2}{5})(\tfrac{1}{143})^{1/2} C_6 U^{(6)} C_{\bar{1}_1}^6$$

$$H_{13} = -(\tfrac{2}{3})(\tfrac{7}{2145})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4 + (\tfrac{3}{2})(\tfrac{1}{1365})^{1/2} C_6 U^{(6)} C_{\bar{1}_0}^6 - (\tfrac{2}{5})(\tfrac{13}{231})^{1/2} C_6 U^{(6)} C_{\bar{1}_1}^6$$

$$H_{22} = (\tfrac{9}{10})(\tfrac{1}{165})^{1/2} C_2 U^{(2)} C_{\bar{1}}^2 - (\tfrac{1}{2})(\tfrac{21}{715})^{1/2} C_4 U^{(4)} C_0^4 + (\tfrac{3}{5})(\tfrac{1}{429})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4$$
$$+ (\tfrac{2}{5})(\tfrac{6}{715})^{1/2} C_6 U^{(6)} C_0^6 - (\tfrac{21}{5})(\tfrac{1}{2145})^{1/2} C_6 U^{(6)} C_{\bar{1}_1}^6$$

$$H_{23} = -(\tfrac{2}{15})(\tfrac{7}{55})^{1/2} C_2 U^{(2)} C_{\bar{1}}^2 + 2(\tfrac{1}{715})^{1/2} C_4 U^{(4)} C_0^4 + (\tfrac{2}{15})(\tfrac{7}{143})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4$$
$$- (\tfrac{3}{10})(\tfrac{7}{1430})^{1/2} C_6 U^{(6)} C_0^6 + (\tfrac{5}{6})(\tfrac{1}{91})^{1/2} C_6 U^{(6)} C_{\bar{1}_0}^6 + (\tfrac{4}{5})(\tfrac{1}{5005})^{1/2} C_6 U^{(6)} C_{\bar{1}_1}^6$$

$$H_{33} = -(\tfrac{3}{5})(\tfrac{1}{165})^{1/2} C_2 U^{(2)} C_{\bar{1}}^2 + (\tfrac{1}{3})(\tfrac{7}{2145})^{1/2} C_4 U^{(4)} C_0^4 + (\tfrac{2}{15})(\tfrac{13}{33})^{1/2} C_4 U^{(4)} C_{\bar{1}}^4$$

$$- (\tfrac{16}{5})(\tfrac{2}{2145})^{1/2}C_6U^{(6)}C_0^6 + (\tfrac{7}{10})(\tfrac{1}{2145})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{44} = -(\tfrac{9}{10})(\tfrac{1}{165})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 - (\tfrac{1}{2})(\tfrac{21}{715})^{1/2}C_4U^{(4)}C_0^4 - (\tfrac{3}{5})(\tfrac{1}{429})^{1/2}C_4U^{(4)}C_{\bar{1}}^4$$
$$+ (\tfrac{2}{5})(\tfrac{6}{715})^{1/2}C_6U^{(6)}C_0^6 + (\tfrac{21}{5})(\tfrac{1}{2145})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

$$H_{45} = \tfrac{2}{5}(\tfrac{7}{495})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + 2(\tfrac{7}{715})^{1/2}C_4U^{(4)}C_0^4 - (\tfrac{2}{15})(\tfrac{7}{143})^{1/2}C_4U^{(4)}C_{\bar{1}}^4$$
$$- (\tfrac{3}{10})(\tfrac{7}{1430})^{1/2}C_6U^{(6)}C_0^6 - (\tfrac{5}{6})(\tfrac{1}{91})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6 - (\tfrac{4}{5})(\tfrac{1}{5005})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$
$$+ \mathrm{i}[(\tfrac{2}{3})(\tfrac{7}{110})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{1}{3})(\tfrac{7}{286})^{1/2}C_4U^{(4)}C_{\bar{1}}^4 + (\tfrac{1}{3})(\tfrac{1}{182})^{1/2}C_6U^{(6)}C_{\bar{1}_0}^6$$
$$+ 2(\tfrac{1}{10010})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6]$$

$$H_{55} = -(\tfrac{1}{5})(\tfrac{3}{55})^{1/2}C_2U^{(2)}C_{\bar{1}}^2 + (\tfrac{1}{3})(\tfrac{7}{2145})^{1/2}C_4U^{(4)}C_0^4 - (\tfrac{2}{15})(\tfrac{13}{33})^{1/2}C_4U^{(4)}C_{\bar{1}}^4$$
$$- (\tfrac{16}{5})(\tfrac{2}{2145})^{1/2}C_6U^{(6)}C_0^6 - (\tfrac{7}{10})(\tfrac{1}{2145})^{1/2}C_6U^{(6)}C_{\bar{1}_1}^6$$

where $C_k = \langle l\|C_k\|l\rangle = (-1)^l(2l+1)\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}$, and $U^{(k)} = \langle f^n SLJ\|U^{(k)}\|f^n SLJ\rangle$
$(k = 2, 4, 6)$ are reduced matrix elements with rank k. For the Nd^{3+} ion considered, $l = 3$
and C_k are calculated to be

$$C_2 = -2(\tfrac{7}{15})^{1/2}$$

$$C_4 = (\tfrac{14}{11})^{1/2}$$

$$C_6 = -10(\tfrac{7}{429})^{1/2}.$$

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