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Experimental and Theoretical Study of the Low-Lying Energy-Level Structure of Sm^{3+} in CaF_2†

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The optical spectrum exhibited by the Sm^{3+} ion in CaF_2 is analyzed assuming both octahedral and trigonal site symmetries. Calculations were performed using a tensor operator technique in the complete intermediate-coupling scheme. The crystal field parameters and the root-mean-square (rms) deviations obtained are $B^{(4)}=-906$ cm^{-1} and $B^{(6)}=618$ cm^{-1}, with rms deviations of 48.1 cm^{-1} for the octahedral site symmetry; $B_0^{(2)}=118$ cm^{-1}, $B_0^{(4)}=-272$ cm^{-1}, $B_3^{(4)}=-296$ cm^{-1}, $B_0^{(6)}=38$ cm^{-1}, $B_4^{(6)}=-128$ cm^{-1}, and $B_6^{(6)}=1556$ cm^{-1}, with rms deviation of 35.4 cm^{-1} for the trigonal site symmetry. It is suggested that the sample on which the measurements were carried out contains Sm^{3+} ions occupying both octahedral and trigonal symmetry sites. It is also shown that crystal field theory with a single set of $B_q^{(k)}$ parameters is quite adequate to describe the energy levels lying below 11 000 cm^{-1}, above which a fairly large energy gap follows.

I. INTRODUCTION

The optical absorption, fluorescence, and paramagnetic resonance spectra of Sm^{3+} in CaF_2 have been investigated by several authors.[1–3] In particular, Rabbiner[2] investigated the florescence of Sm^{3+} in CaF_2 at tetragonal site symmetry and gave a theoretical interpretation.

The $CaF_2:Sm^{3+}$ system is of special interest as the strength of the crystal field is believed to be comparable to that of the spin-orbit interaction. This situation suggests that, in analyzing the experimental spectra, one should treat the system on the basis of the *complete* intermediate-coupling scheme. Fortunately, very accurate free-ion energy eigenvectors[4] are now available, and this treatment is possible in principle. This treatment, however, requires that very large matrices be diagonalized.

A fairly large energy gap of about 7500 cm^{-1} separates the lower-lying levels from higher ones. Crystal field matrix elements between the lower and upper groups of levels are small compared with the gap of 7500 cm^{-1}, and may be neglected. The lower group of levels may then be treated separately. Therefore one can work with matrices of considerably smaller dimensions, enabling one to perform the calculations of the type above.

Since the Sm^{3+} ion substitutes for Ca^{2+} ions in the CaF_2 crystal, there must be some kind of charge compensator so as to preserve charge neutrality. The actual site symmetry of the Sm^{3+} in the CaF_2 matrix will depend on the charge compensation mechanisms, which in turn depend on type and amount of impurities, growing conditions, thermal history, etc. Three main site symmetries[5] are possible for Sm^{3+} in CaF_2, namely, octahedral (O_h), tetrahedral (C_{4v}), and trigonal (C_{3v}) symmetries. Careful study of the influence of heat treatments[3] along with theoretical calculations enables one to classify the lines in the spectra according to their site symmetries. The heat treatment technique, however, is not practical for absorption lines lying below about 11 000 cm^{-1} because of opaque milkiness which is introduced in the crystals as a result of heat treatment. In this paper, where we are primarily concerned with the energy region up to 11 000 cm^{-1}, we shall at-

tempt to analyze the spectra in "as received" Harshaw crystals assuming the three most probable site symmetries O_h, C_{4v}, and C_{3v}. Analysis including the higher levels, where more detailed experimental information is available,[3] will be published in a subsequent paper.

In recent papers[6,7] published by our group, it was shown that in the case of Gd^{3+} in CaF_2, the crystal field parameters should have different values for energy levels with different J manifolds in order to obtain a reasonable fit with experiment. This means that crystal field theory, assuming the ligands as point charges, will not fully apply to the CaF_2: Gd^{3+} system. The present investigation will show, however, that in contrast to the CaF_2: Gd^{3+} case, crystal field theory will be applicable in the case of Sm^{3+} in CaF_2, at least in the energy region up to 11 000 cm^{-1} where 12 different J manifolds are involved.

II. EXPERIMENTAL

The crystals used in the present work were CaF_2: Sm^{3+} single crystals supplied by the Harshaw Chemical Co. The Sm^{3+} concentration was 0.2% in these samples.

Absorption measurements were carried out in a Cary model 14 spectrophotometer with the crystals cut into platelets (approximately of 5×8×2 mm size) and held in the crystal holder of an Andonian custom-made vacuum cryostat. The tail of the cryostat was adapted to fit the sample compartment of the spectrophotometer. All measurements were carried out with the crystal at 77 °K.

Figure 1 is a low-resolution (about 25 Å) absorption spectrum of the CaF_2:Sm^{3+} crystal in the 9000–17000 Å region.

In the figure the peaks are numbered for purposes of identification, and their wavelengths and photon energies are given in Table I.

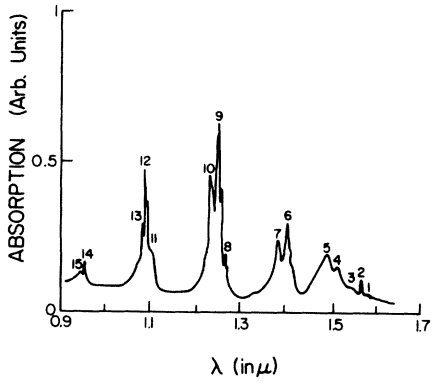

FIG. 1. Low-resolution absorption spectrum exhibited by Sm^{3+} in CaF_2 at 77 °K.

TABLE I. Experimental energy levels of Sm^{3+} in CaF_2 (see Fig. 1).

	λ in Å	Energy in cm^{-1}
1	15 730	6357
2	15 665	6383
3	15 450	6472
4	15 085	6629
5	14 860	6730
6	13 980	7153
7	13 700	7257
8	12 615	7927
9	12 440	8039
10	12 268	8151
11	10 970	9116
12	10 825	9238
13	10 730	9320
14	9 505	10 521
15	9 425	10 610

III. CALCULATIONS

The crystal field potential for the five f electrons of the Sm^{3+} ion (f^5 configuration) in CaF_2 may be expanded in terms of tensor operators $C_q^{(k)}$,

$$V=\sum_i{}'\left(\sum_{k,q} B_q^{(k)} C_q^{(k)}\right)_i , \tag{1}$$

where i runs over the five f electrons. This potential has the following explicit forms for the Sm^{3+} ion with O_h (octahedral), C_{4v} (tetragonal), and C_{3v} (trigonal) site symmetries in the CaF_2 matrix:

$$V(O_h)=\sum_i{}'\{B^{(4)}[C_0^{(4)}+(\tfrac{5}{14})^{1/2}(C_4^4+C_{-4}^4)] + B^{(6)}[C_0^{(6)}-(\tfrac{7}{2})^{1/2}(C_4^{(6)}+C_{-4}^{(6)})]\}_i , \tag{2}$$

where

$$B^{(4)}=B_0^{(4)}=(\tfrac{5}{14})^{-1/2}B_4^{(4)},$$

$$B^{(6)}=B_0^{(6)}=-(\tfrac{7}{2})^{-1/2}B_4^{(6)},$$

$$V(C_{4v})=\sum_i{}'[B_0^{(2)}C_0^{(2)}+B_0^{(4)}C_0^{(4)}+B_4^{(4)}(C_4^{(4)}+C_{-4}^{(4)}) + B_0^{(6)}C_0^{(6)}+B_4^{(6)}(C_4^{(6)}+C_{-4}^{(6)})]_i , \tag{3}$$

$$V(C_{3v})=\sum_i{}'[B_0^{(2)}C_0^{(2)}+B_0^{(4)}C_0^{(4)}+B_3^{(4)}(C_{-3}^{(4)}-C_3^{(4)}) + B_0^{(6)}C_0^{(6)}+B_3^{(6)}(C_{-3}^{(6)}-C_3^{(6)}) + B_6^{(6)}(C_{-6}^{(6)}+C_6^{(6)}]_i . \tag{4}$$

Therefore we are to determine two B parameters in the case of O_h symmetry, five for C_{4v}, and six for C_{3v} symmetries.

Let

$$\phi_J(\mathcal{LS}) = \sum_{\alpha LS} U_{J\mathcal{LS}}(\alpha LS)\,\phi^0(\alpha LS)$$

be the free-ion wave function (intermediate-coupling state) with eigenvalue $E_J(\mathcal{LS})$. Here $(J\mathcal{LS})$ is a set of quantum numbers specifying an intermediate-coupling state, the ϕ^0's are the pure LS basis states, and $U_{J\mathcal{LS}}(\alpha LS)$ represents the unitary matrix which diagonalizes the free-ion Hamiltonian. In this representation we can write the matrix element of the crystal field potential (1) using the standard tensor operator method in the form

$$V(JM\mathcal{LS};J'M'\mathcal{L}'\mathcal{S}') = \sum_{k,q} B_q^{(k)} F_q^k(JM;J'M')\,G^k(J\mathcal{LS};J'\mathcal{L}'\mathcal{S}'), \qquad (5)$$

where

$$F_q^k(JM;J'M') = (3\,\|C^{(k)}\|\,3)(-1)^{J-M}\begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix}, \qquad (6)$$

$$G^k(J\mathcal{LS};J'\mathcal{L}'\mathcal{S}') = \sum_{\alpha\alpha' LL'S} U^*_{J\mathcal{LS}}(\alpha LS)\,U_{J'\mathcal{L}'\mathcal{S}'}(\alpha' L'S') \times (\alpha SLJ\,\|\,U^{(k)}\,\|\,\alpha' SL'J'). \qquad (7)$$

Detailed descriptions of the above notations in (6) and (7) are given in Wybourne.[8] By writing the matrix element in this form, the function $F_q^k(JM;J'M')$ on the right-hand side of (5) is M dependent and also symmetry dependent. On the other hand, the functions $G^K(J\mathcal{LS};J'\mathcal{L}'\mathcal{S}')$ represent M- and symmetry-independent matrices and are obtained by transforming the reduced matrices $(\alpha SLJ\,\|\,U^{(k)}\,\|\,\alpha' SL'J')$ by the unitary matrix $U_{J\mathcal{LS}}(\alpha LS)$. Once the matrices represented by (7) are obtained, they can be used for calculating energy levels of Sm^{3+} in CaF_2 with any symmetry within the f^5 configuration.[9]

The determination of the crystal field parameters requires the knowledge of the intermediate-coupling states and their eigenvalues. Fortunately, Carnall and his co-workers[4] have calculated the *free*-ion energy states[10] for most of the trivalent rare-earth ions. The usefulness of these in the study of crystal field splittings has been proved in the $CaF_2:Gd^{3+}$ system.[7] Therefore we have used the *free*-ion eigenvectors of the Sm^{3+} ion calculated by Carnall *et al.*[4,11]

The reduced matrix elements $(\alpha SLJ\,\|\,U^{(k)}\,\|\,\alpha' SL'J')$ in (7) can be taken from Nielson and Koster[12] or can be calculated by the method of fractional parentage.[13] We have calculated $(\alpha SLJ\,\|\,U^{(k)}\,\|\,\alpha' SL'J')$ using the coefficients of fractional parentage (CFP) of the f^5 configuration (taken from Nielson and Koster).[12]

Group-theoretical considerations reduce considerably the sizes of the Hamiltonian matrices. There are 12 different $(J\mathcal{LS})$ states in the energy region of our present interest. Since, for each one of 12 $(J\mathcal{LS})$ states, there are $(2J+1)$ degenerate $(JM\mathcal{LS})$ states, the total number of $(JM\mathcal{LS})$ basis states is 108, as shown in Table II. The set of $(2J+1)$ states for each J, however, forms a basis set of irreducible representations of the point group to which the site symmetry of Sm^{3+} ion in CaF_2 belongs. Decomposition of the set of $(2J+1)$ states for each J into the irreducible representations of the O_h, C_{4v}, and C_{3v} point groups are also shown in Table II. Accordingly, the sizes of the Hamiltonian matrices to be diagonalized are two 9×9 (Γ_6 and Γ_7) and one 18×18 (Γ_8) in the case of O_h symmetry, two 27×27 (Δ_6 and Δ_7) in C_{4v}, and one 36×36 (Γ_4) and one 18×18 ($\Gamma_5+\Gamma_6$)[14] in C_{3v}.

As usual, we define the rms deviation δ of calculated energy levels by

$$\delta = \left[\sum_i (E^i_{\text{expt}} - E^i_{\text{theor}})^2/(m-N)\right]^{1/2}, \qquad (8)$$

where E^i_{expt} is the ith of the experimentally known levels, E^i_{theor} is the corresponding level obtained theoretically, m is the number of known levels, and N is the number of the $B_q^{(k)}$ parameters introduced in the Hamiltonian and is equal to 2, 5, and 6 in the case of O_h, C_{4v}, and C_{3v} symmetries, respectively. We attempted to determine a set of the $B_q^{(k)}$ parameters for each symmetry considered so as to minimize the rms deviation defined by (8).

IV. RESULTS AND DISCUSSIONS

The results of our calculations for Sm^{3+} in CaF_2 with O_h and C_{3v} site symmetries are given in Figs. 2 and 3 along with the experimental Stark components and the free-ion levels. Figure 2 shows the gross features of the set of energy levels lying in the energy region of interest (compare to Fig. 1). In Fig. 3 more detailed comparison between the calculated and experimental Stark split levels is presented. In Tables III and IV we list the numerical values of the calculated Stark components and the irreducible representations of the respective point groups to which they belong. Results for C_{4v} symmetry are not presented as we could not fit our calculated levels to experiment within reasonable agreement. (The rms deviation in this case was about 180 cm^{-1}.)

We obtained the following crystal field parameters and rms deviations for Sm^{3+} occupying O_h and C_{3v} sites in CaF_2 lattice:

$$O_h:\quad B^{(4)} = -906\ \text{cm}^{-1},\quad B^{(6)} = 618\ \text{cm}^{-1},$$
$$\text{rms deviation} = 48.1\ \text{cm}^{-1}. \qquad (9)$$

TABLE II. Decomposition of intermediate-coupling manifolds into irreducible representations of point groups O_h, C_{4v}, and C_{3v}.

			Decomposition into irreducible representations of the point group [a]		
$J\mathcal{L}\mathcal{S}$ [b]	$E_J(\mathcal{L}\mathcal{S})$ [c]	$2J+1$	O_h	C_{4v}	C_{3v}
$^6H_{5/2}$	0	6	$\Gamma_7+\Gamma_8$	$\Delta_6+2\Delta_7$	$2\Gamma_4+(\Gamma_5+\Gamma_6)$ [d]
$^6H_{7/2}$	1038	8	$\Gamma_6+\Gamma_7+\Gamma_8$	$2\Delta_6+2\Delta_7$	$3\Gamma_4+(\Gamma_5+\Gamma_6)$
$^6H_{9/2}$	2253	10	$\Gamma_6+2\Gamma_8$	$3\Delta_6+2\Delta_7$	$3\Gamma_4+2(\Gamma_5+\Gamma_6)$
$^6H_{11/2}$	3592	12	$\Gamma_6+\Gamma_7+2\Gamma_8$	$3\Delta_6+3\Gamma_7$	$4\Gamma_4+2(\Gamma_5+\Gamma_6)$
$^6H_{13/2}$	5014	14	$\Gamma_6+2\Gamma_7+2\Gamma_8$	$3\Delta_6+4\Delta_7$	$5\Gamma_4+2(\Gamma_5+\Gamma_6)$
$^6F_{1/2}$	6376	2	Γ_6	Δ_6	Γ_4
$^6H_{15/2}$	6485	16	$\Gamma_6+\Gamma_7+3\Gamma_8$	$4\Delta_6+4\Delta_7$	$5\Gamma_4+3(\Gamma_5+\Gamma_6)$
$^6F_{3/2}$	6620	4	Γ_8	$\Delta_6+\Delta_7$	$\Gamma_4+(\Gamma_5+\Gamma_6)$
$^6F_{5/2}$	7112	6	$\Gamma_7+\Gamma_8$	$\Delta_6+2\Delta_7$	$2\Gamma_4+(\Gamma_5+\Gamma_6)$
$^6F_{7/2}$	7960	8	$\Gamma_6+\Gamma_7+\Gamma_8$	$2\Delta_6+2\Delta_7$	$3\Gamma_4+(\Gamma_5+\Gamma_6)$
$^6F_{9/2}$	9121	10	$\Gamma_6+2\Gamma_8$	$3\Delta_6+2\Delta_7$	$3\Gamma_4+2(\Gamma_5+\Gamma_6)$
$^6F_{11/2}$	10 506	12	$\Gamma_6+\Gamma_7+2\Gamma_8$	$3\Delta_6+3\Delta_7$	$4\Gamma_4+2(\Gamma_5+\Gamma_6)$
Total		108	$9\Gamma_6+9\Gamma_7+18\Gamma_8$	$27\Delta_6+27\Delta_7$	$36\Gamma_4+18(\Gamma_5+\Gamma_6)$

[a] Notations for various irreducible representations are consistent with those given by Koster (Ref. 13).

[b] Intermediate-coupling (free-ion) state.

[c] Eigenvalue of intermediate-coupling state.

[d] Γ_5 and Γ_6 form Kramer's pair.

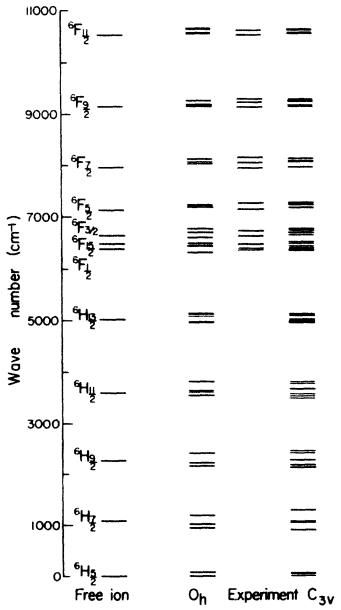

FIG. 2. "Gross feature" comparison of calculated energy-level diagrams with experiment for Sm^{3+} in O_h site and C_{3v} sites, in the energy region up to 11 000 cm^{-1}.

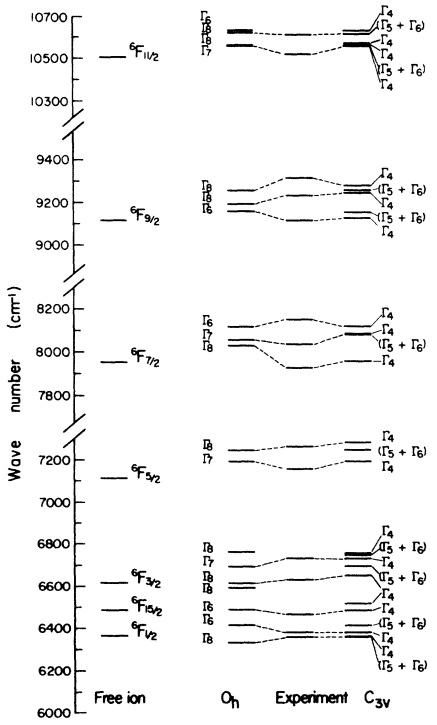

FIG. 3. Detailed comparison of theoretical and experimental energy levels of Sm^{3+} ion in O_h and C_{3v} point-symmetry sites.

C_{3v}: $B_0^{(2)} = 118\ \text{cm}^{-1}$, $B_0^{(4)} = -272\ \text{cm}^{-1}$,

$B_3^{(4)} = -296\ \text{cm}^{-1}$,

$B_0^{(6)} = 38\ \text{cm}^{-1}$, $B_4^{(6)} = -128\ \text{cm}^{-1}$, $B_6^{(6)} = 1556\ \text{cm}^{-1}$,

TABLE III. Crystal field energy levels of Sm^{3+} in CaF_2 assuming O_h site symmetry. [Number of experimental levels[a] = 15 (14); rms deviation[a] = 48.1 (39.6) cm^{-1}.]

$J\mathcal{L}\mathcal{S}$[b]	$E_J(\mathcal{L}\mathcal{S})$[c]	Calculated Stark components	Experimental Stark components	Representation[d]
$^6H_{5/2}$	0	0		Γ_8
		75		Γ_7
$^6H_{7/2}$	1038	944		Γ_6
		1016		Γ_7
		1201		Γ_8
$^6H_{9/2}$	2253	2175		Γ_6
		2257		Γ_8
		2418		Γ_8
$^6H_{11/2}$	3592	3527		Γ_8
		3650		Γ_6
		3672		Γ_8
		3789		Γ_7
$^6H_{13/2}$	5014	4966		Γ_8
		4986		Γ_7
		5096		Γ_8
		5123		Γ_6
		5140		Γ_7
$^6F_{1/2}$	6373[e]	6331	6357	Γ_8
$^6H_{15/2}$	6485	6420	6384	Γ_6
		6495	6472	Γ_6
		6590		Γ_8
		6619	6629	Γ_8
		6696	6730	Γ_7
$^6F_{3/2}$	6620	6767		Γ_8
$^6F_{5/2}$	7112	7192	7153	Γ_7
		7245	7257	Γ_8
$^6F_{7/2}$	7960	8027	(7927)	Γ_8
		8058	8039	Γ_7
		8115	8151	Γ_6
$^6F_{9/2}$	9121	9169	9116	Γ_6
		9191	9238	Γ_8
		9255	9319	Γ_8
$^6F_{11/2}$	10506	10599	10521	Γ_7
		10561		Γ_8
		10622	10610	Γ_8
		10630		Γ_6

[a] See discussions in text.

[b] Intermediate-coupling (free-ion) state.

[c] Eigenvalue of intermediate-coupling state.

[d] Notations for irreducible representations are consistent with those given by Koster (Ref. 13).

[e] See discussions in text.

TABLE IV. Crystal field energy levels of Sm^{3+} in CaF_2 assuming C_{3v} site symmetry. (Number of experimental levels = 15; rms deviation = 35.4 cm^{-1}.)

$J\mathcal{L}\mathcal{S}$[a]	$E_J(\mathcal{L}\mathcal{S})$[b]	Calculated Stark components	Experimental Stark components	Representation[c]
$^6H_{5/2}$	0	0		Γ_4
		24		$(\Gamma_5 + \Gamma_6)$[d]
		30		Γ_4
$^6H_{7/2}$	1038	891		Γ_4
		1058		Γ_4
		1064		$(\Gamma_5 + \Gamma_6)$
		1304		Γ_4
$^6H_{9/2}$	2253	2133		Γ_4
		2199		$(\Gamma_5 + \Gamma_6)$
		2275		Γ_4
		2413		$(\Gamma_5 + \Gamma_6)$
		2462		Γ_4
$^6H_{11/2}$	3592	3481		Γ_4
		3516		$(\Gamma_5 + \Gamma_6)$
		3559		Γ_4
		3691		Γ_4
		3751		$(\Gamma_5 + \Gamma_6)$
		3775		Γ_4
$^6H_{13/2}$	5014	4963		Γ_4
		4969		Γ_4
		4970		$(\Gamma_5 + \Gamma_6)$
		5010		Γ_4
		5102		Γ_4
		5121		$(\Gamma_5 + \Gamma_6)$
		5127		Γ_4
$^6F_{1/2}$	6373[e]	6360	6357	$(\Gamma_5 + \Gamma_6)$
$^6H_{15/2}$	6485	6369		Γ_4
		6384	6384	Γ_4
		6418		$(\Gamma_5 + \Gamma_6)$
		6490	6472	Γ_4
		6518		Γ_4
		6651	6629	Γ_4
		6698		$(\Gamma_5 + \Gamma_6)$
		6725	6730	Γ_4
$^6F_{3/2}$	6620	6750		$(\Gamma_5 + \Gamma_6)$
		6761		Γ_4
$^6F_{5/2}$	7112	7193	7153	Γ_4
		7248		$(\Gamma_5 + \Gamma_6)$
		7277	7257	Γ_4
$^6F_{7/2}$	7960	7956	7927	Γ_4
		8082	8039	$(\Gamma_5 + \Gamma_6)$
		8088		Γ_4
		8121	8151	Γ_4
$^6F_{9/2}$	9121	9126	9116	Γ_4
		9164		$(\Gamma_5 + \Gamma_6)$
		9248	9238	Γ_4
		9264	9319	$(\Gamma_5 + \Gamma_6)$
		9276		Γ_4

rms deviation = 35.4 cm^{-1}. (10)

In the case of O_h symmetry, fitting to a particular

TABLE IV. (*continued*)

$J\mathcal{LS}$ [a]	$E_J(\mathcal{LS})$ [b]	Calculated Stark components	Experimental Stark components	Representation [c]
$^6F_{11/2}$	105 06	105 59	10 521	Γ_4
		105 76		$(\Gamma_5 + \Gamma_6)$
		105 83		Γ_4
		105 92		Γ_4
		106 14	10 610	$(\Gamma_5 + \Gamma_6)$
		106 27		Γ_4

[a] Intermediate-coupling (free-ion) state.

[b] Eigenvalue of intermediate-coupling state.

[c] Notations for irreducible representations are consistent with those given by Koster (Ref. 13).

[d] Γ_5 and Γ_6 form Kramer's pair.

[e] See discussions in text.

level at 7927 cm^{-1} which belongs to the $^6F_{7/2}$ multiplet was not good in all stages of the iteration. If we omit this level from our calculation, then the rms deviation reduces to 39.6 cm^{-1}.

It is quite possible that there exist two types of Sm^{3+} ion sites in the CaF_2 lattice simultaneously, one with O_h symmetry and the other with C_{3v} symmetry. If the charge compensator is far from the Sm^{3+} ion, the local symmetry around Sm^{3+} will be O_h. The C_{3v} site symmetry will be achieved by a charge compensator replacing one of the eight F^- ions nearest to the Sm^{3+} ion. The charge compensator in this case will most probably[15] be in an "as-received" crystal the OH^- complex. As discussed in the Introduction, by studying effects of heat treatment, one is able to obtain the information[3] about the "symmetry development" of the rare-earth ion site. Unfortunately this type of study is not practical for absorption lines in the present region of interest. Furthermore, the optical resolution achieved by the spectrophotometer in this wavelength region is relatively poor. This fact may mean that not all Stark components present in a given manifold will actually be resolved. Hence one will not be able to determine beyond reasonable doubt the site symmetry responsible for the given spectra. In fact, the rms deviations of the calculated levels for O_h and C_{3v} symmetries are both of the same order of magnitude, and it is difficult to say which symmetry is more suitable to interpret the experimental peaks. Rather, one may interpret the results in the following way: The fact that we obtained reasonable fits for both O_h and C_{3v} symmetries might be the consequence of the sample containing both types of Sm^{3+} sites, one with O_h symmetry and the other with C_{3v} symmetry. However, because of "poor" resolution, one is not able to resolve all Stark components.

In his study of the fluorescence spectra of Sm^{3+} in CaF_2 at tetragonal sites, Rabbiner[2] obtained the calculated splitting of the ground state ($^6H_{5/2}$ multiplet) to be of 223 cm^{-1}. Prener and Kingsley[16] investigated the fluorescence spectra of Sm^{3+} in CdF_2, which is isomorphous to CaF_2, and gave the experimental values for the ground-state splitting of 147 cm^{-1}. They suggested that the splitting should be associated with a tetragonal field surrounding the Sm^{3+} ion in CdF_2. In the present work we do not have direct information concerning the splittings of the ground state of Sm^{3+} in CaF_2. Our *calculated* splittings of the ground state for O_h and C_{3v} symmetries, however, are 75 cm^{-1} and 30 cm^{-1}, respectively. In view of the rms deviations of our calculated levels, we feel that the splitting of the ground state in either case will be of about 100 cm^{-1} or less. Under those circumstances, then, the "upper" ground states will be sufficiently populated even at 77 °K to give absorption lines associated with them. Thus, each peak will be a composite peak composed of two lines, and of three lines for O_h and C_{3v} symmetries, respectively, making a detailed analysis of the absorption spectrum even more complicated. Studying the temperature variations and relative intensities of these components using high-resolution spectrometers might provide information concerning the ground-state splittings and site symmetries of the Sm^{3+} ion.

The results listed in Tables III and IV show that the absolute deviations of the calculated levels from the experimental ones are distributed rather randomly over the different J manifolds. In addition, the gross feature of the whole spectrum is represented fairly well by the calculations in both cases of O_h and C_{3v} symmetries (see Fig. 2). It should be noted here that the above results were obtained using a single set of crystal field parameters to describe the energy levels involving 12 different J manifolds. This, we suggest, means that crystal field theory with a single set of parameters "works" well in the CaF_2: Sm^{3+}systems at least in the energy region of the present interest. In the case of Gd^{3+} in CaF_2, the situation is quite different, as was discussed in the Introduction. Probably this difference comes from the following two reasons: (i) In the present paper, we are only concerned with the low-lying levels up to 11 000 cm^{-1}. In the case of Gd^{3+} in CaF_2, however, energies involved are much higher ranging from $\approx$ 32 000 to $\approx$ 37 000 cm^{-1}. (ii) There is a fairly large energy gap of $\approx$ 7500 cm^{-1} separating the low-lying levels from higher ones in the present case. There is no such gap in CaF_2: Gd^{3+} system.

Inspection of the eigenvectors obtained in our calculation shows that, in spite of working in the complete intermediate-coupling scheme, the J mixing effects are not too serious except for a group of levels ranging from $\approx$ 6300 to $\approx$ 6800 cm^{-1}. In other words, the total angular momentum J is still a rea-

sonably good quantum number to even specify the Stark split levels of Sm^{3+} except for the above mentioned levels. In this group of levels, which originates from three different J manifolds $^6F_{1/2}$, $^6H_{15/2}$, and $^6F_{3/2}$, the effect of J mixing is considerable, i.e., probably due to the closeness of these levels.

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[10]The vectors of Carnall *et al.* are not really for the free ion, but are instead vectors for aqueous solution involving some loosely bonded species. We also assume that the free-ion E_k and ζ values do not depend on coordination, environment, etc.

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Positron Annihilation Rates in Lanthanum Hydrides†

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Positron annihilation rates λ_1 and λ_2 are reported for a series of lanthanum hydride samples of compositions from $LaH_{2.0}$ to $LaH_{2.9}$. From $LaH_{2.0}$ to $LaH_{2.7}$, λ_1 was approximately constant at 3.36 $nsec^{-1}$. At higher compositions, λ_1 increased with increasing hydrogen content. A slower rate component λ_2 was observed for annihilation in lanthanum hydrides, but the associated intensity was very low. New data are also reported for lithium hydride as follows: $\lambda_1 = 3.12$ $nsec^{-1}$, $\lambda_2 = 0.68$ $nsec^{-1}$, and $I_2 = 6.30\%$.

INTRODUCTION

Positron annihilation provides an attractive approach to the study of bonding in solids. Two types of measurements have been extensively used to characterize the annihilation process in solids: the measurement of positron lifetimes and the measurement of the two-photon angular correlations. Positronium formation is precluded in ionic solids.[1] The formation of a positron-anion bound state remains a subject of discussion[2,3] and has been most extensively treated for the case of the hydride ion. Gol'danski *et al.*[4] treated a bound state consisting of a positron–hydride-ion pair in relation to the fast component of the lifetime spectrum of lithium hydride. Ivanovna and Prokop'ev[5] attempted to account for additional lifetime components in lithium hydride in terms of additional excited states of this bound state. More recently,