LONGITUDINAL FIELD INFLUENCE ON THE PHASE TRANSITION AND PHYSICAL PROPERTIES OF THE KH$_2$PO$_4$ FAMILY FERROELECTRICS

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Abstract

We verify whether the previously developed model of a KD$_2$PO$_4$ crystal, with the shear strain $\varepsilon_6$ taken into account, is able to describe the longitudinal electric field $E_3$ influence on the KH$_2$PO$_4$ family ferroelectrics. Major effects of the strain $\varepsilon_6$ are splitting of the Slater energies of the short-range correlations and the effective field created by piezoelectric coupling. Calculated $T_C - E_3$ phase diagrams, field dependences of polarization, susceptibility, and elastic constant of deuterated KD$_2$PO$_4$ and pure KH$_2$PO$_4$ well accord with the available experimental data. For a consistent description of all dielectric and piezoelectric characteristics of the crystals, phonon degrees of freedom must be taken into account.

1 Introduction

Studies of ferroelectric crystals behavior under different external factors such as pressure or electric field provide an important information about the phase transition mechanisms in these crystals as well as of their dielectric and piezoelectric responses. Thus, studies of the transition temperature dependence on the geometry of a hydrogen bond revealed a universal dependence of the transition temperature on the distance between equilibrium proton (deuteron) positions on a bond in several crystals of the KH$_2$PO$_4$ family [1, 2]. Studies of the effects produced by external fields conjugate to the order parameter (shear stress $\sigma_6$ and electric field $E_3$ in these crystals) permit to elucidate the role of structural changes occurring at the phase transition, such as appearance of the shear strain $\varepsilon_6$.

In our recent paper [3] we modified the proton ordering model for deuterated KD$_2$PO$_4$ type crystals so that the shear strain $\varepsilon_6$ was taken into account. We obtained a fair agreement of the theoretical results for associated with strain $\varepsilon_6$ dielectric, elastic, and piezoelectric characteristics of KD$_2$PO$_4$ (piezoelectric constants $d_{36}$, $e_{36}$, $h_{36}$, $g_{36}$, elastic constants $c_{P66}^E$, $c_{E66}^P$ and compliances $s_{P66}^E$, $s_{E66}^P$, and dielectric permittivity $\varepsilon_{33}$) with the relevant experimental data.

A consistent taking into account of the changes caused by the strain $\varepsilon_6$ in the system symmetry revealed that this strain splits the energies of short-range deuteron configurations. Thus, the lowest level of the so-called up and down configurations and the energies of lateral and single-ionized configurations are split. Splitting of up/down and ionized configurations gives rise to single- and three-particle spin terms in the short-range Hamiltonian. Our numerical calculations have shown that by fitting to experimental data one is not able to determine the magnitude of the splitting of up/down configurations $\delta_{36}$, since if a certain ratio between $\delta_{36}$ and the magnitude of piezoelectric internal field $\psi_6$ [4], the experiment is well described in a rather wide range of $\delta_{36}$. A good agreement with the experimental data for temperature behavior of the above mentioned physical characteristics of KD$_2$PO$_4$ is also obtained in a simplified version of the model [5], where we neglected splitting of the up/down and ionized configurations and took into account only splitting of lateral configurations and piezoelectric internal fields.

In [6] we show that the transition temperature of KD$_2$PO$_4$ type crystals is increased by the stress $\sigma_6$, and the jumps of the order parameter are decreased. At the constructed phase diagram there are two
critical points where the phase equilibrium curves terminate. Stresses above critical smear off the phase transition and lead to smooth temperature dependences of polarization and strain. Correspondingly, the peak values of those characteristics of the crystal that have peculiarities at the transition points (the longitudinal dielectric permittivity, compliance \( s_{\text{L}} \), piezomodules \( d_{36} \) and \( e_{36} \), and specific heat) increase with stress. These peaks are the highest at the critical stress, whereas at stresses above critical their temperature curves are smooth. Such a behavior is peculiar to the ferroelectrics with the first order phase transition in external fields conjugate to the order parameter.

Studies of the stress \( \sigma_6 \) influence on the \( \text{KH}_2\text{PO}_4 \) family crystals, though interesting they are, remain quite abstract, since their experimental verification appears to be very difficult. Instead, measurements in electric fields are a more accessible experimental technique. The longitudinal electric field \( E_3 \) should be considered, since its influence on the physics of the phase transition the relevant characteristics of the \( \text{KH}_2\text{PO}_4 \) type crystals is analogous to the influence of the shear stress \( \sigma_6 \) and is well studied experimentally.

In this paper we shall show that the developed theory is capable, without introducing any additional fitting parameter, of describing the behavior of the phase transition, polarization, and other characteristics of a deuterated KD\(_2\)PO\(_4\) in electric field \( E_3 \), and attempt to apply this theory also for the description of the relevant characteristics of a pure \( \text{KH}_2\text{PO}_4 \), with tunneling neglected.

### 2 Phenomenological analysis

Strictly speaking, for the \( \text{KH}_2\text{PO}_4 \) type crystals a expansion of thermodynamic potential \( G \) in polarization \( P_3 \) and strain \( \varepsilon_6 \)

\[
G = G_0 + \frac{1}{2} \left( a_1 P_3^2 + a_2 P_3 \varepsilon_6 + a_3 \varepsilon_6^2 \right) + \frac{1}{4} \left( b_1 P_3^4 + b_2 P_3^3 \varepsilon_6 + b_3 P_3^2 \varepsilon_6^2 \right) + \\
+ \frac{1}{6} \left( c_1 P_3^6 + c_2 P_3^5 \varepsilon_6 + c_3 P_3^4 \varepsilon_6^2 \right) - \bar{v} E_3 P_3 - \bar{v} \sigma_6 \varepsilon_6
\]  

is the most consistent. It allows one to perform the analysis for the both fields conjugate to the order parameter – electric field \( E_3 \) and shear stress \( \sigma_6 \). Then the relevant order parameter, after which the phase transition takes place is a certain linear combination of \( P_3 \) and \( \varepsilon_6 \). To determine it, a linear transformation \((P_3, \varepsilon_6) \rightarrow (\xi, \zeta)\) is performed, which diagonalizes the quadratic form \((P_3, \varepsilon_6)\) in the expansion 2.1. Among \( \xi \) and \( \zeta \), the relevant order parameter is that one, which prefactor in 2.1 vanishes at the Curie point.

However, in practical calculations for the only experimentally accessible field conjugate to the order parameter – the electric field \( E_3 \), one usually uses the expansion in powers of polarization \( P_3 \)

\[
G = G_0 + \frac{d'(T - T_0)}{2} P^2 + \frac{b}{4} P^4 + \frac{c}{6} P^6 - EP,
\]  

and the higher order terms can be also taken into account. For the sake of simplicity, in this section we omit indices near polarization \( P_3 \) and field \( E_3 \).

In the vicinity of the transition temperature at \( E = 0 \), the thermodynamic potential \( G(P) \) has three minima \( P_{1,3}^2 = (-b \pm \sqrt{b^2 - 4ac})/2c \) and \( P_2 = 0 \), the depths of which become equal at the transition point. Hence, the temperature of the first order phase transition \( T_{C0} \) at \( E = 0 \) is found from the conditions

\[
\frac{\partial G}{\partial P} = 0, \quad G(P_{1,3}) = G(0),
\]

that are equivalent to

\[
3b^2 = 16ac, \quad T_{C0} = T_0 + \frac{3b^2}{16ca'},
\]

The extremum points of the thermodynamic potential \( G(P) \) at \( E \neq 0 \) are given by the equation

\[
E = aP + bP^3 + cP^5.
\]  

(2.3)
Among five solutions of this equations, two correspond to maxima, and three \( P_1 < 0, \) \( P_2 \simeq 0, \) and \( P_3 > 0 \) correspond to minima of \( G(P) \). From the condition

\[
G(P_2) = G(P_3) \quad \text{at} \quad E > 0, \quad G(P_1) = G(P_1) \quad \text{at} \quad E < 0,
\]

in a linear in \( E \) approximation we find a field dependence of the first order phase transition temperature (the phase equilibrium curve)

\[
T_C = T_C^0 - E \frac{12c}{7a'b} \sqrt{\frac{4c}{-3b}}.
\]

### 2.1 Critical point. Experimental measurements

The phase equilibrium curves (the first order phase transition lines) terminate in two critical points, which coordinates \( (\pm E^*, T^*) \) follow from the thermodynamic conditions – equation of state and the equilibrium condition

\[
\left( \frac{\partial G}{\partial P} \right)_{E} = 0, \quad \frac{\partial E}{\partial P} = 0, \quad \frac{\partial^2 E}{\partial P^2} = 0.
\]

In these points a difference between the truly ferroelectric and pseudo-“paraelectric” with a non-zero polarization \( P_3 \) and strain \( \varepsilon_6 \) phases disappears, so that the transition from one to the other takes place smoothly without jumps of the thermodynamic quantities.

Experimentally the coordinates of the critical points are usually found using the phenomenological theory, by measuring in some way the coefficients of the Landau expansion. To determine the critical field \( E^* \) and temperature \( T^* \), the following formulas are used \[6\],

\[
E^* = a^* P^* + b(P^*)^3 + c(P^*)^5 + d(P^*)^7;
\]

\[
T^* = T_0^* + \frac{a^*}{a'} = T_0^* - \frac{3b(P^*)^2 + 5c(P^*)^4 + 7d(P^*)^6}{a'},
\]

where the higher order terms in the expansion are also taken into account, and \( P^* \) depends on the number of terms in the expansion \[6\]

\[
P^* = \frac{5c}{2d} \left[ \sqrt{1 - \frac{63}{25} \frac{bd}{c^2}} - 1 \right], \quad c \neq 0, d \neq 0;
\]

\[
P^* = \frac{-b}{7d}, \quad c = 0, d \neq 0;
\]

\[
P^* = \frac{-3b}{10c}, \quad c \neq 0, d = 0.
\]

The simplest is to find the coefficient \( a' \), which is nothing but the inverse Curie constant of a crystal. The coefficients at higher terms in the expansion are determined by analyzing the field and temperature dependences of the crystal polarization. Usually, the analysis of the so-called \( \Gamma \)-plots is performed. If one restricts the Landau expansion by the \( P^6 \) term, then from the equation for field \( (2.3) \) it follows \[10\], that the dependence of the quantity

\[
\Gamma(P^2) = \frac{E - aP}{P^3} = b + cP^2
\]

on \( P^2 \) must be linear and independent of the magnitude of the applied field. The intersection of this line with the ordinate axis \( (P^2) \) gives a value of \( b \), and its slope gives the coefficient \( c \). Hence, by analyzing the experimentally measured dependence \( \Gamma(P^2) \) one is able to determine two coefficients of the Landau expansion.

When the dependence \( \Gamma(P^2) \) is closer to a quadratic one rather than to linear one, we should neglect the term \( cP^5 \) in the Landau expansion and take into account the term \( dP^7 \), instead. Then the dependence

\[
\Gamma(P^4) = \frac{E - aP}{P^3} = b + dP^4
\]

must be linear.
Another, somewhat more sophisticated method of determination of the Landau coefficients was proposed by Schmidt [6]. Instead of the Γ-plots, the so-called isopols – lines of a constant polarization in the (E, T) plane should be analyzed. From (2.3) it follows that
\[ T = \frac{E}{a'P} + T_0 - \frac{bP^2 + cP^4}{a'}, \]
that is, the dependence \( T(E) \) at constant polarization is linear. Approximating the experimental paraelectric isopols, one can find the coefficient \( a' \) from the expression
\[ a' = \frac{1}{P} \left( \frac{\partial E}{\partial T} \right)_P. \]
It should be noted that at the first order phase transition the isopols do intersect, whereas at the second order phase transition they do not. Therefore, this analysis permits one to determine the order of the phase transition and estimate the coordinates of the critical point (the point where the order of the phase transition changes), if one exists.

Unfortunately, the described method of determination of the critical point coordinates according to the Landau coefficients does not allow to find more or less trustworthy values of the critical quantities. In Table 1 we presented the measured in different papers Landau coefficients and calculated coordinates of the critical points for KH₂PO₄ (the Table is taken from [6]). All the present results agree as for the magnitude of the critical field in this crystal about 100-300 V/cm. We did not present here the data obtained within dilatometric X-rays studies [1], giving the critical field in KH₂PO₄ of about 8500V/cm.

Table 1: Landau coefficients and calculated coordinates of the critical point for KH₂PO₄ (the data are taken from [6]).

| Ref. | \( a \) (10⁻³ esu) | \( b \) (10⁻¹¹ esu) | \( c \) (10⁻¹₅ esu) | \( d \) (10⁻²⁷ esu) | \( E^* \) (V/cm) | \( T^* - T_0 \) (K) | method |
|------|------------------|------------------|------------------|------------------|------------------|------------------|--------|
| [12] | 3.9 | -1.9 | 6.3 | 0 | 120 | 0.07 | F-plot |
| [13] | 4.2 ± 0.1 | -1.9 ± 0.1 | 5.4 ± 0.4 | 0 | 160 | 0.07 | F-plot |
| [14] | 4.3 ± 0.2 | -2.35 ± 0.4 | 5.91 ± 1.5 | 0 | 232 ± 70 | 0.10 ± 0.03 | Isopols |
| [15] | 4.0 ± 0.2 | -1.48 ± 0.2 | 3.1 ± 0.4 | 0 | 186 ± 60 | 0.08 ± 0.03 | Isopols |
| [16] | 3.91 ± 0.04 | -1.26 ± 0.05 | 3.2 ± 0.1 | 0 | 123 ± 18 | 0.057 ± 0.007 | Isopols |
| [17] | 3.8 ± 0.1 | -3.0 ± 0.8 | 6.5 ± 1.1 | 0 | 370 | 0.16 | F-plot |
| [18] | 3.8 ± 0.1 | -0.5 ± 0.3 | 0 | 3.8 ± 0.4 | 87 | 0.036 | F-plot |
| [19] | 3.9 | -0.54 ± 0.05 | 0 | 2.85 ± 0.10 | 124 | 0.046 |
| [20] | 3.9 | -1.85 ± 0.25 | 3.3 ± 0.5 | 0.87 ± 0.5 | 280 | 0.11 |

As we see, a considerable discrepancy between values of the Landau coefficients takes place, and values of the critical point coordinates are very sensitive to the choice of the Landau coefficients. Thus, a 1.5 times increase of the \( b \) coefficient leads to a 3 times as large value of the critical field and twice as large the quantity \( T^* - T_0 \). The main sources of differences in the values of critical coordinates determined via the Landau coefficients are the following

1. Inadequacy of the Landau expansion as such. It is known to be suitable for the second order phase transitions, only. For crystals, where the first order phase transition is observed, a large number of terms in the expansion should be taken into account, and even then it is valid only in the narrow vicinity of the transition point. Even for KH₂PO₄, where the jump of polarization at the transition point is not as large as in deuterated KD₂PO₄, the Landau expansion is not quite adequate.

2. Ambiguity of the Landau expansion. At interpretation of the same experimental data by different expansions [14] (with \( c = 0, d \neq 0 \) or with \( c \neq 0, d = 0 \)) the critical field can change to more than 124 times. The expansion with \( c = 0, d \neq 0 \) yields considerably smaller values of the critical field than the expansion with \( c \neq 0, d = 0 \).
3. A large numerical error in calculations of the expansion coefficients at a given form of the expansion. Thus, at determining the coefficient $b$ from $\Gamma$-plots, the error arises due to the data dispersion for $\Gamma(P^2)$ at small values of polarization.

4. Changes in the Landau coefficients from sample to sample. First, a quite large dispersion of the data (for determination of the critical point coordinates) takes place for the inverse Curie constant (the coefficient $a'$) \cite{3}. Similarly, the values of $b$ for different samples of the crystal do differ, even though they are obtained by the same method. Here, the dispersion of the data may exceed the error of measurement \cite{1, 4, 5}. Apparently, the Landau coefficients and, thereby, the coordinates of the critical point, essentially depend on a quality of the sample, its history, presence of inner defects, etc.

5. Different experimental methodics of polarization measurements (pyroelectric, dilatometric, hysteresis loops) give values of the coefficient $b$, which may significantly differ.

Comparison with experimental data of other quantities, calculated with the Landau expansion (for instance, temperature and field curves of polarization) does not allow to ascertain these coefficients, because these other quantities are not that sensitive to the values of the Landau coefficients, as the coordinates of the critical point.

Hence, due to a large error in determination of the Landau coefficients and ambiguity of the Landau expansion, the method of calculation of the critical fields and temperatures via the phenomenologic theory allows one only to estimate the coordinates of the critical point (order of magnitude of the critical field).

3 Microscopic model

We consider a ferroelectric crystal of the KH$_3$PO$_4$ type to which external electric field $E_3$, inducing polarization $P_3$ and strain $\varepsilon_6$ in the high-temperature phase, is applied.

The entire Hamiltonian of the model \cite{13} consists of a “seed” part, independent of a hydrogen subsystem configuration and attributed to a host lattice of heavy ions, and of pseudospin short-range and long-range hydrogen Hamiltonians, tunneling being neglected

$$H = N\bar{v}\left(\varepsilon_3^0 + \varepsilon_3^0 E_3 \varepsilon_6 - \varepsilon_3^3 \varepsilon_6^2 - \frac{3}{2} \varepsilon_6^3 \right) + H_{\text{long}} + H_{\text{short}}.$$ (3.4)

The “seed” energy expressed in terms of the electric field $E_3$ and strain $\varepsilon_6$ includes the elastic, piezoelectric, and electric counterparts. $\varepsilon_3^0$, $\varepsilon_3^0$, and $\chi_6^3$ are the so-called “seed” elastic constant, coefficient of the piezoelectric stress, and dielectric susceptibility, respectively; $\bar{v} = v/k_B$, $v$ is the primitive cell volume; $k_B$ is the Boltzmann constant; $N$ is the number of primitive cells.

$H_{\text{long}}$ is the mean field Hamiltonian of the long-range dipole-dipole and lattice mediated \cite{1} interactions between deuterons plus a linear in strain $\varepsilon_6$ molecular field \cite{13} induced by piezoelectric coupling

$$H_{\text{long}} = \frac{1}{2} \sum_{q'f'qf} J_{ff'}(q'q) \langle \sigma_{gf} \rangle \frac{\langle \sigma_{q'f'} \rangle}{2} - \sum_{qf} \left[ \left( \sum_{q'f'} J_{ff'}(q'q) \langle \sigma_{q'f'} \rangle \frac{\langle \sigma_{gf} \rangle}{2} \right) \frac{\sigma_{gf}}{2} - 2\psi_6 \varepsilon_6 \frac{\sigma_{gf}}{2} \right],$$ (3.5)

where

$$4\nu = J_{11} + 2J_{12} + J_{13}$$

is the eigenvalue of the long-range interaction matrix Fourier transform $J_{f'f} = \sum_{R_q} R_q \cdot J_{f'f}(q'q)$;

$$\eta = \langle \sigma_{q1} \rangle = \langle \sigma_{q2} \rangle = \langle \sigma_{q3} \rangle = \langle \sigma_{q4} \rangle$$

is the mean value of the Ising pseudospin $\sigma_{gf} = \pm 1$ which two eigenvalues are assigned to two equilibrium positions of a hydrogen on the $f$-th bond in the $q$-th unit cell.
The Hamiltonian of the short-range configurational interactions between hydrogens is usually chosen such as to reproduce the energy levels of the Slater-type model for KDP (see, for instance Ref. [19]) – the energy levels of up-down \( \varepsilon_a \) (twice degenerate at \( \varepsilon_a = 0 \) and \( \varepsilon_0 = 0 \)), lateral \( \varepsilon_l \) (four-fold degenerate), single-ionized \( \varepsilon_1 \) (eight-fold degenerate), and double-ionized \( \varepsilon_0 \) (twice degenerate) hydrogen configurations (\( \varepsilon_a < \varepsilon_l \ll \varepsilon_1 \ll \varepsilon_0 \)).

Since the system is no longer symmetric with respect to the reflection \( \sigma_h \) in the \( ab \) plane and mirror rotation \( S_4 \) around the \( c \) axis (both operations change the sings of polarization and strain), in presence of strain \( \varepsilon_6 \) and in the electric field \( E_3 \) a splitting of the energies of up and down \( (i = 1 \text{ and } i = 2) \), lateral \( (i = 5, 6) \) and \( (i = 7, 8) \), and single ionized \( (i = 9, 10, 11, 12 \text{ and } i = 13, 14, 15, 16) \) configurations takes place (configuration numbers \( i \) are given in Appendix). Since strain \( \varepsilon_6 \) and polarization \( P_3 \) transform after the same irreducible representation \( (B_2 \text{ in the paraelectric phase and } A_1 \text{ in the ferroelectric phase}) \), the field \( E_3 \) does not split those levels which remain degenerate in presence of the strain \( \varepsilon_6 \).

That part of the splitting, which origin is the distortion of the PO\(_4\) groups and changes of the angle between perpendicular in the paraelectric phase hydrogen bonds is described by linear functions of the strain \( \varepsilon_6 \). The contribution of the electric field \( E_3 \) to the splitting is taken to be equal to the difference between the energy levels of the groups dipoles in the longitudinal field \( E_3 \). Since the groups K-D\(_n\)PO\(_4\) with hydrogens in up \((i = 1)\) and down \((i = 2)\) configurations and in single-ionized configurations (configurations \( i = 9, 10, 11, 12 \text{ and } i = 13, 14, 15, 16 \) ) have opposite directions projections of the dipole moments \( \mu_i \) on the axis \( c \), these groups have also different energies \( \mu_i E \) in external electric field. Usually, the absolute values of the \( c \)-projections of the dipole moments of up/down configurations \( \mu_3 \) are assumed to be twice as large as the corresponding projections of single-ionized configurations. The \( c \)-projections of dipole moments of lateral and double-ionized groups are zero.

Finally, the Hamiltonian of the short-range interactions rewritten in terms of pseudospins according to standard rules \([19, 2]\) and taken into account within the most appropriate for these crystals four-particle cluster approximation, is

\[
\hat{H}_{\text{short}} = -\left[ \Delta + \mu_3 E_3 - \frac{2\delta_{6} - \delta_{66}}{2} \varepsilon_6 \right] \sum_{q} \sum_{j=1}^{4} \frac{\sigma_{qj}}{2} + \sum_{q} \left\{ U \left[ \frac{\sigma_{q1} + \sigma_{q3}}{2} \frac{\sigma_{q4}}{2} \frac{\sigma_{q2}}{2} \frac{\sigma_{q4}}{2} \right] + \Phi \frac{\sigma_{q1} + \sigma_{q2} + \sigma_{q3} + \sigma_{q4}}{2} \frac{\sigma_{q4}}{2} \frac{\sigma_{q4}}{2} \frac{\sigma_{q4}}{2} \frac{\sigma_{q4}}{2} \right\}.
\]

Detailed derivation of the Hamiltonian and the table of the split energy levels in presence of external electric field (longitudinal and transverse) are given in Appendix.

In Eq. (3.6) the following notations are used

\[
V = -\frac{1}{2}w_1, \quad U = \frac{1}{2}w_1 - \varepsilon, \quad \Phi = 4\varepsilon + 2w_1 - 8w;
\]

where

\[
\varepsilon = \varepsilon_a - \varepsilon_s, \quad w = \varepsilon_1 - \varepsilon_s, \quad w_1 = \varepsilon_0 - \varepsilon_s
\]

are the so-called Slater energies. Splitting of the energy levels due to lowering the system symmetry is the only changes in the short-range interactions that we take into account within this model. Therefore, \( \varepsilon, w, w_1 \) do not depend on strain \( \varepsilon_6 \) of field \( E_3 \).

The condition of equality of the mean values of pseudospins \( \eta = \langle \sigma_{qf} \rangle \) calculated with the four-particle \([19, 2]\) and single-particle deuteron Hamiltonians (see \([2]\) ) permits to exclude the self-consistency parameter \( \Delta \). The order parameter \( \eta \) and strain \( \varepsilon_6 \) can be found by minimization of the thermodynamic potential (Gibbs’ function) \( g_{1E}(T, \sigma_6, E_3, \eta) \)

\[
g_{1E}(T, \sigma_6, E_3, \eta) = \frac{\bar{E}}{2} \varepsilon_6^2 + \bar{E} \varepsilon_6 \varepsilon_6 - \frac{\bar{E}}{2} \varepsilon_6^2 - \frac{\bar{E}}{2} \varepsilon_6^2 + 2T \ln 2 + 2\eta^2 - 2T \ln(1 - \eta^2)D - \bar{E} \varepsilon_6 \varepsilon_6,
\]

where

\[
D = \cosh(2z + \beta \delta_{66} \varepsilon_6) + 4b \cosh(z - \beta \delta_{16} \varepsilon_6) + a \varepsilon_6 + \frac{a}{\varepsilon_6} + d,
\]
The conjugate to the strain $\varepsilon_6$ stress $\sigma_6$ is introduced for the sake of simplicity; in numerical calculations $\sigma_6 = 0$.

Using the system of equations

$$
\sigma_6 = c_{66}^0 \varepsilon_6 - c_{36}^0 E_3 + \frac{4\psi_6}{v} \frac{m}{D} + 2M_6^2 \varepsilon_6, \\
P_3 = e_{36}^0 \varepsilon_6 + \chi_3^0 E_3 + \frac{2\mu_3}{v} \frac{m}{D},
$$

which follows from the thermodynamic equilibrium conditions

$$
\frac{1}{v} \left( \frac{\partial g_1}{\partial \varepsilon_6} \right)_{T,E_3,\sigma_6} = 0, \quad \frac{1}{v} \left( \frac{\partial g_1}{\partial E_3} \right)_{T,\sigma_6} = -P_3
$$

we find the isothermal dielectric susceptibility of a free crystal (at $\sigma_6 = \text{const}$)

$$
\chi_{33}^{T\sigma} = \left( \frac{\partial P_3}{\partial E_3} \right)_{T,\sigma_6} = \chi_{33}^0 \left( \frac{c_{36}^0}{c_{66}^0} \right)^2, \quad (3.7)
$$

expressed via the isothermal dielectric susceptibility of a clamped crystal (at $\varepsilon_6 = \text{const}$)

$$
\chi_{33}^{T\varepsilon} = \left( \frac{\partial P_3}{\partial E_3} \right)_{T,\varepsilon_6} = \chi_{33}^0 \left( \frac{2\beta \varphi}{v} \right), \quad (3.8)
$$

the isothermal coefficient of piezoelectric stress

$$
e_{36}^T = \left( \frac{\partial P_3}{\partial \varepsilon_6} \right)_{T,E_3} = e_{36}^0 \left( \frac{2\mu_3}{v} \right) \beta \theta \frac{D}{D - 2\varphi}, \quad (3.9)
$$

and the isothermal elastic constant at constant field

$$
c_{66}^{TE} = \left( \frac{\partial \sigma_6}{\partial \varepsilon_6} \right)_{T,P_3} = c_{66}^0 + \frac{8\beta \psi_6 - \varphi \psi_6 + \frac{r}{v} \frac{M_6^2}{D - 2\varphi} + \frac{2\beta \varphi}{v} \frac{D^2}{D - 2\varphi}}{D - 2\varphi} + \frac{2\beta \varphi}{v} \frac{D^2}{D - 2\varphi}
$$

The other isothermal dielectric and piezoelectric characteristics can be recalculated via the found above by using the known formulas

the constant of piezoelectric stress $h_{36}$

$$
h_{36} = - \left( \frac{\partial E_3}{\partial \varepsilon_6} \right)_{T,P_3} = - \left( \frac{\partial \sigma_6}{\partial P_3} \right)_{T,\varepsilon_6} = \frac{e_{36}^0}{\chi_{33}^T}, \quad (3.10)
$$

the elastic constant $c_{66}^{P\sigma}$ at constant polarization

$$
c_{66}^{P\sigma} = \left( \frac{\partial \sigma_6}{\partial \varepsilon_6} \right)_{T,P_3} = c_{66}^{TE} + e_{36}^T h_{36}. \quad (3.11)
$$

compliance at constant field

$$
s_{66}^{TE} = \left( \frac{\partial \varepsilon_6}{\partial \sigma_6} \right)_{T,E_3} = \frac{1}{c_{66}^{TE}}, \quad (3.12)
$$

the coefficient of the piezoelectric strain

$$
d_{36}^{T\sigma} = \left( \frac{\partial P_3}{\partial \varepsilon_6} \right)_{T,E_3} = e_{36}^{T\sigma} c_{66}^{TE}, \quad (3.13)
$$
the constant of piezoelectric strain

\[ g_{36} = -\left( \frac{\partial E_3}{\partial \sigma_6} \right)_{TP_3} = \frac{h_{36}}{c_{66}}, \]  

(3.14)

When dynamic experimental methodologies are used (measuring frequency exceeds the thermal relaxation frequency), not the isothermal but adiabatic characteristics of the crystals are measured. In the paraelectric phase in absence of electric field the adiabatic and isothermal quantities coincide, but they may essentially differ in the ferroelectric phase or in the electric field. The adiabatic quantities can be obtained from the isothermal analogs with the help of the following formulas [20]

\[
\frac{1}{\chi_{33}^P} = \frac{1}{\chi_{33}^E} \left[ 1 + \frac{1}{\chi_{33}^E} \left( \frac{\partial P_3}{\partial T} \right)_{E_3}^2 \right] = \frac{1}{\chi_{33}^E} \left[ 1 + \frac{T}{\chi_{33}^E} \frac{p_\sigma^2}{c_{P_3, \sigma}} \right];
\]

\[
d_{36}^S = d_{36}^E \frac{\chi_{33}^S}{\chi_{33}^E};
\]

\[
(c_{66}^{SE})^{-1} = (c_{66}^{TE})^{-1} - \left( 1 - \frac{\chi_{33}^S}{\chi_{33}^E} \right) \frac{(d_{36}^P)^2}{\chi_{33}^E},
\]

where

\[ S = R(-2 \ln 2 + 2 \ln[1 - \eta^2] + 2 \ln D + 4T \varphi^T \eta + \frac{2 \tilde{M}_6}{D}) \]

is the entropy of the hydrogen subsystem, \( p_\sigma \) is the pyroelectric coefficient, \( c_{P_3, \sigma} \) is the specific heat at constant polarization and pressure. From (3.13) it follows that the most prominent difference between the adiabatic and isothermal quantities takes place in the range of rapid temperature changes of polarization (where \( \frac{\partial P_3}{\partial T} \) is large) – in the vicinity of the transition point or of the permittivity maximum.

Using (3.13) and the relations (3.7)-(3.14) we can show that the adiabatic and isothermal “true” constants of the crystals – the elastic constant at constant polarization \( c_{P_3} \) and piezomodules \( h_{36} \) and \( g_{36} \) – coincide.

The pyroelectric coefficient and the contribution of the hydrogen subsystem into the specific heat at constant pressure and polarization are given by the following expressions

\[ p_6^\sigma = p_6^\varepsilon + c_{36} \alpha_6, \]  

(3.16)

and

\[ \Delta c_{P_3, \sigma} = \frac{T}{v} \left( \frac{\partial S}{\partial T} \right)_{\sigma} = \Delta c_{P_3} + \frac{q_6^P \alpha_6}{v}, \]  

(3.17)

where \( \Delta c_{P_3} \) is the specific heat at constant polarization and strain

\[
\Delta c_{P_3, \varepsilon} = \frac{T}{v} \left( \frac{\partial S}{\partial T} \right)_{P_3, \varepsilon} = \frac{2R}{D} \left( 4T \varphi^T [\alpha T \varphi^T + \tilde{q}_6] + N_6 - \frac{\tilde{M}_6^2}{2D} \right),
\]

\[ R \] is the gas constant; \( q_6^P \) is the strain heat at constant \( P_3 \),

\[ q_6^P = \left( \frac{\partial S_4}{\partial \varepsilon_6} \right)_{P_3, T} = \frac{4R}{D} \left( T \varphi^T r - 2\varphi_0 \psi_6 - \tilde{q}_6 \psi_6 \lambda_6 + \frac{\tilde{M}_6 \tilde{M}_5}{2D} \right), \]

\( \alpha_6 \) is the factor produced by temperature variation of the strain \( \varepsilon_6 \)

\[ \alpha_6 = \left( \frac{\partial \varepsilon_6}{\partial T} \right)_{\sigma} = -\frac{q_6^P + h_{36} p_6^\varepsilon}{c_{66}^E}, \]

(true thermal expansion, which invokes the diagonal strains, is not considered here. We used the following notations

\[ N_6 = \frac{1}{T^2} \left[ (\varepsilon + \delta_{66} \varepsilon_6)^2 a a_6 + (\varepsilon - \delta_{66} \varepsilon_6)^2 \frac{a}{a_6} + 4b w \delta_{16} \varepsilon_6 \sinh(\varepsilon - \beta \delta_{16} \varepsilon_6) + \right], \]
points for the piezoelectric constants \( c_{16} \) and \( \varepsilon_{tr} \) for KH, respectively, given by Mason [28] but closer to the deQuervain value \( \varepsilon_{tr} = 50 \) for the dielectric permittivity \( \varepsilon_{c} \) capable of describing behavior of the physical characteristics of an undeuterated KH without taking into account tunneling effects.

R is the gas constant.

Having the pyroelectric coefficient and the specific heat at constant polarization, we can find the total molar specific heat at constant pressure

\[
\Delta c_6^\sigma = T \left( \frac{\partial S}{\partial T} \right)_\sigma = \Delta c_6^P + \varrho_6^P \varphi_6^\sigma.
\]

(3.18)

\[
\varrho_6 = \left( \frac{\partial S}{\partial T} \right)_{\varepsilon_6,T} = \frac{\nu}{\mu_3} \frac{2RT}{D} \varphi \{ 2\varphi T \varphi^T + \varrho_6 \}
\]

is the polarization heat at given \( \varepsilon_6 \),

4 Discussion

4.1 Fitting procedure

The presented in previous Section theoretical results will be used to description of the physical characteristics of a highly deuterated crystal KD2PO4. We shall also verify whether the presented theory is capable of describing behavior of the physical characteristics of an undeuterated KH2PO4 without taking into account tunneling effects.

For a highly deuterated crystal K(H1−xDx)2PO4 with the transition temperature in zero field \( T_{C0} = 211.73 \) K (a nominal deuteration level \( x = 0.89 \), hereafter abbreviated as KD2PO4) we use the values of the theory parameters found in [3], providing a fair quantitative description of temperature of several associated with strain \( \varepsilon_6 \) dielectric, piezoelectric, and elastic characteristics of the crystal at atmospheric pressure, namely, the dielectric permittivitities of a free and clamped crystals, elastic constants \( c_{16}^E \) and \( c_{16}^P \) of open-circuited and short-circuited crystals, and piezomodules \( e_{36}, d_{36}, g_{36} \) and \( h_{36} \). Details of the fitting procedure are given in [3].

For and undeuterated crystal KH2PO4 we also chose the theory parameters such as to fit the temperature behavior of the elastic constants \( c_{16}^E \) and \( c_{16}^P \), piezomodules \( e_{36}, d_{36}, g_{36} \), and \( h_{36} \), as well as the longitudinal static dielectric permittivity of a clamped crystal \( \varepsilon_{33}^E \), and of [27] for the elastic constant \( s_{16}^E \) are direct experimental points for KH2PO4. Using Eqs. (3.7) – (3.14) and having the values of \( d_{36}, \varepsilon_{33}, \) and \( c_{16}^E \), we find “experimental” points for the piezoelectric constants \( c_{36}, h_{36} \), elastic characteristics \( c_{16}^E, s_{16}^E, s_{16}^P \), and clamped dielectric permittivity \( \varepsilon_{33}^E \). Recalculated thus values of the piezoelectric constants \( g_{36} \sim 53 \cdot 10^{-8} \) cm2/esu and \( h_{36} \sim 3.8 \cdot 10^{-4} \) dyn/esu above the transition point are greater than \( 44 \cdot 10^{-8} \) cm2/esu and \( 3.0 \cdot 10^{-4} \) dyn/esu, respectively, given by Mason [28] but closer to the deQuervain values \( 50 \cdot 10^{-8} \) cm2/esu for \( h_{36} \).

By this set of the parameters we also try to describe the field dependences of polarization \( P_3 \), longitudinal static dielectric susceptibility \( \chi_{33}^E \), and elastic constant \( c_{16}^E \) of KH2PO4, obtained in [3]. It should be noted that in [3] only the elastic constant was measured directly by the ultrasonic technique, whereas the susceptibility was recalculated using the known thermodynamic relations and the data of [29] for the piezomodules.

A scheme of choosing the theory parameters for KH2PO4 was analogous to that for KD2PO4. At chosen \( \varepsilon \) and \( w \), close to those used in theories where the piezoelectricity and tunneling effects are not
taken into account [33], and setting the Curie temperature of a clamped crystal $T_0^{\text{clamp}} = 118.65$ K, we found the value of the long-range interaction parameter $\nu$. Setting the values of the deformation potentials $\psi_6, \delta_{a6}, \delta_{16}$, we found the value $\delta_{a6}$ by fitting to experimental value of the piezomodule $e_{36}$ at a certain temperature. The parameters $\varepsilon, w, \psi_6, \delta_{a6}, \delta_{16}, c_{66}^{(0)}, \mu_3/\nu$ were chosen such as to obtain the correct values of the transition temperature $T_{C_0} = 122.8$ K of a free crystal, ratio of the polarization jump at the temperature point to saturation polarization (jump of the order parameter), correct temperature curves of the elastic constants $c_{66}^{E}$ and $c_{66}^{P}$, piezomodules $d_{36}$, $g_{36}$, and $h_{36}$, longitudinal static dielectric permittivities of a free $\varepsilon_{33}^{(0)}$ [23, 37, 23, 24, 36] and clamped $\varepsilon_{33}$ crystals, as well as specific heat. Properly chosen parameters $e_{36}^{(0)}, \chi_{33}$ yield the correct values of the piezomodules $d_{36}$, $e_{36}$, $g_{36}$, and $h_{36}$ in the high-temperature limit.

In Table 2 we present the adopted values of the theory parameters for KD$_2$PO$_4$ and KH$_2$PO$_4$.

### Table 2: The theory parameters.

|          | $\varepsilon$ | $w$ | $\nu$ | $\psi_6$ | $\delta_{a6}$ | $\delta_{16}$ | $c_{66}^{(0)} \cdot 10^{-10}$ | $\frac{\mu_3}{\nu}$ | $e_{36}$ | $\chi_{33}^{(0)}$ |
|----------|---------------|-----|-------|---------|---------------|---------------|-------------------------------|-----------------------|---------|-----------------|
| KD$_2$PO$_4$ | 0.13781 | 34.615 | -500 | -692.5 | 1350 | 50 | 6.7 | 6.9 | 0.42 $\cdot$ 10$^4$ | 0.4 |
| KH$_2$PO$_4$ | 0.525 | 383 | 20.58 | -380 | -257 | 300 | 40 | 7.3 | 6.4 | 0.3 $\cdot$ 10$^4$ |

#### 4.2 Effective dipole moment

In our calculations, as well as in earlier theories (see, for instance. [8]) two different values of the effective dipole moment $\mu_3^+ < \mu_3^-$ must be used in the ferroelectric and paraelectric phases. The value of $2\mu_3^-/\nu$ in the ferroelectric phase is given by the experimental value of saturation polarization. The paraelectric values of $2\mu_3^+/\nu$, listed in Table 2, are set by the relation between the experimental and theoretical values of the Curie constant for the longitudinal static dielectric permittivity. In the present theory, $\mu_3^-$ must also provide an agreement with experiment for the piezomodules

$$e_{36} \sim \mu_3, \quad d_{36} \sim \mu_3, \quad h_{36} \sim \mu_3^{-1}, \quad g_{36} \sim \mu_3^{-1}$$

in the paraelectric phase. In KH$_2$PO$_4$ and KD$_2$PO$_4$ the ratio $\mu^+/\mu^-$ is about 1.2. Neither in the present model nor in simpler versions of the proton ordering models it is possible to choose the theory parameters such as to fit the temperature curves of polarization and permittivity with a single value of the parameter $\mu_3$.

The necessity to use in calculations two different values of $\mu$ for paraelectric and ferroelectric phases is not a problem while we do not consider behavior of the system in external fields conjugate to the order parameter. These fields smear out the phase transition; therefore, when the difference between the phases becomes only quantitative (in fields above the critical one), it does not make sense to distinguish the paraelectric and ferroelectric phases and the corresponding $\mu^+$ and $\mu^-$.

Tokunaga [33] relates the deviation of the ratio $\mu^+/\mu^-$ from unity with the existence of an underdamped soft mode in a crystal. In the displacive type ferroelectrics $\mu^+/\mu^- \gg 1$, whereas in the order-disorder type ferroelectrics $\mu^+/\mu^- \sim 1$. Failure of the order-disorder model to describe both polarization and dielectric permittivity without invoking two values of $\mu$ for different phases shows the limits of the model suitability. Since the KH$_2$PO$_4$ family crystals undergo phase transitions of a mixed ordering-displacive type (it is believed that hydrogen ordering triggers displacements of heavy ions), for a consistent description of dielectric properties of these crystals, we need to sophisticate the model and include phonon degrees of freedom and anharmonicity into consideration. Moreover, we need to go further than Kobayashi model (mixed proton-phonon model with only one optical mode taken into account), which is known only to renormalize parameters of the proton ordering model.
4.3 Zero field case

Figures 3 and 2 illustrate how the proposed theory describes experimental data for the physical characteristics of KD$_2$PO$_4$ and KH$_2$PO$_4$ crystals in absence of external electric field. Polarization of a pure KH$_2$PO$_4$ $P_3$ is calculated with $2\mu_3^*/\nu = 5.0 \ \mu$C/cm. To obtain the total specific heat, we added a constant term 60 J/mol K, describing the background specific heat of a host lattice of heavy ions, to the calculated from [18] contribution of the hydrogen subsystem to the specific heat.

4.4 Non-zero field case

In figure 3 we plot the $T_C - E_3$ phase diagrams of the KD$_2$PO$_4$ and KH$_2$PO$_4$ crystals. These diagrams are of the same topology as the $T_C - \sigma_6$ diagram of KD$_2$PO$_4$ [3]. The coordinates of the critical point, calculated within the microscopic theory, essentially depend on the magnitude of the order parameter jump $\Delta \eta$ (the ratio of the polarization jump to the saturation polarization) at the transition point in zero field. Since the order of the phase transition in a pure KH$_2$PO$_4$ is close to the second one, while in a deuterated KD$_2$PO$_4$ a pronounced jump of polarization at the transition point takes place, the critical field in KH$_2$PO$_4$ is much lower than that in KD$_2$PO$_4$.

For KD$_2$PO$_4$ we obtain a good agreement with experimental data for a field dependence of the transition temperature [3]: $\partial T_C/\partial E_3 = 0.13$ K/kVcm in our model and 0.125 ± 0.1 in [3]. Theoretical value of the critical field $E_3^* = 7.0$ kV/cm, where the phase transition in the system disappears, accords fairly well with the experimental estimate $7.1 \pm 0.6$ kV/cm [3]. The critical temperature $T^* = 212.6$ K is close to that from the $T_C - \sigma_6$ diagram.

For an undeuterated crystal, the theory gives the following characteristics of the phase diagram

\[ E^* = 105 \ \text{V/cm}, \quad T^* - T_0 = 0.05 \ \text{K}, \quad \partial T_C/\partial E_3 = 0.23 \ \text{K/kVcm}. \]

The calculated critical field in KH$_2$PO$_4$ agrees with the the estimates $80 \div 370$ V/cm [3], obtained via experimentally measured coefficients of Landau expansions. However, at varying the microscopic $\Delta \eta$ within experimentally estimated limits (for which slight changes in the theory parameters are required), the calculated critical field is significantly increased, while more or less precisely measured macroscopic characteristics (e.g. permittivity) remain practically unchanged. We may conclude that the microscopic theory is able only to estimate the coordinates of the critical point.

In addition, in fields close to critical, peaks of the longitudinal permittivity or other characteristics having peculiarities at the transition point are very sharp. Therefore, even small changes of temperature ($\sim 10^{-3}$ K) can change the permittivity value several times. The maximal temperature step in calculations, yielding more or less correct value of the permittivity maximum, is $\sim 10^{-4}$ K.

As we have already mentioned, we cannot describe polarization of the crystals, without introducing the “ferroelectric” values of the dipole moment $\mu_3$. Nevertheless, we can compare the field behavior of the order parameter $\eta$ with the experimental data for the ratio $P_3/P_s$. Here $P_s = 5.0 \ \mu$C/cm$^2$ for KH$_2$PO$_4$ and $6.2 \ \mu$C/cm$^2$ for KD$_2$PO$_4$ are the experimental values of saturation polarization, practically independent of external field [3]. Such comparison is justified, since the contributions to polarization from the terms $\chi_{33}^0 E_3$ and $\epsilon_{36}^0 \sigma_6$ are not essential. Figure 4 shows a fair accordance of theoretical temperature and field dependences of $P_3/P_s$ for KH$_2$PO$_4$ and KD$_2$PO$_4$ with the experimental data. Increase of polarization and vanishing of polarization jump are well reproduced by the theory.

In figure 5 we depicted the temperature dependences of two characteristics – isothermal static dielectric permittivity of a free crystal $\epsilon_{33}^{T_\sigma}$ and the piezomodule $h_{36}$ of a deuterated crystal at different values of external electric field. Temperature curves of other characteristics of the crystal exhibiting peculiarities at the transition point – compliance $s_{66}^E$ and piezomodules $d_{36}$ and $\epsilon_{36}$ – are similar to those of the permittivity $\epsilon_{33}^{T_\sigma}$. Temperature and field behavior of the piezomodule $g_{36}$ to those of $h_{36}$. The corresponding curves for a undeuterated are qualitatively similar, however, due to closeness of the order of the phase transition to the second one, the temperature and field intervals where all these changes take place are much more narrow.

Maximal values of $\epsilon_{33}^{T_\sigma}$ and similar quantities shift to higher temperatures with field. As the field approaches its critical value, the peak values of these quantities in the transition points increase and are maximal at the critical point. The higher fields smear out the phase transition and round off and lower down the peaks.
Figure 1: Temperature dependences of the strain $\varepsilon_6$-related physical characteristics. Lines and solid symbols correspond to a deuterated KD$_2$PO$_4$; open symbols representing pure KH$_2$PO$_4$ are shown for comparison. Experimental points are taken from □ - [28]; ◦ - [27]; ○ - [21, 22]; ■ - [32]; • - [33]; △ and ▲ are recalculated from Eqns. (3.7) – (3.14) using experimental data of Refs. [28, 27] and Refs. [32, 33], respectively.
Figure 2: Temperature dependences of the physical characteristics of an undeuterated crystal KH$_2$PO$_4$.

Experimental points:
- for polarization: □ - [23]; ○ - [34]; △ - [35]; ▽ - [12];
- for the permittivity: □ - [25]; ○ - [37]; △ - [28]; ▽ - [24];
- for specific heat: □ - [8]; ○ - [8]; △ - [26];
- for the others: □ - [28]; ○ - [27]; ▽ are recalculated from Eqs. (3.7) – (3.14) using experimental data of Refs. [21, 22, 27, 23].
Figure 3: \( T_C - E_3 \) phase diagrams of KD\(_2\)PO\(_4\) and KH\(_2\)PO\(_4\). Experimental points are taken from [9].

Figure 4: Ratio of polarization to saturation polarization \( P_3/P_s \) as a function of temperature for KD\(_2\)PO\(_4\) (left) and KH\(_2\)PO\(_4\) (right) at different values of electric field \( E_3 \) (kV/cm) (left): 1 – 0; 2 – 2.82; 3 – 5.64; 4 – 8.46; 5 – 11.28; (right): 1 – 0; 2 – 5.813; 3 – 12.54 – 20.31. Experimental points are taken from [10] for KH\(_2\)PO\(_4\) and from [8] for KH\(_2\)PO\(_4\).

The field effects on piezomodules \( h_{36} \) and \( g_{36} \) is similar to its effects on polarization. On increasing the field, jumps of these quantities at the transition point decrease and vanish at the critical field. At higher fields, these quantities exhibit smooth temperature dependences.

It is interesting to note that field dependences of adiabatic quantities are stronger than those of the isothermal quantities. Thus, as fig. 6 where we present temperature curves of the adiabatic and isothermal piezomodule \( d_{36}^S \) of a pure KH\(_2\)PO\(_4\) shows, the peak values of the adiabatic piezomodule (as well as of \( s_{66}^{SE} , c_{36}^S , \varepsilon_{33}^S \)) decrease with the external field (above the critical point) much stronger than the peak values of the isothermal \( d_{36}^T \), and the maxima of the adiabatic quantities shift with the field much more perceptibly than those of the isothermal quantities.

As one can see (Fig. 7), the proposed theory yields a fair agreement with experiment for the field effects on the adiabatic longitudinal dielectric susceptibility of a free crystal and elastic constant \( c_{66}^{SE} \) in a pure KH\(_2\)PO\(_4\) [7]. Deviation of the theoretical curves from experimental points in the vicinity of the “transition” (maximum of the permittivity) is attributed to our neglecting tunneling effects. Such neglecting worsens an agreement with an experiment for the temperature curve of order parameter \( P_3/P_s \) and, thereby, of \( \chi_{33}^{SE} \) and \( c_{66}^{SE} \).
5 Concluding remarks

In this paper we apply the previously developed microscopic theory to description of effects produced by the longitudinal electric field $E_3$ on the phase transition and physical properties of the KH$_2$PO$_4$ family ferroelectrics. Calculations are performed in the four-particle cluster approximation within the proton ordering model without taking into account the tunneling effects. The developed model takes into account the existence of the shear strain $\varepsilon_6$, which is spontaneous in the ordered phase and induced by the stress $\sigma_6$ and electric field $E_3$ (via the piezoeffect) in the disordered phase. We also take into account other effects induced by this strain – the splitting of short-range proton correlation energies and appearance of effective molecular fields, created by piezoelectric coupling.

The presented model provides a fair agreement with experimental data for temperature behavior (at zero field) of the dielectric, piezoelectric, elastic, and thermal characteristics – second derivatives of thermodynamic potentials (dielectric permittivity, piezomodules, elastic constants, specific heat) of the crystals. Such agreement takes place for a deuterated crystal KD$_2$PO$_4$ and for a pure KH$_2$PO$_4$ without taking into account the tunneling.

The model satisfactorily reproduced the parameters of experimental $T_C - E_3$ phase diagrams of KD$_2$PO$_4$ and KH$_2$PO$_4$. The transition temperature increases with field; this is accompanied by increase.
in polarization in the high-temperature phase and decrease of its jump at the transition point. The phase equilibrium curves terminate in the critical points, where the polarization (order parameter) jump vanishes. At higher fields the temperature curves of polarization and strain $\varepsilon_6$ are smooth. Such behavior is typical for the systems undergoing the first order phase transitions in external fields conjugate to the order parameter.

The magnitude of the critical field essentially depends on the degree of the “first-orderness” of the phase transition. Thus, in KH$_2$PO$_4$ where the phase transition is close to the tricritical point, the critical field is several times smaller than in KD$_2$PO$_4$, where a pronounced first order phase transition takes place. Experimental method of the critical coordinates determination based in the phenomenologic analysis allows only to estimate the critical field. The calculated within the microscopic theory value of the critical field is determined by the magnitude of the order parameter at the transition point. Since on changing this quantity (at the proper and slight change of the relations between the theory parameters) within the limits of experimental estimates the calculated critical field significantly increases, the microscopic approach also permits only to estimate the coordinates of the critical point, though this estimate is better than the phenomenologic one.

As the field approaches the critical point, the peak values of thermodynamic quantities that have peculiarities at the transition point (the longitudinal dielectric permittivity $\varepsilon_{33}$, piezomodules $d_{36}$ and $e_{36}$, and the elastic compliance $s_{66}^{E}$) increase, while the jumps of “true” constants of the crystals (piezomodules $g_{36}$ and $h_{36}$, and elastic constant $c_{66}^{E}$) decrease. At the critical point the peak values of the formers are maximal, whereas the jumps of the latters vanish. In fields above the critical one, temperature dependences of all thermodynamic quantities are smooth, and the maximal values of the characteristics that have peculiarities at the transition point decrease.

In presence of external field, there arise a difference between isothermal and adiabatic characteristics (dynamic methods of measurements yield the adiabatic quantities), which have peculiarities at the transition point. The field dependences of the adiabatic quantities are stronger than those of the isothermal quantities. Thus, in fields above the critical one, the peak values of the adiabatic quantities decrease with the field much faster that the peaks of the isothermal quantities, and the maxima of the adiabatic quantities shift to higher temperatures that the maxima of the isothermal quantities at the same field. Within the proposed theory we obtain a fair description of the experimental data for the field dependences of the adiabatic dielectric susceptibility and elastic constant of KH$_2$PO$_4$.

The developed model, as well all earlier used versions of proton ordering model, requires two different values of effective dipole moment to be introduced for description of polarization and dielectric permittivity of the crystals (in paraelectric and ferroelectric phases). For a consistent description of dielectric properties of these crystals, phonon degrees of freedom and anharmonicity must be taken into account.
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