Based on the vibronic theory of heteroligand complexes a new model Hamiltonian is proposed for the ferroelectrics of KDP (KH$_2$PO$_4$) family. In local representation three items of this Hamiltonian describe the H-bond protons, the potential energy of lattice’s oscillators and the coupling of these two subsystems respectively. In Ising form, convenient for numerical calculations, the Hamiltonian offered includes explicitly the characteristics of the electronic structure as well as the orbital vibronic constants of the AO$_4$ tetrahedra. The Ising version of theory is then applied to numerical studying of some questions for KDP thermodynamics.

**Introduction**

Recently [1,2 and references therein] we demonstrated that vibronic theory of heteroligand molecular systems (VTHS) may be applied in the microscopic theory of H-bonded ferroelectrics like KDP and squaric acid H$_2$C$_4$O$_4$. In present work we use this approach to handle some thermodynamic problems for the KDP family materials. With the account for proton-lattice coupling (PLC) on the base of four-particle Bethe cluster approximation we consider the PLC contribution to the critical temperature $T_c$ value for KDP, this family forefather.

![Fig.1. KDP crystal structure](image)
Two subsystems in KDP-like materials.

The space structure of the KDP-like ferroelectrics (FE) $\text{MH}_2\text{AO}_4$ (M=K,Rb; A=P,As) (Fig.1) clearly includes two main subsystems – a “non-hydrogen” frame that is formed by mutually bounded tetrahedral anionic complexes $\text{AO}_4$ and a set of hydrogen atoms on the symmetric double-well H-bonds $\text{O–H} \cdots \text{O} \leftrightarrow \text{O} \cdots \text{H–O}$, that connect the $\text{AO}_4$ tetrahedra. Two equilibrium positions of H-atom at each H-bond are close to the minima of the proton’s adiabatic potential (here and below for brevity’s sake we say ‘hydrogen’ and ‘proton’ meaning hydrogen as well as deuterium or its nuclei). We don’t include the M atoms in the non-hydrogen subsystem although it is possible, see [3,4]. From structural chemistry viewpoint these atoms may play most probably the role of electron donors for the $\text{AO}_4$-framework rather than of complex-forming agents like P and As, thus for materials at hand we handle the PLC only with due account taken of protons and $\text{AO}_4$-tetrahedra.

Protons’ mobility for the FE considered (according to conventional theory [5,6]) is related to their tunneling between the minima of the potential curves. Thus several (not more than four) H atoms may be situated at the nearest sites around each $\text{AO}_4$-tetrahedron. Hence each oxygen atom in the crystal may be ascribed to one of two kinds: O (-) or else O(...) in dependence on the character of its bonding with the nearest hydrogen – covalent (O-H) or hydrogen (O...H). Then any $\text{AO}_4$-tetrahedron may be considered as a heteroligand complex $\text{AO}(-)_{k}O(...)_{4-k}$ ($k=0,1...4$) and be treated by means of the VTHS approaches.

VTHS basics.

The VTHS [2] treats the heteroligand complex $\text{AL}_N^k\text{XY}…\text{Z}$ by means of the second-order perturbation theory as the derivative of the homoligand $\text{AL}_N$ and for our purposes one may restrict itself with the case of closed electron shells for both complexes. Then the lowest energy surface $E(Q)$ of the adiabatic potential (APES) for the heteroligand complex has the form

$$E(Q) = S_0 + \frac{1}{2} \sum_k k \hat{Q}_k^2 - 2 \sum_{n,m} S_{nm}^2 \frac{\omega_{nm}}{\omega_{nm}} - 4 \sum_{n,m} S_{nm} A_{nm}' \frac{\omega_{nm}}{\omega_{nm}} \hat{Q}_n \hat{Q}_m.$$

(1)

Here $Q = \{Q_i\}$ is the set of normal (or symmetry) coordinates for the $\text{AL}_N$ system, $k$, and $A_{nm}'$ are its force constants and orbital vibronic constants, written in the basis of occupied (n) and vacant (m) molecular orbitals (MO) of the non-perturbed complex $\text{AL}_N$ and $\omega_{nm}$ -
energy gaps between these MO. Notations $S_{nm}$ in (1) respond to matrix elements in the MO basis for the “substitution operator” $H_S$ [2], that defines the influence of ligand substitution and $S_0$ is the first-order perturbation term. One can easily find from (1) the main parameters of the APES considered – its minimum coordinates $Q_f$ and the depth $E(Q_f)$ of this minimum - with regard to the analogous parameters of unperturbed homoligand system:

$$Q_f^i = \frac{4}{k_{iv}} \sum_{n,m} S_{nm} A_{nm}^v \omega_{nm}^{-1}.$$  \hspace{1cm} (2)

$$E(Q_f) = S_0 - 2 \sum_{n,m} \frac{S_{nm}^2}{\omega_{nm}} - 8 \sum_v k_v \left( \sum_{n,m} \frac{S_{nm} A_{nm}^v}{\omega_{nm}} \right)^2 ,$$  \hspace{1cm} (3)

where relation (2) describes the geometry change of homoligand complex upon complete or partial ligand replacement and (3) – the corresponding change of its potential energy. To use (2), (3) we need to determine $S_{nm}$. Let’s adopt [2] that the replacement of an atom in the complex is equivalent to the replacement of the AOs’ energies of the eliminated atom by the AO’s energies of the atom-substituent. Then one has for $S_{nm}$

$$S_{nm} = \sum_i c_{in} c_{im} \Delta \alpha_i.$$  \hspace{1cm} (4)

where $c_{in}, c_{im}$ are the coefficients at the $i$-th AO in $n$-th and $m$-th substituted atom MO and $\Delta \alpha_i$ - the change of AO’s orbital energy (one-center Coulomb integral) upon this replacement. Let’s mention in this connection that comparison with experiments confirms the use of (2) and (4) to describe quite well the observed geometry changes upon ligands’ substitution [2].

**The use of VTHS for KDP**

In KDP-like FE any proton distribution determines a definite distribution of two kinds of oxygens over the lattice i.e. over the vertices of every AO$_4$ tetrahedron. The «inner» potential energies of such complexes are determined by (3) if compared with standard unperturbed tetrahedral complex in the hypothetic “protophase”, where all protons are situated at the centres of H-bonds. Then it seems reasonable to consider the potential energy $H$ of the macroscopic FE pattern to be equal to the sum of the “inner” energies of the tetrahedral complexes [1,7]. In so doing one should keep in mind that two oxygens of different kinds
always participate in each H-bond. This reason restricts the composition of neighbouring complexes and removes the first-order terms as $S_0$ in (3) and (1) from the Hamiltonian. Another important property of $H$ deals with $S_{nm}$ matrix elements in relations (2), (3). It seems clear that proton transfer from the H-bond centre to the position correspondent to O(-) and O(...) formation at the ends of this bond influence oppositely the levels of the AOs for these two oxygens. Thus the valence levels of oxygens through the whole crystal depend on proton distribution. In particular, it concerns the $\sigma$-orbitals of O atoms that take part in the bonds A-O(-) and A-O(...). For these AO’s the changes of the Coulomb integrals may be written as:

$$\Delta \alpha_i = |\Delta \alpha| \sigma_i^z$$

(5),

where $\sigma_i^z = \pm 1$ are the discrete dichotomic variables (pseudospins) [1].

Local representation of the Hamiltonian.

The relations above yield in two different forms of $H$. The first one may be obtain by summation of (3) for all AO$_4$ tetrahedra (t) of the KDP pattern over the points of the APES’es minima. Taking into account the H-bonds connections between the tetrahedra and using the formulae (3), (4) and (5) then gives [7]

$$H = -\frac{1}{2} \sum_{t,\alpha \neq \beta} J_{\alpha\beta} \sigma_{\alpha t}^z \sigma_{\beta t}^z + \frac{1}{2} \sum_{t, \nu} k_{\nu} \sigma_{\nu t}^z - \sum_{l, \nu, \alpha} k_{l, \alpha \nu} Q_{\nu t}^3 \sigma_{\alpha t}^z.$$  

(6)

It is seen from (6), that the obtained Hamiltonian includes three terms. The first one deal with the proton subsystem of the material, the second one characterises the harmonic potential energy of the ‘lattice’ described. Finally the third term contains the products of pseudospins and oscillator variables and responds to PLC in its local form [3,4]. The obtained form of $H$ clearly demonstrates that the use of VTHS leads ‘automatically’ to the account of PLC with resulting Hamiltonian (6) describing coupled proton-lattice system. Here let’s mention that relation (6) resembles that suggested for KDP in the frames of local single-mode model [3,4]. The difference is in the fact that the model considered here is not supposed to be single-mode one and admits the presence of several distortional modes describing the A(=P or As) atoms displacements not only along z axis but maybe along all three axes of the crystal lattice. Besides the relations obtained do not include indefinite constants thus all terms in the rhs of (6) may be calculated by quantum chemistry methods.
The Ising model for Hamiltonian.

An Ising-type representation [5,6] may be constructed for $H$ by the following way. Let’s write the (potential) energy of the macroscopic KDP-type crystal as the sum of inner potential energies $E_t$ of the AO$_4$ tetrahedra:

$$H = \sum_t E_t$$

(7),

and after it let’s use for each $E_t$ relations (3), (4) and (5).

Fig. 2. Numeration of O and H atoms in the PO$_4$ tetrahedron

Then an expression for $H$ arises:

$$H = - \frac{1}{2} \sum_{(i,j)} J_{ij} \sigma_i \sigma_j,$$

(8),

where $J_{ij}$ are the Ising model interaction parameters. In the theory of KDP-like FE one usually takes into account only two of them, the largest by absolute value, denoted as U and V [5,6]. Here U describes the effective pairwise interaction between two ‘upper’ or two ‘lower’ protons connected with a chosen tetrahedron, and V – the interaction between one ‘upper’ and one ‘lower’ proton (see Fig. 2), while the explicit relations for U and V are the following [7]:

$$U = c^2_a \Delta \alpha^2 \left( \frac{l^2_b}{4\omega_\perp} \frac{l^2_e}{2\omega_\parallel} + \frac{l^2_b}{\omega_\perp^2 k_\perp} \frac{l^2_e A^2_\parallel}{\omega_\parallel^2 k_\parallel} - \frac{2l^2_e A^2_\parallel}{\omega_\parallel^2 k_\parallel} \right)$$

(9)
\[ V = c^2 \Delta \alpha^2 \left( \frac{l_b^2}{4\omega_\perp} + \frac{l_b^2 A_\perp^2}{\omega_\perp^2 k_\perp} \right) \]  

(10)

Symbols \( \omega_\parallel \) and \( \omega_\perp \) denote the energy gaps \( e-a^* \) and \( b-a^* \) between the \( e, b \) MO’s (HOMO) and \( a^* \) MO (LUMO) for the \( AO_4 \)-tetrahedron with \( S_4 \) symmetry in protophase, see Fig.3. The electronic structure of a tetrahedron is also characterised in (9) and (10) by the \( |\Delta \alpha| \) value and the coefficients \( l_e, l_b, c_a \) of the symmetrized oxygen AOs in the MOs. Here the values \( k_\perp, k_\parallel \) and \( A_\perp, A_\parallel \) denote force constants and orbital vibronic constants [8] of the tetrahedron responding to its central atom displacement perpendicular to xy plane (\( \perp \)) or within this plane (\( \parallel \)). Then in accordance with (9), (10) each Ising parameter contains two components:

\[ U = U_{el} + U_{vib} \quad V = V_{el} + V_{vib}, \]  

(11)

one of them depends only on the MOs of the tetrahedron in protophase while the other however depends on force and vibronic constants as well due to the PLC account.

Fig.3. The MO diagram for PO\(_4\) unit in protophase; \( \sigma \) – MO approximation

**Numerical data for Ising parameters**

To use the relations (9)-(10) for the analysis of the thermodynamics of KDP-like materials we need the values of \( U \) and \( V \) together with its electronic (el) and vibronic (vib) components. In fact we’ve already calculated earlier [9] these these \( U \) and \( V \) by means of \textit{ab initio} methods
using different types of clusters, modelling the space structure of KDP/DKDP in protophase. The details of the geometry for the clusters were borrowed from neutron diffraction data [10] for an averaged paraelectric (disordered) phase, its structure is believed to reproduce all possible interactions in crystals, PLC including. The results of the most reliable calculations are collected in Table 1.

Table 1. The Ising parameters (all in K) for KDP and DKDP evaluated by cluster MP2 calculations *.

| Parameter | KDP | | DKDP | |
|-----------|-----|--|-----|--|
| Basis | \(-U\) | \(V\) | \(-U\) | \(V\) |
| cluster \([P[O-H...OPH]_{4}]^{+}\) | | | | |
| 6-311+G(d,p) | 311 | 353 | 444 | 504 |
| 6-311+G(2d,2p) | 302 | 349 | 422 | 488 |
| 6-311++G(2d,2p) | 301 | 348 | 422 | 488 |
| cluster \([P[O-H...OP(OH)]_{4}]^{+}\) | | | | |
| 6-311+G(d,p) | 301 | 345 | 430 | 491 |
| 6-311+G(2d,2p) | 296 | 343 | 412 | 477 |
| 6-311++G(2d,2p) | 295 | 342 | 412 | 477 |

* results for three largest basis sets are presented

The el- and vib- components values for \(U\) and \(V\) may be obtained in principle directly from (9), (10) though it requires additional calculations of MOs and of force and orbital vibronic constants. However the useful estimates for these values may be found much easier. As shown in [7] the \(V_{\text{vib}}\) value may be estimated from the data [10] on relative displacement of phosphorous atom along z axis upon the temperature variation at the vicinity of the point of FE transition. In particular, for KDP the correspondent estimate of \(V_{\text{vib}}\) gives the value 120K and, if compared with Table 1, yields in the ratio \(V_{\text{vib}}/V \approx 0.35\).

Although there is no similar way to estimate \(U_{\text{vib}}\) (as the FE transition causes the P displacement namely along z and not along the orthogonal axes), it seems conceivable that

\[
U_{\text{vib}}/U \approx V_{\text{vib}}/V
\]

This approximated equality is bolstered by the following reasoning. In the protophase considered any AO\(_4\) tetrahedron (Fig.2) with actual S\(_4\) symmetry is in fact close to an ideal form with T\(_d\) symmetry, its three local axes \(x, y, z\) being almost equivalent. As a result, one-electron b,e levels arise due to only slight splitting of triple-degenerated level t\(_2\) into double-degenerated e and non-degenerated b, that leads to relation (12) (see also [11]).
Proton tunneling and $T_c$ calculation.

The Ising parameters determination are necessary but not enough to study the role of PLC in thermodynamics of H-bonded FE, as one should also take into account the tunneling of protons along H-bonds. In the FE microscopic theory [5, 6] it is done by the replacement of classical Hamiltonian (8) by its quantum analogue:

$$H = -\Omega \sum_i \sigma_i^+ - \frac{1}{2} \sum_{i<j} J_{ij} \sigma_i^+ \sigma_j^+.$$  (13)

Here $\Omega$ is the tunneling parameter describing the frequency of proton quantum motion along the H-bond and $\sigma_i^+, \sigma_i^-$ are treated as Pauli operators for the spin $\frac{1}{2}$ that act on the wavefunctions of protons, localized at the minima of its adiabatic potential along $i$-th H-bond. Then for $T_c$ calculation the numerical procedure may be applied [12] that uses Bethe cluster method with tunneling and allows to obtain $T_c$ value as a function on $\Omega$ and Ising parameters utilized.

PLC influence on critical temperature

The results of such calculation for KDP are shown in Fig.4 for three cases including the simplest one that takes into account only the nearest-neighbours interactions of pseudospins, i.e. at $\gamma=0$. For Ising parameters the values $U=-300K$, $V=345K$ were used, calculated ab initio by MP2 procedure (see Table 1) and for tunneling parameter the value $\Omega=370K$ [13] was adopted.

![Fig.4. $T_c$(KDP) versus $\Omega$ using $U = -300K$, $V = 345K$ as the Ising parameters.](image)
As we see from Fig.4 the corresponding $T_c$ is about 150K that is in reasonable agreement with the experimental data (123K) thus corroborating the use of the averaged diffraction data of the paraelectric phase to obtain the parameters of (13).

To estimate in theory the PLC influence over $T_c$ value an analogous calculation ($\gamma=0$) was performed with the U, V values substituted by the values which it would have had without PLC, i.e. by the pure electronic components $U_{el} = U - U_{vib}$, $V_{el} = V - V_{vib}$. The results are presented at Fig.5 and suggest the absence of the structural phase transition into an ordered phase due to its complete suppression by tunneling. Hence Figs.4 and 5, taken together, evidence that both the presence of the ferroelectric phase transition in KDP and the value of its critical temperature are determined mainly by PLC.

![Graph showing T_c(KDP) versus Ω using U_{el}, V_{el} components as the Ising parameters.](image)

Up to now we proceeded from assumption that the (averaged) geometry of the paraelectric phase reflects completely all the interactions in the materials considered, including PLC. Let’s discuss here an opposite situation – what if the paraelectric phase geometry doesn’t reproduce the PLC effect so the paper [9] and Table 1 present in fact namely electronic components of the Ising parameters. If so, in accordance with (11), complete U, V values are to be obtained by adding $U_{vib}$, $V_{vib}$ to the data from Table 1. The corresponding calculations for KDP (Fig.6, $\gamma=0$) give however for $T_c$ the value about 300K that overestimates at least twice both the
experimental data and our result obtained above. Similar but less drastic variations of $U$, $V$ values and $T_c$ estimate are to be observed also if the geometry of paraelectric phase reflects PLC partially. Thus one may conclude that initially adopted assumption about “complete reflection” of PLC by the structure of paraelectric phase of KDP yields (within the frames of model used) in the best approximation of the theoretical estimate for $T_c$ to the experimental value.

**Fig.6.** $T_c$(KDP) versus $\Omega$ treating $U = -300K$, $V = 345K$ as electronic components of the Ising parameters. Conclusions above are made by the examination of the curves from Figs.4-6 with $\gamma = 0$.

Meanwhile it is clear that these conclusions remain valid also for $\gamma = \pm 15K$ i.e. despite some variations of the Ising parameters set due to approximate modeling of non-neighboring pseudospin couplings, tangible influencing the Hamiltonian (13). It is seen from Fig. 4 that $\gamma = 15K$ leads to the worsening of agreement between the calculated $T_c \approx 150K$ and the experiment. At the same time $\gamma = -15K$ slightly improves this agreement that maybe indicates some preference of ‘negative contribution’ in long-range coupling of pseudospins for KDP alike mentioned earlier in [14].

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