Transition Probabilities of Europium(III) in Zirconium and Beryllium Fluoride Glasses, Phosphate Glass, and Pentaphosphate Crystals*

B. BLANZAT

Laboratoire CNRS de Chimie métallurique et spectroscopie des terres rares, F 92190 Bellevue-Meudon, France

L. BOEHM

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel

C. K. JØRGENSEN AND R. REISFELD

Département de Chimie minérale, anlytique et appliquée, University of Geneva, Switzerland

AND N. SPECTOR

Soreq Nuclear Research Center, Yavne, Israel

Eigenvectors of Eu^{3+} were obtained by a least-squares fitting procedure to the measured transitions from the two lowest J levels to a multitude of excited levels up to $41\ 000\ cm^{-1}$. The Judd–Ofelt parameters $\Omega_t(t = 2, 4, 6)$ were obtained by comparison between the $U^{(t)}$ calculated from the eigenvectors, and the observed oscillator strengths. Radiative transition probabilities and branching ratios were evaluated for the excited states $^5D_J(J = 0, 1, 2, 3)$ and $^5L_6$ to ^7F_J. The agreement between the calculated and observed lifetimes and branching ratios is better in oxide glasses than in the pentaphosphate crystal and fluoride glasses. This can be understood on the basis of the higher variety of sites and hence, better averaging.

1. Introduction

Rare earth-doped glasses and crystals are of both theoretical and practical interest because of their properties as lasers (*1, 2*). It was pointed out that owing to the low multiphonon relaxation rate of fluoride glasses (*3*)

their luminescent quantum efficiencies will be increased in comparison to those of oxide glasses in the cases where the distances between the fluorescent level and the adjacent lower levels are small. Recently, this hypothesis was verified (*4*) in lanthanide-doped beryllium fluoride glasses, where an exponential dependence of the multiphonon relaxation rates on this energy gap was observed, typically five times lower than in oxide glasses.

The spectroscopic properties of neodymium in various fluorozirconate glasses were

studied by Lucas *et al.* (5) who suggest that because of the relatively low refractive index, such materials may find applications in high-intensity lasers, owing to the absence of self-focusing due to nonlinear effect. The local symmetry of the lanthanide ions in fluoride glasses is somewhat controversial. Hence, it is interesting to study the absorption and emission spectra of Eu^{3+} in such glasses, and compare them with oxide glasses. The levels with $J = 0, 1$, and 2 (spherical symmetry being a remarkably good approximation) of the two lowest terms ^7F and ^5D of the ground configuration $4f^6$ are particularly suitable (6–8) for investigating the influence of the nearest-neighbor atoms on Eu^{3+}. Pentaphosphate crystals (also called ultraphosphates) such as EuP_5O_{14} (9, 10) have the advantage of high optical transparency for wavelengths down to 240 nm. Therefore, the set of observed J-levels could be extended up to 41 000 cm^{-1}. These newly observed energy levels were incorporated in the least-squares fit thus providing new radial parameters, better established free-ion eigenvectors, and reduced matrix elements which are used in the calculation of spectroscopic properties.

II. Materials

The beryllium glass was kindly provided by Dr. J. Portier, CNRS, Talence (Bordeaux), and its composition (as mole percentage) is

25% BeF_2, 35% AlF_3, 24% CaF_2, 15% BaF_2, and 1% EuF_3.

The zirconium fluoride glass was kindly provided by Dr. J. Lucas, Université de Rennes. Its preparation is described in Ref. (5) and its composition (as mole percentage) is

60% ZrF_4, 33% BaF_2, 5% LaF_3, and 2% EuF_3.

The crystal of EuP_5O_{14} was grown as described in Ref. (9).

The phosphate glasses (6) were prepared by melting a mixture of $NaH_2PO_4 \cdot H_2O$ with 0.5 to 3.5 wt% Eu_2O_3 in a platinum crucible at 1000°C producing $NaPO_3$ glass containing 0.4 to 2.8 mole% europium. The absorption spectra were measured on a sample containing 2 wt% Eu_2O_3.

III. Spectroscopic Measurements

The fluorescence spectra of all the samples were measured on a 50-cm Jarrel Ash grating monochromator equipped with a cooled photomultiplier. As previously described (9) the absorption spectrum of crystalline EuP_5O_{14} was measured on the same instrument, whereas the absorption spectra of the glasses were measured (at room temperature) on a Cary 17 recording spectrophotometer.

Narrow-line selective excitation of the europium excited levels were performed with a dye laser Moletron DL100 using Rhodamine 6G for $^5D_0$ in the yellow, and various substituted coumarines for $^5D_1$ and $^5D_2$ in the green and the blue. The rise time of the laser flash is $5 \cdot 10^{-9}$ sec.

The lifetimes τ were determined by feeding the luminescence signal (after passing a monochromator) in a PAR 162/164 boxcar averager.

Figures 1 and 2 give the observed fluorescence spectra of the zirconium fluoride and beryllium fluoride glasses. In the latter case the broad emission centered around 400 nm is due to a small part of the europium present in its divalent form.

IV. Energy Levels and Eigenvectors

Table I gives the barycenters of J-levels of Eu^{3+} (in cm^{-1}) derived from the absorption spectra of EuP_5O_{14} relative to the (structureless) ground state $^7F_0$ as zero point. In the next nine J-levels, the individual $(2J + 1)$ sublevels have all been observed and assigned symmetry types in the site symmetry
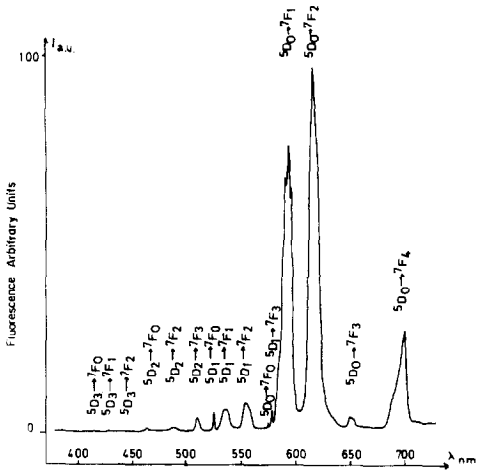
FIG. 1. Steady-state luminescence spectrum of Eu^{3+} in the zirconium fluoride glass under 254-nm ultraviolet excitation by a mercury lamp.

C_{2v} based on absorption spectra in polarized light. Thus, the levels of $^7F_1$ occur at 267, 403, and 480 cm^{-1} and those of $^7F_2$ at 940, 960, 1075, 1101, and 1180 cm^{-1}, whereas the total spreading is around 300 cm^{-1} in $^7F_4$ and $^7F_5$ and 466 cm^{-1} in $^7F_6$. As usual, $^5D_1$ is only split to a very small extent, with sublevels at 19,026, 19,053, and 19,072 cm^{-1}. The barycenters of the 30 subsequent J-levels (from $^5D_3$ to $^5G_5$ have
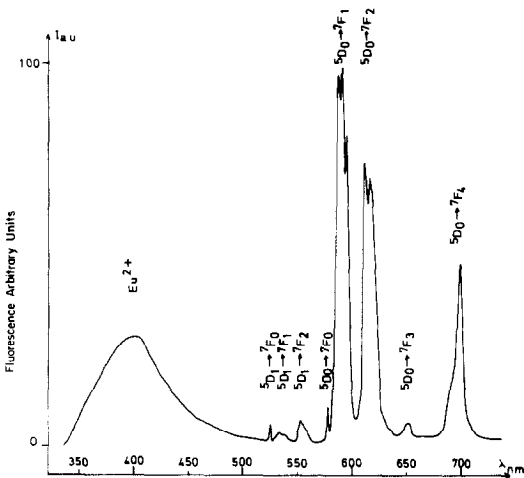

FIG. 2. Luminescence spectrum of Eu^{3+} in beryllium fluoride glass under the same conditions as in Fig. 1.

been obtained from the centre of gravity of the (very narrow) absorption band. In the two cases, where two J-levels are indicated with a distance smaller than 40 cm^{-1}, the calculated distances are given.

The manifold of 40 observed J-level barycenters was compared with the Condon–Shortley parameters (including the Trees corrections, α, β, and γ of comparatively minor importance) with a least-squares fitting program like that previously used for the $4f^{12}$ system Tm^{3+} (11) and for $4f^3Nd^{3+}$ incorporated in $Gd_2(MoO_4)_3$ (12) resulting in the parameters (in cm^{-1})

$$F_2 = 381.0, \qquad F_4 = 61.3, \qquad F_6 = 6.2,$$

$$\alpha = 36, \qquad \beta = -815, \qquad \gamma = 700, \quad (1)$$

$$\zeta_{4f} = 1327,$$

with an rms deviation of ~ 100 cm^{-1}. The corresponding eigenvectors of the J-levels were also evaluated, and Table II gives the predominant components in terms of Russell–Saunders coupling with the last integer being a file number in the standard order of diagonal elements in Racah's theory. The calculation is done in full intermediate coupling.

V. Matrix Elements of Intensities

The qualitative ideas (from 1945) of Broer *et al.* (13) on the origin of the finite transition probabilities (as electric dipolar transitions) from the ground state to excited J-levels (observed in absorption spectra) were expressed independently by Judd (14) and Ofelt (15) in a theory, where the oscillator strength P of a given transition is the sum of three contributions

$$P = \frac{8\pi^2 mc\sigma}{3h(2J+1)} \cdot \frac{(n^2+2)^2}{9n} \cdot \sum_{t=2,4,6} \Omega_t |U^{(t)}|^2,$$
$$(2)$$

where σ is the wavenumber, $(2J+1)$ the number of states in the lower level, and n the refractive index. The matrix elements $U^{(2)}$,

TABLE I

OSERVED ENERGY LEVELS (J-LEVEL BARYCENTERS) OF Eu^{3+} IN EuP_5O_{14}

Level	E (cm^{-1})	Level	E (cm^{-1})	Level	E (cm^{-1})	Level	E (cm^{-1})
$^7F_0$	0	$^5D_3$	24,490	$^5H_4$	31,250	$^5K_6$	37,425
$^7F_1$	383	$^5L_6$	25,379	$^5H_6$	31,526	$^3P_1$	38,117
$^7F_2$	1,051	$^5G_2$	26,410	$^3P_0$	32,793	$^5K_7$	38,410
$^7F_3$	1,927	$^5L_7$	26,420	$^5F_2$	33,134	$^5G_2$	38,760
$^7F_4$	2,896	$^5G_3$	26,573	$^5F_1$	33,452	$^5K_8$	38,956
$^7F_5$	3,922	$^5G_4$	26,594	$^5F_4$	33,596	$(^3K, {}^3I)_6$	39,093
$^7F_6$	5,026	$^5G_6$	26,715	$^5I_4$	33,852	$^5G_3$	39,162
$^5D_0$	17,289	$^5D_4$	27,643	$^5F_5$	34,137	$^5G_4$	39,850
$^5D_1$	19,050	$^5H_3$	30,675	$(^5I, {}^3H)_6$	35,014	$(^5D, {}^5P)_3$	40,000
$^5D_2$	21,528	$^5H_7$	31,056	$^5K_5$	36,206	$^5G_5$	40,399

$U^{(4)}$, and $U^{(6)}$ can be evaluated, for instance, in Russell–Saunders coupling (where they are constrained by several selection rules; $U^{(t)}$ can only be different from zero if J is changed by at most t units and if S does not change at all). Such matrix elements do not depend on chemical bonding to the neighbor atoms and were tabulated (16, 17) and compared with absorption spectra of aqua ions. In this work matrix elements of $U^{(2)}$, $U^{(4)}$. and $U^{(6)}$ were evaluated with the new eigenvectors of Table II for more than 50 transitions and used for all subsequent spec-

troscopic calculations. They differ by several percent from previously tabulated ones and are available upon request.

At first, it may seem surprising that the absorption band intensities can be described by a fixed set of $U^{(t)}$ for a given M^{3+} combined with only three parameters Ω_t characterizing the compound or (solid or liquid) solution, when it is realized that the energy levels (neglecting their separation in sublevels by "ligand field" effects) depend on four to seven parameters, as in Eq. (1). A general trend is recognized from a large

TABLE II

EIGENVECTORS OF LOW-LYING J-LEVELS OF Eu^{3+} IN INTERMEDIATE COUPLING

E (cm^{-1})	J	
0	0	$0.9713|^7F\rangle-0.1736|^5D_1\rangle+0.1561|^5D_3\rangle\cdots$
17,289	0	$-0.2247|^7F\rangle-0.5465|^5D_1\rangle-0.1787|^5D_2\rangle+0.6949|^5D_3\rangle\cdots$
383	1	$0.9766|^7F\rangle-0.1580|^5D_1\rangle+0.1388|^5D_3\rangle\cdots$
19,050	1	$-0.1992|^7F\rangle-0.5674|^5D_1\rangle-0.1889|^5D_2\rangle+0.7268|^5D_3\rangle$ $-0.1183|^3P_1\rangle+0.1539|^3P_3\rangle+0.1769|^3P_6\rangle\cdots$
1,051	2	$0.9832|^7F\rangle-0.1313|^5D_1\rangle+0.1102|^5D_3\rangle\cdots$
21,527	2	$-0.1557|^7F\rangle-0.5835|^5D_1\rangle-0.1883|^5D_2\rangle+0.7488|^5D_3\rangle+0.1010|^3P_6\rangle\cdots$
1,927	3	$0.9888|^7F\rangle-0.0973|^5D_1\rangle\cdots$
24,490	3	$-0.1049|^7F\rangle-0.5912|^5D_1\rangle-0.1699|^5D_2\rangle+0.7539|^5D_3\rangle-0.0862|^5F_1\rangle-0.1348|^5F_2\rangle\cdots$
2,896	4	$0.9903|^7F\rangle-0.0581|^5D_1\rangle+0.0738|^5F_2\rangle\cdots$
3,922	5	$0.9888|^7F\rangle+0.0709|^5F_2\rangle+0.0853|^5G_1\rangle-0.0824|^5G_3\rangle\cdots$
5,020	6	$0.9839|^7F\rangle+0.1175|^5G_1\rangle-0.1168|^5G_3\rangle\cdots$
25,379	6	$-0.0652|^5G_1\rangle+0.0713|^5G_2\rangle+0.0761|^5G_3\rangle-0.0623|^5H_1\rangle$ $-0.1098|^5K\rangle+0.9396|^5L\rangle+0.1377|^3K_1\rangle+0.1286|^3K_2\rangle+0.1637|^3K_5\rangle\cdots$

number of examples. Thus, crystalline fluorides, and aqua ions in water, have values of Ω_4 and Ω_6 of comparable magnitude, whereas Ω_2 usually is not larger than the experimental uncertainty. On the other hand, more covalent compounds (1) have much higher Ω_2, producing "hypersensitive pseudoquadrupolar transitions" having intensities (proportional to the genuine electric quadrupolar transitions, but with a huge factor) dependent almost exclusively on the square of $U^{(2)}$. In Russell–Saunders coupling, each tervalent lathanide shows only one pronounced hypersensitive psuedoquadrupolar transition, from the ground state (S, L, J) to the level $(S, L-2, J-2)$. However, because of the effects of intermediate coupling mixing different (S, L) combinations in the same eigenvector, both $4f^{10}Ho^{3+}$ and $4f^{11}Er^{3+}$ have two such transitions, to levels with $J = 6$ and $11/2$, respectively. It is well recognized that the Judd–Ofelt theory works with a precision of some 20%, but also that the agreement in certain cases (16, 18, 19) is conspicuously ameliorated if one transition (say $^3H_4 \rightarrow {}^3P_2$ in Pr^{3+}) is eliminated.

Whereas Eq. (2) originally was intended for absorption spectra only, the radiative lifetimes of excited states (related to the oscillator strength by Einstein's 1917 formula) and the branching ratios indicating the probability of forming various lower J-levels (1) (including the groundstate) can also be described by Eq. (2) to a reasonable approximation. Thus, the luminescence of Ho^{3+} (20), Er^{3+} (21), and Tm^{3+} (22) in various phosphate, silicate, germanate, and tellurite glasses can be treated along these lines. It is not surprising that the much larger number of data described by the same three Ω_t and an "objective" set of $U^{(t)}$ matrix elements produced a higher dispersion of the agreement, typically within a factor of 1.5 or 2.

The intensity parametrs Ω_t characterizing each material were derived by fitting the experimentally observed oscillator strengths of the transitions obtained by integrating the absorption bands with the calculated values of $U^{(\lambda)2}$. Their values (in the unit 10^{-20} cm^2) are

	Ω_2	Ω_4	Ω_6
Zirconium fluoride glass	0.93	2.61	2.17
Phosphate glass	4.12	4.69	1.83
Pentaphosphate crystal	3.66	1.43	3.07

$$(3)$$

The Nd^{3+} in the zirconium fluoride type B (5) shows $\Omega_2 = 1.93$, $\Omega_4 = 3.8$, and $\Omega_6 = 4.35$ for comparison. Table III gives the calculated luminescent properties of the zirconium fluoride glass, oscillator strength P (in the unit 10^{-8}), the radiative transition probability A (in the unit sec^{-1}), and the branching ratio $\beta = A_i/\Sigma A_i$. Table IV gives the same type of data for the phosphate glass with $n = 1.48$ (22) and Table V for crystalline EuP_5O_4 having $n = 1.62$.

The nonradiative deexcitation from a given electronic level E_2 to the next lower electronic level E_1 is given by

$$W_{NR} = B \exp\{-\alpha(E_2 - E_1)\}, \qquad (4)$$

where B and α are phenomenological parameters (22) which are

	α	B (sec^{-1})	$\hbar\omega$ (cm^{-1})
ZrF_4	0.007	4×10^{-9}	500
Phosphate	0.005	5.4×10^{-12}	1300

and $\hbar\omega$ is the phonon energy.

The nonradiative relaxation rates thus obtained for the deexcitation of the higher levels were higher than 10^6 sec^{-1} leading to a rapid depopulation of all higher levels to the $^5D_0$ with a small contribution to the $^5D_1$ and $^5D_2$ levels.

Table VI combines the measured and calculated values of the radiative lifetimes and branching ratios from $^5D_0$ to levels of the ^7F multiplet in the zirconium fluoride and

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TABLE III

SPECTROSCOPIC PARAMETERS OF Eu^{3+} IN ZIRCONIUM FLUORIDE GLASS

Transition	$P(\times 10^{-8})$	A (sec^{-1})	β
$^5L_6 \rightarrow {}^5D_3$	0.36	0.004	0
$^5D_2$	15.7	3.58	0.0162
$^5D_1$	21.6	13.4	0.0604
$^5D_0$	46.8	47.3	0.2141
$^7F_6$	0.32	2.02	0.0091
$^7F_5$	0.36	2.55	0.0115
$^7F_4$	2.46	19.2	0.0868
$^7F_3$	0.65	5.50	0.0249
$^7F_2$	0.01	0.09	0.0004
$^7F_1$	4.72	45.4	0.2057
$^7F_0$	8.24	81.9	0.3707
$^5D_2 \rightarrow {}^5D_1$	31.7	3.00	0.0279
$^5D_0$	1.58	0.44	0.0041
$^7F_6$	0.11	0.44	0.0041
$^7F_5$	1.87	8.92	0.0830
$^7F_4$	1.45	7.76	0.0722
$^7F_3$	10.5	62.1	0.5781
$^7F_2$	3.00	19.4	0.1805
$^7F_1$	0.32	2.22	0.0206
$^7F_0$	0.44	3.16	0.0294
$^5D_1 \rightarrow {}^5D_0$	20.2	0.97	0.0089
$^7F_6$	0.46	1.40	0.0129
$^7F_5$	1.18	4.17	0.0385
$^7F_4$	5.02	20.2	0.1866
$^7F_3$	6.20	28.0	0.2590
$^7F_2$	7.79	38.9	0.3592
$^7F_1$	1.94	10.4	0.0964
$^7F_0$	0.74	4.16	0.0384
$^5D_0 \rightarrow {}^7F_6$	0.88	2.04	0.0197
$^7F_5$	0	0	0
$^7F_4$	10.9	34.8	0.3364
$^7F_3$	0	0	0
$^7F_2$	6.16	25.0	0.2419
$^7F_1$	9.44	41.6	0.419
$^7F_0$	0	0	0

TABLE IV

SPECTROSCOPIC PARAMETERS OF Eu^{3+} IN PHOSPHATE GLASS

Transition	$P(\times 10^{-8})$	A (sec^{-1})	β
$^5D_2 \rightarrow {}^5D_1$	33.5	3.01	0.0150
$^5D_0$	6.8	1.79	0.0089
$^7F_6$	0.09	0.35	0.0018
$^7F_5$	3.25	14.7	0.0732
$^7F_4$	4.88	24.8	0.1233
$^7F_3$	16.7	93.6	0.4655
$^7F_2$	7.54	46.2	0.2299
$^7F_1$	0.57	3.73	0.0185
$^7F_0$	1.90	12.9	0.0641
$^5D_1 \rightarrow {}^5D_0$	19.7	0.89	0.0043
$^7F_6$	0.38	1.08	0.0052
$^7F_5$	2.03	6.79	0.0327
$^7F_4$	8.76	33.4	0.1607
$^7F_3$	17.4	74.8	0.3597
$^7F_2$	9.42	44.6	0.2145
$^7F_1$	8.35	42.5	0.2045
$^7F_0$	0.72	3.84	0.0185
$^5D_0 \rightarrow {}^7F_6$	0.72	1.58	0.0079
$^7F_5$	0	0	0
$^7F_4$	19.0	57.6	0.2884
$^7F_3$	0	0	0
$^7F_2$	26.5	102.0	0.5113
$^7F_1$	9.19	38.4	0.1924
$^7F_0$	0	0	0

phosphate glasses and pentaphosphate crystal. For the beryllium fluoride only the observed values are given.

Calculations of the results given in Table VI could not be performed for the beryllium fluoride glass, because the three Ω_t from Eq. (3) evaluated from the absorption spectrum had a large uncertainty. It may be due to the fact (found by diffuse light scattering) that

this glass was on the limit of heterogeneous precipitation, forming a vitro-ceramic (1). Nevertheless, we have included this material in the present paper, because we find the observed branching ratios and a few other experimental quantities interesting.

Two transitions play an unusual role in the specific case of Eu^{3+}. One is the pseudoquadrupolar hypersensitive emission $^5D_0 \rightarrow {}^7F_2$ taking over a large proportion of the total luminescence intensity if Ω_2 is large. The other is (the usually very weak) $^5D_0 \rightarrow {}^7F_0$ which is forbidden in all approximations in spherical symmetry. It is frequently argued that it occurs nevertheless because of mixing of sublevels belonging to different J-levels by nondiagonal elements of "ligand field" perturbations, but it is at the same time an experimental fact that "chem-

TABLE V

SPECTROSCOPIC PARAMETERS OF Eu^{3+} IN CRYSTALLINE PENTAPHOSPHATE

Transition	$P\,(\times 10^{-8})$	$A\,(\mathrm{sec}^{-1})$	β
$^5L_6 \rightarrow {}^5D_3$	0.56	~0	0
$^5D_2$	23.5	6.10	0.0160
$^5D_1$	33.0	23.2	0.0607
$^5D_0$	71.6	82.1	0.2148
$^7F_6$	0.49	3.58	0.0094
$^7F_5$	0.54	4.37	0.0114
$^7F_4$	3.62	32.1	0.0839
$^7F_3$	0.99	9.54	0.0250
$^7F_2$	0.01	0.13	0.0004
$^7F_1$	7.21	78.9	0.2065
$^7F_0$	12.6	142.0	0.3720
$^5D_3 \rightarrow {}^5D_2$	42.8	6.58	0.0407
$^5D_1$	0.91	4.70	0.0291
$^5D_0$	0	0	0
$^7F_6$	0.02	0.15	0.0009
$^7F_5$	1.08	7.99	0.0495
$^7F_4$	10.6	86.7	0.5369
$^7F_3$	2.29	20.4	0.1263
$^7F_2$	1.83	17.6	0.1093
$^7F_1$	1.70	17.3	0.1074
$^7F_0$	0	0	0

TABLE V —*Continued*

Transition	$P\,(\times 10^{-8})$	$A\,(\mathrm{sec}^{-1})$	β
$^5D_2 \rightarrow {}^5D_1$	36.4	3.91	0.0213
$^5D_0$	6.73	2.12	0.0115
$^7F_6$	0.16	0.76	0.0042
$^7F_5$	1.11	6.04	0.0329
$^7F_4$	4.23	25.7	0.1402
$^7F_3$	13.1	87.9	0.4785
$^7F_2$	5.08	37.3	0.2032
$^7F_1$	0.59	4.61	0.0251
$^7F_0$	1.88	15.2	0.0830
$^5D_1 \rightarrow {}^5D_0$	21.6	1.17	0.0058
$^7F_6$	0.70	2.43	0.0121
$^7F_5$	0.73	2.93	0.0146
$^7F_4$	2.97	13.6	0.0678
$^7F_3$	13.2	67.6	0.3377
$^7F_2$	10.1	57.1	0.2851
$^7F_1$	8.25	50.4	0.2516
$^7F_0$	0.79	5.04	0.0252
$^5D_0 \rightarrow {}^7F_6$	1.34	3.54	0.0179
$^7F_5$	0	0	0
$^7F_4$	6.45	23.4	0.1181
$^7F_3$	0	0	0
$^7F_2$	26.2	121.0	0.6099
$^7F_1$	10.1	50.4	0.2541
$^7F_0$	0	0	0

ically polarizable" materials (1) have a special propensity for showing both these transitions.

It is seen from Table VI that the branching ratio β for $^5D_0 \rightarrow {}^7F_2$ agrees with experiment for the phosphate glass, but is underestimated for the zirconium fluoride glass, and overestimated for crystalline EuP_5O_{14}. With the exception of the latter case, the calculated and observed values of β usually agree within a factor of 1.5. This may not be as surprising as one would expect at first for

TABLE VI

OBSERVED AND CALCULATED LIFETIMES (msec) OF EXCITED LEVELS OF Eu^{3+} AND BRANCHING RATIOS β

	Zirconium fluoride glass		Beryllium fluoride glass		Phosphate glass		Pentaphosphate crystal	
	obs	calc	obs	calc	obs	calc	obs	calc
$^5D_2$	0.50	—	—	—	—	—	—	—
$^5D_1$	1.0	—	0.17	—	—	—	0.006	—
$^5D_0$	5.0	9.7	8.78	—	2.95	5.00	4.8	5.05
$\beta\,{}^5D_0\text{-}{}^7F_4$	0.196	0.336	0.132	—	0.194	0.288	0.335	0.118
$^7F_3$	0.010	0	0.015	—	0.041	0	0.029	0
$^7F_2$	0.464	0.242	0.406	—	0.568	0.511	0.254	0.610
$^7F_1$	0.290	0.419	0.422	—	0.189	0.192	0.374	0.254
$^7F_0$	0.0017	0	0.005	—	0.007	0	0.007	0

the vitreous systems with a dispersion of local site symmetries, as clearly shown by the $^4I_{9/2} \to ^2P_{1/2}$ band of Nd^{3+} in zirconium fluoride glass (5) having a half-width of $93 \, cm^{-1}$ at liquid helium temperature, compared with 1 or $2 \, cm^{-1}$ for crystalline NdF_3 and $NdZrF_7$. This inhomogeneous line broadening is typical for glasses (1, 23) but does not, by itself, demonstrate that a distinction between network-forming and-modifying cations is well-defined in fluoride glasses. Both in fluoride and in oxide glasses, the individual site may deviate more, on the average, from spherical symmetry than would be true for the crystalline pentaphosphate; but at the same time, the consequences of deviations from spherical symmetry may cancel out to a large extent in the multiple sites in glasses.

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