SHORT COMMUNICATION

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1990). B46, 573–575

Jahn–Teller phase transitions.

By Martin Breza, *Department of Inorganic Chemistry, Slovak Technical University, CS-*81237 *Bratislava, Czechoslovakia*

(*Received* 6 *May* 1989; *accepted* 2 *February* 1990)

Abstract

Phase transitions are studied in terms of the theory of consecutive descent in symmetry resulting from the Jahn–Teller effect. This theory has been successfully applied to some transition-metal compounds. The criteria for Jahn–Teller phase transitions are defined.

Introduction

The Jahn–Teller (JT) effect represents an important phenomenon in physics and chemistry. The generally accepted formulation of the JT theorem (Jahn & Teller, 1937; Jahn, 1938) consists of the assertion that a non-linear nuclear configuration in a 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 cooperative JT effect (Englman, 1972; Bersuker, 1984; Bersuker & Polinger, 1983) is the collective influence of correlated JT-active centres on the crystal structure. As a consequence of their mutual interaction an anisotropic force field is formed and distortion in one direction is preferred. The energetically most advantageous nuclear arrangement in a crystal occurs when every JT centre is distorted and the distortions are correlated. At higher temperatures the JT-active centres may adopt a higher symmetry owing to the dynamic JT effect and the symmetry of the JT force field is changed. This change corresponds to a structural phase transition. In reality, the situation is more complicated, since lattice vibrations and thermal fluctuations tend to destroy the correlation of JT centres. Various defects in crystals, external forces and other effects may cause the adoption of non-JT symmetry. Thus only a limited number of observed phase transitions are a consequence of the pure JT effect.

On the other hand, according to present theories only order–disorder phase transitions (*i.e.* those 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 (Pelikán & Breza, 1985*a,b*) a complete classification of possible symmetries of JT systems for all molecular symmetry point groups was elaborated. This is based on the principle of consecutive splitting of the multidimensional irreducible representations describing the symmetry of electronic terms resulting from the symmetry descent (loss of some symmetry elements) of the system.

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

(i) Let G_m be an immediate subgroup of G_n and Γ_m, Γ'_m ... be irreducible representations of G_m correlating with Γ_n of G_n

$$\dim \Gamma_n = \dim \Gamma_m + \dim \Gamma'_m + \ldots . \tag{1}$$

(ii) If $\dim \Gamma_m = 1$ then symmetry group G_m 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 Γ_m.

The order of the G_n group is an integral multiple of its G_m subgroup order:

$$O(G_n) = kO(G_m) \tag{2}$$

where the integer k corresponds to a number of equivalent configurations of subgroup symmetry. This method is also applicable to pseudo-JT systems; the pseudo-JT effect being a JT effect in the excited electronic state.

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

Real systems are not described by a single electronic state; the populations of excited states are, in principle, non-zero and increase with temperature. Thus, all the symmetries of electronic states have 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

0108-7681/90/040573-03$03.00

not be in the thermodynamically most stable energetic state.

The symmetry descent to the same symmetry group may proceed in various ways. As is implied by (2), the electronic degeneracy is transformed into configurational degeneracy: the same symmetry descent may be caused by k different changes of nuclear configurations. This number, k, depends on the orders of both symmetry groups (G_m and 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 as are the related structure parameters. Otherwise Z is multiplied by small integral numbers k_i for all the translational directions

$$Z_m = k_a k_b k_c Z_n \qquad (3)$$

where Z_n and Z_m are the number of formula units in the unit cell for space groups G_n and G_m, respectively, and k_a, k_b and k_c are small integers, each most probably equal to 1 or to k of equation (2) or its multiples. Similar relations hold for the unit-cell dimensions.

According to group-theoretical criteria, the JT phase transitions with decrease in temperature may be characterized as follows:

(i) Group–subgroup relations hold for both the space symmetry groups.

(ii) The symmetry descent is connected with a multidimensional irreducible representation split.

(iii) The number of formula units in the unit cell may be changed.

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

This theory does not cover phase-stability conditions. It only indicates the possibility that a phase exists. Thus only a few of the phases predicted by the theory have been observed.

Results and discussion

In Table 1 some data (Landolt–Börnstein, 1976, 1977) on various phases of some d-transition-metal compounds are collected. The data are restricted to compounds that are known to exist in three or more phases of different symmetry (at least three different point groups), with well defined phase-transition temperatures and constant composition. The phases are ordered according to decreasing stability temperatures. All these phase transitions may be explained in terms of the present theory as a combination of several chains of symmetry descent (Table 2). Some detailed examples of the use of the theory are demonstrated below.

$BaTiO_3$. This compound is a typical pseudo-JT system (Bersuker, 1984; Bersuker & Polinger, 1983). Its phase transitions (except phase V) may be explained as a combination of two symmetry descent chains (consecutive splitting three-dimensional irreducible representations) resulting in C_{2v} and C_{3v} symmetry groups, respectively. T_d and D_{4h} symmetry groups are not observed. Phase V results from a superposition of C_{2v} and C_{3v} groups owing to the influence of Mn admixtures (Landolt–Börnstein, 1976). This assertion is also supported by the large Z value of phase V. This implies that phase V cannot be the starting point of a symmetry descent chain. Only the phase transitions I→II and II→III are JT ones.

Table 1. *Phase-transition characteristics of some compounds* (*Landolt–Börnstein*, 1976, 1977)

Where appropriate, a range of data from various authors is given for the phase-transition temperatures.

Compound	Phase	Symmetry	Z	Phase transition	Temperature (K)
$BaTiO_3$	V*	D^4_{6h}–$P6_3/mmc$	6	I → V	~1330
	I	O^1_h–$Pm3m$	1	II → I	~395
	II	C^1_{4v}–$P4mm$	1	III → II	273
	III	C^{14}_{2v}–$C2mm$	2	IV → III	153–173
	IV	C^5_{3v}–$R3m$	3		
$NaNbO_3$	I	O^1_h–$Pm3m$	1	II″ → I	~910
	II″	D^5_{4h}–$P4/mbm$	2	II″ → II′	~850
	II′	D^{17}_{2h}–$Cmcm$	8	II → II′	~790
	II	D^{13}_{2h}–$Pnmm$	8	III → II	~740–750
	III′	D^{13}_{2h}–$Pnmm$	24	III → III′	~620–650
	III	D^{11}_{2h}–$Pbma$	8		
$KNbO_3$	I	O^1_h–$Pm3m$	1	II → I	~710
	II	C^1_{4v}–$P4mm$	1	III → II	~500
	III	C^{14}_{2v}–$Bmm2$	2	IV → III	263
	IV	C^5_{3v}–$R3m$	3		
Rb_2WO_4	I	D^3_{3d}–$P\bar{3}m1$	2	I → II	738
	II	D^{16}_{2h}–$Pnma$	4	III → II	663
	III	D^{16}_{2h}–$Pnma$	4	IV → III	513–568
	IV	C^3_{2h}–$C2/m$	4		
$FeNbO_4$	I	D^{14}_{4h}–$P4_2/mnm$	1	I → II	~1620
	II	D^{14}_{2h}–$Pnab$	2	II → III	~1270
	III	C^4_{2h}–$P2/c$	2		
K_2MoO_4	I	D^3_{3d}–$P\bar{3}m1$	2	I → II	713
	II	D^{16}_{2h}–$Pnma$	4	II → III	~580–590
	III	C^3_{2h}–$C2/m$	4		
Rb_2MoO_4	I	D^3_{3d}–$P\bar{3}m1$	2	I → II	772
	II	D^{16}_{2h}–$Pnma$	4	II → III	~370–570
	III	C^3_{2h}–$C2/m$	4		
K_2WO_4	I	D^3_{3d}–$P\bar{3}m1$	3	I → II	700
	II	D^{16}_{2h}–$Pnma$	4	II → III	643
	III	C^3_{2h}–$C2/m$	4		
$RbIn(WO_4)_2$	I	D^3_{3d}–$P\bar{3}m1$	2	I → II	1098
	II	D^{16}_{2h}–$Pnma$	4	II → III	723
	III	T^4_h–$Fd3$	4		
$NaFeO_2$	I	D^4_4–$P4_12_12_1$	4	I → II	~1260–1370
	II	C^9_{2v}–$Pna2_1$	4	II → III	~1030
	III	D^5_{3d}–$R\bar{3}m$	3		

* Pure crystals cannot be obtained (stabilized by Mn).

Table 2. *The symmetry descent scheme for phase transitions*

Γ_0 is the starting multidimensional irreducible representation to be split. Space symmetry groups (in Schönflies and Hermann-Mauguin notation) are listed only if group–subgroup relations hold. Unobserved phases in descent chains are in parentheses.

Compound	dim(Γ_0)	Symmetry descent chains	Remarks
$BaTiO_3$	3	O^1_h–$Pm3m \rightarrow (D_{4h}) \rightarrow C^1_{4v}$–$P4mm \rightarrow C_{2v}$ O^1_h–$Pm3m \rightarrow (T_d) \rightarrow C^6_{3v}$–$R3m$ O^1_h–$Pm3m \rightarrow (D_{3d}) \rightarrow C^6_{3v}$–$R3m \rightarrow (C_s)$	$D_{6h} \simeq C_{3v} \otimes C_{2v}$
$NaNbO_3$	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_2WO_4	2 or 3	$(O_h) \rightarrow D^3_{3d}$–$P\bar{3}m1 \rightarrow C^3_{2h}$–$C2/m$ $(O_h) \rightarrow (T_h$ or $D_{4h}{}^*) \rightarrow D_{2h}$	
$FeNbO_4$	2	$D_{4h} \rightarrow D_{2h}$ $D_{4h} \rightarrow (C_{4h}) \rightarrow C_{2h}$	
M_2MoO_4	2 or 3	$(O_h) \rightarrow D^3_{3d}$–$P\bar{3}m1 \rightarrow C^3_{2h}$–$C2/m$	M = K, Rb
K_2WO_4	2 or 3	See M_2MoO_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	$(O_h) \rightarrow (O$ or $D_{4h}) \rightarrow D_4 \rightarrow (D_2)$ $(O_h) \rightarrow (T_d$ or $D_{4h}) \rightarrow D_{2h}$ $(O_h) \rightarrow D_{3d}$	

* Only for the three-dimensional starting irreducible representation.

$NaNbO_3$ *and* $KNbO_3$. It is interesting that the descent chains for these compounds are not identical (Table 2) in spite of the common starting space symmetry group (not only in the sense of observed or unobserved phases). $KNbO_3$ phase transitions are analogous to those of $BaTiO_3$. Only the two highest phase transitions of $NaNbO_3$ are JT transitions.

$RbIn(WO_4)_2$. Phase III of T_h symmetry is stable at lower temperatures than phase II of its subgroup D_{2h} symmetry. This fact can be explained by another chain of symmetry descent (D_{2h} and T_h must therefore not be in the same chain).

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 irreducible representations of the O_h group in the same way. Our results indicate that the influence of excited electronic states decreases very steeply with excitation energy. 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 may be caused by admixtures in crystals (*e.g.* phase V of $BaTiO_3$).

Concluding remarks

This theory is restricted only to the symmetry properties of individual compounds. It says nothing about the kinetics and gives only a limited amount of information on the thermodynamics of phase transitions. On the other hand, the theory is capable of explaining all the observed transitions and predicting all the possible symmetry changes during the phase transitions.

References

BERSUKER, I. B. (1984). *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*. New York: Plenum Press.

BERSUKER, I. B. & POLINGER, V. Z. (1983). *Vibronnye Vzaimodeistvia v Molekulach i Kristallach*. Moscow: Nauka.

ENGLMAN, R. (1972). *The Jahn–Teller Effect in Molecules and Crystals*. New York: Wiley–Interscience.

JAHN, H. A. (1938). *Proc. R. Soc. London Ser. A*, **164**, 117–131.

JAHN, H. A. & TELLER, E. (1937). *Proc. R. Soc. London Ser. A*, **161**, 220–235.

LANDOLT–BÖRNSTEIN (1976). New series, Vol. III/7e. *Crystal Structures of Inorganic Compounds. Key-Elements*: *d^9-, d^{10}-, d^1 ... d^3-, f-Elements*. Berlin: Springer.

LANDOLT–BÖRNSTEIN (1977). New series, Vol. III/7f. *Crystal Structures of Inorganic Compounds. Key-Elements*: *d^4 ... d^8-Elements*. Berlin: Springer.

PELIKÁN, P. & BREZA, M. (1985*a*). *Chem. Pap.* **39**, 255–270.

PELIKÁN, P. & BREZA, M. (1985*b*). *J. Mol. Struct. Theochem.* **124**, 231–237.

Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (R. O. Gould, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland). As far as practicable books will be reviewed in a country different from that of publication.

Acta Cryst. (1990). B**46**, 575–576

Biomineralisation: chemical and biochemical perspectives. Edited by S. MANN, J. WEBB and R. J. P. WILLIAMS. Pp. xiv + 541. Weinheim, New York: VCH Verlag, 1988. Price DM 274.00.

Biomineralization is the controlled formation of inorganic minerals (such as calcite, hydroxyapatite, magnetite *etc.*) by living organisms. The functions of these 'biominerals' are many and varied; ranging from the obvious protection and support provided by exoskeletons and skeletons, to the more intricate role of acting as gravitational and magnetic sensors. The physical and chemical properties of biominerals are therefore of great interest to researchers in fields as diverse as bioinorganic chemistry, materials science, geology, medicine and biology.

The increasing interest in biomineralization has resulted in the need for a comprehensive reference text on the subject. This book goes some way to filling this requirement. It is comprised of 15 chapters and is essentially a collection of reviews dealing with various aspects of current research into biomineralization. It begins with two chapters providing a useful introduction to the more general aspects of the control of mineral formation in biological systems: essential reading for a newcomer to the subject. This is followed by a number of chapters each of which deals in depth with a particular area of research on biomineralization. The subjects covered range from carbonate calcification in algae to studies on vertebrate tooth mineralization, with the appropriate emphasis placed on the organic matrices which control the mineralization process.

The analytical techniques which are now increasingly important in the study of biominerals, such as electron microscopy, EXAFS (extended X-ray absorption fine structure) and proton-beam analysis, are considered in the latter part of the book. A complete chapter is devoted to proton-beam analysis in which the basis behind techniques such as PIXE (proton-induced X-ray emission) is explained. The book ends with a consideration of the relevance of research into biomineralization to materials science and technology.

The editors have done a reasonable job in ordering the various contributions to the book in a logical way. In general the chapters are well planned, although with over 20 contributors there is, not surprisingly, some variation in standards and some of the chapters are hard going. Most chapters are well referenced, as one would expect from the