

Ligand field splitting in ninefold coordination: application to synthetic analogues of monazite

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The splitting of the energy levels of d^1 ions in a field of nine ligands is calculated for the tricapped trigonal prism (TTP) and for the pentagonal interpenetrating tetrahedral polyhedron (PITP). Comparison of the results, as well as those for the monocapped square antiprism (MSAP), with the theoretical splittings in two synthetic analogues of monazite, LaPO_4 and CePO_4 , shows that in both orthophosphates the polyhedron surrounding the lanthanide ion is best described as a distorted PITP.

1. Introduction

In a recent study [1], the structures of lanthanum orthophosphate (LaPO_4) and cerium orthophosphate (CePO_4), which are synthetic analogues of the naturally occurring mineral monazite, were compared with those of three nine-coordination polyhedra: the monocapped square antiprism (MSAP), the tricapped trigonal prism (TTP) and the pentagonal interpenetrating tetrahedral polyhedron (PITP). The conclusion, supported by a semiquantitative analysis, was that the structures of LaPO_4 and CePO_4 are closer to the PITP than to the other geometries. In the present work, another criterion is used to determine which polyhedron best describes the structures of the two compounds: that of the splitting of the d-orbital energies in the electrostatic field of the ligands. The problem is of interest because monazite analogues have been proposed [2, 3] as possible hosts for the long-term storage of actinide wastes.

2. Results and discussion

2.1. Ligand field splitting: TTP

The structure of the tricapped trigonal prism (TTP) is shown in Fig. 1. Assuming that the cation Ln is in the centre and the ligands O_1 and O_9 in the vertex positions, the coordinates of the ten ions are: $\text{Ln}(0, 0, 0)$; $O_1(0, -a, -a)$; $O_2(-3^{1/2} a/2, \frac{a}{2}, -a)$; $O_3(3^{1/2} a/2, \frac{a}{2}, -a)$; $O_4(0, -a, a)$; $O_5(-3^{1/2} a/2, \frac{a}{2}, a)$; $O_6(3^{1/2} a/2, \frac{a}{2}, a)$; $O_7(6^{1/2} a/2, -2^{1/2} a/2, 0)$; $O_8(-6^{1/2} a/2, -2^{1/2} a/2, 0)$; $O_9(0, 2^{1/2} a, 0)$, where $a = 2^{1/2} d/2$, d is the cation-ligand distance and the coordinate system is the same as in Fig. 1.

The potential due to the ligand O_i of coordinates (x_i, y_i, z_i) is given by:

$$V_i = e_i/4\pi\epsilon_0 R_i = e_i/4\pi\epsilon_0 [(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2]^{1/2} \quad (1)$$

where e_i is the effective charge of the ion O_i and R_i is the distance between O_i and the point (x, y, z) .

Equation 1 may be written in the form:

$$V_i = e_i/4\pi\epsilon_0 [r^2 + r_i^2 - 2(x_i x + y_i y + z_i z)]^{1/2} \quad (2)$$

where $r^2 = x^2 + y^2 + z^2$ is the distance from the origin to the point (x, y, z) and $r_i^2 = x_i^2 + y_i^2 + z_i^2$ is the distance from the origin to the ligand O_i .

Assuming there is no overlap of the cation orbitals onto the ligands, i.e., that $r \ll r_i$, the denominator of Equation 2 may be replaced by a binomial expansion in terms of the form $r/r_i, x_i x/r_i$, etc. For a d electron, it can be shown [4] that only the powers 2 and 4 of the coordinates need be included in the expansion.

In the case of the TTP structure, the expansion described above leads to the following potential:

$$V_{\text{TTP}} = \sum_{i=1}^9 V_i = -\frac{e}{4\pi\epsilon_0} \frac{21}{128d^3} [8z^4 + 3(x^4 + y^4) + 21x^2y^2 + 36z^2(x^2 + y^2)] \quad (3)$$

In order to determine the matrix elements of the Hamiltonian associated with the potential V_{TTP} , we use the method proposed by Randić [5] and compute matrix elements of the form $\langle \ell | V_k | \ell \rangle$, where $\ell = 0, 1, \pm 2$, V_k are the functions of the coordinates x, y, z that appear in the expression for the potential and the orbitals are expressed in the form:

$$\psi(0) = \left(\frac{5}{16\pi}\right)^{1/2} R(r)(3 \cos^2 \theta - 1) \quad (4)$$

$$\psi(1) = \left(\frac{15}{8\pi}\right)^{1/2} R(r) \sin \theta \cos \theta \exp(i\phi) \quad (5)$$

$$\psi(\pm 2) = \left(\frac{15}{32\pi}\right)^{1/2} R(r) \sin^2 \theta \exp(\pm 2i\phi) \quad (6)$$

The integrations over r lead to constants of the form $G_n = e \langle r^n \rangle / 4\pi\epsilon_0 d^{n+1}$. The results of the integrations over θ and ϕ are shown in Table I. Using this table, we obtain the following matrix elements for the Hamiltonian associated with the potential V_{TTP} :

$$H_{00} = -\frac{183}{128} G_4 \quad (7)$$

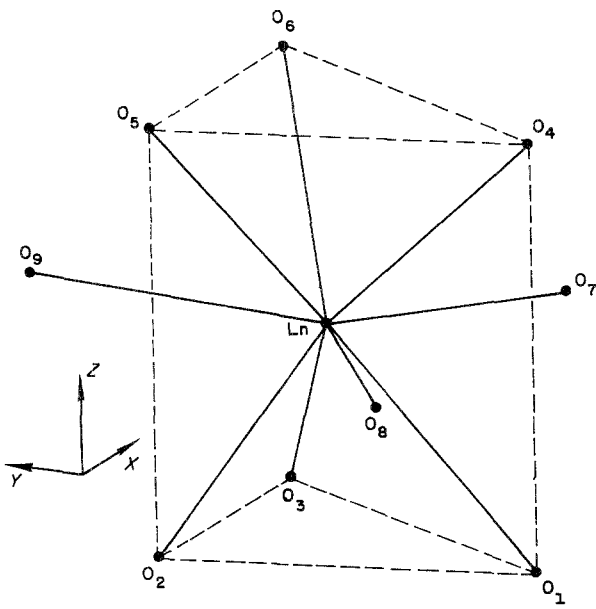


Figure 1 Tricapped trigonal prism (TTP) structure.

$$H_{11} = -\frac{223}{128} G_4 \quad (8)$$

$$H_{22} = -\frac{158}{128} G_4 \quad (9)$$

$$H_{2-2} = \frac{15}{128} G_4 \quad (10)$$

where $G_4 = \langle r^4 \rangle / 4\pi\epsilon_0 d^5$.

The eigenfunctions of the Hamiltonian may be written in the usual form $d_{z^2} \equiv |0\rangle$, $d_{xz,yz} \equiv (1/2^{1/2})(|1\rangle \pm |-1\rangle)$, $d_{xy} \equiv (1/2^{1/2})(|2\rangle - |-2\rangle)$, $d_{x^2-y^2} \equiv (1/2^{1/2})(|2\rangle + |-2\rangle)$. The corresponding eigenvalues are:

$$E(xy) = -(143/128)G_4 \simeq -1.12G_4 \quad (11)$$

$$E(x^2 - y^2) = -(173/128)G_4 \simeq -1.35G_4 \quad (12)$$

$$E(z^2) = -(183/128)G_4 \simeq -1.43G_4 \quad (13)$$

$$E(xz, yz) = -(223/128)G_4 \simeq -1.74G_4 \quad (14)$$

2.2. Ligand field splitting: PITP

The structure of the pentagonal interpenetrating polyhedron (PITP) is shown in Fig. 2. Assuming that the cation Ln is in the centre and the ligands O₁ to O₉ in the vertex positions, the coordinates of the ten ions are: Ln(0, 0, 0); O₁(-d, 0, 0); O₂(-d cos 72°, d sin 72°, 0); O₃(d sin 54°, d cos 54°, 0); O₄(d sin 54°, -d cos 54°, 0); O₅(-d cos 72°, -d sin 72°, 0); O₆(-d/2, 0, 3^{1/2}d/2); O₇(d/2, 0, 3^{1/2}d/2); O₈(0, d/2, -3^{1/2}d/2); O₉(0, -d/2, -3^{1/2}d/2), where d is the cation-ligand distance and the coordinate system is the same as in Fig. 2.

TABLE I Integrals over θ and ϕ for orbitals $\psi(\ell)$ and different perturbation potentials V_k

V_k	$\langle 0 V_k 0\rangle$	$\langle 1 V_k 1\rangle$	$\langle 2 V_k 2\rangle$	$\langle 2 V_k -2\rangle$
z^4	9/21	5/21	1/21	0
$x^4 + y^4$	6/21	6/21	12/21	2/21
x^2y^2	1/21	1/21	2/21	-1/21
$(x^2 + y^2)z^2$	2/21	4/21	2/21	0

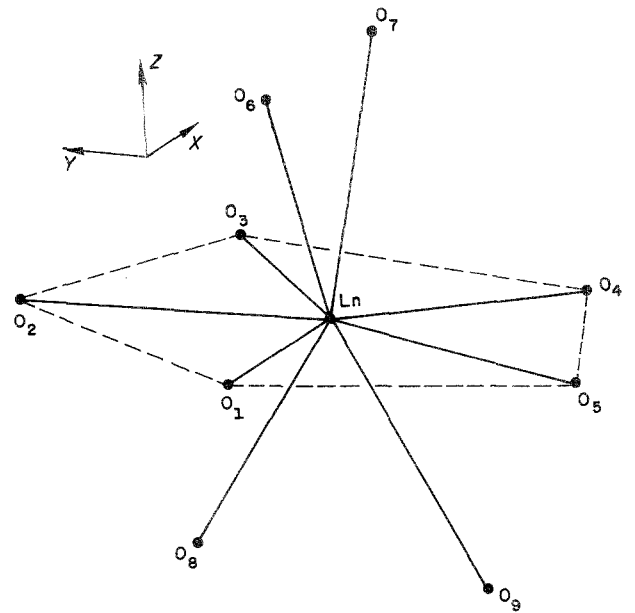


Figure 2 Pentagonal interpenetrating tetrahedral polyhedron (PITP) structure.

In the case of the PITP structure, the potential due to the nine ligands is given by:

$$V_{\text{PITP}} = \frac{e}{4\pi\epsilon_0} \frac{63}{32d^5} [9z^4 + 4(x^4 + y^4) + 3x^2y^2 - 27z^2(x^2 + y^2)] \quad (15)$$

Using Table I, we find the following matrix elements for the Hamiltonian associated with the potential V_{PITP} :

$$H_{00} = \frac{162}{32} G_4 \quad (16)$$

$$H_{11} = -\frac{108}{32} G_4 \quad (17)$$

$$H_{22} = \frac{27}{32} G_4 \quad (18)$$

$$H_{2-2} = \frac{15}{32} G_4 \quad (19)$$

The corresponding eigenvalues are:

$$E(z^2) = (162/32)G_4 \simeq 5.06G_4 \quad (20)$$

$$E(xy) = (42/32)G_4 \simeq 1.31G_4 \quad (21)$$

$$E(x^2 - y^2) = (12/32)G_4 \simeq 0.38G_4 \quad (22)$$

$$E(xz, yz) = -(108/32)G_4 \simeq -3.38G_4 \quad (23)$$

2.3. Ligand field splitting: MSAP

The structure of the monocapped square antiprism (MSAP) is shown in Fig. 3. Assuming that the cation Ln is in the centre and the ligands O₁ and O₉ in the vertex positions, the coordinates of the ten ions are: Ln(0, 0, 0); O₁(-a, -a, -a); O₂(-a, a, -a); O₃(a, a, -a); O₄(a, -a, -a); O₅(0, -2^{1/2}a, a); O₆(-2^{1/2}a, 0, a); O₇(0, 2^{1/2}a, a); O₈(2^{1/2}a, 0, a); O₉(0, 0, d), where $a = 3^{1/2}d/3$, d is the cation-ligand distance and the coordinate system is the same as in Fig. 3.

In the case of the MSAP, the ligand field splitting,

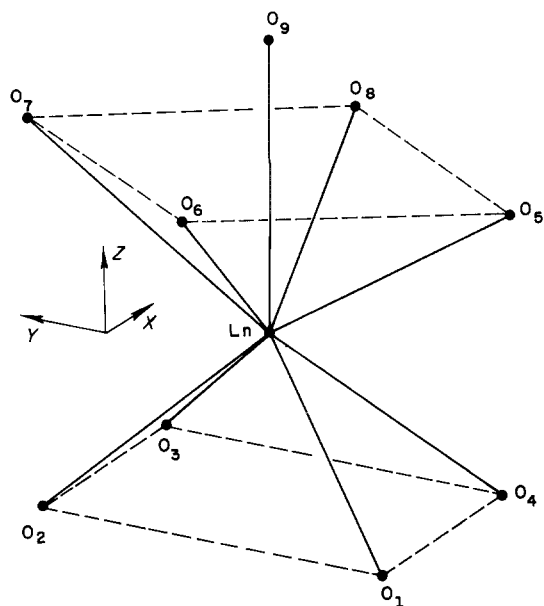


Figure 3 Monocapped square antiprism (MSAP) structure.

assuming $G_4/G_2 = 0.1$, the value appropriate to the V^{4+} ion, is given by [6]:

$$E(z^2) = 2.25G_4 \quad (24)$$

$$E(xz, yz) = 1.83G_4 \quad (25)$$

$$E(xy) = E(x^2 - y^2) = -2.96G_4 \quad (26)$$

2.4. Ligand field splitting: LaPO_4 and CePO_4

In the case of the real compounds LaPO_4 and CePO_4 , the theoretical potential due to the ligands can be computed directly from the atomic positions, as determined by X-ray diffraction [1, 7]. When the result is rounded up to two significant places and the small terms are dropped, the potential is the same for both orthophosphates:

$$V = \frac{e}{4\pi\epsilon_0} \frac{1}{d^5} [2.4z^4 + 2.4(x^4 + y^4) - 4.6x^2y^2 - 11z^2(x^2 + y^2)] \quad (27)$$

Using Table I, we find the following matrix elements for the Hamiltonian associated with the potential V :

$$H_{00} = 0.45G_4 \quad (28)$$

$$H_{11} = -1.06G_4 \quad (29)$$

$$H_{22} = 0 \quad (30)$$

$$H_{2-2} = 0.01G_4 \quad (31)$$

The corresponding eigenvalues are:

$$E(z^2) = 0.45G_4 \quad (32)$$

$$E(x^2 - y^2) = 0.01G_4 \quad (33)$$

$$E(xy) = -0.01G_4 \quad (34)$$

$$E(xz, yz) = -1.06G_4 \quad (35)$$

The splittings for the TTP, PITP and MSAP geometries (Equations 11 to 14, 20 to 23 and 24 to 26, respectively) are compared with the splitting for LaPO_4 and CePO_4 (Equations 32 to 35) in Fig. 4. In order to make the comparison easier, the largest splitting in each case was normalized to unity and a

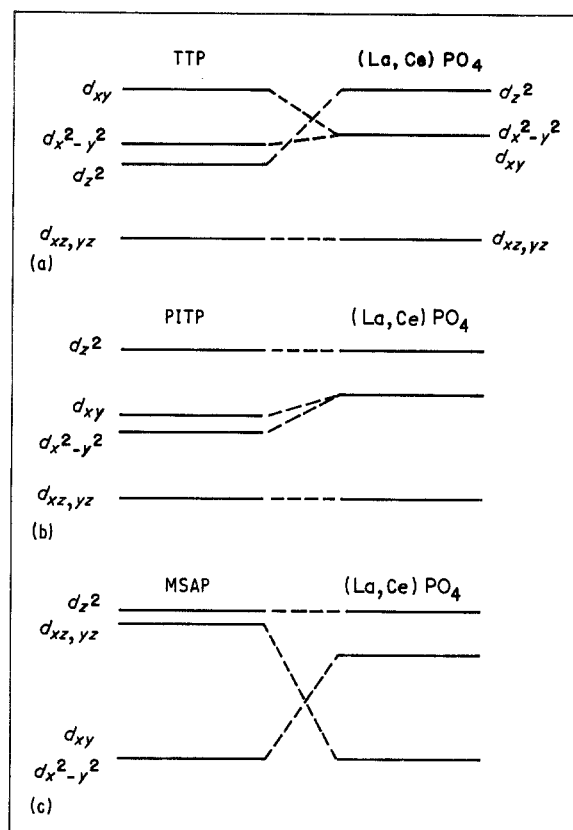


Figure 4 Energy splitting of the d orbitals for three possible arrangements of nine equivalent charges, as compared with the splitting in LaPO_4 and CePO_4 . (a) Tricapped trigonal prism (TTP); (b) pentagonal interpenetrating tetrahedral polyhedron (PITP); (c) monocapped square antiprism (MSAP).

constant energy was added to all levels so that the largest and the smallest level would be at the same position in all four cases. As Fig. 4 shows, the splittings for the PITP geometry are much closer to those in the orthophosphates than the splittings for the other geometries. The fact that the energy of the orbital $d_{x^2-y^2}$ is slightly higher than the energy of the orbital d_{xy} in the orthophosphates indicates that the main distortion in the real compounds is a compression of the pentagon along the x -axis. We are thus led to the conclusion that, as suggested by Mullica *et al.* [1], the polyhedron surrounding the lanthanide ion in LaPO_4 and CePO_4 is best described as a distorted PITP.

References

1. D. F. MULLICA, W. O. MILLIGAN, D. A. GROSSIE, G. M. BEALL and L. A. BOATNER, *Inorg. Chim. Acta* **95** (1984) 231.
2. G. J. McCARTHY, W. B. WHITE and D. E. PFOERTSCH, *Mater. Res. Bull.* **13** (1978) 1239.
3. L. A. BOATNER, G. W. BEALL, M. M. ABRAHAM, C. B. FINCH, P. G. HURAY and M. RAPPAPZ, in "The Scientific Basis for Nuclear Waste Management", Vol. III, edited by C. J. Northrup (Plenum, New York, 1980) p. 289.
4. J. W. ORTON, "Electron Paramagnetic Resonance" (Gordon and Breach, New York, 1968).
5. M. RANDIC, *J. Chem. Phys.* **36** (1962) 2094.
6. R. S. DE BIASI and J. C. DE LIMA, *J. Magn. Magn. Mater.* **46** (1985) 305.
7. G. W. BEALL, L. A. BOATNER, D. F. MULLICA and W. O. MILLIGAN, *J. Inorg. Nucl. Chem.* **43** (1981) 101.

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