

# Jahn—Teller effect and phase transitions theory

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*Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday*

Phase transitions are studied in terms of the theory of consecutive descent in symmetry due to the Jahn—Teller effect. This theory has been successfully applied to some transition metal compounds.

Изучались фазы переходов в согласии с теорией последовательного снижения симметрии по эффекту Яна—Теллера. Эта теория была с успехом применена для некоторых соединений переходных металлов.

The Jahn—Teller (JT) effect represents an important phenomenon in stereochemistry and crystallochemistry. The generally accepted formulation of the JT theorem [1, 2] consists of the assertion that a nonlinear nuclear configuration in the degenerate electronic state is energetically unstable (except Kramers degeneracy). This theorem implies the existence of at least one stable nuclear configuration in which the electronic degeneracy is removed so that the system relaxes to an energetically more advantageous configuration.

The static JT effect [3—6] is such a phenomenon when the system under study is observed in a single stable configuration. The dynamic JT effect [3—6] is considered in the case of the transition of the system among more stable configurations. Such a transition may be so fast that only the averaged nuclear configuration of higher symmetry is registered. It may be difficult or practically impossible to distinguish experimentally the static and dynamic behaviour of real systems.

The cooperative JT effect [3—6] is the collective influence of correlated JT active centres on the crystal structure. As a consequence of their mutual interaction a nonisotropic force field is formed and the distortion in one direction is preferred. Energetically most advantageous nuclear arrangement in a crystal corresponds to such a situation when every JT centre is distorted and the distortions of various centres are correlated. At higher temperatures the JT active centres may adopt a higher symmetry due to the dynamic JT effect and the symmetry of JT force field is changed. This change corresponds to a structural phase transition in crystals. In reality, the situation is more complicated. Lattice vibrations and thermal fluctuations act in order to destroy the correlation of JT centres. Various defects in crystals, external forces and other

effects may cause the preference of non-JT symmetry. Thus only a limited number of the observed phase transitions is a consequence of pure JT effect.

On the other hand, according to present theories only the order—disorder phase transitions (*i.e.* destroying the correlations of JT centres as a consequence of lattice vibrations and thermal fluctuations) are denoted as the JT ones.

### Method

In our previous papers [7, 8] a complete classification of possible symmetries of JT systems for all molecular symmetry point groups was elaborated. This one is based on the principle of the consecutive splitting of multidimensional irreducible representations (IR) describing the symmetry of electronic terms due to the descent in symmetry (loss of some symmetry elements) of the system.

Let  $\Gamma_n$  be multidimensional IR ( $\dim \Gamma_n > 1$ ) describing the actual degenerate electronic term of original (unperturbed) nuclear configuration of  $G_n$  symmetry group. The procedure of determining the symmetries of stable JT nuclear configuration may be summarized as follows:

i) Let  $G_m$  be an immediate subgroup of  $G_n$  and  $\Gamma_m, \Gamma'_m \dots$  are IR's of  $G_m$  correlating with  $\Gamma_n$  of  $G_n$

$$\dim \Gamma_n = \dim \Gamma_m + \dim \Gamma'_m + \dots \quad (1)$$

ii) If  $\dim \Gamma_m = 1$  then  $G_m$  symmetry group may describe the stable nuclear configuration.

If  $\dim \Gamma_m > 1$  then the symmetry descent continues and the whole procedure should be repeated for  $G_m$  and  $\Gamma_m$ .

The order of the  $G_n$  group is an integer multiple of its  $G_m$  subgroup order

$$O(G_n) = k O(G_m) \quad (2)$$

where the little integer  $k$  corresponds to a number of equivalent configurations of the subgroup symmetry.

Application of this procedure to 32 crystallographic point groups [9] with triple and/or double electronic degeneracy has been published elsewhere [7, 8].

The above method is applicable to all symmetries of nuclear arrangements which allow the degeneracy of electronic states or, in other words, their symmetry groups contain at least one multidimensional IR.

This method has been used for investigation of JT centres so far (molecules, complex ions). Since it is based on the group-theoretical analysis, it is applicable to crystals as well. Symmetry properties of the crystal are determined by its unit cell symmetry.

Real systems are not described by the single electronic state, the populations of excited states are, in principle, nonzero and increase with temperature. Moreover, JT centres in the unit cell may be nonequivalent and/or of different symmetries. Thus, the combinations of all the possible symmetries of electronic states are to be taken into account. Moreover, the behaviour of real systems is complicated by defects and other fluctuations, by the influence of various forces of non-JT symmetry, *etc.* The system may not be in the thermodynamically most stable energetic state.

On the other hand, the symmetry descent in 32 crystallographic point groups is the same for IR's with the same dimensions. Thus, the degenerate electronic state of the parent system may be described by reducible representation as a sum of three- and two-dimensional IR's (one-dimensional IR's may be omitted for our purposes). The symmetry descent scheme for such a reducible representation is the sum of symmetry descent schemes for individual IR's.

The symmetry descent to the same symmetry group may proceed in various ways. As implied by eqn (2), the electronic degeneracy is transformed into the configuration degeneracy: The same symmetry descent may be caused by  $k$  different changes of nuclear configurations. This number  $k$  depends on the orders of both the symmetry groups ( $\mathbf{G}_m$  and  $\mathbf{G}_n$ ). If all the JT centres lower their symmetry in the same way, the number of formula units in the unit cell  $Z$  is conserved and similarly are the related structure parameters. Otherwise  $Z$  is multiplied by small integer  $k_Z$

$$Z_m = k_Z Z_n \quad (3)$$

where  $Z_n$  and  $Z_m$  are the numbers of formula units in the unit cell for  $\mathbf{G}_n$  and  $\mathbf{G}_m$  space groups, respectively;  $k_Z$  depends on the number and symmetries of JT centres in the  $\mathbf{G}_n$  unit cell. Similar relations hold for the unit cell dimensions.

According to group-theoretical criteria all the phase transitions related to JT effect may be divided as follows:

#### A. Correlative phase transitions.

The symmetry of JT active centres is changed in the same way. Group-subgroup relations hold for the space symmetry groups ("translationgleiche" t-subgroups are meant [10]). The number of the formula units in the unit cell is conserved.

#### B. Reorientation phase transitions.

The symmetry of individual JT active centres is conserved but their mutual orientations are changed. Point group symmetries (and IR dimensions) are conserved. Only the space symmetry groups may be changed. The number of formula units in the unit cell is usually changed.

### C. Noncorrelative phase transitions.

The symmetry descent chains are changed due to the effects of non-JT character. Group-subgroup relations do not hold.

Correlative phase transitions may be divided as follows:

#### A1. Pure JT phase transitions.

They are connected with multidimensional IR split.

#### A2. Dynamical phase transitions.

IR dimensions are conserved.

In reality, there are often combinations of various types of phase transitions, mostly of A1—B type (reorientation JT phase transitions). This is implied by eqn (3) and/or by possible nonexistence of some phases.

The symmetry descent usually goes in two or more parallel chains and results into different symmetries. These may dynamically interact to form some higher symmetry which corresponds to their supergroup.

This theory does not cover the problem of phase stability conditions. It only indicates the possibility of the phase existence. Thus only few structure phases predicted by the theory have been registered.

## Results and discussion

In Table 1 some data [11, 12] on various phases of some transition metal compounds are collected. The collection is restricted only to the compounds that are known in three or more phases of different symmetries (at least three different point groups), with well defined temperatures of phase transitions and with constant composition. The phases are ordered according to decreasing temperature of stability. All these phase transitions may be explained in terms of the presented theory as the combination of several chains of symmetry descent. Table 2 summarizes the shortest possible symmetry descent chains that include both the parent symmetry and at least one of the observed phase symmetries.

The use of our theory may be demonstrated by some examples in details:

**BaTiO<sub>3</sub>.** This compound is a typical pseudo-JT system [4—6]. Its phase transitions (except phase V) may be explained as a combination of the symmetry descent chains (consecutive splitting three-dimensional IR's) resulting in  $C_{2v}$  and  $C_{3v}$  symmetry groups, respectively.  $T_d$  and  $D_{4h}$  symmetry groups are not observed. Phase V results as a supergroup of  $C_{2v}$  and  $C_{3v}$  groups due to the influence of certain admixtures (this phase must be stabilized by Mn admixtures [11]). This assertion is supported also by large  $Z$  value of phase V. It implies that this phase cannot be the starting point of a symmetry descent chain. Phase transition I → II is pure JT one (A1 type), II → III is the combination of A1 and B type, the remaining ones are of C type.

Table 1

Phase transition characteristics of some compounds [11, 12]

Where appropriate, the range of data of various authors is given for phase transition temperatures

Compound	Phase	Symmetry	Z	Phase transition	T/K
BaTiO <sub>3</sub>	V*	D <sub>6h</sub> <sup>4</sup> -P6 <sub>3</sub> /mmc	6	I → V	≈ 1330
	I	O <sub>h</sub> <sup>1</sup> -Pm3m	1	II → I	≈ 395
	II	C <sub>4v</sub> <sup>1</sup> -P4mm	1	III → II	273
	III	C <sub>2v</sub> <sup>14</sup> -C2mm	2	IV → III	153 ... 173
NaNbO <sub>3</sub>	IV	C <sub>3v</sub> <sup>5</sup> -R3m	3		
	I	O <sub>h</sub> <sup>1</sup> -Pm3m	1	II'' → I	≈ 910
	II''	D <sub>4h</sub> <sup>5</sup> -P4/mbm	2	II'' → II''	≈ 850
	II'	D <sub>2h</sub> <sup>17</sup> -Cmcm	8	II → II'	≈ 790
	II	D <sub>2h</sub> <sup>13</sup> -Pnmm	8	III' → II	≈ 740 ... 750
	III'	D <sub>2h</sub> <sup>13</sup> -Pnmm	24	III → III'	≈ 620 ... 650
KNbO <sub>3</sub>	III	D <sub>2h</sub> <sup>11</sup> -Pbma	8		
	I	O <sub>h</sub> <sup>1</sup> -Pm3m	1	II → I	≈ 710
	II	C <sub>4v</sub> <sup>1</sup> -P4mm	1	III → II	≈ 500
	III	C <sub>2v</sub> <sup>14</sup> -Bmm2	2	IV → III	263
Rb <sub>2</sub> WO <sub>4</sub>	IV	C <sub>3v</sub> <sup>5</sup> -R3m	3		
	I	D <sub>3d</sub> <sup>3</sup> -P3m1	2	I → II	738
	II	D <sub>2h</sub> <sup>16</sup> -Pnma	4	III → II	663
	III	D <sub>2h</sub> <sup>16</sup> -Pnma	4	IV → III	513 ... 568
FeNbO <sub>4</sub>	IV	C <sub>2h</sub> <sup>3</sup> -C2/m	4		
	I	D <sub>4h</sub> <sup>14</sup> -P4 <sub>2</sub> /mnm	1	I → II	≈ 1620
	II	D <sub>2h</sub> <sup>14</sup> -Pnab	2	II → III	≈ 1270
	III	C <sub>2h</sub> <sup>4</sup> -P2/c	2		
LaCrO <sub>3</sub>	I	O <sub>h</sub> <sup>1</sup> -Pm3m	1	I → II	≈ 1300
	II	D <sub>6h</sub> <sup>4</sup> -P6 <sub>3</sub> /mmc	6	II → III	563
	III	D <sub>2h</sub> <sup>16</sup> -Pbnm	4		
K <sub>2</sub> MoO <sub>4</sub>	I	D <sub>3d</sub> <sup>3</sup> -P3m1	2	I → II	713
	II	D <sub>2h</sub> <sup>16</sup> -Pnma	4	II → III	≈ 580 ... 590
	III	C <sub>2h</sub> <sup>3</sup> -C2/m	4		
Rb <sub>2</sub> MoO <sub>4</sub>	I	D <sub>3d</sub> <sup>3</sup> -P3m1	2	I → II	773
	II	D <sub>2h</sub> <sup>16</sup> -Pnma	4	II → III	≈ 370 ... 570
	III	C <sub>2h</sub> <sup>3</sup> -C2/m	4		
Pr <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	I	D <sub>2d</sub> <sup>3</sup> -P42 <sub>1</sub> m	2		
	II	C <sub>2h</sub> <sup>6</sup> -C2/c	12	I → II	1260
	III	C <sub>2v</sub> <sup>8</sup> -Pba2	4	I → III	508
Nd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	I	D <sub>2d</sub> <sup>3</sup> -P42 <sub>1</sub> m	2		
	II	C <sub>2h</sub> <sup>6</sup> -C2/c	12	I → II	≈ 1230
	III	C <sub>2v</sub> <sup>8</sup> -Pba2	4	I → III	498
Sm <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	I	D <sub>2d</sub> <sup>3</sup> -P42 <sub>1</sub> m	2		
	II	C <sub>2h</sub> <sup>6</sup> -C2/c	4	I → II	≈ 1180
	III	C <sub>2v</sub> <sup>8</sup> -Pba2	4	I → III	470

Table 1 (Continued)

Compound	Phase	Symmetry	Z	Phase transition		T/K
Eu <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	I	D <sub>2d</sub> <sup>3</sup> -P $\bar{4}$ 2 <sub>1</sub> m	2			
	II	C <sub>2h</sub> <sup>6</sup> -C2/c	4	I	→ II	1054
	III	C <sub>2v</sub> <sup>8</sup> -Pba2	4	I	→ III	453
Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	I	D <sub>2d</sub> <sup>3</sup> -P $\bar{4}$ 2 <sub>1</sub> m	2			
	II	C <sub>2h</sub> <sup>6</sup> -C2/c	4	I	→ II	≈ 1120 ... 1140
	III	C <sub>2v</sub> <sup>8</sup> -Pba2	4	I	→ III	≈ 430
Tb <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	I	D <sub>2d</sub> <sup>3</sup> -P $\bar{4}$ 2 <sub>1</sub> m	2			
	II	C <sub>2h</sub> <sup>6</sup> -C2/c	4	I	→ II	≈ 1070 ... 1100
	III	C <sub>2v</sub> <sup>8</sup> -Pba2	4	I	→ III	≈ 430
Dy <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	I	D <sub>2d</sub> <sup>3</sup> -P $\bar{4}$ 2 <sub>1</sub> m	2			
	II	C <sub>2h</sub> <sup>6</sup> -C2/c	4	I	→ II	1048 ... 1078
	III	C <sub>2v</sub> <sup>8</sup> -Pba2	4	I	→ III	418
K <sub>2</sub> WO <sub>4</sub>	I	D <sub>3d</sub> <sup>3</sup> -P $\bar{3}$ m1	3	I	→ II	700
	II	D <sub>2h</sub> <sup>16</sup> -Pnma	4	II	→ III	643
	III	C <sub>2h</sub> <sup>3</sup> -C2/m	4			
RbIn(WO <sub>4</sub> ) <sub>2</sub>	I	D <sub>3d</sub> <sup>3</sup> -P $\bar{3}$ m1	2	I	→ II	1098
	II	D <sub>2h</sub> <sup>16</sup> -Pnma	4	II	→ III	723
	III	T <sub>h</sub> <sup>4</sup> -Fd3	4			
RbPr(WO <sub>4</sub> ) <sub>2</sub>	I	D <sub>4h</sub> <sup>4</sup> -P4/nnc	2	I	→ II	≈ 1220
	II	D <sub>2h</sub> <sup>14</sup> -Pbna	4	II	→ III	1098
	III	C <sub>2h</sub> <sup>6</sup> -C2/c	4			
NaFeO <sub>2</sub>	I	D <sub>4</sub> <sup>4</sup> -P4 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	4	I	→ II	≈ 1260 ... 1370
	II	C <sub>2v</sub> <sup>9</sup> -Pna2 <sub>1</sub>	4	II	→ III	≈ 1030
	III	D <sub>3d</sub> <sup>3</sup> -R $\bar{3}$ m	3			

\* Stabilized by Mn admixtures.

NaNbO<sub>3</sub> and KNbO<sub>3</sub>. Symmetry descent chains are described in Table 2. It is interesting that the chains for both the compounds are not identical in spite of the common starting symmetry space group (not only in the sense of observed or unobserved phases). KNbO<sub>3</sub> phase transitions are analogous to the BaTiO<sub>3</sub> ones. NaNbO<sub>3</sub> phase transitions are of B type except two highest ones of combined A1 and B type.

M<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>. These lanthanoide compounds may be described by the same symmetry descent chains. The existence of higher symmetry phases at higher temperatures is probable.

LaCrO<sub>3</sub>. Phase II of this compound may result as a supergroup of stable D<sub>2h</sub> symmetries (compare BaTiO<sub>3</sub>).

RbIn(WO<sub>4</sub>)<sub>2</sub>. Phase III of T<sub>h</sub> symmetry is more stable at lower temperatures than phase II of its subgroup D<sub>2h</sub> symmetry. This fact can be explained by another chain of symmetry descent (D<sub>2h</sub> and T<sub>h</sub> must not be in the same chain).

Table 2

The symmetry descent scheme for phase transitions

Compound	dim $\Gamma_0$	Symmetry descent chains	Note
BaTiO <sub>3</sub>	3	$O_h^1$ -Pm3m $\rightarrow$ ( $D_{4h}$ ) $\rightarrow$ $C_{4v}^1$ -P4mm $\rightarrow$ $C_{2v}$	$D_{6h} \approx C_{3v} \times C_{2v}$
	3	$O_h^1$ -Pm3m $\rightarrow$ ( $T_d$ ) $\rightarrow$ $C_{3v}^5$ -R3m	
	2, 3	$O_h^1$ -Pm3m $\rightarrow$ ( $D_{3d}$ ) $\rightarrow$ $C_{3v}^5$ -R3m $\rightarrow$ ( $C_s$ )	
NaNbO <sub>3</sub>	2, 3	$O_h^1$ -Pm3m $\rightarrow$ ( $T_d$ ) $\rightarrow$ $C_{3v}^5$ -R3m $\rightarrow$ ( $C_s$ )	
	3	$O_h \rightarrow D_{4h} \rightarrow D_{2h}$	
	2, 3	$O_h \rightarrow T_h \rightarrow D_{2h}$	
KNbO <sub>3</sub>	2	$O_h \rightarrow D_{4h}$	
	2, 3	see BaTiO <sub>3</sub> (except $D_{6h}$ )	
	2, 3	$(O_h) \rightarrow D_{3d}^3$ -P $\bar{3}$ m1 $\rightarrow$ $C_{2h}^3$ -C2/m	
Rb <sub>2</sub> WO <sub>4</sub>	2, 3	$(O_h) \rightarrow (T_h) \rightarrow D_{2h}$	
	3	$(O_h) \rightarrow D_{3d}^3$ -P $\bar{3}$ m1	
	3	$(O_h) \rightarrow (D_{4h}) \rightarrow D_{2h}$	
FeNbO <sub>4</sub>	2	$D_{4h} \rightarrow D_{2h}$	
	2	$D_{4h} \rightarrow (C_{4h}) \rightarrow C_{2h}$	
LaCrO <sub>3</sub>	2, 3	$O_h \rightarrow (T_h) \rightarrow D_{2h}$	$D_{6h} \approx D_{2h} \times 3$
	3	$O_h \rightarrow (D_{4h}) \rightarrow D_{2h}$	
M <sub>2</sub> MoO <sub>4</sub>	2, 3	$(O_h) \rightarrow D_{3d}^3$ -P $\bar{3}$ m1 $\rightarrow$ $C_{2h}^3$ -C2/m	M = K, Rb
	3	$(O_h) \rightarrow D_{3d}^3$ -P $\bar{3}$ m1	
M <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	2	$(D_{4h}) \rightarrow D_{2d} \rightarrow C_{2v}$	M = Pr, Nd, Sm, Eu, Gd, Tb, Dy
	2	$(D_{4h}) \rightarrow (C_{4h}) \rightarrow C_{2h}$	
K <sub>2</sub> WO <sub>4</sub>	3	see M <sub>2</sub> MoO <sub>4</sub>	
	3	$(O_h) \rightarrow D_{3d}$	
	3	$(O_h) \rightarrow (D_{4h}) \rightarrow D_{2h}$	
RbIn(WO <sub>4</sub> ) <sub>2</sub>	3	$(O_h) \rightarrow T_h \rightarrow (S_6)$	
	2, 3	$(O_h) \rightarrow D_{3d} \rightarrow (C_{2h})$	
	3	see FeNbO <sub>4</sub>	
RbPr(WO <sub>4</sub> ) <sub>2</sub>	3	$(O_h) \rightarrow (O) \rightarrow D_4$	
	3	$(O_h) \rightarrow (D_{4h}) \rightarrow D_4 \rightarrow (D_2)$	
	3	$(O_h) \rightarrow (D_{4h}) \rightarrow D_{2h}$	
	3	$(O_h) \rightarrow D_{3d}$	
	2, 3	$(O_h) \rightarrow (T_d) \rightarrow D_{2h}$	
	2, 3	$(O_h) \rightarrow (O) \rightarrow D_4 \rightarrow (D_2)$	

$\Gamma_0$  is the starting multidimensional IR to be split. Space symmetry groups (in Schönflies and Hermann—Mauguin notation) are listed only if group-subgroup relations hold also for them. Unobserved phases in descent chains are in parentheses.

Explanations of phase transitions of other compounds may be understood very simply from Table 2. Some of them can be explained assuming either two- or three-dimensional IR's of  $O_h$  group in the same way. The possibility of  $O_h$  and  $D_{6h}$  starting symmetries for the same compounds (explained here as a

dynamical superposition of static structures at different conditions) is rare and can be caused by admixtures in crystals (*e.g.* phase V of BaTiO<sub>3</sub>).

### Conclusion

The phase transitions based on JT effect were studied using group-theoretical treatment. The theory of consecutive splitting of multidimensional IR due to the symmetry descent [7, 8] was applied to some compounds of transition metals. A good agreement of this theory and experimentally observed structures was demonstrated. New classification of phase transitions according to group-theoretical criteria was proposed.

This theory seems to be more general. It may be applied to all compounds of such a symmetry space group that enables the existence of multidimensional IR's. On the other hand, this theory is restricted only to the symmetry properties of individual compounds. It says nothing about the kinetics and gives only a little information about the thermodynamics of phase transitions. This theory is capable to predict all the possible symmetry changes at phase transitions but only few of them are observed in real systems.

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