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Fluorescence of Dy^{3+} in CaF_2

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The fluorescent "Spectra I" of Dy^{3+} in CaF_2 consisting of approximately 45 lines are found to originate from the crystal-field split levels of the ${}^4F_{11/2}$ and ${}^6H_{15/2}$, ${}^6H_{13/2}$ and ${}^6H_{11/2}$ free-ion states, in accord with energy-level schemes which indicate the crystal-field symmetry for Spectra I about the Dy ion to be type O_h group. These schemes also give information on the crystal-field energy level representations and energies to 3 cm^{-1}, preliminarily.

TRIVALENT rare-earth-doped fluorite crystal fluorescent line spectra have been observed to fall into two distinct types, "I and II," according to the method of crystal preparation.[1] The theoretical bases for "Spectra I and II" are not completely understood.

A preliminary analysis[2] of Spectra I and II of Sm^{3+} in CaF_2 has indicated that in this case the fluorescent lines can be accounted for largely as transitions between the crystal-field split levels of the upper fluorescent and lower ground multiplet Russell-Saunders states of the Sm^{3+} free-ion. Based on a frequency shift between corresponding subgroups of Spectra I and II these two spectra were identified[2] as originating from two different upper fluorescent states of Sm^{3+}.

However, there are several other trivalent rare-earth-doped fluorite spectra for which the approximate spectral location of the subgroups are the same[1] for types I and II; and the analysis of the Spectra I and II of one such crystal such as Dy^{3+} in CaF_2 could be helpful in this regard. The purpose of this paper is to indicate the crystal-field symmetry and crystal-field energy level origins, preliminarily, of the Dy^{3+} in CaF_2 Spectra I.[3] The basis for this analysis will be several spectrograms obtained in conjunction with a recent investigation[4]; these spectrograms (shown in Fig. 1) record the fluorescent Spectrum I of a crystal of 0.1% Dy^{3+} in CaF_2 with 0.1% NaF, at liquid-nitrogen temperature, to an accuracy of 5 cm^{-1}.

Since, in rare-earths the crystal field is much smaller than the spin-orbit interaction, each Russell-Saunders state splits independently into crystal-field levels. Group theory may be easily used to find the amount of this splitting and the allowed transitions between such split levels if the group theoretical symmetry about the rare-earth ion is known.[5]

In general, it is theoretically possible, in principle, to solve this spectral problem completely, using perturbation theory, by obtaining the wave functions and energies of the crystal-field split states. However, the amount of labor is prohibitive here and some information required to obtain such exact results may be lacking for a many-electron atom in crystal fields such

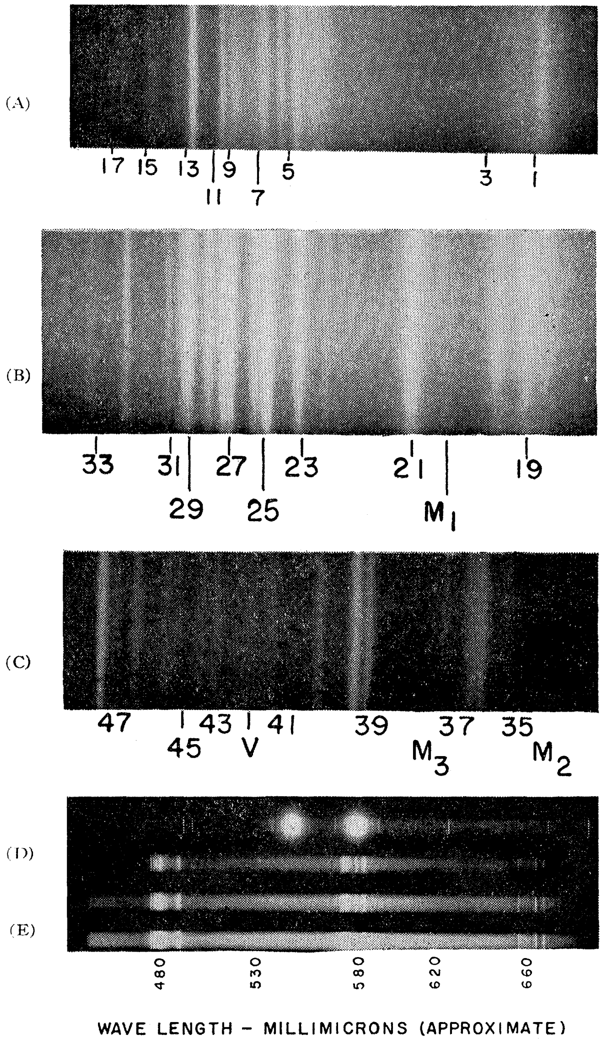

FIG. 1. Fluroescence of Dy^{3+} in CaF_2, Spectrum I. The line numbers are identified in Table I. (A) Enlargment of the spectrogram of Subgroup *A*. (B) Enlargement of the spectrogram of Subgroup *B*. (C) Enlargement of the spectrogram of Subgroup *C*. (D) Mercury comparison spectrogram. (E) Spectrograms showing the relative positions and intensities of Subgroups *A*, *B*, and *C*.

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[1] I. V. Stepanov and P. P. Feofilov, Doklady Akad. Nauk. SSSR 4, 615 (1957) [translation: Soviet Phys.—Dokl. 1, 350 (1956)].

[2] N. Rabbiner, Phys. Rev. 130, 502 (1963).

[3] The general crystal-field symmetry type of Dy^{3+} in CaF_2, Spectra II will be seen likely to be of a lower symmetry than that for Spectra I.

[4] H. H. Theissing, P. Caplan, T. Ewanizky, and G. deLhery, Appl. Opt. 2, 291 (1963).

[5] H. Bethe, Ann Physik 3, 133 (1929).

TABLE I. Frequencies of fluorescent lines of Dy^{3+} in CaF_2, Spectrum I.[a]

Line	λ (Å)	$\bar{\nu}$ (cm⁻¹)
	I–A	
*B*1	4895	20 429
*WBB*2	4884	20 475
*WW*3	4864	20 559
*BB*4	4799	20 838
5	4792	20 868
6	4787	20 890
7	4780	20 921
*W*8	4774	20 947
9	4769	20 969
10	4767	20 978
11	4764	20 991
*W*12	4758	21 017
*B*13	4750–3	21 053–40
*W*14	4746	21 070
*W*15	4735	21 119
*W*16	4722	21 177
*WW*17	4717	21 200
	I–B	
*WB*18	5827	17 161
*B*19	5819	17 185
*B*20	5810	17 212
*B*21	5781	17 298
*W*22	5751	17 388
23	5742	17 416
24	5732	17 446
25	5727	17 461
26	5719	17 486
27	5717	17 492
28	5712	17 507
29	5706	17 525
30	5703	17 535
31	5698	17 550
32	5684	17 593
*W*33	5673	17 627
	I–C	
34	6719	14 883
35	6707	14 910
36	6697	14 932
37	6692	14 943
*S*38	6658	15 020
*S*39	6654	15 029
40	6642	15 056
41	6627	15 090
42	6607	15 135
43	6602	15 147
44	6595	15 164
45	6590	15 175
46	6581	15 195
47	6574	15 211
*S*48	6569	15 223

[a] See Appendix

as in the trivalent rare-earth doped fluorites. In such cases group theory can provide vital information with comparatively little effort and is a powerful and elegant tool.

It is known that the CaF_2 lattice is octahedral without any rare-earth doping. If the Dy^{3+} ion is then incorporated, lattice distortion ensues. But if the distortions introduced by placing of Dy^{3+} into the CaF_2 lattice are comparatively small, the crystal field will remain O_h. A recent investigation[6] has indicated this to be the case. In this paper the assumption of O_h symmetry for Dy^{3+} in CaF_2 is made; and the deduced crystal-field energy level schemes are found to be in accord with the 45 observed lines to within the accuracy of 5 cm⁻¹. This tends to confirm the O_h crystal symmetry, and, in addition, provides information on the crystal-field level energies and representations.

Referring to Fig. 1, the fluorescent spectra of a crystal of Dy^{3+} in CaF_2 is seen to be composed of three subgroups, *A*, *B*, and *C*, and resembles[1] Spectrum I. These spectrograms came from a diffraction grating a linear dispersion averaging 19.5 Å/mm. The frequencies of these lines are listed in Table I under the subgroups *A*, *B*, and *C* to an accuracy of 5 cm⁻¹.

Using Table I, the mean frequencies of these *A*, *B*, and *C* subgroups are found to be 20 900, 17 400, 15 100 cm⁻¹, thus identifying them as the sets of transitions between the free-ion states of known energies (*E*): the $^6F_{11/2}$ fluorescent state and the $^6H_{15/2}$, $^6H_{13/2}$, and $^6H_{11/2}$ ground-multiplet states of Dy^{3+}. This is in accord with the energies of these states which have been previously established[7] as follows:

$^6F_{11/2}$; $E\sim 20\,900$ cm⁻¹: (*A*, *B*, *C* subgroup origins)

$^6H_{11/2}$; $E\sim 5800$ cm⁻¹: (*C* subgroup terminus)

$^6H_{13/2}$; $E\sim 3500$ cm⁻¹: (*B* subgroup terminus)

$^6H_{15/2}$; $E\sim 000$ cm⁻¹: (*A* subgroup terminus).

TABLE II. Crystal-field splittings and allowed transitions in O_h field[a] [$\Gamma_6 \leftrightarrow \Gamma_7$ transition forbidden].

State	Crystal-field split representations	Transitions to $^6F_{11/2}$ state		Total number allowed transitions to $^6F_{11/2}$ state		
		$^6H_{15/2}$	$^6F_{11/2}$		(Observed)	Dev.
$^6H_{15/2}$	$\Gamma_6, \Gamma_7, \Gamma_8, \Gamma_8, \Gamma_8$	Γ_6	Γ_6	$20-2=18$	(17)	−1
		Γ_7	Γ_7			
		Γ_8	Γ_8			
		Γ_8	Γ_8			
		Γ_8				
		$^6H_{13/2}$	$^6F_{11/2}$			
$^6H_{13/2}$	$\Gamma_6, \Gamma_7, \Gamma_7, \Gamma_8, \Gamma_8$	Γ_6	Γ_6	$20-3=17$	(16)	−1
		Γ_7	Γ_7			
		Γ_7				
			Γ_8			
		Γ_8	Γ_8			
		Γ_8				
		$^6H_{11/2}$	$^6F_{11/2}$			
$^6H_{11/2}$	$\Gamma_6, \Gamma_7, \Gamma_8, \Gamma_8$	Γ_6	Γ_6	$16-2=14$	(15)	+1
		Γ_7	Γ_7			
		Γ_8	Γ_8			
		Γ_8	Γ_8			

[a] See Ref. 5.

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[6] W. Low, Proc. Phys. Soc. (London) **76**, 307 (1960).

[7] G. H. Dieke and S. Singh, J. Opt. Soc. Am. **46**, 495 (1956); and G. H. Dieke, H. M. Crosswhite, and B. Dunn, *ibid.* **51**, 826 (1961).

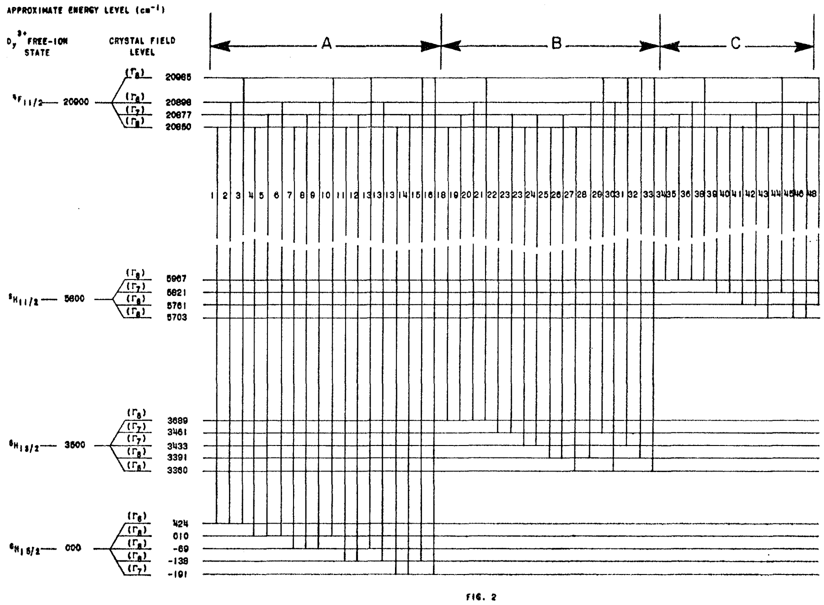

FIG. 2. O_h-crystal-field energy-level scheme in accordance with fluorescence frequencies observed for Spectrum I of Dy^{3+} in CaF_2.

The approximate numbers of the lines listed in Table I are those expected for transitions between levels of these free-ion states split (cf Table II) by a crystal field of O_h symmetry using the group-theory splittings and selection rules for $J=11/2$, $13/2$, $15/2$ free-ion states. The maximum theoretically allowed number of transitions (cf Table II) according to group theory for subgroups A, B, and C (using the above J-value assignments) are 18, 17, and 14 lines, respectively, compared with the observed numbers of 17, 16, and 15 lines (Table I.)

Using the data listed in Table II for O_h symmetry, energy level schemes (Fig. 2) are deduced which correspond to the observed frequencies to within 3 cm^{-1} (Table III). These schemes (Fig. 2) seem quite unique for the observed frequencies and may be used to give the level energies and group theory representations[5] of the crystal-field levels. The above appears to be strong evidence in support of O_h symmetry for Spectra I of Dy^{3+} in CaF_2. This energy level scheme type of check may be helpful in finding or corroborating the crystal-field symmetry in other such crystals.

The general characteristics of Spectra II of Dy^{3+} in CaF_2 which show[1] many more lines than Spectrum I in the same spectral locations, tend to support the notion that the crystal-field symmetry of Spectra II is of a lower symmetry than O_h, allowing greater crystal field splittings of the same Dy^{3+} free-ion states given[7] above, with a consequently greater number of theoretically allowable transitions.[2,5]

Note added in proof. Since the writing of this paper, it has come to the attention of the author that investigations by R. W. Bierig and M. J. Weber of the EPR spectrum of Dy^{3+} in CaF_2 at liquid helium temperature have indicated Γ_8 and not Γ_7 (as reported previously in Ref. 6 by Low) to be the ground state of the cubic-field type crystals. In addition, other EPR resonances due to ions of Dy^{3+} in CaF_2 sites of tetragonal and trigonal local crystal-field symmetries have been reported by these authors. As indicated in this paper, such crystals of lower symmetry spectra are probably associated with type II crystals of Dy^{3+} in CaF_2.

Bierig and Weber have also suggested that the crystal field of Sm^{3+} in CaF_2 may be trigonal or tetragonal (instead of the C_2 and C_3 symmetries proposed previously in Refs. 1 and 2).

In Ref. 2 it had been indicated that Spectrum I originated from four crystal-field-split levels of the second lowest fluorescent state of Sm^{3+} labeled as a $J=\frac{7}{2}$ state, effectively. Now, according to Fig. 2 of Ref. 2, the two states adjacent to $J=\frac{7}{2}$ (labeled $J=\frac{5}{2}$ and $\frac{9}{2}$) have energy separations from the $J=\frac{7}{2}$ state comparable with the crystal-field-split energy splittings of the $J=\frac{7}{2}$ state itself. In such cases where the crystal-field splittings are comparable with separations between free-ion states, J is no longer a good quantum number due to mixing of free-ion states (here the mixing of $J=\frac{5}{2}$ and $\frac{9}{2}$ states with the $J=\frac{7}{2}$ state). The simple group-theoretical analysis based on the splitting an unmixed J state should then be modified for a precise solution; in the above Dy^{3+} case where the crystal-field splittings are small this simple group theory method is precise.

ACKNOWLEDGMENT

I am grateful for the support of the authors of Ref. 4, and in particular to T. Ewanizky for the spectrograms.

TABLE III. Deviation of frequencies of energy-level schemes from frequencies observed (cm^{-1}).

Line	Exp.	Scheme	Dev.
1	20 429	20 426	−3
2	20 475	20 474	−1
3	20 559	20 561	2
4	20 838	20 840	2
5	20 868	20 867	−1
6	20 890	20 888	−2
7	20 921	20 919	−2
8	20 947	20 946	−1
9	20 969	20 967	−2
10	20 978	20 975	−3
11	20 991	20 988	−3
12	21 017	21 015	−2
13	21 053–40	21 054, 41, 36	1, 0, −4
14	21 070	21 068	−2
15	21 119	21 123	4
16	21 177	21 176	−1
17	21 200		
18	17 161	17 161	0
19	17 185	17 188	3
20	17 212	17 209	−3
21	17 298	17 296	−2
22	17 388	17 389	1
23	17 416	17 416, 17	0, 1
24	17 446	17 444	−2
25	17 461	17 459	−2
26	17 486	17 486	0
27	17 492	17 490	−2
28	17 507	17 507	0
29	17 525	17 524	−1
30	17 535	17 538	3
31	17 550	17 552	2
32	17 593	17 594	1
33	17 627	17 625	−2
34	14 883	14 883	0
35	14 910	14 910	0
36	14 932	14 931	−1
37	14 943		
38	15 020	15 019	−1
39	15 029	15 029	0
40	15 056	15 056	0
41	15 090	15 089	−1
42	15 135	15 137	2
43	15 147	15 147	0
44	15 164	15 163	−1
45	15 175	15 174	−1
46	15 195	15 195	0
47	15 211		
48	15 223	15 224	1

APPENDIX: NOTES TO TABLE I

Referring to Fig. 1, the lines of Subgroup *B* are the strongest and those of Subgroup *C*, the weakest (on the average). The strength of a line relative to others in the same subgroup is indicated by the letters: *S*-stronger, *W*-weaker, and *WW*-much weaker. Broad lines are denoted by letters: *B*-broad and *BB*-very broad; such broad lines have an observed accuracy which is less than that of the other lines, which are all sharp.

In Subgroup *A*, line No. 3 at 4864 Å is indicated in Fig. 1(A); it was obscured by the light background.

In Subgroup *B*, Fig. 1(B) shows a very weak mercury line (M_1) at 5790 Å [Fig. 1(D)].

In Subgroup *C*, Fig. 1(C) shows weak mercury lines (M_2) at 6716 Å and a second-order mercury line 3341.5 Å at 6683 Å (M_3). These were also indicated in spectrograms not shown here. In the region between line Nos. 41 and 42, there appears to be two very weak lines (labeled '*V*') at 6616 Å and 6620 Å. Line No. 37 [6692 Å] which is unaccounted for in Fig. 2, may have originated from lines of the exciting ultraviolet source [which had a filter transparent to the long-wavelength part of the spectrum] which are suspected to have shown up on the spectrograms at wavelengths >6683 Å.

The scheme (in Fig. 2) for Subgroup *C* and for the $^6H_{11/2}$ state is considered uncertain due to the number of unaccounted-for lines in Subgroup *C*, which may be due to the general weak intensity of the lines of Subgroup *C*; as it is possible that the lines of Dy^{3+} for Subgroup *C* had the same intensity as lines not due to Dy^{3+}. For example, it is possible that, if line no. 35 was due to the exciting source while the possible line indicated (*V*) above at 6616 Å actually exists, and is due to Dy^{3+}, the Γ_8 and Γ_6 designations for the levels, respectively, at 5967 and 5761 cm^{-1} would be interchanged [since 6616 Å equals 15115 cm^{-1}, and the transition would be: 20877 → 5761 cm^{-1}]. The result in this case is that the 5967 cm^{-1} level would have no transition to the $^4F_{11/2}$, (Γ_7) 20877 cm^{-1} level indicating Γ_6 for the 5967 cm^{-1} level; and the 5761 cm^{-1} level would have transitions to all the levels of the $^4F_{11/2}$ state indicating it to be Γ_8.

The unaccounted-for weak lines Nos. 17 and 47 may be vibrational lines. Lines Nos. 29 and 30, Nos. 9 and 10 which appear as a single one in Fig. 1 were resolved on weaker spectrograms (not shown). Line No. 13 appeared broadened by a weaker component ~4750 Å on stronger spectrograms than Fig. 1(A) [cf. Fig. 1(E)].

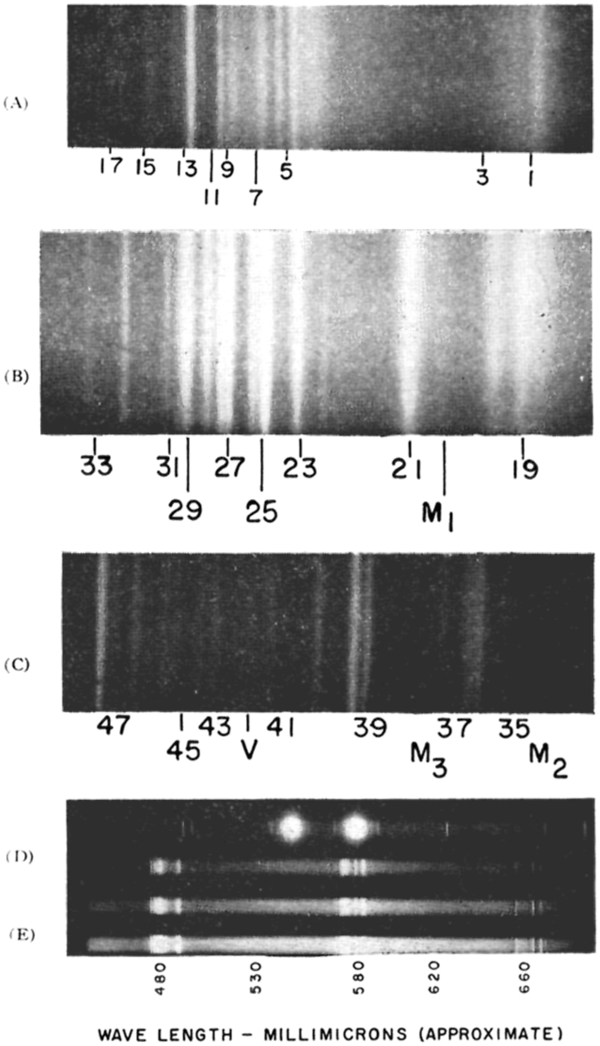

FIG. 1. Fluroescence of Dy^{3+} in CaF_2, Spectrum I. The line numbers are identified in Table I. (A) Enlargment of the spectrogram of Subgroup *A*. (B) Enlargement of the spectrogram of Subgroup *B*. (C) Enlargement of the spectrogram of Subgroup *C*. (D) Mercury comparison spectrogram. (E) Spectrograms showing the relative positions and intensities of Subgroups *A*, *B*, and *C*.