# Symmetry, instability, stereochemistry and phase transitions in coordination compounds

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<u>Abstract</u> – A general model is worked out comprising direct
correlations between symmetry, vibronic instability, stereo-
chemistry and structural phase transformations in condensed
media. The different phases of the latter are shown to oc-
cur as a result of consequent sudden breaks of symmetry with
transitions from the higher symmetry to the lower one by de-
crease of temperature, the micromechanism triggering all
these transformations being the same: the Jahn-Teller (pse-
udo Jahn-Teller) effect. In addition to the previous results,
it is shown rigorously that the Jahn-Teller effects are the
only possible sources of dynamic instability of high symme-
try polyatomic systems with respect to lower symmetry dis-
tortions, and thus these effects control all the stereoche-
mical and structural transformations of matter. The visual
reason of instability is due to formation of new covalent
bonds (strong effect) and polarization of surrounding atoms
(small effect) by distortion. Besides the vibronic origin of
structural phase transitions in crystals and the transition
liquid-crystal (melting) considered earlier, the electroni-
cally controled vibronic nature of the transition gas –
liquid is discussed.

## INTRODUCTION

The goal of this short (partly review) paper is to show that both
the stereochemistry of high symmetry configurations and all the
phase transformations in condensed matter are controled by the
electronic ground and low-lying excited states through the vibronic
Jahn-Teller effects. Although the fact that the instability of the
high symmetry configurations is caused by the Jahn-Teller and pseudo
Jahn-Teller effects is well known, the statement that all the phase
transformations are also electronically (vibronically) controlled is
novel. The idea is that by decrease of temperature the vibronic in-
stability causes a chain of consequent sudden breaks of symmetry
(emerging as phase transitions), which thus have the same micro-
mechanism: the Jahn-Teller (pseudo Jahn-Teller) effect. The states
of broken symmetry are well known, especially in the theory of
elementary particles. Just these states are responsible for the
fact that we are living in a universe of particles, and not of

antiparticles: the absence of symmetry between the equivalent states of
particles and antiparticles testifies to the great energy barrier between
them due to which the system, at low temperatures, is in one of two (or
more) equivalent states (and thus, in a nonstationary state). At high enough
temperatures the barrier is overcome and the system becomes symmetric (it
is assumed that immediately after the Great Explosion at extremely high tem-
peratures the distribution on all kind of elementary particles, including
particles and antiparticles, was quite symmetric, and only after a consider-
able cooling during a set of symmetry breaks the universe acquired its
contemporane broken-symmetry state).

In condensed states of matter such processes of break of symmetry are
observed in the form of structural phase transformations gas ⟷liquid,
liquid⟷ crystal and structural phase transitions in crystals (in a sense
chemical reactions can be considered in a similar way). Although many
papers are devoted to these processes, so far there is no general model
formulated to reveal the unitive electronic mechanism initiating all these
transformations with symmetry breaks.

## JAHN-TELLER AND PSEUDO JAHN-TELLER EFFECTS AS SOURCES OF BREAKS OF SYMMETRY

One of the well known effects of instability of high symmetry configur-
ations of polyatomic systems in degenerate electronic states is the Jahn-
Teller effect. In the absence of electronic degeneracy similar instability
can be caused by the pseudo Jahn-Teller effect. Both effects, schemati-
cally represented in Fig. 1, have a common nature: mixing of electronic
states under nuclear displacements - vibronic mixing (the Jahn-Teller
effect can be considered as a limiting case of the pseudo Jahn-Teller
effect whe the energy gap between the mixing states $2\Delta = 0$). The theory of
these effects and their applications in various areas of physics and
chemistry of molecules and crystals is widely worked out by different
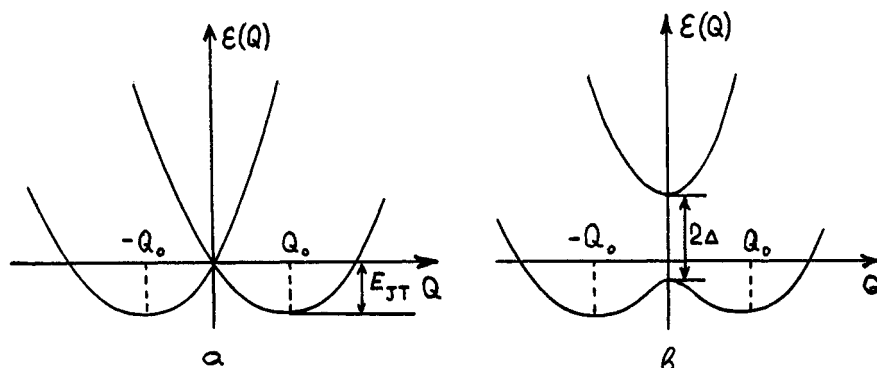authors (for reviews see refs. 1-4 and references therein).



Fig. 1. Schematical illustration of the Jahn-Teller (a) and
pseudo Jahn-Teller (b) effects

One of the distinguished features of the vibronic effects under consideration is the preservation of the high symmetry of the problem. Although in each of the minima of Fig. 1 the system possesses lower symmetry, than that at the initial $Q=0$ configuration, the number of such equivalent minima and their positions are always such, as they complete each other up to high symmetry at $Q=0$. But if the barrier between them is big enough, one can prepare the system in one of the minima, and then it will be there a long enough time (quasistationary state). The state of the system corresponding to one of the minima of the adiabatic potential, having a symmetry lower than that of the Hamiltonian, is just a state of broken symmetry. Denote by $E_{sym}$, $U_{sym}$ and $S_{sym}$, respectively, the free energy, potential energy and entropy of the high symmetry configuration, while $E_{ls}$, $U_{ls}$ and $S_{ls}$ stand for the same values in the lower symmetry configuration appropriate to one of the equivalent minima. Then we have:

$$E_{sym} = U_{sym} - TS_{sym}, \qquad E_{ls} = U_{ls} - TS_{ls} \tag{1}$$

$$E_{sym} - E_{ls} = E_{JT} - T\Delta S_{JT} \tag{2}$$

where it is taken into account that $U_{sym} - U_{ls} = E_{JT}$ in the Jahn-Teller stabilization energy, and I introduce also the Jahn-Teller stabilization entropy $\Delta S_{JT} = S_{sym} - S_{ls}$. Since the entropy of the high symmetry configuration (which can be regarded as an average on all the equivalent low symmetry ones appropriate to the equivalent minima) is always larger, than that of the lower symmetry one in the minimum, $\Delta S_{JT} > 0$. Denoting $T_0 = E_{JT}/\Delta S_{JT}$ we have:

$$E_{sym} - E_{ls} = \Delta S_{JT}(T_0 - T) \tag{3}$$

Herefrom it is obvious that if $T > T_0$ the high symmetry configuration is more stable, whereas for $T < T_0$ the low symmetry one is preferable. It can be shown that when the cooperative interactions between the distortions at different Jahn-Teller centers in condensed matter are taken into a count, the transition from the high symmetry configuration to the lower one takes place at a certain temperature as a sudden break of symmetry - a phase transition.

Thus the Jahn-Teller and pseudo Jahn-Teller effects may lead to states of broken symmetry. The higher the initial (starting) symmetry of the system, the higher the degeneracy (pseudodegeneracy) of the electronic states, and the more complex (multiform) the adiabatic potential, allowing several (many) types of states with broken symmetry ocurring at different temperatures. We obtain thus a direct correlation between the full symmetry of the system and possible states of broken symmetry. The possible occurence of these latter and the transition temperatures depend on the $E_{JT}$ and $\Delta S_{JT}$ values at appropriate minima (or sadlepoints) of the adiabatic potential and on the parameters of cooperative interactions of Jahn-Teller distortions.

## UNIQUENESS OF THE VIBRONIC ORIGIN OF DYNAMIC INSTABILITY

One of the most important questions arising in the topic under consideration is whether the Jahn-Teller and pseudo Jahn-Teller effects are the only possible sources of instability of high symmetry configurations resulting in symmetry breakdown and phase transitions, or this instability may have other roots in the electronic structure of matter. The answer to this question stating that the vibronic origin of dynamic instability is unique for all polyatomic systems was given recently in a series of papers (ref. 5-8). I give here a more general and rigorous proof of this statement (theorem) for any polyatomic system of cubic symmetry. Let us consider a coordination compound or a crystal of cubic symmetry in a nondegenerate state $\Psi$ , containing s types of atoms (s sublattices), and investigate its stability (instability) with respect to limiting nuclear displacements shifting one sublattice as a whole with respect to the others. The (normal) coordinates of 3s-3 limiting displacements of the sublattices can be taken as follows ( $x_{k\alpha}$, $y_{k\alpha}$, $z_{k\alpha}$ are the Cartezian coordinates of the nuclei):

$$X_k' = N^{-1/2} \sum_{\alpha} x_{k\alpha} \cdots, \qquad k = 1, 2, \ldots, s$$

$$X_j = \sum_k c_{jk}^x X_k', \ldots, \qquad j = 1, 2, \ldots, s-1 \qquad (4)$$

the last s-th coordinate being of the type $X_s = C \sum_k X_k'$, of which the energy is independent. Separate in the electronic Hamiltonian of the adiabatic approximation the terms containing the coordinates (4):

$$H = \sum_k V_k(\vec{r_i}, \vec{R_k}) + W \qquad (5)$$

Here

$$V_k(\vec{r_i}, \vec{R_{k\alpha}}) = -\mathcal{G}_k \sum_{i,\alpha} |\vec{r_i} - \vec{R_k}|^{-1}, \quad W = \sum_{\alpha,\beta} \sum_{k,l} \mathcal{G}_k \mathcal{G}_l R_{k\alpha,1\beta}^{-1}, \qquad (6)$$

$V_k$ is the energy of interaction between the electrons with the coordinates $\vec{r_i}$ ($x_i$, $y_i$, $z_i$) and the k type nuclei with the coordinates $\vec{R_{k\alpha}}$($x_{k\alpha}$, $y_{k\alpha}$, $z_{k\alpha}$) and charges $\mathcal{G}_k$ (it is assumed that e = 1), and W represents the nuclei - nuclei interactions.

In the adiabatic approximation the potential energy can be determined as follows: $E(x_j, y_j, z_j) = \langle \Psi | H | \Psi \rangle$ . In order to evaluate the curvature $K_{X_j X_j}$ of this surface in the direction $X_j$ at the point of highest symmetry $X_j = X_j^0$ , ... it is necessary first to expand the Hamiltonian H with respect to the nuclear displacements from this point, and then, using the perturbation theory up to the second order, we get the following exact formula for the curvature:

$$K_{X_j X_j} = \left( \frac{\partial^2 E}{\partial x_j^2} \right)_0 = K_{0X_j X_j} + K_{vX_j X_j} ; \qquad (7)$$

$$K_{0X_jX_j} = \left\langle 0 \left| \left( \frac{\partial^2 H}{\partial x_j^2} \right)_0 \right| 0 \right\rangle ; \qquad K_{vX_jX_j} = -\sum_1 F_{X_j}^{(oi)\,2} / \Delta_{io} \qquad (8)$$

$$F_{X_j}^{(oi)} = \left\langle 0 \left| \left( \frac{H}{X_j} \right)_0 \right| i \right\rangle , \quad 2\Delta_{io} = E_i - E_0 \qquad (9)$$

where $|0\rangle$ is the electronic wave function $\Psi$ in the ground state for fixed at the point $X_j^0$, ... nuclei, and $|i\rangle$ is the same for the excited states at this point, $E_0$ and $E_i$ being their energies. The $K_0$ component of the curvature is the nonvibronic contribution (the quantum-mechanical average of the operator of curvature in the ground electronic state), while $K_v$ is the contribution of the vibronic mixing with the excited states ($F_X^{(oi\,v)}$ is the nondiagonal vibronic constant, ref. 1). Since $K_v < 0$, the instability of the high symmetry configuration $K < 0$ can obviously take place when $|K_v| > |K_0|$. But if $K_0 > 0$, the inequality $K < 0$ can be hold only due to the vibronic contribution. If it takes place due to the contribution of only one term of Eq. (12), than the instability coincides exactly with that predicted in the two-level problem of the pseudo Jahn-Teller effect. Let us prove in a general way that always $K_0 > 0$ and hence the instability of the high symmetry configuration can take place only due to the vibronic mixing of the ground state with the excited ones.

According to the unitarity of the transformation (4) we have:

$$\frac{\partial^2 H}{\partial x_j^2} = \sum_k (c_{jk}^x)^2 \frac{\partial^2 V_k}{\partial x'^2} + \frac{\partial^2 W}{\partial x_j^2} \qquad (10)$$

For any polyatomic system $\left\langle 0 \left| \partial^2 V_k / \partial x_k'^2 \right| 0 \right\rangle = (4\pi/3) \mathscr{F}_k \rho_k + \mathscr{F}_k Q_{kXX}$ , where $\rho_k$ is the electronic density at the nuclei of the k sublattice, and $Q_{kXX}$

is the component of the gradient of the electric field produced by the electrons on the nuclei of this sublattice. Since $Q_{XX} + Q_{YY} + Q_{ZZ} = 0$,

$$\left\langle 0 \left| \frac{\partial^2 V_k}{\partial x'^2} + \frac{\partial^2 V_k}{\partial y'^2} + \frac{\partial^2 V_k}{\partial z'^2} \right| 0 \right\rangle = 4\pi \mathscr{F}_k \rho_k \geqslant 0 \qquad (11)$$

For a cubic system the three components along the three Cartezian axes are equal to each other and hence $\left\langle 0 \left| \partial^2 V_k / \partial x_k'^2 \right| 0 \right\rangle = (4\pi/3) \mathscr{F}_k \rho_k \geqslant 0$.

For the same reason it follows from the relation $\nabla^2 R^{-1} = 0$ that $(\partial^2 W / \partial x_j^2)_0 = 0$. Substituting this relation into Eq.(8) we obtain the inequality sought for:

$$K_{0X_jX_j} \geqslant 0 \qquad (12)$$

and similarly $K_{0Y_jY_j} \geqslant 0$, $K_{0Z_jZ_j} \geqslant 0$.

Analogous proofs of $K_0 \geqslant 0$ were obtained for anisotropic crystals, linear chains and in general for any system using quite convincing estimates (inequalities) for the parameters and ab initio numerical calculations. Thus the following theorem can be formulated: The only source of dynamic

instability of high symmetry configurations of polyatomic systems is the
vibronic mixing of its electronic states by nuclear displacements (Jahn-
Teller and pseudo Jahn-Teller effects).

Since $K_0 > 0$, the instability occurs when $|K_v| > K_0$, i.e.

$$\sum_i |F^{(oi)}|^2 / \Delta_{io} > K_0 \qquad (13)$$

Usually only one or a few number of terms in the left hand side of this
inequality are important to the instability.

## VISUAL INTERPRETATION OF THE INSTABILITY AS DUE TO FORMATION
## OF NEW COVALENT BONDS BY DISTORTION

It is important to analyse the reason of instability of high symmetry
configurations in terms of chemical bonding. In Fig. 2 the ground state
(highest occupied $p_x(1) + p_x(2)$ orbitals of two oxygen atoms) and first
excited one (lowest unoccupied $d_{xz}$ orbital of the $Ti^{4+}$ ion) of the fragment
$O^{2-}-Ti^{4+}-O^{2-}$ of the cluster $TiO_6^{8-}$ in barium titanate are shown
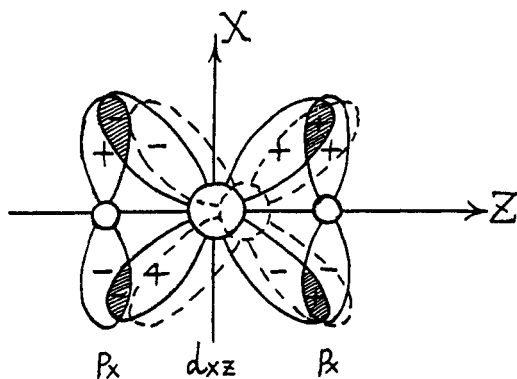schematically (ref. 1,2). One can see that if the titanium atom is in the



Fig. 2

center between the two oxygen atoms, the total overlap of the $d_{xz}$ orbital
(appertaining to the $t_{2g}$ symmetry of the octahedron) with the appropriate
combination of the two $p_x$ orbitals (of $t_{1u}$ symmetry) equals zero by
symmetry. But if the titanium atom is displaced along Z with respect to the
oxygen ones ($t_{1u}$ displacement) this overlap becomes nonzero, and an
additional chemical $\pi$-bond Ti—O is produced (see also ref. 1). The sense
of the criterion (20) is that if the energy of this new bonding is larger
than that lost by distortion of the other bonds (which are responsible for
the equilibrium of forces in the high symmetry configuration), then the
initial configuration is unstable with respect to this distortion. Besides
the formation of new covalent bonds the vibronic contribution (8) to the
curvature contains also terms of atomic polarization effects when the
states $|0\rangle$ and $|i\rangle$ (mixed by the nuclear displacement) appertain mainly to
one atom (or to the same type of atoms). For the above example of barium

titanate the closest-in-energy oxygen atomic states mixing under the
titanium displacement are 2p and 3s, the appropriate contribution being
$K_v^p = |F_z(2p,3s)|^2/\Delta_{3s,3p}$. We estimated this magnitude and compared it
with the covalency contribution $K_v^c = |F_z(2p^O,3d^{Ti})|^2/\Delta_{2p,3d}$. It emerged
that $|K_v^p/K_v^c| \approx 0.1$. Note that for the $NH_3$ molecule in planar configuration
ab initio calculations 6 yield a similar relation: $|K_v^p/K_v^c| = 0.06/0.62 \approx 0.1$.
Thus the contribution of polarization effects toward the instability is by
an order of magnitude smaller than the contribution of formation of new
covalent bonding.

## GENERAL MODEL OF ELECTRONICALLY CONTROLED STRUCTURAL TRANSFORMATION IN CONDENSED MATTER

The discussion given above, and especially the proof of the uniqueness of
the vibronic origin of dynamic instability, allow to formulate the
following general scheme of structural phase transformations in condensed
matter presented as a consequence of sudden symmetry breaks controlled by
the electronic structure of the high symmetry configuration, the
micromechanism of these processes being the Jahn-Teller (pseudo Jahn-
Teller) effect. This statement is equally applicable to any structural
phase transformations in matter. With respect to structural phase
transitions in crystals it was discussed in quite a number of publications
and confirmed experimentally (see ref. 1-3,8-10). Recently (ref. 11) it was
shown that in the same vibronic approach the origin of liquid↔crystal
(melting) transitions, as well as glass↔crystal ones, can be explained.
The authors (ref. 11) employ the results of previous works in which the
liquid state is considered as consisting of mobile and relative low-stable
formations of near-neighbour order, mostly icosahedrons. Then using the
method of $X_\alpha$ (scattered waves), they calculated the electronic structure of
19-atomic almost icosahedral model clusters of a series of elements, and
show that the $e_g-t_{2g}$ degeneracy (pseudodegeneracy) of the molecular states
in accordance with the Jahn-Teller (pseudo Jahn-Teller) effect is
responsible for the instability of the system with respect to the nuclear
displacements toward the cubic structure. Assuming a certain model for the
interaction between the clusters in the liquid state they succeeded to
evaluate the melting temperature for a series of crystals (Ar, Al, Cd, Co,
Pb, Ru, Si, W) in good agreement with the experimental data. If the
freezing of the liquid state due to the interaction of desordered clusters
takes place at higher temperatures than the phase transition to the cubic
configuration, then we obtain also an amorphous state.

The electronically (vibronically) controled transition gas↔liquid can be
treated in a similar way. Some general ideas for this treatment are given
below. Consider first the formation of a diatomics from this point of view.
The system of two atoms without interaction between them has the symmetry
of $R(3)\cdot\mathcal{T}(2)$, where R(3) is group of rotations of the free atom, and $\mathcal{T}(2)$
is the group of permutations of two atoms. This symmetry produces high
degenerate electronic states which, when the interatomic interaction is

included, at low enough temperatures become unstable with respect to the only symmetrized displacement approaching the two atoms. In this process the symmetry is reduced from $R(3) \times T(2)$ to $C_{\infty v}$, while the potential energy, due to the chemical bonding, also decreases, quite similar to the Jahn-Teller effect. This procedure can be extended to any number of atoms in the gas phase, in particular, to 19-atomic groups leading to the formation of the above-mentioned icosahedral near- neighbour ordering in the liquid phase. The group of symmetry of such a set of noninteracting atoms is $R(3) \cdot T(19)$. This group allows high degeneracies of the orbital states (including 19-fold degenerate ones), and it contains the icosahedral group as a subgroup. In accordance with the vibronic effects, described above, at low enough temperatures the system becomes unstable with respect to phase transformations to another system with lower (icosahedral or more low) symmetry and formation of chemical bonds between the atoms, initiating thus the phase transition gas ⟷ liquid.

Thus all the phase transformations in condensed matter can be presented as initiated by the vibronic interactions, and in each of these processes the electronic states, responsible for the vibronic mixing initiating the phase transition, can be revealed. We obtain thus a general picture of phase transformations controlled by the electronic structure with a unique micromechanism: the Jahn-Teller (pseudo Jahn-Teller) effect.

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