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Low-Symmetric Coordination Polyhedra – Pseudosymmetry and Idealization

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Abstract

A method is described for the analysis of symmetryless or low-symmetric coordination polyhedra with respect to their pseudosymmetry, regardless of coordination number. With lattice sums of spherical harmonics, symmetry-adapted orientations of the real polyhedra in the various point groups are ascertained by fitting procedures. The idealized polyhedra can then be constructed by averaging and optimizing the positional parameters of those atoms which are symmetry equivalent in the idealized arrangements. The degree of distortion of the real polyhedra with regard to the idealized polyhedra is specified by the mean value of relative atom displacements. The method can assist in the investigation of factors affecting crystal structure and in the interpretation of spectroscopic and magnetic properties of compounds with *d* and *f* elements. The analysis is applied to LiCeO₂ where a symmetryless arrangement of the O atoms around the Ce atom occurs with coordination number seven.

1. Introduction

In the discussion of crystal structures the description of the existing coordination polyhedra (CP) and their

comparison with known ideal arrangements are of great importance (Wells, 1984). The investigation of the relationship between real, *i.e.* normally distorted, polyhedra and ideal polyhedra can be useful in various ways such as the ascertainment of factors affecting crystal structure. In the case of complexes the shape of the CP will depend on the chemical bonding between the central atom and the ligands, on mutual repulsions of the ligands, and on the packing relations in the crystal structure (Hoard & Silverton, 1963). The consequences of these influences are in most cases distortions relative to those polyhedron models that are predicted, for example, from the pure electrostatic point of view (point charges) or from the packing of rigid spheres. In intermetallic compounds deviations from Laves principles (Laves, 1956) can occur if covalent bonds, *i.e.* bonds with directional character, exist (Pearson, 1972). Idealizations of low-symmetric arrangements with a special pseudosymmetry also facilitate the investigation of spectroscopic and magnetic properties of transition-metal and rare-earth compounds. Raising the symmetry normally leads to a drastic decrease of the number of crystal-field parameters and therefore reduces the problem.

The description and idealization of low-symmetric CP can be complicated by a high degree of distortion, by an unsuitable orientation of the CP to the cell edges and/or by high coordination numbers (CN).

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An increase in the distortion from ideal conformation and an increase in the CN generally speaking leads to an increasing number of possible idealizations. In order to distinguish between different idealized polyhedra (for instance between square antiprism and dodecahedron in the case of CN 8), various suggestions were made in the past. So-called shape parameters were introduced such as angles between connecting lines $M-X$ and the main axis of symmetry (M central atom, X ligand), the ratio of interatomic distances, and dihedral angles between appropriate planes (Hoard & Silverton, 1963; Kepert, 1965; Lippard, 1967; Lippard & Russ, 1968; Muetterties & Wright, 1967; Porai-Koshits & Aslanov, 1972; Muetterties & Guggenberger, 1974). The disadvantages of these methods are the following: (i) the choice of appropriate shape parameters depends on the polyhedron type; (ii) the choice of shape parameters becomes more and more complicated with increasing CN; (iii) it is hard to define a unit of measure by which to determine numerically the best possible idealized polyhedra. Some of these disadvantages are avoided in the approach of Dollase (1974). In his method the distortion of a real coordination polyhedron is determined by comparison with a set of idealized coordinates which are ascertained from an initial set of the required symmetry by least-squares fit. This method can be applied especially in the case of high symmetries and small CN.

We, however, are searching for a method of general application which determines rapidly the pseudosymmetry of a distorted coordination polyhedron, independent of CN and any starting sets of idealized coordinates. To start with we describe the main ideas of the method and the computer program. After that we present some results of calculations on a polyhedron with seven vertices.

2. Analysis of pseudosymmetry and method of idealization

2.1. Outline

In order to analyse low-symmetric arrangements with respect to their pseudosymmetry, calculations are carried out in two steps as illustrated in Fig. 1. A central atom M is irregularly surrounded by four ligands X ; for simplicity all five atoms are in the same plane. The quadrangle can be idealized for instance by an arrangement with point symmetry $4/mmm$, i.e. a square [other possibilities are mmm (rectangle) or $2/m$ (parallelogram)]. In the first step position B , which is related to a Cartesian coordinate system with the central atom at the origin and adapted to the symmetry $4/mmm$, is derived from the real position A . In the second step the idealized structure C is constructed under two constraints: (i) the four symmetry-equivalent and therefore identical dis-

tances $M-X$ of C are obtained from the mean value of the four different distances in the real structure; (ii) going from the real to the idealized structure the sum of ligand displacements has to be a minimum. The minimum total can serve to measure the quality of idealization.

If the same pattern is applied to three dimensions the first step of the calculations obviously is to ascertain (by spatial rotations around M) the suitable position B (see § 2.2) which is adapted to a distinct point symmetry P and which can serve in the second step as a basis of the idealization C (see § 2.3).

2.2. Determination of the symmetry-adapted orientations of the real coordination polyhedron (CP)

The symmetry-adapted orientations of the real CP can be achieved through the lattice sums

$$S(k, q) = \sum_{j=1}^{\text{CN}} (1/R_j^{k+1}) P_k^q(\cos \theta_j) \exp(-iq\varphi_j),$$

where CN is the number of coordinated ligands; R_j , θ_j and φ_j are polar coordinates of the j th ligand, and the functions $P_k^q(\cos \theta) \exp(-iq\varphi)$ are spherical harmonics apart from a constant factor.* In the case of symmetryless CP (point symmetry 1), in principle all $S(k, q)$ with $k = 1, 2, \dots, \infty$; $0 \leq q \leq k$ can make contributions to $V = \sum_k \sum_q S(k, q)$. With increasing point symmetry the number of terms decreases; in a characteristic manner for each point group P terms with distinct (k, q) values are absent in accordance with group theory (Gerloch & Slade, 1973). In Fig. 2 some examples are presented ($1, 2/m, mmm, 4/mmm$). In order to reduce computation time we have only used the terms with $k \leq 6$. They are sufficient to distinguish between the symmetries of the normally occurring polyhedra as the arrays of the corresponding (k, q) values are different (the only exceptions are the pairs $622-6/mmm$ and $432-m3m$ which, by using $k \leq 6$, lead to the same (k, q) pattern and are therefore

* The lattice sums $S(k, q)$ multiplied by electric charges are the ligand factors of the crystal-field operator and describe the charge distribution in the vicinity of a metal ion (Judd, 1963; Hutchings, 1964).

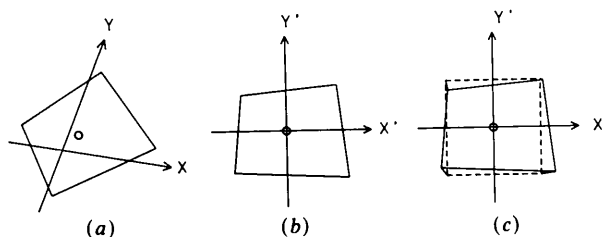


Fig. 1. Idealization of a quadrangle by a square; (a) real conformation; (b) symmetry-adapted conformation; (c) idealized conformation.

indistinguishable). Since the $S(k, q)$ are complex quantities (with the exception of terms with $q=0$ which are real), they are separated into real and imaginary parts, $S_r(k, q)$ and $S_i(k, q)$ respectively.

1

q	0	1	2	3	4	5	6
k	re	re	im	re	im	re	im
1	■	■	■				
2	■	■	■	■	■		
3	■	■	■	■	■	■	■
4	■	■	■	■	■	■	■
5	■	■	■	■	■	■	■
6	■	■	■	■	■	■	■

2/m

q	0	1	2	3	4	5	6
k	re	re	im	re	im	re	im
1							
2	■			■	■		
3							
4	■			■	■		
5							
6	■			■	■		

mmm

q	0	1	2	3	4	5	6
k	re	re	im	re	im	re	im
1							
2	■			■	■		
3							
4	■			■	■		
5							
6	■			■	■		

4/mmm

q	0	1	2	3	4	5	6
k	re	re	im	re	im	re	im
1							
2	■						
3							
4	■						
5							
6	■						

Fig. 2. Arrays of k and q for the point symmetries 1, 2/m, mmm and 4/mmm.

The arrays of Fig. 2 are obtained only if the ligands hold distinct positions with respect to the axes of a Cartesian coordinate system (e.g. the main symmetry axis coincide with the z axis etc.). From these ideal positions, small displacements of the ligands produce relatively small contributions of those $S_r(k, q)$ and $S_i(k, q)$ that are absent in the ideal structure.

This behaviour of the lattice sums can be exploited for the determination of a convenient orientation of the real structure with regard to the point group P of interest: in low-symmetric polyhedra with a distinct pseudosymmetry P the symmetry-adapted orientation is characterized by the smallest total of those lattice sums that are quenched in the ideal structure. This orientation is gained by rotating the real CP around the central atom. In this process it is necessary that the various lattice sums are entered into the fitting procedures* with comparable weight. Because the range of the individual lattice sums can differ widely [e.g. $|S(4, 4)_{\max}|/|S(4, 0)_{\max}| \approx 10^2$; $|S(6, 6)_{\max}|/|S(6, 0)_{\max}| \approx 10^5$] normalization factors $f(k, q)$ have to be introduced. In our calculations we have chosen $f(k, q) = 1/|S(k, q)_{\max}|^s$ where the index s indicates a reference to one single $M-X$ group. The distance R_{M-X} which is necessary to calculate the $f(k, q)$ is chosen to be the mean value of all distances $M-X$ of the real CP. In order to compare fits on the basis of several P differing among other things in the number $N(P)$ of the lattice sums entering the minimization process, and in order to be independent of CN, normalizations with respect to $N(P)$ and CN are also carried out. Consequently, in the fitting procedure we are looking for an orientation of the real CP with regard to P that minimizes the function

$$W(P) = 1/\{N(P) \times \text{CN}\} \left[\sum_{k'} f(k', 0) |S(k', 0)| \right. \\ \left. + \sum_{k' q' \neq 0} f(k', q') |S_r(k', q')| \right. \\ \left. + \sum_{k' q' \neq 0} f(k', q') |S_i(k', q')| \right].$$

The summations k' and q' extend over those lattice sums that are quenched in the ideal structure.† In general the real and imaginary parts have different (k', q') combinations (see Fig. 2).

For practical use, i.e. for reducing computer time (see Appendix 2), it is sufficient to calculate $W(P)$ only for a few of the infinite number of possible

* The fitting program is based on standard methods (Späth, 1974).

† In the cubic and icosahedral point groups constant ratios between some of the remaining terms exist, i.e. $S_r(4, 4)/S(4, 0) = 120$ and $S_r(6, 4)/S(6, 0) = -2520$ in the cubic groups, and $S_r(6, 5)/S(6, 0) = 5040$ in the icosahedral point group I_h . In order to achieve adaptations with respect to these point groups additional terms corresponding to deviations from these ideal ratios have to be included in the optimization process.

orientations. A convenient method is to choose special points such as the position of single atoms X or the centre of gravity of pairs $X-X$, triangles $\begin{matrix} X-X \\ \diagdown \diagup \\ X \end{matrix}$ etc. which are then set on the positive z axis by rotation around the central atom. In each case this operation is followed by rotations around the z axis from 0 to 180° in steps of 1° . In each orientation $W(P)$ is calculated. Finally the best orientation with lowest $W(P)$ value can be determined.

2.3 Construction of the idealized coordination polyhedra

Once the best symmetry-adapted orientation of the real CP has been found, it is possible to construct the idealized CP. Since the orientation of the symmetry elements of P with regard to the real structure is now fixed the ligands can be associated with the idealized positions of P . To begin with the average is calculated of each of the real spherical coordinates of those n ligands which occupy a site with multiplicity n in the idealized polyhedra, i.e. which are symmetry equivalent.* These positional parameters can serve as initial values in order to obtain the ideal parameters which give a minimum in the relative atom displacements $\overline{\Delta R^i}$.

$$\overline{\Delta R^i} = (1/\text{CN}) \sum_{j=1}^{\text{CN}} \{ |\mathbf{R}_j(\text{real}) - \mathbf{R}_j(\text{ideal})| / |\mathbf{R}_j(\text{real})| \}.$$

$\overline{\Delta R^i}$ is the measure of the quality of idealization. It can be minimized (i) by optimization of the coordinates θ and φ and (ii) by rotations of the real CP around the three coordinate axes changing rotation angles by $\leq 0.1^\circ$. The reason for (ii) is that in general the position found in §2 using normalized lattice sums is not necessarily the best orientation with respect to the new minimization condition $\overline{\Delta R^i}$.

The optimization procedures and the association of the atoms with the various sites are best explained by an example and are described in more detail in § 3.2 and the Appendix.

3. Application of the method to heptacoordination in LiCeO_2

3.1. Ideal coordination polyhedra

In the case of heptacoordination four ideal polyhedra (Fig. 3) have been discussed (Muetterties & Wright, 1967) which are the trigonal prism capped on a rectangle ($mm2$), the capped octahedron ($3m$), the pentagonal bipyramid ($\overline{10}m2$), and the tetragonal base-trigonal base (m). The last model consists of a

Table 1. LiCeO_2 ; Fractional atomic parameters (Schiller, 1985)

	x	y	z
Li	0.649 (4)	0.138 (4)	0.158 (4)
Ce	0.20028 (6)	0.06802 (7)	0.30630 (7)
O(1)	-0.0859 (10)	0.2612 (10)	0.4886 (10)
O(2)	0.4295 (10)	0.1275 (10)	0.7137 (11)

square and a triangle (with equal sides) on parallel planes. In idealized form there are two alternatives depending on the relative orientation of the square and the triangle, both having $P = m$. A fifth CP with $P = 2$ is possible from energetic considerations (Claxton & Benson, 1966); up to now, however, in real structures, it has not to our knowledge been found and therefore is not discussed here (but see § 3.3).

3.2. Analysis of the CeO_7 polyhedron

LiCeO_2 [δ - LiSmO_2 (Gondrand, 1970)] crystallizes on a monoclinic lattice (space group $P12_1/c1$) with the cell parameters $a = 5.824$ (1), $b = 6.166$ (1), $c = 5.793$ (1) Å, $\beta = 102.48$ (2) $^\circ$ and $Z = 4$ (Schiller, 1985). All atoms in the unit cell occupy the general position with parameters shown in Table 1. The Ce atom is surrounded by seven O atoms at distances of 2.43–2.54 Å (Fig. 4). The polyhedron consists of four O(1) (nos. 2, 3, 6, 7) and three O(2) (nos. 1, 4, 5) atoms. With respect to a Cartesian coordinate system with the Ce atom at the origin the O atoms have coordinates and distances to the central atom as shown in Table 2.

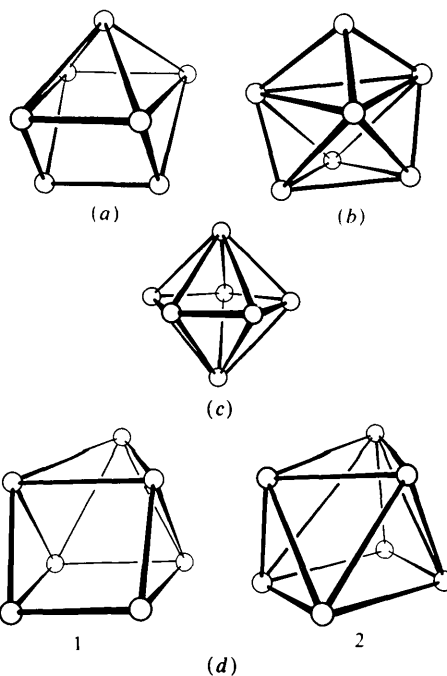


Fig. 3. Ideal polyhedra for coordination number 7; (a) trigonal prism capped on a rectangle (point symmetry $mm2$); (b) capped octahedron ($3m$); (c) pentagonal bipyramid ($\overline{10}m2$); (d) tetragonal base-trigonal base (m), two conformations.

* A ligand is set on a distinct special position of P if its real position is less distant than 0.6 Å from the idealized position. In our experience 0.6 Å is a suitable distance, but can be changed to lower or higher values, depending on the problem.

Table 2. LiCeO_2 ; Cartesian coordinates (Å) of the seven O atoms and their distances from Ce (at the origin)

O atom no.*	x	y	z	R
1	2.11	-1.21	-0.58	2.49
2	-0.65	-2.03	1.33	2.51
3	-1.63	1.19	1.42	2.46
4	1.30	1.88	-0.83	2.43
5	1.30	0.37	2.07	2.47
6	-1.63	1.05	-1.48	2.44
7	-0.65	-1.89	-1.56	2.54

* See Fig. 4.

3.2.1. $mm2$. In order to determine the symmetry-adapted orientation of the CeO_7 polyhedron with respect to $mm2$, 33 normalized lattice sums must be considered in the minimization process [see (k, q) array in Fig. 5a]. Since the atomic positions of the point group $mm2^*$ have multiplicities 1, 2 and 4 respectively, it is convenient to choose either single O atoms or the centre of gravity of all pairs or quadrangles which are then set on the positive z axis by rotation around the central atom (see § 2.2). Details of the best orientations obtained in the three cases are summarized in Table 3. The data are supplemented by the mean value $V(P)$ of all normalized lattice sums and by the ratio $\rho(P) = W(P)/V(P)$. The latter gives a fair indication whether a convenient adaptation to P has been achieved. The second (k, q) array in Fig. 5(b) illustrates the normalized lattice sums related to orientation I in a quantitative form [in order to underline the differences between the lattice sums they are also normalized to the maximum contribution produced by $f(6, 4)S(6, 4)$, which term is represented as a circle]. Obviously all normalized lattice sums that are quenched in $mm2$ yield only small contributions.

* General position: $(x, y, z; \bar{x}, \bar{y}, z; x, \bar{y}, z; \bar{x}, y, z)$; special positions: $(x, 0, z; \bar{x}, 0, z)$; $(0, y, z; 0, \bar{y}, z)$; $(0, 0, z)$.

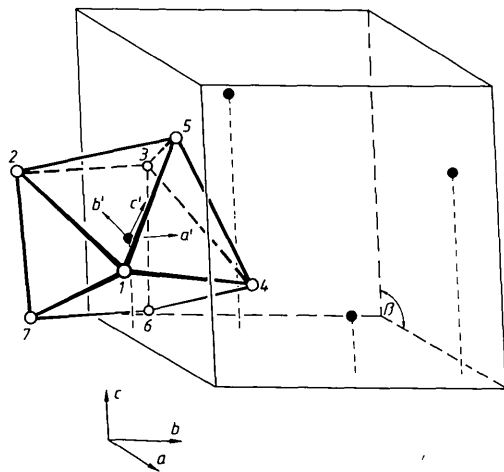


Fig. 4. Unit cell of LiCeO_2 ; only the Ce atoms (●) and the next O-atom neighbours (○) for one Ce atom are shown.

Table 3. LiCeO_2 ; Symmetry-adapted orientation of the CeO_7 polyhedron with respect to $mm2$

Orientation	Points* on positive z axis	Nos. of O atoms	$W^\dagger(mm2)$	$V^\dagger(mm2)$	$\rho^\dagger(mm2)$
I	Single atoms	5	0.042	0.094	0.44
II	Pairs	6, 7	0.040	0.094	0.43
III	Quadrangles	1, 2, 3, 4	0.076	0.102	0.75

* Centre of gravity.

† See text.

Inspecting Table 3, one notes that

(i) the relatively low ratios $\rho(mm2)$ indicate what have in our experience been satisfactory adaptations to the point group of interest;

$mm2$

q	0	1	2	3	4	5	6
k	re	re	im	re	im	re	im
1	■						
2	■		■				
3	■		■				
4	■		■		■		
5	■		■		■		
6	■		■		■		■

q	0	1	2	3	4	5	6
k	re	re	im	re	im	re	im
1	-	-	-				
2		-	-	△	-		
3		-	△	△	-	△	△
4	△	△	△	△	△	△	△
5	△	-	△	△	△	△	△
6	△	-	△	△	△	△	△

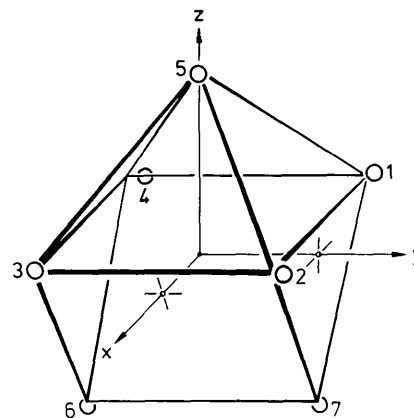


Fig. 5. Symmetry-adapted orientation and idealization of the CeO_7 polyhedron with respect to $mm2$; (a) (k, q) array for $mm2$; (b) normalized lattice sums related to orientation I (see Table 3); (c) real and idealized structures.

Table 4. LiCeO_2 ; Cartesian coordinates (\AA) of real and idealized positions of O atoms in the CeO_7 polyhedron (Ce at origin) with respect to $mm2$

O atom no.	Multiplicity	Real structure				Idealized structure				$\Delta R'$	ΔR (\AA)
		x	y	z	R	x	y	z	R		
5	1	0.11	0.02	2.47	2.47	0	0	2.47	2.47	0.045	0.11
6	2	0.15	-1.48	-1.94	2.44	0	-1.55	-1.94	2.49	0.070	0.17
7	2	0.04	1.63	-1.95	2.54	0	1.55	-1.94	2.49	0.035	0.09
1	4	-1.69	1.77	0.51	2.49	-1.80	1.64	0.42	2.48	0.076	0.19
2	4	1.77	1.75	0.38	2.51	1.80	1.64	0.42	2.48	0.048	0.12
3	4	1.81	-1.62	0.44	2.46	1.80	-1.64	0.42	2.48	0.012	0.03
4	4	-1.94	-1.42	0.38	2.43	-1.80	-1.64	0.42	2.48	0.107	0.26
										$\overline{\Delta R'} = 0.056$	$\overline{\Delta R} = 0.14 \text{ \AA}$

(ii) obviously, the three orientations I, II and III correspond to nearly equivalent positions of the polyhedron with respect to the z axis. O atom 5 has to be associated with the ideal special position with multiplicity one of the point group $mm2$; by the same token, atoms 6, 7 and 1, 2, 3, 4 correspond to the twofold and fourfold ideal positions respectively. Consequently, any of the three orientations can serve as a basis for the same idealization.

To give an example, the results of the calculation of the idealized positions with respect to orientation I after minimizing $\overline{\Delta R'}$ are shown in Table 4 and Fig. 5(c) ($\overline{\Delta R'} = 0.056$; The corresponding absolute mean displacement is $\overline{\Delta R} = 0.14 \text{ \AA}$). The construction of the idealized polyhedron is described in more detail in the Appendix.

3.2.2. $3m$. The symmetry-adapted orientation of the CeO_7 polyhedron corresponding to $3m$ can be determined in a fashion analogous to that described for the adaptation to $mm2$. The number of lattice sums considered in the minimization process of § 2 is 37. Instead of choosing pairs and quadrangles as in the case of $mm2$ the centre of gravity of triangles (besides single atoms) is set on the positive z axis. The ratios $\rho(3m)$ are greater than in the adaptation to $mm2$, i.e. the $3m$ adaptation is less successful. The construction of the idealized polyhedron can be carried out with $\overline{\Delta R'} = 0.104$ ($\overline{\Delta R} = 0.26 \text{ \AA}$), which is

twice as much as in the adaptation to $mm2$ (see Fig. 6).

3.2.3. $\overline{10}m2$. The adaptation of the CeO_7 polyhedron to $\overline{10}m2$ is unprofitable because $\rho(\overline{10}m2)$ is relatively high (≈ 0.95). Therefore, we do not discuss the idealization related to this point group (but, in principle, the construction of an idealized polyhedron with respect to $\overline{10}m2$ would be possible).

3.2.4. m . With respect to this symmetry* a better adaptation of the real polyhedron than in the case of $mm2$ is possible [$\rho(m) \approx 0.25$; $\overline{\Delta R'} = 0.033$, $\overline{\Delta R} = 0.08 \text{ \AA}$]; this is reasonable because m is a subgroup of $mm2$ (see § 3.3).

In order to get a symmetry adaptation to the tetragonal base-trigonal base (Fig. 3d) which is of great importance in the discussion of structural relationships (see e.g. Rinck, 1982), the extinction conditions of the lattice sums have to be modified. In the case of a square and a triangle (with equal sides) orientated on planes parallel to the xy plane and with the mirror in the xz plane additional lattice sums with $q = 1, 2$ and 5 are quenched [we take the symbol $m(4, 3)$ for this special case of m].

The idealization process yields a tetragonal base-trigonal base of conformation (1) with $\overline{\Delta R'} = 0.047$

* If the mirror plane corresponding to the point group m lies in the xz plane all imaginary parts of the lattice sums are quenched.

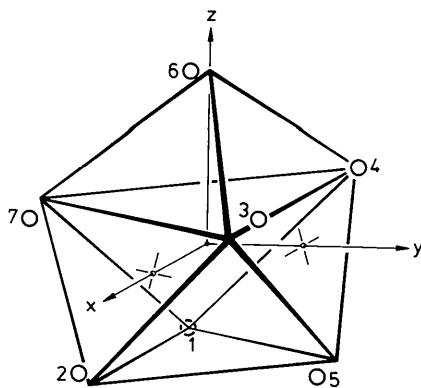


Fig. 6. Symmetry-adapted orientation and idealization of the CeO_7 polyhedron with respect to $3m$.

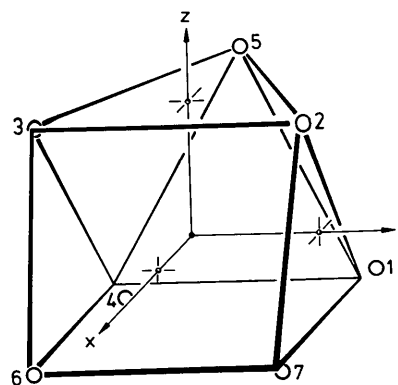


Fig. 7. Symmetry-adapted orientation and idealization of the CeO_7 polyhedron with respect to $m(4, 3)$.

[see Figs. 3(d) and 7].* The atoms have to be displaced by an average of $\overline{\Delta R} = 0.12 \text{ \AA}$, i.e. by nearly the same extent as in the $mm2$ model. This result confirms that the tetragonal base-trigonal base is very similar to the capped trigonal prism.

3.3. Résumé

In addition to the m , $mm2$ and $3m$ models, idealizations of the CeO_7 polyhedron with respect to the point groups 2 and 3 have been undertaken. All results are summarized in Table 5. A comparison of $\overline{\Delta R}'$ values in different idealizations shows that they undergo characteristic changes: from the various pairs of idealizations with respect to point groups which are related in the sense of group-subgroup, the polyhedron model with the smaller number of symmetry elements (i.e. with the greater number of independent parameters R , θ , φ of the polyhedron vertices) always has the lower $\overline{\Delta R}'$ value.†

4. Interpretation of the magnetic properties of LiCeO_2

According to the matter of investigation, parameters like $\overline{\Delta R}'$ lend themselves to various purposes: In the cases where the points of interest are factors affecting crystal structure, high-symmetric polyhedra are often suitable as standards of comparison. Relatively high $\overline{\Delta R}'$ values may occur if the real structures are sufficiently distorted. In the case of models which are applied to the interpretation of physical properties idealizations with a high $\overline{\Delta R}'$ value may lead to oversimplification and loss of accuracy which have to be avoided. We have applied the idealization program in order to obtain an interpretation of the magnetic properties of LiCeO_2 on the basis of a point-charge model.‡ Susceptibility measurements (temperature range 3.8 to 295 K; see Fig. 8) show that the magnetic moment of the Ce^{3+} ($4f^1$) ion depends on temperature, resulting in strong deviations from Curie-Weiss behaviour (Lueken, Hannibal & Stamm, 1984). The reason for this is that crystal-field effects perturb the free-ion ground-state term ${}^2F_{5/2}$. It would be rather involved to give an accurate description of this

* In order to distinguish between the two conformations of the tetragonal base-trigonal base the signs of lattice sums with $q=4$ have to be scrutinized. In conformation (1) $S_r(4,4)$ and $S_r(6,4)$ are negative and $S_r(5,4)$ is positive whereas in conformation (2) the signs are reversed.

† In principle, the lower-symmetric polyhedron must lead at least to the same $\overline{\Delta R}'$ value as the higher symmetric model (Hamilton, 1965).

‡ The point-charge model is a highly simplifying approach to reality. Nevertheless, it is a valuable tool in magnetochemistry of the rare earths because it can often predict crystal-field splittings in a satisfactory manner and is easily applied. In more extended models, e.g. the angular overlap model (Gerloch, 1983), overlap of the charge clouds of the central atom with the ligands is considered. In this model idealization of the metal environment with respect to symmetry is not necessary.

Table 5. LiCeO_2 ; Results of all idealization processes

Point group	m	$m(4,3)^*$	2	$mm2$	3	$3m$	$\overline{10}m2$
Number of symmetry elements	2	2	2	4	3	6	20
Number of independent atomic parameters	12	4	10	6	7	5	2
$\rho(P)^\dagger$	0.25	0.40	0.45	0.55	0.60	0.65	0.95
$\overline{\Delta R}'$	0.033	0.047	0.054	0.056	0.101	0.104	‡
$\overline{\Delta R}$ (Å)	0.08	0.12	0.13	0.14	0.25	0.26	—

* Special case of m with additional symmetries of parts of the polyhedron (see text).

† Mean value of several orientations.

‡ No idealization was carried out because of the high ρ value.

influence because of the low point symmetry of the Ce atoms. In order to simplify the problem the geometry of the seven surrounding O atoms (which represent the strongest factor in the crystal field) has to be idealized, without giving up the necessary accuracy. To keep displacements to a minimum the m model is the most suitable. In order to simplify the magnetochemical analysis it is on the other hand convenient to describe the crystal-field effects by a Hamiltonian $\hat{H}_{CF} = \sum_k \sum_q B(k, q) \hat{O}(k, q)$ [with the operator equivalents $\hat{O}(k, q)$ of Stevens (1952) and the crystal-field intensity parameters $B(k, q)$] containing as small a number of terms as possible, i.e. with arrangements of high symmetry like $3m$ (three terms in \hat{H}_{CF}). Owing to the relatively large $\overline{\Delta R}'$ value, however, an idealization to this point symmetry has to be rejected because the loss in accuracy of the $B(k, q)$ exceeds the acceptable limit with regard to chemical-bonding discussions. On the other hand, it is justified to take the $mm2$ model rather than the m or 2 model (five instead of eight terms) because differences in the corresponding $\overline{\Delta R}'$ values are small. In the $mm2$ model the magnetic properties can be explained with $B(k, q)$ parameters that agree satisfactorily with a simple point-charge model. The consistency of experimental and calculated data is illustrated in Fig. 8.

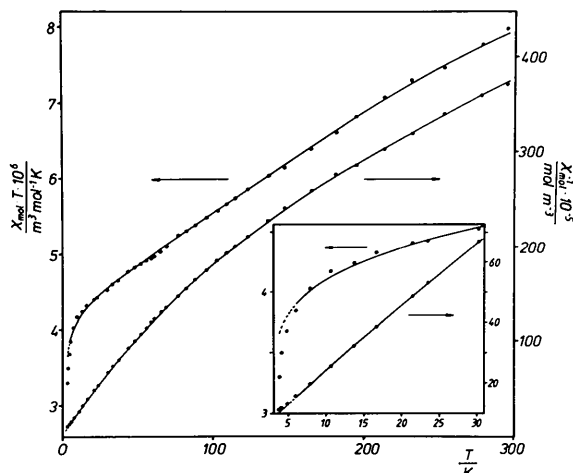


Fig. 8. $\chi_{\text{mol}} T$ vs T and $1/\chi_{\text{mol}}$ vs T diagrams for LiCeO_2 ; • experimental, — calculated.

APPENDIX

In order to construct an idealized polyhedron from a distorted arrangement the atoms of the real structure have to be associated with the special and general positions in the point group of interest. As a general rule the determination of the (idealized) atomic coordinates starts with the position(s) of lowest multiplicity and goes on to positions of increasing multiplicity. To illustrate this procedure the idealization with respect to $mm2$ can be used as an example: The position of lowest multiplicity is $0, 0, z$ (multiplicity 1). In the orientations obtained by step 1 (see Table 3) only O atom 5 of the CeO_7 polyhedron is less distant than 0.6 \AA from the z axis (in orientation I this atom lies exactly on the axis). If the real atomic polar coordinates are in general R_5, θ_5 and φ_5 the idealized coordinates are $R_5^{\text{id}} = R_5, \theta_5^{\text{id}} = 0$ or 180° and $\varphi_5^{\text{id}} = 0^\circ$ and the displacements ΔR_5 and $\Delta R_5' = \Delta R_5/R_5$ can be calculated. Finally O atom 5 is rejected from the set.

The two positions with multiplicity 2 are (i) $0, y, z; 0, \bar{y}, z$ and (ii) $x, 0, z; \bar{x}, 0, z$. In orientation I only the atoms 6 and 7 fulfil the 0.6 \AA criterion with respect to position (i), whereas in the case of (ii) no atoms are found. From the real coordinates R_6, θ_6 and R_7, θ_7 the mean values $R_{6,7}^{\text{av}}$ and $\theta_{6,7}^{\text{av}}$ can be calculated. The idealized coordinates are obtained in the following way. Owing to the special position of the O atoms, φ_6^{id} must be $\pm 90^\circ$ (the sign depends on the sign of y_6) and $\varphi_7^{\text{id}} = -\varphi_6^{\text{id}}$. Because of the condition concerning the idealized $M-X$ distances (see § 2.1), $R_{6,7}^{\text{id}} = R_{6,7}^{\text{av}}$, whereas $\theta_{6,7}^{\text{id}}$ has in principle to be optimized in order to determine $\theta_{6,7}^{\text{id}}$ and to reduce the displacements ΔR or $\Delta R'$ to a minimum (in case of $LiCeO_2$ the difference between R_6 and R_7 is small and therefore $\theta_{6,7}^{\text{av}}$ and $\theta_{6,7}^{\text{id}}$ are nearly identical). From our experience, θ^{av} has to be varied in steps of $\leq 0.01^\circ$. After this procedure O atoms 6 and 7 are rejected from the set. (In more complicated situations where, for instance, three atoms are found with the 0.6 \AA criterion, the twofold position will be occupied by those two atoms that have the smallest total relative displacement.)

Since in the case of the CeO_7 polyhedron no further atoms are found in the vicinity of symmetry axes and planes the remaining four atoms (1-4) have to be associated with the general position. From the real coordinates the mean values $R_{1,2,3,4}^{\text{av}}$, $\theta_{1,2,3,4}^{\text{av}}$ and φ^{av} (with the four individual φ values $\pm \varphi^{\text{av}}$ and $180 \pm \varphi^{\text{av}}$) can be calculated. By the same token, as in the case of the twofold position $R_{1,2,3,4}^{\text{id}} = R_{1,2,3,4}^{\text{av}}$ and, owing to the general position of the O atoms, $\theta_{1,2,3,4}^{\text{id}}$ and φ^{id} must be varied in order to get $\theta_{1,2,3,4}^{\text{id}}$ and φ^{id} which reduce ΔR or $\Delta R'$ to a minimum. Depending on the sign of the parameters x_j and y_j ($j = 1-4$), the

four idealized φ parameters are then associated with the corresponding atoms. (If more than four atoms have to be associated with general positions those four atoms are selected that lead to the smallest total relative displacement.)

After calculating ΔR and $\Delta R'$ the sum of all seven displacements is known. Finally, the average relative displacement $\Delta \bar{R}'$ is minimized by rotating the real arrangement around the three axes of the Cartesian coordinate system.

The calculations were carried out using a DEC PDP 11/23 computer with a 64 K core memory. In the first step of the program the computation of $W(P)$ needs approximately 1 min for a single orientation. In the second step the idealization process needs 5 s for a single iteration. The computer program described is available from the authors on request.

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