Symmetry II - Point defects

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WFS-2025 - Wave function methods for solid state matter
Gdańsk, March 2025

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Founding fathers

1967

1977

ANNALEN DER PHYSIK

5. FOLGE, 1929, BAND 3, HEFT 2

Termaufspaltung in Kristallen

Von H. Bethe

(Mit 8 Figuren)

JULY 15, 1932 *PHYSICAL REVIEW* *VOLUME 41*

Theory of the Variations in Paramagnetic Anisotropy Among Different Salts of the Iron Group

By J. H. Van Vleck

University of Wisconsin

(Received June 6, 1932)

https://www.nobelprize.org/

Crystal field theory

Point groups

- Symmetry lowered by “crystal field”: $G \subset O(3)$
- Discrete set of symmetry operations remain
- Conjugacy classes: $R, S \in \mathcal{C}$ if $\exists T \in G : R = T^{-1}ST$
- Representations:

$$P_R \psi_j = \sum_{i=1}^{l_\Gamma} [\Gamma(R)]_{ij} \psi_i$$

- Characters:

$$\chi_\Gamma(R) = \sum_{i=1}^{l_\Gamma} [\Gamma(R)]_{ii} = \mathrm{Tr}[\Gamma(R)]$$

Crystal field theory

Point groups

- Example: character table of $O_h = O \otimes \{E, i\}$

O_h	E	$8C_3$	$6C_2'$	$6C_4$	$3C_2$	i	$8S_6$	$6\sigma_d$	$6S_4$	$3\sigma_h$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	1	-1	-1	1
E_g	2	-1	0	0	2	2	-1	0	0	2
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1
T_{2g}	3	0	1	-1	-1	3	0	1	-1	-1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	-1	1	1	-1
E_u	2	-1	0	0	2	-2	1	0	0	-2
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1
T_{2u}	3	0	1	-1	-1	-3	0	-1	1	1

Crystal field theory

Point groups

- Example: character table of $O_h = O \otimes \{E, i\}$

O_h	E	$8C_3$	$6C_2'$	$6C_4$	$3C_2$	i	$8S_6$	$6\sigma_d$	$6S_4$	$3\sigma_h$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	1	-1	-1	1
E_g	2	-1	0	0	2	2	-1	0	0	2
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1
T_{2g}	3	0	1	-1	-1	3	0	1	-1	-1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	-1	1	1	-1
E_u	2	-1	0	0	2	-2	1	0	0	-2
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1
T_{2u}	3	0	1	-1	-1	-3	0	-1	1	1

Crystal field theory

Point groups

- Symmetry lowered by "crystal field": $O(3) \supset G$
- IRs of $O(3)$ (i.e. atomic states) reducible in G:

$$\mathcal{D}^{(\mathcal{I})} = \bigoplus_{j=1}^{r} a_j \Gamma^{(j)} = a_1\Gamma^{(1)} \oplus a_2\Gamma^{(2)} \oplus \ldots \oplus a_r\Gamma^{(r)}$$

($\mathcal{I}$ angular momentum of interest, r number of IR for group G)

- Simply calculable thanks to character table:

$$a_j = \frac{1}{h}\sum_{i=1}^{r} N_i \underbrace{\chi(\mathcal{C}_i)}_{O(3)} \underbrace{\left[\chi^{(j)}(\mathcal{C}_i)\right]^*}_{G}$$

(N_i number of symm. operations in class $\mathcal{C}_i$; $h = \sum_{i=1}^{r} N_i$ = order of G)

Crystal field theory

Point groups

- Characters of $SO(3)$ for rotation over α:

$$\chi^{(\mathcal{I})}(\alpha) = \frac{\sin(2\mathcal{I}+1)\frac{\alpha}{2}}{\sin\frac{\alpha}{2}}$$

- Problematic for half integer spin: $\chi^{(\mathcal{I})}(\alpha + 2\pi) = (-1)^{2\mathcal{I}}\chi^{(\mathcal{I})}(\alpha)$
- Introduce double groups (G^*) with new element:
  - R, Rotation over 2π
  - $R \neq E$
  - $R^2 = E$
- Additional conjugacy classes and IRs needed

Crystal field theory

Point groups

- Example: additional classes and IRs of O_h^*:

O_h^*	E	R	$8C_3$	$8RC_3$	$6C_2' + 6RC_2'$	$6C_4$	$6RC_4$	$3C_2 + 3RC_2$	i	$\cdots$
$E_{1/2g}$	2	-2	1	-1	0	$\sqrt{2}$	$-\sqrt{2}$	0	2	$\cdots$
$E_{5/2g}$	2	-2	1	-1	0	$-\sqrt{2}$	$\sqrt{2}$	0	2	$\cdots$
$F_{3/2g}$	4	-4	-1	1	0	0	0	0	4	$\cdots$
$E_{1/2u}$	2	-2	1	-1	0	$\sqrt{2}$	$-\sqrt{2}$	0	-2	$\cdots$
$E_{5/2u}$	2	-2	1	-1	0	$-\sqrt{2}$	$\sqrt{2}$	0	-2	$\cdots$
$F_{3/2u}$	4	-4	-1	1	0	0	0	0	-4	$\cdots$

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Crystal field theory

Symmetry-adapted basis states

- Different choices rationalized from "coupling schemes"

$$\hat{H} = \hat{H}_0' + \hat{H}_1' + \hat{H}_2 + \hat{H}_3$$

	term splitting (RS)	multiplet splitting (SO)	crystal field splitting
$3d$	1-10 eV	0.1 eV	1 eV
$4d$	1-10 eV	0.1-1 eV	1 eV
$5d$	1-10 eV	1 eV	1 eV
$4f$	1-10 eV	0.1-1 eV	0.01 eV
$5f$	1-10 eV	1 eV	0.01-0.1 eV
$5p$	1-10 eV	1 eV	1 eV
$6p$	1-10 eV	1 eV	1 eV

Crystal field theory

Symmetry-adapted basis states: weak field

- Natural for $4f^N$ (lanthanides) and $5f^N$ (heavy actinides) configurations
- $2J+1$ degenerate atomic multiplet ${}^{2S+1}L_J$ split by CF:

$$\mathcal{D}^{(J)} = \bigoplus_{j=1}^{r} a_j \Gamma^{(j)}$$

- Reduction coefficients:

$$|\alpha SLJ;\ a\Gamma\gamma\rangle = \sum_{M=-J}^{J} \langle JM|\, Ja\Gamma\gamma\rangle\, |\alpha SLJM\rangle$$

- Example: Pr^{3+}; $4f^2$; ${}^3H_4$:

$${}^3H_4 = A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g} \qquad (O_h)$$

Crystal field theory

Symmetry-adapted basis states: intermediate field

- Natural for $3d^N$ (transition metals) configurations
- $(2L+1)(2S+1)$ degenerate atomic term ${}^{2S+1}L$ split by CF:

$$\mathcal{D}^{(L)} = \bigoplus_{i=1}^{r} a_i \Gamma^{(i)}$$

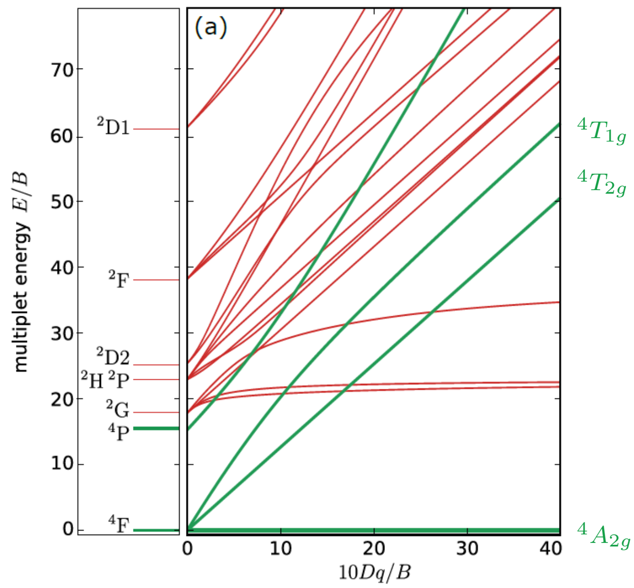
- Example: Cr^{3+}; $3d^3$; ${}^4F$:

$${}^4F = {}^4A_{2g} \oplus {}^4T_{1g} \oplus {}^4T_{2g} \qquad (O_h)$$

Crystal field theory

Symmetry-adapted basis states: intermediate field

- Tanabe-Sugano diagrams



Crystal field theory

Symmetry-adapted basis states: intermediate field

- Spin degeneracy further reduced through spin-orbit coupling:

$$\mathcal{D}^{(S)} = \bigoplus_{j=1}^{r} a_j \Gamma^{(j)}$$

- CF multiplets obtained from direct product (spin-orbit interaction):

$$\Gamma^{(i)} \to \Gamma^{(i)} \otimes \mathcal{D}^{(S)} = \bigoplus_{j=1}^{r} a_j \left(\Gamma^{(i)} \otimes \Gamma^{(j)} \right) = \bigoplus_{j=1}^{r} \bigoplus_{k=1}^{r} a_j a_k \Gamma^{(k)}$$

- Clebsch-Gordan and reduction coefficients:

$$\begin{aligned} |\alpha(S a_s \Gamma^{(j)}, L a_L \Gamma^{(i)}) a \Gamma^{(k)} \gamma^{(k)}\rangle \quad = \quad & \sum_{M_S M_L \gamma^{(i)} \gamma^{(j)}} \langle S M_S |\, a_s \Gamma^{(j)} \gamma^{(j)} \rangle \langle L M_L |\, a_L \Gamma^{(i)} \gamma^{(i)} \rangle \\ & \langle \Gamma^{(i)} \gamma^{(i)} \Gamma^{(j)} \gamma^{(j)} |\, a \Gamma^{(k)} \gamma^{(k)} \rangle \, |\alpha S M_S L M_L \rangle \end{aligned}$$

Crystal field theory

Symmetry-adapted basis states: intermediate field

- Spin degeneracy further reduced through spin-orbit coupling:

$$\mathcal{D}^{(S)} = \bigoplus_{j=1}^{r} a_j \Gamma^{(j)}$$

- CF multiplets obtained from direct product (spin-orbit interaction):

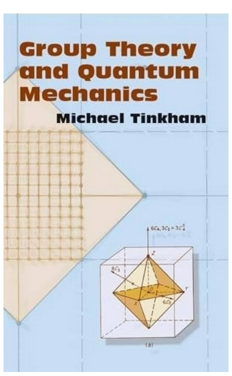
$$\Gamma^{(i)} \rightarrow \Gamma^{(i)} \otimes \mathcal{D}^{(S)} = \bigoplus_{j=1}^{r} a_j \left(\Gamma^{(i)} \otimes \Gamma^{(j)} \right) = \bigoplus_{j=1}^{r} \bigoplus_{k=1}^{r} a_j a_k \Gamma^{(k)}$$

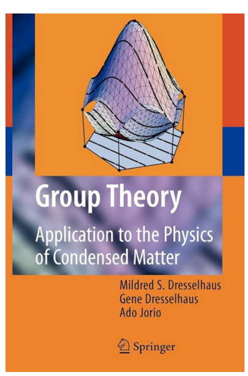
- Example: Cr^{3+}; $3d^3$; ${}^4F$; ${}^4T_{1g}$:

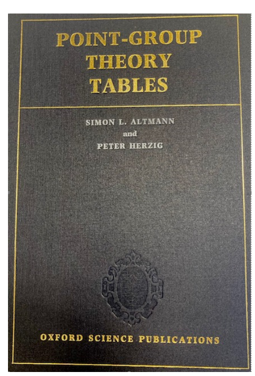
$$\begin{aligned} \mathcal{D}^{3/2} &= F_{3/2g} \\ T_{1g} \otimes F_{3/2g} &= E_{1/2g} \oplus E_{5/2g} \oplus 2F_{3/2g} \end{aligned}$$

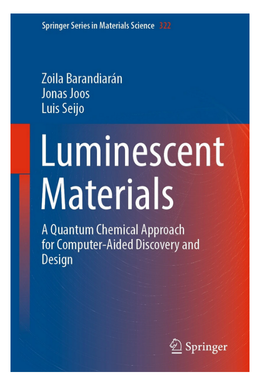
Literature

Point symmetry









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Exercise: Configurations, terms and multiplets for Pr^{3+}

1. Determine the ground and first excited configuration of a free Pr^{3+} ion.
2. For both configurations, determine which LS terms and LSJ multiplets are expected.
3. Draw a qualitatively correct energy level scheme, assuming Hunds' rules, showing:
   - The effects of $\hat{H}_0'$, $\hat{H}_1'$ and $\hat{H}_2$.
   - A suitable label for every energy level.
   - The degeneracy of every energy level.
4. Check your result using `https://www.nist.gov/pml/atomic-spectra-database`. Explain possible deviations.

Solution: Configurations, terms and multiplets for Pr^{3+}

Configurations

- The ground state configuration is readily found from the *aufbau* principle ($Z = 59$).
  - Pr: $[Xe]4f^3 6s^2$
  - Pr^+: $[Xe]4f^3 6s$
  - Pr^{2+}: $[Xe]4f^3$
  - Pr^{3+}: $[Xe]4f^2$

  taking care to ionize the outermost (largest n) shells first.
- The first excited configurations are found by exciting one valence electron to the first empty shell:
  - Pr^{3+}: $[Xe]4f5d$
  - Pr^{3+}: $[Xe]4f6s$

Solution: Configurations, terms and multiplets for Pr^{3+}

Terms

- Number of Slater determinants: $\frac{14!}{2!12!} = 91$
- Pauli's exclusion principle must be respected: use M_L, M_S table

Solution: Configurations, terms and multiplets for Pr^{3+}

(M_L, M_S) table for the [Xe]$4f^2$ configuration

	6	5	4	3	2	1	0
1		$(\overset{+}{3},\overset{+}{2})$ ^3H	$(\overset{+}{3},\overset{+}{1})$ ^3H	$(\overset{+}{3},\overset{+}{0})$, $(\overset{+}{2},\overset{+}{1})$ ^3H ^3F	$(\overset{+}{3},\overset{+}{-1})$, $(\overset{+}{2},\overset{+}{0})$ ^3H ^3F	$(\overset{+}{3},\overset{+}{-2})$, $(\overset{+}{2},\overset{+}{-1})$, $(\overset{+}{1},\overset{+}{0})$ ^3H ^3F ^3P	$(\overset{+}{3},\overset{+}{-3})$, $(\overset{+}{2},\overset{+}{-2})$, $(\overset{+}{1},\overset{+}{-1})$ ^3H ^3F ^3P
0	$(\overset{+}{3},\overset{-}{3})$ ^1I	$(\overset{+}{3},\overset{-}{2})$ $(\overset{-}{3},\overset{+}{2})$ ^1I ^3H	$(\overset{+}{3},\overset{-}{1})$ $(\overset{-}{3},\overset{+}{1})$ $(\overset{+}{2},\overset{-}{2})$ ^1I ^1G ^3H	$(\overset{+}{3},\overset{-}{0})$, $(\overset{-}{3},\overset{+}{0})$ $(\overset{+}{2},\overset{-}{1})$, $(\overset{-}{2},\overset{+}{1})$ ^1I ^1G ^3H ^3F	$(\overset{+}{3},\overset{-}{-1})$, $(\overset{-}{3},\overset{+}{-1})$ $(\overset{+}{2},\overset{-}{0})$, $(\overset{-}{2},\overset{+}{0})$ $(\overset{+}{1},\overset{-}{1})$ ^1I ^1G ^1D ^3H ^3F	$(\overset{+}{3},\overset{-}{-2})$, $(\overset{-}{3},\overset{+}{-2})$, $(\overset{+}{2},\overset{-}{-1})$ $(\overset{-}{2},\overset{+}{-1})$, $(\overset{+}{1},\overset{-}{0})$, $(\overset{-}{1},\overset{+}{0})$ ^1I ^1G ^1D ^3H ^3F ^3P	$(\overset{+}{3},\overset{-}{-3})$, $(\overset{-}{3},\overset{-}{-3})$, $(\overset{+}{2},\overset{-}{-2})$ $(\overset{-}{2},\overset{+}{-2})$, $(\overset{+}{1},\overset{-}{-1})$, $(\overset{-}{1},\overset{+}{-1})$ $(\overset{+}{0},\overset{-}{0})$ ^1I ^1G ^1D ^1S ^3H ^3F ^3P

Solution: Configurations, terms and multiplets for Pr^{3+}

Terms

- $4f^2$ configuration
  - Number of Slater determinants: $\frac{14!}{2!12!} = 91$
  - Pauli's exclusion principle must be respected: use M_L, M_S table
  - In summary:
    - Triplets: ^3H, ^3F, ^3P
    - Singlets: ^1I, ^1G, ^1D, ^1S
- $4f5d$ configuration
  - Number of Slater determinants: $14 \times 10 = 140$
  - Pauli's exclusion principle is automatically respected: straightforward coupling
    - $S = |s_1 - s_2|, \ldots, s_1 + s_2 = 0, 1$ or $1/2 \otimes 1/2 = 0 \oplus 1$
    - $L = |\ell_1 - \ell_2|, \ldots, \ell_1 + \ell_2 = 1, 2, 3, 4, 5$ or $3 \otimes 2 = 1 \oplus 2 \oplus 3 \oplus 4 \oplus 5$
  - All combintations:
    - Triplets: ^3H, ^3G, ^3F, ^3D, ^3P
    - Singlets: ^1H, ^1G, ^1F, ^1D, ^1P

Solution: Configurations, terms and multiplets for Pr^{3+}

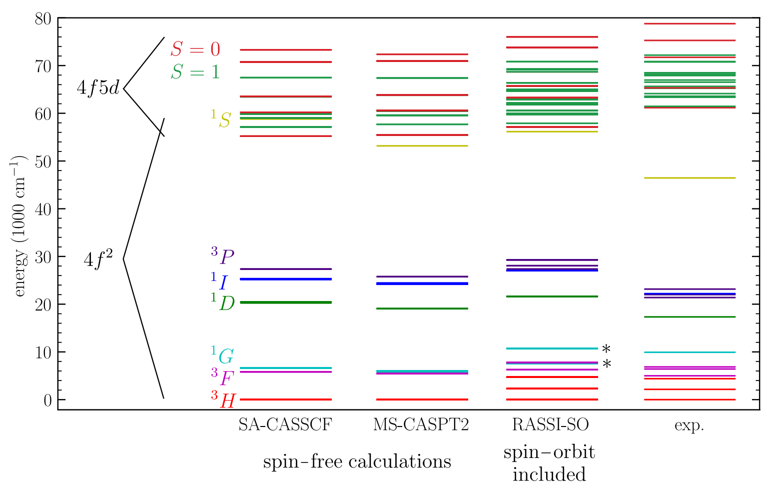
Multiplets

- Angular momentum coupling: $J = |L - S| \dots L + S$
- Example: ^3H $(L = 5,\ S = 1)$
  - Total degeneracy $= (2L + 1)(2S + 1) = 33$
  - $J = 4, 5, 6 \quad$ or $\quad 5 \otimes 1 = 4 \oplus 5 \oplus 6$
  - $^3H_4$, degeneracy $= 2J + 1 = 9$
  - $^3H_5$, degeneracy $= 2J + 1 = 11$
  - $^3H_6$, degeneracy $= 2J + 1 = 13$
- Singlets do not split $(S = 0,\ J = L)$
- ...

Solution: Configurations, terms and multiplets for Pr^{3+}

Energy level scheme

- Compare with experiment / empirical assignment
- Compare with *ab initio* wave function calculations (see also later lectures):



$*$ strong spin-orbit interaction between $^1G_4$ and $^3F_4$

Exercise: Crystal field levels Pr^{3+} in YAG

Assume that the Pr^{3+} ion is incorporated on an Y^{3+} site of a YAG crystal.

1. Predict how the atomic ${}^{2S+1}L$ terms split in the crystal field (with D_2 symmetry). How many occurrences of every spin-symmetry combination ${}^{2S+1}\Gamma$ do you expect for both considered electron configurations?
2. Derive how every ${}^{2S+1}\Gamma$ is further split by spin-orbit coupling. What are the corresponding symmetry labels?

D_2^*	E	R	$C_2 + RC_2\ (z)$	$C_2 + RC_2\ (y)$	$C_2 + RC_2\ (x)$
A	1	1	1	1	1
B_1	1	1	1	-1	-1
B_2	1	1	-1	1	-1
B_3	1	1	-1	-1	1
$E_{1/2}$	2	-2	0	0	0

Solution: Crystal field levels Pr^{3+} in YAG

- Descent from spherical symmetry (L part):
  - S term: $\mathcal{D}^{(0)} = A$
  - P term: $\mathcal{D}^{(1)} = B_1 \oplus B_2 \oplus B_3$
  - D term: $\mathcal{D}^{(2)} = 2A \oplus B_1 \oplus B_2 \oplus B_3$
  - F term: $\mathcal{D}^{(3)} = A \oplus 2B_1 \oplus 2B_2 \oplus 2B_3$
  - G term: $\mathcal{D}^{(4)} = 3A \oplus 2B_1 \oplus 2B_2 \oplus 2B_3$
  - H term: $\mathcal{D}^{(5)} = 2A \oplus 3B_1 \oplus 3B_2 \oplus 3B_3$
  - I term: $\mathcal{D}^{(6)} = 4A \oplus 3B_1 \oplus 3B_2 \oplus 3B_3$

Solution: Crystal field levels Pr^{3+} in YAG

- Descent from spherical symmetry (L part)
- $4f^2$ configuration: $3\,{}^3A$, $6\,{}^3B_1$, $6\,{}^3B_2$, $6\,{}^3B_3$, $10\,{}^1A$, $6\,{}^1B_1$, $6\,{}^1B_2$, $6\,{}^1B_3$

	${}^3A$	${}^3B_1$	${}^3B_2$	${}^3B_3$	${}^1A$	${}^1B_1$	${}^1B_2$	${}^1B_3$
${}^3H$	2	3	3	3				
${}^3F$	1	2	2	2				
${}^3P$	0	1	1	1				
${}^1I$					4	3	3	3
${}^1G$					3	2	2	2
${}^1D$					2	1	1	1
${}^1S$					1	0	0	0

Solution: Crystal field levels Pr^{3+} in YAG

- Descent from spherical symmetry (L part)
- $4f^2$ configuration: $3\,{}^3A$, $6\,{}^3B_1$, $6\,{}^3B_2$, $6\,{}^3B_3$, $10\,{}^1A$, $6\,{}^1B_1$, $6\,{}^1B_2$, $6\,{}^1B_3$
- $4f5d$ configuration: $8\,{}^3A$, $9\,{}^3B_1$, $9\,{}^3B_2$, $9\,{}^3B_3$, $8\,{}^1A$, $9\,{}^1B_1$, $9\,{}^1B_2$, $9\,{}^1B_3$

	${}^{2S+1}A$	${}^{2S+1}B_1$	${}^{2S+1}B_2$	${}^{2S+1}B_3$
${}^{2S+1}H$	2	3	3	3
${}^{2S+1}G$	3	2	2	2
${}^{2S+1}F$	1	2	2	2
${}^{2S+1}D$	2	1	1	1
${}^{2S+1}P$	0	1	1	1

Solution: Crystal field levels Pr^{3+} in YAG

- Descent from spherical symmetry (L part)
- $4f^2$ configuration: $3\,{}^3A$, $6\,{}^3B_1$, $6\,{}^3B_2$, $6\,{}^3B_3$, $10\,{}^1A$, $6\,{}^1B_1$, $6\,{}^1B_2$, $6\,{}^1B_3$
- $4f5d$ configuration: $8\,{}^3A$, $9\,{}^3B_1$, $9\,{}^3B_2$, $9\,{}^3B_3$, $8\,{}^1A$, $9\,{}^1B_1$, $9\,{}^1B_2$, $9\,{}^1B_3$
- Descent from spherical symmetry (S part)
  - Multiplicity 1: $\mathcal{D}^{(0)} = A$
  - Multiplicity 3: $\mathcal{D}^{(1)} = B_1 \oplus B_2 \oplus B_3$
- Spin-orbit splitting:

Solution: Crystal field levels Pr^{3+} in YAG

- Descent from spherical symmetry (L part)
- $4f^2$ configuration: $3\,{}^3A$, $6\,{}^3B_1$, $6\,{}^3B_2$, $6\,{}^3B_3$, $10\,{}^1A$, $6\,{}^1B_1$, $6\,{}^1B_2$, $6\,{}^1B_3$
- $4f5d$ configuration: $8\,{}^3A$, $9\,{}^3B_1$, $9\,{}^3B_2$, $9\,{}^3B_3$, $8\,{}^1A$, $9\,{}^1B_1$, $9\,{}^1B_2$, $9\,{}^1B_3$
- Descent from spherical symmetry (S part)

	A	B_1	B_2	B_3
${}^3A$		1	1	1
${}^3B_1$	1		1	1
${}^3B_2$	1	1		1
${}^3B_3$	1	1	1	
${}^1A$	1			
${}^1B_1$		1		
${}^1B_2$			1	
${}^1B_3$				1

Solution: Crystal field levels Pr^{3+} in YAG

- Descent from spherical symmetry (L part)
- $4f^2$ configuration: $3\,^3A$, $6\,^3B_1$, $6\,^3B_2$, $6\,^3B_3$, $10\,^1A$, $6\,^1B_1$, $6\,^1B_2$, $6\,^1B_3$
- $4f5d$ configuration: $8\,^3A$, $9\,^3B_1$, $9\,^3B_2$, $9\,^3B_3$, $8\,^1A$, $9\,^1B_1$, $9\,^1B_2$, $9\,^1B_3$
- Descent from spherical symmetry (S part)
- $4f^2$ configuration: $28A$, $21B_1$, $21B_2$, $21B_3$ (91 SO states in total)
- $4f5d$ configuration: $35A$, $35B_1$, $35B_2$, $35B_3$ (140 SO states in total)