Optical Absorption Spectrum of Nd³⁺-Doped LaF₃ Single Crystal: The Evidence of a Hidden Selection Rule*

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The symmetry of the La^{+3} site in LaF_3 has been determined by x-ray and paramagnetic resonance. The x-ray results show a C_{2v} site symmetry in agreement with paramagnetic resonance. The optical absorption spectrum shows conclusive evidence of a selection rule contrary to the fact that a C_{2v} site symmetry gives no selection rule. Hence, there exists a hidden selection rule.

INTRODUCTION

THE spectra of magnetically diluted rare-earth crystals have been studied extensively. Selection rules derived from the site symmetry group for the pure electronic transitions are in good agreement with observed spectra except some of the allowable transitions were missing in the observed spectra. There are two possible reasons, either the transition intensity was too low to be observed or there exists an unknown hidden selection rule. We present the spectrum of Nd³⁺-doped LaF₃ single crystals and show that there is very strong evidence of a hidden selection rule.

THE SITE SYMMETRY OF LaF₃

The structure of LaF_3 is known. X-ray data[1] have shown that there are six molecules in a unit cell. The space symmetry is D_{6h}^3 and the site symmetry for all La^{3+} site is C_{2v}, but not too far from D_{3h}. One could consider the La^{3+} site to be distorted from a D_{3h} symmetry to a C_{2v} symmetry. The distortion destroys the threefold axis, two of the twofold axes, and some of the reflection planes. The remaining twofold axis would be the twofold axis of the C_{2v} site symmetry. Since this remaining twofold axis could be any of the three twofold axes of the D_{3h} symmetry, there are at least three La^{3+} sites with their twofold axis $\pi/3$ from each other and perpendicular to the c axis or the optical axis of the crystal in a unit cell. This idea has been confirmed by paramagnetic resonance results reported by Jones and co-workers[2] and Baker and Rubins.[3] The paramagnetic resonance experiments have not only shown that the site symmetry for the paramagnetic ions is C_{2v}, but quite far from D_{3h} or any axial symmetry. If the paramagnetic ions see a D_{3h} or any axial symmetry, the g tensor can be represented by $g_{11}=g_z$ and $g_\perp=g_x=g_y$. If the site symmetry in not too far from an axial symmetry, one would expect g_x to be not too far from g_y. Baker and Rubins have shown that this is not the case for several rare-earth ions doped into the LaF_3 crystal. We have re-

peated their experiment for Nd³⁺-doped LaF₃, the same crystal from which we took the absorption spectrum, and the results agree with their reported values. Figure 1 shows the positions of the resonance signals when the magnetic field was rotated in a plane perpendicular to the c axis of the crystal. The maximum g factors are 2.183 and 2.349. The minimum g factor was not observed because of the limited range of the magnet. The dashed line in Fig. 1 is calculated from results reported by Baker and Rubins. Our maximum g factors differ from Baker and Rubins by approximately 100 G. This we believe to be because of slight deviations from exact perpendicular orientation of the c axis of the crystal with respect to the magnetic field. If the site symmetry is an axial symmetry, Fig. 1 should be a straight line. It is clear that the site symmetry is quite far from an axial symmetry.

Additional evidence from paramagnetic resonance is the zero-field splitting parameters of the Gd³⁺ ion. Jones and co-workers reported a large B_2^2 term when quan-
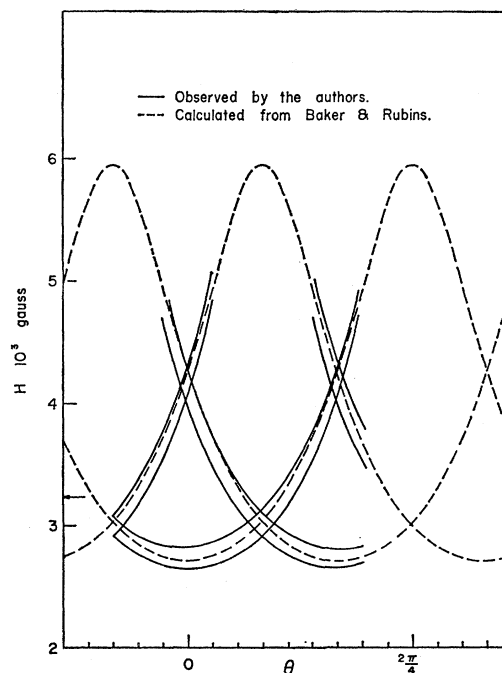
[1] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. II.
[2] D. A. Jones, J. M. Baker, and D. F. D. Pope, Proc. Phys. Soc. (London) **74**, 249 (1959).
[3] J. M. Baker and R. S. Rubins, Proc. Phys. Soc. (London) **78**, 1353 (1961).

FIG. 1. Paramagnetic resonance of 1% Nd³⁺ in LaF₃.

TABLE I. Character table for C_{2v} site symmetry.

C_{2v}	E	E'	C_2	σ_v	$\sigma_v{}'$
Γ_1	1	1	1	1	1
Γ_2	1	1	−1	−1	1
Γ_3	1	1	1	−1	−1
Γ_4	1	1	−1	1	−1
Γ_5	2	−2	0	0	0

tized along the c axis of the crystal. If the Gd^{3+} ion site symmetry is not too far from D_{3h} symmetry, there should be a small $B_2{}^2$ term.

SELECTION RULE FOR C_{2v} SITE SYMMETRY

The character table for C_{2v} site symmetry reported by Satten[4] is shown in Table I. It has only one two-dimensional irreducible representation in addition to the four one-dimensional irreducible representations of the simple group. The Nd^{3+} has an odd number of electrons so all of the pure electronic states must transform according to this two-dimensional irreducible representation. This means that there is only one crystal field quantum number and there is no selection rule.

It is easy to see that the double group of C_{2v} has only one irreducible representation in addition to the simple group. The two generators for the double group in a spin space of χ_+ and χ_- are

$$C_2=\begin{pmatrix}+i & 0 \\ 0 & -i\end{pmatrix}, \quad \sigma_v=\begin{pmatrix}0 & 1 \\ -1 & 0\end{pmatrix},$$

and they do not commute with each other. The double group is not an Abelian group even though the simple group is an Abelian group. If the double group is not an Abelian group then there are five irreducible representations because $1^2+1^2+1^2+1^2+2^2=8$. Thus, there is only one additional irreducible representation in the double group.

OPTICAL ABSORPTION SPECTRUM

Some of the crystals used here were grown by one of the authors, Stafsudd, at Atomics International and Futurecraft by Czochralski and Epitaxial techniques.[5] The crystals show a metallic reflection plane just like those described in the paramagnetic resonance work of Jones and co-workers and Baker and Rubins. Other crystals were obtained from Crystallonic. The latter does not show the metallic reflection plane but gives the same spectra.

The c axis of the crystal was identified by three methods, cross polarized light, the cleavage plane and x ray. The spectra were taken by a 21-ft grating spectrograph at liquid-nitrogen and liquid-helium temperatures. The results from the 1% Nd^{3+}-doped LaF_3

[4] R. A. Satten, Hughes Research Report No. 207 (1961).
[5] K. Nassau, J. Appl. Phys. **32**, 1820 (1961).

TABLE II. Absorption spectrum of 1% Nd^{3+} in LaF_3 at liquid-N_2 temperature. Asterisks denote the lines which show up in liquid-He temperature spectrum.

J	Line	λ Å	ν cm⁻¹	I	Pol	cm⁻¹
$^4F_{3/2}$	$R1$	8657.7	11 547.2	w	σ	$R2-R1=44.4$
	$R2^*$	8624.6	11 591.6	s	$\pi\sigma$	
	$R3^*$	8593.9	11 633.6	s	σ	
	$S1$	7976.5	12 533.4	w	π	
	$S2$	7965.2	12 551.2	s	π	$S6-S2=44.4$
	$S3$	7954.1	12 576.3	m	σ	$S7-S3=44.2$
$^4F_{5/2}$	$S4$	7950.9	12 573.7	w	σ	
	$S5$	7949.3	12 576.3	m	$\pi\sigma$	$S8-S5=44.4$
	$S6^*$	7937.1	12 595.6	s	σ	
	$S7^*$	7926.2	12 612.9	w	σ	
	$S8^*$	7921.3	12 620.7	s	$\pi\sigma$	
	$S9$	7915.4	12 630.1	s	σ	$S11-S9=44.4$
	$S10$	7904.1	12 648.2	s	σ	$S12-S10=44.5$
$^2H_{9/2}$	$S11^*$	7887.6	12 674.6	s	$\pi\sigma$	
	$S12^*$	7876.4	12 692.6	s	$\pi\sigma$	
	$S13^*$	7837.7	12 755.3	m	σ	
	$A1$	7421.8	13 470.1	s	π	$A2-A1=44.7$
	$A2^*$	7397.2	13 514.8	s	σ	
$^4F_{7/2}$	$A3$	7380.1	13 546.2	s	π	$A4-A3=44.6$
	$A4^*$	7355.9	13 590.8	s	σ	
	$A5$	7336.0	13 627.7	w	σ	$A6-A5=43.2$
$^4S_{3/2}$	$A6^*$	7312.8	13 670.9	s	$\pi\sigma$	
	$A7^*$	7309.7	13 676.7	s	σ	
	$A8^*$	7291.9	13 710.1	s	σ	
	$A9^*$	7289.7	13 714.2	s	σ	
	$B1$	6759.4	14 790.1	m	π	$B3-B1=44.6$
	$B2$	6747.0	14 817.3	w	$\pi\sigma$	$B4-B2=44.5$
	$B3^*$	6739.1	14 834.7	m	$\pi\sigma$	
$^4F_{9/2}$	$B4^*$	6726.8	14 861.8	w	$\pi\sigma$	
	$B5^*$	6713.8	14 890.6	w	π	
	$B6$	6701.9	14 917.0	w	π	
	$B7^*$	6682.9	14 959.4	w	$\pi\sigma$	
$^2H_{11/2}$	$C1^*$	6249.0	15 998.1	w	$\pi\sigma$	
	$C2^*$	6230.2	16 046.4	w	π	
	$D1$	5825.1	17 162.3	w	σ	
	$D2$	5792.2	17 259.8	s	$\pi\sigma$	$D4-D2=44.8$
	$D3$	5788.4	17 271.2	s	π	$D5-D3=44.8$
$^2G_{7/2}$	$D4^*$	5777.2	17 304.6	s	$\pi\sigma$	
	$D5^*$	5773.4	17 316.0	s	$\pi\sigma$	
	$D6^*$	5757.8	17 362.9	m	σ	
	$D7$	5720.6	17 475.8	m	π	$D9-D7=44.5$
$^4G_{5/2}$	$D8^*$	5709.7	17 509.2	w	π	
	$D9^*$	5706.1	17 520.3	s	σ	
	$D10$	5693.6	17 558.7	m	$\pi\sigma$	
	$D11^*$	5679.2	17 603.2	m	$\pi\sigma$	
	$E1$	5233.4	19 102.7	m	σ	$E2-E1=44.7$
	$E2^*$	5221.2	19 147.4	s	$\pi\sigma$	
	$E3$	5209.1	19 191.8	w	$\pi\sigma$	$E5-E3=44.4$
	$E4$	5204.8	19 207.7	m	π	$E6-E4=44.4$
$^4G_{7/2}$	$E5^*$	5197.1	19 236.2	s	$\pi\sigma$	
	$E6^*$	5192.8	19 252.1	s	$\pi\sigma$	
	$E7$	5185.1	19 280.7	w	π	$E8-E7=44.7$
	$E8^*$	5173.1	19 325.4	s	σ	
	$E9$	5168.5	19 342.6	w	π	
	$F1$	5120.8	19 522.8	w	π	$F2-F1=45.4$
	$F2^*$	5108.9	19 568.2	w	$\pi\sigma$	
	$F3^*$	5087.4	19 650.9	w	σ	
$^3G_{9/2}$	$F4^*$	5078.3	19 686.2	w	σ	
	$F5$	5076.0	19 695.1	w	π	$F7-F5=44.3$
	$F6^*$	5073.7	19 704.0	w	σ	
	$F7^*$	5064.6	19 739.4	w	$\pi\sigma$	

The S group
a
b
c
d
e

The D group
a
b
c
d
e

← λ

The A group
a
b
c
d
e

←——— 50 Å ———→

FIG. 2. Absorption spectrum of the S, D, and A group.

a π polarization
b σ polarization   } liquid N_2
c   light through c axis   } temperature
d π polarization   } liquid He
e σ polarization   } temperature

crystal are listed in Table II. The lines with an asterisk are the lines which show up at liquid helium temperature. Figure 2 shows the spectra of the S, D, and A groups. Figure 3 shows a densitometer trace of the E group. The spectra clearly show polarized lines in contradiction to the fact that a C_{2v} site symmetry gives no selection rule.

DISCUSSION

There is no question that there exists a hidden selection rule. Rather the question is what causes the selection rule. We have considered the following possibility which may or may not be the explanation. The selection rules arising from space groups are well known.[6] The pure translational symmetry gives a $\Delta k = 0$ selection rule, and the rest of the selection rules for the unit cell are given by the point group. The point group for LaF$_3$ is D_{6h}. It is possible to obtain a selection rule from this point group.

The criterion for using the point group instead of the site group depends on the interaction between the rare-earth ions. If there is strong enough coupling to be detected experimentally, then the point group should be used. If the interaction is small, all of the rare-earth ions can be considered as isolated systems and the site group should be used. It is believed that when the rare-earth ions are diluted by diamagnetic ions such as La^{3+}, then the rare-earth ions would be isolated. However, there is no proof that the paramagnetic ions would not form clusters.

[6] S. A. Pollack and R. A. Satten, J. Chem. Phys. **36**, 804 (1962).

Figure 1 shows three sets of double lines. Baker and Rubins believe there are six rare-earth ions in a unit cell, and three of them see a slightly different crystalline field from the other three. Thus, there would be two slightly different g tensors.

Some of the absorption lines appear as doublets, for example, $D4$ and $D5$ of the D group. These doublets can be explained using two slightly different crystalline field parameters as suggested by Baker and Rubins. If this is true, the two lines of the doublet must obey the same selection rule. However, this is not the case. These doublets are $\sigma\pi$ transition from the ground state, but from the 44.5 cm^{-1} excited state one line of the doublet is $\pi\sigma$ and the other line is π only, for example, $D2$ and $D3$. If the rare-earth ions are coupled together and the coupling is large enough to be resolved into two lines, it is possible that the state or states transform according to different irreducible representations of the point group. Thus, it is possible to have different selection rules within the doublet. It is very difficult to see whether the spectrum follows the D_{6h} point group selection rule because the coupling between rare-earth ions is small, and one would expect several states which transform according to different irreducible representation to be very close to one another and not necessarily resolvable in the spectrum.

Without more knowledge of the coupling between rare-earth ions it is very difficult to prove the validity of the point group selection rule; in other words, the authors do not think the evidence is sufficient to satisfy the criterion for the application of the point group selection rule.
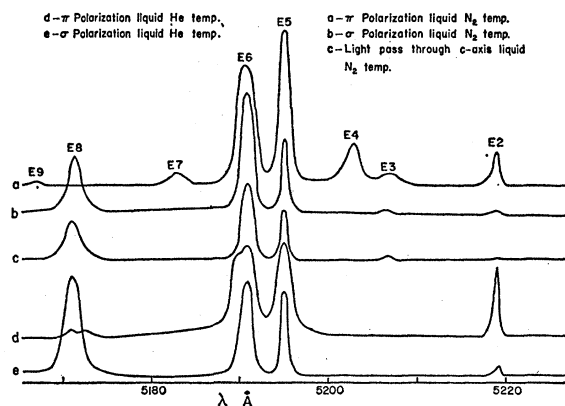

d-π Polarization liquid He temp.
e-σ Polarization liquid He temp.
a-π Polarization liquid N_2 temp.
b-σ Polarization liquid N_2 temp.
c-Light pass through c-axis liquid N_2 temp.

E9   E8   E7   E6   E5   E4   E3   E2

5180   5200   5220
λ Å

FIG. 3. Densitometer trace of the E group absorption lines of 1% Nd^{3+} in LaF$_3$.

The S group

The D group

← λ

The A group

← 50 Å →

FIG. 2. Absorption spectrum of the S, D, and A group.

a π polarization

b σ polarization   } liquid N_2

c   light through c axis   temperature

d π polarization   } liquid He

e σ polarization   temperature