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NOTES

Fluorescence of Sm^{3+} in CaF_2

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(Received 27 November 1962)

JUL 9 1963

The fluorescent "Spectra I and II" of Sm^{3+} in CaF_2 , consisting of approximately eighty lines, are found to fall naturally into six subgroups each of which has a mean frequency tending to identify it as a set of transitions between the crystal field split levels of one upper fluorescent and one lower ground multiplet free-ion state of known energies. Substantiation of the free-ion origins of these six subgroups is obtained by deducing crystal field energy level schemes, based on the group theoretical symmetry surrounding the Sm ion, which are in accord with the frequencies of the eighty observed lines to within the experimental tolerance of 5 cm^{-1} , maximum. This preliminary analysis indicates that Spectrum II originates from the lowest fluorescent state, $^4F_{5/2}$, and that Spectrum I originates from the second lowest fluorescent state.

INTRODUCTION

present, the theory of the spectra of trivalent rare-earth doped fluorite crystals has not been entirely established. In a significant experimental study¹ the fluorescent line spectra of fluorite crystals activated by rare earth trivalent ions had been observed to fall into two groups called "Spectrum I" and "Spectrum II," which have qualitative similarities. However, the theoretical basis for these two groups is not completely known. Therefore, some preliminary analysis of "Spectra I and II" for one trivalent rare earth would be useful; and it is the main purpose of this paper to indicate the energy level origins for the Sm^{3+} in CaF_2 fluorescent "Spectra I and II." The basis for this analysis will be the spectrograms obtained in a recent investigation² in which approximately eighty fluorescent lines of Sm^{3+} in CaF_2 were photographed at liquid nitrogen temperature (three of these spectrograms³ are shown in Fig. 1).

Using the known energies of the free-ion Russell-Saunders states of Sm^{3+} and the symmetry characteristics of the crystalline electric field about the Sm^{3+} ion in CaF_2 , unique crystal field energy level schemes will be derived which account for the eighty observed lines to within their experimental accuracy of 5 cm^{-1} maximum deviation. The crystalline electric field is much smaller than the spin-orbit interaction in rare earths, and thus, it can be considered as a perturbation which splits a single Russell-Saunders (R-S) state but does not mix different R-S states. Therefore, group theory can easily be used to find the amount of the crystal field splitting of any Russell-Saunders free-ion state and the allowed transitions between such crystal

field split levels. The resulting energy level schemes point to the lowest and second lowest 4F fluorescent free-ion states as the origins of "Spectra II and I", respectively, for Sm^{3+} in CaF_2 .

EXPERIMENTAL PROCEDURES

Referring to Fig. 1, the first spectrogram, which resembles Spectrum I, records the fluorescent spectrum of a light green crystal of Sm^{3+} in CaF_2 with about 0.001 mole % of Sm . The second spectrogram records the fluorescent spectrum of Sm^{2+} , mixed with some Sm^{3+} , in CaF_2 for comparison; and it shows the spectrum of Sm^{2+} , at frequencies³ greater than $6830 \text{ \AA}$, in addition to some of the Sm^{3+} Spectra I and II. The third spectrogram was obtained from a colorless crystal of Sm^{3+} in CaF_2 and resembles Spectrum II. Upon comparison with the second spectrogram, the first and third spectrograms are seen to have Sm^{2+} lines (greater than $6830 \text{ \AA}$); evidently, this is due to amounts of Sm^{2+} in the light green crystal and traces of Sm^{2+} in the colorless crystal which are insufficient to give it any color. The spectrograms³ of Fig. 1 came from a diffraction grating having a linear dispersion averaging $19.5 \text{ \AA/mm}$. On other such spectrograms having shorter exposures the intense overexposed lines of Fig. 1 appear much narrower and sharper.

The frequencies of the Sm^{3+} in CaF_2 lines of the first and third spectrograms of Fig. 1 are listed in Table I as Spectrum I and Spectrum II, respectively, under three subgroups to an accuracy better than 5 cm^{-1} . The subgroups of Spectrum I, i.e., A, B, and C, have mean frequencies which are approximately 300 cm^{-1} less than the mean frequencies of the corresponding subgroups of Spectrum II, i.e., A', B', and C'.

FREE-ION STATES

Based on this frequency shift and the known energies of free-ion states it is possible to identify the subgroups of Spectrum I and Spectrum II as transitions between the crystal field split levels of one of the lowest two of three excited fluorescent states, and the appropriate three of the five nearly equally spaced states of the

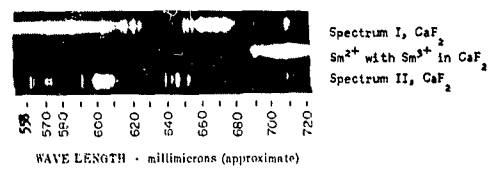


FIG. 1. Fluorescence of Sm^{3+} in CaF_2 .

¹ I. V. Stepanov and P. P. Feofilov, Doklady Akad. Nauk I, 340 (1957).
² H. H. Thelma, P. J. Caplan, T. Ewanizky, and G. de Lhery, Applied Optics (to be published).

³ D. L. Wood and W. Kaiser, Phys. Rev. 126, 2079 (1962).

TABLE I. Frequencies of fluorescent lines of Sm^{3+} in CaF_2 *

Spectrum I			Spectrum II		
Line	λ (Å)	$\bar{\nu}$ (cm^{-1})	Line	λ (Å)	$\bar{\nu}$ (cm^{-1})
I—C			II—C'		
B1	6802	14 702	W52	6549	15 270
B2	6775	14 760	S53	6537	15 298
B3	6764	14 784	W54	6517	15 344
S4	6747	14 821	W55	6507	15 368
S5	6721	14 879	W56	6494	15 399
S6	6699	14 928	S57	6477	15 440
S7	6662	15 011	S58	6468	15 461
S8	6650	15 039	W59	6450	15 504
S9	6639	15 063	S60	6438	15 533
S10	6623	15 099	S61	6402	15 620
S11	6614	15 119	S62	6372	15 694
B12	6595	15 163	II—B'		
W13	6586	15 184	W63	6121	16 337
S14	6565	15 232	S64	6093	16 412
S15	6562	15 239	S65	6069	16 477
W16	6555	15 256	S66	6056	16 513
S17	6537	15 298	S67	6040	16 556
S18	6529	15 316	68	6029	16 586
S19	6516	15 347	69	6015	16 625
W20	6491	15 406	S70	5999	16 669
W21	6472	15 451	W71	5934	16 852
I—B			W72	5920	16 892
B22	6446	15 513	S73	5908	16 926
B23	6354	15 738	II—A'		
B24	6306	15 858	S74	5665	17 652
B25	6268	15 954	W75	5656	17 680
B26	6255	15 987	W76	5643	17 721
S27	6250	16 000	S77	5621	17 790
S28	6219	16 080	S78	5605	17 841
B29	6198	16 134	S79	5598	17 864
S30	6177	16 189	S80	5583	17 912
S31	6168	16 213	Diffuse group		
S32	6149	16 263	~5716	~17 495	
W33	6137	16 295	~5724	~17 470	
S34	6088	16 426	~5733	~17 443	
S35	6069	16 477			
36	6057	16 510			
S37	6040	16 556			
I—A					
38	5906	16 933			
S39	5851	17 091			
B40	5837	17 132			
B41	5823	17 173			
B42	5789	17 274			
43	5744	17 409			
44	5735	17 437			
45	5728	17 458			
S46	5723	17 473			
S47	5711	17 511			
S48	5678	17 612			
W49	5674	17 624			
W50	5663	17 658			
W51	5649	17 702			

* In Fig. 1, Spectrum I spectrogram, the following eight weak lines are not accounted for by Fig. 2(b). Subgroup A: 5683 Å, 5800 Å (B), 5919 Å, Subgroup B: 6029 Å, 6122 Å (B), 6362 Å, Subgroup C: 6477 Å, 6837 Å (B). In the Fig. 1 Spectrum II spectrogram, the several diffuse lines in the "Diffuse" subgroup of Table I are excluded from subgroup A' which comprises sharp lines. The weak line 5945 Å of subgroup B' is not accounted for by Fig. 2(c). The letters preceding the line numbers indicate the following relative line strengths. S-strong; W-weak; B-broad and weak. The spectrograms of Fig. 1 all show a second order 3341.5 Å mercury line at 6683 Å.

^b The unaccounted-for lines of one spectrum may possibly be due to lines from centers of the other spectrum present. For example, the "diffuse" group (Spectrum II) may be connected with the five lines of Spectrum I ranging from 5711 to 5742 Å; while the lines 5919 and 6477 Å, that are unaccounted for in Spectrum I, may be identical with the 5920 Å and 6477 Å (S) lines of Spectrum II, Table I. Also, the lines 6029, 6040, 6057, and 6069 Å all occur both in Subgroup B of Spectrum I and Subgroup B' of Spectrum II; if any of these four pairs of lines is not really two lines, it would help to explain the unaccounted-for lines both in Subgroups B and B'. Some of the unaccounted-for lines may be due to transitions from the

ground (6H) multiplet of the $4f$ configuration of Sm^{3+} [Fig. 2(a)]. Then, using the group theoretically predicted amount of splittings of the free-ion states in crystal fields of known symmetry about the Sm^{3+} ion in CaF_2 , crystal field energy levels consistent with the observed fluorescent frequencies can be deduced; this further substantiates that these free-ion states are the origins of the subgroups of Spectrum I and Spectrum II.

The approximate numbers and frequencies of the lines in Table I are those expected for transitions between the crystal field split levels of the upper three fluorescent free-ion states and the free-ion states of the ground (6H) multiplet. The energies of all of these free-ion states have been approximately established in the literature. In the (6H) ground multiplet the $J=7/2$, $9/2$, $11/2$, and $13/2$ states are approximately 1200, 2400, 3500, and 4800 cm^{-1} above the ($^6H_{5/2}$) ground state.⁴ The first fluorescent state $^4F_{5/2}$ is approximately 17 800 cm^{-1} above ground; the second and third fluorescent states (unidentified) are approximately 18 700 and 19 900 cm^{-1} above the $^6H_{5/2}$ ground state.⁴ The three sets of transitions between the $^4F_{5/2}$ and the $J=5/2$, $7/2$, and $9/2$ states of the 6H multiplet, are consistent with the average observed frequencies (Table I) of the three subgroups of Spectrum II. Transitions from either of the other two fluorescent states to any free-ion state of the ground multiplet do not have frequencies corresponding to those of Spectrum II [Fig. 2(a)]. Thus, these three sets of transitions appear to be the origin of the subgroups of Spectrum II.

Referring to Fig. 2(a), Spectrum I is shown to originate only from either of the two highest fluorescent free-ion states, since the observed frequencies of Spectrum I (Table I) are in accord with these transitions, but do not correspond to those obtained for transitions between the $^4F_{5/2}$ lowest fluorescent state and any state of the ground multiplet. In addition, it will be shown that the number of lines observed for Spectrum I (Table I) are less than could arise theoretically from a $J=7/2$ fluorescent state, but are much greater than the maximum theoretically allowed using $^4F_{5/2}$.

CRYSTAL FIELD SPLITTINGS

First, a maximum crystal field splitting is assumed, i.e., the crystal field is assumed to remove half of the degeneracy of each of the free-ion states leaving only Kramers' degeneracy, which cannot be lifted by only an electric field in an atom with an odd number of electrons. Second, all transitions between these crystal field split levels are assumed to be allowed, giving the maximum number of transitions. Then, the resulting crystal

⁴ G. H. Dieke, H. M. Crosswhite, and B. Dunn, J. Opt. Soc. Am. 51, 826 (1961), and references therein.

highest fluorescent state (dashed in Fig. 2(a)). If some lines of Table I do not originate from the identified fluorescent levels, (Fig. 2), e.g., vibrational lines, different energies than now assigned to the pertinent crystal-field-split 4H energy levels might be consistent with now unaccounted-for lines. Some unaccounted-for lines may be due to Sm^{3+} centers which are present [e.g., 6837 Å (B)]. In any case, the unaccounted-for lines are among the weakest observable lines on the spectrograms.

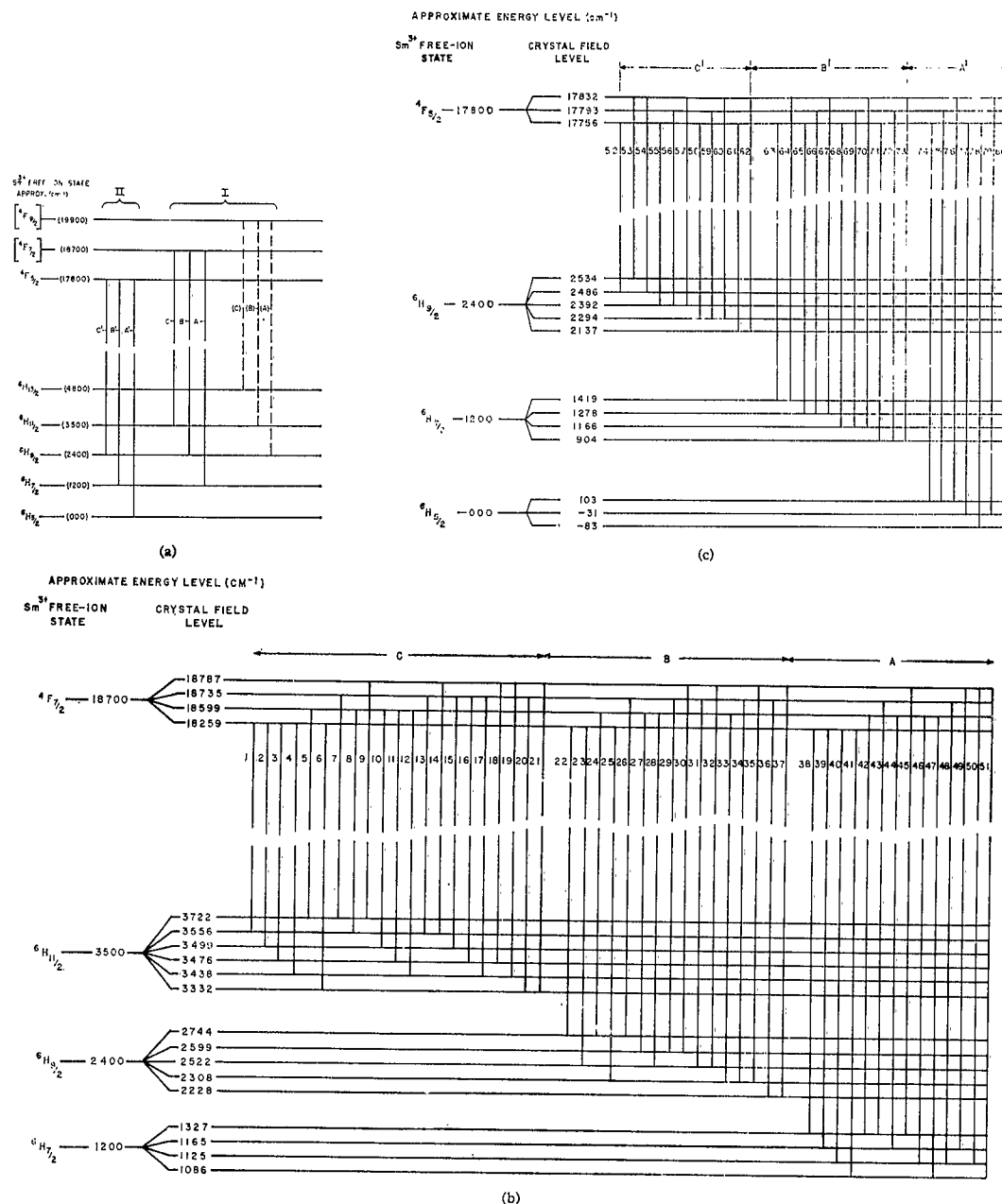


FIG. 2(a) Free-ion Sm^{3+} energy level schemes in accord with fluorescence frequencies of Spectra I and II of Sm^{3+} in CaF_2 . (b) Crystal field energy level schemes in accord with fluorescence frequencies, Spectrum I of Sm^{3+} in CaF_2 . (c) Crystal field energy level schemes in accord with fluorescence frequencies, Spectrum II of Sm^{3+} in CaF_2 .

field splittings are for the upper or lower $J=5/2$ state, a threefold splitting; for an upper or lower $J=7/2$ state, a fourfold splitting, and for a $J=9/2$ state, a fivefold splitting, etc. The resulting maximum number of allow-

able transitions, assuming no forbidden transitions, and using only the $4F_{5/2}$ fluorescent state are: nine, twelve, and fifteen for the A' , B' , and C' subgroups, respectively, which is far short of the observed number

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

Line	Exper.	Scheme	Dev.	Line	Exper.	Scheme	Dev.
1	14 702	14 703	1	41	17 173	17 173	0
2	14 760	14 760	0	42	17 274	17 272	-2
3	14 784	14 783	-1	43	17 409	17 408	-1
4	14 821	14 821	0	44	17 437	17 434	-3
5	14 879	14 877	-2	45	17 458	17 460	2
6	14 928	14 927	-1	46	17 473	17 474	1
7	15 011	15 013	2	47	17 511	17 513	2
8	15 039	15 043	4	48	17 612	17 610	-2
9	15 063	15 065	2	49	17 624	17 622	-2
10	15 099	15 100	1	50	17 658	17 662	4
11	15 119	15 123	4	51	17 702	17 701	-1
12	15 163	15 161	-2	52	15 270	15 270	0
13	15 184	15 179	-5	53	15 298	15 298	0
14	15 232	15 231	-1	54	15 344	15 346	2
15	15 239	15 236	-3	55	15 368	15 364	-4
16	15 256	15 259	3	56	15 399	15 401	2
17	15 298	15 297	-1	57	15 440	15 440	0
18	15 316	15 311	-5	58	15 461	15 462	1
19	15 347	15 349	2	59	15 504	15 499	-5
20	15 406	15 403	-3	60	15 533	15 538	5
21	15 451	15 455	4	61	15 620	15 619	-1
22	15 513	15 515	2	62	15 694	15 695	1
23	15 738	15 737	-1	63	16 337	16 337	0
24	15 858	15 855	-3	64	16 412	16 413	1
25	15 954	15 951	-3	65	16 477	16 478	1
26	15 987	15 991	4	66	16 513	16 515	2
27	16 000	16 000	0	67	16 556	16 554	-2
28	16 080	16 077	-3	68	16 586	16 590	4
29	16 134	16 136	2	69	16 625	16 627	2
30	16 189	16 188	-1	70	16 669	16 666	-3
31	16 213	16 213	0	71	16 852	16 852	0
32	16 263	16 265	2	72	16 892	16 889	-3
33	16 295	16 291	-4	73	16 926	16 928	2
34	16 426	16 427	1	74	17 652	17 648	-4
35	16 477	16 479	2	75	17 680	17 685	5
36	16 510	16 507	-3	76	17 721	17 724	3
37	16 556	16 559	3	77	17 790	17 787	-3
38	16 933	16 932	-1	78	17 841	17 839	-2
39	17 091	17 094	3	79	17 864	17 863	-1
40	17 132	17 134	2	80	17 912	17 915	3

of lines for Spectrum I, although sufficient for Spectrum II. However, it is apparent that the resulting maximum number of allowable transitions similarly computed for a $J=7/2$ fluorescent upper state to a lower $J=7/2, 9/2$, and $11/2$ set of lower states are sixteen, twenty, and twenty-four for A, B, and C, respectively, thus slightly exceeding the observed number of frequencies of Spectrum I. Thus, transitions from the second (or possibly third) highest fluorescent state having a $J>5/2$ value seem likely to be the origin of Spectrum I. The most likely situations are assumed⁵ as examples in Figs. 2(a) and 2(b), i.e., that the second fluorescent state is $^4F_{7/2}$ and is the origin of nearly all of Spectrum I, and that the third fluorescent state is $^4F_{9/2}$, which may contribute a few weak lines to Spectrum I.

Referring to Fig. 2(c) and to Table II, it is apparent that almost all of the observed frequencies of Spectrum II can be accounted for by a unique set of crystal field energy levels split from the $^4F_{5/2}$ and $J=5/2, 7/2$ and

⁵ The $^4F_{7/2}$ assignment although the most likely for the second upper fluorescent states is not proven. However, if Spectrum I is assumed to originate from a $J>7/2$ fluorescent state the resulting additional crystal-field-split levels would more than account for all the observed lines to within 5 cm^{-1} .

$9/2$ states of the 6H ground multiplet by a crystalline electric field about the ion having a symmetry sufficient to remove all but Kramers' degeneracy from these states. It seems likely¹ that such is the type of symmetry. One symmetry group which would accomplish this is an Abelian group. Now, the C_3 and C_2 symmetries are Abelian groups which are likely to be the symmetries of Spectra I and II.

C_2 may be justified as the symmetry of such crystals where two Sm^{3+} ions can replace three Ca^{2+} ions in three cubes of F^- neighbors, allowing four possible arrangements of three adjacent $8F^-$ cubes with central Ca each. Of these four possible arrangements, the one with the three cubes all on a line going through the center and midpoints of opposite edges of all three cubes is the most symmetrical giving C_2 , the theoretical symmetry of the field about the ion.

In crystals made with oxygen not completely excluded, O^{2-} can replace one of eight fluorine (F^-) neighbors of the ion, effecting charge compensation, with the seven remaining neighbors each moving on a line connecting it with the rare earth ion; and the rare earth ion itself moves on a line connecting it with the newly instituted O^{2-} . Here, C_3 is the resultant symmetry.¹ Since C_3 is an Abelian group, all but Kramers' degeneracy is lifted for all the free-ion states.

It can be assumed that Spectrum I is due to transitions originating from the levels of the second highest fluorescent free-ion state split by the crystal field. This assumption may be justified by the results obtained thereby, i.e., that the crystal-field-split levels of the states involved can be assigned energies to account for the observed frequencies.

Referring to Fig. 2(b), in which the second highest fluorescent state is assigned a $J=7/2$ value, almost all the observed lines are accounted for, and almost all the level energies are defined uniquely to within the tolerance of 5 cm^{-1} (Table II). Some of the weak unaccounted-for lines (see Table I) may, in this case, originate from the highest fluorescent state.⁶ It is to be noted that the group theoretically derived selection rules for the assumed symmetries of C_3 and C_2 give no forbidden transitions between any of the crystal field split levels of the free-ion states having any of the J values mentioned herein.⁶ The lines predicted assuming all transi-

⁶ The derivation of the selection rules is based on the fact that the transition probability is proportional to the square of the matrix element of the perturbation for electric or magnetic dipole radiation connecting the two states in question, i.e., transition probability $\propto |\int \psi_A H' \psi_B dT|^2$ where the two states are ψ_A and ψ_B and the dipole operator is H' . The transition probability is nonzero for allowed transitions only between those two states for which the above matrix element is nonzero. To find such allowed transitions, one may use group theory by employing a theorem which states that the wave functions of two different irreducible representations of a symmetry group are orthogonal. Thus, to determine the nonzero values of the above matrix element we note that ψ_B belongs to a particular representation of the symmetry group, H' belongs to another representation of the group, and thus the direct product $H' \times \psi_B$ must belong also to a representation of the symmetry group, say ψ_C . The matrix element reduces to $\int \psi_A \psi_C dT$ and, therefore, is nonzero only if there is

tions allowed and not experimentally observed [not shown in Figs. 2(b) and 2(c)] may be too weak to be recorded on the spectrograms.⁷

CONCLUSIONS

Spectrum II of Sm^{3+} in CaF_2 originates from transitions between the crystal-field-split levels of the $^4F_{5/2}$

some component irreducible representation of ψ_A which is the same as at least one component irreducible representation of ψ_C . In practice, all the above (including decomposition of ψ_A and ψ_C into component irreducible representations) is done using the table of characters of the particular symmetry group.

⁷ Also, there may be masking of such lines expected (in Fig. 2) by the background of light in certain regions on the spectrograms, e.g., $18\,599 \rightarrow 2228\text{ cm}^{-1}$ and $18\,259 \rightarrow 2599\text{ cm}^{-1}$ transitions in Subgroup B, are in such background regions of the Spectrum I spectrograms.

state and those of the $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ states of the free ion. Spectrum I originates from transitions between the crystal-field-split levels of the second, and possibly the third, highest free-ion fluorescent state and those of the ground multiplet (6H) states.

The energies of crystal field split levels of the fluorescent states from which Spectra I and II originate are determined uniquely (to within 5 cm^{-1}) by the observed fluorescent frequencies.

ACKNOWLEDGMENTS

I gratefully acknowledge the help of the authors of reference 2 and, in particular, T. Ewanizky who made the spectrograms.