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# Group-chain scheme analysis of the energy levels and magnetic properties of $\text{Er}^{3+}$ in the $\text{LiYF}_4$ crystal

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**Abstract.** Based on the analysis of group-chain scheme wavefunctions and the use of the constraint condition set down by the ratios of crystal-field parameters calculated by the point-charge model, the crystal-field-level fitting and the study of Zeeman interaction characterized by the  $g$ -factor in  $\text{Er}^{3+} : \text{LiYF}_4$  have been carried out, in which the  $\text{Er}^{3+}$  ions occupy positions with point symmetry  $S_4$ . The RMS of energy-level fitting is less than  $8 \text{ cm}^{-1}$ , and the corresponding wavefunctions of Stark sublevels are useful in the calculation of the  $g$ -factors of the ground and excited states. The calculated results agree well with the experiment and confirm Karayianis' partial  $g$ -sum rule. The method proposed turned out to be effective in the study of not only the spectroscopic and laser properties but also the magnetic properties of rare-earth ions in crystals.

## 1. Introduction

The scheelite crystal lithium yttrium fluoride ( $\text{LiYF}_4$ ) is one of the most versatile materials investigated thus far. As for triply ionized rare-earth ions in  $\text{LiYF}_4$ , Kaminskii [1] list 36 lasers at different wavelengths. Interest in  $\text{Er}^{3+} : \text{LiYF}_4$  stems from several factors including efficient quantum counter action, long-lived strong fluorescent levels and a wide range of laser emission at infrared wavelengths ( $0.85\text{--}2.8 \mu\text{m}$ ) [2–5]. Very recently, the room-temperature-pumped continuous green wave laser emission demonstrated in  $\text{Er}^{3+} : \text{LiYF}_4$  is even more fascinating [6, 7]. It is important to study the detailed structure of energy levels in order to improve the device efficiency in the above mentioned application. We would like to use the method of a group-chain scheme + constraint condition by the ratios of crystal-field (CF) parameters, which was proposed by one of the present authors before, to investigate fully the energy levels of  $\text{Er}^{3+} : \text{LiYF}_4$ . However, this time we study its magnetic properties rather than its spectroscopic characteristics to show that the method introduced is widely applicable.

Conventional CF theory has been extensively used in energy-level and spectroscopy analysis of rare-earth crystals. Karayianis [8] has analysed the energy levels and magnetic splitting of  $\text{Er}^{3+}$ . His theoretical calculations yielded excited-state  $g$ -factors for all levels of the  $^4I$  term. Additionally, Karayianis [9] and Kulpa and Karayianis [10] discussed a partial  $g$ -sum rule which could allow the use of  $g$ -factors for spectral interpretation without the need for elaborate calculations. It was Butler [11] who first introduced the group-chain scheme to investigate how the effect of the environment of the ions may be written in terms of tensor operators which have point-group symmetry. Since the coupling coefficients and

the tables in Butler's book offer fundamental simplification, it is more convenient to fit the energy levels of the localized centres in crystals, which generalize the calculation of matrix elements.

In previous work, the CF of low-symmetry active ions in laser crystals, such as  $\text{Nd}^{3+}$  in  $\text{YVO}_4$  [12],  $\text{NdAl}_3(\text{BO}_3)_4$ , and  $\text{YAl}_3(\text{BO}_3)_4$  [13], was analysed in detail based on the group-chain scheme. In  $\text{Nd}^{3+} : \text{YVO}_4$ ,  $\text{Nd}^{3+}$  ions substitute on the  $D_{2d}$  sites of  $\text{Y}^{3+}$  ions. Naturally, a group-subgroup chain is selected as  $O_3 \supset O_h \supset T_d \supset D_{2d}$ . In  $\text{Er}^{3+} : \text{LiYF}_4$ ,  $\text{Er}^{3+}$  ions occupy positions of  $S_4$  site symmetry. Noting that the  $S_4$  point group is the subgroup of  $D_{2d}$ , we choose the extended group chain  $O_3 \supset O_h \supset T_d \supset D_{2d} \supset S_4$ . In actual calculation of the energy levels of  $\text{Er}^{3+} : \text{LiYF}_4$ , we may utilize the results for  $\text{Nd}^{3+} : \text{YVO}_4$ .

## 2. Group-chain scheme analysis

Consider the group chain  $O_3 \supset O_h \supset T_d \supset D_{2d} \supset S_4$ ; the detailed CF Hamiltonian can be expressed in Butler's notation as

$$H_{cf} = C_{2^+20}^{2^+} b_{2^+20}^{2^+} + C_{0^+00}^{4^+} b_{0^+00}^{4^+} + i C_{1^+1\bar{0}}^{4^+} b_{1^+1\bar{0}}^{4^+} + C_{2^+20}^{4^+} b_{2^+20}^{4^+} + C_{0^+00}^{6^+} b_{0^+00}^{6^+} + i C_{1^+1\bar{0}}^{6^+} b_{1^+1\bar{0}}^{6^+} + C_{2^+20}^{6^+} b_{2^+20}^{6^+}. \quad (1)$$

Here  $b_{\mu\nu\xi}^k$  are the basis functions of the group chain  $O_3 \supset O_h \supset T_d \supset D_{2d} \supset S_4$  and are identical with  $|k\mu\nu\xi 0\rangle$  in [11];  $C_{\mu\nu\xi}^k$  are the expansion coefficients of  $H_{cf}$  by these bases. Because all the basis functions belong to the 0 representation of  $S_4$  in the calculation concerned, the index 0 for the  $S_4$  group has been omitted in equation (1).

Based on the conventional CF analysis [14],  $H_{of}$  can also be expressed as [15]

$$H_{cf} = B_{20}C_{20} + B_{40}C_{40} + RB_{44}(C_{44} + C_{4-4}) + iIB_{44}(C_{44} - C_{4-4}) + B_{60}C_{60} + RB_{64}(C_{64} + C_{6-4}) + iIB_{64}(C_{64} - C_{6-4}) \quad (2)$$

where  $RB_{kq}$  and  $IB_{kq}$  represent the real and imaginary components, respectively, of the CF parameter  $B_{kq}$ . It can be easily shown that the relationship between the CF parameters of the two different schemes will be

$$\begin{aligned} B_{20} &= -\left(\frac{2}{3}\right)^{1/2} C_{2^+20}^{2^+} & C_{2^+20}^{2^+} &= -\left(\frac{3}{2}\right)^{1/2} B_{20} \\ B_{40} &= 2\left(\frac{2}{35}\right)^{1/2} \left[ \frac{1}{2} \left(\frac{7}{3}\right)^{1/2} C_{0^+00}^{4^+} + \frac{1}{2} \left(\frac{5}{3}\right)^{1/2} C_{2^+20}^{4^+} \right] \\ C_{0^+00}^{4^+} &= \frac{1}{2} \left(\frac{35}{2}\right)^{1/2} \left( \frac{21^{1/2}}{6} B_{40} + \frac{30^{1/2}}{6} RB_{44} \right) \\ RB_{44} &= 2\left(\frac{2}{35}\right)^{1/2} \left[ \frac{1}{2} \left(\frac{5}{6}\right)^{1/2} C_{0^+00}^{4^+} - \frac{1}{2} \left(\frac{7}{6}\right)^{1/2} C_{2^+20}^{4^+} \right] & C_{1^+1\bar{0}}^{4^+} &= \frac{35^{1/2}}{2} IB_{44} \\ IB_{44} &= 2\left(\frac{2}{35}\right)^{1/2} \left(\frac{1}{2}\right)^{1/2} C_{1^+1\bar{0}}^{4^+} & C_{2^+20}^{4^+} &= \frac{1}{2} \left(\frac{35}{2}\right)^{1/2} \left( \frac{15^{1/2}}{6} B_{40} - \frac{42^{1/2}}{6} RB_{44} \right) \end{aligned} \quad (3)$$

and

$$\begin{aligned}
 B_{60} &= 4\left(\frac{1}{231}\right)^{1/2}\left[-\frac{1}{2}\left(\frac{1}{2}\right)^{1/2}C_{0+00}^{6+} + \frac{1}{2}\left(\frac{7}{2}\right)^{1/2}C_{2+20}^{6+}\right] \\
 C_{0+00}^{6+} &= \frac{231^{1/2}}{4}\left(-\frac{2^{1/2}}{4}B_{60} + \frac{7^{1/2}}{2}RB_{64}\right) \\
 RB_{64} &= 4\left(\frac{1}{231}\right)^{1/2}\left(\frac{7^{1/2}}{4}C_{0+00}^{6+} + \frac{1}{4}C_{2+20}^{6+}\right) \quad C_{1+1\bar{0}}^{6+} = \frac{462^{1/2}}{4}IB_{64} \\
 IB_{64} &= 4\left(\frac{1}{231}\right)^{1/2}\left(\frac{1}{2}\right)^{1/2}C_{1+1\bar{0}}^{6+} \quad C_{2+20}^{6+} = \frac{231^{1/2}}{4}\left(\frac{14^{1/2}}{4}B_{60} + \frac{1}{2}RB_{64}\right).
 \end{aligned} \tag{4}$$

In  $Er^{3+} : LiYF_4$ , the  $Er^{3+}$  ion contains 11 4f-shell electrons and is an odd-electron system. So its CF Hamiltonian is a time-reversal invariant, which leads to Kramers degeneracy of the energy levels.

As shown later, all the Stark levels are doubly degenerate and their wavefunctions have the following conjugate relationship:

$$\begin{aligned}
 \Psi &= \sum_{aa_1a_2a_3a_4} C_{aa_1a_2a_3a_4}^a |aa_1a_2a_3a_4\rangle \\
 \bar{\Psi} &= \sum_{aa_1a_2a_3a_4} (C_{aa_1a_2a_3a_4}^a)^* |aa_1a_2a_3\bar{a}_4\rangle
 \end{aligned} \tag{5}$$

and so only one set of basis functions  $\Psi$  need to be taken into consideration during the calculation of the Hermitian matrix elements.

The matrix elements of the CF Hamiltonian in the group-chain scheme can be calculated by means of the Wigner–Eckart theorem and the factorization lemma of the  $3jm$  factors [11]:

$$\begin{aligned}
 \langle aa_1a_2a_3a_4 | H_{cf} | bb_1b_2b_3b_4 \rangle &= \sum_{k\mu\nu\xi} C_{k\mu\nu\xi}^k \begin{bmatrix} a \\ a_1 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \begin{bmatrix} a_2 \\ a_3 \end{bmatrix} \begin{bmatrix} a_3 \\ a_4 \end{bmatrix} \\
 &\times \sum_{r_1r_2r_3r_4} \begin{bmatrix} a^* & k & b \\ a_1^* & \mu & b_1 \end{bmatrix} r \begin{bmatrix} a_1^* & \mu & b_1 \\ a_2^* & \nu & b_2 \end{bmatrix} r_1 \begin{bmatrix} a_2^* & \nu & b_2 \\ a_3^* & \xi & b_3 \end{bmatrix} r_2 \\
 &\times \begin{bmatrix} a_3^* & \xi & b_3 \\ a_4^* & 0 & b_4 \end{bmatrix} r_3 \langle a || b^k || b \rangle
 \end{aligned} \tag{6}$$

$$\langle a || b^k || b \rangle = \langle f^n SLa || U^{(k)} || f^n SL'b \rangle \langle 4f || C^{(k)} || 4f \rangle. \tag{7}$$

As usually adopted in this field, the reduced matrix elements (RME)  $\langle f^n SLa || U^{(k)} || f^n SL'b \rangle$  are calculated under the intermediate-coupling approximation [16–18] and are listed in appendix 1. All the  $2jm$  and  $3jm$  factors can be found from [11].

### 3. Energy levels fitting and wavefunctions

Because the separation of the concerned low-lying spectroscopic terms of the  $Er^{3+}$  ion are sufficiently large, the effect of  $J$  mixing is small in the  $Er^{3+} : LiYF_4$  crystal.  $J$  remains as a fairly ‘good’ quantum number [16]. Therefore  $J$  mixing was ignored in the following calculation.

The method introduced here differs from Karayianis’ [8] method. The energy-level fitting is performed by two steps instead of by diagonalizing a combined spin–orbit and CF Hamiltonian. First, free-ion wavefunctions in a Russell–Saunders basis of  $J$  states are obtained by diagonalizing a Hamiltonian containing the Coulomb and spin–orbit interactions, and thus we can compute the RME of  $U^{(k)}$  ( $k = 2, 4, 6$ ) between all the intermediate-coupled

wavefunctions representing the multiplets of the electronic ground configuration of the free ion. Second, matrices (such as  $8 \times 8$  of  ${}^4I_{15/2}$ ,  $7 \times 7$  of  ${}^4I_{13/2}$ , etc) representing the CF interaction are diagonalized simultaneously for several  ${}^{2S+1}L_J$  states for which data on the experimental energy levels exist, and the CF parameters are determined in a least-squares fit to the data. Here we assume that the centres of gravity of  $J$  multiplets are invariant even in the CF interaction, because the effect of  $J$  mixing is negligible.

On the basis of the group-subgroup chain  $O_3 \supset O_h \supset T_d \supset D_{2d} \supset S_4$ , some of the wavefunctions of the  $4f_{11}$  configuration in  $\text{Er}^{3+}$  at the  $S_4$  symmetry position are expressed as linear combinations of the basis  $|f^n SLJ \mu \nu \xi \eta\rangle$  in the group-chain scheme, where  $\mu$ ,  $\nu$ ,  $\xi$  and  $\eta$  are the irreducible representations of  $O_h$ ,  $T_d$ ,  $D_{2d}$  and  $S_4$ , respectively. From equation (6), the detailed matrix elements of the  ${}^4S_{3/2}$ ,  ${}^4F_{9/2}$ ,  ${}^4I_{9/2}$ ,  ${}^4I_{11/2}$ ,  ${}^4I_{13/2}$  and  ${}^4I_{15/2}$  spectroscopic terms can be obtained. Taking into account the structure distortion when the  $\text{Er}^{3+}$  ions occupy some of the  $Y^{3+}$  sites [19], the CF parameters are calculated by the simple point-charge model:

$$A_{nm} = \sum_j \frac{e^2}{R_j^{n+1}} \frac{4\pi}{2n+1} (-1)^m Y_n^{-m}(\theta_j, \varphi_j). \quad (8)$$

Consider the shielding factors of  $5s^25p^6$  shells and the scaling parameters of the bare Hartree-Fock wavefunction [20]:

$$B_{nm} = \rho_n A_{nm}. \quad (9)$$

With  $\text{Er}^{3+}$ ,  $\rho_2 = 0.1706$ ,  $\rho_4 = 0.4126$  and  $\rho_6 = 0.9826$ . During the lattice sum of  $A_{nm}$ ,  $B_{44}$  can be made real by a rotation about the  $Z$  axis, i.e.  $IB_{44} = 0$ . Thus the fitting number of CF parameters is reduced to six. Using equation (4), the initial values and  $r_0$ ,  $r_1$ ,  $r_2$ , the ratios of the same rank of group-chain parameters can be obtained, which are listed in tables 1 and 2. Note that

$$r_0 = \frac{C_{2+20}^{4+}}{C_{0+00}^{4+}} \quad r_1 = \frac{C_{1+10}^{6+}}{C_{0+00}^{6+}} \quad r_2 = \frac{C_{2+20}^{6+}}{C_{0+00}^{6+}}.$$

The absolute values of these ratios can be seen as a measure of the degree of symmetry distortion of the system [13].

**Table 1.** CF parameters  $B_{kq}$  for  $\text{Er}^{3+} : \text{LiYF}_4$ .

| $B_{20}$ | $B_{40}$ | $B_{44}$ | $B_{60}$ | $RB_{64}$ | $IB_{64}$ | Reference           |
|----------|----------|----------|----------|-----------|-----------|---------------------|
| 361.59   | -621.29  | 1141.97  | -100.65  | 326.56    | 66.51     | Point Charged model |
| 314      | -625     | 982      | -32.4    | 584       | 171       | [21]                |
| 364.13   | -281.41  | 493.35   | -45.51   | 155.70    | 31.67     | Fitting results     |

**Table 2.** Group-chain parameters and constraint ratios

| $C_{2+20}^{2+}$ | $C_{0+00}^{4+}$ | $C_{2+20}^{4+}$ | $C_{0+00}^{6+}$ | $C_{1+10}^{6+}$ | $C_{2+20}^{6+}$ | $r_0$   | $r_1$  | $r_2$  | Reference           |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|---------|--------|--------|---------------------|
| -442.86         | 1185.52         | -3419.0         | 1758.97         | 357.39          | 262.67          | -2.8839 | 0.2032 | 0.1493 | Point Charged model |
| -445.97         | 492.44          | -1494.5         | 843.79          | 170.17          | 134.05          | -3.0349 | 0.2017 | 0.1589 | Fitting results     |

By using the ratios listed in table 2 as constraints in the least-squares fitting, only one minimum was obtained. Further work in the fitting is to adjust the ratios to minimize the

**Table 3.** Comparison of the observed and calculated energy levels and  $g$ -factors of  $Er^{3+}$  in  $LiYF_4$  at 77 K.

| $J$<br>multiplet | Energy ( $cm^{-1}$ ) |                           |                          | $g_{\parallel}$           |                          |                          |
|------------------|----------------------|---------------------------|--------------------------|---------------------------|--------------------------|--------------------------|
|                  | $\Gamma$             | Experimental <sup>a</sup> | Theoretical <sup>b</sup> | Experimental <sup>c</sup> | Theoretical <sup>b</sup> | Theoretical <sup>d</sup> |
| $^4S_{3/2}$      | 7,8                  | 18 497                    | 18 495.24                |                           | 2.00                     | 2.00                     |
|                  | 5,6                  | 18 438                    | 18 439.76                | $-5.26 \pm 0.04$          | -6.00                    | -6.00                    |
| $^4F_{9/2}$      | 5,6                  | 15 477                    | 15 480.35                |                           | 1.73                     |                          |
|                  | 7,8                  | 15 425                    | 15 426.87                |                           | -4.07                    |                          |
|                  | 7,8                  | 15 349                    | 15 343.63                |                           | -3.62                    |                          |
|                  | 5,6                  | 15 333                    | 15 332.97                |                           | 0.94                     |                          |
|                  | 7,8                  | 15 314                    | 15 314.19                | $9.84 \pm 0.25$           | 11.69                    |                          |
| $^4I_{9/2}$      | 7,8                  | 12 667                    | 12 671.66                |                           | 1.21                     |                          |
|                  | 7,8                  | 12 572                    | 12 559.07                |                           | -2.28                    |                          |
|                  | 5,6                  | 12 546                    | 12 541.13                |                           | 1.63                     |                          |
|                  | 5,6                  | 12 483 <sup>f</sup>       | 12 496.49                |                           | -0.17                    |                          |
|                  | 7,8                  | 12 369                    | 12 369.00                |                           | 3.25                     |                          |
| $^4I_{11/2}$     | 7,8                  | 10 355                    | 10 355.26                |                           | 5.88                     |                          |
|                  | 5,6                  | 10 320                    | 10 323.44                |                           | -8.43                    |                          |
|                  | 7,8                  | 10 303                    | 10 305.62                |                           | -3.89                    |                          |
|                  | 5,6                  | 10 285                    | 10 284.58                |                           | 2.12                     |                          |
|                  | 5,6                  | 10 239                    | 10 240.85                |                           | -2.37                    |                          |
|                  | 7,8                  | 10 222                    | 10 234.23                | $1.44 \pm 0.07$           | 0.89                     | 1.23                     |
|                  |                      |                           |                          |                           |                          |                          |
| $^4I_{13/2}$     | 5,6                  | 6738                      | 6746.98                  |                           | -8.99                    | -9.35                    |
|                  | 7,8                  | 6724                      | 6725.73                  | $5.86 \pm 0.10$           | 5.93                     | 7.13                     |
|                  | 5,6                  | 6696                      | 6700.51                  |                           | 9.69                     | 9.48                     |
|                  | 7,8                  | 6672                      | 6656.05                  | $-4.07 \pm 0.11$          | -3.80                    | -5.37                    |
|                  | 5,6                  | 6580                      | 6587.11                  |                           | 4.03                     | 5.57                     |
|                  | 7,8 <sup>g</sup>     | 6540                      | 6535.46                  | $1.37 \pm 0.18$           | 1.20                     | 1.54                     |
|                  | 5,6 <sup>g</sup>     | 6536                      | 6534.15                  | $-1.13 \pm 0.47$          | -0.30                    | -1.24                    |
| $^4I_{15/2}$     | 5,6                  | 354                       | 361.74                   |                           | 12.00                    | 10.58                    |
|                  | 5,6                  | 326                       | 327.38                   |                           | -9.65                    | -8.77                    |
|                  | 7,8                  | 289                       | 282.07                   |                           | -9.62                    | -12.03                   |
|                  | 7,8                  | 250                       | 240.85                   |                           | 4.12                     | 7.89                     |
|                  | 7,8                  | 55                        | 62.00                    | $-2.38 \pm 0.13$          | -0.73                    | -0.81                    |
|                  | 5,6                  | 26                        | 30.83                    | $0.11 \pm 0.13$           | -0.45                    | -0.37                    |
|                  | 7,8                  | 16                        | 7.72                     | $-7.97 \pm 0.20$          | -8.17                    | -11.06                   |
|                  | 5,6                  | 0                         | 3.41                     | $3.137 \pm 0.003^e$       | 2.91                     | 3.35                     |
|                  | RMS                  |                           |                          |                           | 1.09                     | 2.01                     |

<sup>a</sup> Spectrum observed by Petrov and Tkachuk [22].<sup>b</sup> Present results.<sup>c</sup> Kulpa's [23] electron paramagnetic resonance EPR data.<sup>d</sup> Karayianis' [8] parametrized fit.<sup>e</sup> EPR data of Sattler and Nemarich [24].<sup>f</sup> Estimated value according to our fitting.<sup>g</sup> Fitting results of this paper. In Kulpa's paper, the ground state of  $^4I_{13/2}$  is  $\Gamma_{7,8}$ .

RMS deviation of the energy levels. In table 2, comparisons of the initial and final even- $k$  parameters  $C_{\mu\nu\xi}^k$  ( $cm^{-1}$ ) and the corresponding ratios are given. The experimental and fitting energy levels are compared in table 3. The group irreducible representations of Stark

sublevels are also shown.

$$\text{RMS} = \sum_{i=1}^{28} \frac{(E_i^{\text{exp}} - E_i^{\text{theo}})^2}{28 - 6}. \quad (10)$$

The RMS of fitting results is less than  $8 \text{ cm}^{-1}$ , which shows that calculated eigenvalues agree well with the experimental energy levels [22].

The eigenfunctions of the Stark sublevels of the  ${}^4S_{3/2}$ ,  ${}^4F_{9/2}$ ,  ${}^4I_{9/2}$ ,  ${}^4I_{11/2}$ ,  ${}^4I_{13/2}$  and  ${}^4I_{15/2}$  manifolds are normalized and listed in the order of decreasing energy in appendix 2. In the case of the  $S_4$  point group, Butler's notations  $\frac{1}{2}$  and  $\frac{3}{2}$  correspond to  $\Gamma_5$  and  $\Gamma_8$  respectively, of Bethe's notation.

Owing to Kramers degeneracy, another set of conjugate eigenfunction of Stark sublevels, which belongs to  $\Gamma_6$  and  $\Gamma_7$  (or  $-\frac{1}{2}$  and  $-\frac{3}{2}$ ) of the  $S_4$  point-group irreducible representations, is omitted in appendix 2. By using the eigenfunctions above, the  $g$ -factors of EPR can be further calculated.

#### 4. The Zeeman interaction

Because of the existence of time-reversal symmetry in  $\text{Er}^{3+}:\text{LiYF}_4$ , all the Stark sublevels are doubly degenerate even if all these levels completely split by the CF interaction of  $S_4$  point symmetry. Degenerate CF levels will be split in a magnetic field, and the magnitude of the splitting, which can be characterized by a  $g$ -tensor, depends on the external magnetic field and eigenfunctions of CF concerned.

Karayianis [8] had reported a theoretical calculation of  $g$ -factors of the Stark sublevels of the  ${}^4I$  term by the conventional CF method, which did not agree well with Kulpa's [23] experimental values. In this paper, the  $g$ -factors of the ground and excited states of the  ${}^4S_{3/2}$ ,  ${}^4F_{9/2}$ ,  ${}^4I_{9/2}$ ,  ${}^4I_{11/2}$ ,  ${}^4I_{13/2}$  and  ${}^4I_{15/2}$  terms are calculated on the basis of group-chain scheme analysis.

According to equation (4.2.9) of Butler [11], the Zeeman Hamiltonian can be expressed as follows by the basis of the group chain  $O_3 \supset O_h \supset T_d \supset D_{2d} \supset S_4$ :

$$H_Z = \sum_{\alpha_1 J_1 \alpha_2 J_2} (C_0 U^{1+1+\tilde{0}0} + C_1 U^{1+1+111} + C_{-1} U^{1+1+11-1}) \langle \alpha_1 J_1 \| H_Z \| \alpha_2 J_2 \rangle \quad (11)$$

where  $U^{1+1+1\xi\beta}$  ( $\xi\beta = \tilde{0}0, 11, 1-1$ ) is an  $O_3$  unit tensor of the above group-chain scheme, and  $C_i$  ( $i = 0, \pm 1$ ) depends on the relationship between the laboratory (Zeeman)  $z$  axis and the crystal  $x, y, z$  axes.

Generally, the Zeeman interaction is much less than the CF interaction so that we can deal with the external magnetic field as a perturbation and use the wavefunctions of the CF energy levels as zeroth-order approximate wavefunctions to analyse the magnetic splitting. There are two different situations which should be discussed separately.

##### 4.1. Magnetic field $H$ along the crystal $Z$ axis

In this situation, the Zeeman Hamiltonian can be written as

$$H_Z = \sum_{\alpha_1 J_1 \alpha_2 J_2} U^{1+1+\tilde{0}0} \langle \alpha_1 J_1, \alpha_2 J_2 | \langle \alpha_1 J_1 \| H_Z \| \alpha_2 J_2 \rangle. \quad (12)$$

Using bases of the group chain  $O_3 \supset O_h \supset T_d \supset D_{2d} \supset S_4$ , the matrix elements of Zeeman effect can be expanded as

$$\langle \alpha SL J a_1 a_2 a_3 a_4 | H_Z | \alpha SL J b_1 b_2 b_3 b_4 \rangle$$

$$= \sum_{\alpha_1 J_1 \alpha_2 J_2} \langle \alpha SL J a_1 a_2 a_3 a_4 | U^{1^+1^+1\bar{0}0}(\alpha_1 J_1, \alpha_2 J_2) | \alpha SL J b_1 b_2 b_3 b_4 \rangle \times \langle \alpha_1 J_1 || H_Z || \alpha_2 J_2 \rangle. \quad (13)$$

The matrix elements of the unit tensor  $U^{1^+1^+1\bar{0}0}(\alpha_1 J_1, \alpha_2 J_2)$  are zero unless all operator parentage labels match the state parentage labels. Using this, the summation vanishes and equation (13) is given by

$$\langle \alpha SL J a_1 a_2 a_3 a_4 | U^{1^+1^+1\bar{0}0}(\alpha SL J, \alpha SL J) | \alpha SL J b_1 b_2 b_3 b_4 \rangle \langle \alpha SL J || H_Z || \alpha SL J \rangle. \quad (14)$$

By using the Wigner–Eckart theorem it can be factorized as

$$\langle \alpha SL J | U^{1^+}(\alpha SL J, \alpha SL J) | \alpha SL J \rangle \langle \alpha SL J || H_Z || \alpha SL J \rangle \begin{bmatrix} J \\ a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} \begin{bmatrix} J^* & 1^+ & J \\ a_1^* & 1^+ & b_1 \\ a_2^* & 1 & b_2 \\ a_3^* & \tilde{0} & b_3 \\ a_4^* & 0 & b_4 \end{bmatrix} \begin{matrix} O_3 \\ O_h \\ T_d \\ D_{2d} \\ S_4 \end{matrix}. \quad (15)$$

Now the RME of the unit tensor operator is unity and thus vanishes. By further factorizing the  $2jm$  and  $3jm$  factors, we obtain

$$\sum_{r_1 r_2 r_3 r_4} \langle \alpha SL J || H_Z || \alpha SL J \rangle \begin{bmatrix} J \\ a_1 \end{bmatrix} \begin{bmatrix} J^* & 1^+ & J \\ a_1^* & 1^+ & b_1 \end{bmatrix} r_1 \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \begin{bmatrix} a_1^* & 1^+ & b_1 \\ a_2^* & 1 & b_2 \end{bmatrix} r_2 \begin{bmatrix} a_2 \\ a_3 \end{bmatrix} \times \begin{bmatrix} a_2^* & 1 & b_2 \\ a_3^* & \tilde{0} & b_3 \end{bmatrix} r_3 \begin{bmatrix} a_3 \\ a_4 \end{bmatrix} \begin{bmatrix} a_3^* & \tilde{0} & b_3 \\ a_4^* & 0 & b_4 \end{bmatrix} r_4 \quad (16)$$

where

$$\langle \alpha SL J || H_Z || \alpha SL J \rangle = \beta H g_{SLJ} \sqrt{J(J+1)(2J+1)}$$

$$g_{SLJ} = 1 + (g_S - 1) \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (17)$$

$$g_S \approx 2.00232.$$

Observe that the Zeeman interaction is an  $S_4$  scalar; so a  $\delta_{a_4 b_4}$  arises in the above formula. If we use  $jm$  tables and consider the eigenfunction of each Stark sublevel which belongs to the  $\Gamma_8(3/2)$  or  $\Gamma_5(1/2)$  irreducible representation of the  $S_4$  then we have

$$\langle \alpha SL J a_1 a_2 a_3 a_4 | H_Z | \alpha SL J b_1 b_2 b_3 b_4 \rangle = \frac{1}{\sqrt{2}} \beta H g_{SLJ} [J(J+1)(2J+1)]^{1/2} \times \sum_{r_1 r_2 r_3} \begin{bmatrix} J & 1^+ & J \\ a_1 & 1^+ & b_1 \end{bmatrix} r_1 \begin{bmatrix} a_1 & 1^+ & b_1 \\ a_2 & 1 & b_2 \end{bmatrix} r_2 \begin{bmatrix} a_2 & 1 & b_2 \\ a_3 & \tilde{0} & b_3 \end{bmatrix} r_3. \quad (18)$$

The corresponding matrix element of another degenerate eigenfunction which belongs to the  $\Gamma_7(-\frac{3}{2})$  or  $\Gamma_6(-\frac{1}{2})$  irreducible representation of the  $S_4$  group can be obtained similarly:

$$\langle \alpha SL J a_1 a_2 a_3 - a_4 | H_Z | \alpha SL J b_1 b_2 b_3 - b_4 \rangle = \frac{-1}{\sqrt{2}} \beta H g_{SLJ} [J(J+1)(2J+1)]^{1/2} \times \sum_{r_1 r_2 r_3} \begin{bmatrix} J & 1^+ & J \\ a_1 & 1^+ & b_1 \end{bmatrix} r_1 \begin{bmatrix} a_1 & 1^+ & b_1 \\ a_2 & 1 & b_2 \end{bmatrix} r_2 \begin{bmatrix} a_2 & 1 & b_2 \\ a_3 & \tilde{0} & b_3 \end{bmatrix} r_3. \quad (19)$$

So the  $g_{\parallel}$ -values, which characterize the splitting energy of the doublet for a given magnetic field, can be written as

$$g_{\parallel}(\Gamma_{5,6}) = \frac{\Delta E(\Gamma_{5,6})}{\beta H} = \frac{2 \langle \alpha SL J a_1 a_2 a_3 a_4 | H_Z | \alpha SL J b_1 b_2 b_3 b_4 \rangle}{\beta H}$$

$$g_{\parallel}(\Gamma_{7,8}) = \frac{\Delta E(\Gamma_{7,8})}{\beta H} = -\frac{2 \langle \alpha SL J a_1 a_2 a_3 a_4 | H_Z | \alpha SL J b_1 b_2 b_3 b_4 \rangle}{\beta H}. \quad (20)$$



Here a convention is established by which positive or negative  $g_{\parallel}$  are defined [9]. The expression for  $g_{\parallel}$ -values of all the Stark sublevels of the  ${}^4S_{3/2}$ ,  ${}^4F_{9/2}$ ,  ${}^4I_{9/2}$ ,  ${}^4I_{11/2}$ ,  ${}^4I_{13/2}$  and  ${}^4I_{15/2}$  terms are listed in appendix 3. The  $g_{\parallel}$ -values are listed in table 3.

Comparing the results obtained with the experimental values of Kulpa [23] and the theoretical values of Karayianis [8], the RMS of the present paper (1.09) is obviously less than that of Karayianis (2.01). The  $g_{\parallel}$ -value of the ground state  ${}^4I_{15/2}$  (2.91) is also in good agreement with experiment (3.137).

In order to confirm the reliability of the analysis, we may sum all the  $g$ -factors over levels belonging to a particular irreducible representation (e.g.  $\Gamma_{5,6}$ ) of a particular  $2S+1L_J$  state to check the partial  $g$ -sums rule [9]. In essence this rule refers to an approximate invariance of the trace of the Zeeman interaction when the summation is taken over states of the same group characterization within a given JLS multiplet. The results of the sums are compared in table 4. The good agreement shows that group-chain scheme analysis, by using one set of the CF parameter ratios as the constraint condition, is not only useful in the study of spectroscopic properties of laser crystals [12,13] but also valid in the theoretical calculation of magnetic properties.

**Table 4.** Comparison of partial  $g$  sums with theoretical values for the  ${}^4I$  term of  $\text{Er}^{3+}$  in  $\text{LiYF}_4$ , where  $\mu$  is the crystal quantum number.

| $J$                | $\Gamma_7(-\frac{3}{2})$ |               | $\Gamma_5(\frac{1}{2})$ |               |
|--------------------|--------------------------|---------------|-------------------------|---------------|
|                    | $\mu = \frac{1}{2}^a$    | $\text{Er}^b$ | $\mu = \frac{3}{2}^a$   | $\text{Er}^b$ |
| ${}^4I_{9/2}$      | 2.18                     | 2.18          | 1.45                    | 1.45          |
| ${}^4I_{11/2}$     | 2.90                     | 2.88          | -8.69                   | -8.68         |
| ${}^4I_{13/2}$     | 3.32                     | 3.32          | 4.43                    | 4.43          |
| ${}^4I_{15/2}$     | -14.40                   | -14.41        | 4.80                    | 4.81          |
| $G_{4\mu}(6, 3/2)$ | -6.00                    | -6.03         | 2.00                    | 2.01          |

<sup>a</sup> From table VI of [9].

<sup>b</sup> Our present fitting results.

#### 4.2. Magnetic field $H$ perpendicular to the crystal $Z$ axis

Suppose that the external field is along the direction of the  $X$  axis; then the Zeeman Hamiltonian will be

$$H_Z = \sum_{\alpha_1 J_1 \alpha_2 J_2} \frac{1}{\sqrt{2}} [U^{1^+1^+111}(\alpha_1 J_1, \alpha_2 J_2) - U^{1^+1^+11-1}(\alpha_1 J_1, \alpha_2 J_2)] \langle \alpha_1 J_1 \| H_Z \| \alpha_2 J_2 \rangle. \quad (21)$$

For example, consider the  $g_{\perp}$ -factor of the  ${}^4I_{15/2}$  ground state, i.e.  ${}^4I_{15/2}(\Gamma_{5,6})$ . The derivation of the Zeeman matrix elements is similar to section 4.1. Also we have

$$\begin{aligned} & \langle \alpha SLJ a_1 a_2 a_3 a_4 | H_Z | \alpha SLJ b_1 b_2 b_3 b_4 \rangle \\ &= \frac{1}{\sqrt{2}} \sum_{r_1 r_2 r_3 r_4} \langle \alpha SLJ \| H_Z \| \alpha SLJ \rangle \begin{bmatrix} a_3 \\ a_4 \end{bmatrix} \text{D}_{2d} \begin{bmatrix} J & 1^+ & J \\ a_1 & 1^+ & b_1 \end{bmatrix} \begin{matrix} r \\ r_1 \end{matrix} \\ & \times \begin{bmatrix} a_1 & 1^+ & b_1 \\ a_2 & 1 & b_2 \end{bmatrix} \begin{matrix} r_1 \\ r_2 \end{matrix} \begin{bmatrix} a_2 & 1 & b_2 \\ a_3 & 1 & b_3 \end{bmatrix} \begin{matrix} r_2 \\ r_3 \end{matrix} \\ & \times \left( \begin{bmatrix} a_3 & 1 & b_3 \\ a_4^* & 1 & b_4 \end{bmatrix} \begin{matrix} r_3 \\ r_4 \end{matrix} - \begin{bmatrix} a_3 & 1 & b_3 \\ a_4^* & -1 & b_4 \end{bmatrix} \begin{matrix} r_3 \\ r_4 \end{matrix} \right). \end{aligned} \quad (22)$$

Dissimilar to section 4.1, the diagonal matrix elements are all zero (table 5)

$$\begin{aligned}
 H_{12} &= \frac{1}{2} \beta H g ({}^{2S+1}L_J) [J(J+1)(2J+1)]^{1/2} \\
 &\times \sum_{r_1 r_2 r_3} \begin{bmatrix} J & 1^+ & J \\ a_1 & 1^+ & b_1 \end{bmatrix} r_1 \begin{bmatrix} a_1 & 1^+ & b_1 \\ a_2 & 1 & b_2 \end{bmatrix} r_2 \begin{bmatrix} a_2 & 1 & b_2 \\ \frac{1}{2} & 1 & \frac{1}{2} \end{bmatrix} r_3 \\
 &= \beta H g ({}^4I_{15/2}) F(C_1, C_2, C_3, C_4)
 \end{aligned} \tag{23}$$

where  $F(C_1, C_2, C_3, C_4)$  is a function of  $C_i$  ( $i = 1, 2, 3, 4$ ), the linear coefficients of corresponding group-chain wavefunctions, and can be calculated using appendix 2.  $g_{\perp}$  can be obtained by diagonalizing the above  $2 \times 2$  matrix. Finally we obtain  $g_{\perp} = 8.28$ , which agrees well with the experimental value (8.105) [24]. The value of  $g_{\perp}$  is much larger than that of  $g_{\parallel}$  (3.137). It shows large anisotropy of the ground-state  $g$  tensor.

**Table 5.** The Zeeman matrix elements of the  ${}^4I_{15/2}(\Gamma_{5,6})$  ground term.

| $H_Z$      | $\Gamma_5$ | $\Gamma_6$ |
|------------|------------|------------|
| $\Gamma_5$ | 0          | $H_{12}$   |
| $\Gamma_6$ | $H_{12}$   | 0          |

## 5. Conclusion

Group-chain scheme analysis has been carried out for the  $Er^{3+}$  ion  $LiYF_4$  in  $S_4$  low-symmetry sites and the CF energy-level fitting has been performed by using the constraint condition introduced by the ratios of the CF parameters calculated by the simple point-charge model. With the aid of the least-squares fitting programs, the group-chain parameters with real physical meaning and the wavefunctions of Stark sublevels belonging to the manifolds  ${}^4S_{3/2}$ ,  ${}^4F_{9/2}$ ,  ${}^4I_{9/2}$ ,  ${}^4I_{11/2}$ ,  ${}^4I_{13/2}$  and  ${}^4I_{15/2}$  have been obtained.

The existence of an external magnetic field lifts the Kramers' degeneracy of spectroscopic terms of  $Er^{3+} : LiYF_4$ , and Zeeman splitting occurs in CF energy levels. The theoretical formula for the  $g$ -factor has been completely deduced from the analysis introduced. On the basis of the wavefunctions obtained, the  $g$ -factors of ground and excited states of the terms concerned are calculated, which agrees well with the experiment and confirms the partial  $g$ -sums rule of Karayianis. As shown in table 3, the RMS value for  $g$ -factors calculated in this paper is half that published in [8]. This fully demonstrates that the constraint condition used certainly represents the physical reality, which not only can be used in the study of the optical properties but also can be applied to investigate the magnetic properties of crystals doped with rare-earth ions. It also can be seen that the observable macromagnetic properties are connected with the group-chain parameters determined by the microstructures of the crystal.

One of the great advantages of group-chain scheme analysis is that the system's symmetry properties of the irreducible subspaces and eigenstates can be obtained by utilizing simple group theory. The same method can be introduced into the study of other physical properties of localized centres in the crystals.

## Appendix 1

The reduced matrix elements of  $U^{(k)}$  for  $Er^{3+}$  are given in table A1.1.

**Table A1.1.** Reduced matrix elements of  $U^{(k)}$  for  $Er^{3+}$ .

| $\alpha SLJ - \alpha SL'J'$   | $\langle f^n SLJ    U^{(k)}    f^n SL'J' \rangle$ |         |         |
|-------------------------------|---|---------|---------|
|                               | $k = 2$   | $k = 4$ | $k = 6$ |
| ${}^4S_{3/2} - {}^4S_{3/2}$   | 0.2036  | 0       | 0       |
| ${}^4S_{3/2} - {}^4I_{9/2}$   | 0   | 0.2700  | 0.5060  |
| ${}^4S_{3/2} - {}^4I_{11/2}$  | 0   | 0.0608  | 0.2809  |
| ${}^4S_{3/2} - {}^4I_{13/2}$  | 0   | 0       | 0.5900  |
| ${}^4S_{3/2} - {}^4I_{15/2}$  | 0   | 0       | 0.4780  |
| ${}^4F_{9/2} - {}^4F_{9/2}$   | 0.3132  | 0.2883  | 0.2017  |
| ${}^4I_{9/2} - {}^4I_{9/2}$   | 0.0015  | 0.2674  | -0.8637 |
| ${}^4I_{11/2} - {}^4I_{11/2}$ | -0.2697   | 0.1703  | -0.1553 |
| ${}^4I_{13/2} - {}^4I_{13/2}$ | -0.4161   | 0.4161  | -0.4783 |
| ${}^4I_{15/2} - {}^4I_{15/2}$ | -0.4996   | 0.6180  | -1.3582 |

## Appendix 2

The wavefunctions for the CF energy levels ( $O_3 \supset O_h \supset T_d \supset D_{2d} \supset S_4$ ) are as follows:

$${}^4S_{3/2}(b) \quad \left| \frac{3^-}{2} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_8)$$

$$(a) \quad \left| \frac{3^-}{2} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle \quad (\Gamma_5)$$

$${}^4F_{9/2}(e) \quad (0.1677 - 0.0226i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle + 0.9856 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle \quad (\Gamma_5)$$

$$(d) \quad (0.6907 + 0.0644i) \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle + (0.6692 + 0.0209i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\ + 0.2656 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_8)$$

$$(c) \quad (0.4250 + 0.1503i) \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle + (-0.6746 - 0.1353i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\ + 0.5687 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_8)$$

$$(b) \quad (0.9768 - 0.1315i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle - 0.1692 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle \quad (\Gamma_5)$$

$$(a) \quad (-0.5461 - 0.1318i) \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle + (0.2645 + 0.0917i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\ + 0.5687 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_8)$$

$${}^4I_{9/2}(e) \quad (-0.6846 - 0.6708i) \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle + (-0.1404 - 0.2360i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\ + 0.0766 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_8)$$

$$(d) \quad (0.0472 + 0.2665i) \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle + (0.0692 - 0.9577i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\ - 0.0686 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_8)$$

$$(c) \quad (-0.5865 + 0.6486i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle + 0.4851 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle \quad (\Gamma_5)$$

$$(b) \quad (0.3253 - 0.3598i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle + 0.8745 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle \quad (\Gamma_5)$$

$$(a) \quad (0.0560 + 0.0701i) \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle + (0.0156 - 0.0479i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\ + 0.9947 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_8)$$

$${}^4I_{11/2}(f) \quad (-0.4349 + 0.0106i) \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle + (-0.4387 + 0.0186i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\ - 0.7860 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_8)$$

$$(e) \quad (-0.0853 + 0.0399i) \left| \frac{1^-}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \right\rangle + (-0.1972 + 0.0299i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle \\ + 0.9754 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{1}{2} \frac{1}{2} \right\rangle \quad (\Gamma_5)$$

$$(d) \quad (-0.5384 + 0.0111i) \left| \frac{1^-}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \right\rangle + (0.8262 - 0.0264i) \left| \frac{3^-}{2_0} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \\ - 0.1637 \left| \frac{3^-}{2_1} \frac{3}{2} \frac{3}{2} \frac{3}{2} \right\rangle \quad (\Gamma_8)$$

- (c)  $(0.7168 + 0.4180i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.4964 - 0.2507i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle - 0.0470|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )
- (b)  $(-0.5428 + 0.0893i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.7842 + 0.1900i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle - 0.2155|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )
- (a)  $(0.7212 - 0.0241i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2}\rangle + (0.3516 - 0.0173i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle - 0.5962|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle$  ( $\Gamma_8$ )
- $^4I_{13/2}(g)$   $(-0.1697 - 0.01392i)|\frac{\bar{1}}{2_0} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.7232 - 0.0492i)|\frac{\bar{1}}{2_1} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (0.0703 + 0.0386i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle + 0.6627|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )
- (f)  $(0.6203 - 0.0276i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2}\rangle + (0.4526 + 0.0006i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle + 0.6400|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle$  ( $\Gamma_8$ )
- (e)  $(0.0076 - 0.0545i)|\frac{\bar{1}}{2_0} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.5570 + 0.0047i)|\frac{\bar{1}}{2_1} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.6294 - 0.0401i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle - 0.5375|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )
- (d)  $(0.0625 + 0.0072i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2}\rangle + (-0.8421 - 0.0148i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle + 0.5354|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle$  ( $\Gamma_8$ )
- (c)  $(0.9422 - 0.2565i)|\frac{\bar{1}}{2_0} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.0626 + 0.0780i)|\frac{\bar{1}}{2_1} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.0644 + 0.0057i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle + 0.1798|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )
- (b)  $(0.7810 - 0.0251i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2}\rangle + (-0.2924 - 0.0136i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle - 0.5511|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle$  ( $\Gamma_8$ )
- (a)  $(-0.1080 + 0.0533i)|\frac{\bar{1}}{2_0} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (0.3904 + 0.0431i)|\frac{\bar{1}}{2_1} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.7628 - 0.0984i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle + 0.4895|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )
- $^4I_{15/2}(h)$   $(-0.7065 + 0.3776i)|\frac{\bar{1}}{2_0} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (0.1604 + 0.0047i)|\frac{\bar{1}}{2_1} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.5254 + 0.1075i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle - 0.2117|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )
- (g)  $(0.3768 - 0.3575i)|\frac{\bar{1}}{2_0} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (0.5246 - 0.3514i)|\frac{\bar{1}}{2_1} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (-0.5310 + 0.2067i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle - 0.0827|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )
- (f)  $(0.7712 + 0.3717i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2}\rangle + (-0.3715 - 0.1331i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle + (0.2402 + 0.0867i)|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle + 0.2146|\frac{\bar{3}}{2_2} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle$  ( $\Gamma_8$ )
- (e)  $(0.2041 + 0.0567i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2}\rangle + (-0.3024 - 0.0430i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle + (-0.8065 - 0.0564i)|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle - 0.4564|\frac{\bar{3}}{2_2} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle$  ( $\Gamma_8$ )
- (d)  $(-0.2455 - 0.0319i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2}\rangle + (-0.5382 - 0.0958i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle + (0.4939 + 0.0509i)|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle - 0.6271|\frac{\bar{3}}{2_2} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle$  ( $\Gamma_8$ )
- (c)  $(-0.0090 - 0.2139i)|\frac{\bar{1}}{2_0} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (0.2230 + 0.5158i)|\frac{\bar{1}}{2_1} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (0.2698 + 0.3942i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle - 0.6405|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )
- (b)  $(-0.3813 - 0.1245i)|\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2}\rangle + (-0.6668 - 0.0861i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle + (-0.1851 - 0.0209i)|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle + 0.5936|\frac{\bar{3}}{2_2} \frac{\bar{3}}{2} \frac{\bar{3}}{2}\rangle$  ( $\Gamma_8$ )
- (a)  $(-0.1693 - 0.1181i)|\frac{\bar{1}}{2_0} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (0.3001 + 0.4121i)|\frac{\bar{1}}{2_1} \frac{\bar{1}}{2} \frac{\bar{1}}{2}\rangle + (0.0241 + 0.3986i)|\frac{\bar{3}}{2_0} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle + 0.7335|\frac{\bar{3}}{2_1} \frac{\bar{3}}{2} \frac{\bar{1}}{2}\rangle$  ( $\Gamma_5$ )

### Appendix 3

The group-chain scheme calculation of  $g_{\parallel}$ -values of Stark sublevels of  $\text{Er}^{3+} : \text{LiYF}_4$  is as follows.

$$\begin{aligned}
 g_{\parallel}(^4I_{15/2}, \Gamma_{5,6}) &= 2\sqrt{510}g(^4I_{15/2}) \left( \frac{\sqrt{17}}{6\sqrt{30}}|C_1|^2 - \frac{99}{20\sqrt{510}}|C_2|^2 - \frac{17}{90\sqrt{510}}|C_3|^2 \right. \\
 &\quad + \frac{31\sqrt{5}}{36\sqrt{102}}|C_4|^2 - \frac{\sqrt{13}}{15\sqrt{17}}C_{12} + \frac{\sqrt{1001}}{45\sqrt{34}}C_{13} + \frac{\sqrt{11}}{9\sqrt{17}}C_{14} \\
 &\quad \left. + \frac{\sqrt{77}}{15\sqrt{1020}}C_{23} + \frac{\sqrt{143}}{12\sqrt{510}}C_{24} + \frac{\sqrt{91}}{9\sqrt{1020}}C_{34} \right) \\
 g_{\parallel}(^4I_{15/2}, \Gamma_{7,8}) &= -2\sqrt{510}g(^4I_{15/2}) \left( \frac{\sqrt{5}}{2\sqrt{102}}|C_1|^2 - \frac{43}{20\sqrt{510}}|C_2|^2 + \frac{321}{90\sqrt{510}}|C_3|^2 \right. \\
 &\quad + \frac{15\sqrt{5}}{36\sqrt{102}}|C_4|^2 + \frac{1}{\sqrt{34}}C_{13} - \frac{3\sqrt{77}}{15\sqrt{1020}}C_{23} - \frac{3\sqrt{143}}{12\sqrt{510}}C_{24} - \frac{3\sqrt{91}}{9\sqrt{1020}}C_{34} \left. \right) \\
 g_{\parallel}(^4I_{13/2}, \Gamma_{5,6}) &= \sqrt{1365}g(^4I_{13/2}) \left( \frac{\sqrt{5}}{\sqrt{273}}|C_1|^2 - \frac{\sqrt{13}}{3\sqrt{105}}|C_2|^2 + \frac{23\sqrt{2}}{7\sqrt{2730}}|C_3|^2 \right. \\
 &\quad \left. + \frac{\sqrt{2}}{21\sqrt{2730}}|C_4|^2 + \frac{2\sqrt{2}}{\sqrt{273}}C_{13} + \frac{4\sqrt{2}}{3\sqrt{105}}C_{24} + \frac{12\sqrt{33}}{7\sqrt{2730}}C_{34} \right) \\
 g_{\parallel}(^4I_{13/2}, \Gamma_{7,8}) &= -\sqrt{1365}g(^4I_{13/2}) \left( \frac{-\sqrt{5}}{\sqrt{273}}|C_1|^2 + \frac{25\sqrt{2}}{7\sqrt{2730}}|C_2|^2 - \frac{11\sqrt{2}}{7\sqrt{2730}}|C_3|^2 \right. \\
 &\quad \left. + \frac{2\sqrt{22}}{7\sqrt{195}}C_{12} - \frac{8}{7\sqrt{65}}C_{13} - \frac{4\sqrt{33}}{7\sqrt{2730}}C_{23} \right) \\
 g_{\parallel}(^4I_{11/2}, \Gamma_{5,6}) &= \sqrt{858}g(^4I_{11/2}) \left( \frac{-\sqrt{11}}{3\sqrt{78}}|C_1|^2 + \frac{87}{33\sqrt{858}}|C_2|^2 - \frac{263}{33\sqrt{858}}|C_3|^2 \right. \\
 &\quad \left. - \frac{\sqrt{10}}{\sqrt{429}}C_{12} + \frac{8}{3\sqrt{429}}C_{13} + \frac{4\sqrt{10}}{11\sqrt{858}}C_{23} \right) \\
 g_{\parallel}(^4I_{11/2}, \Gamma_{7,8}) &= -\sqrt{858}g(^4I_{11/2}) \left( \frac{\sqrt{11}}{3\sqrt{78}}|C_1|^2 - \frac{151}{33\sqrt{858}}|C_2|^2 - \frac{69}{33\sqrt{858}}|C_3|^2 \right. \\
 &\quad \left. - \frac{\sqrt{14}}{3\sqrt{19}}C_{12} + \frac{12\sqrt{10}}{11\sqrt{858}}C_{23} \right) \\
 g_{\parallel}(^4I_{9/2} \text{ or } ^4F_{9/2}, \Gamma_{5,6}) &= \sqrt{495}g(^4I_{9/2} \text{ or } ^4F_{9/2}) \left( \frac{-1}{5\sqrt{55}}|C_1|^2 + \frac{39}{15\sqrt{495}}|C_2|^2 \right. \\
 &\quad \left. - \frac{4\sqrt{14}}{5\sqrt{330}}C_{12} \right) \\
 g_{\parallel}(^4I_{9/2} \text{ or } ^4F_{9/2}, \Gamma_{7,8}) &= -\sqrt{495}g(^4I_{9/2} \text{ or } ^4F_{9/2}) \left( \frac{-11}{9\sqrt{55}}|C_1|^2 + \frac{9}{5\sqrt{55}}|C_2|^2 \right. \\
 &\quad \left. - \frac{71}{15\sqrt{495}}|C_3|^2 + \frac{4}{5\sqrt{33}}C_{12} + \frac{8\sqrt{7}}{45\sqrt{11}}C_{13} - \frac{4\sqrt{14}}{5\sqrt{330}}C_{23} \right) \\
 g_{\parallel}(^4S_{3/2}, \Gamma_{5,6}) &= \sqrt{30}g(^4S_{3/2}) \frac{-3}{\sqrt{30}} = -6 \\
 g_{\parallel}(^4S_{3/2}, \Gamma_{7,8}) &= -\sqrt{30}g(^4S_{3/2}) \frac{-1}{\sqrt{30}} = 2
 \end{aligned}$$

where  $C_i$  ( $i = 1, 2, 3, 4$ ) is the linear coefficient of the corresponding group-chain wavefunction, and  $C_{ij}(i, j = 1, 2, 3, 4) = C_i^* C_j + C_j^* C_i$ .

## References

- [1] Kaminskii A A 1981 *Laser Crystals: Their Physics and Properties* (New York: Springer)
- [2] Brown M R and Shand W A 1969 *J. Phys. C: Solid State Phys.* **2** 1908
- [3] Brown M R, Roots K G and Shand W A 1969 *J. Phys. C: Solid State Phys.* **2** 593
- [4] Chicklis E P, Folweiler R C and Naiman C S 1973 *Air Force Avionics Laboratory Reports* AFAL-TR-73-94, Nos. 1 and 2
- [5] Chiclis E P 1973 *Laser Focus* (August) 30
- [6] Brode R, Heumann E, Koetke J, Danger T and Huber G 1993 *Appl. Phys. Lett.* **63** 2030
- [7] Heine F, Heumann E, Danger T, Schweizer T, Huber G and Chai B 1994 *Appl. Phys. Lett.* **65** 383
- [8] Karayianis N 1971 *J. Phys. Chem. Solids* **32** 2385
- [9] Karayianis N 1971 *J. Chem. Phys.* **55** 3734
- [10] Kulpa S M and Karayianis N 1972 *Proc. 1972 Army Sci. Conf.* vol II (West Point, New York) 217
- [11] Butler P H 1981 *Point Group Symmetry Application: Method and Tables* (New York: Plenum)
- [12] Luo Zundu and Huang Yidong 1994 *J. Phys.: Condens. Matter* **6** 3737
- [13] Luo Zundu and Huang Yidong 1993 *J. Phys.: Condens. Matter* **5** 6949
- [14] Yu Jiaqi 1984 *Lumin. Display Dev.* **5** 102 (in Chinese)
- [15] Sachs M 1963 *Solid State Theory* (New York: McGraw-Hill) ch 4
- [16] Wybourne B G 1961 *J. Chem. Phys.* **34** 279
- [17] Rotenberg M, Bivins R, Metropolis N and Wooten J K 1959 *The 3j and 6j Symbols* (Reading, MA: MIT)
- [18] Nielson C W and Koster G F 1963 *Spectroscopic Coefficients for the  $p^n$  and  $d^n$  and  $f^n$  Configurations* (Reading, MA: MIT)
- [19] Thoma R E, Weaver C F, Friedman H A, Insley H, Harris L A and Yakel H A 1961 *J. Phys. Chem.* **65** 1096
- [20] Morrison C A and Leavitt R P 1979 *J. Chem. Phys.* **71** 2366
- [21] Morrison C A and Leavitt R P 1982 *Handbook on the Physics and Chemistry of Rare Earths* vol 5, ed K A Gschneidner and L Eyring (Amsterdam: North-Holland) 627
- [22] Petrov M V and Tkachuk 1978 *Opt. Spectrosc.* **45** 81
- [23] Kulpa S M 1975 *J. Phys. Chem. Solids* **36** 1317
- [24] Sattler J P and Nemanich J 1971 *Phys. Rev. B* **4** 1