COMPETITIVE INTERACTIONS AND PHASE STATES OF MIXED JAHN–TELLER SYSTEMS

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1. Introduction

There is a large class of systems containing centers, whose ground state is degenerate, quasi-degenerate or orientationally degenerate. As examples, we can mention centers with charge transfer between nearest to non-isovalent substitution ions, splitting configurations, off-center ions, impurity pairs consisting of substitution and interstitial ions in high symmetry lattices, systems with orbital degeneracy etc. Distinctive feature of all these centers is multi-well profile of their potential energy. Physical and chemical properties of such systems are determined by splitting of energy levels in equivalent potential wells due to the tunneling effects, external fields, random crystal fields and molecular fields of various types. Our interest to these systems is stipulated by the following circumstances.

1) The anomalously large contribution of such centers to different properties of condensed systems and the unusual character of these properties in comparison with the non-degenerate systems. Jahn-Teller (JT) ions occupy the special position among the multi-well potential centers [1,2,3,4,5,6,7,8]. The microscopic nature of multi-well potential is known for the JT systems (unlike other ones) and the exhibitions of multi-well potential in different properties (magnetic, thermodynamic, spectral and other) are very diverse. The JT centers can have simultaneously spin and orbital degeneracy, the dipole moment, that is why as a degenerate subsystem they make available the high susceptibility of crystal to the various external actions. Besides, JT states are extended enough widely, e.g., in oxides with cubic lattice one of the 3d ion charge state can be orbitally degenerate.

2) Crystalline systems containing orbitally degenerate (Jahn–Teller) ions are an ideal object for modeling various phase transitions in systems with cooperative interactions. The Jahn–Teller mechanism of inter-atomic interactions is responsible for various types of phase transitions in mixed crystalline systems, namely, structural, spin-reorientation, and decay transitions. The model of cooperative Jahn–Teller interactions enables the diversity of crystal states related to the specified phase transitions, including immiscibility diagrams.

In present work the ground attention is focused on the special features of phase transitions in crystals with Jahn–Teller ions in which competitive interactions of different types take place. In particular, the crystal solutions are considered where substituting cations can occupy crystallographic nonequivalent sites. In this case, the roles of competing interactions play the cooperative Jahn–Teller interaction and the preference energy of cationic distribution on nonequivalent sublattices. The main object of study is spinel-type systems with structural Jahn–Teller transitions of first and second type to the ferrodistortion phase. The Kanamori model describes structural
phase transitions. The topology of equilibrium and metastable states and phase boundaries were found for such crystals. The results obtained allow to describe typical fragments of experimental phase diagrams of the solutions based on Mn₃O₄. The developed model enables to understand the special features of the phase diagrams and the nature of equilibrium and metastable states of the mixed Jahn–Teller systems. It was shown that the type of the phase states of the systems under consideration, the temperatures of structural and phase decay transitions, and the topology of phase boundaries and absolute immiscibility regions depend to a substantial extent on the character and conditions of the redistribution of mixed cations between the crystallographic sublattices as the temperature and system composition change.

As an illustration of another type of systems with competing interactions we investigated crystals whose structural phase transition is accompanied by change of charge configurations on 3d-ions. It was shown that such effects can be described on the basios of model of cooperative Jahn–Teller phase transitions and can be predetermined by stabilization of Jahn–Teller valence states of cations in the low-temperature phase.

2. Jahn-Teller states

The JT theorem claims that for orbitally degenerate ions and molecules the symmetric configuration of environment is unstable with respect to deformations. As a result, the adiabatic potential of such ions or molecules (systems with pseudo-degeneracy) turns out to be of multi-well type (see Fig. 1).

\[ W(\varphi) = W_0 \cos 3\varphi, \quad \cot \varphi = e(E_\varphi)/e(E_\varepsilon). \] (1)

The characteristic displacements of nearest to JT center anions in states corresponding to minimums of adiabatic potential \((\varphi = -2\pi/3, 0, 2\pi/3)\) are presented on Fig. 2.
3. Magnetic systems with JT ions. Magnetic anisotropy and magnetostriction. Competing anisotropy

3.1. JT ions with ground cubic E-term. In comparison with the non-magnetic crystals splitting of orbitally degenerate state in magnets depends essentially on the direction of exchange fields at JT ion. The Hamiltonian of magnetic anisotropy in view of three lowest states of JT ion with cubic E-term can be written as follows.

\[
H_{\text{anis}} = \frac{2}{3} D S(S-1/2) \left( 3n_z^2 - 1 \right) U_{Eg,s} + \sqrt{3} \left( n_x^2 - n_y^2 \right) U_{Ee,s},
\]

where \( D \) is the single-ion anisotropy constant, \( S \) is the spin, \( n \) is the unit vector of magnetization.

The anisotropy energy plays the role of splitting energy of three lowest vibronic states by the spin-orbit interaction in the second order. As a result the angular dependence of the free energy of magnetic anisotropy \( \Delta F_{\text{anis}} \) has unusual form at temperature \( k_B T < D \). For example, in the case of static limit of Jahn-Teller effect this free energy is equal to (see also Fig. 3):

\[
\Delta F_{\text{anis}} = -2 D S(S-1/2) \max \left\{ \frac{n_x^2}{2} - \frac{1}{3}, \frac{n_y^2}{2} - \frac{1}{3}, \frac{n_z^2}{2} - \frac{1}{3} \right\}
\]

This angle dependence leads to the stepwise changing of \( \Delta F_{\text{anis}} \) (anisotropy of “light axis”-type) with the magnetization direction (see Fig. 3a).
The anomalously large value of this contribution to the magnetic crystallographic anisotropy energy is caused by the fact that the constants of single-ion anisotropy for orbitally degenerate centers are proportional to $\lambda$ or $\lambda^2/\Delta_{\text{cub}}$, where $\Delta_{\text{cub}}$ is the cubic crystal field parameter. For usual non-degenerate ions the anisotropy constants are proportional to $\lambda^4/\Delta_{\text{cub}}^3$ in cubic crystals.

The magnetostrictive properties of these systems have specific features as well. The spin-orbit interaction removes the degeneracy from the directions of local JT deformations at given direction of magnetization which were initially equivalent and this leads to the magnetostriction distortion of the crystal. The JT ions contribution to the magnetostriction constants in the absence of random fields is equal to $x_{\text{JT}}e_{\text{JT}}$, where $e_{\text{JT}}$ is the characteristic local JT deformation ($e_{\text{JT}} \sim 10^{-1}-10^{-2}$).

Only tetragonal deformations can take place at the centers under consideration and each of these three energy levels turns to be the lowest in the definite region of magnetization angles. The transfer of magnetization through the boundary of these regions is accompanied at low temperatures by the change of the type of tetragonal deformation at JT ions, that is the JT ion contribution to magnetostriction (Fig 3b). Such effects were observed in the system YIG: Mn$^{3+}$ [9].

3.2. **Centers containing 3d-ion of mixed valence in cubic magnets.** The indicated results (besides JT systems) have the direct relation to magnetic properties of cubic magnets with mixed valence (MV) centers determined by non-isovalent substitutions or vacancies (see, for example, [10]). Such centers of several 3d-ions with the charge, localized on them, arise in the case of non-isovalent substitutions and in the presence of anion or cation vacancies. The MV complexes in addition to traditional properties of JT centers have peculiarities caused by reorientation of extra charge (electron or hole) between ions of a complex, when the degeneracy is taken out at the expense of external perturbations or cooperative interactions.
First of all it concerns to occurrence of essential electrical dipole moment at MV center. The example of MV center with C<sub>3v</sub> symmetry is presented in Fig. 6 for the case of cubic crystal lattice (in particular for spinel structure). It consists of three cations (3d-ions) with localized t<sub>2g</sub> - hole on them.

In the case of small hopping integrals b of an excess charge (|b|<|D| or |λ|) reorientation of MV center (the transfer of an extra charge) is similar to the tunneling of JT ion between minimums of adiabatic potential. These systems are characterized by anomalously strong contribution into constants of magnetic anisotropy and magnetostriction as well as unusual angular dependence of the free energy from magnetic anisotropy [11].

3.3. Competing anisotropy. This peculiarity of the magnetic behavior of JT or mixed valence subsystems leads to the appearance of oblique phases in systems with competing anisotropy (for example, due to the JT term proportional to n<sub>i</sub><sup>2</sup> in contrast to n<sub>i</sub><sup>4</sup> in magnetic anisotropy energy of matrix).

The typical phase diagram (relative temperature - concentration) for systems where the competition of magnetic anisotropy of matrix and MV centers takes place is presented in Fig. 5.

**Fig. 5.** Magnetic phase diagram of a system with mixed valence centers (for example, Cr<sup>4+</sup>-Cr<sup>3+</sup>, Cr<sup>2+</sup>-Cr<sup>3+</sup>).

*Solid and dashed curves represent the lines of first and second order phase transitions, respectively.*
Thus, presented example illustrates, that the presence of competing anisotropic interactions in degenerate systems results in occurrence of the intermediate (or angular) phase.

4. Structural phase transitions (cooperative JT effect)

4.1. Hamiltonian. We shall confine the consideration to JT ferro elastic with doubly degenerate ions. In this case the simple model was proposed by Kanamori [6] for the description of structure phase transitions, caused by the cooperative Jahn-Teller effect:

\[
H = E_0 + \sum_s \left[ V_2 e_{E,g} + h_{E,g,s} + V_2 \left( e_{E,g}^2 - e_{E,e}^2 \right) \right] U_{E,g,s} + \left[ V e_{E,e} + h_{E,e,s} - 2V_2 e_{E,g} e_{E,e} \right] U_{E,e,s},
\]

\[
E_0 = N \Omega \left[ \frac{1}{2} C_{JT}^0 \left( e_{E,g}^2 + e_{E,e}^2 \right) + V_3 e_{E,g} \left( e_{E,g}^2 - e_{E,e}^2 \right) \right], \quad U_{E,g} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, \quad U_{E,e} = \begin{bmatrix} 0 & 1/2 \\ 1/2 & 0 \end{bmatrix},
\]

where \( N \) is the number of elementary cells in crystal; \( V_2 \) and \( V_3 \) are the parameters of anharmonic interaction of the doubly degenerate term with uniform JT deformations \( e_{E,g} \) and \( e_{E,e} \); \( h_{E,g,s} \) and \( h_{E,e,s} \) are the components of two-dimensional random field at the JT ion, index \( s \) labels JT ions.

4.2. Random fields distribution. The low-symmetry crystal fields may be one of the dominating mechanism of removing degeneracy on the JT ion. The distinctive property of these functions is their many-component character. For centers with cubic E-term we have the following random fields distribution function \( f(h_{E,g},h_{E,e}) \) [12],

\[
f(h_{E,g},h_{E,e}) = \sum_s \delta(h_{E,g} - h_{E,g,s}) \delta(h_{E,e} - h_{E,e,s}),
\]

where \( h_{E,\mu,s} (\mu = g, e) \) are the components of random field at the JT center with index \( s \), \( U_{E,\mu,s} \) are orbital operators. The explicit form of these functions can be obtained in cases when the nature of random field source are known and the law of low-symmetry field decreasing with increasing distance from the source are established. For example, the random field distribution function of deformational nature \( f(h_{E,g},h_{E,e}) \) for small concentrations of these field sources \( x_i \ll 1 \) has the following form

\[
f(h_{E,g},h_{E,e}) = f(h) = \frac{N_{JT}}{2\pi} \Gamma \left[ h_{E,g}^2 + h_{E,e}^2 + \Gamma^2 \right]^{-3/2},
\]

\[
\Gamma = \sum_i x_i \left[ V_E \frac{\partial \Omega}{\partial \mu} \right] \frac{1 + \sigma}{\Omega 1 - \sigma},
\]

where \( N_{JT} \) is the number of JT ions in crystal, \( V_E \) is the parameter of vibronic interaction of JT ion with JT active deformations, \( \Omega \) is the volume of the unit cell, \( \sigma \) is the Poisson coefficient. At high concentrations of random field sources \( x_i \sim 1 \) we have for \( f(h_{E,g},h_{E,e}) \)

\[
f(h_{E,g},h_{E,e}) = f(h) = \frac{N_{JT}}{\pi \Delta^2} \exp \left[ - \left( h_{E,g}^2 + h_{E,e}^2 \right)/\Delta^2 \right],
\]

where the dispersion \( \Delta \) is equal to the random field value at the nearest position to the source of such field, \( h \equiv (h_{E,g},h_{E,e}) \).

4.3. Phase transitions type. In absence of anharmonic interactions the model
describes the structure phase transitions of the second order, while transitions of the first order are described when anharmonic interactions are taken into account. The cubic crystals with the spinel structure, containing JT ions of the iron group (Mn$^{3+}$, Cu$^{2+}$, etc.) in octahedral sites can serve as an example of considered ferroelastics. The analogous model may be developed for the rare-earth metal compounds with the zircon structure (for example, TmVO$_4$). As a rule, the structure phase transitions of the first order occur in the cubic crystals while of the second order - in compounds with zircon structure.

In the theory of the cooperative Jahn-Teller effect the role of the order parameter is played by the deformation $\langle e_{E,\bar{g}} \rangle$, which is defined by the equation [6, 13]

$$E(e, h) = \left( V_E e + h_{E,\bar{g}} - V_2 e^2 \right)^{1/2} + h_{E,\bar{g}}^2 , \quad e = \langle e_{E,\bar{g}} \rangle .$$

Here $c_{JT}$ is the concentration of JT ions, the line over the expression means the configuration averaging with random field distribution function $f(h)$ (6)-(7), for simplicity the quantity $V_3$ is set to zero, $\langle...\rangle$ is the symbol of the quantum-statistical average. Typical temperature dependencies of the order parameter $e$ for different values of dispersion $\Delta$ are presented in Fig. 6.

The phase transition can be described analytically when the anharmonic parameter is small. Then, in the absence of random fields, the phase transitions are nearly of the second order and their characteristics describe by the following:

$$T_D \approx (V_E e_0)(1 + 6 p^2) , \quad \langle e_{E,\bar{g}}(T_D) \rangle \approx -6 p e_0 , \quad \langle e_{E,\bar{g}}(T = 0) \rangle \approx -(1 + 2|p|) e_0 \text{sign}(p) ,$$

$$p = \frac{V_2}{C_{JT}^0 \Omega} , \quad e_0 = c_{JT} \frac{|V_E|}{C_{JT}^0 \Omega} ,$$

where $T_D$ is the temperature of the structural phase transition, $e_0$ is the parameter, describing JT deformation at $T \to 0$K, the anharmonicity parameter $|p| << 1$.

![Fig. 6. Temperature dependencies of the order parameter.](image)

_The following dimensionless variables and values of parameter $p$ are used:_
\[ x = \langle e_{x3} \rangle / e_0, \quad t = k_B T (V_{e0} / 2), \quad \Delta (V_{e0}) = 0.05 (1), 0.25 (2), 0.5 (3), 0.7 (4); \quad p = -0.2. \]

4.4. Phase transitions in the case of competing interactions: cooperative JT interaction and random fields. Random crystal fields and dilution of JT systems by nondegenerate ions reduce the temperature of phase transition and value of the order parameter in the low-symmetry phase. The phase transition temperature \( T_D \) is equal to zero, when the critical value of the dispersion arrives at \( \Delta_{crit} \), which has the same order as the quantity \( V e_0 \)

\[
\frac{T_D}{\Delta} \approx A \left[ 1 - \frac{\Delta}{\Delta_{crit}} \right]^{1/3}, \quad \Delta_{crit} \approx \frac{\pi}{2} V e_0 \left( 1 - 2 p^2 \right), \quad A^3 \approx 2 \frac{\pi}{3}. \quad (10)
\]

The critical concentration of JT ions can be determined if the dependence of the dispersion as a function of \( c_{JT} \) is defined, e.g.: \( \Delta^2 (c_{JT}) = \Delta^2 (0) + (1 - c_{JT}) \Delta^2 \).

Such calculations have been performed for the solid crystal solution \( Tm_{1-x} Lu_x VO_4 \), where the critical concentration of JT ions \( Tm^{3+} \) is situated in the interval \( 0.18 < x_{crit} < 0.28 (x = 1 - c_{JT}) \) [14,15].

Quite analogous JT model was used for the analysis of the structure phase transitions in doped quasi two-dimensional crystal \( La_2 MeO_4 - \delta \) (Me = Cu, Co). Phase transition from the high-temperature tetragonal phase to the low-temperature octahedral phase occurs due to the rotation of the oxygen octahedron around the [110] axis and anti-phase rotations of oxygen octahedrons in the neighboring cells [16-17]. For the description of such phase transitions model of multi-well potential centers was developed on the basis of pseudo Jahn-Teller effect [18]. In this model the expressions for the order parameter and temperature of the structure transition \( T_D \) are similar to (9)-(10). If main contribution to the dispersion is made by one type of random field source, e.g. Sr impurities, the corresponding expressions for \( T_D \) are transformed to the form:

\[
T_D = T_D (x = 0) \left[ 1 - (2 / \pi) x / x_{crit} \right], \quad T_D >> \Delta; \quad T_D = (2 / \sqrt{\pi}) T_D (x = 0) \left[ 1 - x / x_{crit} \right]^{1/2}, \quad T_D < \Delta; \quad (11)
\]

where \( x_{crit} \) is the critical dopant concentration. The comparison of the theoretical dependence \( T_D(x) \) with experimental data is shown in Fig. 7. The resulting theoretical curves are in good agreement with experimental data without any fitting parameters.
Fig. 7. Concentration dependence of the transition temperature from tetragonal phase to orthorhombic phase in La$_{2-x}$Sr$_x$CuO$_{4-\delta}$.

5. Decomposition or immiscibility of degenerate systems

5.1. Nature of Decomposition. Now let us consider the phase transition such as decomposition of degenerate systems and analyze the origin of immiscibility (or rather weak miscibility) of different components in crystals with the cooperative JT effect. In such systems the substitution of JT ions by orbitally nondegenerate ions can lead to the separation into phases with higher and lower concentrations of JT ions. The relationship between structural phase transformations and phase transitions of separation type always takes place. This connection appears in JT crystals because in both cases the system has the tendency to decrease its free energy as a result of maximum possible splitting of degenerate states. The possibility of microscopic description of certain variety of immiscibility phase diagrams using simplest JT subsystem models with structural phase transitions (SPT) of first and second orders was shown in [19,20,21].

5.2. Model of mixture. Phase instability regions in quasi-binary system. The model of mixture in which free energy is determined by splitting of degenerate levels and the configuration entropy corresponds to chaotic distribution of JT ions in the mixture can be considered. In this case, the free energy of a quasi-binary system per structural unit can be written as follows:

\[
F = x_{JT} F_{JT} + F_{id} + C_{JT}^0 \frac{e^2}{2}, \quad F_{JT} = -k_B T \ln \left( 2 \cosh \left( \frac{E(e,h)}{k_B T} \right) \right),
\]

\[
F_{id} = T \left[ x_{JT} \ln x_{JT} + (1-x_{JT}) \ln (1-x_{JT}) \right].
\]

Expressions (12) allow one to calculate the chemical potentials $\mu_a$ (of components with JT ions), $\mu_b$ (of component with orbitally nondegenerate ions), and the exchange chemical potential $\mu = \mu_a - \mu_b$ of the quasi-binary system under investigation [22,23,24]:

\[
\mu = \frac{\partial F}{\partial x_{JT}} = \mu_a - \mu_b = F_{JT} + x_{JT} \frac{\partial F_{JT}}{\partial x_{JT}} + T \ln \left[ \frac{x_{JT}}{1-x_{JT}} \right],
\]
The standard equilibrium conditions can be used for the calculation of the coexisting phase concentrations of components over binodal:

\[
\mu_a^I = \mu_a^{II}, \quad \mu_b^I = \mu_b^{II},
\]

where indexes I and II correspond to the phases with tetragonal and cubic symmetry respectively. The absolute instability boundaries (spinodal) of the homogeneous solution are determined by known equation \[^{[25]}\]:

\[
\frac{\partial^2 F}{\partial x_{JT}^2} = \frac{\partial \mu}{\partial x_{JT}} = 0.
\]

Corresponding equilibrium phase diagram (binodal) as well as the spinodal curve are shown in Fig. 8 for the case of the structural phase transition of the second order. The critical point of mixing is occured at temperature \(k_B T_{crit} = \left| V E 0 \right| / 3 \) and concentration \(x_{JT crit} = 1/3\).

The results of calculation of the phase boundaries (binodal lines) for the cooperative JT systems with the first order structural phase transitions are shown in Fig. 9. In contrast to the system considered above, the critical point of mixing coincides with the structural phase transition temperature of the pure compound with JT ions \[^{[26]}\]. This phase diagram is in good qualitative agreement with the distinctive fragments of the experimental diagram for the stratified JT systems (see, for example \[^{[26]}\]).

Thus, it is shown that the model of degenerate system with substitutions allows one to describe the separation of such mixed systems into phases with higher and lower concentrations of degenerate centers in temperature range below \(T_{crit}\).

**Fig. 8.** Phase diagram of the quasi-binary JT systems with structural phase transitions of second order.

*Solid curve shows the bimodal one and dashed is the spinodal one.*

**Fig. 9.** Phase diagram of the quasi-binary JT systems with structural phase transitions of the first order.

**5.3. The systems with competing anharmonic couplings.** It is possible to show, that the class of the immiscibility phase diagrams described by JT model of interparticle interaction can be much larger. It follows, in particular, from the analysis of phase equilibriums of crystalline systems with two types of JT ions. The typical phase
diagrams of such mixed JT systems is presented in Fig. 10-11. These systems are considered with common type of anharmonic coupling (Fig. 10) and competing or alternative ones (Fig. 11) [27].

**Fig. 10.** The phase diagram of the quasi-binary JT system without competing anisotropy ($p_1 = 0.3$, $p_2 = 0.05$).

_Dashed curve at the top of the diagram shows line of structural phase changes in system with random distribution of two types of JT ions. The dashed-dotted line at the bottom of the diagram corresponds to the curve of absolute (spinodal) instability of “ferro” phase._

**Fig. 11(a,b).** The phase diagrams of the quasi-binary JT system with the competing anisotropy ($p = p_1 = -p_2 = 0.25$ (a), 0.35 (b)).

_Solid curves correspond to the phase coexistence boundaries. The dashed curve at the top of diagram shows the line of structural phase transitions in system with random distribution of two types of JT ions. The dashed-dotted curves at the bottom of diagrams show boundaries of the angular phase._

The cigar-shaped two-phase regions in the upper parts of the diagrams (Fig. 10-11) represent equilibria of the para–ferro type of cubic and tetragonal phases of the ferro elastic. In the lower part of the diagram the two-phase regions are associated with the equilibrium between ferrodistortive states with different types or signs of tetragonal distortion. It is interesting to note that the angular phase of the solid solution always lies inside the region of the two-phase immiscible state of the system. In other words, at equilibrium the decomposition of the solution is preferable in comparison with the formation of angular phase. One can expect, however, that in real solutions because of kinetic limitations the equilibrium state should not be realized and the tendency towards decomposition should be manifested in the formation of complexes with higher concentration of one or another components of the mixture at certain concentration range.

The phase diagrams presented at Fig. 11a,b illustrate the topology evolution of the phase diagram from one type to another: namely, from azeotropic to eutectic. Therefore the above analysis has shown that the phenomenon of limited solubility is a
characteristic feature of degenerate systems, and the JT model of cooperative inter-center interactions enables one to describe wide class of immiscibility phase diagrams. It is established that the topological features of the decomposition phase diagrams in JT and other similar crystalline systems can be deduced from anisotropic, anharmonic interactions [27].

5.4. Phase transitions in mixed Jahn-Teller systems with crystallographically non-equivalent sub-lattices. The phase diagrams of mixed crystalline systems with orbitally degenerate ions that can occupy two nonequivalent crystallographic sites were studied as well. It was shown that the Jahn-Teller interaction between the ions can influenced substantially the character of the distribution of the cations over the nonequivalent sub-lattices [28]. The corresponding preference energy is determined by the stabilization of degenerate electronic states in the cooperative or low-temperature, low-symmetry phase. Phase states of systems under consideration, the temperatures of structural and phase separation transitions as well as the topology of phase boundaries and absolute immiscibility regions depend on the character and conditions of the redistribution of mixed cations between the crystallographic sublattices as the temperature and system composition change to a great extent. The most interesting situation arises when the preference and the Jahn-Teller interaction energies compare and compete with each other for governing the distribution of the cations over sublattices in the low-symmetry phase. Spinel-like mixtures with the structural Jahn-Teller transitions to the ferrodistortion phase were chosen as the objects of study. The crystals were considered in which Jahn-Teller ions (for example, Mn$^{3+}$) are replaced by orbitally nondegenerate ions B$^{2+}$ = Zn$^{2+}$, Mg$^{2+}$ and other: 

$$A_{1-\eta}^2 B_{\eta}^{2+} \text{tet} + A_{2-2c-\eta}^3 B_{c-\eta}^{2+} A_{4-\eta}^{4+} \text{oct} O_{4-}^2.$$

Analogously to the expression (12) the free energy of considered system per structural unit can be written in the form:

$$F = \eta E_p + F_{JT} + F_{conf}, \quad e \equiv (e_E g),$$

$$F_{JT} = C_{JT} \frac{e^2}{2} + V_3 e^3 + k_B T (2 - 2c - 2\eta) \ln 2 \cosh \left( \frac{V_E e - V_2 e^2}{k_B T} \right),$$

$$F_{conf} = k_B T \left[ -2 \ln 2 + (1 - \eta) \ln (1 - \eta) + \eta \ln \eta + \frac{1}{2c - \eta} \ln (c - \eta) + (2 - 2c - 2\eta) \ln (2 - 2c + 2\eta) \right],$$

where $E_p$ is the preference energy of the substituting ions for occupying tetrahedral sites (the energy difference between the ions in tetrahedral and octahedral sites).

The contribution of Jahn--Teller ions to the Helmholtz free energy $F \equiv F(c, T)$ is represented in as the sum of three terms. The first describes the preference energy of the cations that are mixed for selecting definite (tetrahedral) coordination, the second is related to the removal of orbital degeneracy (splitting of degenerate levels), and the third is the configurational contribution corresponding to chaotic distribution of mixed cations over octahedral and tetrahedral crystallographic sites. This model is characterized by two order parameters. As usual, the role of the order parameter for structural Jahn-Teller transitions is played by the tetragonal deformation $e \equiv e(c, T)$ according to the equation (8). The second order parameter is the concentration of the substituting atoms in tetrahedral sites $\eta \equiv \eta(c, T)$. The equilibrium values of the specified long-range order parameter can easily be found by minimizing the Helmholtz energy (16) of the mixed crystalline system.
\[
\frac{\eta(1-c-\eta)^2}{(1-\eta)(c-\eta)^2} = \exp\left(-\frac{E_p}{k_BT}\right) \cosh^2\left(\frac{V_0e - V_2e^2}{k_BT}\right).
\] (17)

It is visible, that at positive sign of the value \(E_p\) the energy of preference and cooperative JT energy represent competing interactions. In general case, equations (8) and (17) must be resolved self-consistently at given temperature and substituting component content.

It was shown that two types of tetragonal states could take place in the low-temperature phase of such systems. Accordingly, there is additional first-order phase transition related to drop of the Jahn-Teller strain value and, as a result, the drop of \(\eta\) parameter (see Fig. 12 a-b) in the tetragonal phase. The structural phase transition of this type occurs if equilibrium distribution of the cations between the octahedral and tetrahedral sites is established and phase decomposition does not take place in the system. The region of the phase II existence increases while that of the phase I decreases as the parameter describing the ratio of the preferring energy to the Jahn-Teller one \(\varepsilon = \frac{E_p}{|E_{JT}(T \to 0K)|}\) grows.

The typical temperature dependences of parameters \(\eta(c, T)\) and \(e(c, T)\) are shown on fig. 13 for the case of the second order phase transition. It can be readily seen, that unusual behaviour of JT deformations take place with temperature. Namely, two-phase temperature intervals become much displayed: the first lies in low temperature region in which JT ion content in octahedral coordination remains practically as much as possible and at higher temperatures is the second where the change of cation distribution determines behaviour of temperature dependence of JT deformations. The behaviour of system close to the critical point in tetragonal phase (see Fig. 12b) is characterized by mean-field or Landau-type temperature dependence. We can mention in this connection the phase transitions of liquid-vapor or martensic transformations in In-Tl alloys as known analogies [29].

The example of the equilibrium phase diagram of the system under consideration which takes into account the decomposition to phases with higher and lower Jahn-Teller ion concentrations is shown in Fig. 13 for \(\varepsilon = 1.5\).

![Fig. 12. Phase diagram for model system with \(E_p/|E_{JT}(T \to 0K)| = 1.5\). It is illustrated the situation when the equilibrium distribution of cations over octahedral and tetrahedral sites is established as the temperature varies and the phase decomposition does not occur. I and II are the tetragonal phases and III is the cubic one. The cases a and b correspond to the phase transitions of the first and second orders.](image)
Fig. 13. The temperature dependences of the order parameters $\eta(c, T)$ and $e(c, T)$ for the case of crystals with the second order JT phase transition. ($E_p/|E_{JT}(T\to0K)| = 1.5$)

The examples of the equilibrium phase diagrams of the systems under consideration which take into account the immiscibility onto the phases with high and low Jahn-Teller ion concentrations is shown in Fig. 14 for the ratio $E_p/|E_{JT}(T\to0K)| = 1.5$. One can see that the single-phase low-symmetry state of the crystal corresponds to the tetragonal phase of type I.

Fig 14a-b. The equilibrium phase diagram (a) and concentration dependences of free energy of the mixed systems (b); $E_p > 0$: $E_p/|E_{JT}(T\to0K)| = 1.5$.

The meta-stable phase states of the above-mentioned Jahn-Teller systems are characterized by the presence of tetragonal phases of both types, I and II. The occurrence of the several types of Jahn-Teller phases in meta-stable states of substituted Jahn-Teller systems was described in monograph [26].

To summarize, the analysis of phase equilibria in multi-component Jahn-Teller systems performed above shows that Jahn-Teller interactions can substantially influenced the distribution of cations over non-equivalent crystallographic sub-lattices as well as the topology of equilibrium and meta-stable phase states. The formation of certain phase states of the systems under consideration should be determined to a great extent by the conditions of heating or cooling them during experiments. The model developed above enables one to describe the specific features of the phase diagrams as well as the nature of equilibrium and meta-stable states of the specified mixed Jahn-Teller systems.
5. Phase transformations of JT systems with competing charging configurations

Let us consider systems in which change of charging configurations on 3d ions or disproportionation reaction can take place. For example the crystal compound RbMn[Fe(CN)₆] has structural phase transition accompanied by electron transfer between ionic pairs Fe²⁺, Mn³⁺ on Fe³⁺, Mn²⁺ [30]; several oxides in which disproportionation processes take place over 3d ions of manganese or copper (for example 2Mn³⁺ ↔ Mn²⁺ + Mn⁴⁺). If one suppose, that corresponding recharging reaction results in the \( E_p \) energy change regarding to formula unit then the approach developed earlier can be generalized for these purposes. We shall consider an opportunity of 3d ions valences varying in above-mentioned JT systems on following example:

\[
\left( A^{2+}_{\text{tet}} [B^3_2]_{\text{oct}} O_4^{2-} \right) \leftrightarrow \left( A^{2+}_{1-\eta}, A^{3+}_\eta \right)_{\text{tet}} [B^{2+}_{2-\eta}, B^{2+}_\eta]_{\text{oct}} O_4^{2-}
\]

where \( B^{3+} \) is the JT ion, and value \((2-\eta)\) plays the role of concentration of JT ions. In comparison with expression (12) the configuration contribution into the free energy becomes for this case:

\[
F = \eta E_p + F_{JT} + F_{\text{conf}}, \quad F_{\text{conf}} = 3k_B T \left[ (1-\eta) \ln(1-\eta) + \eta \ln \eta \right].
\]  

(18)

It is obvious, that negative \( E_p \) value generates the competition between the cooperative JT interactions hopeful to stabilize JT state of ion \( B^{3+} \) and the preference ones \( \sim E_p \) responsible for adjustment of charging states between \( B^{3+} \rightarrow B^{2+} \) and \( A^{2+} \rightarrow A^{3+} \) octa to tetra. The temperature dependences of the order parameters \( \eta(T) \) and \( \epsilon(T) \) (calculated for this case as the most interesting) are shown on Fig. 14. For brevity the results are presented only for systems with structural phase transition of the second order.

![Fig. 14a-b. Temperature dependences of the order parameters \( \epsilon(T) \) and \( \eta(T) \) for values \( E_p/E_{JT}(T\rightarrow0\text{K}) = 0.5 \) (1) and 1.0 (2), correspondingly.](image)

It can be seen, that the presence of the competing above-mentioned interactions determines non-monotonic character of temperature dependences of the order parameters. The growth of JT deformation with temperature on a curve 2 of fig. 14 is caused by the increasing in concentration of JT ions at corresponding decreasing in number of pairs \( B^{2+}\rightarrow A^{3+} \). Fig. 15 illustrates the influence of recharging effects in cation subsystem onto the temperature of cooperative JT transition of the second order.
Fig. 15. The dependence of the cooperative JT phase transformation temperature from the ratio $E_p/|E_J(T→0K)|$.

Fig. 16. Dependence of the order parameter $\eta(T_D)$ at the transition point from the ratio $E_p/|E_J(T→0K)|$.

Therefore, the developed JT model of phase transformations allows us to analyze the effects caused by changing of valence state of the cation subsystem consistently with the description of structural phase transformations and the immiscibility phenomena. More detailed consideration of this question will be reported soon.

6. Conclusion.

Presented analysis of phase states of multi-component JT systems has shown, that JT interactions can influence to a large extent to the cation distribution over non-equivalent crystal sub-lattices and over possible electron transfer of 3d ionic pairs as well as to the topology of equilibrium and meta-stable phase states. Thus realization of one or another processes of phase formation in considered systems should be determined substantially by the rate of their heating or cooling during experimental preparation.

The results approved by the consideration of the immiscibility in JT systems are easily generalized on wider class of the condensed ionic systems. It is experimentally established, that dominating type of the nearest anion environment configuration of cations or character of their distribution over such configurations can vary significantly by the replacements in crystal or liquid ionic systems. In this connection the analysis of phase transformations such as restricted solubility or melting (in systems where as well as in JT solutions the effect of redistribution of configurations of the nearest anion environment with concentration or temperature takes place) has been carried out \([31-32]\). The idea of spent generalization is based on established for JT systems the interrelation of structural phase transformations with character of cation distribution on non-equivalent positions, including an example of dependence of energy of system from cation distribution. The configuration part of the free energy has traditional form and the internal energy has modeled by expression

$$E = E_p \eta + E_1 c + E_2, \quad E_p = E_p(c) = E_0(1 - \epsilon c), \quad \epsilon > 0. \quad (19)$$

where $E_0$, $E_1$, $E_2$ – energy parameters which can be expressed through anion and cation energies in tetrahedral and octahedral positions.

It was established that decreasing temperature leads to specific concavity of the free energy dependence upon concentration which is concerned directly with the presence of decomposition region. Therefore the internal energy of the solution might have positive, negative and changing sign deviations from ideal behavior (Fig. 17-18).
Corresponding calculations of absolute instability regions and equilibrium phase diagrams of considered ionic systems for both types of the condensed states have been performed. Within the framework of this qualitatively simple model it was possible to analyze relationship between the character of nearest cationic environment and thermodynamic properties of mixture. It was established that the sign-change of the cation preference energy to certain coordination is accompanied by occurrence of the absolute (spinodal) instability region of the solution and the miscibility gap on phase diagram of these mixed ionic systems. The obtained results have even broader range of applications. It is enough to specify calculations of immiscibility region in spinel systems NiFe₂O₄ - NiCr₂O₄ [33] and estimations of the configuration contribution in melting entropy [32]. We can see many examples confirming such point of view.

We hope that the developed microscopic theory of JT system will provide a model basis for calculations of phase equilibriums of structural, thermodynamic, magnetic and other properties of composite systems with various types of the degenerate states.

*The work was supported by Russian Foundation for Basic Research (grants 04-03-32120 and 04-03-32390).*

**REFERENCES**


17. Plakida N.M. High temperature superconductors [in Russian]. Moscow: 
18. Kaplan M.D., Khomskii D.I. The peculiarities of electronic 3d-states and 
structural transition in high temperature superconductors of La2CuO4 type. Pis’ma 
Kaplan M.D. Symmetrical aspects of the cooperative pseudo Jahn-Teller effect in 
Interactions: Jahn-Teller Effect in Crystals and Molecules, Eds. M.D.Kaplan and 
analysis of two-phase region “spinel-hausmannite” in solid solutions Mn3-cBeO4 
22. Prigogine I., Defay R. Chemische Thermodynamik. Leipzig: Deutsche Verlag fur 
Grundstoffindustrie. 1962.
24. Zhdanov G.S., Khudzhua A.G. Lectures in solid state physics: principles of 
26. Balakirev V.F., Barhatov V.P., Golikov Yu.V., Maisel S.G. Manganites: 
2000.
type in systems with orbital degeneracy. Low Temperature Physics. 2002. V. 28, 
850–859.
Transitions in Mixed Jahn--Teller Systems with Crystallographically 
29. Hultgren R, Desai P, Hawkins D, Gleiser M, Kelley K. Selected values of the 
30. Hiroko Tokoro, Shin-ichi Ohkoshi, Tomoyuki matsuda, Kazuhiro Hashimoto. A 
Large Thermal Hysteresis Loop Produced by a Charge-transfer Phase Transition in 
Ionic Systems with a Varied Coordination of Cations. Reports of Academy of 
Immiscibility in condensed ionic systems with competing coordination of cations. 
Melts (in Russian), № 2, 2004, c. 40-49
33. Ziemniak S.E., Gaddipati A.R., Sander P.S. Immiscibility in the NiFe2O4 - 
NiCr2O4 spinel binary. Journal of Physics and Chemistry of solids. 2005, 66, 
1112-1121.