PHYSICAL REVIEW VOLUME 170, NUMBER 2 10 JUNE 1968

Symmetry Selection Rules of Electric-Dipole Transitions of Eu^{3+} and Sm^{2+} in Crystals: A Solid-State Infrared Quantum Counter-Amplifier[*]

FRANCIS K. FONG,[†] LAWRENCE A. VREDEVOE, AND ROGER E. DE WAMES
Science Center/Aerospace and Systems Group, North American Rockwell Corporation, Thousand Oaks, California

(Received 12 February 1968)

A practical scheme for a 10-μ infrared quantum counter-amplifier is proposed, where the infrared frequency is converted into an easily detectable optical frequency. Detailed analysis of the electric-dipole transitions within the $4f^6$ ground configuration of Eu^{3+} and Sm^{2+} ions in various symmetries reveals that these ions have selection rules in C_{3h}, D_{3h}, and D_3 symmetries which allow for significant amplification. This scheme could provide a means of detecting the 10-μ photons generated by the CO_2 laser.

I. INTRODUCTION

THE direct detection of infrared photons is much more difficult than that of optical photons. Therefore, a practical scheme for an infrared (ir) counter would involve a mechanism for converting the ir photons into optical photons, which could then be readily measured. If, in the process of frequency conversion, the scheme also provides amplification of the optical output over the ir input, one would have a quantum counter-amplifier. Bloembergen[1] proposed a theoretical model for such a counter-amplifier as an alternative to maser-type amplification, with the specific advantage that the proposed model would eliminate the troublesome spontaneous-emission noise characteristic to maser operation. It is the purpose of this paper to examine the amplification that one could obtain from a generalization of such a scheme, and to show how the selection rules peculiar to Eu^{3+} and Sm^{2+} in C_{3h}, D_{3h}, and D_3 symmetries will make these ion-symmetry combinations the best candidates for the detection of 10-μ photons, with Eu^{3+} being the better of the two because of energy considerations. Although the detection of 10-μ photons is of primary interest since this is the energy of the CO_2 laser emission, this system can also be used to detect 25- and 5-μ infrared photons. The electric-dipole transitions of Eu^{3+} and Sm^{2+} in various symmetries will be discussed in some detail.

II. AMPLIFICATION SCHEME AND RATE EQUATIONS

We will consider a five-level scheme (Fig. 1), which, as will be shown later, describes the electric-dipole coupled levels within the $4f^6$ configuration of Eu^{3+} and Sm^{2+} in C_{3h}, D_{3h}, and D_3 symmetries. The five states are denoted by $|1\rangle$, $|2\rangle$, $|3\rangle$, $|4\rangle$, and $|5\rangle$, and their spectroscopic notation for the case of Eu^{3+} is also given in Fig. 1. The spontaneous-emission rates between the levels are denoted by σ_{ij}'s, while the stimulated transitions (pumping rates) are denoted by R_{ij}'s. Incoming ir photons excite electrons from the ground state $|1\rangle$ to state $|2\rangle$. A strong optical pumping R_{23} (e.g., a laser) between states $|2\rangle$ and $|3\rangle$ will excite these electrons to the excited state $|3\rangle$ with greater probability than for the spontaneous relaxation back to the ground state. From the excited state $|3\rangle$ the electrons can relax to states $|1\rangle$, $|2\rangle$, $|4\rangle$, or $|5\rangle$ via optical emission processes. Those electrons that relax to states $|2\rangle$, $|4\rangle$, or $|5\rangle$ have high probabilities of being re-excited to $|3\rangle$ by the optical pumping R_{23}, R_{43}, and R_{53}, and therefore could "recycle" many times, emitting optical photons to a photomultiplier during each cycle. This, then, is the source of the amplification that can be achieved by such a scheme.

The main leakage from the amplification cycle is the spontaneous rate σ_{31}. This leakage cannot be suppressed by optical pumping, as was done in the case of states $|2\rangle$, $|4\rangle$, and $|5\rangle$, since pumping on the ground state would add extraneously excited electrons to the excited states. One would expect, therefore, that the greatest amplification would be achieved for a system where the ion-symmetry properties would forbid the electric-dipole transitions $|3\rangle \rightarrow |1\rangle$. This fact, and many less obvious features of the scheme, is obtained from the solutions of the rate equations. For this five-level scheme, the rate equations are

$$\dot{N}_1 = -(N_1-N_2)R_{12}+N_2\sigma_{21}+N_3\sigma_{31}+N_4\sigma_{41}+N_5\sigma_{51}, \quad (1)$$

$$\dot{N}_2 = (N_1-N_2)R_{12}-(N_2-N_3)R_{23}-N_2\sigma_{21}+N_3\sigma_{32} + N_4\sigma_{42}+N_5\sigma_{52}, \quad (2)$$

$$\dot{N}_3 = (N_2-N_3)R_{23}-N_3(\sigma_{31}+\sigma_{32}+\sigma_{34}+\sigma_{35}) - (N_3-N_4)R_{43}-(N_3-N_5)R_{53}, \quad (3)$$

$$\dot{N}_4 = N_3\sigma_{34}-N_4(\sigma_{41}+\sigma_{42})+N_5\sigma_{54}+(N_3-N_4)R_{43}, \quad (4)$$

$$\dot{N}_5 = N_3\sigma_{35}-N_5(\sigma_{54}+\sigma_{52}+\sigma_{51})+(N_3-N_5)R_{53}. \quad (5)$$

We will assume that the incoming ir signal is of sufficient duration so that the steady-state solutions of (1)-(5) prevail. The solution, then, for the emission/

---

[*] A preliminary version of this work was given in a meeting of the Materials Advisory Board, National Academy of Science, December, 1967.

[†] Present address: Department of Chemistry, Purdue University, Lafayette, Ind. 47907.

[1] N. Bloembergen, Phys. Rev. Letters 2, 84 (1959).

absorption ratio is

$$\frac{N_3(\sigma_{32}+\sigma_{34}+\sigma_{35})}{N_1R_{12}}=\Bigg[\frac{R_{12}+\sigma_{12}}{R_{23}}\left(1+\frac{R_{23}+R_{43}+R_{53}+\sigma_{31}}{\sigma_{32}+\sigma_{34}+\sigma_{35}}\right)-\frac{R_{12}+\sigma_{12}}{R_{23}(\sigma_{32}+\sigma_{34}+\sigma_{35})}\left(\frac{R_{43}(R_{43}+\sigma_{34})}{R_{43}+\sigma_{41}+\sigma_{42}}+\frac{R_{53}(R_{53}+\sigma_{35})}{R_{53}+\sigma_{54}+\sigma_{52}+\sigma_{51}}\right)$$

$$+\frac{1}{\sigma_{32}+\sigma_{34}+\sigma_{35}}\Bigg(\sigma_{31}+\frac{\sigma_{41}(R_{43}+\sigma_{34})}{R_{43}+\sigma_{41}+\sigma_{42}}+\frac{\sigma_{41}\sigma_{54}(R_{53}+\sigma_{35})}{(R_{53}+\sigma_{54}+\sigma_{52}+\sigma_{51})(R_{43}+\sigma_{41}+\sigma_{42})}+\frac{\sigma_{51}(R_{53}+\sigma_{35})}{R_{53}+\sigma_{54}+\sigma_{52}+\sigma_{51}}$$

$$-\frac{R_{43}\sigma_{54}(R_{53}+\sigma_{35})(R_{12}+\sigma_{12})}{R_{23}(R_{53}+\sigma_{54}+\sigma_{52}+\sigma_{51})(R_{43}+\sigma_{41}+\sigma_{42})}\Bigg)\Bigg]^{-1}. \tag{6}$$

In order for any amplification to occur, the bracket on the rightside of Eq. (6) must be <1. Since the transitions $|3\rangle \rightarrow |1\rangle$ cross the largest energy gap, one would expect, for all cases where the selection rules allow this electric-dipole relaxation to occur, that the ratio $\sigma_{31}/(\sigma_{32}+\sigma_{34}+\sigma_{35})$ will not be small, thus preventing any significant amplification. If, however, σ_{31} vanishes, then significant amplification can occur. For this case, the largest amplification occurs for weak ir signals and strong optical-pumping rates, R_{23}, R_{43}, $R_{53} \gg \sigma_{ij} \gg R_{12}$, whereupon Eq. (6) simplifies to

$$\frac{N_3(\sigma_{32}+\sigma_{34}+\sigma_{35})}{N_1R_{12}}=\frac{\sigma_{32}+\sigma_{34}+\sigma_{35}}{\sigma_{12}+\sigma_{41}+\sigma_{51}}. \tag{7}$$

The spontaneous radiative emission rates are proportional to the cube of the transition frequency.[2] Substituting the values[3] for Eu^{3+} (see Fig. 1) in Eq. (7), we find

$$N_3(\sigma_{32}+\sigma_{34}+\sigma_{35})/N_1R_{12} \cong 100. \tag{8}$$

III. ELECTRIC-DIPOLE COUPLING BETWEEN ENERGY LEVELS OF Eu^{3+} AND Sm^{2+} IONS IN CRYSTALS

The energy-level schemes in crystalline lattices (Fig. 2) of the isoelectronic ions Eu^{3+} and Sm^{2+}, both with the ground configuration $4f^6$ and the first excited configuration $4f^5\,5d$, are similar in many details.[4] The ground multiplet ${}^7F$ in $4f^6$ has seven spin-orbit levels $J=0, 1, 2, \cdots, 6$. The first excited multiplet ${}^5D$ lies approximately 10^4 cm^{-1} above ${}^7F$. In Eu^{3+}, the lower edge of the $4f^5\,5d$ configuration lies $\sim 5\times10^4$ cm^{-1} above the ground J level ${}^7F_0$, thus making it possible to resolve all of the five spin-orbit levels of the ${}^5D$ multiplet. In Sm^{2+}, the ${}^5D_J$ levels with $J\geq 1$ are sometimes hidden in the broad $4f^5\,5d$ bands, which lie lower than those in Eu^{3+}. This is a result of the lower effective nuclear charge in Sm^{2+}. In the present scheme for a solid-state ir quantum counter-amplifier, we shall utilize electric-dipole transitions within the $4f^6$ ground configuration. Specifically, we shall be concerned with electric-dipole couplings between the ${}^5D_0$ and the ${}^7F_J$ levels.

The oscillator strength f of an electric-dipole transition between states $\langle f^6\alpha_1S_1L_1J_1M_1|$ and $|f^6\alpha_2S_2L_2J_2M_2\rangle$ is given by

$$f(\alpha_1S_1L_1J_1M_1,\ \alpha_2S_2L_2J_2M_2)$$
$$=4\pi mc\omega\hbar^{-1}e^{-2}\,|\langle f^6\alpha_1S_1L_1J_1M_1|\,D_q^{(1)}\,|f^6\alpha_2S_2L_2J_2M_2\rangle|^2, \tag{9}$$

where α denotes all the quantum numbers not specified explicitly, ω is the wave number of the transition, m is the mass of the electron, and the other symbols have their usual significance. The matrix element

$$\langle f^6\alpha_1S_1L_1J_1M_1|\,D_q^{(1)}\,|f^6\alpha_2S_2L_2J_2M_2\rangle$$

is the transition-dipole moment

$$\mu(\alpha_1S_1L_1J_1M_1,\ \alpha_2S_2L_2J_2M_2),$$

with the electric-dipole operator written in the tensor notation $D_q^{(1)}$. This transition-dipole moment of the two states becomes nonvanishing when an electric-

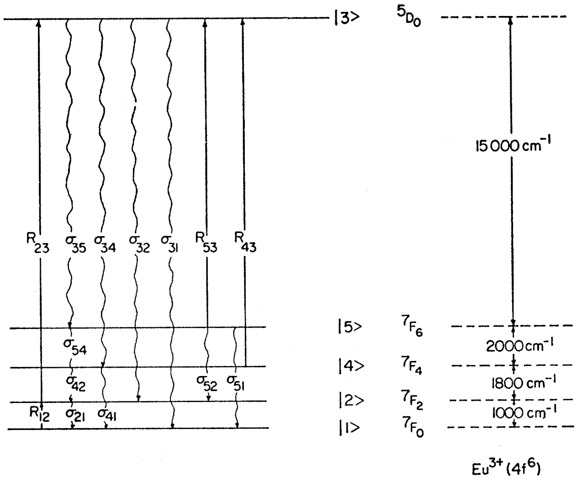

FIG. 1. The five-level scheme. The approximate energy gaps for Eu^{3+} are taken from Dieke, Crosswhite, and Dunn (Ref. 3).

---

[2] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), p. 261.

[3] G. H. Dieke, H. M. Crosswhite, and B. Dunn, J. Opt. Soc. Am. **51**, 820 (1961).

[4] G. H. Dieke and R. Sarup, J. Chem. Phys. **36**, 371 (1962).

dipole transition between them is allowed. This is the case when opposite parity states of the $4f^5\,5d$ configuration are admixed into the states of the $4f^6$ configuration through the presence of odd-parity potential terms in the crystal field. We shall treat this strong crystal-field mixing as a perturbation on the free-ion states, as has been done by previous authors, but will shortly point out the difficulties which one encounters when trying to draw conclusions from such an approach. An arbitrary crystal-field potential may be expressed in terms of spherical harmonics $Y_{km}(\theta_i,\phi_i)$ in the form

$$V_c=\sum_{i,k,m} a_{km}Y_{km}(\theta_i,\phi_i), \tag{10}$$

where the allowed values of l and m are obtained for a given point-group symmetry by requiring that V_c transforms according to the identity representation A_1 of the group. Crystal-field potentials of all the point-group symmetries with odd-parity terms are listed in Table I.[5]

If $S_1\neq S_2$, as is the case here for transitions between the ^5D and ^7F multiplets, it is necessary to invoke a first-order spin-orbit interaction term so as to allow for the selection rule $\Delta S=0$. If the admixing of opposite-parity states occurs through the presence of the $V_{\mathrm{odd}}{}^{(k)}$ terms, then we arrive at a third-order term of the type

$$\begin{aligned}\sum_{\Gamma,L,M,\Gamma',J',M'} &(f^6\,{}^5D_{J_1=0,M_1=0}\mid V_{\mathrm{odd}}{}^{(k)}\mid f^5d\,{}^5\Gamma_{J,M})(f^5d\,{}^5\Gamma_{J,M}\mid \sum_i(\mathbf{s}\cdot\mathbf{l})_i\mid f^5d\,{}^7\Gamma'_{J',M'})\\ &\times(f^5d\,{}^7\Gamma'_{J',M'}\mid D_q{}^{(1)}\mid f^6\,{}^7F_{J_2,M_2})[E(f^6\,{}^5D_{J_1=0,M_1=0})-E(f^5d\,{}^5\Gamma_{J,M})]^{-1}[E(f^6\,{}^5D_{J_1=0,M_1=0})-E(f^5d\,{}^7\Gamma'_{J',M'})]^{-1}\end{aligned} \tag{11}$$

in the transition-dipole moment. If the opposite-parity admixing is achieved via even as well as odd crystal-field terms, the result may be exemplified by a fourth-order term such as

$$\begin{aligned}\sum_{J,'M',\Gamma,J,M,\Gamma',J'',M''} &(f^6\,{}^5D_{J_1=0,M_1=0}\mid V_{\mathrm{even}}{}^{(k)}\mid f^6\,{}^5D_{J',M'})(f^6\,{}^5D_{J',M'}\mid V_{\mathrm{odd}}{}^{(k)}\mid f^5d\,{}^5\Gamma_{J,M})\\ &\times(f^5d\,{}^5\Gamma_{J,M}\mid \sum_i(\mathbf{s}\cdot\mathbf{l})_i\mid f^5d\,{}^7\Gamma'_{J'',M''})(f^5d\,{}^7\Gamma'_{J'',M''}\mid D_q{}^{(1)}\mid f^6\,{}^7F_{J_2,M_2})[E(f^6\,{}^5D_{J_1=0,M_1=0})-E(f^6\,{}^5D_{J',M'})]^{-1}\\ &\times[E(f^6\,{}^5D_{J_1=0,M_1=0})-E(f^5d\,{}^5\Gamma_{J,M})]^{-1}[E(f^6\,{}^5D_{J_1=0,M_1=0})-E(f^5d\,{}^7\Gamma'_{J'',M''})]^{-1},\end{aligned} \tag{12}$$

which will contribute to the transition-dipole moment. The $\langle\mid$ and $\mid\rangle$ in Eq. (9) denote symmetrized crystal states, while the $(\mid$ and $\mid)$ in (11) and (12) denote free-ion states.

When considering nth-order transition-dipole moments, there are $n!$ different permutations of the n operators. In the cases of third- and fourth-order transitions, there are, respectively, six and 24 terms, each containing sums over intermediate states. Because of the energy denominators that appear in the perturbation expansions, however, the largest terms will be those in which the photon is emitted in the last step, since then all the energy differences from the ground state to the intermediate excited states of the system will not be increased in magnitude by the photon energy. By similar reasoning, the smallest terms are those with the photon emitted in the first step. To exemplify this fact, we write a typical term of each type for the transition $^5D_0\rightarrow{}^7F_0$:

$$\begin{aligned}&({}^5D_0\mid V_{\mathrm{odd}}{}^{(k)}\mid {}^5\Gamma_J)({}^5\Gamma_J\mid V_{\mathrm{even}}{}^{(k)}\mid {}^5\Gamma'_{J'})({}^5\Gamma'_{J'}\mid \sum_i(\mathbf{s}\cdot\mathbf{l})_i\mid {}^7\Gamma''_{J''})({}^7\Gamma''_{J''}\mid D_q{}^{(1)}\mid {}^7F_0)\\ &\qquad\times[E({}^5D_0)-E({}^5\Gamma_J)]^{-1}[E({}^5D_0)-E({}^5\Gamma'_{J'})]^{-1}[E({}^5D_0)-E({}^7\Gamma''_{J''})]^{-1},\end{aligned}$$

and

$$\begin{aligned}&({}^5D_0\mid D_q{}^{(1)}\mid {}^5\Gamma_J)({}^5\Gamma_J\mid V_{\mathrm{even}}{}^{(k)}\mid {}^5\Gamma'_{J'})({}^5\Gamma'_{J'}\mid \sum_i(\mathbf{s}\cdot\mathbf{l})_i\mid {}^7\Gamma''_{J''})({}^7\Gamma''_{J''}\mid V_{\mathrm{odd}}{}^{(k)}\mid {}^7F_0)\\ &\qquad\times[E({}^5D_0)-E({}^5\Gamma_J)-\hbar\omega]^{-1}[E({}^5D_0)-E({}^5\Gamma'_{J'})-\hbar\omega]^{-1}[E({}^5D_0)-E({}^7\Gamma''_{J''})-\hbar\omega]^{-1}.\end{aligned} \tag{13}$$

Since $E(\Gamma)>E({}^5D_0)$ and $\hbar\omega=E({}^5D_0)-E({}^7F_0)$, we see that the denominators in the second term have a much larger magnitude than those in the first. The same conclusion, of course, applies to the third-order processes, and the two dominant third-order terms are given by (11) and a similar term in which the order of the crystal-field and spin-orbit operators are permuted.

The crystal-field splittings within the $4f^n$ configurations are typically of the order of 10–100 cm^{-1}, while those within the $4f^{n-1}\,5d$ configurations are of the order of 10^4 cm^{-1}. Therefore, the matrix element of $V_{\mathrm{even}}{}^{(k)}$ between the excited $4f^{n-1}\,5d$ states will be two to three orders of magnitude greater than that between the $4f^n$ ground states. There are six terms in which the $D_q{}^{(1)}$ operator appears in the last transition. Of these, only three terms exist in which the $V_{\mathrm{even}}{}^{(k)}$ operator occurs in the second or third (intermediate) transitions within the excited $4f^{n-1}\,5d$ configuration. These will be the three leading terms of all the 24 fourth-order per-

---

[5] Details of Table I were worked out by R. Satten, M. Sachs, and A. Mencher in 1954 (unpublished).

mutations, since they will be several orders of magnitude larger than the other three terms.

We now compare the orders of magnitude of the leading third- and fourth-order terms for the ${}^5D_0 \rightarrow {}^7F_0$ transitions in Sm^{2+} and Eu^{3+}. For Sm^{2+}, the free-ion energy gap $E(\Gamma)-E({}^5D_0) \sim 6000$ cm^{-1} while for Eu^{3+} it is $\sim$35000 cm^{-1}. The matrix elements of the spin-orbit coupling, the electric-dipole moment, and the odd crystal-field potential are between similar states in the leading third- and fourth-order terms. Thus the ratios of the magnitudes of the third- and fourth-order contributions to the electric-dipole transition moment are of the order

$$\frac{\text{third-order moment}}{\text{fourth-order moment}} \sim \frac{E(\Gamma)-E({}^5D_0)}{\langle \Gamma \mid V_{\text{even}}^{(k)} \mid \Gamma' \rangle} \sim \begin{cases} 0.6 \ \mathrm{Sm}^{2+} \\ 3.5 \ \mathrm{Eu}^{3+} \end{cases}. \tag{14}$$

These estimates are contradictory to the expectations of Wybourne[6] that the fourth-order terms would be predominant in the case of Eu^{3+} and that the third-order terms would be predominant in Sm^{2+}. From our estimates above, we find that the third- and fourth-order processes in Sm^{2+} and Eu^{3+} are of the same order of magnitude.

A perturbation approach using the *free-ion* states as initial basis functions leads to a very slowly converging series where many successive terms may be of the same order. This is due to the fact that the crystal-field potential has a very large effect (10^4 cm^{-1}) on the excited configuration free-ion states and cannot be treated as a small perturbation.

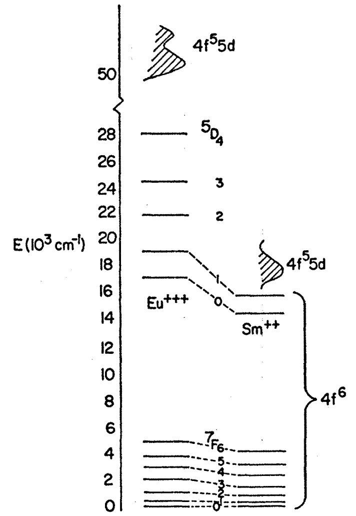

FIG. 2. Schematic energy-level diagrams of Sm^{2+} and Eu^{2+} in crystals.

TABLE I. Set of potentials for the noncubic point groups (Ref. 5).

Group	$V_c = \sum_i{}_{k,m} a_{km} Y_{km}(\theta_i, \varphi_i)$
C_1	All k, m
C_i	k even
C_s	$k+m$ even
C_2	m even
C_{2h}	k even m even
C_{2v}	m even
D_2	k even m even
D_{2h}	k even m even
S_4	k even $m=4n$ k odd $m=4n+2$ $(n=0, \pm 1, \pm 2, \cdots)$
D_{2d}	k even $m=4n$
C_4	$m=4n$
C_{4h}	k even, $m=4n$
C_{4v}	$m=4n$
D_4	k even, $m=4n$
D_{4h}	k even, $m=4n$
C_3	$m=3n$
C_{3i}	k even, $m=3n$
C_{3v}	$m=3n$
D_3	k even, $m=6n$ k odd, $m=6n+3$
D_{3d}	k even, $m=6n$
C_{3h}	k even, $m=6n$ k odd, $m=6n+3$
D_{3h}	k even, $m=6n$ k odd, $m=6n+3$
C_6	$m=6n$
C_{6h}	k even, $m=6n$
C_{6v}	$m=6n$
D_6	k even, $m=12n$
D_{6h}	k even, $m=12n$

The observation[4,7–11] of the electric-dipole transitions ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_1$ have been cited[9] as evidence for the physical presence[12] of the Y_{1m} term in the crystal-field expansions of C_n, C_{nv}, and C_s symmetries. To justify this claim, it was necessary to assume the predominance of the third-order processes given by (11). As seen by the preceding discussion, however, it is evident that higher-order processes also play a major role in these transitions when one treats the crystalline potential as a perturbation on the free-ion states. In this case, the allowed presence of a Y_{1m} term in the crystal potential is clearly *not* solely responsible for the

---

[6] B. G. Wybourne, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience Publishers, Inc., New York, 1967), p. 35.

[7] B. R. Judd, J. Chem. Phys. **44**, 839 (1966).

[8] W. E. Bron and W. R. Heller, Phys. Rev. **136**, A1433 (1964).

[9] Z. J. Kiss and H. A. Weakliem, Phys. Rev. Letters **15**, 457 (1965).

[10] W. C. Nieuwpoort and G. Blasse, Solid State Commun. **4**, 227 (1966).

[11] F. K. Fong and E. Y. Wong, Phys. Rev. **162**, 348 (1967).

C_{3h}

	A'	A''	E'		E''	
A'		π	σR	σL		
A''	π				σR	σL
E'	σL			σR	π	
	σR		σL			π
E''		σL	π			σR
		σR		π	σL	

D_{3h}

	A_1'	A_2'	A_1''	A_2''	E'	E''
A_1'				π	σ	
A_2'			π		σ	
A_1''		π				σ
A_2''	π					σ
E'	σ	σ			σ	π
E''			σ	σ	π	σ

D_3

	A_1	A_2	E
A_1		π	σ
A	π		σ
E	σ	σ	πσ

FIG. 3. Selection-rule tables of the C_{3h}, D_{3h}, and D_3 groups for electric-dipole transitions, where σ, π, σR, and σL correspond to the operators x or y, z, $x+iy$, and $x-iy$, respectively.

0–0 and 0–1 electric-dipole transitions as was previously speculated.[9]

In the expansion of the crystal states $\langle f^6S_1L_1J_1M_1|$ and $|f^6S_2L_2J_2M_2\rangle$, one notes that they can be expanded only in terms of those free-ion states or those linear combinations of free-ion states which transform according to their respective irreducible representations. When this is properly done, with the help of Table I, it can readily be verified that the electric-dipole coupling of the above states, via a first-order spin-orbit coupling, obeys the rigid predictions of the group-theoretical matrix-element theorem.[13] For example, $\langle {}^5D_0|$ and $|{}^7F_0\rangle$ both transform according to the identity irreducible representation A_1. In C_{nv} symmetry, this fact results in an allowed 0–0 electric-dipole transition with a π polarization, the coordinate z having the transformation properties of A_1. On the other hand, an electric-dipole transition between the states $\langle {}^5D_0|$ and $|{}^7F_0\rangle$ is forbidden in, for example, C_{3h} symmetry, since R_z forms the basis of A_1 in this case, and only a magnetic dipole is allowed. A survey of the noncubic point symmetries listed in Table I readily reveals that in S_4, C_{3h}, D_{3h}, and D_3 symmetries, $\langle {}^5D_0|D_q^{(1)}|{}^7F_0\rangle=0$, and in C_{3h}, D_{3h} and D_3, we obtain the additional selection rule that $\langle {}^5D_0|D_q^{(1)}|{}^7F_1\rangle=0$. In the remaining point-group symmetries listed in Table I, electric-dipole transitions from ${}^5D_0$ to all the ${}^7F_J$ levels are allowed. The selection rules for electric-dipole transitions between irreducible representations of C_{3h}, D_{3h} and D_3 are summarized in Fig. 3, which can be constructed by invoking the matrix-element theorem. To determine the ΔJ selection rules of ${}^5D_0\leftrightarrow{}^7F_J$ transitions in a given symmetry, all that is needed is the proper decomposition of the quantum number J into the irreducible representations of the given symmetry.

The forbidden 0–0 and 0–1 transitions of Sm^{2+} and Eu^{3+} ions in C_{3h}, D_{3h}, and D_3 symmetries give the desired properties of the quantum counter-amplifier schemes outlined in Sec. II, i.e., the selection rules $0\not\leftrightarrow 0$ and $0\not\leftrightarrow 1$ assure the condition $\sigma_{31}=0$. In the case of S_4 symmetry one would need to observe, and pump, the ${}^5D_0\leftrightarrow{}^7F_1$ optical transitions, in addition to those transitions allowed in C_{3h}, D_{3h}, and D_3 symmetries. The ${}^7F_0$-${}^7F_1$ energy splitting is $\sim$400 cm^{-1}, and, unless one were interested in detecting ir photons of this energy, the S_4 symmetry system would be needlessly more complicated to operate than that for C_{3h}, D_{3h}, and D_3 symmetries. Therefore, for the case of 10-μ photons, we limit our considerations to the latter three symmetries. When closure properties are invoked,[12–14] the numerators in (11), for example, may be replaced by terms of the form

$$\{f^6\,{}^5D_{J_1=0,M_1=0}|(V_{\text{odd}}^{(k)})[\sum_i(\mathbf{s}\cdot\mathbf{l})_i](D_q^{(1)})|f^6\,{}^7F_{J_2,M_2}\}.$$

There, the product

$$(V_{\text{odd}}^{(k)})[\sum_i(\mathbf{s}\cdot\mathbf{l})_i](D_q^{(1)})$$

can be expanded in terms of spherical harmonics $Y_{j\mu}$ with j even. In this approximation, we see that the transitions $0\leftrightarrow 2$, $0\leftrightarrow 4$, and $0\leftrightarrow 6$ are dominant. This is why the crystal states $|{}^7F_4\rangle$ and $|{}^7F_6\rangle$ have been included, while the states $|{}^7F_3\rangle$ and $|{}^7F_5\rangle$ have not, in the discussion of the rate equations in Sec. II.

IV. DISCUSSION

The scheme we have proposed for a quantum counter, in which all the levels to which the optical relaxations

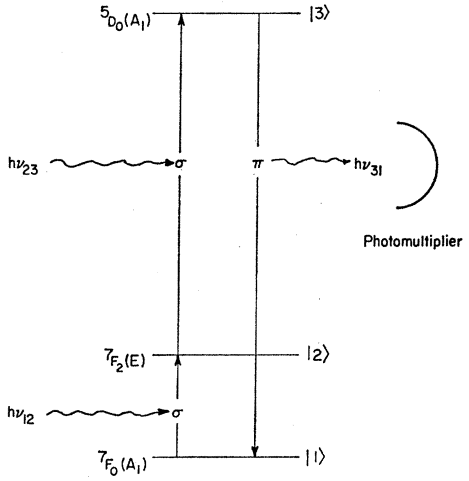

FIG. 4. Frequency conversion scheme utilizing Sm^{2+} or Eu^{3+} in C_{4v} symmetry without amplification.

---

[12] B. R. Judd, Phys. Rev. **127**, 750 (1962).
[13] M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill Book Co., New York, 1964), p. 80.
[14] J. D. Axe, J. Chem. Phys. **39**, 1154 (1963).

occur are pumped, yields the highest emission/absorption ratio. However, detection is complicated by the fact that the optical photons emitted to the photomultiplier will be accompanied by an intense pumping flux at the same frequencies. It seems quite possible that this difficulty could be resolved by placing the direction of propagation of the pumping light at right angles to the orientation of the photomultipliers. Bloembergen[1] has suggested polarization discrimination (i.e., pumping with one polarization and detecting only the other polarization with the photomultiplier) as an additional means of distinguishing between the pumping photons and the relaxation photons. In the present case, however, such discrimination cannot be achieved because the states $|2\rangle$, $|4\rangle$, and $|5\rangle$ have finite electric-dipole matrix elements to the excited state $|3\rangle$ only via a pure π or σ polarization.

An alternative scheme that avoids the above difficulty is to pump only the $|2\rangle\rightarrow|3\rangle$ transition and observe only the optical photons emitted in the $|3\rangle\rightarrow|5\rangle$ and $|3\rangle\rightarrow|4\rangle$ relaxations. For this scheme, the emission/absorption ratio is

$$\frac{N_3(\sigma_{34}+\sigma_{35})}{N_1R_{12}}=\left[\frac{R_{12}+\sigma_{21}}{R_{23}}\left(1+\frac{R_{23}+\sigma_{31}+\sigma_{32}}{\sigma_{34}+\sigma_{35}}\right)+\frac{(\sigma_{54}+\sigma_{52}+\sigma_{51})\left(\sigma_{31}(\sigma_{41}+\sigma_{42})+\sigma_{41}\sigma_{34}\right)+\sigma_{35}\sigma_{54}\sigma_{41}+\sigma_{51}\sigma_{35}(\sigma_{41}+\sigma_{42})}{(\sigma_{54}+\sigma_{52}+\sigma_{51})(\sigma_{41}+\sigma_{42})(\sigma_{34}+\sigma_{35})}\right]^{-1}. \tag{15}$$

Again taking the optimum case, where $\sigma_{31}=0$ and $R_{12}\ll\sigma_{ij}\ll R_{23}$, and specializing the result to the Eu^{3+} levels of Fig. 1, the above ratio is

$$N_3(\sigma_{34}+\sigma_{35})/N_1R_{12}=1.35, \tag{16}$$

which is much smaller than that of the previous scheme. The reason is clear: By not pumping levels $|4\rangle$ and $|5\rangle$ to the exited level $|3\rangle$ there is substantial "leakage" to the ground state via the spontaneous rates σ_{41} and σ_{51}. By providing for a simple means of discrimination between the optical pumping and optical emission, we sacrifice the emission/absorption ratio. If, however, amplification is not important, this latter scheme has the advantage of eliminating the problems of pumping and observing optical transitions between the same levels.

Where amplification is not emphasized, another scheme of interest may be described (Fig. 4). In C_{4v} symmetry, for example, the $|3\rangle\rightarrow|1\rangle$ electric-dipole relaxation corresponding to the transition ${}^5D_0(A_1)\leftrightarrow{}^7F_0(A_1)$, occurs via a π polarization (Sec. III). The two-photon absorption $|1\rangle\rightarrow|2\rangle$ and $|2\rangle\rightarrow|3\rangle$, however, corresponds to the transitions ${}^7F_0(A_1)\leftrightarrow{}^7F_2(E)$ and ${}^7F_2(E)\leftrightarrow{}^5D_0(A_1)$, which occur via σ polarizations. Thus if both pumping processes $|1\rangle\rightarrow|2\rangle$ and $|2\rangle\rightarrow|3\rangle$ are achieved with σ-polarized light, whereas the detection is sensitive only to π-polarized light, then it will no longer be necessary to energy select with the photomultiplier.

If the ir signal (in either scheme) becomes so strong that the rate R_{12} becomes comparable to the spontaneous relaxation rates σ_{32}, σ_{34}, and σ_{35}, the quantum counter begins to saturate and the emission/absorption ratio decreases. This is simply the result of pumping electrons into excited state $|3\rangle$ faster than they can relax to the lower states $|2\rangle$, $|4\rangle$, and $|5\rangle$. Since the spontaneous rates σ_{32}, σ_{34}, and σ_{35} are generally quite large, the response of the system should be linear for all but the most intense ir signals.

The quantum counter-amplifier which we have described will also respond to ir energies corresponding to the ${}^7F_0\rightarrow{}^7F_4$ (5.6 μ) and ${}^7F_0\rightarrow{}^7F_6$ (5.0 μ) excitations, and, as pointed out in Sec. III, by using S_4 symmetry, a ${}^7F_0-{}^7F_1$ (25 μ) excitation could be detected.

ACKNOWLEDGMENTS

Two of us (F. K. F. and L. A. V.) are grateful to Professor R. A. Satten for illuminating discussions on the subject of symmetry selection rules. A detailed check of the rate equations by C. R. Chilver is gratefully acknowledged.