
A COMPLETE CLASSIFICATION OF STABLE SYMMETRIES OF THE JAHN–TELLER SYSTEMS

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The classification of stable symmetries of the Jahn–Teller systems for common symmetry groups with degenerate relativistic and non-relativistic electronic states is elaborated. The results obtained by epikernel principle and by the method of step-by-step symmetry descent are compared. The deficiency of the epikernel principle is demonstrated on some examples of the Jahn–Teller phase transitions.

The Jahn–Teller (JT) effect has a prominent role in many branches of physics and chemistry. H. A. Jahn and E. Teller discovered the energetic instability^{1,2} of the non-linear geometric configuration of nuclei in degenerate electronic state – except Kramers degeneracy due to relativistic effects. Such an electronic state is hereafter denoted as the unstable one. In such a way formulated JT theorem implies the existence of at least one stable nuclear configuration in non-degenerate non-relativistic electronic state or in double degenerate relativistic electronic state (Kramers degeneracy). Such an electronic state is hereafter denoted as the stable one. The rise of a stable electronic state may be mathematically formulated as a consequence of splitting the original unstable electronic state of the parent symmetry group simultaneously with the symmetry descent of the whole nuclear system (some symmetry elements are destroyed).

In this context the problem arises how to determine the stable nuclear configurations of JT systems. It may be solved, in principle, by two alternative treatments based on the study of

- (i) JT active coordinates,
- (ii) unstable electronic states.

The oldest treatments are based on the study of an analytic shape of the adiabatic potential surface which may be derived by the perturbation theory³. However, these are handicapped by enormous complexity for larger systems. In addition the obtained results never may be regarded as complete. Among the methods based on the group-theoretical analysis of JT active coordinates, the method of epikernel principle⁴ is the most elaborated one. It may be applied to pseudo-JT systems, too.

The theory of step-by-step descent in symmetry^{5,6} belongs to the methods based on the analysis of symmetry properties of the electronic state. It represents the most complete solution of the problem and it may be applied to such pseudo-JT systems which are treatable as the JT systems in excited electronic state, too.

The results of the methods based on group-theoretical analysis may be directly applied to the crystals⁶, too. The symmetry properties of the crystal are determined by its unit cell symmetry. For real crystals all the electronic states (their probabilities depend on temperature) and likewise also all the mutual orientations of JT centres are to be considered. The practical verification of the obtained results may be carried out by the phase transitions scheme for the compounds with JT active centres⁹ that has been elaborated under these assumptions and that has been successfully applied to some complex compounds of transition metals.

THEORETICAL

The symmetry properties of electronic states and nuclear coordinates may be described as the representations of the pertinent symmetry group of the nuclear system. In accordance with the rule of JT instability^{1,2}, the following relations hold for the symmetries of JT active coordinates, A , and the electronic states, Γ .

(i) $A \in [\Gamma \otimes \Gamma]$ for non-relativistic electronic states described by single-valued Γ representations,

(ii) $A \in \{\Gamma \otimes \Gamma\}$ for relativistic electronic states described by double-valued Γ representations.

The symbols $[]$ and $\{ \}$ denote the symmetrized and antisymmetrized direct product, respectively. The system symmetry is not changed by the fully-symmetric coordinates of a_1 type therefore they are usually not included among the JT active coordinates.

If A corresponds to the degenerate or reducible representation, i.e. if it contains some symmetry components, the multidimensional distortion space⁴ is treated instead of the single distortion coordinate. The symmetry operation under consideration is conserved during the nuclear displacement change only if the invariance of pertinent nuclear coordinates under change is preserved. It means that its representation has the same character values as the identity operation. The minimal symmetry subgroup preserved during the coordinates change like this is denoted as the kernel, $K(G, A)$, where G is the parent (unperturbed) group and A is the pertinent coordinate representation. The epikernels are the intermediate subgroups during this distortion between the parent group existing in the origin of the distortion space only and the kernel group preserved in all distorted structures. There are often several epikernels for the pertinent G group and A representation. These epikernels may represent the independent symmetry descent ways that lead in different routes to the

kernel group. If the coordinate representation is reducible, i.e. composed of two or more different irreducible representations, the kernels of the pertinent subspaces are the epikernels of the aggregative representation.

In accordance with the epikernel principle⁴ the stable symmetries correspond to kernels and/or epikernels, as a rule of maximal symmetry. The epikernels correspond also to unstable symmetries lying on the symmetry descent route to the stable symmetries. All the above mentioned kernels and epikernels refer to non-fully symmetric vibronic active coordinates only.

In accordance with the theory of step-by-step descent in symmetry^{5,6} the unstable electronic state is split simultaneously with the symmetry descent of G^0 parent group till the G^n symmetry subgroup with pertinent stable electronic state is reached. The whole method is based on the following procedure:

(i) The symmetry elements of the „perturbed” system constitute the immediate G^n subgroup of the parent system: $G^n \subset G^0$.

(ii) The irreducible Γ^n representation describing the electronic state of G^n subgroup originates in splitting the multidimensional Γ^0 irreducible representation corresponding to pertinent unstable electronic state in the G^0 parent symmetry group.

(iii) If Γ^n corresponds to the stable electronic state (one-dimensional single-valued or two-dimensional double-valued irreducible representation) then the G^n subgroup corresponds to the stable system geometry. Otherwise the system continues in the symmetry descent and the whole procedure is repeated for the G^{n+1} subgroup that is the immediate subgroup of G^n group: $G^{n+1} \subset G^n$.

Considering that the symmetry groups usually have several immediate subgroups and the irreducible representations of dimension higher than two may be split into the irreducible representation of different dimensions, usually there are several symmetry descent routes. Only few of them have been observed in real systems.

Individual symmetry descent routes, the above mentioned methods are dealing with, may be applied to the structure phase transitions^{6,9}. All phase transitions that may be described by these symmetry descent routes or by their combinations are denoted as the JT phase transitions. The above mentioned theory does not solve the problem of phase stability, it indicates the possibility of the phase existence only. It implies that only some of the predicted phase transitions will be observed.

RESULTS AND DISCUSSION

The obtained results are shown in Tables I–V. For each of the symmetry point groups, G^0 , both the possible irreducible representations of electronic states, ES, and corresponding JT active coordinates, JTC, and stable symmetry subgroups according to epikernel principle, EP, and according to the method of step-by-step descent in symmetry, SD, are presented. The representation dimensions are as follows

TABLE I
 Cyclic groups

Group	ES ^a	JTC ^b	EP ^c	SD ^d
C_3	E	e	C_1	C_1
C_4	E	b	C_2	C_2
C_5	E_1	e_2	C_1	C_1
	E_2	e_1	C_1	C_1
C_6	E_1, E_2	e_2	C_2	C_1, C_2
C_7	E_1	e_2	C_1	C_1
	E_2	e_3	C_1	C_1
	E_3	e_1	C_1	C_1
C_8	E_1, E_3	e_2	C_2	C_2
	E_2	e_1	C_4	C_4
S_4	E	b	C_2	C_2
S_6	E_g, E_u	e_g	C_i	C_1, C_i
S_8	E_1, E_3	e_2	C_2	C_2
	E_2	b	C_4	C_4
S_{10}	E_{1g}, E_{1u}	e_{2g}	C_i	C_1, C_i
	E_{2g}, E_{2u}	e_{1g}	C_i	C_1, C_i
S_{12}	E_1, E_5	e_2	C_2	C_1, C_2
	E_2, E_4	e_4	S_4	C_1, C_2, S_4
	E_3	b	C_6	C_6, C_2
C_{3h}	E', E''	e'	C_s	C_1, C_s
C_{4h}	E_g, E_u	b_g	C_{2h}	C_2, C_{2h}
C_{5h}	E'_1, E''_1	e'_2	C_s	C_1, C_s
	E'_2, E''_2	e'_1	C_s	C_1, C_s
C_{6h}	$E_{1g}, E_{2g}, E_{1u}, E_{2u}$	e_{2g}	C_{2h}	$C_1, C_i, C_s, C_2, C_{2h}$
C_{7h}	E'_1, E''_1	e'_2	C_s	C_1, C_s
	E'_2, E''_2	e'_3	C_s	C_1, C_s
	E'_3, E''_3	e'_1	C_s	C_1, C_s
C_{8h}	$E_{1g}, E_{1u}, E_{3g}, E_{3u}$	e_{2g}	C_{2h}	C_2, C_{2h}
	E_{2g}, E_{2u}	b_g	C_{4h}	C_4, C_{4h}
C_{3v}	E	e	C_1, C_s	C_1, C_s
C_{4v}	E	b_1, b_2	C_2, C_{2v}	C_2, C_{2v}
C_{5v}	E_1	e_2	C_1, C_s	C_1, C_s
	E_2	e_1	C_1, C_s	C_1, C_s

TABLE I
 (Continued)

Group	ES ^a	JTC ^b	EP ^c	SD ^d
C_{6v}	E_1, E_2	e_2	C_2, C_{2v}	C_1, C_s, C_2, C_{2v}
C_{7v}	E_1	e_2	C_1, C_s	C_1, C_s
	E_2	e_3	C_1, C_s	C_1, C_s
	E_3	e_1	C_1, C_s	C_1, C_s
C_{8v}	E_1, E_3	e_2	C_2, C_{2v}	C_2, C_{2v}
	E_2	b_1, b_2	C_4, C_{4v}	C_4, C_{4v}

^c Degenerate electronic states^{3,7,8}; ^b Jahn–Teller active coordinates (except fully-symmetric ones)^{3,7,8}; ^c subgroup symmetries obtained according to the epikernel principle⁴; ^d stable subgroup symmetries obtained according to the symmetry descent theory^{5,6}.

(the indices are omitted for the sake of simplicity): $A(1)$, $B(1)$, $E(2)$, $T(3)$, $G(4)$, $H(5)$, $I(6)$. The electronic states are denoted by capitals and the coordinates by small letters. In the tables such groups are omitted which cannot have any multidimensional irreducible representations, i.e. the unstable electronic states. The fully symmetric coordinates of a_1 type are not presented among the coordinates that can be active in the Jahn–Teller effect, too. Besides the two-dimensional irreducible representations of electronic states of E type and such symmetry groups which can have the one- and two-dimensional double-valued irreducible representations only are omitted for the double groups.

At a glance it is evident that the stable symmetry groups according to the epikernel principle method coincide with these ones according to the method of step-by-step descent in symmetry for some simple parent symmetry group only (C_n , C_{nv} , D_n for $n \neq 6$, D_{2d} , D_{4d} , D_{8d}). For most cases the results obtained by the epikernel principle method are included in the results obtained by the method of step-by-step descent in symmetry. This fact is apparent as the epikernel principle method is restricted to the JT active coordinates resulting from the first-order perturbation method. From this point of view the method of step-by-step descent in symmetry is more complete.

In some cases any groups obtained according to the epikernel principle do not occur among the stable subgroups according to the step-by-step descent in symmetry. As a matter of fact, in D_{6d} parent group for E_2 electronic state in the case of S_6 subgroup and for E_3 electronic state in the case of C_6 subgroup the degeneracy is already removed at their supergroups. D_{3d} subgroup for G_g or G_u electronic states

TABLE II
 Dihedral groups

Group	ES ^a	JTC ^b	EP ^c	SD ^d
D_3	E	e	C_1, C_2	C_1, C_2
D_4	E	b_1, b_2	C_2, D_2	C_2, D_2
D_5	E_1	e_2	C_1, C_2	C_1, C_2
	E_2	e_1	C_1, C_2	C_1, C_2
D_6	E_1, E_2	e_2	C_2, D_2	C_1, C_2, D_2
D_7	E_1	e_2	C_1, C_2	C_1, C_2
	E_2	e_3	C_1, C_2	C_1, C_2
	E_3	e_1	C_1, C_2	C_1, C_2
D_8	E_1, E_3	e_2	C_2, D_2	C_2, D_2
	E_2	b_1, b_2	C_4, D_4	C_4, D_4
D_{3h}	E', E''	e'	C_s, C_{2v}	C_1, C_2, C_s, C_{2v}
D_{4h}	E_g, E_u	b_{1g}, b_{2g}	C_{2h}, D_{2h}	$C_2, D_2, C_{2v}, C_{2h}, D_{2h}$
D_{5h}	E'_1, E''_1	e'_2	C_s, C_{2v}	C_1, C_2, C_s, C_{2v}
	E'_2, E''_2	e'_1	C_s, C_{2v}	C_1, C_2, C_s, C_{2v}
D_{6h}	$E_{1g}, E_{1u}, E_{2g}, E_{2u}$	e_{2g}	C_{2h}, D_{2h}	$C_1, C_2, C_s, C_i, D_2, C_{2v}, C_{2h}, D_{2h}$
D_{7h}	E'_1, E''_1	e'_2	C_s, C_{2v}	C_1, C_2, C_s, C_{2v}
	E'_2, E''_2	e'_3	C_s, C_{2v}	C_1, C_2, C_s, C_{2v}
	E'_3, E''_3	e'_1	C_s, C_{2v}	C_1, C_2, C_s, C_{2v}
D_{8h}	$E_{1g}, E_{1u}, E_{3g}, E_{3u}$	e_{2g}	C_{2h}, D_{2h}	$C_2, D_2, C_{2v}, C_{2h}, D_{2h}$
	E_{2g}, E_{2u}	b_{1g}, b_{2g}	C_{4h}, D_{4h}	$C_4, D_4, C_{4v}, D_{4h}, C_{4h}$
D_{2d}	E	b_1, b_2	C_2, D_2, C_{2v}	C_2, D_2, C_{2v}
D_{3d}	E_g, E_u	e_g	C_i, C_{2h}	$C_1, C_s, C_2, C_i, C_{2h}$
D_{4d}	E_1, E_2	e	C_2, D_2, C_{2v}	C_2, D_2, C_{2v}
	E_2	b_1, b_2	C_4, D_4, C_{4v}	C_4, D_4, C_{4v}
D_{5d}	E_{1g}, E_{1u}	e_{2g}	C_i, C_{2h}	$C_1, C_i, C_2, C_s, C_{2h}$
	E_{2g}, E_{2u}	e_{1g}	C_i, C_{2h}	$C_1, C_i, C_2, C_s, C_{2h}$
D_{6d}	E_1, E_5	e_2	C_2, D_2, C_{2v}	$C_1, C_s, C_2, D_2, C_{2v}$
	E_2, E_4	e_4	S_4, D_{2d}	$C_1, C_s, C_2, D_2, C_{2v}, D_{2d}$
	E_3	b_1, b_2	C_6, D_6, C_{6v}	$C_2, D_2, C_{2v}, D_6, C_{6v}$
D_{7d}	E_{1g}, E_{1u}	e_{2g}	C_i, C_{2h}	$C_1, C_i, C_2, C_s, C_{2h}$
	E_{2g}, E_{2u}	e_{3g}	C_i, C_{2h}	$C_1, C_i, C_2, C_s, C_{2h}$
	E_{3g}, E_{3u}	e_{1g}	C_i, C_{2h}	$C_1, C_i, C_2, C_s, C_{2h}$

TABLE II
(Continued)

Group	ES ^a	JTC ^b	EP ^c	SD ^d
<i>D</i> _{8d}	<i>E</i> ₁ , <i>E</i> ₇	<i>e</i> ₂	<i>C</i> ₂ , <i>C</i> _{2v} , <i>D</i> ₂	<i>C</i> ₂ , <i>C</i> _{2v} , <i>D</i> ₂
	<i>E</i> ₂ , <i>E</i> ₆	<i>e</i> ₄	<i>C</i> ₄ , <i>D</i> ₄ , <i>C</i> _{4v}	<i>C</i> ₄ , <i>D</i> ₄ , <i>C</i> _{4v}
	<i>E</i> ₃ , <i>E</i> ₅	<i>e</i> ₆	<i>C</i> ₂ , <i>C</i> _{2v} , <i>D</i> ₂	<i>C</i> ₂ , <i>C</i> _{2v} , <i>D</i> ₂
	<i>E</i> ₄	<i>b</i> ₁ , <i>b</i> ₂	<i>C</i> ₈ , <i>D</i> ₈ , <i>C</i> _{8v}	<i>C</i> ₈ , <i>D</i> ₈ , <i>C</i> _{8v}

^c Degenerate electronic states^{3,7,8}; ^b Jahn-Teller active coordinates (except fully-symmetric ones^{3,7,8}); ^c subgroup symmetries obtained according to the epikernel principle⁴; ^d stable subgroup symmetries obtained according to the symmetry descent theory^{5,6}.

TABLE III
Cubic groups

Group	ES ^a	JTC ^b	EP ^c	SD ^d
<i>T</i>	<i>E</i>	<i>e</i>	<i>D</i> ₂	<i>D</i> ₂ , <i>C</i> ₁
	<i>T</i>	<i>e</i> , <i>t</i>	<i>C</i> ₁ , <i>D</i> ₂	<i>C</i> ₁ , <i>C</i> ₃ , <i>D</i> ₂
<i>T</i> _h	<i>E</i> _g , <i>E</i> _u	<i>e</i> _g	<i>D</i> _{2h}	<i>C</i> ₁ , <i>C</i> _i , <i>D</i> ₂ , <i>D</i> _{2h}
	<i>T</i> _g , <i>T</i> _u	<i>e</i> _g , <i>t</i> _g	<i>C</i> _i , <i>D</i> _{2h}	<i>C</i> ₁ , <i>C</i> _i , <i>C</i> ₃ , <i>D</i> ₂ , <i>S</i> ₆ , <i>D</i> _{2h}
<i>T</i> _d	<i>E</i>	<i>e</i>	<i>D</i> ₂ , <i>D</i> _{2d}	<i>C</i> ₁ , <i>C</i> _s , <i>D</i> ₂ , <i>D</i> _{2d}
	<i>T</i> ₁ , <i>T</i> ₂	<i>e</i> , <i>t</i> ₂	<i>C</i> ₁ , <i>C</i> _s , <i>C</i> ₂ , <i>D</i> ₂	<i>C</i> ₁ , <i>C</i> _s , <i>C</i> ₂ , <i>C</i> ₃ , <i>D</i> ₂ ,
			<i>C</i> _{2v} , <i>C</i> _{3v} , <i>D</i> _{2d}	<i>C</i> _{2v} , <i>C</i> _{3v} , <i>D</i> _{2d}
<i>O</i>	<i>E</i>	<i>e</i>	<i>D</i> ₂ , <i>D</i> ₄	<i>C</i> ₁ , <i>C</i> ₂ , <i>D</i> ₂ , <i>D</i> ₄
	<i>T</i> ₁ , <i>T</i> ₂	<i>e</i> , <i>t</i> ₂	<i>C</i> ₁ , <i>C</i> ₂ , <i>D</i> ₂ , <i>D</i> ₃ , <i>D</i> ₄	<i>C</i> ₁ , <i>C</i> ₂ , <i>C</i> ₃ , <i>D</i> ₂ , <i>D</i> ₃ , <i>D</i> ₄
<i>O</i> _h	<i>E</i> _g , <i>E</i> _u	<i>e</i> _g	<i>D</i> _{2h} , <i>D</i> _{4d}	<i>C</i> ₁ , <i>C</i> _i , <i>C</i> _s , <i>C</i> ₂ , <i>C</i> _{2h} ,
				<i>D</i> ₂ , <i>D</i> ₄ , <i>D</i> _{2h} , <i>D</i> _{2d} , <i>D</i> _{4h}
	<i>T</i> _{1g} , <i>T</i> _{1u} , <i>T</i> _{2g} , <i>T</i> _{2u}	<i>e</i> _g , <i>t</i> _{2g}	<i>C</i> _i , <i>C</i> _{2h} , <i>D</i> _{2h} , <i>D</i> _{3d} , <i>D</i> _{4h}	<i>C</i> ₁ , <i>C</i> _i , <i>C</i> _s , <i>C</i> ₂ , <i>C</i> ₃ , <i>C</i> _{2h} , <i>C</i> _{2v} , <i>D</i> ₂ , <i>C</i> _{3v} , <i>S</i> ₆ , <i>D</i> ₃ , <i>D</i> ₄ , <i>D</i> _{2d} , <i>D</i> _{2h} , <i>D</i> _{3d} , <i>D</i> _{4h}

^c Degenerate electronic states^{3,7,8}; ^b Jahn-Teller active coordinates (except fully-symmetric ones)^{3,7,8}; ^c subgroup symmetries obtained according to the epikernel principle⁴; ^d stable subgroup symmetries obtained according to the symmetry descent theory^{5,6}.

and I_h subgroup for H_g or H_u electronic states are unstable in the case of I_h parent group (the unstable electronic states described by degenerate irreducible representations arise by splitting unstable electronic states of the parent group), thus the symmetry descent continues.

Diametrically opposite situation arises for the double groups. Supposing the same JT active coordinates the method of epikernel principle predicts the same results for single-valued and double-valued irreducible representations. According to the method of step-by-step in descent symmetry, however, these cases cannot be identified because the electronic state instability is removed immediately after the symmetry descent leaves the cubic or icosahedral groups.

Under these circumstances such a requirement arises how to solve the problem of deciding between both the treatments, preferably on the basis of experimental data. For this purpose the scheme of phase transitions based on Jahn–Teller effect may be used that has been elaborated generalizing the theory of step-by-step descent in symmetry⁹. In Table VI some data on phase transitions of some transition metal compounds are collected^{9–11}. The above mentioned phase transitions may be explained as a combination of some symmetry descent routes (Table VII) finalized by a stable symmetry.

TABLE IV
Icosahedral groups

Group	ES ^a	JTC ^b	EP ^c	SD ^d
I	T_1, T_2	h	C_1, C_2, D_2, D_3, D_5	$C_1, C_2, C_3, D_2, D_3, D_5$
	G	g, h	$C_1, C_2, C_3, D_2, D_3, D_5, T$	$C_1, C_2, C_3, D_2, D_3, D_5, T$
	H	g, h	$C_1, C_2, C_3, D_2, D_3, D_5, T$	$C_1, C_2, C_3, D_2, D_3, D_5, T$
I_h	$T_{1g}, T_{1u}, T_{2g}, T_{2u}$	h_g	$C_i, C_{2h}, D_{2h}, D_{3d}, D_{5d}$	$C_1, C_i, C_s, C_2, C_3, D_2, S_6, C_{2h}, D_3, D_{2h}, D_5, D_{3d}, D_{5d}$
	G_g, G_u	g_g, h_g	$C_i, C_{2h}, S_6, D_{2h}, D_{3d}, D_{5d}, T_h$	$C_1, C_s, C_i, C_2, C_3, D_2, S_6, C_{2h}, D_3, D_{2h}, D_5, D_{3d}, T, T_h$
	H_g, H_u	g_g, h_g	$C_i, C_{2h}, S_6, D_{2h}, D_{3d}, D_{5d}, T_h$	$C_1, C_s, C_i, C_2, C_3, D_2, S_6, C_{2h}, D_3, D_{2h}, D_5, D_{3d}, D_{5d}$

^a Degenerate electronic states^{3,7,8}; ^b Jahn–Teller active coordinates (except fully-symmetric ones)^{3,7,8}; ^c subgroup symmetries obtained according to the epikernel principle⁴; ^d stable subgroup symmetries obtained according to the symmetry descent theory^{5,6}.

BaTiO_3 . This compound is a typical pseudo-JT system. Their phase transitions (except phase V) may be explained as a combination of two basic symmetry descent routes finished by stable C_{2v} and C_{3v} groups. T_d and D_{4h} symmetry groups have not been observed. Phase V existence is explained as the combination of C_{2v} and C_{3v} stable groups and due to the presence of Mn admixtures. Too large number of formula units in the unit cell, Z , excludes the phase V as an origin of the symmetry descent route. The epikernel principle does not predict the existence of stable C_{2v} and C_{3v} symmetries. As the unstable C_{4v} symmetry is no epikernel of O_h group the epikernel principle does not predict it as the unstable one.

NaNbO_3 . The phase transitions may be explained by two symmetry descent routes into single stable D_{2h} symmetry point group which satisfies the epikernel principle, too. The unstable T_h group does not belong to the epikernels of O_h group, thus it cannot be the unstable symmetry group according to epikernel principle.

KNbO_3 . The phase transitions are analogous to BaTiO_3 (except phase V).

TABLE V
Some double groups

Group	ES ^a	JTC ^b	EP ^c	SD ^d
T	$G_{3/2}$	e, t	C_1, D_2	C_3, D_2
T_h	$G_{3/2g}, G_{3/2u}$	e_g, t_g	C_i, D_{2h}	C_3, D_2, S_6, D_{2h}
T_d	$G_{3/2}$	t, t_2	$C_1, C_2, C_3, D_2,$ C_{2v}, C_{3v}, D_{2d}	C_3, D_2, C_{3v}, D_{2d}
O	$G_{3/2}$	e, t_2	C_1, C_2, D_2, D_3, D_4	C_3, D_2, D_3, D_4
O_h	$G_{3/2g}, G_{3/2u}$	e_g, t_{2g}	$C_i, C_{2h}, D_{2h},$ D_{3d}, D_{4h}	$C_3, D_2, C_{3v}, S_6, D_3, D_4,$ $D_{2d}, D_{2h}, D_{3d}, D_{4h}$
I	$G_{3/2}$ $I_{5/2}$	h g, h	C_1, C_2, D_2, D_3, D_5 $C_1, C_2, C_3, D_2,$ D_3, D_5, T	C_3, D_2, D_3, D_5 C_3, D_2, D_3, D_5, T
I_h	$G_{3/2g}, G_{3/2u}$ $I_{5/2g}, I_{5/2u}$	h_g g_g, h_g	$C_i, C_{2h}, D_{2h},$ D_{3d}, D_{5d} $C_i, C_{2h}, S_6, D_{2h},$ D_{3d}, D_{5d}, T_h	$C_3, D_2, S_6, D_3, D_5,$ D_{3d}, D_{5d} $C_3, D_2, S_6, D_3, D_{2h}, D_5,$ D_{3d}, D_{5d}, T, T_h

^a Degenerate electronic states^{3,7,8}; ^b Jahn–Teller active coordinates (except fully-symmetric ones)^{3,7,8}; ^c subgroup symmetries obtained according to the epikernel principle⁴; ^d stable subgroup symmetries obtained according to the symmetry descent theory^{5,6}.

TABLE VI

Phase transition characteristics of some compounds¹⁰⁻¹². Where appropriate, the range of data of various authors is given for phase transition temperatures.

Compound	Phase	Symmetry	Z ^a	Phase transition	Temperature K
BaTiO ₃	V ^b	$D_{6h}^4-P6_3/mmc$	6	I → V	≈ 1 330
	I	O_h^1-Pm3m	1	II → I	≈ 395
	II	C_{4v}^1-P4mm	1	III → II	273
	III	C_{2v}^1-C2mm	2	IV → III	153...173
	IV	C_{3v}^5-R3m	3		
NaNbO ₃	I	O_h^1-Pm3m	1	II'' → I	≈ 910
	II''	D_{4h}^5-P4/mbm	2	II'' → II'	≈ 850
	II'	D_{2h}^7-Cmcm	8	II → II'	≈ 790
	II	D_{2h}^3-Pnmm	8	III → II	≈ 740...750
	III'	D_{2h}^1-Pnmm	24	III → III'	≈ 620...650
	III	D_{2h}^1-Pbma	8		
KNbO ₃	I	O_h^1-Pm3m	1	II → I	≈ 710
	II	C_{4v}^1-P4mm	1	III → II	≈ 500
	III	C_{2v}^1-Bmm2	2	IV → III	263
	IV	C_{3v}^5-R3m	3		
Rb ₂ WO ₄	I	$D_{3d}^2-P\bar{3}m1$	2	I → II	738
	II	D_{2h}^6-Pnma	4	III → II	663
	III	D_{2h}^6-Pnma	4	IV → III	513...568
	IV	C_{2h}^3-C2/m	4		
FeNbO ₄	I	$D_{4h}^1-P4_2/mnm$	1	I → II	≈ 1 620
	II	D_{2h}^1-Pnab	2	II → III	≈ 1 270
	III	C_{4h}^2-P2/c	2		
K ₂ MoO ₄	I	$D_{3d}^3-P\bar{3}m1$	2	I → II	713
	II	D_{2h}^6-Pnma	4	II → III	≈ 580...590
	III	C_{2h}^3-C2/m	4		
Rb ₂ MoO ₄	I	$D_{3d}^3-P\bar{3}m1$	2	I → II	772
	II	D_{2h}^6-Pnma	4	II → III	≈ 370...570
	III	C_{2h}^3-C2/m	4		
K ₂ WO ₄	I	$D_{3d}^3-P\bar{3}m1$	3	I → II	700
	II	D_{2h}^6-Pnma	4	II → III	643
	III	C_{2h}^3-C2/m	4		
RbIn(WO ₄) ₂	I	$D_{3d}^3-P\bar{3}m1$	2	I → II	1 098
	II	D_{2h}^6-Pnma	4	II → III	723
	III	T_h^4-Fd3	4		

TABLE VI
(Continued)

Compound	Phase	Symmetry	Z^a	Phase transition	Temperature K
NaFeO ₂	I	$D_{4h}^4-P4_12_12_1$	4	I → II	≈ 1 260 ··· 1 370
	II	$C_{2v}^9-Pna2_1$	4	II → III	≈ 1 030
	III	$D_{3d}^2-R\bar{3}m$	3		

^a Number of formula units in the unit cell; ^b pure crystals cannot be obtained (stabilized by Mn)

TABLE VII

The symmetry descent scheme for phase transitions¹⁰. Space symmetry groups (in Schönflies and Hermann–Mauguin notation) are listed only if group-subgroup relations hold also for them. Unobserved phases are in parentheses

Compound	IR ^a	Symmetry descent routes
BaTiO ₃	3	$O_h^1-Pm\bar{3}m \rightarrow (D_{4h}) \rightarrow C_{4v}^1-P4mm \rightarrow C_{2v}$ $O_h^1-Pm\bar{3}m \rightarrow (T_d) \rightarrow C_{3v}^5-R\bar{3}m$ $O_h^1-Pm\bar{3}m \rightarrow (D_{3d}) \rightarrow C_{3v}^5-R\bar{3}m \rightarrow (C_s)$ $D_{6h} \approx C_{3v} \times C_{2v}$
NaNbO ₃	3	$O_h \rightarrow D_{4h} \rightarrow D_{2h}$ $O_h \rightarrow (T_h) \rightarrow D_{2h}$
KNbO ₃	3	see BaTiO ₃ (except D_{6h})
Rb ₂ WO ₄	2 or 3	$(O_h) \rightarrow D_{3d}^3-P\bar{3}m1 \rightarrow C_{2h}^3-C2/m$ $(O_h) \rightarrow (T_h \text{ or } D_{4h}^b) \rightarrow D_{2h}$
FeNbO ₄	2	$D_{4h} \rightarrow D_{2h}$ $D_{4h} \rightarrow (C_{4h}) \rightarrow C_{2h}$
K ₂ MoO ₄	2 or 3	$(O_h) \rightarrow D_{3d}^3-P\bar{3}m1 \rightarrow C_{2h}^3-C2/m$
Rb ₂ MoO ₄	2 or 3	see K ₂ MoO ₄
K ₂ WO ₄	2 or 3	see K ₂ MoO ₄
RbIn(WO ₄) ₂	3	$(O_h) \rightarrow D_{3d}$ $(O_h) \rightarrow (D_{4h}) \rightarrow D_{2h}$ $(O_h) \rightarrow T_h \rightarrow (S_6)$
NaFeO ₂	3	$(O_h) \rightarrow (O \text{ or } D_{4h}) \rightarrow D_4 \rightarrow (D_2)$ $(O_h) \rightarrow (T_d \text{ or } D_{4h}) \rightarrow D_{2h}$ $(O_h) \rightarrow D_{3d}$

^a Starting IR dimensions of the unstable electronic states; ^b only for three-dimensional starting IR.

$\text{RbIn}(\text{WO}_4)_2$. The phase III of T_h symmetry exists at lower temperatures than the phase II of its D_{2h} symmetry subgroup. This fact is explained by another symmetry descent routes (D_{2h} and T_h must not be on the same symmetry descent route). The observed stable symmetries satisfy the epikernel principle, too. The unstable T_h group is not included into the epikernels of O_h group, thus the epikernel principle is not satisfied (see above).

NaFeO_2 . The phase transitions of this compound may be explained in various ways (see Table VII). The observed unstable T_h group does not belong to the epikernels of O_h group what is at variance with the epikernel principles (see above).

The explanation of phase transitions of the remaining compounds may be understood simply from Table VII. Some of them may be equivalently explained assuming either two- or three-dimensional irreducible representations of O_h group. The observed phase transitions are explainable by the epikernel principle as well.

CONCLUSIONS

The methods of step-by-step descent in symmetry and epikernel principle provide the equal results for some simple symmetry groups with non-relativistic electronic states only. In many cases, mostly for relativistic electronic states, the obtained results are significantly different. In most cases the results obtained by the method of epikernel principle are contained in the results obtained by the method of step-by-step descent in symmetry. This fact is a consequence of the perturbation treatment restrictions (JT active coordinates result from the first-order perturbation theory). Applying the obtained results to the experimentally observed phase transitions due to JT effect⁹, the method of step-by-step descent in symmetry may be successfully verified.

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