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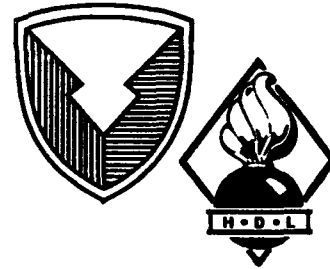
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# Theoretical Crystal-Field Calculations for Rare-Earth Ions in III-V Semiconductor Compounds

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13. ABSTRACT (Maximum 200 words) <p>This report presents preliminary crystal-field calculations showing the splitting of the Stark levels of three rare-earth-doped III-V semiconductor compounds: <math>\text{Yb}^{3+}:\text{InP}</math>, <math>\text{Er}^{3+}:\text{GaAs}</math>, and <math>\text{Nd}^{3+}:\text{GaP}</math>. The crystal-field parameters were obtained from a lattice-sum calculation including monopole, self-induced dipole, and self-induced quadrupole contributions. The effects of varying the effective ionic charges and the ionic polarizabilities are explored. For each of the systems considered, these parameters were adjusted to match available experimental data on the ordering of the levels according to irreducible representation, the magnitude of crystal-field splitting, and intensities. A consistent set of parameters was found that gave reasonable results for all the systems considered. Refinements in the crystal-field model may be necessary when more experimental data become available.</p>				
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# Contents



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<b>1. Introduction</b> .....	5
<b>2. Material Properties</b> .....	6
2.1 Crystallographic Data .....	6
2.2 Effective Charges .....	6
2.3 Polarizabilities .....	7
2.4 Index of Refraction .....	9
<b>3. Yb<sup>3+</sup>:InP</b> .....	9
<b>4. Er<sup>3+</sup>:GaAs</b> .....	12
<b>5. Nd<sup>3+</sup>:GaP</b> .....	16
<b>6. Conclusions</b> .....	17
<b>Acknowledgements</b> .....	18
<b>References</b> .....	18
<b>Bibliography of Erbium-, Ytterbium-, and Neodymium-Doped III-V Semiconductors</b> ....	21
<b>Distribution</b> .....	23

## Figures

1. Energy level diagram for Yb <sup>3+</sup> :InP .....	11
2. Branching ratios for Yb <sup>3+</sup> :InP at 6 K calculated using electric and magnetic dipole transition probabilities .....	12
3. Energy level diagram for Er <sup>3+</sup> :GaAs .....	14
4. Branching ratios for Er <sup>3+</sup> :GaAs at 6 K calculated using electric and magnetic dipole transition probabilities .....	15
5. Multiplet branching ratios for Nd <sup>3+</sup> :GaP calculated using electric dipole transition probabilities only .....	17

## Tables

1. Fractional positions of atoms in unit cell .....	6
2. Multipole contributions to crystal-field components, $A_{kq}$ .....	8
3. Dipole ionic polarizabilities deduced from experimental measurements of dielectric constant .....	8
4. Best-fit Sellmeier coefficients for specified wavelength range .....	9
5. Crystal-field parameters for Yb <sup>3+</sup> :InP with $Q(\text{In}) = +3$ , and $Q(\text{P}) = -3$ , and phosphorus polarizabilities $\alpha_D = 2.0 \text{ \AA}^3$ and $\alpha_Q = 4.0 \text{ \AA}^5$ .....	10
6. Energy levels for Yb <sup>3+</sup> :InP computed using crystal-field parameters of table 5 .....	10
7. Crystal-field parameters for Er <sup>3+</sup> :GaAs, for $Q(\text{Ga}) = +3$ , and $Q(\text{As}) = -3$ .....	13
8. Energy levels for Er <sup>3+</sup> :GaAs computed using crystal-field parameters of table 7b .....	14

**Tables (cont'd)**

	Page
9. Crystal-field parameters for $\text{Nd}^{3+}:\text{GaP}$ with $Q(\text{Ga}) = +3$ , and $Q(\text{P}) = -3$ , and phosphorus polarizabilities $\alpha_D = 2 \text{ \AA}^3$ and $\alpha_Q = 4 \text{ \AA}^5$ .....	16
10. Energy levels for $\text{Nd}^{3+}:\text{GaP}$ computed using crystal-field parameters from table 9 .....	16

# 1. Introduction

The incorporation of rare-earth ions into III-V semiconductor compounds has recently generated a great deal of interest, motivated primarily by potential applications in optoelectronic devices. Many groups have reported photoluminescence and photoluminescence excitation measurements of rare-earth ions in these systems. The systems for which the most published data are available are  $\text{Yb}^{3+}:\text{InP}$ ,  $\text{Er}^{3+}:\text{GaAs}$ , and  $\text{Nd}^{3+}:\text{GaP}$  (we provide bibliographies for each of these). In addition, two review articles have been written [1,2], and some work has been done on theory [3].

The symmetry of the site occupied by the rare-earth ion depends on the growth conditions. For the samples listed above, the sample preparation has been optimized to minimize the number of lines seen in the spectrum. It is assumed that under favorable growth conditions, the rare-earth ion substitutes for a cation. For unfavorable growth conditions, it has been speculated that the rare-earth ion occupies an interstitial site or defect site instead of substituting for a cation. The location of the rare-earth ion in a III-V lattice is discussed by Kozanecki et al [4,5]. Because Yb is the smallest rare-earth ion and In is larger than Ga or Al,  $\text{Yb}^{3+}:\text{InP}$  grows relatively easily with Yb substituting for indium in the InP lattice. For the other systems considered, the optimum conditions for sample growth are still under investigation, but many of the spectral features can be explained assuming cubic symmetry.

The starting point for each sample considered is a simple point-charge model with full valence charges ( $\pm 3$ ) for the constituent ions. Variations of the simple point-charge model are considered that give improved agreement to the experimental data. The irreducible representations are obtained from group theory, assuming  $T_d$  symmetry of the rare-earth site. Varying the effective ionic charge changes the relative splitting of the levels but not the ordering of the irreducible representations. Introducing self-induced contributions to the simple point-charge model allows the relative ordering of the irreducible representations to be changed, as well as the magnitude of the level splittings.

Physically reasonable values for the material parameters (the effective charge and the dipole and quadrupole polarizabilities) are discussed in section 2. For each of the three systems considered, the parameters  $Q = 3$ ,  $\alpha_D = 2 \text{ \AA}^3$ , and  $\alpha_Q = 4 \text{ \AA}^5$  provide a good starting point for interpreting experimental data, and the results of the calculations using these parameters are presented in sections 3 to 5. For  $\text{Er}^{3+}:\text{GaAs}$ , sufficient experimental data are available so that we can deviate from this parameter combination to improve agreement with the data. For all the systems considered, the identification of the levels is uncertain because of the presence of extra lines, and further optimization of

the model may be more profitable after more experimental work is done. As a complement to the energy level calculation, the relative intensities of transitions measured in fluorescence are also calculated directly from the theoretical model. The intensity calculations were done at 6 K to correspond to experimental fluorescence measurements. At this temperature, essentially all transitions originate at the lowest level of the upper multiplet. These calculations are compared directly with the photoluminescence spectra and provide a further check on the model.

## 2. Material Properties

### 2.1 Crystallographic Data

The III-V semiconductor compounds considered in this report crystallize in the zinc-blende structure, which belongs to space group  $F\bar{4}3m$ , 216 in the *International tables for x-ray crystallography* [6]. The lattice is described in Wyckoff [7] with two sites, the cation and anion sites, each having  $T_d$  symmetry. The crystallographic information is summarized in table 1. The lattice parameters for these compounds are also given by Wyckoff as 5.6537 Å for GaAs, 5.8687 Å for InP, and 5.4505 Å for GaP.

**Table 1. Fractional positions of atoms in unit cell**

Site	Symmetry	x	y	z	Charge	Dipole polarizability	Quadrupole polarizability
Cation site (Ga, In)	$T_d$	0	0	0	+Q	$\alpha_D(+)$	$\alpha_Q(+)$
Anion site (As, P)	$T_d$	0.25	0.25	0.25	-Q	$\alpha_D(-)$	$\alpha_Q(-)$
Interstitial sites	$T_d$	0.50	0.50	0.50	—	—	—
	$T_d$	0.75	0.75	0.75	—	—	—

### 2.2 Effective Charges

To maintain charge neutrality, the effective cation charge,  $Q$ , is balanced by an anion charge,  $-Q$ , giving only one free parameter for the effective charge. Various models have been developed to describe the effective charge in III-V compounds [8,9]. In the simplest approximation, the static effective charge can be written  $Q^* = -\Delta Q + 4p$ , where  $0 \leq p \leq 1$ , and  $\Delta Q = 1$  for III-V compounds. For  $p = 1$ , the effective cation charge is the full valence charge of +3 (in units of the electronic charge). The models predict an effective cation charge somewhat smaller than the full valence charge  $Q = 3$ , but not a great deal smaller. The effective charges calculated from a band-structure model [9] range from 2.0 to 2.5.

In  $T_d$  symmetry, there are four nonzero even- $k$  crystal-field components, but only  $B_{40}$  and  $B_{60}$  are independent;  $B_{44} = (5/14)^{1/2} B_{40}$  and  $B_{64} = -(7/2)^{1/2} B_{60}$ . If dipole and quadrupole polarizabilities as well as the effective charge

are allowed to vary, there are more free parameters in the model than independent crystal-field components. For this reason, the effective charge was fixed at  $Q = 3$ . A point-charge model with effective charge  $Q = 3$  and no self-induced terms is subsequently referred to as a simple point-charge model.

### 2.3 Polarizabilities

In sites with cubic symmetry, there are no point-dipole or point-quadrupole contributions because of the high symmetry of the lattice [10]. However, the cubic symmetry does not prevent self-induced effects. We have calculated these effects following Morrison et al [11]. Table 2 lists the contributions to the crystal-field components,  $A_{kq}$ , for each ion from the monopole, self-induced dipole, and self-induced quadrupole terms, with unit charge and unit polarizabilities for all ionic species. The contributions are multiplied by the parameters  $Q$ ,  $\alpha_D$ , and  $\alpha_Q$  for each species and added to compute the total crystal field. Very nearly all the self-induced contributions come from the anion, and to a good approximation, the cation contributions to the self-induced fields can be neglected, even though the calculated polarizabilities for the cations are larger than for the anions. This gives two parameters for the anion polarizabilities,  $\alpha_D$  and  $\alpha_Q$ , in addition to the effective charge,  $Q$ , for each compound.

Dipole polarizabilities have been computed by Pandey et al [12] for several III-V compounds and are given in table 3. They used the Clausius-Mossotti relation, which is of questionable applicability to III-V compounds. It should be possible to repeat these calculations with an effective electric field appropriate to semiconductors [13]. Theoretical dipole ionic polarizabilities for positive ions can be calculated from Hartree-Fock theory and have been tabulated by Fraga, Karwowski, and Saxena [14]. However, since the positive ionic contributions to the self-induced fields are not significant, we have not made use of these values. Dipole and quadrupole polarizabilities for several ions are given by Schmidt et al [15]. Although neither  $P^{3-}$  nor  $As^{3-}$  is included in this study,  $N^{3-}$  is, and one may assume that the values for the other column-V elements are comparable. For  $N^{3-}$ ,  $\alpha_D = 2.65 \text{ \AA}^3$  and  $\alpha_Q = 12.12 \text{ \AA}^5$ . These values are large, and in light of previous experience [11], we reduced these values in simulating the experimental data. The splittings produced by these parameters for each of the compounds considered are described in the following sections.

If the formulas in the paper by Morrison et al [11] are used, the higher order multipoles could also be included, but there are no reliable estimates of polarizabilities for higher order multipoles. The quality of the fluorescence data at this time does not warrant the determination of polarizabilities from spectral analysis, so estimates of the magnitude of the multipolar polarizabili-



ties need to come from other measurements. It is expected that the contributions from higher order multipoles will become progressively weaker, although we have no data to substantiate this claim.

**Table 2. Multipole contributions to crystal-field components,  $A_{kq}$**

These contributions are multiplied by the parameters  $Q$ ,  $\alpha_D$ , and  $\alpha_Q$ , respectively, for each ionic species and added to compute the total crystal field.

a. In site in InP

$A_{kq}$ ( $\text{cm}^{-1}/\text{\AA}^k$ )	Monopole		Self-induced dipole		Self-induced quadrupole	
	In	P	In	P	In	P
Im $A_{32}$	0	-5492	0	-848.9	0	-331.3
$A_{40}$	125.9	1659	8.65	428.4	1.58	199.7
$A_{44}$	75.3	992	5.17	256.0	0.94	119.3
$A_{60}$	12.9	-151	1.58	-78.3	0.37	-48.5
$A_{64}$	-24.1	283	-2.95	146.5	-0.69	90.7
Im $A_{72}$	0	86.2	0	57.6	0	40.1
Im $A_{76}$	0	79.3	0	53.0	0	36.9

b. Ga site in GaAs

$A_{kq}$ ( $\text{cm}^{-1}/\text{\AA}^k$ )	Monopole		Self-induced dipole		Self-induced quadrupole	
	Ga	As	Ga	As	Ga	As
Im $A_{32}$	0	-6376.4	0	-1102.4	0	-463.5
$A_{40}$	151.8	1999.7	11.7	577.4	2.29	290.0
$A_{44}$	90.7	1195.0	6.97	345.1	1.37	173.3
$A_{60}$	16.8	-196.2	2.29	-113.7	0.58	-75.9
$A_{64}$	-31.3	367.0	-4.28	212.7	-1.08	141.9
Im $A_{72}$	0	116.2	0	86.9	0	65.1
Im $A_{76}$	0	106.9	0	79.9	0	59.9

c. Ga site in GaP

$A_{kq}$ ( $\text{cm}^{-1}/\text{\AA}^k$ )	Monopole		Self-induced dipole		Self-induced quadrupole	
	Ga	P	Ga	P	Ga	P
Im $A_{32}$	0	-7381.8	0	-1424.3	0	-644.4
$A_{40}$	181.9	2400.9	15.63	773.9	3.30	418.2
$A_{44}$	108.7	1434.8	9.34	462.5	1.97	249.9
$A_{60}$	21.6	-253.5	3.30	-163.9	0.89	-117.7
$A_{64}$	-40.5	474.2	-6.18	306.8	-1.67	220.2
Im $A_{72}$	0	155.7	0	129.9	0	104.8
Im $A_{76}$	0	143.2	0	119.5	0	96.4

**Table 3. Dipole ionic polarizabilities deduced from experimental measurements of dielectric constant (Pandey et al [12])**

Ion	$\alpha_D$ ( $\text{\AA}^3$ )
Ga	4.435
In	6.489
P	2.659
As	3.786

## 2.4 Index of Refraction

The index of refraction is not included in the lattice model and is not necessary for calculating energy levels. It is used in the branching ratio calculations to evaluate the Lorentz inner-field correction:

$$X_{ij} = \frac{n_{ij}(n_{ij}^2 + 2)^2}{9} \text{ for electric dipole transitions, and}$$

$$X'_{ij} = n_{ij}^3 \text{ for magnetic dipole transitions.}$$

Empirical fits were made to the index of refraction data from the *CRC Handbook of Laser Science and Technology* [16] to the following Sellmeier dispersion relation:

$$n^2 = A + \frac{B\lambda^2}{\lambda^2 - C}.$$

For  $A$  not equal to one, the equation is only valid for restricted wavelength range, and the wavelength range of the input data is given in table 4 with the resulting parameter values.

**Table 4. Best-fit Sellmeier coefficients for specified wavelength range**

Compound	Sellmeier coefficients			Wavelength range ( $\mu\text{m}$ )
	A	B	C ( $\mu\text{m}^2$ )	
GaAs	7.14	3.78	0.27	1.13–1.65
InP	5.74	3.75	0.299	0.925–2.0
GaP	5.29	3.79	0.142	0.8–3.8

## 3. $\text{Yb}^{3+}:\text{InP}$

The simple point-charge model predicts the irreducible representation of the ground state of  $\text{Yb}^{3+}:\text{InP}$  to be  $\Gamma_6$ . This determination is substantiated by electron paramagnetic resonance (EPR) measurements of an isotropic  $g$ -value for the ground state by Masterov et al [17] of  $g = 3.29$ . In pure cubic symmetry with no  $J$ -mixing, the  $g$ -values for the ground state doublets are  $\Gamma_7 = 2.666$  and  $\Gamma_6 = 3.4$ . In order to reconcile the experimental and calculated  $g$ -value for a  $\Gamma_6$  doublet, we can include an orbital reduction factor  $k < 1$  in calculating the  $J = 7/2$  Lande  $g$ -factor [18]. It is impossible to reconcile a  $\Gamma_7$  ground state with the experimental measurement of the  $g$ -value. Combinations of parameters that give a  $\Gamma_7$  or  $\Gamma_8$  ground state have therefore been ruled out. Because of the large energy separation of the  ${}^2F_{7/2}$  and  ${}^2F_{5/2}$  and the small crystal-field splitting, the  $J$ -mixing by the crystal field has a negligible effect on the  $g$ -factors.

The contributions of the monopole and self-induced terms to the crystal-field parameters for  $\text{Yb}^{3+}:\text{InP}$  are given in table 5. The crystal-field parameters,  $B_{kq}$ , are related to the crystal-field components,  $A_{kq}$ , by  $B_{kq} = \rho_k A_{kq}$ . Values of  $\rho_k$  for  $\text{Yb}^{3+}$  ( $\rho_4 = 0.3938$  and  $\rho_6 = 0.912$ ) are given by Morrison and Leavitt [19]. All the nonzero tensor components,  $A_{kq}$  and  $B_{kq}$ , are listed in table 5 for the sake of completeness, even though they are not all independent. The theoretical energies and irreducible representations corresponding to these crystal-field parameters are given in table 6 and depicted schematically in figure 1.

The first point of comparison with the experimental data is the ordering of the irreducible representations. As mentioned above, theory and EPR measurements both give  $\Gamma_6$  as the ground state. Several papers [20–23] have identified the lowest state in the upper multiplet as a  $\Gamma_8$  quartet. This is stated most explicitly by Aszodi et al [22], where two different sets of crystal-field parameters are used to describe the upper and lower multiplets. Using the present approach, we cannot justify the use of the two sets of parameters from a microscopic point of view. For all parameter combinations that give a  $\Gamma_6$  ground state, the lowest level in the  ${}^2F_{5/2}$  multiplet is also a  $\Gamma_6$  doublet. The present results suggest that the line chosen for Zeeman analysis was not the line corresponding to a transition from the lowest  ${}^2F_{5/2}$  level to the ground state, as assumed by the authors.

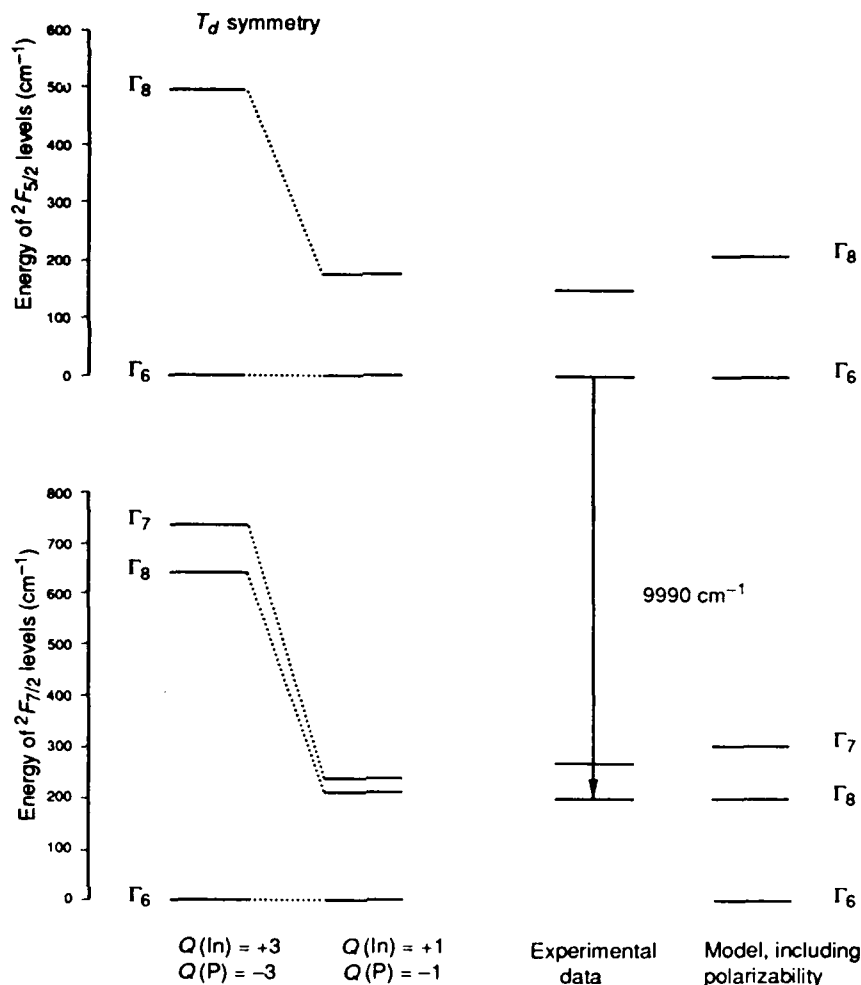
**Table 5.** Crystal-field parameters for  $\text{Yb}^{3+}:\text{InP}$  with  $Q(\text{In}) = +3$ , and  $Q(\text{P}) = -3$ , and phosphorus polarizabilities  $\alpha_D = 2.0 \text{ \AA}^3$  and  $\alpha_Q = 4.0 \text{ \AA}^5$

$A_{kq}$ ( $\text{cm}^{-1}/\text{\AA}^k$ )	Monopole	Self-induced dipole	Self-induced quadrupole	Total crystal field	$B_{kq}$ ( $\text{cm}^{-1}$ )
Im $A_{32}$	16,476.3	-1697.8	-1325.2	13,453.3	—
$A_{40}$	-4,599.9	856.7	798.6	-2,944.5	-1159.5
$A_{44}$	-2,749.0	512.0	477.3	-1,759.7	-693.0
$A_{60}$	491.9	-156.6	-193.9	141.4	128.9
$A_{64}$	-920.3	292.9	362.8	-264.5	-241.2
Im $A_{72}$	-258.6	115.3	160.4	17.1	—
Im $A_{76}$	-237.9	106.0	147.6	15.7	—

**Table 6.** Energy levels for  $\text{Yb}^{3+}:\text{InP}$  computed using crystal-field parameters of table 5

$2S+1L_J$ (centroid)	Level	$\Gamma_n$	Theoretical energy ( $\text{cm}^{-1}$ )	Theoretical energy shifted by $10,338 \text{ cm}^{-1}$	Experimental energy ( $\text{cm}^{-1}$ )
${}^2F_{7/2}$ (294.7)	1	6	0.1	-10,338	—
	2	8	348	-9,990	-9,990
	3	7	475	-9,863	-9,921
${}^2F_{7/2}$ (10,553.4)	4	6	10,338	0	0
	5	8	10,665	327	—

**Figure 1. Energy level diagram for Yb<sup>3+</sup>:InP.**



The second point of comparison is the magnitude of the crystal-field splittings. The strongest lines in the spectrum are seen at 9990 and 9921  $\text{cm}^{-1}$ , yielding a splitting between the second and third lines in the lower multiplet of 69  $\text{cm}^{-1}$  [20–22]. A peak is seen 35  $\text{cm}^{-1}$  below the strong peak at 9990  $\text{cm}^{-1}$  in photoluminescence measurements [20–22] and was identified as the transition to the ground state. However, the theoretical calculation places the ground state 348  $\text{cm}^{-1}$  below the  $\Gamma_8$  level. The transition to the ground state connects two  $\Gamma_6$  states, and since this transition is not allowed by electric dipole selection rules, it is expected to be weak. A line at a higher frequency was reported by Kozanecki et al [23] and shown (on a scale expanded by a factor of 15) together with the strong transitions at 9921 and 9990  $\text{cm}^{-1}$ . Kozanecki et al did not report a numerical value for the energy, but from the plot of their data, the line is at approximately 10,135  $\text{cm}^{-1}$ , and the line at this energy is a possible candidate for the transition connecting the two  $\Gamma_6$  states. Because the transition to the ground state is expected to be very weak, it is easily confused with other extra lines in the spectra and may be difficult to identify experimentally.

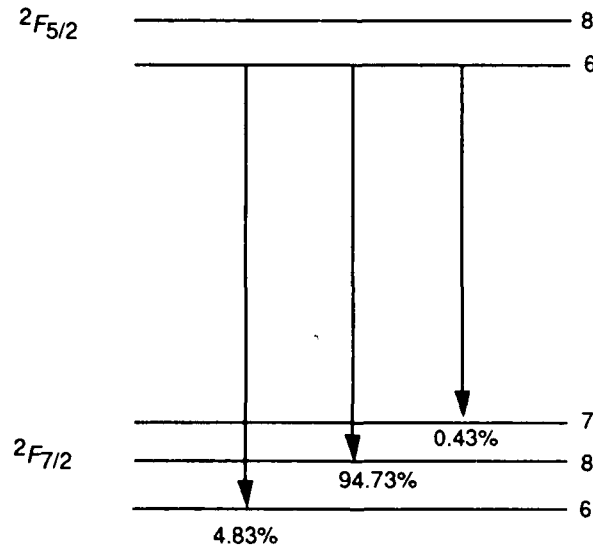
The centroid for the  ${}^2F_{5/2}$  multiplet is adjusted in table 6 to reproduce  ${}^1e$  splitting at  $9990\text{ cm}^{-1}$ . This raises the center of gravity of the upper multiplet by around  $100\text{ cm}^{-1}$  from what was reported elsewhere [20–22], bringing it into closer agreement with the center of gravity for this multiplet in other insulating crystals (see, for example, the review article in Gschneidner and Eyring [24]). Since the host material, rather than the atomic parameters, should have the largest influence on the crystal-field splittings, the higher placement of the centroid has more credibility.

Figure 2 shows branching ratios for  $\text{Yb}^{3+}:\text{InP}$  calculated using the odd-fold crystal-field components given in table 5. The strongest transition is predicted as the transition from  $\Gamma_6$  ( $J = 5/2$ ) to a  $\Gamma_8$  ( $J = 7/2$ ) at  $9990\text{ cm}^{-1}$ . Experimentally, the line at  $9990\text{ cm}^{-1}$  is strong, but the line at  $9921\text{ cm}^{-1}$  is almost as strong and has structure. No detailed quantitative comparison is made with the experimental luminescence spectra at this time.

#### 4. $\text{Er}^{3+}:\text{GaAs}$

The simple point-charge model predicts the irreducible representation of the ground state of  $\text{Er}^{3+}:\text{GaAs}$  to be  $\Gamma_6$ . However, EPR measurements of  $\text{Er}^{3+}:\text{GaAs}$  [25] indicate that the  $g$ -value of the ground state is isotropic ( $g_{\parallel} = g_{\perp} = 5.921$ ) and corresponds well with the value appropriate for a  $\Gamma_7$  state in  $T_d$  symmetry ( $g(\Gamma_7) = 6.0$  and  $g(\Gamma_6) = 6.8$  for perfect cubic symmetry). EPR measurements of  $\text{Er}^{3+}:\text{InP}$  [26] also indicate a  $\Gamma_7$  ground state ( $g_{\parallel} = 5.699 \pm 0.005$  and  $g_{\perp} = 5.954 \pm 0.005$ ). The anisotropy was attributed to a slight axial distortion of the symmetry of the  $\text{Er}^{3+}$  site. One of the most successful aspects of this model is that when self-induced effects are included in the theory, the  $\Gamma_7$  state is predicted to be the lowest state in the ground multiplet.

**Figure 2. Branching ratios for  $\text{Yb}^{3+}:\text{InP}$  at 6 K calculated using electric and magnetic dipole transition probabilities.**



The various contributions for the monopole and self-induced terms for two different parameter sets are given in table 7. The crystal-field parameters,  $B_{kq}$ , are related to the crystal-field components,  $A_{kq}$ , by  $B_{kq} = \rho_k A_{kq}$ . Values of  $\rho_k$  for  $\text{Er}^{3+}$  ( $\rho_4 = 0.4126$  and  $\rho_6 = 0.9826$ ) are given by Morrison and Leavitt [19]. In table 7, all the nonzero tensor components are listed for the sake of completeness, even though they are not all independent. The theoretical energies and irreducible representations of the  $^4I_{15/2}$  and  $^4I_{13/2}$  multiplets of  $\text{Er}^{3+}$  corresponding to the crystal-field parameters of table 7b are compared with experimental splittings in table 8, and a schematic diagram of the energy levels is shown in figure 3.

Experimental lines for the  $^4I_{15/2}$  multiplet were measured by photoluminescence by Ennen et al [27]. More lines are observed in emission than expected for  $\text{Er}^{3+}$  in a cubic site. We have assumed that some of the lines are due to  $\text{Er}^{3+}$  ions in cubic sites. Extra lines may be due to ions in minority sites and phonon sidebands, especially the lines that replicate splittings observed in the upper manifold. Values for levels belonging to the  $^4I_{15/2}$  multiplet not included in our calculation are 112.3, 178, 217.3, 427.9, and 449.9  $\text{cm}^{-1}$ . A line around 30  $\text{cm}^{-1}$  that is predicted by the model was not reported by Ennen et al [27]. Another group (Zhao et al [28]) has reported values for some of the smaller peaks with smaller splittings at 15,448, 15,482, 15,547, 15,647, and 15,685  $\text{\AA}$ . Their most intense line is the second, at 15,482  $\text{\AA}$ , which should correspond to the transition to the ground state. If splittings are measured from

Table 7. Crystal-field parameters for  $\text{Er}^{3+}:\text{GaAs}$ , for  $Q(\text{Ga}) = +3$ , and  $Q(\text{As}) = -3$

a. Arsenic polarizabilities  $\alpha_D = 2 \text{\AA}^3$  and  $\alpha_Q = 4 \text{\AA}^5$

$A_{kq}$ ( $\text{cm}^{-1}/\text{\AA}^k$ )	Monopole	Self-induced dipole	Self-induced quadrupole	Total crystal field	$B_{kq}$ ( $\text{cm}^{-1}$ )
Im $A_{32}$	19,129.2	-2204.7	-1854.2	15,070.3	—
$A_{40}$	-5,543.7	1154.9	1159.9	-3,228.9	-1332.2
$A_{44}$	-3,313.0	690.2	693.2	-1,929.6	-796.2
$A_{60}$	638.8	-227.4	-303.5	107.9	106.0
$A_{64}$	-1,195.1	425.5	567.8	-201.8	-198.3
Im $A_{72}$	-348.6	173.8	260.6	85.8	—
Im $A_{76}$	-320.6	159.8	239.7	78.9	—

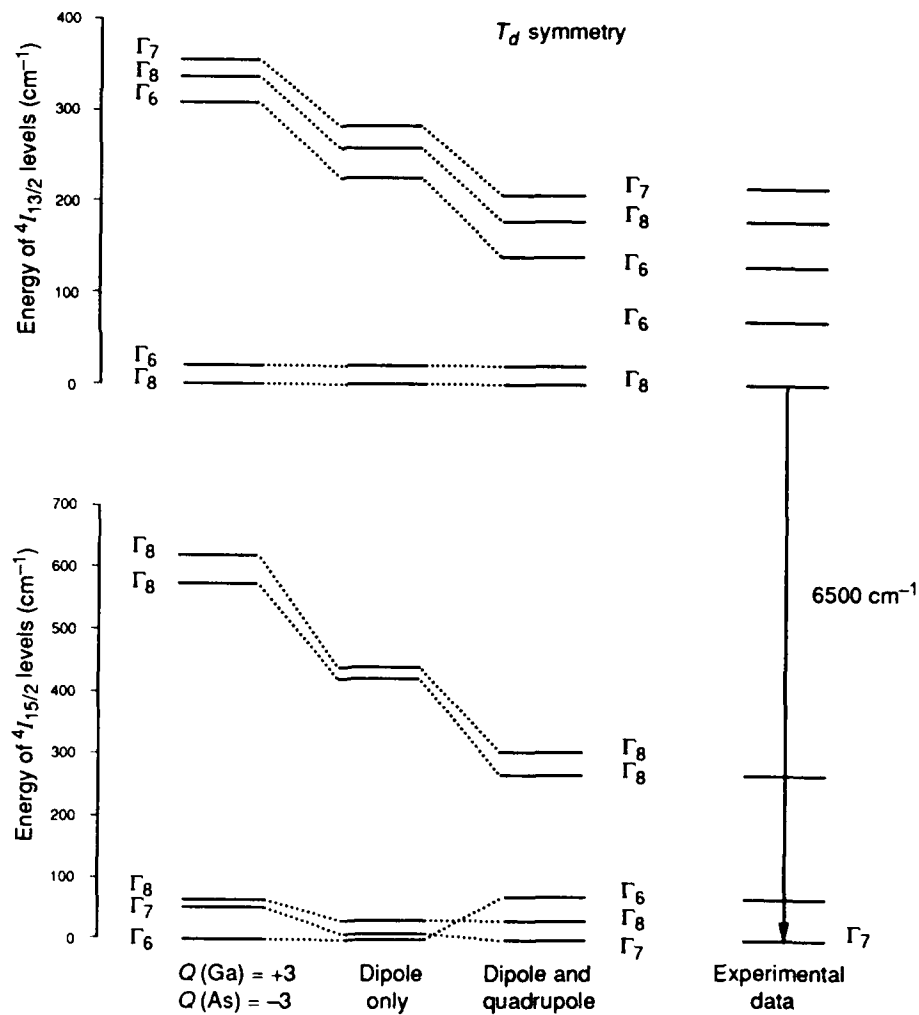
b. Arsenic polarizabilities  $\alpha_D = 1.7 \text{\AA}^3$  and  $\alpha_Q = 3.4 \text{\AA}^5$

$A_{kq}$ ( $\text{cm}^{-1}/\text{\AA}^k$ )	Monopole	Self-induced dipole	Self-induced quadrupole	Total crystal field	$B_{kq}$ ( $\text{cm}^{-1}$ )
Im $A_{32}$	19,129.2	-1874.0	-1576.1	15,679.1	—
$A_{40}$	-5,543.7	981.7	986.0	-3,576.1	-1475.5
$A_{44}$	-3,313.0	586.7	589.2	-2,137.1	-881.8
$A_{60}$	638.8	-193.3	-258.0	187.5	184.2
$A_{64}$	-1,195.1	361.6	482.6	-350.8	-344.7
Im $A_{72}$	-348.6	147.7	221.5	20.6	—
Im $A_{76}$	-320.6	135.9	203.7	19.0	—

**Table 8. Energy levels for Er<sup>3+</sup>:GaAs computed using crystal-field parameters of table 7b**

$2S+1L_J$ (centroid)	Level	$\Gamma_n$	Theoretical energy (cm <sup>-1</sup> )	Experimental energy (cm <sup>-1</sup> ) strongest lines
$4I_{15/2}$ (162.8)	1	7	0.0	0
	2	8	29.0	—
	3	6	71	69.4
	4	8	265	268.5
	5	8	301	—
$4I_{13/2}$ (6610.8)	6	8	6501	6500.7
	7	6	6528	6569.0
	8	6	6639	6627.3
	9	8	6679	6680.5
	10	7	6708	6715.0

**Figure 3. Energy level diagram for Er<sup>3+</sup>:GaAs.**

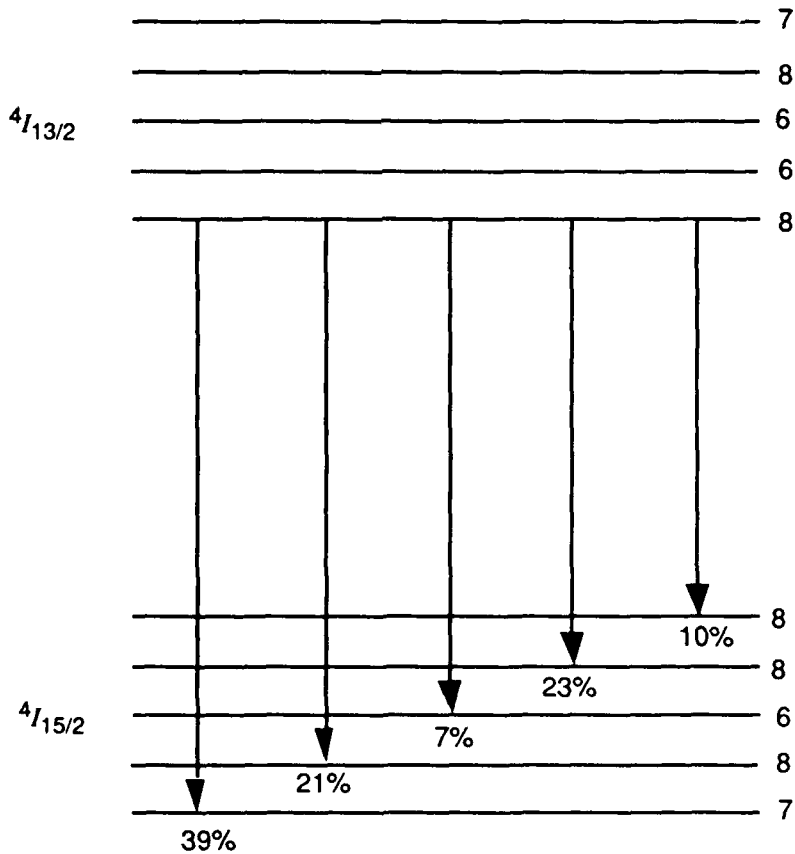


this line, the next three lines are at 26, 68, and 83  $\text{cm}^{-1}$ . These peaks are visible in the spectrum of Ennen et al, but were not labelled as erbium peaks. If their three lowest levels (0, 69, and 112  $\text{cm}^{-1}$ ) are fit assuming cubic symmetry, the parameter values again correspond to ionic charges larger than  $\pm 3$ . In general, it is more difficult to fit data measured in emission than in absorption, and it is hard to conclude anything from the emission spectrum alone.

Experimental lines for the  $^4I_{13/2}$  multiplet were measured by photoluminescence excitation spectroscopy by Ennen et al [27]. The weak pair of levels at 6840.4 and 6854.3  $\text{cm}^{-1}$  was not included in table 8. Splitting the upper manifold this strongly, assuming cubic symmetry, would require a point-charge model with ionic charges larger than  $\pm 3$ . The other levels in the upper multiplet correlate reasonably well with the levels predicted by the model.

Branching ratios for  $\text{Er}^{3+}:\text{GaAs}$  are given in figure 4. In agreement with experiment, the model predicts the strongest intensity at low temperatures in the transition from the lowest state of the upper multiplet to the ground state.

**Figure 4. Branching ratios for  $\text{Er}^{3+}:\text{GaAs}$  at 6 K calculated using electric and magnetic dipole transition probabilities.**





## 5. Nd<sup>3+</sup>:GaP

Of the three systems described in this report, the least amount of experimental work has been published for Nd<sup>3+</sup>:GaP. In computing the theoretical levels, the same parameter values giving reasonable results for the other two ions were used in the lattice sum for GaP:  $Q = 3.0$ ,  $\alpha_D = 2.0 \text{ \AA}^3$ , and  $\alpha_Q = 4.0 \text{ \AA}^5$ ; the results are presented in table 9. The crystal-field calculation based on these parameters is given in table 10. No EPR data were found for this system. Photoluminescence data have been reported by Müller et al [29] and Donegan [30]. Müller et al have reported that two sets of lines are evident in the spectrum, but one set decreases in intensity upon annealing. The values of the more prominent set are given in table 10 (labelled as levels from the A complex), and the strongest lines from this set are compared with the theory.

Multiplet branching ratios for Nd<sup>3+</sup>:GaP were computed for electric dipole transitions only, and the results are shown in figure 5. These results are remarkably similar to the corresponding results for the cubic material LaOF [31]. No quantitative measurements of integrated intensities are available, but one can get a qualitative estimate of the branching ratios from the photoluminescence spectra of Müller et al. The fluorescence to the <sup>4</sup>I<sub>9/2</sub> multiplet is stronger than the fluorescence to the <sup>4</sup>I<sub>11/2</sub> multiplet, in agreement with the calculations. Until the origin of the extra lines is better understood, it is hard to draw any strong conclusions, but the experimental results so far are consistent with a model assuming cubic symmetry.

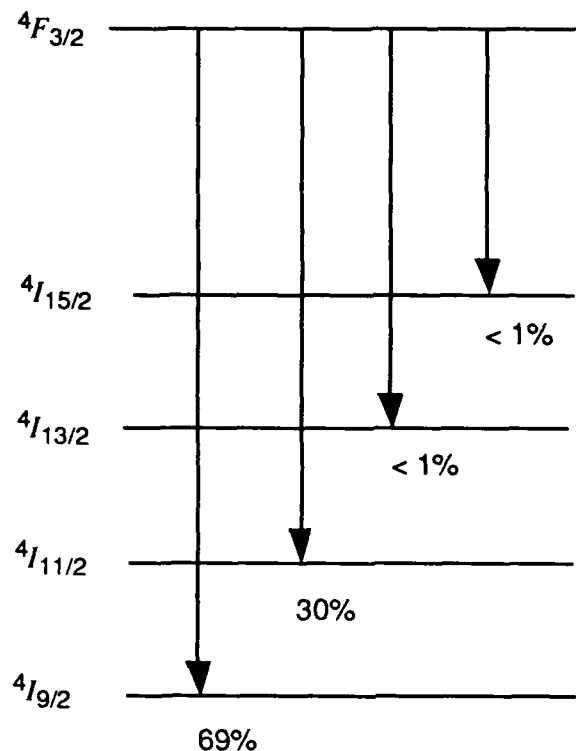
**Table 9.** Crystal-field parameters for Nd<sup>3+</sup>:GaP with  $Q(\text{Ga}) = +3$  and  $Q(\text{P}) = -3$ , and phosphorus polarizabilities  $\alpha_D = 2 \text{ \AA}^3$  and  $\alpha_Q = 4 \text{ \AA}^5$

$A_{kq}$ (cm <sup>-1</sup> /Å <sup>k</sup> )	Monopole	Self-induced dipole	Self-induced quadrupole	Total crystal field	$B_{kq}$ (cm <sup>-1</sup> )
Im $A_{32}$	22,145.4	-2848.7	-2577.6	16,719.1	—
$A_{40}$	-6,657.0	1547.8	1672.6	-3,436.6	-1985.0
$A_{44}$	-3,978.3	925.0	999.6	-2,053.8	-1186.3
$A_{60}$	825.3	-327.9	-470.9	26.5	42.1
$A_{64}$	-1,544.1	613.5	881.0	-49.6	-78.8
Im $A_{72}$	-467.2	259.9	419.4	212.1	—
Im $A_{76}$	-429.7	239.1	385.7	195.1	—

**Table 10.** Energy levels for Nd<sup>3+</sup>:GaP computed using crystal-field parameters from table 9

$2S+1L_J$ (centroids)	Level	$\Gamma_n$	Theoretical energy (cm <sup>-1</sup> )	Experimental energy A complex (cm <sup>-1</sup> )	Experimental energy (cm <sup>-1</sup> )
<sup>4</sup> I <sub>9/2</sub> (160.3)	1	8	0.1	0	0
	2	8	198.1	174, 204	174
	3	7	335.3	372, 409	372
<sup>4</sup> I <sub>11/2</sub> (2022.3)	4	7	1894	1894	1894
	5	8	1941.5	2058, 2069	2069
	6	6	2052.8	2144	—
	7	8	2128.2	2211, 2277	—

Figure 5. Multiplet branching ratios for Nd<sup>3+</sup>:GaP calculated using electric dipole transition probabilities only.



## 6. Conclusions

The salient experimental features that need to be explained by any crystal-field model are (1) the ordering of levels according to symmetry labels, particularly correct identification of the ground state, (2) the magnitude of the crystal-field splittings, and (3) the intensities of transitions between  $4f$  states.

The magnitude of the crystal-field splittings in all rare-earth ions in III-V semiconductor compounds examined so far is smaller than that produced by a point-charge model with the full valence charges. The reduced splitting can be achieved by reducing the effective ionic charges of ions in the lattice or by including self-induced contributions to the total crystal field. We have shown that the second method can better explain the experimental data and gives a more complete model of the semiconductor compounds. The rare-earth impurity ions can be used in this way as a probe to study the host in which they are embedded.

Our primary objective has been to find physically reasonable values of the parameters that accurately predict the ordering of the Stark levels. We have found that  $Q = 3$ ,  $\alpha_D = 2 \text{ \AA}^3$ , and  $\alpha_Q = 4 \text{ \AA}^5$  give reasonable results for all compounds considered here, and the crystal-field splittings calculated from this set of starting parameters give a good starting place for analyzing experimental data. This has worked particularly well for Er<sup>3+</sup>:GaAs, where

this parameter set predicts a  $\Gamma_7$  ground state in agreement with experimental EPR measurements. A point-charge model alone does not predict the correct ground state for  $\text{Er}^{3+}$ . In order to get a  $\Gamma_7$  ground state without the self-induced quadrupole contribution, one must use unreasonably large values of the dipole polarizability. With physically reasonable values of dipole and quadrupole polarizabilities, the correct ground state for  $\text{Er}^{3+}$  is obtained.

More work needs to be done on the intensities, but this cannot be done until the theoretical and experimental energies are in better agreement. Several ions have shown a hypersensitivity of the optical transitions to their crystal-line environment [32,33]. The theoretical intensities are not reconciled here with experimental observations, but it is noted that the intensities calculated for electric dipole transitions are sensitive to the  $A_{72}$  and  $A_{76}$  crystal-field components as well as the  $A_{32}$  component, making a complete description of the crystal field necessary.

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