Possible symmetries of Jahn—Teller distortions for O_h parent group

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Classification of the stable symmetries of Jahn—Teller systems of O_h parent group is done both for double and triple degenerate nonrelativistic electronic states and for fourfold degenerate relativistic ones. The results produced by the epikernel principle and by the method of step-by-step descent in symmetry connected with degenerate states splitting are compared. The results obtained on the basis of epikernel principle are incomplete and for relativistic electronic states even incorrect.

Jahn—Teller (JT) effect plays a key role in the stereochemistry of metal complexes. According to the JT theorem [1, 2] a nonlinear geometrical arrangement of nuclei in degenerate electronic state — except Kramers' degeneracy caused by relativistic effects — is unstable. It implies the existence of at least one stable configuration of nuclei in a nondegenerate electronic state or double degenerate relativistic electronic state (Kramers' degeneracy). Such a state is related by splitting to the original degenerate electronic state of the parent symmetry group. The splitting is connected with a symmetry descent of nuclear configuration, *i.e.* some symmetry elements vanish.

The principal question is what are the stable nuclear configurations of JT systems. This problem may be solved in various ways.

The most common treatment is to investigate the analytic form of the adiabatic potential surface generated by the perturbation theory [3]. However, it may be successfully applied only to very simple systems and the results may never be complete.

Other treatments are based on the group theoretical analysis of

i) JT active coordinates and

ii) (degenerate) electronic states.

Among the methods based on the symmetry properties of JT active coordinates the epikernel principle represents the most elaborated one [4]. Unfortunately, in all applications its range is limited for JT active modes. On the other hand, it may be applied also to pseudo-JT systems.

The theory of step-by-step descent in symmetry [5, 6] belongs to the methods based on the symmetry properties of the electronic state. It represents the most complex solution of the problem and it is applicable to such pseudo-JT systems which may be considered as the JT systems in excited electronic states, too.

The aim of this study is to compare the results of the above-mentioned group-theoretical treatments.

Method

Electronic states and nuclear coordinates may be described by their symmetry properties as representations of the proper symmetry group. The rule of JT instability [1, 2] states that the JT active distortion coordinate of a degenerate electronic state of symmetry type Γ must span representations Λ belonging to the nontotally symmetric part of the symmetrized direct product of Γ for single-valued representations, $[\Gamma \times \Gamma]$, or antisymmetrized direct product of Γ for double-valued representations, $\{\Gamma \times \Gamma\}$.

If the representations of the displacement coordinates are degenerate or reducible, *i.e.* if several symmetry components are involved, one is no longer dealing with a single distortion coordinate but with a distortion space, covering several dimensions [4]. A symmetry operation will be conserved during a nuclear displacement if and only if it leaves the displacement coordinate invariant (it has the same character values as the identity operation). The conserved (minimal) subgroup is called the kernel of the coordinate representation. It is symbolized as $\mathbf{K}(\mathbf{G}, \Lambda)$ where $\mathbf{G}$ is the parent (undistorted) group and Λ the representation. Such a subgroup, which is only conserved in a part of the distortion space, is termed an epikernel of Λ in $\mathbf{G}$, $\mathbf{E}(\mathbf{G}, \Lambda)$. Clearly epikernels are intermediate subgroups between the parent group (which exists only in the origin of the space), and the kernel group, which is conserved in all distorted structures. There are often several epikernels corresponding to one specific group $\mathbf{G}$ and one specific representation Λ. These epikernels may represent independent ways of symmetry lowering, leading to the kernel group along different paths. If the coordinate representation is reducible, *i.e.* composed of two or more different irreducible representations, the subspace kernels become epikernels of the sum representation.

The epikernel principle may be formulated as follows [4]: Extremum points on a JT surface prefer epikernels to kernels; they prefer maximal epikernels to lower ranking ones. As a rule stable minima are to be found with structures of maximal epikernel symmetry.

In the theory of step-by-step descent in symmetry the correlation among symmetry point groups is investigated for individual JT active systems from the viewpoint of the pertinent electronic state [5, 6]. The JT distortion causes a descent in the symmetry, $\mathbf{G}^0 \rightarrow \mathbf{G}^n$, and the original degenerate electronic state, $S_D(\mathbf{G}^0)$, is split yielding the nondegenerate single-valued one or double degenerate double-valued one, $S_N(\mathbf{G}^n)$. The symbol $\mathbf{G}^0$ denotes the symmetry point group of the parent system. A symmetry descent generates the n-th level subgroup, $\mathbf{G}^n$.

$$\subset \mathbf{G}^n \subset \ldots \subset \mathbf{G}^2 \subset \mathbf{G}^1 \subset \mathbf{G}^0 \tag{1}$$

The method is based on the following procedure:

i) The symmetry elements of the distorted geometry form a subgroup $\mathbf{G}^n$ of the parent system: $\mathbf{G}^n \subset \mathbf{G}^0$

ii) The irreducible representation $\Gamma(S^n)$ describing the electronic state in the distorted geometry $\mathbf{G}^n$ originates in the splitting of the multidimensional irreducible representation, $\Gamma(S_D^0)$, which corresponds to the actual degenerate electronic state in the parent geometry $\mathbf{G}^0$.

iii) The stable (equilibrium) geometry corresponds to the nondegenerate nonrelativistic or double degenerate relativistic electronic state, $S_N(\mathbf{G}^n)$, described by the one-dimensional single-valued or two-dimensional double-valued irreducible representation, $\Gamma(S_N)$. Otherwise the system continues in the symmetry descent and the procedure is repeated for $\mathbf{G}^{n+1} \subset \mathbf{G}^n$.

Because the symmetry point groups may have two or more subgroups and more than two-dimensional representations may be split into representations of different dimensions, there are various ways of symmetry descent. Only few of them have been observed among real systems.

Results and discussion

The symmetry group of an ideal octahedron, $\mathbf{O}_h$, contains ten single-valued irreducible representations describing the symmetries of electronic states and/or nuclear coordinates [7]. There are four one-dimensional (A_{1g}, A_{1u}, A_{2g}, and A_{2u}), two two-dimensional (E_g and E_u) and four three-dimensional (T_{1g}, T_{1u}, T_{2g}, and T_{2u}) ones. For their symmetrized direct products the following relations hold [3, 7, 8]

$$[A_{ij} \times A_{ij}] = A_{1g} \qquad i = 1, 2; j = \mathrm{g}, \mathrm{u} \tag{2}$$

$$[E_j \times E_j] = A_{1g} + E_g \qquad j = \mathrm{g}, \mathrm{u} \tag{3}$$

$$[T_{ij} \times T_{ij}] = A_{1g} + E_g + T_{2g} \qquad i = 1, 2; j = \mathrm{g}, \mathrm{u} \tag{4}$$

In describing the relativistic effects the double groups with double-valued representations are used [3]. Thus four two-dimensional ($E_{1/2g}$, $E_{1/2u}$, $E_{5/2g}$, and

$E_{5/2u}$) and two four-dimensional ($G_{3/2g}$ and $G_{3/2u}$) double-valued irreducible representations must be considered for this double group, too. The following relations hold for their antisymmetrized direct products [3, 7, 8]

$$\{E_{ij} \times E_{ij}\} = A_{1g} \qquad i = 1/2,\ 5/2;\ j = \mathrm{g, u} \tag{5}$$

$$\{G_{3/2j} \times G_{3/2j}\} = A_{1g} + E_g + T_{2g} \qquad j = \mathrm{g, u} \tag{6}$$

Thus only the coordinates of e_g and t_{2g} symmetries are JT active in $\mathbf{O}_h$ group and degenerate electronic states of E_g, E_u, T_{1g}, T_{1u}, T_{2g}, T_{2u}, $G_{3/2g}$, and $G_{3/2u}$ may be split due to the JT effect.

Table 1

Kernel, $\mathbf{K}(\mathbf{O}_h, \Lambda)$, and epikernel, $\mathbf{E}(\mathbf{O}_h, \Lambda)$, subgroups of $\mathbf{O}_h$ parent group for Λ irreducible representations of distortion coordinate [4]

Λ	$\mathbf{K}(\mathbf{O}_h, \Lambda)$	$\mathbf{E}(\mathbf{O}_h, \Lambda)$
a_{1g}	$\mathbf{O}_h$	
a_{1u}	$\mathbf{O}$	
a_{2g}	$\mathbf{T}_h$	
a_{2u}	$\mathbf{T}_d$	
e_g	$\mathbf{D}_{2h}$	$\mathbf{D}_{4h}$
e_u	$\mathbf{C}_2$	$\mathbf{C}_4$, $\mathbf{S}_4$
t_{1g}	$\mathbf{C}_i$	$\mathbf{S}_6$, $\mathbf{C}_{4h}$, $\mathbf{C}_{2h}$
t_{1u}	$\mathbf{C}_1$	$\mathbf{C}_{3v}$, $\mathbf{C}_{4v}$, $\mathbf{C}_{2v}$, $\mathbf{C}_s$
t_{2g}	$\mathbf{C}_i$	$\mathbf{D}_{3d}$, $\mathbf{D}_{2h}$, $\mathbf{C}_{2h}$
t_{2u}	$\mathbf{C}_1$	$\mathbf{D}_3$, $\mathbf{D}_{2d}$, $\mathbf{C}_{2v}$, $\mathbf{C}_2$, $\mathbf{C}_s$
$e_g + t_{2g}$	$\mathbf{C}_i$	$\mathbf{D}_{2h}$, $\mathbf{C}_{2h}$

Similar relations hold also for other cubic groups, only the subscripts are changed [3, 7, 8]. Axial symmetry groups may contain maximally two-dimensional irreducible representations and among them only two-dimensional single-valued ones may be a subject of JT effect [3, 7, 8].

The kernels and epikernels of $\mathbf{O}_h$ parent group are collected in Table 1. Figs. 1—3 show the distortion routes for the same parent group according to the theory of step-by-step descent in symmetry applied to various degenerate electronic states. And now let us compare the results of both the treatments.

For triple degenerate electronic states, according to eqn (*4*), it is $\Lambda = e_g$, t_{2g} or ($e_g + t_{2g}$). The epikernel principle predicts the stable nuclear arrangements of $\mathbf{D}_{4h}$, $\mathbf{D}_{3d}$, $\mathbf{D}_{2h}$, $\mathbf{C}_{2h}$, and $\mathbf{C}_i$ symmetry groups (Table 1). In addition, the step-by-

-step descent theory predicts stable geometries of $\mathbf{D}_4$, $\mathbf{D}_{2d}$, $\mathbf{S}_6$, $\mathbf{D}_3$, $\mathbf{C}_{3v}$, $\mathbf{D}_2$, $\mathbf{C}_{2v}$, $\mathbf{C}_3$, $\mathbf{C}_2$, $\mathbf{C}_s$, and $\mathbf{C}_1$ symmetries (Fig. 1). These may be obtained including coordinates composed of all the possible symmetries in the sense of epikernel principle (as partly indicated in Table 1 for non-JT active coordinates), but this principle says nothing about the possible electronic degeneracy (and JT stability or instability) of resulting nuclear arrangements.

For double degenerate electronic states only e_g coordinates are JT active (eqn (*3*)). According to epikernel principle there are stable geometries of $\mathbf{D}_{4h}$ and $\mathbf{D}_{2h}$

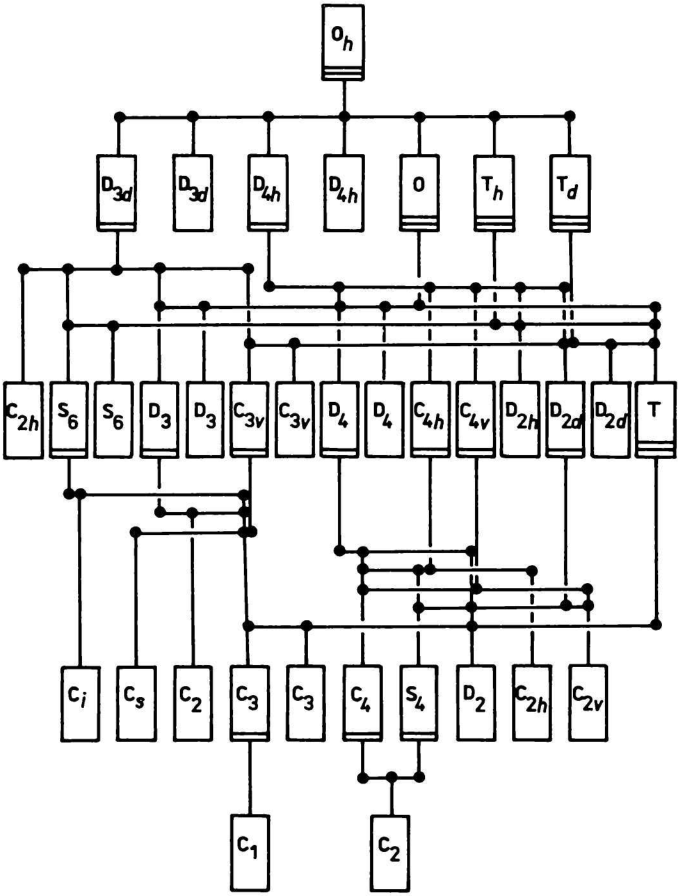

Fig. 1. Possible symmetry descent routes for triple degenerate nonrelativistic electronic states of $\mathbf{O}_h$ parent group according to the theory of step-by-step descent in symmetry [5] (double and triple lines at the bottom of rectangles denoting individual symmetry groups correspond to double and triple degenerate electronic states, respectively).

symmetries only. The step-by-step descent theory predicts additional nuclear arrangements of $\mathbf{D}_4$, $\mathbf{D}_{2d}$, $\mathbf{D}_2$, $\mathbf{C}_{2h}$, $\mathbf{C}_2$, $\mathbf{C}_s$, $\mathbf{C}_i$, and $\mathbf{C}_1$ symmetry. All the symmetry groups are included in the previous example, too.

For fourfold degenerate relativistic electronic states the predictions of the epikernel principle are the same as for triple degenerate nonrelativistic ones (*cf.* eqns (*4*) and (*6*)). Among them the step-by-step descent theory excludes the $\mathbf{C}_{2h}$ and $\mathbf{C}_i$ symmetry groups (the fourfold degeneracy is destroyed in their supergroups). On the other hand, the geometries of $\mathbf{D}_4$, $\mathbf{D}_{2d}$, $\mathbf{S}_6$, $\mathbf{D}_3$, $\mathbf{C}_{3v}$, $\mathbf{D}_2$, and $\mathbf{C}_3$ symmetries are to be included, too.

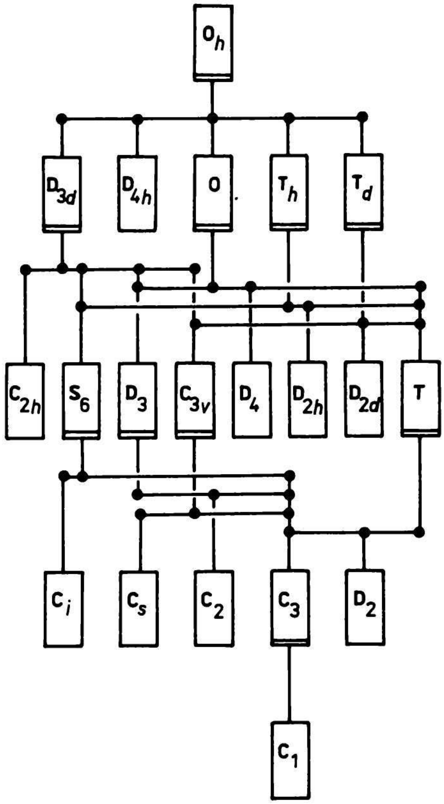

Fig. 2. Possible symmetry descent routes for double degenerate nonrelativistic electronic states of $\mathbf{O}_h$ parent group according to the theory of step-by-step descent in symmetry [5] (double lines at the bottom of rectangles denoting individual symmetry groups correspond to double degenerate electronic states).

Finally we may conclude that the epikernel principle is able to predict the stable symmetries of the highest probability. However, all the possible stable symmetries cannot be found according to this principle. This may be caused by perturbation origin of JT active coordinates. Moreover, incorrect results are obtained for relativistic electronic states described by double-valued representations.

Naturally the final decision must be said by an experiment. Applying the JT symmetry descent scheme to phase transitions [6, 9] such unit cell symmetries may be obtained which do not satisfy the epikernel principle. Nevertheless, further investigations in this field are desired.

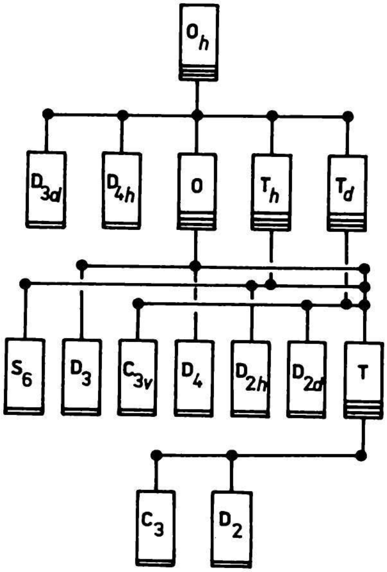

Fig. 3. Possible symmetry descent routes for fourfold degenerate relativistic electronic states of $\mathbf{O}_h$ parent group according to the theory of step-by-step descent in symmetry [5] (double and quadruple lines at the bottom of rectangles denoting individual symmetry groups correspond to double and fourfold degenerate electronic states, respectively).

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