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The Orbit–Lattice Interaction for Lanthanide Ions. III* Superposition Model Analysis for Arbitrary Symmetry

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Abstract

Explicit formulae are obtained for the superposition model contributions to phenomenological orbit–lattice parameters for sites of arbitrary symmetry. As an example, these results are applied to derive expressions for the orbit–lattice parameters in C_{3h} and D_{3h} symmetry, without the assumption of uniform strain.

1. Introduction

The first paper of this series (Newman 1978; referred to as Part I) determined values of the intrinsic parameters and power law exponents from static crystal field data so that orbit–lattice parameters could be calculated without reference to dynamic coupling experiments. This approach was used in Part II (Newman 1980) to analyse the results of static strain experiments in cubic systems (Baker and Currell 1976). In the course of carrying out that work it became clear that the limitations of the uniform strain assumption were making it difficult to make proper comparison between theory and experiment. These limitations have been described at length by Newman and Chen (1982). It is thus necessary to be able to derive superposition model expressions for the orbit–lattice coupling parameters where the lattice distortions correspond to arbitrary displacements of the neighbouring ions. An examination of two cubic systems (Chen and Newman 1981; Newman and Chen 1982) shows that only those ions which are coordinated to the lanthanide ions (i.e. the ligands) need to be taken into account. Even the long-range quadrupole contributions can usually be neglected. In doubtful cases Buisson and Borg (1970) parameters can be introduced following the suggestion in Part II.

Another problem which arises in the quantitative analysis of experimental data is the uncertain magnitude of the local distortions in the neighbourhood of a substituted paramagnetic ion. In the case of orbit–lattice coupling this can result in uncertainty in the strength of the coupling between lattice and local distortions. It has been suggested (Newman and Chen 1982) that additional coupling parameters could be inserted in some favourable cases, where the number of experimental data is in excess of the number of unknown superposition model parameters. Nevertheless,

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there is clearly no substitute in the long run for refining the procedures for making local distortion calculations. The main difficulty in making such calculations is the provision of adequate experimental checks. It is hoped that the empirically determined coupling parameters, referred to above, will be useful in this respect.

In this paper we present general expressions for the superposition model contributions to orbit–lattice parameters and then, as an example, we use these expressions to determine these parameters for nine-fold coordinated C_{3h} and D_{3h} sites. The latter results generalize the electrostatic, uniform strain expressions derived by Borg and Mlik (1975).

Table 1. Static coordination factors $K_n^m(\theta, \phi)$ and their differentials $\partial K_n^m/\partial\theta$

The corresponding factors for negative values of m are obtained by replacing $\cos m\phi$ by $\sin m\phi$

m	K_n^m	$\partial K_n^m/\partial\theta$
	$n = 2$	
0	$\frac{1}{2}(3\cos^2\theta - 1)$	$-\frac{3}{2}\sin 2\theta$
1	$3\sin 2\theta\cos\phi$	$6\cos 2\theta\cos\phi$
2	$\frac{1}{2}3\sin^2\theta\cos 2\phi$	$\frac{3}{2}\sin 2\theta\cos 2\phi$
	$n = 4$	
0	$\frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$	$-\frac{5}{2}\sin\theta(7\cos^3\theta - 3\cos\theta)$
1	$5(7\cos^3\theta - 3\cos\theta)\sin\theta\cos\phi$	$5(28\cos^4\theta - 27\cos^2\theta + 3)\cos\phi$
2	$\frac{5}{2}(7\cos^2\theta - 1)\sin^2\theta\cos 2\phi$	$5(7\cos^2\theta - 4)\sin 2\theta\cos 2\phi$
3	$35\cos\theta\sin^3\theta\cos 3\phi$	$35\sin^2\theta(4\cos^2\theta - 1)\cos 3\phi$
4	$\frac{35}{8}\sin^4\theta\cos 4\phi$	$\frac{35}{2}\cos\theta\sin^3\theta\cos 4\phi$
	$n = 6$	
0	$\frac{1}{16}(231\cos^6\theta - 315\cos^4\theta + 105\cos^2\theta - 5)$	$-\frac{21}{8}\sin\theta(33\cos^5\theta - 30\cos^3\theta + 5\cos\theta)$
1	$\frac{21}{4}(33\cos^5\theta - 30\cos^3\theta + 5\cos\theta)\sin\theta\cos\phi$	$\frac{21}{4}(198\cos^6\theta - 285\cos^4\theta + 100\cos^2\theta - 5)\cos\phi$
2	$\frac{105}{32}(33\cos^4\theta - 18\cos^2\theta + 1)\sin^2\theta\cos 2\phi$	$\frac{105}{16}(99\cos^5\theta - 102\cos^3\theta + 19\cos\theta)\sin\theta\cos 2\phi$
3	$\frac{105}{8}(11\cos^3\theta - 3\cos\theta)\sin^3\theta\cos 3\phi$	$\frac{315}{8}(22\cos^4\theta - 15\cos^2\theta + 1)\sin^2\theta\cos 3\phi$
4	$\frac{63}{16}(11\cos^2\theta - 1)\sin^4\theta\cos 4\phi$	$\frac{63}{8}(33\cos^3\theta - 13\cos\theta)\sin^3\theta\cos 4\phi$
5	$\frac{693}{8}\cos\theta\sin^5\theta\cos 5\phi$	$\frac{693}{8}(6\cos^2\theta - 1)\sin^4\theta\cos 5\phi$
6	$\frac{231}{32}\sin^6\theta\cos 6\phi$	$\frac{693}{16}\cos\theta\sin^5\theta\cos 6\phi$

2. General Formulation

In this section we present tables of the angle-dependent coefficients that are required in any application of the superposition model to the orbit–lattice interaction. By using Stevens' (1952) normalization of the parameters, the static superposition model equation may be written as

$$A_n^m\langle r^n\rangle = \sum_i K_n^m(\theta_i, \phi_i)\,\bar{A}_n(R_i),$$

where the sum is over the contributions of the ligands at $\boldsymbol{R}_i = (R_i, \theta_i, \phi_i)$. If the $\boldsymbol{R}_i$ are known (e.g. from X-ray determinations) then the 'coordination factors' $K_n^m(\theta_i, \phi_i)$ for each ligand i can be calculated using the expressions given in Table 1. The simple form of the above equation comes about because of the assumption of axial symmetry of the single ligand contributions. Note that the results in Table 1 assume that the $\bar{A}_n$ also have Stevens' normalization, so that $A_n^0\langle r^n\rangle = \bar{A}_n$ for a single ligand on the z-axis.

The dynamic crystal field parameters are changes in the $A_n^m\langle r^n\rangle$ due to arbitrary distortions $\boldsymbol{R}_i \rightarrow \boldsymbol{R}_i + \delta\boldsymbol{R}_i$ of the complex of ions which contribute to one or more of the above sums. We write

$$\begin{aligned}\delta A_n^m\langle r^n\rangle &= \sum_i \delta\boldsymbol{R}_i \cdot \frac{\partial}{\partial \boldsymbol{R}_i} A_n^m\langle r^n\rangle \\ &= \sum_i \delta\boldsymbol{R}_i \cdot \left\{\left(\frac{\partial}{\partial \boldsymbol{R}_i} K_n^m(i)\right)\bar{A}_n + K_n^m(i)\frac{\partial \bar{A}_n}{\partial \boldsymbol{R}_i}\right\}.\end{aligned}$$

The displacements $\delta\boldsymbol{R}_i$ depend on the model being used to relate the distortion of the complex to the lattice distortions (see e.g. Stedman and Minard 1981; Newman and Chen 1982).

In order to use the equation for $\delta A_n^m\langle r^n\rangle$ it is necessary to evaluate the coefficients $\partial K_n^m(i)/\partial \boldsymbol{R}_i$. We shall refer to these as the dynamic coordination factors. It is convenient to adopt a common set of cartesian coordinates related to the structure of the ion complex, so we are particularly interested in the cartesian derivatives $R\,\partial K_n^m/\partial x$, $R\,\partial K_n^m/\partial y$, $R\,\partial K_n^m/\partial z$. These are given in Tables 2, 3 and 4 for all values of n and m relevant in the coupling of lanthanide 4f electrons. The same results may also be used to determine the coupling coefficients of the iron group 3d electrons.

3. Description of Local Distortions in Ninefold Coordination

The ninefold coordinated system consists of two shells, a three-ion shell in the xy plane and a six-ion shell in two parallel planes above and below the three-ion system (see Fig. 1). The symmetry of each of these shells is D_{3h}, but their C_2' axes may be out of alignment in the xy plane, reducing the overall symmetry to C_{3h}. For example, C_{3h} symmetry would be produced by rotating the threefold shell ions labelled 1, 2 and 3 rigidly in the xy plane so that ion 1 no longer lies on the x-axis. The angle between the bond of ion 1 and the x-axis produced by this rotation will be denoted β. The angle subtended at the origin by the positive z-axis and ions 4, 5 and 6 will be denoted θ.

The D_{3h} symmetry coordinates have been derived using the unique labelling scheme method developed by Newman (1981). The permutation representations for each subsystem are given in Table 5. These have been used to generate the symmetry coordinates listed in Table 6. By using the D_{3h}/C_{3h} correlations given in Table 7, C_{3h} labels can also be associated with the same set of symmetry coordinates.

4. Orbit–Lattice Parameters for C_{3h} and D_{3h} Symmetries

Systems with C_{3h} symmetry have been very important in the development of lanthanide crystal field theory (see e.g. Hüfner 1978). There also exists a considerable amount of spin–lattice relaxation data for such systems, so they provide a possible testing ground for theories which attempt to correlate quantitatively static and dynamic crystal field parameters. The main problem is that we only have a limited knowledge of the photon dispersion curves for such systems.

Table 2. Expressions for $R\partial K_2^m/\partial\alpha$

$\|m\|$	α	$m \geqslant 0$	$m < 0$	$\|m\|$	α	$m \geqslant 0$	$m < 0$
0	x	$-3\cos^2\theta\sin\theta\cos\phi$	—	2	x	$3\sin\theta\cos\phi(\cos^2\theta\cos 2\phi+2\sin^2\phi)$	$3\sin\theta\sin\phi(1-2\sin^2\theta\cos^2\phi)$
	y	$-3\cos^2\theta\sin\theta\sin\phi$	—		y	$3\sin\theta\sin\phi(\cos^2\theta\cos 2\phi-2\cos^2\phi)$	$3\sin\theta\cos\phi(1-2\sin^2\theta\sin^2\phi)$
	z	$3\cos\theta\sin^2\theta$	—		z	$-3\sin^2\theta\cos\theta\cos 2\phi$	$-3\sin^2\theta\cos\theta\sin 2\phi$
1	x	$6\cos\theta(1-2\cos^2\phi\sin^2\theta)$	$-6\cos\theta\sin^2\theta\sin 2\phi$				
	y	$-6\cos\theta\sin^2\theta\sin 2\phi$	$6\cos\theta(1-2\sin^2\theta\sin^2\phi)$				
	z	$-6\cos 2\theta\sin\theta\cos\phi$	$-6\cos 2\theta\sin\theta\sin\phi$				

Table 3. Expressions for $R\partial K_4^m/\partial\alpha$

$\|m\|$	α	$m \geqslant 0$	$m < 0$
0	x	$\frac{5}{2}(3-7\cos^2\theta)\cos^2\theta\sin\theta\cos\phi$	—
	y	$\frac{5}{2}(3-7\cos^2\theta)\cos^2\theta\sin\theta\sin\phi$	—
	z	$-\frac{5}{2}(3-7\cos^2\theta)\cos\theta\sin^2\theta$	—
1	x	$5\cos\theta[2(14\cos^4\theta-17\cos^2\theta+3)\cos^2\phi+(7\cos^2\theta-3)]$	$5\cos\theta\sin 2\phi(14\cos^4\theta-17\cos^2\theta+3)$
	y	$5\cos\theta\sin 2\theta(14\cos^4\theta-17\cos^2\theta+3)$	$5\cos\theta[7\cos^2\theta-3+2\sin^2\phi(14\cos^4\theta-17\cos^2\theta+3)]$
	z	$-5\sin\theta\cos\theta(28\cos^4\theta-27\cos^2\theta+3)$	$-5\sin\theta\sin\phi(28\cos^4\theta-27\cos^2\theta+3)$
2	x	$10\cos\phi\sin\theta[(7\cos^2\theta-4)\cos^2\theta\cos 2\phi+(7\cos^2\theta-1)\sin^2\phi]$	$5\sin\theta\sin\phi[4(7\cos^2\theta-4)\cos^2\theta\cos^2\phi-(7\cos^2\theta-1)\cos 2\phi]$
	y	$10\sin\phi\sin\theta[(7\cos^2\theta-4)\cos^2\theta\cos 2\phi-(7\cos^2\theta-1)\cos^2\phi]$	$5\sin\theta\cos\phi[4(7\cos^2\theta-4)\cos^2\theta\sin^2\phi+(7\cos^2\theta-1)\cos 2\phi]$
	z	$-10(7\cos^2\theta-4)\sin^2\theta\cos\theta\cos 2\phi$	$-10\sin^2\theta\cos\theta(7\cos^2\theta-4)\sin 2\phi$
3	x	$35\sin^2\theta\cos\theta(3\cos 2\phi-4\sin\theta\cos 3\phi\cos\phi)$	$35\sin^2\theta\cos\theta(3\sin 2\phi-4\sin^2\theta\sin 3\phi\cos\phi)$
	y	$-35\sin^2\theta\cos\theta(3\sin 2\phi+4\sin^2\theta\cos 3\phi\sin\phi)$	$35\sin^2\theta\cos\theta(3\cos 2\phi-4\sin^2\theta\sin 3\phi\sin\phi)$
	z	$-35\sin^2\theta\sin 3\theta\cos 3\theta$	$-35\sin^2\theta\sin 3\theta\sin 3\phi$
4	x	$\frac{35}{2}\sin^3\theta(\cos 3\phi-\sin^2\theta\cos 4\phi\cos\phi)$	$\frac{35}{2}\sin^3\theta(\sin 3\phi-\sin^2\theta\sin 4\phi\cos\phi)$
	y	$-\frac{35}{2}\sin^3\theta(\sin 3\phi+\sin^2\theta\cos 4\phi\sin\phi)$	$\frac{35}{2}\sin^3\theta(\cos 3\phi-\sin^2\theta\sin 4\phi\sin\phi)$
	z	$-\frac{35}{2}\sin^4\theta\cos\theta\cos 4\phi$	$-\frac{35}{2}\cos\theta\sin^4\theta\sin 4\phi$

Table 4. Expressions for $R\partial K_6^m/\partial\alpha$

m	α	Differential
0	x	$-\frac{21}{8}(33\cos^4\theta - 30\cos^2\theta + 5)\cos^2\theta\sin\theta\cos\phi$
	y	$-\frac{21}{8}(33\cos^4\theta - 30\cos^2\theta + 5)\cos^2\theta\sin\theta\sin\phi$
	z	$\frac{21}{8}(33\cos^4\theta - 30\cos^2\theta + 5)\cos\theta\sin^3\theta$
1	x	$\frac{21}{4}\cos\theta[\cos^2\theta(99\cos^4\theta - 126\cos^2\theta + 35) + \cos 2\phi(99\cos^6\theta - 159\cos^4\theta + 65\cos^2\theta - 5)]$
	y	$\frac{21}{4}\cos\theta\sin 2\phi(99\cos^6\theta - 159\cos^4\theta + 65\cos^2\theta - 5)$
	z	$-\frac{21}{4}(198\cos^6\theta - 285\cos^4\theta + 100\cos^2\theta - 5)\sin\theta\cos\phi$
2	x	$\frac{105}{16}\sin\theta[(99\cos^4\theta - 102\cos^2\theta + 19)\cos^2\theta\cos 2\phi\cos\phi$ $+ (33\cos^4\theta - 18\cos^2\theta + 1)\sin 2\phi\sin\phi]$
	y	$\frac{105}{16}\sin\theta[(99\cos^4\theta - 102\cos^2\theta + 19)\cos^2\theta\cos 2\phi\sin\phi$ $- (33\cos^4\theta - 18\cos^2\theta + 1)\sin 2\phi\cos\phi]$
	z	$-\frac{105}{16}(99\cos^4\theta - 102\cos^2\theta + 19)\cos\theta\sin^2\theta\cos 2\phi$
3	x	$\frac{315}{8}\sin^2\theta\cos\theta[(22\cos^4\theta - 15\cos^2\theta + 1)\cos 3\phi\cos\phi + (11\cos^2\theta - 3)\sin 3\phi\sin\phi]$
	y	$\frac{315}{8}\sin^2\theta\cos\theta[(22\cos^4\theta - 15\cos^2\theta + 1)\cos 3\phi\sin\phi - (11\cos^2\theta - 3)\sin 3\phi\cos\phi]$
	z	$-\frac{315}{8}(22\cos^4\theta - 15\cos^2\theta + 1)\sin^3\theta\cos 3\phi$
4	x	$\frac{63}{8}\sin^3\theta[(33\cos^2\theta - 13)\cos^2\theta\cos 4\phi\cos\phi + 2(11\cos^2\theta - 1)\sin 4\phi\sin\phi]$
	y	$\frac{63}{8}\sin^3\theta[(33\cos^2\theta - 13)\cos^2\theta\cos 4\phi\sin\phi - 2(11\cos^2\theta - 1)\sin 4\phi\cos\phi]$
	z	$-\frac{63}{8}(33\cos^2\theta - 13)\cos\theta\sin^4\theta\cos 4\phi$
5	x	$\frac{693}{8}\sin^4\theta\cos\theta(5\cos 4\phi - 6\sin^2\theta\cos\phi\cos 5\phi)$
	y	$-\frac{693}{8}\sin^4\theta\cos\theta(5\sin 4\phi + 6\sin^2\theta\sin\phi\cos 5\phi)$
	z	$-\frac{693}{8}\sin^5\theta(6\cos^2\theta - 1)\cos 5\phi$
6	x	$\frac{693}{16}\sin^5\theta(\cos 5\phi - \sin^2\theta\cos 6\phi\cos\phi)$
	y	$-\frac{693}{16}\sin^5\theta(\sin 5\phi + \sin^2\theta\cos 6\phi\sin\phi)$
	z	$-\frac{693}{16}\sin^6\theta\cos\theta\cos 6\phi$
-1	x	$\frac{21}{4}\sin 2\phi\cos\theta(99\cos^6\theta - 159\cos^4\theta + 65\cos^2\theta - 5)$
	y	$\frac{21}{4}\cos\theta[\cos^2\theta(99\cos^4\theta - 126\cos^2\theta + 35) - \cos 2\phi(99\cos^6\theta - 159\cos^4\theta + 65\cos^2\theta - 5)]$
	z	$-\frac{21}{4}(198\cos^6\theta - 285\cos^4\theta + 100\cos^2\theta - 5)\sin\theta\sin\phi$
-2	x	$\frac{105}{16}\sin\theta[(99\cos^4\theta - 102\cos^2\theta + 19)\cos^2\theta\sin 2\phi\cos\phi$ $- (33\cos^4\theta - 18\cos^2\theta + 1)\cos 2\phi\sin\phi]$
	y	$\frac{105}{16}\sin\theta[(99\cos^4\theta - 102\cos^2\theta + 19)\cos^2\theta\sin 2\phi\sin\phi$ $+ (33\cos^4\theta - 18\cos^2\theta + 1)\cos 2\phi\cos\phi]$
	z	$-\frac{105}{16}(99\cos^4\theta - 102\cos^2\theta + 19)\cos\theta\sin^2\theta\sin 2\phi$
-3	x	$\frac{315}{8}\sin^2\theta\cos\theta[(22\cos^4\theta - 15\cos^2\theta + 1)\sin 3\phi\cos\phi - (11\cos^2\theta - 3)\cos 3\phi\sin\phi]$
	y	$\frac{315}{8}\sin^2\theta\cos\theta[(22\cos^4\theta - 15\cos^2\theta + 1)\sin 3\phi\sin\phi + (11\cos^2\theta - 3)\cos 3\phi\cos\phi]$
	z	$-\frac{315}{8}(22\cos^4\theta - 15\cos^2\theta + 1)\sin^3\theta\sin 3\phi$
-4	x	$\frac{63}{8}\sin^3\theta[(33\cos^2\theta - 13)\cos^2\theta\sin 4\phi\cos\phi - 2(11\cos^2\theta - 1)\sin\phi\cos 4\phi]$
	y	$\frac{63}{8}\sin^3\theta[(33\cos^2\theta - 13)\cos^2\theta\sin 4\phi\sin\phi + 2(11\cos^2\theta - 1)\cos\phi\cos 4\phi]$
	z	$-\frac{63}{8}(33\cos^2\theta - 13)\cos\theta\sin^4\theta\sin 4\phi$
-5	x	$\frac{693}{8}\sin^4\theta\cos\theta(5\sin 4\phi - 6\sin^2\theta\cos\phi\sin 5\phi)$
	y	$\frac{693}{8}\sin^4\theta\cos\theta(5\cos 4\phi - 6\sin^2\theta\sin\phi\sin 5\phi)$
	z	$-\frac{693}{8}(6\cos^2\theta - 1)\sin^5\theta\sin 5\phi$
-6	x	$\frac{693}{16}\sin^5\theta(\sin 5\phi - \sin^2\theta\sin 6\phi\cos\phi)$
	y	$\frac{693}{16}\sin^5\theta(\cos 5\phi - \sin^2\theta\sin 6\phi\sin\phi)$
	z	$-\frac{693}{16}\cos\theta\sin^6\theta\sin 6\phi$

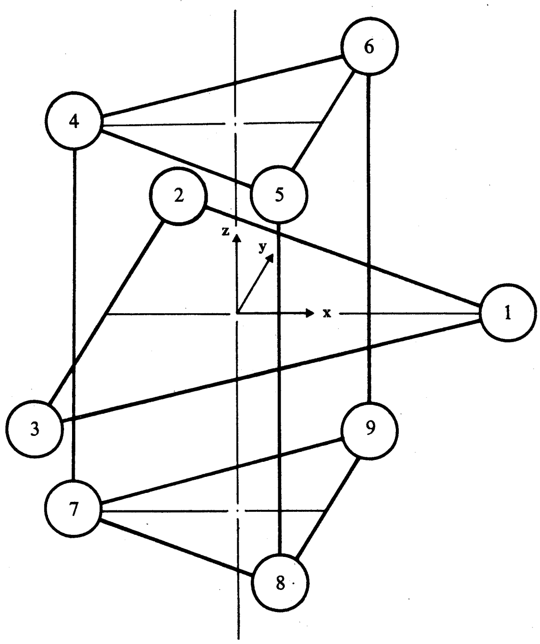

Fig. 1. Atom labels for the D_{3h} (C_{3h}) cluster. These define the symmetry coordinates listed in Table 6.

Table 5. D_{3h} **symmetry coordinates for ion permutations in threefold and sixfold coordination**

Rep.	Row no.	Ion label 1	2	3	Norm. factor	Rep.	Row no.	Ion label 4	5	6	7	8	9	Norm. factor
	3-fold coordination							6-fold coordination						
A_1'	1	+	+	+	$\sqrt{\frac{1}{3}}$	A_1'	4	+	+	+	+	+	+	$\sqrt{\frac{1}{6}}$
$E'(x)$	2	+2	−	−	$\sqrt{\frac{1}{6}}$	A_2''	5	+	+	+	−	−	−	$\sqrt{\frac{1}{6}}$
$E'(y)$	3	0	+	−	$\sqrt{\frac{1}{2}}$	$E'(x)$	6	−2	+	+	−2	+	+	$\frac{1}{2}\sqrt{\frac{1}{3}}$
						$E'(y)$	7	0	−	+	0	−	+	$\frac{1}{2}$
						$E''(xz)$	8	−2	+	+	+2	−	−	$\frac{1}{2}\sqrt{\frac{1}{3}}$
						$E''(yz)$	9	0	−	+	0	+	−	$\frac{1}{2}$

We have derived expressions for the parameters associated with the symmetry coordinates described in Table 6 and have compared these with the uniform strain results of Borg and Mlik (1975), which were based on the point charge electrostatic model. This involves relating our symmetry coordinates to those adopted by Borg and Mlik (1975) and using the usual electrostatic expressions for the intrinsic parameters (Newman 1978, equation 6). The method of derivation is illustrated in the Appendix.

In systems of D_{3h}/C_{3h} symmetry, some uniform strain parameters involve a mixture of two modes with the same irreducible representation (e.g. both E'' representations as in the Appendix). Borg and Mlik (1975) have given the appropriate linear combinations in their definition of the strain tensor (equation 21 of their paper). According

Table 6. D_{3h}/C_{3h} symmetry coordinates corresponding to the unique labelling scheme

The corresponding C_{3h} labels are given by omitting suffices from A' and A''

D_{3h} label		No. of ions in shell	Symmetry coordinate
$(A_2''\otimes A_1')A_2''$		3	$z^1 = \sqrt{\tfrac{1}{3}}(z_1+z_2+z_3)$
		6	$z^4 = \sqrt{\tfrac{1}{6}}(z_4+z_5+z_6+z_7+z_8+z_9)$
$(A_2''\otimes E')E''$	zx	3	$z^2 = \sqrt{\tfrac{1}{6}}(2z_1-z_2-z_3)$
		6	$z^6 = \tfrac{1}{2}\sqrt{\tfrac{1}{3}}\{(-2z_4+z_5+z_6)+(-2z_7+z_8+z_9)\}$
	zy	3	$z^3 = \sqrt{\tfrac{1}{2}}(z_2-z_3)$
		6	$z^7 = \tfrac{1}{2}(-z_5+z_6-z_8+z_9)$
$(E'\otimes A_1')E'$	x	3	$x^1 = \sqrt{\tfrac{1}{3}}(x_1+x_2+x_3)$
		6	$x^4 = \sqrt{\tfrac{1}{6}}(x_4+x_5+x_6+x_7+x_8+x_9)$
	y	3	$y^1 = \sqrt{\tfrac{1}{3}}(y_1+y_2+y_3)$
		6	$y^4 = \sqrt{\tfrac{1}{6}}(y_4+y_5+y_6+y_7+y_8+y_9)$
$(E'\otimes E')A_1'$		3	$\sqrt{\tfrac{1}{2}}(x^2+y^3) = \sqrt{\tfrac{1}{2}}\{\sqrt{\tfrac{1}{6}}(2x_1-x_2-x_3)+\sqrt{\tfrac{1}{2}}(y_2-y_3)\}$
		6	$\sqrt{\tfrac{1}{2}}(x^6+y^7) = \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}\sqrt{\tfrac{1}{3}}(-2x_4+x_5+x_6-2x_7+x_8+x_9) +\tfrac{1}{2}(-y_5+y_6-y_8+y_9)\}$
$(E'\otimes E')A_2'$		3	$\sqrt{\tfrac{1}{2}}(x^3-y^2) = \sqrt{\tfrac{1}{2}}\{\sqrt{\tfrac{1}{2}}(x_2-x_3)-\sqrt{\tfrac{1}{6}}(2y_1-y_2-y_3)\}$
		6	$\sqrt{\tfrac{1}{2}}(x^7-x^6) = \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}(-x_5+x_6-x_8+x_9) -\tfrac{1}{2}\sqrt{\tfrac{1}{3}}(-2y_4+y_5+y_6-2y_7+y_8+y_9)\}$
$(E'\otimes E')E'$	x	3	$\sqrt{\tfrac{1}{2}}(x^2-y^3) = \sqrt{\tfrac{1}{2}}\{\sqrt{\tfrac{1}{6}}(2x_1-x_2-x_3)-\sqrt{\tfrac{1}{2}}(y_2-y_3)\}$
		6	$\sqrt{\tfrac{1}{2}}(x^6-y^7) = \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}\sqrt{\tfrac{1}{3}}(-2x_4+x_5+x_6-2x_7+x_8+x_9) -\tfrac{1}{2}(-y_5+y_6-y_8+y_9)\}$
	y	3	$\sqrt{\tfrac{1}{2}}(x^3+y^2) = \sqrt{\tfrac{1}{2}}\{\sqrt{\tfrac{1}{2}}(x_2-x_3)+\sqrt{\tfrac{1}{6}}(2y_1-y_2-y_3)\}$
		6	$\sqrt{\tfrac{1}{2}}(x^7+y^6) = \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}(-x_5+x_6-x_8+x_9) +\tfrac{1}{2}\sqrt{\tfrac{1}{3}}(-2y_4+y_5+y_6-2y_7+y_8+y_9)\}$
$(A_2''\otimes A_2'')A_1'$		6	$z^5 = \sqrt{\tfrac{1}{6}}(z_4+z_5+z_6-z_7-z_8-z_9)$
$(A_2''\otimes E'')E'$	x	6	$z^8 = \tfrac{1}{2}\sqrt{\tfrac{1}{3}}(-2z_4+z_5+z_6+2z_7-z_8-z_9)$
	y	6	$z^9 = \tfrac{1}{2}(-z_5+z_6+z_8-z_9)$
$(E'\otimes A_2'')E''$	xz	6	$x^5 = \sqrt{\tfrac{1}{6}}(x_4+x_5+x_6-x_7-x_8-x_9)$
	yz	6	$y^5 = \sqrt{\tfrac{1}{6}}(y_4+y_5+y_6-y_7-y_8-y_9)$
$(E'\otimes E'')A_1''$		6	$\sqrt{\tfrac{1}{2}}(x^8+y^9) = \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}\sqrt{\tfrac{1}{3}}(-2x_4+x_5+x_6+2x_7-x_8-x_9) +\tfrac{1}{2}(-y_5+y_6+y_8-y_9)\}$
$(E'\otimes E'')A_2''$		6	$\sqrt{\tfrac{1}{2}}(x^9-y^8) = \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}(-x_5+x_6+x_8-x_9) -\tfrac{1}{2}\sqrt{\tfrac{1}{3}}(-2y_4+y_5+y_6+2y_7-y_8-y_9)\}$
$(E'\otimes E'')E''$	xz	6	$\sqrt{\tfrac{1}{2}}(x^8-y^9) = \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}\sqrt{\tfrac{1}{3}}(-2x_4+x_5+x_6+2x_7-x_8-x_9) -\tfrac{1}{2}(-y_5+y_6+y_8-y_9)\}$
	yz	6	$\sqrt{\tfrac{1}{2}}(x^9+y^8) = \sqrt{\tfrac{1}{2}}\{\tfrac{1}{2}(-x_5+x_6+x_8-x_9) +\tfrac{1}{2}\sqrt{\tfrac{1}{3}}(-2y_4+y_5+y_6+2y_7-y_8-y_9)\}$

Table 7. D_{3h}/C_{3h} correlations and alternative irreducible representation labels

D_{3h}	C_{3h}	D_{3h}	C_{3h}	D_{3h}	C_{3h}
A_1', Γ_1	A', Γ_1	A_1'', Γ_3	A'', Γ_4	E'', Γ_5	${}^2E''$, Γ_5 and ${}^1E''$, Γ_6
A_2', Γ_2	A', Γ_1	A_2'', Γ_4	A'', Γ_4	E', Γ_6	${}^2E'$, Γ_2 and ${}^1E'$, Γ_3

to these equations, noting that the E'' displacements δz^6 and δx^5 transform as the strains δzx and δxz respectively, the uniform strain parameters may be written

$$V(n, \Gamma_5 A) = -\sqrt{\tfrac{1}{2}}(V_{\mathrm{N},1} - V_{\mathrm{N},2}) \quad \text{and} \quad V(n, \Gamma_5 B) = \sqrt{\tfrac{1}{2}}(V_{\mathrm{N},1} + V_{\mathrm{N},2}).$$

All the parameters $V(n, \Gamma_\alpha A/B)$ in Tables 8 and 9 can be obtained in a similar way using the technique described in the Appendix.

Table 8. Superposition model expressions for the orbit–lattice parameters of the D_{3h} system with Borg and Mlik (1975) labels

Representation	Parameter	Threefold shell	Sixfold shell[A]
$(E'\otimes E')A_1'$	$V(2,\Gamma_1 A)$	$\frac{1}{3}\sqrt{2}\,t_2\bar{A}_2$	$-\frac{1}{3}\sqrt{2}\,t_2\bar{A}_2$
and	$V(2,\Gamma_1 B)$	$-\frac{1}{3}t_2\bar{A}_2$	$3(1-\frac{1}{18}t_2)\bar{A}_2$
$(A_2''\otimes A_2'')A_1'$	$V(4,\Gamma_1 A)$	$-\sqrt{2}\,t_4\bar{A}_4$	$\frac{13}{6}\sqrt{2}\,t_4\bar{A}_4$
	$V(4,\Gamma_1 B)$	$t_4\bar{A}_4$	$5\sqrt{6}\,(1-\frac{13}{60}t_4)\bar{A}_4$
	$V(6,\Gamma_1 aA)$	$\frac{5}{3}\sqrt{2}\,t_6\bar{A}_6$	$\frac{19}{12}\sqrt{2}\,t_6\bar{A}_6$
	$V(6,\Gamma_1 aB)$	$-\frac{5}{3}t_6\bar{A}_6$	$-\frac{147}{4}(1-\frac{19}{882}t_6)\bar{A}_6$
	$V(6,\Gamma_1 bA)$	$-\frac{1}{3}\sqrt{231}\,t_6\bar{A}_6$	$-\frac{1}{12}\sqrt{231}\,t_6\bar{A}_6$
	$V(6,\Gamma_1 bB)$	$\frac{1}{6}\sqrt{462}\,t_6\bar{A}_6$	$-\frac{3}{8}\sqrt{462}\,(1+\frac{1}{18}t_6)\bar{A}_6$
$(E'\otimes E')A_2'$	$V(6,\Gamma_2)$	$3\sqrt{154}\,\bar{A}_6$	$\frac{3}{4}\sqrt{154}\,\bar{A}_6$
$(A_2''\otimes E')E''$	$V(2,\Gamma_5 A)$	$-\bar{A}_2$	$\bar{A}_2$
and	$V(2,\Gamma_5 B)$	$\bar{A}_2$	$-(1-t_2)\bar{A}_2$
$(E'\otimes A_2'')E''$	$V(4,\Gamma_5 A)$	$\sqrt{30}\,\bar{A}_4$	$-\frac{13}{6}\sqrt{30}\,\bar{A}_4$
	$V(4,\Gamma_5 B)$	$-\sqrt{30}\,\bar{A}_4$	$\frac{1}{6}\sqrt{30}\,(1-t_4)\bar{A}_4$
	$V(6,\Gamma_5 aA)$	$-5\sqrt{7}\,\bar{A}_6$	$-\frac{19}{4}\sqrt{7}\,\bar{A}_6$
	$V(6,\Gamma_5 aB)$	$5\sqrt{7}\,\bar{A}_6$	$-\frac{7}{4}\sqrt{7}\,(1-t_6)\bar{A}_6$
	$V(6,\Gamma_5 bA)$	$\frac{1}{2}\sqrt{462}\,\bar{A}_6$	$\frac{1}{8}\sqrt{462}\,\bar{A}_6$
	$V(6,\Gamma_5 bB)$	$-\frac{1}{2}\sqrt{462}\,\bar{A}_6$	$\frac{5}{8}\sqrt{462}\,(1+\frac{1}{5}t_6)\bar{A}_6$
$(E'\otimes E')E'$	$V(2,\Gamma_6)$	$(1-\frac{1}{2}t_2)\bar{A}_2$	$\frac{3}{2}(1-\frac{1}{6}t_2)\bar{A}_2$
	$V(4,\Gamma_6 a)$	$-\frac{2}{3}\sqrt{15}\,(1-\frac{1}{2}t_4)\bar{A}_4$	$\frac{4}{3}\sqrt{15}\,(1-\frac{5}{16}t_4)\bar{A}_4$
	$V(4,\Gamma_6 b)$	$-\frac{2}{3}\sqrt{105}\,(1+\frac{1}{4}t_4)\bar{A}_4$	$-\frac{1}{6}\sqrt{105}\,(1+\frac{1}{4}t_4)\bar{A}_4$
	$V(6,\Gamma_6 a)$	$\frac{1}{2}\sqrt{70}\,(1-\frac{1}{2}t_6)\bar{A}_6$	$-\frac{81}{8}\sqrt{70}\,(1+\frac{1}{54}t_6)\bar{A}_6$
	$V(6,\Gamma_6 b)$	$2\sqrt{21}\,(1+\frac{1}{4}t_6)\bar{A}_6$	$-\frac{29}{8}\sqrt{21}\,(1+\frac{9}{58}t_6)\bar{A}_6$
$(E'\otimes E'')E''$	$V'(2,\Gamma_5)$		$-(1+\frac{1}{2}t_2)\bar{A}_2$
	$V'(4,\Gamma_5)$		$-\frac{4}{3}\sqrt{30}\,(1+\frac{1}{16}t_4)\bar{A}_4$
	$V'(6,\Gamma_5 a)$		$\frac{1}{4}\sqrt{7}\,(1+\frac{7}{2}t_6)\bar{A}_6$
	$V'(6,\Gamma_5 b)$		$-\frac{7}{8}\sqrt{462}\,(1-\frac{1}{14}t_6)\bar{A}_6$
$(E'\otimes A_1')E'$	$V'(2,\Gamma_6)$	$-(1+\frac{1}{2}t_2)\bar{A}_2$	$\frac{1}{2}(1+\frac{1}{2}t_2)\bar{A}_2$
	$V'(4,\Gamma_6 a)$	$-\frac{2}{3}\sqrt{15}\,(1+\frac{1}{2}t_4)\bar{A}_4$	$2\sqrt{15}(1+\frac{5}{24}t_4)\bar{A}_4$
	$V'(4,\Gamma_6 b)$	$\frac{2}{3}\sqrt{105}\,(1-\frac{1}{4}t_4)\bar{A}_4$	$-\frac{1}{2}\sqrt{105}\,(1-\frac{1}{12}t_4)\bar{A}_4$
	$V'(6,\Gamma_6 a)$	$-\frac{1}{2}\sqrt{70}\,(1+\frac{1}{2}t_6)\bar{A}_6$	$\frac{81}{8}\sqrt{70}\,(1-\frac{1}{54}t_6)\bar{A}_6$
	$V'(6,\Gamma_6 b)$	$2\sqrt{21}\,(1-\frac{1}{4}t_6)\bar{A}_6$	$-\frac{43}{8}\sqrt{21}\,(1-\frac{9}{86}t_6)\bar{A}_6$
$(A_2''\otimes E'')E'$	$V'(2,\Gamma_6)$		$(1+\frac{1}{2}t_2)\bar{A}_2$
	$V'(4,\Gamma_6 a)$		$-\frac{2}{3}\sqrt{15}\,(1-\frac{1}{4}t_4)\bar{A}_4$
	$V'(4,\Gamma_6 b)$		$\frac{1}{3}\sqrt{105}\,(1+\frac{1}{4}t_4)\bar{A}_4$
	$V'(6,\Gamma_6 a)$		$\frac{1}{8}\sqrt{70}\,(1+\frac{1}{58}t_6)\bar{A}_6$
	$V'(6,\Gamma_6 b)$		$\frac{7}{4}\sqrt{21}\,(1+\frac{9}{14}t_6)\bar{A}_6$

[A] For the sixfold shell, θ is taken to be equal to $\pi/4$ and $3\pi/4$ and $\beta = 0$.

Table 8 gives the 'strong' (Newman and Chen 1982) superposition model expressions for the coupling to all active modes of the threefold and sixfold shell for the D_{3h} case, and Table 9 gives them for the C_{3h} case. In these tables θ for the sixfold shell is taken to be equal to $\frac{1}{4}\pi$ as a particular case. In the more general case it is more convenient to compute numerical results directly for a given coordination rather than derive complicated algebraic results.

All of the parameters are expressed in terms of the power law exponents t_n and the intrinsic parameters $\bar{A}_n$ which may in principle be obtained from static crystal field data using superposition model expressions for static parameters of D_{3h}/C_{3h} systems. In the case $\theta = 45°$ these are given by

Parameter	Threefold shell	Sixfold shell
$A_2^0\langle r^2\rangle$	$-\frac{3}{2}\bar{A}_2$	$\frac{3}{2}\bar{A}_2$
$A_4^0\langle r^4\rangle$	$\frac{9}{8}\bar{A}_4$	$-\frac{39}{16}\bar{A}_4$
$A_6^0\langle r^6\rangle$	$-\frac{15}{16}\bar{A}_6$	$-\frac{57}{64}\bar{A}_6$
$A_6^6\langle r^6\rangle$	$\frac{693}{32}\bar{A}_6\cos 6\beta$	$\frac{693}{128}\bar{A}_6\cos 6\beta$

as can easily be ascertained from Table 1 ($\beta = 0$ corresponds to D_{3h} symmetry).

The parameters listed in Tables 8 and 9 which correspond to the product representation modes $(A_2''+E')\otimes(A_2''+E')$ for D_{3h} and $(A''+E')\otimes(A''+E')$ for C_{3h} are associated with uniform strain (Newman 1981). They differ from the results of Borg and Mlik (1975) by a common factor $\frac{3}{2}\sqrt{6}$ because of the different normalization imposed by the strain tensor. Note that there exist additional parameters corresponding to the representations Γ_5, Γ_6 of D_{3h} and Γ_2, Γ_3, Γ_5, Γ_6 of C_{3h} in Tables 8 and 9 respectively. We can obtain the parameters corresponding to pure radial or angular modes by making appropriate linear combinations of the parameters $V(n,\Gamma_\alpha)$ with the corresponding extra parameters $V'(n,\Gamma_\alpha)$ as the work of Newman and Chen (1982) has illustrated.

5. Summary

In order to provide a description of the orbit–lattice interaction for sites of arbitrary symmetry, general expressions for the superposition model contributions to the dynamic coupling parameters have been derived. As an example, the method of determining the superposition model expressions for the orbit–lattice coupling parameters associated with the symmetry coordinates of D_{3h}/C_{3h} systems has been given in detail.

The results given in Tables 8 and 9 express the dynamic coupling parameters in terms of power law exponents t_n and the intrinsic parameters $\bar{A}_n$ which may, in principle, be obtained from static crystal field data. In these generalized results, not only the parameters which can be related to the uniform strain results (Borg and Mlik 1975) are included, but the extra parameters corresponding to other active modes in such systems are given as well. This provides the possibility of relating phenomena such as Jahn–Teller effect to static strain and spin–lattice relaxation measurements.

The results presented in this paper, along with the general discussion given in Newman and Chen (1982), lay the groundwork for the future development of a widely applicable quantitative theory of the orbit–lattice interaction for lanthanide ions. It is intended that this theory should provide a unified understanding of the wide range of phenomena which depend essentially on this interaction.

Table 9. Superposition model expressions for the orbit–lattice parameters of the C_{3h} system with Borg and Mlik (1975) labels

Representation	Parameter	Threefold shell	Sixfold shell[A]
$(E'\otimes E')A'$	$V(2,\Gamma_1 A)$	$\frac{1}{3}\sqrt{2}\,t_2\bar{A}_2$	$-\frac{1}{3}\sqrt{2}\,t_2\bar{A}_2$
and	$V(2,\Gamma_1 B)$	0	0
$(A''\otimes A'')A'$	$V(2,\Gamma_1 C)$	$-\frac{1}{3}t_2\bar{A}_2$	$3(1-\frac{1}{18}t_2)\bar{A}_2$
	$V(4,\Gamma_1 A)$	$-\sqrt{2}\,t_4\bar{A}_4$	$\frac{13}{6}\sqrt{2}\,t_4\bar{A}_4$
	$V(4,\Gamma_1 B)$	0	0
	$V(4,\Gamma_1 C)$	$t_4\bar{A}_4$	$5(1+\frac{13}{60}t_4)\bar{A}_4$
	$V(6,\Gamma_1 aA)$	$\frac{5}{3}\sqrt{2}\,t_6\bar{A}_6$	$\frac{19}{12}\sqrt{2}\,t_6\bar{A}_6$
	$V(6,\Gamma_1 aB)$	0	0
	$V(6,\Gamma_1 aC)$	$-\frac{5}{3}t_6\bar{A}_6$	$-\frac{147}{4}(1-\frac{19}{882}t_6)\bar{A}_6$
	$V(6,\Gamma_1 bA)$	$-\frac{1}{6}\sqrt{462}\,t_6\bar{A}_6\cos 6\beta$	$-\frac{1}{24}\sqrt{462}\,t_6\bar{A}_6\cos 6\beta$
	$V(6,\Gamma_1 bB)$	$-3\sqrt{77}\,\bar{A}_6\sin 6\beta$	$-\frac{3}{4}\sqrt{77}\,\bar{A}_6\sin 6\beta$
	$V(6,\Gamma_1 bC)$	$\frac{1}{6}\sqrt{231}\,t_6\bar{A}_6\cos 6\beta$	$-\frac{3}{8}\sqrt{231}\,(1+\frac{1}{18}t_6)\bar{A}_6\cos 6\beta$
	$V(6,\Gamma_1 cA)$	$-\frac{1}{6}\sqrt{462}\,t_6\bar{A}_6\sin 6\beta$	$-\frac{1}{24}\sqrt{462}\,t_6\bar{A}_6\sin 6\beta$
	$V(6,\Gamma_1 cB)$	$-3\sqrt{77}\,\bar{A}_6\cos 6\beta$	$-\frac{3}{4}\sqrt{77}\,\bar{A}_6\cos 6\beta$
	$V(6,\Gamma_1 cC)$	$\frac{1}{6}\sqrt{231}\,t_6\bar{A}_6\sin 6\beta$	$-\frac{3}{8}\sqrt{231}\,(1+\frac{1}{18}t_6)\bar{A}_6\sin 6\beta$
$(E'\otimes E')^2E'$	$V(2,\Gamma_2)$	$-(1-\frac{1}{2}t_2)\bar{A}_2$	$\frac{3}{2}(1-\frac{1}{6}t_2)\bar{A}_2$
	$V(4,\Gamma_2 a)$	$-\frac{2}{3}\sqrt{105}\,(1+\frac{1}{4}t_4)\bar{A}_4\cos 6\beta$	$-\frac{1}{6}\sqrt{105}\,(1+\frac{1}{4}t_4)\bar{A}_4\cos 6\beta$
	$V(4,\Gamma_2 b)$	$-\frac{2}{3}\sqrt{15}\,(1-\frac{1}{2}t_4)\bar{A}_4$	$\frac{4}{3}\sqrt{15}\,(1-\frac{5}{16}t_4)\bar{A}_4$
	$V(6,\Gamma_2 a)$	$2\sqrt{21}\,(1+\frac{1}{4}t_6)\bar{A}_6\cos 6\beta$	$-\frac{29}{8}\sqrt{21}\,(1+\frac{9}{58}t_6)\bar{A}_6\cos 6\beta$
	$V(6,\Gamma_2 b)$	$\frac{1}{2}\sqrt{70}\,(1-\frac{1}{2}t_6)\bar{A}_6$	$-\frac{81}{8}\sqrt{70}\,(1+\frac{1}{54}t_6)\bar{A}_6$
$(E'\otimes E')^1E'$	$V(2,\Gamma_3)$	$-(1-\frac{1}{2}t_2)\bar{A}_2$	$\frac{3}{2}(1-\frac{1}{6}t_2)\bar{A}_2$
	$V(4,\Gamma_3 a)$	$-\frac{2}{3}\sqrt{105}\,(1+\frac{1}{4}t_4)\bar{A}_4\sin 6\beta$	$-\frac{1}{6}\sqrt{105}\,(1+\frac{1}{4}t_4)\bar{A}_4\sin 6\beta$
	$V(4,\Gamma_3 b)$	$-\frac{2}{3}\sqrt{15}\,(1-\frac{1}{2}t_4)\bar{A}_4$	$\frac{4}{3}\sqrt{15}\,(1-\frac{5}{16}t_4)\bar{A}_4$
	$V(6,\Gamma_3 a)$	$2\sqrt{21}\,(1+\frac{1}{4}t_6)\bar{A}_6\sin 6\beta$	$-\frac{29}{8}\sqrt{21}\,(1+\frac{9}{58}t_6)\bar{A}_6\sin 6\beta$
	$V(6,\Gamma_3 b)$	$\frac{1}{2}\sqrt{70}\,(1-\frac{1}{2}t_6)\bar{A}_6$	$-\frac{81}{8}\sqrt{70}\,(1+\frac{1}{54}t_6)\bar{A}_6$
$(A''\otimes E')^2E''$	$V(2,\Gamma_5 A)$	$\bar{A}_2$	$-\bar{A}_2$
and	$V(2,\Gamma_5 B)$	$-\bar{A}_2$	$-(1-t_2)\bar{A}_2$
$(E'\otimes A'')^2E''$	$V(4,\Gamma_5 A)$	$-\sqrt{30}\,\bar{A}_4$	$-\frac{13}{6}\sqrt{30}\,\bar{A}_4$
	$V(4,\Gamma_5 B)$	$\sqrt{30}\,\bar{A}_4$	$\frac{1}{6}\sqrt{30}\,(1-t_4)\bar{A}_4$
	$V(6,\Gamma_5 aA)$	$5\sqrt{7}\,\bar{A}_6$	$\frac{19}{4}\sqrt{7}\,\bar{A}_6$
	$V(6,\Gamma_5 aB)$	$-5\sqrt{7}\,\bar{A}_6$	$-\frac{7}{4}\sqrt{7}\,(1-t_6)\bar{A}_6$
	$V(6,\Gamma_5 bA)$	$-\frac{1}{2}\sqrt{462}\,\bar{A}_6\sin 6\beta$	$-\frac{1}{8}\sqrt{462}\,\bar{A}_6\sin 6\beta$
	$V(6,\Gamma_5 bB)$	$\frac{1}{2}\sqrt{462}\,\bar{A}_6\sin 6\beta$	$-\frac{5}{8}\sqrt{462}\,(1-\frac{1}{5}t_6)\bar{A}_6\sin 6\beta$
$(A''\otimes E')^1E''$	$V(2,\Gamma_6 A)$	$\bar{A}_2$	$-\bar{A}_2$
and	$V(2,\Gamma_6 B)$	$-\bar{A}_2$	$-(1-t_2)\bar{A}_2$
$(E'\otimes A'')^1E''$	$V(4,\Gamma_6 A)$	$-\sqrt{30}\,\bar{A}_4$	$-\frac{13}{6}\sqrt{30}\,\bar{A}_4$
	$V(4,\Gamma_6 B)$	$\sqrt{30}\,\bar{A}_4$	$\frac{1}{6}\sqrt{30}\,(1-t_4)\bar{A}_4$
	$V(6,\Gamma_6 aA)$	$5\sqrt{7}\,\bar{A}_6$	$\frac{19}{4}\sqrt{7}\,\bar{A}_6$
	$V(6,\Gamma_6 aB)$	$-5\sqrt{7}\,\bar{A}_6$	$-\frac{7}{4}\sqrt{7}\,(1-t_6)\bar{A}_6$
	$V(6,\Gamma_6 bA)$	$-\frac{1}{2}\sqrt{462}\,\bar{A}_6\cos 6\beta$	$-\frac{1}{8}\sqrt{462}\,\bar{A}_6\cos 6\beta$
	$V(6,\Gamma_6 bB)$	$\frac{1}{2}\sqrt{462}\,\bar{A}_6\cos 6\beta$	$-\frac{5}{8}\sqrt{462}\,(1+\frac{1}{5}t_6)\bar{A}_6\cos 6\beta$
$(E'\otimes A')^2E'$	$V'(2,\Gamma_2)$	$\frac{1}{2}\sqrt{2}\,(1+\frac{1}{2}t_2)\bar{A}_2$	$-\frac{1}{4}\sqrt{2}\,(1+\frac{1}{2}t_2)\bar{A}_2$
	$V'(4,\Gamma_2 a)$	$-\frac{1}{3}\sqrt{210}\,(1-\frac{1}{4}t_4)\bar{A}_4\cos 6\beta$	$\frac{1}{4}\sqrt{210}\,(1-\frac{1}{12}t_4)\bar{A}_4\cos 6\beta$
	$V'(4,\Gamma_2 b)$	$-\frac{1}{3}\sqrt{30}\,(1+\frac{1}{2}t_4)\bar{A}_4$	$-\sqrt{30}\,(1+\frac{5}{24}t_4)\bar{A}_4$
	$V'(6,\Gamma_2 a)$	$\sqrt{42}\,(1-\frac{1}{4}t_6)\bar{A}_6\cos 6\beta$	$\frac{43}{16}\sqrt{42}\,(1-\frac{9}{86}t_6)\bar{A}_6\cos 6\beta$
	$V'(6,\Gamma_2 b)$	$\frac{1}{2}\sqrt{35}\,(1+\frac{1}{2}t_6)\bar{A}_6$	$-\frac{81}{8}\sqrt{35}\,(1-\frac{1}{54}t_6)\bar{A}_6$

Table 9 (*Continued*)

Representation	Parameter	Threefold shell	Sixfold shell[A]
$(A''\otimes E'')^2E'$	$V'(2,\Gamma_2)$		$-\frac{1}{2}\sqrt{2}\,(1+\frac{1}{2}t_2)\bar{A}_2$
	$V'(4,\Gamma_2\,a)$		$-\frac{1}{3}\sqrt{210}\,(1+\frac{1}{4}t_4)\bar{A}_4\cos 6\beta$
	$V'(4,\Gamma_2\,b)$		$\frac{2}{3}\sqrt{30}\,(1+\frac{1}{4}t_4)\bar{A}_4$
	$V'(6,\Gamma_2\,a)$		$\frac{7}{4}\sqrt{42}\,(1+\frac{9}{14}t_6)\bar{A}_6\cos 6\beta$
	$V'(6,\Gamma_2\,b)$		$-\frac{1}{4}\sqrt{35}\,(1+\frac{1}{58}t_6)\bar{A}_6$
$(E'\otimes A')^1E'$	$V'(2,\Gamma_3)$	$-\frac{1}{2}\sqrt{2}\,(1+\frac{1}{2}t_2)\bar{A}_2$	$\frac{1}{4}\sqrt{2}\,(1+\frac{1}{2}t_2)\bar{A}_2$
	$V'(4,\Gamma_3\,a)$	$\frac{1}{3}\sqrt{210}\,(1-\frac{1}{4}t_4)\bar{A}_4\sin 6\beta$	$-\frac{1}{4}\sqrt{210}\,(1-\frac{1}{12}t_4)\bar{A}_4\sin 6\beta$
	$V'(4,\Gamma_3\,b)$	$\frac{1}{3}\sqrt{30}\,(1+\frac{1}{2}t_4)\bar{A}_4$	$\sqrt{30}(1+\frac{5}{24}t_4)\bar{A}_4$
	$V'(6,\Gamma_3\,a)$	$-\sqrt{42}\,(1-\frac{1}{4}t_6)\bar{A}_6\sin 6\beta$	$-\frac{43}{16}\sqrt{42}\,(1-\frac{9}{86}t_6)\bar{A}_6\sin 6\beta$
	$V'(6,\Gamma_3\,b)$	$-\frac{1}{2}\sqrt{35}\,(1+\frac{1}{2}t_6)\bar{A}_6$	$\frac{81}{8}\sqrt{35}\,(1-\frac{1}{54}t_6)\bar{A}_6$
$(A''\otimes E'')^1E'$	$V'(2,\Gamma_3)$		$\frac{1}{2}\sqrt{2}\,(1+\frac{1}{2}t_2)\bar{A}_2$
	$V'(4,\Gamma_3\,a)$		$\frac{1}{3}\sqrt{210}\,(1+\frac{1}{4}t_4)\bar{A}_4\sin 6\beta$
	$V'(4,\Gamma_3\,b)$		$-\frac{2}{3}\sqrt{30}\,(1+\frac{1}{4}t_4)\bar{A}_4$
	$V'(6,\Gamma_3\,a)$		$-\frac{7}{4}\sqrt{42}\,(1+\frac{9}{14}t_6)\bar{A}_6\sin 6\beta$
	$V'(6,\Gamma_3\,b)$		$\frac{1}{4}\sqrt{35}\,(1+\frac{1}{58}t_6)\bar{A}_6$
$(E'\otimes E'')^2E''$	$V'(2,\Gamma_5)$		$(1+\frac{1}{2}t_2)\bar{A}_4$
	$V'(4,\Gamma_5)$		$-\frac{4}{3}\sqrt{30}\,(1+\frac{1}{16}t_4)\bar{A}_4$
	$V'(6,\Gamma_5\,a)$		$-\frac{1}{4}\sqrt{7}\,(1+\frac{7}{2}t_6)\bar{A}_6$
	$V'(6,\Gamma_5\,b)$		$\frac{7}{8}\sqrt{462}\,(1-\frac{1}{14}t_6)\bar{A}_6\sin 6\beta$
$(E'\otimes E'')^1E''$	$V'(2,\Gamma_6)$		$(1+\frac{1}{2}t_2)\bar{A}_2$
	$V'(4,\Gamma_6)$		$-\frac{4}{3}\sqrt{30}\,(1+\frac{1}{16}t_4)\bar{A}_4$
	$V'(6,\Gamma_6\,a)$		$-\frac{1}{4}\sqrt{7}\,(1+\frac{7}{2}t_6)\bar{A}_6$
	$V'(6,\Gamma_6\,b)$		$\frac{7}{8}\sqrt{462}\,(1-\frac{1}{14}t_6)\bar{A}_6\cos 6\beta$

[A] For the sixfold shell, θ is taken to be equal to $\pi/4$ and $3\pi/4$, and $\phi = \beta,\ \frac{2}{3}\pi+\beta,\ \frac{4}{3}\pi+\beta$ $(\beta \neq 0)$.

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Appendix. Calculation of $V(n,\Gamma_\alpha)$ Parameters

The crystal field Hamiltonian may be expanded as a Taylor series in the local strain $\sigma(\Gamma_\alpha, \beta)$ and the term which is linear in the strain is called the orbit–lattice interaction. It may be written in the general form

$$V_{\mathrm{OL}} = \left(\frac{\partial V(r,\theta,\phi)}{\partial\sigma(\Gamma_\alpha,\beta)}\right)_{\mathrm{eq}} \sigma(\Gamma_\alpha,\beta) = \sum_{n\alpha\beta} V(n,\Gamma_\alpha)\, C(n,\Gamma_\alpha,\beta)\, \sigma(\Gamma_\alpha,\beta).$$

A related definition (Newman and Chen 1982), which uses symmetrized atomic displacements $\delta(\Gamma_\alpha, \beta)$ instead of the local strain, is

$$V_{\mathrm{OL}} = \left(\frac{\partial V(r,\theta,\phi)}{\partial\delta(\Gamma_\alpha,\beta)}\right)_{\mathrm{eq}} \delta(\Gamma_\alpha,\beta) = \sum_{n\alpha\beta} V(n,\Gamma_\alpha)\, C(n,\Gamma_\alpha,\beta)\, \delta(\Gamma_\alpha,\beta). \qquad \text{(A1)}$$

In these equations $C(n, \Gamma_\alpha, \beta)$ are linear combinations of orbital angular momentum operators of order n, which transform as the βth component of the representation Γ_α of the symmetry group; $V(n, \Gamma_\alpha)$ are the dynamic coupling parameters with units of energy. There are 22 or 41 such parameters corresponding to D_{3h} or C_{3h} symmetry respectively. The $\delta(\Gamma_\alpha, \beta)$ are displacements labelled according to the βth component of representation Γ_α. When $\delta(\Gamma_\alpha, \beta)$ are regarded as the normal mode displacements, equation (A1) will be the same as equation (4) in Stedman and Minard (1981). For D_{3h}/C_{3h} symmetry systems the number of $\delta(\Gamma_\alpha, \beta)$ (i.e. the number of cluster symmetry coordinates required) is 27 and the modes labelled by the C_{3h} irreducible representations are $5A'+4A''+5E'+4E''$ ($= S-\tau(s)$ in the notation of Stedman and Minard 1981, Table 2).

Assuming $\delta(\Gamma_\alpha, \beta)$ are normalized displacements (accordingly, the parameters $V(n, \Gamma_\alpha)$ in equation A1 are now written $V_{\mathrm{N}}(n, \Gamma_\alpha)$), we define

$$\delta(\Gamma_\alpha,\beta) = \frac{3}{R}\Delta R(\Gamma_\alpha,\beta) = \sum_i \lambda_i(\Gamma_\alpha,\beta)\frac{3}{R}\Delta u_i, \qquad \text{(A2)}$$

where $i = x, y, z$ and $\lambda_i(\Gamma_\alpha, \beta)$ are the coefficients of symmetry coordinates in Table 6. For instance, in the case of D_{3h} symmetry, two of the normalized displacements for Γ_5 (or E'') representation are

$$\delta(\Gamma_5,a) = \delta z^6 = \tfrac{1}{2}\sqrt{\tfrac{1}{3}}(3/R)\{(-2\Delta z_4+\Delta z_5+\Delta z_6)+(-2\Delta z_7+\Delta z_8+\Delta z_9)\} \qquad \text{(A3a)}$$

(for the mode labelled by $(A_2''\otimes E')E''$, zx component) and

$$\delta(\Gamma_5,b) = \delta x^5 = \sqrt{\tfrac{1}{6}}(3/R)(\Delta x_4+\Delta x_5+\Delta x_6-\Delta x_7-\Delta x_8-\Delta x_9) \qquad \text{(A3b)}$$

(for the mode labelled $(E'\otimes A_2'')E''$, xz component).

The crystal field potential at the site (r, θ, ϕ) is described by

$$V(r,\theta,\phi) = \sum_{n,m} B_n^m Z_n^m,$$

where the Z_n^m are tesseral harmonics (Newman 1971, equation 2·4). By using the superposition model expression, equation (A1) may be written as

$$\sum V_{\mathrm{N}}(n,\Gamma_\alpha)\, C(n,\Gamma_\alpha,\beta) = \sum_{n,m} Z_n^m(\theta,\phi)\left(\frac{\partial B_n^m}{\partial\delta(\Gamma_\alpha,\beta)}\right)_{\mathrm{eq}}$$

$$= \sum_{n,m} Z_n^m(\theta,\phi)\, S_n^m\left(\sum_i \frac{\partial}{\partial\delta(\Gamma_\alpha,\beta)} K_n^m(\theta_i,\phi_i)\,\bar{A}_n(R_i)\right)_{\mathrm{eq}}, \qquad \text{(A4)}$$

where S_n^m are coefficients relating the parameters B_n^m to the Stevens notation $A_n^m\langle r^n\rangle$ (cf. Dieke 1968, Table 8).

As the $C(n,\Gamma_\alpha,\beta)$ are linear combinations of spherical harmonics, they can be expressed in terms of Z_n^m. The values of the $V_N(n,\Gamma_\alpha)$ are then found by equating the coefficients of these tesseral harmonics in equation (A4).

As an illustration, we calculate $V_N(2,\Gamma_5)$ for sixfold coordination of D_{3h} symmetry systems, corresponding to the normalized mode displacements shown in equation (A3). From the table in Appendix I of Borg and Mlik (1975) we find

$$C(2,\Gamma_5) = \sqrt{\tfrac{1}{2}}\,(4\pi/5)^{\frac{1}{2}}(Y_2^{-1}-Y_2^1) = \sqrt{\tfrac{1}{2}}\,Z_2^1$$

and then, according to equation (A4), we have

$$V_{N,a}(2,\Gamma_5) = S_2^1\sqrt{2}\left(\sum_i \frac{\partial}{\partial\delta(\Gamma_5,a)}K_2^1(i)\,\bar{A}_2\right),$$

$$V_{N,b}(2,\Gamma_5) = S_2^1\sqrt{2}\left(\sum_i \frac{\partial}{\partial\delta(\Gamma_5,b)}K_2^1(i)\,\bar{A}_2\right). \tag{A5}$$

By using the definition of $\delta(\Gamma_5,a)$ in equation (A3a) and substituting $S_2^1 = \sqrt{6}/6$, we find

$$\begin{aligned} V_{N,a}(2,\Gamma_5) &= \tfrac{1}{3}\sqrt{3}\sum_i \frac{R}{3}\frac{\partial x_i}{\partial R(\Gamma_5,a)}\left(\bar{A}_2\frac{\partial K_2^1(i)}{\partial x_i}+K_2^1(i)\frac{\partial \bar{A}_2}{\partial x_i}\right) \\ &= \tfrac{1}{9}\sqrt{3}\sum_i \frac{\partial x_i}{\partial R(\Gamma_5,a)}\left(R\frac{\partial K_2^1(i)}{x_i}-K_2^1(i)\frac{\partial R}{\partial x_i}t_2\right)\bar{A}_2 \\ &= \tfrac{1}{9}\sqrt{3}\sum_i \frac{\partial x_i}{\partial R(\Gamma_5,a)}(-6\cos 2\theta_i\sin\theta_i\cos\phi_i-3\sin 2\theta_i\cos\phi_i\cos\theta_i\,t_2)\bar{A}_2\,, \end{aligned}$$

where we have used the appropriate expressions given in Tables 1 and 2. In addition, the terms $\partial x_i/\partial R(\Gamma_5)$ can be obtained by differentiating the relations involving x_i in Table 6 as

$$\partial x_i/\partial R(\Gamma_5,a) = -\sqrt{\tfrac{1}{3}} \qquad \text{for } i = 4,\,7\,,$$

$$\partial x_i/\partial R(\Gamma_5,b) = \tfrac{1}{2}\sqrt{\tfrac{1}{3}} \qquad \text{for } i = 5,\,6,\,8,\,9\,.$$

Finally, substituting the site coordinates (R_i,θ_i,ϕ_i) for each ligand (4–9) (see the footnote to Table 8) we obtain

$$V_{N,a}(2,\Gamma_5) = -\tfrac{1}{2}\sqrt{2}\,t_2\,\bar{A}_2\,.$$

The parameter $V_{N,b}(2,\Gamma_5)$ in equation (A5) is obtained in the same way to give

$$V_{N,b}(2,\Gamma_5) = \sqrt{2}\,(1-\tfrac{1}{2}t_2)\bar{A}_2\,.$$

We notice that linear combinations of these two parameters, $V_{N,a}(2,\Gamma_5)$ and $V_{N,b}(2,\Gamma_5)$, give alternative pairs of independent parameters corresponding to the Γ_5 representation. For example, in Table 8 for sixfold coordination, the parameters

$$V(2,\Gamma_5 A) = \bar{A}_2\,, \qquad V(2,\Gamma_5 B) = -(1-t_2)\bar{A}_2\,,$$

come from appropriate linear combinations of $V_{N,a}$ and $V_{N,b}$ according to the relations given by Borg and Mlik (1975, equation 21).

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