Energy Levels and Crystal-Field Calculations of Er^{3+} in Yttrium Aluminum Garnet*

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The absorption spectrum of erbium-doped yttrium aluminum garnet is reported. From the splitting of J manifolds, the crystal-field parameters $A_2{}^0 = 260$ cm⁻¹, $A_4{}^0 = -160$ cm⁻¹, $A_4{}^4 = 5A_4{}^0$, $A_6{}^0 = 45$ cm⁻¹, and $A_6{}^4 = -710$ cm⁻¹ have been calculated.

1. INTRODUCTION

ENERGY levels of the trivalent Yb^{3+} and Er^{3+} ions in the host-lattice yttrium gallium garnet [YGaG] have been reported in the literature.[1,2] The splittings of some of the J manifolds of Er^{3+}:YGaG have been explained[2] in terms of a crystal field of cubic symmetry. In recent communications[3,4] from this laboratory we have reported on the energy-level diagram of the trivalent rare-earth ions Nd^{3+}, Eu^{3+}, and Tb^{3+} in the host-lattice yttrium aluminum garnet [YAlG]. Crystal-field calculations on the splitting of J manifolds of these ions indicate that rare-earth ions in YAlG experience a crystal field of approximately tetragonal symmetry. The energy-level diagram of Er^{3+}:YAlG up to 23 000 cm⁻¹ is discussed in this paper. Crystal-field calculations on the splitting of various J manifolds has enabled us to evaluate the crystal-field parameters.

2. EXPERIMENTAL TECHNIQUES

The absorption spectrum of Er^{3+}:YAlG has been observed in the visible and infrared using a $\frac{1}{2}$-m Jarell-Ash spectrometer. Spectra were recorded with a maximum resolution of 1 Å in the spectral region of 10 500–4400 Å.

The absorptions in the infrared have also been recorded with a Beckman IR-7 spectrophotometer, using NaCl optics. Spectra of heavily doped Er^{3+}:YAlG samples were studied at room temperature and at 4.2°K.

3. ABSORPTION SPECTRUM AND ENERGY LEVELS OF Er^{3+} : YAlG

The approximate positions of the J manifolds for Er^{3+} are well known and are given in the paper of Dieke and Crosswhite.[5] In Er^{3+}:YAlG, we have been able to obtain the positions of most of the Stark split levels of the J manifolds from the absorption spectrum at 4.2°K. Transitions at this temperature originate predominantly from the ground state (lowest level of the $^4I_{15/2}$ manifold) and terminate on the excited states. The energy of these

states is thus obtained directly from the absorption bands which are observed at 4.2°K. The positions of the various levels of the $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, and $^4F_{3/2}$, as determined from the absorption spectra, are given in Table I.

Transitions to the levels of the $^4F_{3/2}$ manifold are the strongest in the entire spectrum. The absorption at 20 625 cm⁻¹ is unassigned since there are only four transitions possible from the ground state to the $^4F_{7/2}$ manifold. The temperature dependence of this absorption rules out the possibility that it is due to a transition from an excited state of the $^4I_{15/2}$ manifold to one of the $^4F_{7/2}$ levels. In the spectral region investigated, transi-

TABLE I. Absorption spectrum Er^{3+}:$Y_3Al_2(AlO_4)_3$ at 4.2°K.

Absorptions (cm⁻¹)	Intensity[a]	Assignment
6766	st	$^4I_{13/2}$
6858	st	
6949	w	
10 252	st	$^4I_{11/2}$
10 281	m	
10 360	m	
10 370	w	
10 411	w	
		$^4I_{9/2}$
12 298	w	
12 524	vw	
12 573	vw	
12 719	st	
12 765	st	
15 290	m	$^4F_{9/2}$
15 319	w	
15 364	m	
15 485	st	
15 530	st	
18 406	st	$^4S_{3/2}$
18 470	st	
19 100	st	$^2H_{11/2}$
19 124	st	
19 161	st	
19 328	st	
19 350	st	
19 367	st	
20 520	st	$^4F_{7/2}$
20 574	m	
20 625[b]	br m	
20 659	st	
20 709	st	
22 230	st	$^4F_{5/2}$
22 250	st	
22 299	st	
22 601	v. st	$^4F_{3/2}$
22 672	v. st	

[a] The intensities are relative and valid inside a group only. v. st =very strong, st =strong, m =medium, w =weak, br =broad.
[b] Level probably due to an impurity.

[1] R. Pappalardo and D. L. Wood, J. Chem. Phys. **33**, 1734 (1960).
[2] R. Pappalardo, Z. Physik **173**, 374 (1963).
[3] J. A. Koningstein and J. E. Geusic, first preceding paper, Phys. Rev. **135**, A711 (1964).
[4] J. A. Koningstein, second preceding paper, Phys. Rev. **135**, A726 (1964).
[5] G. H. Dieke and H. M. Crosswhite, Appl. Opt. **2**, 675 (1963).

tions to all levels of the J manifolds have been observed with the exception of the $^4I_{13/2}$ and $^4I_{11/2}$ manifolds.

Because the host lattice absorbs below 2000 cm^{-1}, we have been unable to observe transitions within the $^4I_{15/2}$ manifold. Transitions originating in some of the Stark levels of the $^4I_{15/2}$ manifold and terminating on levels of the $^4S_{3/2}$ and $^4F_{5/2}$ manifold have been observed at room temperature. The positions of the ground manifold levels were obtained from the experimental data and are shown in Table II.

TABLE II. Transitions from $^4I_{15/2}-^4F_{5/2}$ and $^4I_{15/2}-^4S_{3/2}$. The position of Stark levels of the $^4I_{15/2}$ manifold are indicated by ( ).

Absorptions at 300°K (cm⁻¹)	Levels of ⁴F₅/₂ 22 299 cm⁻¹	22 250 cm⁻¹	22 230 cm⁻¹	Absorptions at 300°K (cm⁻¹)	Levels of ⁴S₃/₂ 18 470 cm⁻¹	18 406 cm⁻¹	Levels of ⁴I₁₅/₂ (average)
22 272	(27)			18 442	(28)		
22 210			(20)	18 385		(21)	24
22 180		(70)		18 393	(77)		
22 160			(70)	18 336		(70)	72
22 134		(116)					
22 083	(116)						116
21 887	(412)			18 055	(415)		412
21 839		(411)		17 984		(422)	
21 878	(421)			18 041	(429)		426
21 828		(422)		17 974		(432)	
21 813			(417)				
21 779		(471)		17 942		(464)	468
21 736	(563)			17 899	(571)		
21 689		(561)		17 840		(566)	564
21 669			(561)				

4. ANALYSIS OF THE SPECTRUM

The experimental results indicate that the $(J+\frac{1}{2})$-fold degeneracy for most of the J manifolds of Er^{3+}:YAlG is completely removed. The fact that the $(J+\frac{1}{2})$-fold degeneracy is removed indicates that the symmetry of the crystal field is not cubic; however, this fact does not allow us to distinguish a rhombic field from a tetragonal field.[6] The rare-earth ions replace the yttrium ions in the garnet systems. Although crystallographic data are not available for the aluminum garnet or gallium garnet, such data are reported[7,8] for the yttrium iron garnet. The yttrium ions occupy the 24(c) positions of the space group $O_h(10)Ia3d$. In the garnet the yttrium ion is surrounded by 8 oxygen ions which are arranged in a distorted cube. The crystallographic data suggest[8] that the symmetry of the crystal field at the yttrium site belongs to the group D_2. From an interpretation of the spectrum of Nd^{3+}, Eu^{3+}, and Tb^{3+} in YAlG; however, it is found that the symmetry is approximately tetragonal.[3,4]

In our present consideration we are not concerned with the position of the J manifolds of Er^{3+}:YAlG. We are, however, interested in the splitting of J manifolds due to the crystal field. The electric-field potential produced by the surrounding ions contributes to the Hamiltonian of the Er^{3+} ion. It is usual[9] to expand this

part of the Hamiltonian V, in a series of spherical harmonics:

$$V = \sum_n \sum_{m=-n}^{n} \sum_k B_n{}^m r_k{}^n Y_n{}^m(\theta_k, \varphi_k), \qquad (1)$$

where $B_n{}^m$ are constants and given by the positions of the neighbors around the Er^{3+} ion, r_k is the radius of the $4f$ electrons, $\sum_k$ stands for a summation over all electrons, $Y_n{}^m(\theta_k, \varphi_k)$ are spherical harmonics, $n=6$ for $4f$ electrons. From the results of crystal-field calculations of Nd^{3+}, Eu^{3+}, and Tb^{3+} in Y$_3$Al$_2$(AlO$_4$)$_3$, it has been found that the important terms in Eq. (1) are

$$V = \alpha A_2{}^0 Y_2{}^0 + \beta A_4{}^0 [Y_4{}^0 + 5(Y_4{}^{+4} + Y_4{}^{-4})]$$
$$+ \gamma A_6{}^0 [Y_6{}^0 - 21\epsilon(Y_6{}^{+4} + Y_6{}^{-4})]. \qquad (2)$$

In Eq. (2), the Operator Equivalent Method of Stevens, Elliott, and Judd[10–12] has been employed, hence α, β, and γ are operator equivalent constants, and $A_n{}^m = \langle r^n \rangle B_n{}^m$ with $\langle r^n \rangle = \int [R(r)]^2 r^n r^2 dr$, $\epsilon = A_6{}^4/21 A_6{}^0$. The operator equivalent constants for some J states of Er^{3+} have been calculated by Erath[13] taking into account departure from LS coupling. Recent calculations by Wybourne[14] indicate the departure of LS coupling for the $^4I_{15/2}$ states of Nd^{3+} and Er^{3+} to be small. The operator equivalent constants for these two states are thus numerically approximately equal; they differ, however, in sign. The over-all splittings of the $^4I_{15/2}$ manifolds of Nd^{3+} and Er^{3+} YAlG differ considerably. In a previous paper[3] it was shown that J mixing occurred within the ^4I manifolds of Nd^{3+}:YAlG. This occurrence of J mixing was due to the fact that the over-all splitting of the individual ^4I manifolds was comparable to their separation. In Er^{3+}:YAlG, the over-all splittings of ^4I manifolds are small compared to their separation, and hence J mixing should not be appreciable.

Neglecting the contribution of $A_2{}^2$, we calculate (from the splitting of the $^4S_{3/2}$ and $^4F_{3/2}$ states) values of the parameter $A_2{}^0$ of 260 and 215 cm^{-1}, respectively. $A_2{}^0 \approx 260$ cm^{-1} in Er^{3+}:YAlG is comparable with values of this parameter which have been obtained for the rare-earth ions Nd^{3+}, Eu^{3+}, and Tb^{3+} in YAlG.[3,4]

The parameters $A_4{}^0$, $A_4{}^4 = -5A_4{}^0$, $A_6{}^0$, and $A_6{}^4$ have been evaluated from the splitting of the $^4I_{15/2}$ and $^4I_{9/2}$ states and are given in Table III. The calculated and observed splitting for some of the J manifolds is shown in Figs. 1 and 2.

TABLE III. Crystal-field parameters $A_n{}^m = \langle r^n \rangle B_n{}^m$ for Er^{3+}:YAlG.

$A_2{}^0 = 260$ cm⁻¹	$A_4{}^0 = -160$ cm⁻¹ $A_4{}^4 = +800$ cm⁻¹	$A_6{}^0 = 45$ cm⁻¹ $A_6{}^4 = -710$ cm⁻¹

[6] H. A. Bethe, Ann. Physik **3**, 133 (1929).
[7] G. Z. Menzer, Kristallografiya **69**, 300 (1929).
[8] S. Geller and M. A. Gilleo, Phys. Chem. Solids **3**, 30 (1957).
[9] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952).

[10] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).
[11] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).
[12] B. R. Judd, Proc. Roy. Soc. (London) **A227**, 552 (1955).
[13] E. H. Erath, J. Chem. Phys. **34**, 1985 (1960).
[14] B. G. Wybourne, J. Chem. Phys. **32**, 639 (1960).

TABLE IV. The ratio of the sixth-order terms $A_6{}^4$ and $A_6{}^0$ for different rare-earth ions in YAlG.

Ion	$\epsilon = A_6{}^4/21A_6{}^0$
Nd^{3+}:$Y_3Al_2(AlO_4)_3$	0.51
Eu^{3+}:$Y_3Al_2(AlO_4)_3$	0.57
Tb^{3+}:$Y_3Al_2(AlO_4)_3$	0.58
Er^{3+}:$Y_3Al_2(AlO_4)_3$	0.75

A general agreement exists between the calculated and observed splitting patterns. A deviation occurs in the calculated and observed splitting of the ^4F manifolds. In a previous paper[3] we have demonstrated how the splitting of a $J = \frac{7}{2}$ manifold can be used to evaluate the parameter $A_6{}^0$ and the constant $\epsilon = A_6{}^4/21A_6{}^0$. This calculation has been carried out for the $^4F_{7/2}$ manifold of Er^{3+}:YAlG. Results of this calculation show that no unique values for $A_6{}^0$ and ϵ exist if 250 cm^{-1} $< A_2{}^0 <$ 300 and 150 cm^{-1} $< |A_4{}^0| <$ 200 cm^{-1}. This would suggest that the wave function used by Erath to calculate operator equivalent constants for the $^4F_{7/2}$ state is probably inaccurate. It is perhaps worthwhile to note that the $A_n{}^m$ parameters for Er^{3+}:YAlG which are given in Table III represent a crystal field of near tetragonal symmetry. For crystal fields of cubic symmetry, the ratio of the fourth-order terms[15] is $A_4{}^4/A_4{}^0 = 5$, while for such a field $A_2{}^0 = 0$ and $\epsilon = A_6{}^4/21A_6{}^0 = 1.0$. Values of the constant ϵ which we have obtained for
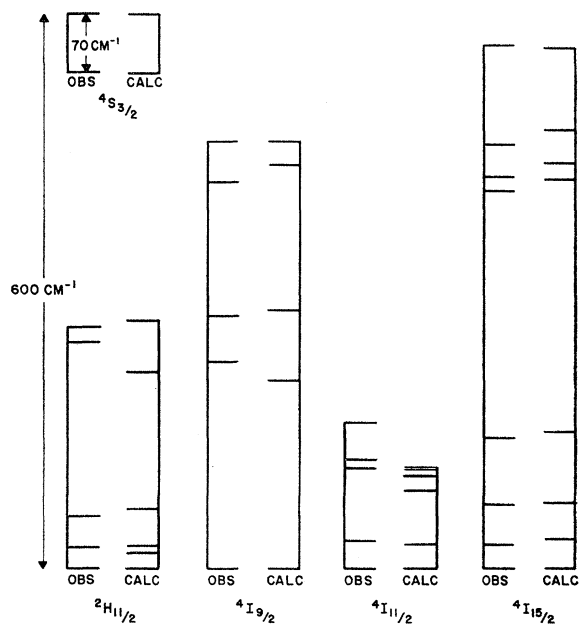
FIG. 1. Observed and calculated splitting patterns of the $^4S_{3/2}$, $^2H_{11/2}$, $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{15/2}$ manifolds of Er^{3+}:YAlG.

[15] K. R. Lea, M. J. M. Leask, and W. P. Wolf, Phys. Chem. Solids **23**, 1381 (1961).
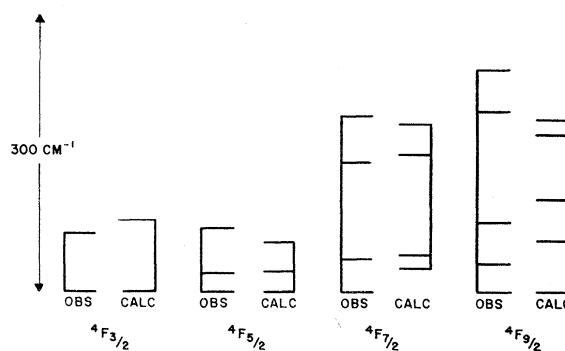
FIG. 2. Observed and calculated splitting patterns of the ^4F manifolds of Er^{3+}:YAlG.

some of the trivalent rare-earth ions in the host lattice YAlG are given in Table IV.

The table shows that ϵ increases as the atomic number Z increases in the series of the lanthanides. Calculations of Freeman and Watson[16] on the radial integrals $\langle r^2 \rangle$, $\langle r^4 \rangle$, and $\langle r^6 \rangle$ have been employed to calculate the constants $B_n{}^m = A_n{}^m/\langle r^n \rangle$ of Eq. (1). Table V

TABLE V. Values of the constants $B_n{}^m = A_n{}^m/r^n$ for the rare-earth ions Nd^{3+}, Eu^{3+}, Tb^{3+}, and Er^{3+} in the host-lattice YAlG.

Ion	$A_2{}^0$ (cm^{-1})	$B_2{}^0 \times 10^{-16}$ (cm^3)	$A_4{}^0$ (cm^{-1})	$B_4{}^0 \times 10^{-32}$ (cm^5)	$A_6{}^0$ (cm^{-1})	$B_6{}^0 \times 10^{-64}$ (cm^7)
Nd^{3+}	270	2.7	-250	-1.0_4	92	7.4
Eu^{3+}	268	3.3	-190	-1.1_3	94	12.7
Tb^{3+}	260	3.5	-184	-1.3_2	93	16.3
Er^{3+}	260	3.9	-160	-1.4_1	45	15.1

shows values of $B_2{}^0$, $B_4{}^0$, and $B_6{}^0$ for some of the trivalent rare-earth ions in YAlG.

CONCLUSIONS

The splitting of J manifolds of Er^{3+}:YAlG has been approximately reproduced using the crystal field constants given in this paper. Slight modification of the wave functions of these J manifolds would influence the crystal-field constants and hence the validity of these parameters depends on the knowledge of the wave functions.

ACKNOWLEDGMENTS

[16] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).