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Fluorescence of Sm^{3+} in CaF_2

Norman Rabbiner
U. S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey

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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

At present, the theory of the spectra of trivalent rare-earth doped fluorite crystals has not been entirely established. In a significant experimental study[1] 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 investigation[2] in which approximately eighty fluorescent lines of Sm^{3+} in CaF_2 were photographed at liquid nitrogen temperature (three of these spectrograms[2] 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.

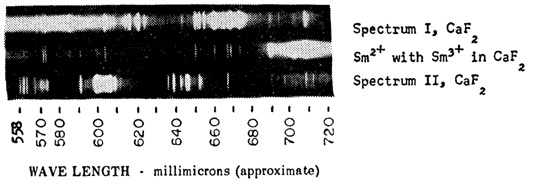

FIG. 1. Fluorescence of Sm^{3+} in CaF_2.

EXPERIMENTAL PROCEDURES

Referring to Fig. 1, the first spectrogram, which resembles[1] 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 frequencies[3] greater than 6830 Å, 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[1] Spectrum II. Upon comparison with the second spectrogram, the first and third spectrograms are seen to have Sm^{2+} lines (greater than 6830 Å); 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 spectrograms[2] of Fig. 1 came from a diffraction grating having a linear dispersion averaging 19.5 Å/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

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[1] I. V. Stepanov and P. P. Feofilov, Doklady Akad. Nauk **1**, 350 (1957).

[2] H. H. Theissing, 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).

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 $^4F_{5/2}$.

TABLE I. Frequencies of fluorescent lines of Sm^{3+} in CaF$_2$.[a]

Spectrum I			Spectrum II		
Line	λ (Å)	$\tilde{\nu}$ (cm^{-1})	Line	λ (Å)	$\tilde{\nu}$ (cm^{-1})
	I—*C*			II—*C*′	
*B*1	6802	14 702	*W*52	6549	15 270
*B*2	6775	14 760	*S*53	6537	15 298
*B*3	6764	14 784	*W*54	6517	15 344
*S*4	6747	14 821	*W*55	6507	15 368
*S*5	6721	14 879	*W*56	6494	15 399
*S*6	6699	14 928	*S*57	6477	15 440
*S*7	6662	15 011	*S*58	6468	15 461
*S*8	6650	15 039	*W*59	6450	15 504
*S*9	6639	15 063	*S*60	6438	15 533
*S*10	6623	15 099	*S*61	6402	15 620
*S*11	6614	15 119	*S*62	6372	15 694
*B*12	6595	15 163			
*W*13	6586	15 184		II–*B*′	
*S*14	6565	15 232	*W*63	6121	16 337
*S*15	6562	15 239	*S*64	6093	16 412
*W*16	6555	15 256	*S*65	6069	16 477
*S*17	6537	15 298	*S*66	6056	16 513
*S*18	6529	15 316	*S*67	6040	16 556
*S*19	6516	15 347	68	6029	16 586
*W*20	6491	15 406	69	6015	16 625
*W*21	6472	15 451	*S*70	5999	16 669
			*W*71	5934	16 852
	I—*B*		*W*72	5920	16 892
*B*22	6446	15 513	*S*73	5908	16 926
*B*23	6354	15 738			
B24	6306	15 858		II—*A*′	
*B*25	6268	15 954	*S*74	5665	17 652
*B*26	6255	15 987	*W*75	5656	17 680
*S*27	6250	16 000	*W*76	5643	17 721
*S*28	6219	16 080	*S*77	5621	17 790
*B*29	6198	16 134	*S*78	5605	17 841
*S*30	6177	16 189	*S*79	5598	17 864
*S*31	6168	16 213	*S*80	5583	17 912
*S*32	6149	16 263			
*W*33	6137	16 295		Diffuse group	
*S*34	6088	16 426		~5716	~17 495
*S*35	6069	16 477		~5724	~17 470
36	6057	16 510		~5733	~17 443
*S*37	6040	16 556			
	I—*A*				
38	5906	16 933			
*S*39	5851	17 091			
*B*40	5837	17 132			
*B*41	5823	17 173			
*B*42	5789	17 274			
43	5744	17 409			
44	5735	17 437			
45	5728	17 458			
*S*46	5723	17 473			
*S*47	5711	17 511			
*S*48	5678	17 612			
*W*49	5674	17 624			
*W*50	5663	17 658			
*W*51	5649	17 702			

[a] In Fig. 1, Spectrum I spectrogram, the following eight weak lines are not accounted[b] 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[b] from subgroup A′ which comprises sharp lines. The weak line 5945 Å of subgroup B′ is not accounted[b] 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 pair 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 highest fluorescent state (dashed in Fig. 2(a). If some lines of Table I do not originate from the identicated fluorescent levels, (Fig. 2), e.g., vibrational lines, different energies than now assigned to the pertinent crystal-field-split ^6H energy levels might be consistent with now unaccounted-for lines. Some unaccounted-for lines may be due to Sm^{2+} 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.

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

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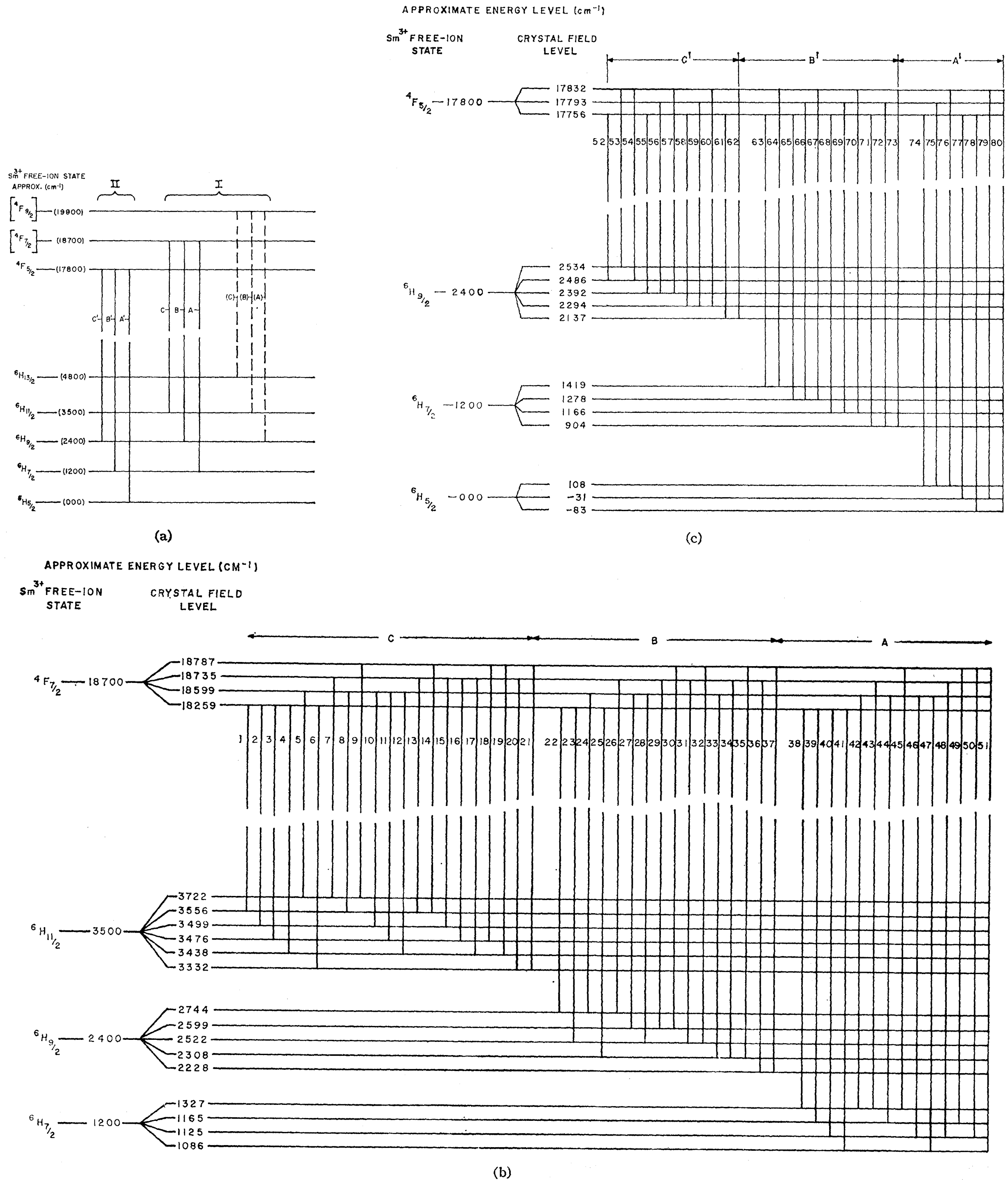
[4] G. H. Dieke, H. M. Crosswhite, and B. Dunn, J. Opt. Soc. Am. **51**, 826 (1961), and references therein.



(a)

(c)

(b)

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

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[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}.

[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 $^4F_{5/2}$ 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

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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 → 2228 cm^{-1} and 18 259 → 2599 cm^{-1} transitions in Subgroup B, are in such background regions of the Spectrum I spectrograms.

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Covalency Effects in $KNiF_3$. I. Nuclear Magnetic Resonance Studies

R. G. SHULMAN
Bell Telephone Laboratories, Murray Hill, New Jersey

AND

S. SUGANO
The Institute for Solid State Physics, The University of Tokyo, Azabu Minato ku, Tokyo, Japan
and
Bell Telephone Laboratories, Murray Hill, New Jersey

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A nuclear magnetic resonance study of the F^{19} resonance in a single crystal of $KNiF_3$ is reported. The internal fields at the fluorine nuclei were measured. Interpretation of the measured fields showed that the spin densities in the fluorine $2s$ and $2p\sigma$ orbitals were $(0.538\pm0.05)\%$ and $(3.78\pm0.2)\%$, respectively. A comparison with the $KMnF_3$ measurements, where $p\pi$ interactions are allowed, indicated the importance of $p\pi$ bonding in these crystals. It is shown that only a model which allows the $2s$, $2p\sigma$, and $2p\pi$ electrons individual degrees of covalency can explain the observations.

I. INTRODUCTION

It is the purpose of this series of papers to present a detailed study of d-electron covalency in a specific example, i.e., a $KNiF_3$ crystal. For this purpose, we have studied experimentally the nuclear magnetic resonance (NMR) of the fluorine and the optical spectrum. The former experiment measures the covalency directly, while the latter determines parameters such as the cubic crystal field splitting which depend upon the covalency. These two experimental studies shall be presented in parts I and II of this series. In part III, a theoretical calculation will be made of the observed quantities such as the NMR frequency shift and the cubic field splitting parameter. The theory is based on the molecular orbital (MO) model of Van Vleck,[1] and will be shown to be very successful.

Previous[2] nuclear magnetic resonance studies of the fluorine nuclei in magnetic crystals have shown the presence of large internal magnetic fields at the fluorine nuclei. These fields arise mainly from hyperfine interactions with the unpaired electrons, and they have been interpreted so as to give information about the wave functions of the unpaired electrons. The isotropic hyperfine fields have determined the spin density in the fluoride ion's $2s$ orbitals and the anisotropic hyperfine fields the spin density in the $2p$ orbitals. For some crystals it was difficult to understand the anisotropy because it was sometimes not possible to assign the unpaired $3d$ electrons to meaningful spatial orbitals, while in other cases it was not possible to distinguish between the contributions of $p\sigma$ and $p\pi$ electrons. By $p\sigma$ electrons we mean those in the σ bond having no angular momentum about the internuclear radius, while the $p\pi$ electrons are in π bonds which do have angular momentum about this axis. It is the purpose of this paper to explain how the measurements in $KNiF_3$ remove these difficulties and allow an unambiguous determination of the

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[1] J. H. Van Vleck, J. Chem. Phys. 3, 803, 807 (1935).

[2] R. G. Shulman, Phys. Rev. 121, 125 (1961); R. G. Shulman and K. Knox, *ibid.* 119, 94 (1960).

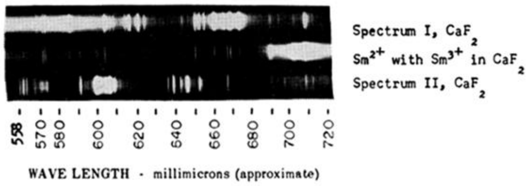

FIG. 1. Fluorescence of Sm^{3+} in CaF$_2$.