

## Second-Order Nonradiative Processes in $\text{CaF}_2:\text{Sm}^{2+}$ †

R. ORBACH

*Department of Physics, University of California, Los Angeles, California*

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It was first shown by Axe and Sorokin that nonradiative decay of the terminal optical maser level ( ${}^7F_1$ )  $\text{CaF}_2:\text{Sm}^{2+}$  is forbidden to first order even though many phonon states are available with the proper energy for the transition. At first sight this would indicate the  ${}^7F_1$  level to be metastable. It is shown that a second-order two-phonon emission transition can alleviate this bottleneck, and the decay process rate is computed. This process, involving virtual transitions to a higher level ( ${}^7F_2$ ), is shown to be very effective and to lead to a nonradiative lifetime of  $\sim 10^{-6}$  sec, in accord with the necessary conditions for the existence of optical maser action in  $\text{CaF}_2:\text{Sm}^{2+}$ .

IN the process of investigating nonradiative processes in rare-earth salts, we have come across an interesting effect of a well-known angular momentum selection rule. This is the so-called "triangle rule," which states<sup>1</sup> that the matrix element of an operator spanning a  $2j+1$  dimensional space is finite between states of dimensionality  $2j'+1$  and  $2j''+1$  if and only if  $j'+j'' \geq j \geq |j'-j''|$ . A clear example of the effect of this rule is  $\text{CaF}_2:\text{Sm}^{2+}$ . The energy levels for  $\text{Sm}^{2+}$  in calcium fluoride are now well known.<sup>2</sup> Sorokin and Stevenson<sup>3</sup> first reported observation of optical maser action in this salt, and a detailed analysis of the fluorescence and optical maser action was subsequently carried out by Kaiser *et al.*<sup>4</sup> One can think of the optical maser system in this salt as being of a four-level type. The ground "reservoir" level is the  ${}^7F_0$  ground state of  $\text{Sm}^{2+}$ , and the excited  $f^5d(\Gamma_{1u})$  level and the  $f^6({}^7F_1, \Gamma_{4g})$  level form the two states between which maser transitions occur, the latter being the terminal state. The intriguing aspect of this system is that Kaiser *et al.* show that the  ${}^7F_1$  terminal level never really becomes a bottleneck serious enough to destroy optical maser action. They state that "there is no evidence at the present time for accumulation in any level between the terminal state and the ground state."

At first sight we find this to be a very surprising result. The orbit-lattice interaction for rare-earth ions in a cubal (or octahedral) environment is given by<sup>5,6</sup>

$$V_{\text{OL}} = \sum_{l=2,4,6} \sum_{m=0,\pm} V(\Gamma_{3g}l)C(\Gamma_{3g}l,m)\epsilon(\Gamma_{3g},m) + \sum_{l=2,4,6} \sum_{m=0,\pm 1} V(\Gamma_{5g}l)C(\Gamma_{5g}l,m)\epsilon(\Gamma_{5g},-m)(-1)^m, \quad (1)$$

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<sup>1</sup> A. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), pp. 34, 47.

<sup>2</sup> D. L. Wood and W. Kaiser, *Phys. Rev.* **126**, 2079 (1962); W. A. Runciman and C. V. Stager, *J. Chem. Phys.* **37**, 196 (1962); P. P. Feofilov and A. A. Kapyanski, *Opt. i Spektroskopiya* **12**, 493 (1962) [translation: *Opt. Spectry. (USSR)* **12**, 272 (1962)].

<sup>3</sup> P. P. Sorokin and M. J. Stevenson, *IBM J. Res. Develop.* **5**, 56 (1961).

<sup>4</sup> W. Kaiser, C. G. B. Garrett, and D. L. Wood, *Phys. Rev.* **123**, 766 (1961); see also P. P. Sorokin, M. J. Stevenson, J. R. Lankard,

where  $C(\Gamma_{ig}l,m)$  and  $\epsilon(\Gamma_{ig},m)$  are linear combinations of Racah's  $C_{lm} = \sum_i [4\pi/(2l+1)]^{1/2} Y_l^m(i)$  and the strain tensor, respectively. They transform as the  $m$ th subvector of the  $\Gamma_{ig}$  irreducible representation of the cubic group. For  $l=2$ ,

$$C(\Gamma_{3g}2,\theta) = C_{20};$$

$$C(\Gamma_{3g}2,e) = (C_{22} + C_{2-2})/\sqrt{2};$$

$$C(\Gamma_{5g}2,1) = C_{2-1};$$

$$C(\Gamma_{5g}2,0) = (C_{22} - C_{2-2})/\sqrt{2};$$

$$C(\Gamma_{5g}2,-1) = -C_{21};$$

and

$$\epsilon(\Gamma_{3g},\theta) = \frac{1}{2}(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy});$$

$$\epsilon(\Gamma_{3g},e) = \frac{1}{2}\sqrt{3}(\epsilon_{xx} - \epsilon_{yy});$$

$$\epsilon(\Gamma_{5g},1) = -i(3/2)^{1/2}(\epsilon_{yz} + i\epsilon_{zx});$$

$$\epsilon(\Gamma_{5g},0) = i\sqrt{3}\epsilon_{xy};$$

$$\epsilon(\Gamma_{5g},-1) = i(3/2)^{1/2}(\epsilon_{yz} - i\epsilon_{zx}).$$

We see immediately that the matrix element for direct nonradiative transitions<sup>7</sup> from the terminal to the ground state,  $\langle J=0 | V_{\text{OL}} | J=1 \rangle$ , necessarily vanishes because of the triangle rule. This occurs even in the presence of intermediate coupling, because the spin-orbit interaction commutes with  $J$ . The existence of lattice vibrations in the vicinity of the energy difference between the  $J=1$  and the  $J=0$  levels is thus irrelevant. They cannot effect transitions directly between the two levels. Nevertheless, the experiments of Kaiser *et al.* do show that the  $J=1$  level, far from being metastable, in fact has a nonradiative lifetime less than  $10^{-6}$  sec.

This apparent paradox is easily removed by examining higher order nonradiative processes. Usually at low

and G. D. Petit, *Phys. Rev.* **127**, 503 (1962), for a study of  $\text{SrF}_2:\text{Sm}^{2+}$ .

<sup>5</sup> We are explicitly assuming the ion to be in a site with a center of inversion, and hence are neglecting terms odd in  $l$  which vanish within the  $f^n$  configuration.

<sup>6</sup> M. Blume and R. Orbach, *Phys. Rev.* **127**, 1587 (1962).

<sup>7</sup> J. D. Axe and P. P. Sorokin, *Phys. Rev.* **130**, 945 (1963) have also noted this point. They show group theoretically [see after Eq. (5)] that the direct relaxation matrix element in a cubic site vanishes, and they point to the results of pulsed maser operation experiments to substantiate their conclusion. Our approach is slightly different, and does go on to discuss the higher order process which allows optical maser action to proceed.

temperatures such processes are unimportant relative to first-order transitions. It is clear that when, for energy reasons or because of vanishing matrix elements, direct transitions are inoperative, higher order terms of this sort must be considered. In this specific case we find them to be surprisingly effective.

We limit ourselves to  $l=2$  terms in (1) for convenience. Our lack of knowledge concerning the  $V(\Gamma_{ig}l)$  makes this expedient though there do exist certain cases where the  $l=2$  static crystalline field terms dominate over the  $l=4$  and the  $l=6$  terms.<sup>8</sup> In the present case, this approximation gives us at least an order of magnitude result for the nonradiative relaxation time between the  $J=1$  and  $J=0$  multiplets.

Because of the triangle rule, the sum over  $i$  in the second-order effective Hamiltonian,

$$\mathcal{H}_{\text{eff}} = \sum_i \frac{\langle J=0 | V_{\text{OL}} | i \rangle \langle i | V_{\text{OL}} | J=1 \rangle}{E_1 - E_i}, \quad (2)$$

(where the energy denominators include the phonon energies) is restricted to the  $J=2$  multiplet alone. Designating the energy splitting between the  $J=2$  and  $J=1$  levels<sup>2</sup> by  $2\Delta = 526 \text{ cm}^{-1}$ , the only important term in (2) at low temperatures is

$$\begin{aligned} \mathcal{H}_{\text{eff}} = & \sum_{m', m'', i', i''} V(\Gamma_{i'g}2) V(\Gamma_{i''g}2) \\ & \times \langle J=0 | C(\Gamma_{i'g}2, m') \epsilon(\Gamma_{i'g}, m') | J=2, M_J = m'' \rangle \\ & \times \langle J=2, M_J = m'' | C(\Gamma_{i''g}2, m''') \\ & \times \epsilon(\Gamma_{i''g}, m''') | J=1, M_J = m \rangle \\ & \times [-2\Delta - \hbar\omega_{i', m''}]^{-1}, \quad (3) \end{aligned}$$

corresponding to the emission of both phonons. The subscripts  $i, m$  on the angular frequencies label the frequency of the phonon created by  $\epsilon(\Gamma_{ig}, m)$ . When we square (3) and integrate over phonon coordinates to get the over-all transition rate we get cross terms which vanish unless the  $i$  and  $m$  indices are equal in pairs. The matrix elements in (3) are evaluated using standard expressions.<sup>9</sup> We find the nonradiative transition probability per unit time  $W_{\text{NR}}$  to be the same for the  $|J=1, M_J = \pm 1\rangle$  and the  $|J=1, M_J = 0\rangle$  levels. We assume a Debye<sup>10</sup> spectrum for the lattice and find

$$\begin{aligned} W_{\text{NR}} = & V^2(\Gamma_{5g}2) [V^2(\Gamma_{3g}2) + V^2(\Gamma_{5g}2)] (2\pi^3 5^6 \rho^2)^{-1} \\ & \times \left( \frac{2}{3v_i^5} + \frac{1}{v_i^5} \right)^2 \int_0^{\omega_D} d\omega_1 \int_0^{\omega_D} d\omega_2 \\ & \times \left[ \frac{1}{2\Delta + \hbar\omega_1} - \frac{1}{2\Delta + \hbar\omega_2} \right]^2 \omega_1^3 \omega_2^3 \\ & \times \{ [1 - \exp(-\hbar\omega_1/kT)] [1 - \exp(-\hbar\omega_2/kT)] \}^{-1} \\ & \times \delta[(\Delta/\hbar) - \omega_1 - \omega_2]. \quad (4) \end{aligned}$$

<sup>8</sup> In addition, for this case, the triangle rule also reduces the effectiveness of the  $l=4, 6$  terms. One must go to multiplets of  $J=4, 6$  respectively, in the intermediate state, for a nonvanishing contribution from these terms. This results in energy denominators

It is clear that the product of  $V^2(\Gamma_{5g}2)$  with a linear combination of  $V^2(\Gamma_{3g}2)$  and  $V^2(\Gamma_{5g}2)$  must occur in (4). This follows from a consideration of the cubic field representation for the  $J=0$  and  $J=1$  levels. We wish the matrix element of the vibration operators which transform as  $\Gamma_{3g}$  and  $\Gamma_{5g}$  between states  $J=0$  and  $J=1$  which, in a cubic field, transform as  $\Gamma_1$  and  $\Gamma_4$ , respectively. Using the well-known relations,

$$\begin{aligned} \Gamma_3 \times \Gamma_3 &= \Gamma_1 + \Gamma_2 + \Gamma_3; \\ \Gamma_3 \times \Gamma_5 &= \Gamma_4 + \Gamma_5; \\ \Gamma_5 \times \Gamma_5 &= \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5; \end{aligned} \quad (5)$$

we see that only the last two cross products contain  $\Gamma_4$ . Transitions are to occur between  $\Gamma_4$  and  $\Gamma_1$ . By virtue of (5), only  $\Gamma_3 \times \Gamma_5$  and  $\Gamma_5 \times \Gamma_5$  products can accomplish this. The direct process from the  $J=1$  to the  $J=0$  multiplet is forbidden group theoretically because  $\Gamma_4 \times (\Gamma_3 + \Gamma_5) \times \Gamma_1$  does not contain the identity representation.<sup>7</sup> Other materials with a low-lying  $\Gamma_4$  excited level and a singlet  $\Gamma_1$  ground state (e.g.,  $\text{U}^{4+}$  in a cubic environment) may thus suffer the same selection rule as  $\text{Sm}^{2+}$  does in  $\text{CaF}_2$ . This rule ought to be lifted slightly in a tetrahedral environment<sup>11</sup> because of the lack of inversion symmetry. States of different parity can be admixed into the atomic wave functions allowing the odd component (in particular the  $l=1$  term) of the orbit-lattice potential to relax the excited  ${}^7F_1$  level.

It is to be noted that a cancellation does occur in (4) if the two emitted phonons were of equal energy. This is an interesting and unexpected feature of this problem which has its roots in the well-known Van Vleck cancellation,<sup>12</sup> because of the transformation properties of the  $C_{lm}$  between different  $J$  states. Using the delta function in (4) to eliminate  $\omega_2$  as a variable, we find the result

$$\begin{aligned} W_{\text{NR}} = & V^2(\Gamma_{5g}2) [V^2(\Gamma_{3g}2) + V^2(\Gamma_{5g}2)] \\ & \times [2^3 \times 3^2 \times 5^6 \times \pi^3 \rho^2 \Delta^4]^{-1} \left( \frac{2}{3v_i^5} + \frac{1}{v_i^5} \right)^2 \\ & \times \int_{0, \Delta/\hbar - \omega_D}^{\Delta/\hbar, \omega_D} \frac{(\Delta - 2\hbar\omega)^2 [(\Delta/\hbar) - \omega]^3 \omega^3 \exp(\Delta/2kT) d\omega}{4 \sinh(\hbar\omega/2kT) \sinh[(\Delta - \hbar\omega)/2kT]}, \quad (6) \end{aligned}$$

where the limits on the integral are from  $0 \rightarrow \Delta/\hbar$  if  $\Delta < \hbar\omega_D$ , and from  $(\Delta/\hbar) - \omega_D \rightarrow \omega_D$  if  $\Delta > \hbar\omega_D$ .

of  $9\Delta$  and  $20\Delta$ , for the  $l=4$  and  $6$  terms, respectively, which are to be compared with  $2\Delta$  for the  $l=2$  term.

<sup>9</sup> J. P. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) A251, 134 (1959); S. R. Polo (to be published).

<sup>10</sup> This is probably the weakest part of our treatment. We shall eventually make use of phonons whose energy is considerably higher than those which may reasonably be expected to behave in the Debye manner. It is for this reason that our treatment must be regarded as only indicating an order of magnitude for the nonradiative relaxation rate.

<sup>11</sup> The vibrations for a tetrahedral cluster transform as  $\Gamma_1 + \Gamma_3 + 3\Gamma_4 + \Gamma_5$  of the group  $T_d$ .

<sup>12</sup> J. H. Van Vleck, Phys. Rev. 57, 426 (1940).

On the assumption that  $\hbar\omega_D$  (the Debye energy)  $\leq \Delta$ , we can simplify the integral in (7) to

$$\left(\frac{\Delta}{\hbar}\right)^3 \int_{\Delta/\hbar-\omega_D}^{\omega_D} \frac{(\Delta-2\hbar\omega)^2\omega^3 d\omega}{[1-\exp(-\hbar\omega/kT)]}, \quad (7)$$

which, at temperatures much less than  $T_D = \hbar\omega_D/k$ , becomes

$$\frac{2}{3} \frac{\Delta^5}{\hbar^7} \left( \Delta - \frac{2}{5} \hbar\omega_D \right) (4\hbar^3\omega_D^3 - 6\hbar^2\omega_D^2\Delta + 4\hbar\omega_D\Delta^2 - \Delta^3). \quad (8)$$

The lack of dependence of (8) upon temperature is a direct consequence of our assumption of two-phonon emission. Any process involving the absorption of phonons would necessarily result in a temperature-dependent contribution which would vanish in the limit  $T \rightarrow 0$ .

We must now estimate a value for the orbit-lattice coefficients  $V(\Gamma_{3g2})$  and  $V(\Gamma_{5g2})$ . To do this we make use of a "rule" which has worked surprisingly well for similar quantities in other rare-earth salts.<sup>13</sup> We note that in the rare-earth trichloride, the splitting of the  $\text{Eu}^{3+}$ ,  $J=1$  multiplet by the axial field amounts to  $50 \text{ cm}^{-1}$ .<sup>14</sup> We compute this splitting for unity strain using (1) and find that a value of  $V(\Gamma_{3g2}) \sim 500 \text{ cm}^{-1}$  would produce this splitting. We then return to our case of  $\text{CaF}_2:\text{Sm}^{2+}$  and set  $V(\Gamma_{3g2}) \sim V(\Gamma_{5g2}) \sim 500 \text{ cm}^{-1}$ . Judging from relative crystal field values for di- and trivalent ions, such an estimate is on the conservative side. Using this value for the  $V(\Gamma_{ig2})$ , letting  $\Delta = 263 \text{ cm}^{-1}$ ,  $\rho = 3.18 \text{ g/cc}$ ,  $v_i = 5 \times 10^5 \text{ cm/sec}$ ,  $v_i = (1/\sqrt{3})v_i$ , and  $\hbar\omega_D \sim 250 \text{ cm}^{-1}$ , we find

$$W_{\text{NR}} = 4.4 \times 10^5 \text{ sec}^{-1}, \quad (10)$$

or a nonradiative time of  $\sim 2 \times 10^{-6} \text{ sec}$  for the

$\text{CaF}_2:\text{Sm}^{2+}$ ,  ${}^7F_1$  level. This value is perilously close to the  $\Gamma_{1u} \rightarrow {}^7F_1$  fluorescence decay time of  $2 \times 10^{-6}$  found by Kaiser *et al.*,<sup>4</sup> and indicates that saturation of optical maser action in  $\text{CaF}_2:\text{Sm}^{2+}$  may occur at relatively weak operating levels. This is indeed found to be the case.<sup>7</sup> In view of this bottleneck, it has been observed<sup>15</sup> that in  $\text{SrF}_2:\text{Sm}^{2+}$ , where the position of the  $d$  band is such that the  ${}^5D_0 \rightarrow {}^7F_2$  fluorescent lifetime is of the order of ten milliseconds,<sup>2</sup> the saturation effect should be absent even at high pump levels. It would be of some interest to check this prediction.

It should now be clear that higher order processes of the type described above may lead to efficient non-radiative transitions whenever direct transitions are forbidden for energy conservation reasons, as well as in cases for which the direct matrix element itself turns out to vanish. The multiphonon emission relaxation process is hardly a new idea, but in this specific case, we have been able to formulate it in a rather quantitative manner. We find such processes to be remarkably effective, and it is hoped that future experiments will accurately estimate the  $V(\Gamma_{igl})$  for the various rare-earth salts. A knowledge of these quantities will then enable one to make quite quantitative predictions for many cases of nonradiative transitions in solids.

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<sup>13</sup> R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961); P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).

<sup>14</sup> L. G. De Shazer and G. H. Dieke, J. Chem. Phys. **38**, 2190 (1963).

<sup>15</sup> Z. J. Kiss (private communication).

<sup>16</sup> G. Breit and E. Teller, Astrophys. J. **91**, 215 (1940); J. A. Wheeler, J. Opt. Soc. Am. **37**, 813 (1947).