

# Contents

<b>1</b>	<b>Introduction and Historical Overview</b>	<b>1</b>
1.1	The Initial Idea	1
1.2	The Unexpected New Results	2
1.3	The Dream Comes True	4
1.4	What to Expect?	4
	References	7
<b>2</b>	<b>F Centers and Rare-Earth Ion Defects in Alkali Halides</b>	<b>9</b>
2.1	F-Center-Related Defects	9
2.2	Divalent Rare-Earth Ions in Alkali Halides	11
2.2.1	Isolated $\text{Yb}^{2+}$ Ions	11
2.2.2	Isolated $\text{Eu}^{2+}$ Ions	15
2.2.3	Isolated $\text{Sm}^{2+}$ Ions	16
	References	20
<b>3</b>	<b>Properties of Molecular Defects</b>	<b>23</b>
3.1	Transition Energies	23
3.1.1	Free Molecules	23
3.1.2	Transition Energies of Molecular Ions in a Solid	24
3.2	Absorption Intensity and Oscillator Strengths	26
3.2.1	Free Molecule	26
3.2.2	Transition Probabilities for Molecular Ions in a Solid	28
3.3	Molecules in Alkali Halides	30
	References	31
<b>4</b>	<b>Theoretical Models for E–V Transfer</b>	<b>33</b>
4.1	Common Features	33
4.2	Förster–Dexter-Type Models	36
4.3	Models for Electronic–Vibrational Coupling	38
4.3.1	Radiative Transitions Including Electronic–Vibrational Coupling	39
4.3.2	Supermolecule Model (Horizontal Tunneling)	42
4.3.3	The Sudden Approximation	43

4.4	Comparison .....	45
4.5	Potential Energy Surfaces .....	47
	References .....	48
<b>5</b>	<b><math>F_H(CN^-)</math> Centers .....</b>	<b>51</b>
5.1	Basic Spectroscopic Properties .....	51
5.1.1	Overview .....	51
5.1.2	Electronic Transitions .....	52
5.1.3	Vibrational Transitions .....	53
5.2	Energy Transfer: Relative and Absolute E–V Transfer Rates .	54
5.2.1	E–V Transfer Efficiency in KCl .....	55
5.2.2	E–V Transfer in CsCl: Time-Dependent Measurement of the EL and VL .....	57
5.3	V–E Energy Transfer .....	60
5.4	Vibrational Coupling of F Centers to the $CN^-$ Stretchmode .	61
5.4.1	KCl .....	61
5.4.2	CsCl and CsBr .....	63
5.5	The Nature of the Relaxed Excited State .....	65
5.6	Putting It All Together: Comparing E–V Transfer Rates with Theoretical Models ....	66
5.6.1	FD Model .....	67
5.6.2	Horizontal-Tunneling Model .....	67
5.6.3	Relative Transfer Rates .....	68
	References .....	69
<b>6</b>	<b><math>CN^-</math> Next to an Anion Vacancy Occupied by No Electron or Two Electrons .....</b>	<b>71</b>
6.1	Background .....	71
6.2	Experimental Results .....	72
6.3	Creation Kinetics .....	74
6.4	Shift in Spectral Position .....	75
6.5	Changes in Absorption Cross Section .....	76
	References .....	76
<b>7</b>	<b><math>F_H(OH^-)</math> Centers .....</b>	<b>77</b>
7.1	Cs Halides .....	77
7.1.1	Electronic Absorption .....	77
7.1.2	Magnetic Resonance .....	80
7.1.3	Vibrational Properties .....	81
7.1.4	The Relaxed Excited State .....	81
7.2	$F_{H_2}$ Center .....	81
7.3	K and Rb Halides: Optical Bistability .....	82
7.3.1	Electronic Absorption .....	82
7.3.2	Vibrational Absorption .....	84
7.3.3	Microscopic Structure .....	86

7.3.4	Entropy-Driven Bistability: Two-Center Model . . . . .	88
7.3.5	Three-Center-Type Model . . . . .	88
7.3.6	Changes in Vibrational Absorption Cross-Section . . . . .	90
7.4	E–V Energy Transfer . . . . .	91
7.5	Dynamic Properties . . . . .	91
	References . . . . .	93
<b>8</b>	<b>Interaction Between F Electrons and Distant OH<sup>−</sup> Molecules . . . . .</b>	<b>95</b>
8.1	The Main Idea . . . . .	95
8.2	OH <sup>−</sup> Defects with a Captured Extra Electron . . . . .	97
8.2.1	Absorption Results . . . . .	97
8.2.2	Optically Detected Magnetic Resonance . . . . .	100
8.3	Vibrational Properties of Molecular Electron Traps . . . . .	101
8.3.1	Shift in Transition Energy and Enhancement of Absorption Intensity . . . . .	101
8.3.2	Mechanical and Electrical Anharmonicity . . . . .	104
8.3.3	Librational Sidebands . . . . .	104
8.3.4	Summary . . . . .	105
8.4	Electron Trapping by OH <sup>−</sup> Pairs . . . . .	105
8.5	Electron Tunneling from F Centers to OH <sup>−</sup> -Related Defects . . . . .	107
8.6	E–V Transfer Between Distant F-centers and OH <sup>−</sup> -Defects . . .	108
8.7	Conclusions and Outlook . . . . .	110
8.8	Further OH <sup>−</sup> -Type Centers in CsI . . . . .	111
	References . . . . .	112
<b>9</b>	<b>Ytterbium Ions and CN<sup>−</sup> Molecules . . . . .</b>	<b>115</b>
9.1	Crystal Growth and Sample Characterization . . . . .	115
9.2	Yb <sup>2+</sup> :(CN <sup>−</sup> ) <sub>n</sub> Defect Complexes: Electronic Transitions . . . .	116
9.2.1	Absorption and Emission Properties . . . . .	117
9.3	Vibrational Transitions of CN <sup>−</sup> Molecules Within Yb <sup>2+</sup> :(CN <sup>−</sup> ) <sub>n</sub> Complexes . . . . .	122
9.3.1	Temperature Dependence . . . . .	123
9.4	Optically Induced Bistability . . . . .	128
9.5	Center Model . . . . .	130
9.6	Interpretation of the Spectral Shifts . . . . .	132
9.6.1	Ligand Field Strength . . . . .	132
9.7	Vibrational Luminescence and E–V Energy Transfer . . . . .	138
9.7.1	Type of Center Involved in the E–V Energy Transfer . .	141
9.8	Dynamics of the E–V Transfer . . . . .	142
9.8.1	Temperature Dependence . . . . .	147
9.8.2	Concentration Variation . . . . .	149
9.9	Properties of Yb <sup>2+</sup> Ions with Excited CN <sup>−</sup> Neighbors . . . . .	152
9.9.1	Experimental Results and Their Interpretation . . . . .	153

9.9.2	Origin of Enhancement of Electronic Transition Probability . . . . .	155
9.10	Putting It All Together: Comparing E–V Transfer Rates with Theoretical Models . . . .	156
9.10.1	The Förster–Dexter Model and the Relative Transfer Rates . . . . .	157
9.10.2	FD Model: Absolute Transfer Rates . . . . .	158
9.10.3	Horizontal-Tunneling Model: Relative Transfer Rates .	158
9.10.4	Horizontal-Tunneling Model: Absolute Transfer Rates .	159
9.11	Possible Application as a Phosphor . . . . .	159
	References . . . . .	162
<b>10</b>	<b>Europium and <math>\text{CN}^-</math> Molecules</b> . . . . .	165
10.1	$\text{Eu}^{2+}:(\text{CN}^-)_n$ Complexes . . . . .	165
10.2	Possible Application as a Phosphor . . . . .	168
10.3	Summary and Interpretation of Experimental Results . . . . .	168
	References . . . . .	169
<b>11</b>	<b>Samarium and <math>\text{CN}^-</math> Molecules</b> . . . . .	171
11.1	Introduction . . . . .	171
11.2	Complexes Involving a Single $\text{CN}^-$ Molecule . . . . .	172
11.2.1	Spectroscopic Characterization . . . . .	172
11.2.2	Preliminary Center Model . . . . .	175
11.2.3	Energy-Level Scheme . . . . .	176
11.3	Complexes Involving Several $\text{CN}^-$ Molecules . . . . .	176
11.3.1	Energy-Level Scheme . . . . .	177
11.4	E–V Energy Transfer . . . . .	177
11.4.1	Vibrational Luminescence . . . . .	178
11.4.2	Interpretation . . . . .	179
11.4.3	Summary and Outlook . . . . .	181
	References . . . . .	181
<b>12</b>	<b>Other Defect Complexes</b> . . . . .	183
12.1	$ns^2$ Ions ( $\text{Tl}^+$ and $\text{Pb}^{2+}$ ) and $\text{CN}^-$ Molecules . . . . .	183
12.2	$\text{Cu}^+$ Ions and $\text{OH}^-$ Molecules . . . . .	185
	References . . . . .	185
<b>13</b>	<b>Summary</b> . . . . .	187
13.1	Comparison of the Defect Systems . . . . .	187
13.2	Potential Applications . . . . .	190
	Reference . . . . .	191
	<b>Index</b> . . . . .	193

Electronic Defect States in Alkali Halides  
Effects of Interaction with Molecular Ions

Dierolf, V.

2003, XII, 196 p., Hardcover

ISBN: 978-3-540-00471-4