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Theoretical analysis of the coupling between 4T_2 and 2E states of the Cr^{3+} ion in tunable laser material

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Abstract. The effective matrix element of the spin-orbit coupling between the 2E and 4T_2 states of the Cr^{3+} ion was calculated according to the C_3i point symmetry that the Cr^{3+} ion occupies in garnets and the Huang-Rhys S factor and phonon energy $\hbar\omega$, which were estimated using the room-temperature absorption and emission spectra by means of a special multi-mode model. Based on the parameters obtained, the ratios of lifetimes $\tau({}^2E)/\tau({}^4T_2)$ for Cr^{3+} in crystals of the garnets GSGG, YSGG, GGG and YGG were calculated by the models proposed by Donnelly *et al* and Wojtowicz *et al*. The results turned out to be satisfactory. All the theoretical models describing the coupling of 2E and 4T_2 states were compared and evaluated.

1. Introduction

Chromium-doped crystals with weak or intermediate crystal field are tunable laser materials [1–3]. The laser action is based on the 4T_2 to 4A_2 transition, which has a broad-band emission, and the 2E to 4A_2 transition, which results in the R line. Although the 2E level is not directly involved in laser action, it provides a particle reservoir for 4T_2 . Therefore, the ratio of $\tau({}^2E)/\tau({}^4T_2)$ is an important parameter for a tunable laser crystal. The 2E to 4A_2 transition corresponds to spin-forbidden luminescence with a lifetime in the millisecond range. The spin-forbidden law is partly broken by the spin-orbit coupling between 2E and 4T_2 states and the electron-phonon interaction, which mixes phonon states of 2E and those of 4T_2 . There is a series of papers concentrating on the mechanism of 2E luminescence that have tried to calculate theoretically the ratio of intensities and lifetimes between 2E and 4T_2 downward transitions [4–8]. An expression for the approximate wavefunction for the perturbed 2E state was given by Donnelly *et al* [5], which took into account both spin-orbit and electron-phonon interactions. According to this expression, the ratio concerned can be calculated, although the authors of [5] did not do so. Wojtowicz *et al* [9] proposed two models to deal with similar problems. Their model A (frozen lattice model) and model B (designated by them as a modified DHGIM model) are different only in the sequence of introducing spin-orbit coupling and electron-phonon interaction. Their model B is basically the same as that proposed by Donnelly *et al*, except that the energy denominators are different. The conclusion of [9] is that their model A is better than model B. Nevertheless, in order to reach a better fit by their model A, a value of $\frac{1}{2}(R_1 + R_2)$, where R_1 and R_2 are equilibrium positions for the system in the 2E and 4T_2 states respectively, should be chosen for R_0 as the frozen

lattice position. This assumption has no clear physical meaning and is somewhat artificial. In fact, the calculation results are dependent on the choice of the values of S , $\hbar\omega$ and W . Therefore, to judge which model is suitable, it is necessary to examine first whether all the chosen parameters are suitable. Obviously, the W value (200 cm^{-1}) used by Wojtowicz [9] is a calculated value for Cr^{3+} ions sited at cubic symmetry positions [10]. However, the actual site symmetry of the Cr^{3+} ion in garnets is C_{3i} and that in ruby is C_3 . It will be shown that the spin-orbit interaction matrix element W corresponding to these point groups needs to be recalculated. On the other hand, the S and $\hbar\omega$ values should be determined by fluorescence and absorption spectra for every kind of crystal; it is unreasonable to choose $S = 6$ and $\hbar\omega = 250\text{ cm}^{-1}$ for all the different crystals.

In this paper, we will first calculate the spin-orbit interaction matrix elements, according to the exact point group symmetry that Cr^{3+} occupies, using the group chain scheme introduced by Butler [11], Prepho and Schatz [12]. Secondly, based on a multi-mode model proposed by Huang Kun [13], S and $\hbar\omega$ can be estimated by using room-temperature spectra [14]. This multi-mode method and the results are also introduced. Finally, all the parameters obtained are used to calculate the ratios of lifetimes and the results are compared with those published in [9] to evaluate the rationality of the models for calculating the ratio of lifetimes.

2. Calculation of spin-orbit interaction matrix elements between 2E and 4T_2 states

As an example, we will calculate the matrix elements of spin-orbit interaction H_{so} , $W = \langle {}^2E, i | H_{\text{so}} | {}^4T_2, i' \rangle$, for garnet crystals, in which Cr^{3+} ions occupy $C_{3i} = S_6$ site symmetry positions, where i and i' denote a series of state labels along the group chain $O_3 \supset O_h \supset D_{3d} \supset C_{3i}$ for 2E and 4T_2 levels respectively. In the calculation of W , the Wigner-Eckart theorem was used to obtain the matrix element for the scalar product of spin and orbit vectors [11]

$$\sum_k (l_k \cdot S_k) = -\{l_k S_k^*\}_0^0 \tag{2.1}$$

$$\begin{aligned} & \langle (\lambda_1 \lambda_2) r_1 \lambda i | \{l_k S_k^*\}_0^0 | (\mu_1 \mu_2) r_2 \mu j \rangle \\ &= \sum_{S_1 S_2} \delta_{ij} \delta_{\lambda\mu} H(\lambda_1 \lambda_2 \lambda) H(\mu_1 \mu_2 \mu) |\kappa|^{-1/2} \{ \lambda_2 \} \{ \lambda_2^* \kappa^* \mu_2 S_2 \} \{ \lambda_1 \lambda_2 \lambda^* r_1 \} \\ & \quad \times \left\{ \begin{matrix} \mu_1 & \mu_2 & \lambda \\ \lambda_2^* & \lambda_1 & \kappa \end{matrix} \right\}_{S_1 S_2 r_1 r_2} \langle \lambda_1 || l || \mu_1 \rangle_{S_1} \langle \lambda_2 || S^* || \mu_2 \rangle_{S_2} \end{aligned} \tag{2.2}$$

and the Racah factorization lemma of 3- j m factors [11, 12]

$$\begin{aligned} & \begin{pmatrix} c \\ c_1 \\ c_2 \end{pmatrix} \begin{matrix} G \\ G_1 \\ G_2 \end{matrix} \begin{pmatrix} a & b & c^* \\ a_1 & b_1 & c_1^* \\ a_2 & b_2 & c_2^* \end{pmatrix}^* \begin{matrix} rG \\ G_1 \\ G_2 \end{matrix} \\ &= \begin{pmatrix} c \\ c_1 \end{pmatrix} \begin{matrix} G \\ G_1 \end{matrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \begin{matrix} G_1 \\ G_2 \end{matrix} \sum_{r_1} \begin{pmatrix} a & b & c^* \\ a_1 & b_1 & c_1^* \end{pmatrix}^* \begin{matrix} rG \\ r_1 G_1 \end{matrix} \begin{pmatrix} a_1 & b_1 & c_1^* \\ a_2 & b_2 & c_2^* \end{pmatrix} \begin{matrix} r_1 G_1 \\ G_2 \end{matrix} \end{aligned} \tag{2.3}$$

can also be used. Then the general formula for the calculation of matrix elements H_{so} can be written as

$$\begin{aligned}
 & \left\langle l^n \alpha \left(\begin{matrix} S & \Gamma_{S_1} & \Gamma_{S_2} & \Gamma_{S_3} \\ L & \Gamma_1 & \Gamma_2 & \Gamma_3 \end{matrix} \right) r t \tau \middle| H_{so} \middle| l^n \alpha' \left(\begin{matrix} S' & \Gamma'_{S_1} & \Gamma'_{S_2} & \Gamma'_{S_3} \\ L' & \Gamma'_1 & \Gamma'_2 & \Gamma'_3 \end{matrix} \right) r' t' \tau' \right\rangle \\
 &= \sum_{g_3} \sum_{S_1} \sum_{S_2} \sum_{r_1} \sum_{r_2} \sum_{r_3} \sum_{r_{S_1}} \sum_{r_{S_2}} \sum_{r_{S_3}} (-1)^{g_3} \delta_{tt'} \delta_{\tau\tau'} H(\Gamma_{S_3} \Gamma_3 t) \\
 & \quad \times H(\Gamma'_{S_3} \Gamma'_3 t') \{ \Gamma_3 \} \{ \Gamma_3^* g_3^* \Gamma_3 S_2 \} \{ \Gamma_{S_3} \Gamma_3 t^* r' \} \left\{ \begin{matrix} \Gamma_3 & \Gamma_{S_3} & t \\ \Gamma_{S_3} & \Gamma_3 & g_3 \end{matrix} \right\}_{S_1 S_2 r r'} \\
 & \quad \times \left(\begin{matrix} S \\ \Gamma_{S_1} \end{matrix} \right) \left(\begin{matrix} \Gamma_{S_1} \\ \Gamma_{S_2} \end{matrix} \right) \left(\begin{matrix} \Gamma_{S_2} \\ \Gamma_{S_3} \end{matrix} \right) \left(\begin{matrix} L \\ \Gamma_1 \end{matrix} \right) \left(\begin{matrix} \Gamma_1 \\ \Gamma_2 \end{matrix} \right) \left(\begin{matrix} \Gamma_2 \\ \Gamma_3 \end{matrix} \right) \left(\begin{matrix} S^* & 1 & S' \\ \Gamma_{S_1}^* & 1 & \Gamma'_{S_1} \end{matrix} \right)_{r_{S_1}} \\
 & \quad \times \left(\begin{matrix} \Gamma_{S_1}^* & 1 & \Gamma'_{S_1} \\ \Gamma_{S_2}^* & g_2^* & \Gamma'_{S_2} \end{matrix} \right)_{r_{S_2}} \left(\begin{matrix} \Gamma_{S_2}^* & g_2^* & \Gamma'_{S_2} \\ \Gamma_{S_3}^* & g_3^* & \Gamma'_{S_3} \end{matrix} \right)_{r_{S_3}} \left(\begin{matrix} L^* & 1 & L' \\ \Gamma_1^* & 1 & \Gamma'_1 \end{matrix} \right)_{r_1} \\
 & \quad \times \left(\begin{matrix} \Gamma_1^* & 1 & \Gamma'_1 \\ \Gamma_2^* & g_2 & \Gamma'_2 \end{matrix} \right)_{r_2} \left(\begin{matrix} \Gamma_2^* & g_2 & \Gamma'_2 \\ \Gamma_3^* & g_3 & \Gamma'_3 \end{matrix} \right)_{r_3} \{ -\zeta [l(l+1)(2l+1)]^{1/2} \} \\
 & \quad \times \left\langle l^n \alpha S L \middle\| \sum_k U_k S_k \middle\| l^n \alpha' S' L' \right\rangle \quad (2.4)
 \end{aligned}$$

where U is the Racah unit tensor and all the symbols used are the same as those adopted by Butler [11]. The labels of the representation for corresponding groups in the group chain are $L(O_3)$, $\Gamma_1(O_h)$, $\Gamma_2(D_{3d})$, $\Gamma_3(C_{3i})$ and $S(O_3)$, $\Gamma_{S_1}(O_h)$, $\Gamma_{S_2}(D_{3d})$, $\Gamma_{S_3}(C_{3i})$; r_i denotes the number of repeat representations in related groups; and ζ is the spin-orbit coupling constant of free Cr^{3+} ions. The irreducible tensor matrix element

$$\left\langle l^n \alpha S L \middle\| \sum_k U_k S_k \middle\| l^n \alpha' S' L' \right\rangle = \langle l^n \alpha S L \| V'' \| l^n \alpha' S' L' \rangle \quad (2.5)$$

can be found from [15]. For the case concerned, $l = 2$, $S = \frac{1}{2}$, $L = 4$, $S' = \frac{3}{2}$, $L' = 3$, so equation (2.5) equals $-\sqrt{3}$.

If Cr^{3+} ions occupy a cubic site symmetry position, then equation (2.4) in this case becomes

$$\begin{aligned}
 & \left\langle d^3 2E \left(\begin{matrix} \frac{1}{2} & \frac{1}{2} \\ 4 & 2 \end{matrix} \right) \frac{3}{2} \middle| H_{so} \middle| d^3 4T_2 \left(\begin{matrix} \frac{3}{2} & \frac{3}{2} \\ 3 & 1 \end{matrix} \right) \frac{3}{2} \right\rangle \\
 &= \left(\begin{matrix} \frac{1}{2} \\ \frac{1}{2} \end{matrix} \right) \left(\begin{matrix} 4 \\ 2 \end{matrix} \right) \left(\begin{matrix} \frac{1}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & 1 & \frac{3}{2} \end{matrix} \right) \left(\begin{matrix} 4 & 1 & 3 \\ 2 & 1 & \bar{1} \end{matrix} \right) \left\{ \begin{matrix} \frac{3}{2} & \bar{1} & \frac{3}{2} \\ 2 & \frac{1}{2} & 1 \end{matrix} \right\} (\sqrt{90} \zeta). \quad (2.6)
 \end{aligned}$$

The values of the 3- j m factor and 6- j m symbol can be found from tables given in [11]:

$$\begin{aligned}
 \text{3-}j\text{m factor} & \quad \left(\begin{matrix} \frac{1}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & 1 & \frac{3}{2} \end{matrix} \right) = 1 & \quad \left(\begin{matrix} 4 & 1 & 3 \\ 2 & 1 & \bar{1} \end{matrix} \right) = \frac{1}{\sqrt{7}} \\
 \text{6-}j\text{m symbol} & \quad \left\{ \begin{matrix} \frac{3}{2} & \bar{1} & \frac{3}{2} \\ 2 & \frac{1}{2} & 1 \end{matrix} \right\} = -\frac{1}{2\sqrt{6}}.
 \end{aligned}$$

All the 2- j m factors concerned are unity. Substituting into (2.6), it is easy to obtain

$$W = -\frac{1}{2} \sqrt{\frac{15}{7}} \zeta. \quad (2.7)$$

With $\zeta = 275 \text{ cm}^{-1}$ [16], the magnitude of W obtained is 201 cm^{-1} , the same as that given by Ruciman and Schroeder [10].

The site symmetry possessed by the Cr^{3+} ion in garnets is C_{3i} . In this case, there are twelve sublevels for 4T_2 and four sublevels for 2E . They are denoted as follows:

$$\begin{aligned}
 |{}^2E, 1\rangle &= \left| \left(\begin{array}{ccc} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ 2 & 1 & -1 \end{array} \right) - \frac{1}{2} \right\rangle & |{}^2E, 2\rangle &= \left| \left(\begin{array}{ccc} \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\ 2 & 1 & 1 \end{array} \right) \frac{1}{2} \right\rangle \\
 |{}^2E, 3\rangle &= \left| \left(\begin{array}{ccc} \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\ 2 & 1 & -1 \end{array} \right) \frac{3}{2} \right\rangle & |{}^2E, 4\rangle &= \left| \left(\begin{array}{ccc} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ 2 & 1 & 1 \end{array} \right) \frac{3}{2} \right\rangle \\
 |{}^4T_2, 1\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & \frac{1}{2} & \frac{1}{2} \\ 1 & 1 & -1 \end{array} \right) - \frac{1}{2} \right\rangle & |{}^4T_2, 2\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} \\ 1 & 0 & 0 \end{array} \right) - \frac{1}{2} \right\rangle \\
 |{}^4T_2, 3\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & -\frac{3}{2} & \frac{3}{2} \\ 1 & 1 & 1 \end{array} \right) - \frac{1}{2} \right\rangle & |{}^4T_2, 4\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & \frac{3}{2} & \frac{3}{2} \\ 1 & 1 & 1 \end{array} \right) - \frac{1}{2} \right\rangle \\
 |{}^4T_2, 5\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} \\ 1 & 1 & 1 \end{array} \right) \frac{1}{2} \right\rangle & |{}^4T_2, 6\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & \frac{1}{2} & \frac{1}{2} \\ 1 & 0 & 0 \end{array} \right) \frac{1}{2} \right\rangle \\
 |{}^4T_2, 7\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & -\frac{3}{2} & \frac{3}{2} \\ 1 & 1 & -1 \end{array} \right) \frac{1}{2} \right\rangle & |{}^4T_2, 8\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & \frac{3}{2} & \frac{3}{2} \\ 1 & 1 & -1 \end{array} \right) \frac{1}{2} \right\rangle \\
 |{}^4T_2, 9\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} \\ 1 & 1 & -1 \end{array} \right) \frac{3}{2} \right\rangle & |{}^4T_2, 10\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & \frac{1}{2} & \frac{1}{2} \\ 1 & 1 & 1 \end{array} \right) \frac{3}{2} \right\rangle \\
 |{}^4T_2, 11\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & -\frac{3}{2} & \frac{3}{2} \\ 1 & 0 & 0 \end{array} \right) \frac{3}{2} \right\rangle & |{}^4T_2, 12\rangle &= \left| \left(\begin{array}{ccc} \frac{3}{2} & \frac{3}{2} & \frac{3}{2} \\ 1 & 0 & 0 \end{array} \right) \frac{3}{2} \right\rangle.
 \end{aligned} \tag{2.8}$$

These wavefunctions are written in the following scheme

$$\left| \left(\begin{array}{ccc} \Gamma_{S_1}(\text{O}_h) & \Gamma_{S_2}(\text{D}_{3d}) & \Gamma_{S_3}(\text{C}_{3i}) \\ \Gamma_1(\text{O}_h) & \Gamma_2(\text{D}_{3d}) & \Gamma_3(\text{C}_{3i}) \end{array} \right) t \right\rangle.$$

By using equation (2.4) and the $2-jm$, $3-jm$ factors and $6-jm$ symbols given in the appendix, all the matrix elements between substates of 4T_2 and those of 2E can be calculated. The results are given in table 1.

Obviously, by the effect of spin-orbit coupling, 4T_2 components are mixed into sublevels of 2E :

$$\begin{aligned}
 |{}^2E, 1\rangle &= |{}^2E, 1\rangle_0 + [\zeta/\Delta E({}^4T_2-{}^2E)][-(5/14)^{1/2}|{}^4T_2, 1\rangle - (5/28)^{1/2}|{}^4T_2, 2\rangle \\
 &\quad - (15/56)^{1/2}|{}^4T_2, 3\rangle - i(15/56)^{1/2}|{}^4T_2, 4\rangle]
 \end{aligned} \tag{2.9}$$

assuming $|{}^4T_2, i\rangle$ ($i = 1, 2, \dots, 12$) are approximately degenerate. Similar expressions for $|{}^2E, 2\rangle$, $|{}^2E, 3\rangle$ and $|{}^2E, 4\rangle$ can be easily written down:

$$\begin{aligned}
 |{}^2E, 2\rangle &= |{}^2E, 2\rangle_0 + [\zeta/\Delta E({}^4T_2-{}^2E)][-(5/14)^{1/2}|{}^4T_2, 5\rangle + (5/28)^{1/2}|{}^4T_2, 6\rangle \\
 &\quad - i(15/56)^{1/2}|{}^4T_2, 7\rangle + (15/56)^{1/2}|{}^4T_2, 8\rangle]
 \end{aligned} \tag{2.10}$$

$$\begin{aligned}
 |{}^2E, 3\rangle &= |{}^2E, 3\rangle_0 + [\zeta/\Delta E({}^4T_2-{}^2E)][(5/14)^{1/2}|{}^4T_2, 9\rangle - (5/28)^{1/2}|{}^4T_2, 10\rangle \\
 &\quad + i(15/56)^{1/2}|{}^4T_2, 11\rangle - (15/56)^{1/2}|{}^4T_2, 12\rangle]
 \end{aligned} \tag{2.11}$$

$$\begin{aligned}
 |{}^2E, 4\rangle &= |{}^2E, 4\rangle_0 + [\zeta/\Delta E({}^4T_2-{}^2E)][(5/28)^{1/2}|{}^4T_2, 9\rangle + (5/14)^{1/2}|{}^4T_2, 10\rangle \\
 &\quad + (15/56)^{1/2}|{}^4T_2, 11\rangle + i(15/56)^{1/2}|{}^4T_2, 12\rangle].
 \end{aligned} \tag{2.12}$$

Table 1. Matrix elements of spin-orbit interaction H_{so} between states of 4T_2 and 2E .

	$ ^4T_2, 1\rangle$	$ ^4T_2, 2\rangle$	$ ^4T_2, 3\rangle$	$ ^4T_2, 4\rangle$
$\langle ^2E, 1 $	$-(5/14)^{1/2}$	$-(5/28)^{1/2}$	$-(15/56)^{1/2}$	$-i(15/56)^{1/2}$
	$ ^4T_2, 5\rangle$	$ ^4T_2, 6\rangle$	$ ^4T_2, 7\rangle$	$ ^4T_2, 8\rangle$
$\langle ^2E, 2 $	$-(5/14)^{1/2}$	$(5/28)^{1/2}$	$-i(15/56)^{1/2}$	$(15/56)^{1/2}$
	$ ^4T_2, 9\rangle$	$ ^4T_2, 10\rangle$	$ ^4T_2, 11\rangle$	$ ^4T_2, 12\rangle$
$\langle ^2E, 3 $	$(5/14)^{1/2}$	$-(5/28)^{1/2}$	$i(15/56)^{1/2}$	$-(15/56)^{1/2}$
$\langle ^2E, 4 $	$(5/28)^{1/2}$	$(5/14)^{1/2}$	$(15/56)^{1/2}$	$i(15/56)^{1/2}$

In the calculation of the lifetime of 2E , the electric-dipole (ED) matrix elements between 4T_2 and 4A_2 are involved. Owing to the fact that the garnet crystal belongs to a cubic space group O_h^{10} , macroscopically, the ED transition rates between each sublevel of 4T_2 to related sublevels of 4A_2 should be the same and equal to those in the case in which Cr^{3+} occupies a cubic point group site, so that on average we have

$$\overline{|\langle ^4T_2, i | M_e | ^4A_2 \rangle|^2} = |\langle ^4T_2 | M_e | ^4A_2 \rangle|^2. \quad (2.13)$$

This statement can also be demonstrated mathematically. Here M_e is the effective electric-dipole moment and $|^4T_2, i\rangle$ for $i = 1, 2, 3, \dots, 12$ are crystal-field (CF) eigenfunctions of C_{3i} symmetry, while the wavefunctions $|^4T_2\rangle$ and $|^4A_2\rangle$ are referred to those of O_h symmetry. For the sake of simplicity, the bar symbol of the average will be omitted in the following equations. Because spin variables are not contained in the dipole moment, in the transition process, all the spin variables involved cannot be changed. Any one of the twelve 4T_2 states can only transit to one of the four 4A_2 states. Then equations (2.9) and (2.13) result in the following equation:

$$|\langle ^2E, 1 | M_e | ^4A_2 \rangle|^2 = [\zeta^2 / (\Delta E)^2] \{ [-(5/14)^{1/2} - (5/28)^{1/2} - (15/56)^{1/2}]^2 + (15/56) \} |\langle ^4T_2 | M_e | ^4A_2 \rangle|^2. \quad (2.14)$$

Similarly, we have

$$|\langle ^2E, 2 | M_e | ^4A_2 \rangle|^2 = [\zeta^2 / (\Delta E)^2] \{ [-(5/14)^{1/2} + (5/28)^{1/2} + (15/56)^{1/2}]^2 + (15/56) \} |\langle ^4T_2 | M_e | ^4A_2 \rangle|^2 \quad (2.15)$$

$$|\langle ^2E, 3 | M_e | ^4A_2 \rangle|^2 = [\zeta^2 / (\Delta E)^2] \{ [(5/14)^{1/2} - (5/28)^{1/2} - (15/56)^{1/2}]^2 + (15/56) \} |\langle ^4T_2 | M_e | ^4A_2 \rangle|^2 \quad (2.16)$$

and

$$|\langle ^2E, 4 | M_e | ^4A_2 \rangle|^2 = [\zeta^2 / (\Delta E)^2] \{ [(5/14)^{1/2} + (5/28)^{1/2} + (15/56)^{1/2}]^2 + (15/56) \} |\langle ^4T_2 | M_e | ^4A_2 \rangle|^2. \quad (2.17)$$

$|\langle ^2E, i \rangle$ ($i = 1, 2, 3, 4$) are approximately degenerate and so the total particle number $N(^2E)$ can be seen as equally populated in each of these four states with probabilities of 1/4. Therefore, the average transition rates $\overline{A(^2E \rightarrow ^4A_2)}$ can be estimated by

$$\overline{A(^2E \rightarrow ^4A_2)} = \left(\frac{1}{4}\right) \sum_i A(^2E, i \rightarrow ^4A_2). \quad (2.18)$$

We can, in another way, assume an effective spin-orbit coupling matrix element W' with

$$W'^2 = (\zeta^2/4) \{ 2[(5/14)^{1/2} + (5/28)^{1/2} + (15/56)^{1/2}]^2 + 2[-(5/14)^{1/2} + (5/28)^{1/2} + (15/56)^{1/2}]^2 + 4(15/56) \} = 1.5088\zeta^2$$

and $W' = 1.2283\zeta = 338 \text{ cm}^{-1}$ assuming $\zeta = 275 \text{ cm}^{-1}$ [16].

Concerning the breaking of the spin-forbidden law of electric dipole transition, detailed theoretical analysis shows that the low-symmetry distortion of the crystal field has a strong effect on the spin-orbit coupling, although it has only a weak effect on the further splitting of the energy levels. In the study of luminescence of 2E states, if the active Cr^{3+} ion occupies a position with a symmetry lower than cubic, one cannot use the value of W for the situation of cubic symmetry.

3. Estimation of Huang-Rhys S factor and phonon energy $\hbar\omega$

It has been pointed out in section 1 that S and $\hbar\omega$ should be determined from detailed spectral information. In order to obtain a reasonable estimation of these parameters, two facts should be considered. First, in reality, the electron-phonon coupling is in fact a multi-mode interaction and the usual single-mode model is too simple to describe physical reality. Second, most of the spectral data were obtained at room temperature or 77 K, but almost all the estimations of S and $\hbar\omega$ published are based on a formula for 0 K. We proposed a model that can take into account these two facts [14]. From the measured half-width B of the fluorescence emission spectrum and the Stokes shift E_S determined from the separation between the emission spectral peak and the absorption spectral peak, the ratio r can be calculated

$$r = B^2 / (E_S/2). \quad (3.1)$$

On the other hand, the Stokes shift E_S is

$$E_S = E_a - E_e = 2S\hbar\omega. \quad (3.2)$$

The average phonon energy $\hbar\omega$ can be defined as

$$\overline{\hbar\omega} = \frac{1}{S} \sum_k \left(\frac{\omega_k}{2\hbar} \right) \Delta_{jik}^2 (\hbar\omega_k) \quad (3.3)$$

$$S = \sum_k \left(\frac{\omega_k}{2\hbar} \right) \Delta_{jik}^2. \quad (3.4)$$

For high temperature and under strong coupling condition, we have

$$B = 2.3548 [S(T) (\overline{\hbar\omega})^2]^{1/2} \quad (3.5)$$

where

$$S(T) = \sum_k \Delta_{jik}^2 \left(\frac{\omega_k}{2\hbar} \right) \coth \left(\frac{\beta\hbar\omega_k}{2} \right) \quad (3.6)$$

and

$$(\overline{\hbar\omega})^2 = \frac{1}{S(T)} \sum_k \left[\Delta_{jik}^2 \left(\frac{\omega_k}{2\hbar} \right) \coth \left(\frac{\beta\hbar\omega_k}{2} \right) \right] (\hbar\omega_k)^2. \quad (3.7)$$

Therefore

$$r = 5.545 \sum_k \left[\Delta_{jik}^2 \left(\frac{\omega_k}{2\hbar} \right) \coth \left(\frac{\beta\hbar\omega_k}{2} \right) \right] (\hbar\omega_k)^2 / \sum_k \Delta_{jik}^2 \left(\frac{\omega_k}{2\hbar} \right) (\hbar\omega_k). \quad (3.8)$$

Based on an approximation proposed by Huang Kun [13], we used a model consisting of five multiple-frequency modes. Let their frequencies differ by a fixed multiple factor and let the product $S_k \hbar\omega_k$ (for $k = 1, 2, 3, 4, 5$) be

$$S_k (\hbar\omega_k) = \Delta_{jik}^2 \left(\frac{\omega_k}{2\hbar} \right) (\hbar\omega_k) = \frac{1}{5} \sum_k \Delta_{jik}^2 \left(\frac{\omega_k}{2\hbar} \right) (\hbar\omega_k) \quad (3.9)$$

and $\hbar\omega_k = k\hbar\omega_1$ for $k = 1, 2, 3, 4, 5$. At room temperature $\beta = 1/kT = 0.005 \text{ cm}^{-1}$. Then

$$r = 1.109 \sum_{k=1}^5 [\coth(0.0025k\hbar\omega_1)(k\hbar\omega_1)]. \quad (3.10)$$

Using the values of r obtained by spectral measurements and equation (3.2), it is easy to determine $\hbar\omega_1$ by equation (3.8). Then S_1 can be obtained by

$$S_1 \hbar\omega_1 = \frac{1}{5}(S\hbar\omega) = \frac{1}{10}(E_S) \quad (3.11)$$

and

$$S = S_1(1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \frac{1}{5}) = 2.28S_1 \quad (3.12)$$

$$\overline{\hbar\omega} = (1/S)(E_S/2). \quad (3.13)$$

The S and $\overline{\hbar\omega}$ values obtained by this method are given in table 2 based on the spectral data from [4]. In the following calculations, the average value $\hbar\omega$ will be seen as the phonon energy and the average symbol will be omitted.

We would like to point out, additionally, that there is a mistake in [14]: the caption of table 1 should be exchanged with that of table 2.

Table 2. Calculated results of Huang-Rhys factor and phonon energy of Cr^{3+} -doped tunable laser garnet crystals.

Crystals	YGG	GGG	YSGG	GSGG
S	5.45	5.04	4.40	4.49
$\hbar\omega$ (cm^{-1})	238.7	252.5	317.8	293.9

Table 3. Comparison of the experimental and model calculation of $\tau(^2E)/\tau(^4T_2)$ for GSGG, YSGG, GGG and YGG garnets doped with Cr^{3+} ; $\tau(^4T_2)$ was taken to be $90 \mu\text{s}$, and the experimental values are taken from [9].

Material	ΔE (cm^{-1})	Experimental $\tau(^2E)/\tau(^4T_2)$	Theoretical $\tau(^2E)/\tau(^4T_2)$		
			DHGIM	Modified DHGIM	Frozen lattice
GSGG	50	2.4	3.5	2.6	1.8
YSGG	350	13.7	15.7	15.4	8.7
GGG	380	16.0	16.4	16.2	10.8
YGG	650	26.1	26.5	26.2	21.0

4. Results and discussion

By using the values of W , S and $\hbar\omega$ obtained by the methods described in previous sections, the models proposed by Donnelly *et al* [5] and Wojtowicz *et al* [9] were used to calculate the ratio of lifetimes and the results are given in table 3. It is at once apparent that the agreement between the experimental results and calculated values of the DHGIM model and modified DHGIM model is satisfactory, but that for the frozen lattice model appears very unsatisfactory. As pointed out by Yamaga *et al* [6], the lattice relaxation energy is fairly large compared with the spin-orbit

interaction, and so it is physically reasonable to introduce first the effect of electron-phonon interaction, which can change the electron distribution in each electronic state. The effect of H_{so} can then be dealt with as a perturbation to the electron-phonon system. On the contrary, the frozen lattice model incorrectly introduces first a perturbation that has a smaller effect on the system; besides, it has assumed unreasonably a prerequisite that the equilibrium position of the frozen lattice R_0 is close to $\frac{1}{2}(R_1 + R_2)$. Apparently, the models that have a correct and clear physical meaning will be those which agree well with experimental results. It is noted that, in the calculation presented, all the parameters used were obtained from an independent theoretical method or experimental results without introduction of any adjustable parameter. Therefore, it is safe to say that the judgment formed upon these models is objective and reasonable. Probably, the reason why the results of modified DHGIM are better than those of DHGIM is that $E_q - E_d$ appearing in the denominator of equation (10) in [9] was substituted by the experimental energy separation between 4T_2 and 2E states in the actual calculation, which is in fact the perturbed energy separation. In other words, in equations (6) and (7) in [5], if one refers Δ to the experimental energy separation, then it seems unnecessary to add a term coming from the effect of H_{so} .

In order to obtain a good result, it is also important to have a correct estimation of the S and $\hbar\omega$ parameters. The method based on the statistical multi-mode model proposed by Huang Kun turned out to be good enough.

It is noteworthy that the crystal energy states, either 4T_2 or 2E , are in fact split into levels with a certain separation. As shown in section 2, they usually have different spin-orbit coupling matrix elements. On the other hand, the particle population in the separated levels of 4T_2 or 2E cannot be the same. Therefore, to obtain a better result, especially in the case of small energy separation between 4T_2 and 2E , it is necessary to calculate the mixing between $|{}^4T_2, i\rangle$ and $|{}^2E, j\rangle$ separately and then to estimate the effective lifetime of 2E according to the following formula:

$$1/\tau({}^2E) = \sum_i \exp(-\Delta_i/kT) A({}^2E, i) / \sum_i \exp(-\Delta_i/kT)$$

where Δ_i for $i = 1, 2, 3, 4$ are energy separations from the lowest level of 2E .

When the separation between 4T_2 and 2E is large enough, it is possible to use an effective spin-orbit coupling matrix element to discuss the mixing of these two states behaving like two single states belonging to related irreducible representations of cubic point symmetry. It is demonstrated in our calculation that this approximation is good enough for the situations in Cr^{3+} -doped garnets with low and intermediate crystal field.

In conclusion we would like also to emphasize that, in the study of luminescence and other related phenomena, if necessary, the spin-orbit coupling should be calculated according to the exact site symmetry that the active centre occupies.

Appendix

The irreducible representations of groups considered in this paper are labelled using Butler's notations [11]. The correspondences among the labels of Butler, Bethe and Mulliken are 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	$\bar{0}$	2	1	$\bar{1}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
	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	$\bar{0}$	1	$\frac{1}{2}$	$\frac{3}{2}$	$-\frac{3}{2}$		
	Mulliken	A_g	E_g		E_u		A_u		
C_3	Bethe	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6		
	Butler	0	1	-1	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{3}{2}$		

The $3-jm$ factors for the group chain $O_3 \supset O_h \supset D_{3d} \supset C_{3i}$ used are as follows:

$O_3 \supset O_h$

$$\begin{pmatrix} 4 & 1 & 3 \\ 2 & 1 & \bar{1} \end{pmatrix} = (1/7)^{1/2} \quad \begin{pmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & 1 & \frac{3}{2} \end{pmatrix} = 1$$

$O_h \supset D_{3d}$

$$\begin{pmatrix} 2 & 1 & \bar{1} \\ 1 & 1 & 0 \end{pmatrix} = -(1/3)^{1/2} \quad \begin{pmatrix} 2 & 1 & \bar{1} \\ 1 & \bar{0} & 1 \end{pmatrix} = -(1/3)^{1/2}$$

$$\begin{pmatrix} 2 & 1 & \bar{1} \\ 1 & 1 & 1 \end{pmatrix} = (1/3)^{1/2} \quad \begin{pmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & \bar{0} & \frac{1}{2} \end{pmatrix} = -(1/3)^{1/2}$$

$$\begin{pmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & 1 & \frac{3}{2} \end{pmatrix} = (1/6)^{1/2} \quad \begin{pmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & 1 & \frac{3}{2} \end{pmatrix} = 1/2$$

$$\begin{pmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & 1 & -\frac{3}{2} \end{pmatrix} = 1/2 \quad \begin{pmatrix} \bar{1} & \bar{0} & 1 \\ 0 & \bar{0} & 0 \end{pmatrix} = (1/3)^{1/2} \quad \begin{pmatrix} \bar{1} & \bar{0} & 1 \\ 1 & \bar{0} & 1 \end{pmatrix} = -(2/3)^{1/2}$$

$D_{3d} \supset C_{3i}$

$$\begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \end{pmatrix} = (1/2)^{1/2} \quad \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \end{pmatrix} = (1/2)^{1/2}$$

$$\begin{pmatrix} 1 & \bar{0} & 1 \\ 1 & 0 & -1 \end{pmatrix} = -(1/2)^{1/2} \quad \begin{pmatrix} 1 & \bar{0} & 1 \\ -1 & 0 & 1 \end{pmatrix} = (1/2)^{1/2}$$

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} = (1/2)^{1/2} \quad \begin{pmatrix} 1 & 1 & 1 \\ -1 & -1 & -1 \end{pmatrix} = (1/2)^{1/2}$$

$$\begin{pmatrix} 0 & \bar{0} & \bar{0} \\ 0 & 0 & 0 \end{pmatrix} = -1 \quad \begin{pmatrix} 1 & 0 & 1 \\ -1 & 0 & 1 \end{pmatrix} = (1/2)^{1/2} \quad \begin{pmatrix} 1 & 0 & 1 \\ 1 & 0 & -1 \end{pmatrix} = -(1/2)^{1/2}$$

$$\begin{pmatrix} 1 & 1 & \bar{0} \\ -1 & 1 & 0 \end{pmatrix} = (1/2)^{1/2} \quad \begin{pmatrix} 1 & 1 & \bar{0} \\ 1 & -1 & 0 \end{pmatrix} = (1/2)^{1/2}$$

$$\begin{pmatrix} \frac{1}{2} & \bar{0} & \frac{1}{2} \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} = (1/2)^{1/2} \quad \begin{pmatrix} \frac{1}{2} & \bar{0} & \frac{1}{2} \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} = (1/2)^{1/2}$$

$$\begin{aligned} \begin{pmatrix} \frac{1}{2} & 1 & \frac{1}{2} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix} &= (1/2)^{1/2} & \begin{pmatrix} \frac{1}{2} & 1 & \frac{1}{2} \\ \frac{1}{2} & -1 & \frac{1}{2} \end{pmatrix} &= (1/2)^{1/2} \\ \begin{pmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & 1 & \frac{3}{2} \end{pmatrix} &= -(1/2)^{1/2} & \begin{pmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ -\frac{1}{2} & -1 & \frac{3}{2} \end{pmatrix} &= -i(1/2)^{1/2} \\ \begin{pmatrix} \frac{1}{2} & 1 & -\frac{3}{2} \\ -\frac{1}{2} & -1 & \frac{3}{2} \end{pmatrix} &= -(1/2)^{1/2} & \begin{pmatrix} \frac{1}{2} & 1 & -\frac{3}{2} \\ \frac{1}{2} & 1 & \frac{3}{2} \end{pmatrix} &= i(1/2)^{1/2}. \end{aligned}$$

The 6- j m symbols of C_{3i} , which exist and are equal to unity in our consideration, are:

for $g_2 = 0$

$$\left\{ \begin{matrix} \frac{1}{2} & -1 & -\frac{1}{2} \\ 1 & \frac{1}{2} & 0 \end{matrix} \right\} \quad \left\{ \begin{matrix} \frac{1}{2} & 1 & \frac{3}{2} \\ -1 & \frac{1}{2} & 0 \end{matrix} \right\} \quad \left\{ \begin{matrix} -\frac{1}{2} & 1 & \frac{3}{2} \\ 1 & -\frac{1}{2} & 0 \end{matrix} \right\} \quad \left\{ \begin{matrix} -\frac{1}{2} & 1 & \frac{1}{2} \\ -1 & -\frac{1}{2} & 0 \end{matrix} \right\}$$

for $g_2 = 1$

$$\left\{ \begin{matrix} \frac{1}{2} & 1 & \frac{3}{2} \\ 1 & -\frac{1}{2} & 1 \end{matrix} \right\} \quad \left\{ \begin{matrix} \frac{3}{2} & 1 & -\frac{1}{2} \\ 1 & \frac{1}{2} & 1 \end{matrix} \right\} \quad \left\{ \begin{matrix} \frac{1}{2} & 0 & \frac{1}{2} \\ -1 & -\frac{1}{2} & 1 \end{matrix} \right\} \quad \left\{ \begin{matrix} \frac{3}{2} & 0 & \frac{3}{2} \\ -1 & \frac{1}{2} & 1 \end{matrix} \right\}$$

for $g_2 = -1$

$$\left\{ \begin{matrix} -\frac{1}{2} & -1 & \frac{3}{2} \\ -1 & \frac{1}{2} & -1 \end{matrix} \right\} \quad \left\{ \begin{matrix} \frac{3}{2} & -1 & \frac{1}{2} \\ -1 & -\frac{1}{2} & -1 \end{matrix} \right\} \quad \left\{ \begin{matrix} -\frac{1}{2} & 0 & -\frac{1}{2} \\ 1 & \frac{1}{2} & -1 \end{matrix} \right\} \quad \left\{ \begin{matrix} \frac{3}{2} & 0 & \frac{3}{2} \\ 1 & -\frac{1}{2} & -1 \end{matrix} \right\}.$$

All of the 2- j m phases used are unity except

$$\begin{pmatrix} \frac{1}{2} \\ -\frac{1}{2} \end{pmatrix} D_{3d} C_{3i} = -1 \quad \begin{pmatrix} \bar{0} \\ 0 \end{pmatrix} D_{3d} C_{3i} = -1.$$

The 3- j m symbols of O_h used in this paper are

$$\begin{pmatrix} \bar{1} & 1 & \bar{0} \\ -1 & -1 & a_2 \end{pmatrix} = \begin{pmatrix} \bar{1} & 1 & \bar{0} \\ 0 & 0 & a_2 \end{pmatrix} = \begin{pmatrix} \bar{1} & 1 & \bar{0} \\ 1 & 1 & a_2 \end{pmatrix} = -(1/3)^{1/2}.$$

References

- [1] Henderson B and Imbusch G F 1988 *Contemp. Phys.* **29** 25
- [2] Deshazer L F, Pinto A and Esterowitz L (ed) 1986 *Tunable Solid State Lasers II* (Berlin: Springer)
- [3] Struve B and Huber G 1985 *J. Appl. Phys.* **57** 45
- [4] Struve B and Huber G 1985 *J. Appl. Phys.* **B 36** 195
- [5] Donnelly C J, Healy S M, Glynn T J, Imbusch G F and Morgan G P 1988 *J. Lumin.* **42** 119
- [6] Yamaga M, Henderson B and O'Donnell K P 1989 *J. Phys.: Condens. Matter* **1** 9175
- [7] Yamaga M, Henderson B and O'Donnell K P 1990 *Appl. Phys.* **B 50** 425
- [8] Yamaga M, Henderson B and O'Donnell K P 1990 *Appl. Phys.* **B 51** 132
- [9] Wojtowicz A J, Grinberg M and Lempicki A 1991 *J. Lumin.* **50** 231
- [10] Ruciman W A and Schroeder K A 1962 *Proc. R. Soc.* **265** 489
- [11] Butler P H 1981 *Point Group Symmetry Application, Methods and Tables* (New York: Plenum)
- [12] Piepho S B and Schatz P N 1983 *Group Theory in Spectroscopy with Application to MCD* (New York: Wiley)
- [13] Huang Kun 1984 *J. Lumin.* **31/32** 738
- [14] Luo Zundu and Chen Jiming 1991 *Chin. Phys. (USA)* **11** 399
- [15] Nielson C W and Kester G F 1953 *Spectroscopic Coefficients for the p^n , d^n , and f^n Configurations* (Cambridge, MA: MIT Press)
- [16] Uyling P H M, Raassen A J J and Wyart J F 1984 *J. Phys. B: At. Mol. Phys.* **17** 4130