Theoretical investigations of thermodynamic properties of partially deuterated K(H$_{1-x}$D$_x$)$_2$PO$_4$ ferroelectrics

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The research of thermodynamic properties of partially deuterated K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals was performed within the framework of proton ordering model with tunnelling within the four-particle cluster approximation for short-range interaction and within the molecular field approximation for long-range interaction. The KD$_2$PO$_4$'s model parameters were derived for the case of acceptable description of the experimental data for crystal thermodynamic characteristics. Based on the introduced procedure of deriving parameters for K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals, the thermodynamic and dielectric properties of these crystals were calculated and the results were compared with the experimental ones. The problem of applying the mean crystal approximation to the analysis of physical characteristics of K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals was discussed.

Key words: KDP, proton ordering model, four-particle cluster approximation, mean crystal approximation

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1. Introduction

The investigations of partially deuterated ferroelectric crystals of the K(H$_{1-x}$D$_x$)$_2$PO$_4$ type make it possible to readily explain the thermodynamic and dynamic properties, peculiarities of the phase transitions, and the isotopic effect in the mixed ferroelectric crystals of the order-disorder type. A relatively simple structure of the KH$_2$PO$_4$ family of ferroelectrics and the peculiarities of their structure, related to the hydrogen bond system, allows us to use the methods and approximations that provide high accuracy of calculation results. Close interplay between the theory and experiment is an essential point in the development of the physics of these crystals which makes it possible to work out adequate theoretical models and ultimately understand their physical properties.

Theoretic studies of the K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals were carried out in the works [1–12]. All studies of the mixed K(H$_{1-x}$D$_x$)$_2$PO$_4$ ferroelectrics were carried out within one of the modifications of the proton ordering model or within the proton-phonon model. The first model was proposed by Slater [13] and was developed and expanded in the works by Blinc [14,15], De Gennes [16], Vaks [17,18] and other researchers. Another model was proposed by Kobayashi [19] and then it was developed in the work [10].

The first attempt to study the K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals was made by Tokunaga and Matsubara [1]. The proton ordering model was exploited for the description of K(H$_{1-x}$D$_x$)$_2$PO$_4$ which was performed within the cluster approximation. In this work the assumption of the equality of all the interaction parameters for the KDP and DKDP crystals was made. The differences in the ferroelectric properties of these crystals were related to the tunnelling effects taking place in KDP: $\Omega \neq 0$. Besides, it was assumed that the $T_c(x)$ dependency can be obtained from the expression $T_c(\Omega)$ derived for pure KDP by replacing $\Omega \rightarrow x \cdot \Omega$. However, the author failed to gain agreement between the theory and experiment for the $T_c(x)$ dependency.

Several other model theories related to the study of the dependencies of ferroelectric phase transition temperature and the Curie-Weiss constant on the deuteration level of K(H$_{1-x}$D$_x$)$_2$PO$_4$...
crystals emerged after this work, such as [2,3,8,9]. The methods and approaches exploited in the works [2,3] were critically assessed in the work [20]. It was noticed that the molecular field approximation used in the works [2,3] is not precise enough. Particularly it concerns the K(H$_{1-x}$D$_x$)$_2$PO$_4$-type crystals, where this approximation is imprecise even for unmixed compounds and the satisfactory description could be achieved within the cluster approximation. In the work [8] the effect of partial deuteration on the phase transition of the plain Slater model (this model does not take into consideration the charged configurations, long-range interaction and the tunnelling) was considered.

In the work [9], different thermodynamic properties of the partially deuterated crystals K(H$_{1-x}$D$_x$)$_2$PO$_4$, Rb(H$_{1-x}$D$_x$)$_2$PO$_4$, Cs(H$_{1-x}$D$_x$)$_2$AsO$_4$ were researched within the framework of the model and the approximations developed in the works [17,18,20]. Here a special approach was developed to the study of partially deuterated ferroelectrics and one of its key points was the assumption of proportionality of interaction constants to the product of the hydrogen bound dipole moments. The second key point of the proposed approach was the assumption of homogeneous distribution of deuterium over the mixed crystal. This assumption contradicts the results of the work [21], where an essential heterogeneous distribution of the deuterium over the mixed crystals in the equilibrium state was observed. In this work the equations on thermodynamic characteristics were derived within the cluster approximation and within the proposed approach. The concentration dependencies of the Curie-Weiss temperature $T_0(x)$ and the Curie constant $C(x)$ were considered in detail and the results of the numerical calculations were compared to the experimental data.

Unfortunately, this work does not provide the results of calculations for polarization and specific heat, for which reliable experimental data are available. The theoretically calculated curve of $C(x)$ shows much steeper behaviour than the experimental one. Thus, the proposed approach to the description of the partially deuterated K(H$_{1-x}$D$_x$)$_2$PO$_4$-type crystals needs more thorough examination. It should be noted that having neglected the charging configurations, long-range configuration and tunnelling we can reproduce the results of the work [8].

In the work [10] some static and dynamic characteristics of the partially deuterated ferroelectric crystals K(H$_{1-x}$D$_x$)$_2$PO$_4$ were described within the coupled proton-phonon model proposed by Kobayashi [19]. In contrast to the Ising model with transverse field, where the interaction of proton motion with the lattice vibrations is taken into account by changing the interaction constants, this model takes into account the interaction of proton motion with the lattice vibrations by adding the terms into the Hamiltonian, which corresponds to the lattice vibration and to the interaction between the lattice and pseudospins. This approach turns out to be more natural.

In the work [10] the following assumptions were made: 1) the eigenfrequencies $\omega_q$ of the vibration of ions at the absence of the conjunction with the pseudospin system are the same for KDP and DKDP; 2) the constants of the interaction of pseudospins $J_{ij}$ along with the constants of the pseudospin-phonon interaction are proportional to the effective dipole moments of the pseudospins; 3) there is no tunnelling on the hydrogen bond of the entirely deuterated compound $\Omega_D = 0$. The assignment was solved within the molecular field approximation. It was shown that this system has the second order phase transition and that the dielectric permittivity complies with Curie-Weiss law. The equation for the phase transition temperature and the expression for the Curie-Weiss constant was derived as well. In particular, the following inequality for the phase transition temperature and for the Curie-Weiss constant was derived: $d^2 T_c(x)/dx^2 < 0$ and $d^2 C(x)/dx^2 > 0$.

Comparing the theoretical results of this work with the experimental data, it should be noticed that a very good agreement was derived for $T_c(x)$ and the sign of the value $d^2 C(x)/dx^2$ was in agreement with the experimental results of the work [21]. However, the fit of the $C(x)$ with the experiment was not satisfactory. The molecular field approximation, exploited in this work, as it was noted above, is inappropriate for the study of KDP-type crystals. Hence, we do not have fair grounds to claim that the coupled proton-phonon model is adequate for describing the KDP-type crystals, as well as for the K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals, in particular.

Moreover, we should make reference to the works [11,12], where the partially deuterated ferroelectrics of K(H$_{1-x}$D$_x$)$_2$PO$_4$-type were studied within the proton ordering model without tun-
nelling in the cluster approximation and under the condition of the linear dependency of the parameters \( \varepsilon \) and \( w \) on the deuterium concentration. The long-range interaction parameter \( \nu_z \) was derived under the condition of the equality between the theoretically calculated phase transition temperatures \( T_c \) and experimental ones. In the work [11] the thermodynamic properties and the static longitudinal dielectric permittivity were studied; in the work [12] the focus was made on the static transverse dielectric permittivity. Generally, a good agreement with the experimental data was derived for polarization, proton-deuteron specific heat, static longitudinal and transverse dielectric permittivity temperature dependencies. However, these works do not take into account the tunnelling and hence they are not quite correct to be applied to the study of the partially deuterated \( \text{K(H}_1\text{x-D}_2\text{)}\text{2PO}_4 \) type ferroelectrics within the four-particle cluster approximation.

In the present work we study the thermodynamic properties of the partially deuterated crystals \( \text{K(H}_1\text{x-D}_2\text{)}\text{2PO}_4 \) within the proton ordering model taking the tunnelling into account. The model was considered within the four-particle cluster approximation for short-range interaction, within the molecular field approximation for the long-range interaction and within the mean crystal approximation for partially deuterated compounds. In this study we used the results obtained in the work [22] for the thermodynamics of the \( \text{KH}_2\text{PO}_4 \) crystals. Theoretically derived thermodynamic properties of the \( \text{K(H}_1\text{x-D}_2\text{)}\text{2PO}_4 \) crystals were compared with the experimental ones. The issue of the mean crystal applicability to the description of the physical properties of the \( \text{K(H}_1\text{x-D}_2\text{)}\text{2PO}_4 \) crystals was discussed.

### 2. Thermodynamic characteristics of the \( \text{KH}_2\text{PO}_4 \) and \( \text{KD}_2\text{PO}_4 \) ferroelectrics

In this section we take a quick look at theoretical results for thermodynamic characteristics of the \( \text{KH}_2\text{PO}_4 \) and \( \text{KD}_2\text{PO}_4 \) type ferroelectrics derived within the framework of the proton ordering model in the four-particle cluster approximation for short-range interaction and in the molecular field approximation for long-range interaction. The analysis of the model with tunnelling, appropriate to the crystals of \( \text{KH}_2\text{PO}_4 \) type, could be found in the work [22]; while the analysis of the model without tunnelling, appropriate to the crystals of \( \text{KD}_2\text{PO}_4 \) type, could be found in the works [11, 12].

To start with, let us present the results for some thermodynamic characteristics of the proton ordering model. The molar free energy of the proton system is of the following form [15, 17, 18, 22]:

\[
f = RT \left( -\ln Z_4 + 2\ln Z_1 + \frac{\beta}{4} \nu_z P^2 \right),
\]

(1)

where \( R \) is the absolute gas constant, \( T \) is the temperature, \( \beta \) is the inverse temperature, \( \nu_z \) is the long-range interaction parameter,

\[
Z_4 = \sum_{i=1}^{16} \exp(-\beta E_i), \quad Z_1 = 2 \cosh \left( \beta \sqrt{K} \right), \quad K = \left( C + \frac{\nu_z P^2}{4} \right)^2 + (2\Gamma + \Omega)^2.
\]

\( E_i \) are the eigen values of the four-particle Hamiltonian matrix \( H_4 \):

\[
H_4 = B_1 \oplus B_2 \oplus B_3 \oplus B_4,
\]

(2)

where

\[
B_1 = \begin{pmatrix}
-2C & 0 & 0 & 2\Gamma & 0 & 0 \\
0 & 2C & 0 & 0 & 2\Gamma & 0 \\
0 & 0 & \varepsilon & 2\Gamma & 2\Gamma & 0 \\
2\Gamma & 0 & 2\Gamma & w - C & 0 & \sqrt{2\Gamma} \\
0 & 2\Gamma & 2\Gamma & 0 & w + C & \sqrt{2\Gamma} \\
0 & 0 & 0 & \sqrt{2\Gamma} & \sqrt{2\Gamma} & w_1 \\
\end{pmatrix}, \quad B_3 = \varepsilon,
\]

\[
B_2 = \begin{pmatrix}
\varepsilon & \sqrt{2\Gamma} & \sqrt{2\Gamma} \\
\sqrt{2\Gamma} & w - C & 0 \\
\sqrt{2\Gamma} & 0 & w + C \\
\end{pmatrix}, \quad B_4 = \begin{pmatrix}
w - C & 0 & \sqrt{2\Gamma} \\
0 & w + C & \sqrt{2\Gamma} \\
\sqrt{2\Gamma} & \sqrt{2\Gamma} & w_1 \\
\end{pmatrix}.
\]
Here $\varepsilon, w, w_1$ are the model theory cluster parameters, $w_1 = 4w - 2\varepsilon$, $\Omega$ is the tunnelling parameter. The fields $\Gamma$ and $C$, contained in the given expression depend on the proton ordering parameter $P = 2\langle S^z \rangle$ and the parameter $X = 2\langle S^x \rangle$:

$$C = \frac{P}{2\beta Q} \ln \frac{1 - Q}{1 + Q} - \frac{1}{4} \nu_z P, \quad \Gamma = \frac{X}{4\beta Q} \ln \frac{1 - Q}{1 + Q} - \frac{\Omega}{2}, \quad Q = \sqrt{P^2 + X^2}.$$  

The parameters $P$ and $X$ are derived under the minimum free energy condition. The molar entropy is derived through the differentiation of the free energy with respect to temperature:

$$S = -\frac{1}{T} f + R\beta \left( \frac{1}{4} \nu_z P^2 + \frac{1}{Z_4} \sum_{i=1}^{16} \exp(-\beta E_i) E_i + 2\sqrt{K} \tanh(\beta \sqrt{K}) \right).$$  

The analytical expression for the specific heat is too cumbersome, so we calculate it by differentiating the entropy with respect to temperature.

The formulas for the components of the static dielectric permittivity tensor for this model along with the equation for the Curie-Weiss temperature $T_0$ can be found in the work [22].

The polarization of the crystal is proportional to the proton ordering parameter:

$$\mathcal{P}(T) = \frac{2\mu_z}{v} P(T),$$  

where $\mathcal{P}(T)$ is the spontaneous polarization, $\mu_z$ is the effective dipole moment of the primitive cell along the ferroelectric axis $z$, $v$ is the volume of the primitive cell, $P(T)$ is the ordering parameter. The saturation of polarization is reached at some non-zero temperature. The corresponding value of the proton ordering parameter is less than one. The saturation of polarization is written as follows:

$$P_{\text{sat}} = \frac{2\mu_z}{v} P_{\text{sat}},$$  

where $P_{\text{sat}}$ is the saturation polarization, $P_{\text{sat}}$ is the value of the parameter $P$ at the saturation point.

Now, let us present the expressions of thermodynamic characteristics of the ferroelectrics crystals KD$_2$PO$_4$ type, derived within the proton ordering model without tunnelling.

The free energy [11,12]:

$$f = RT \left( \frac{\beta}{4} \nu_z P^2 - \ln \frac{(1 - P^2)\mathcal{D}}{2} \right),$$  

where

$$\mathcal{D} = \cosh 2C_d + 4b \cosh C_d + 2a + d, \quad C_d = \frac{1}{2} \ln \frac{1 + P}{1 - P} + \frac{\beta \nu_z}{4} P,$$

$$a = \exp(-\beta \varepsilon), \quad b = \exp(-\beta w), \quad d = \exp(-\beta w_1),$$  

and the ordering parameter $P$ is derived under the minimum free energy condition.

The polarization and the saturation polarization are described as (4) and (5) respectively. However, in case of the model without tunnelling for the ordering parameter saturation we have $P_{\text{sat}} = P(T \to 0) = 1$.

The entropy can be obtained directly by differentiating the free energy with respect to the temperature:

$$S = R \left( \ln \frac{(1 - P^2)\mathcal{D}}{2} + \frac{M}{\mathcal{D}} - \frac{\beta \nu_z}{2} P^2 \right),$$  

where

$$M = \beta(4bw \cosh C_d + 2aw + dw_1).$$  

The expression for the specific heat can be found by differentiating the entropy with respect to the temperature:

$$\Delta C = R \cdot (Y + U \cdot V),$$  

where

$$Y = \frac{1}{T} f, \quad U = R \beta \frac{1}{4} \nu_z P^2, \quad V = \frac{1}{Z_4} \sum_{i=1}^{16} \exp(-\beta E_i) E_i + 2\sqrt{K} \tanh(\beta \sqrt{K}).$$
with
\[
Y = \left( 4T \varphi_1 (T \varphi_1 + Q) + N - M^2 / D \right) / D, \quad U = 2T \varphi_2 (2T \varphi_1 + Q) / D, \\
V = \beta (2T \varphi_1 + Q) / (D - 2 \varphi_2 \varepsilon), \quad \varphi_1 = - \frac{\beta^2 \nu_z}{4} P, \quad \varphi_2 = \frac{1}{1 - P^2} + \frac{\beta \nu_z}{4}, \\
N = \beta^2 (2a \varepsilon^2 + d \omega_1^2 + 4bw^2 \cosh C_d), \quad Q = 2 \beta bw \sinh C_d - M \cdot P, \\
\varepsilon = \cosh 2C_d + b \cosh C_d - P^2 D, \\
\]
where \( M \) is derived according to (9) and \( D, C_d, a, b, d \) are defined in (7).

The diagonal components of the static dielectric permittivity according to [22] are as follows:
\[
\varepsilon_{\alpha} = \varepsilon_{\alpha}(\infty) + 4 \mu^2_\alpha (1 + \delta_{\alpha \sigma}) \frac{2 \beta F_{\alpha}}{D - \frac{1}{1 - P^2} + \frac{\beta \nu_z}{4}} 2F_{\alpha}, \\
\]
where \( \varepsilon_{\alpha}(\infty) \) is the high frequency contribution to the dielectric permittivity, \( \mu_{\alpha} \) are the components of the effective dipole moment of the primitive cell, \( v \) is the volume of the primitive cell and
\[
F_x = F_y = a + b \cosh C_d, \quad F_z = b \cosh C_d + \cosh 2C_d - P^2 D.
\]
All the off-diagonal components are equal to zero.

Setting the denominator of (12) equal to zero at \( P = 0 \), and taking into account that the values \( a, b, d \) are defined by means of (7) we can obtain the equation for the Curie-Weiss temperature \( T_0 \):
\[
2(a + b) + d = 1 + (b + 1) \frac{\beta \nu_z}{2}.
\]

In case of the model without tunnelling we can derive the theory model parameters \( \varepsilon, w, \nu_z \) by defining the phase transition temperature \( T_c \), the Curie-Weiss temperature \( T_0 \) and the jump of the ordering parameter at the phase transition point \( P_c \).

At \( T = T_c \) we can write the following equality for the free energy:
\[
f(\varepsilon, w, \nu_z, P_c, T_c) = f(\varepsilon, w, \nu_z, 0, T_c).
\]
Out of this equality and taking into account (6) we derive the following:
\[
a = \frac{\cosh 2C_d + 4b \cosh C_d - (1 + 4b)L + d(1 - L)}{2(L - 1)},
\]
where
\[
L = \exp \left( \frac{\nu_z \mu^2_\alpha}{4T_c} \right) \frac{1}{1 - P_c^2}.
\]
Here \( C_d, b, d \) are defined by (7) at \( T = T_c, P = P_c \).

Now, if we take into account the minimum free energy condition (the parameter \( P \) is the solution of the equation \( \partial f / \partial P \big|_T = 0 \)) and take into account the relationship (14) then at \( T = T_c \) we shall derive the following:
\[
b = \frac{(L - 1) \sinh 2C_d - P_c L \cosh 2C_d + P_c L}{4P_c L \cosh C_d - 4P_c L - 2(L - 1) \sinh C_d}.
\]
Here the value \( C_d \) is defined as (7) at \( T = T_c, P = P_c \).

The long-range interaction parameter \( \nu_z \) is derived using the equation (13) at certain Curie-Weiss temperature \( T_0 \). Expressing the values \( a, b, d \), defined in the equation (13) at the temperature \( T_0 \) in terms of \( a, b, d \), defined at the temperature \( T_c \), let us rewrite the equation (13) in the following way:
\[
\frac{\nu_z}{2T_0} = \frac{2 \exp \left( \frac{T_c}{T_0} \ln a \right) + 2 \exp \left( \frac{T_c}{T_0} \ln b \right) - 1 + \exp \left( \frac{T_c}{T_0} \ln d \right)}{1 + \exp \left( \frac{T_c}{T_0} \ln b \right)},
\]

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where the values $a$ and $b$ are defined through the $T_c$, $P_c$, $\nu_z$ by means of the equalities (14), (16).

Solving the equation (17) it is proper to omit the term containing $d$ and set $d = 0$ in the expression (14). This is justified by $\epsilon \ll w \ll w_1$, so $d$ is small in comparison to $a$ and $b$, and hence it can be neglected.

Finally, in order to define the values $a$, $b$ and $\nu_z$ we need to numerically solve the equation (17) taking into account the equalities (14), (15), (16). The model theory parameters $\epsilon$ and $w$ will be derived by means of relationships (7):

$$\epsilon = -T_c \ln a, \quad w = -T_c \ln b.$$ (18)

### 3. Model theory parameters for KD$_2$PO$_4$ crystal and thermodynamic characteristics calculated on the basis of the derived results with experiment

The success of the study of partially deuterated K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals to a great extent depends on the success of the theoretical description of physical characteristics of KH$_2$PO$_4$ and KD$_2$PO$_4$ crystals. In particular, the model theory parameters derived for these crystals are significant. Careful theoretical study of KH$_2$PO$_4$ crystal was carried out in the work [22]. For KH$_2$PO$_4$ crystal we use the model theory parameters obtained in this work:

$$\epsilon = 55 \text{ K}, \quad w = 600 \text{ K}, \quad \Omega = 138 \text{ K}, \quad \nu_z = 109.22 \text{ K}, \quad \nu_x = 40 \text{ K};$$
$$\mu_z = \bar{\mu}_z \theta(T_c - T) + \bar{\mu}_z \theta(T - T_c),$$
$$\bar{\mu}_z = 5.017 \cdot 10^{-30} \text{ C} \cdot \text{m}, \quad \bar{\mu}_z = 5.856 \cdot 10^{-30} \text{ C} \cdot \text{m};$$
$$\bar{\epsilon}_z(\infty) = \bar{\epsilon}_x(\infty) \theta(T_c - T) + \bar{\epsilon}_z(\infty) \theta(T - T_c),$$
$$\bar{\epsilon}_z(\infty) = 6.7, \quad \bar{\epsilon}_x(\infty) = 9;$$
$$\mu_x = 13.078 \cdot 10^{-30} \text{ C} \cdot \text{m};$$
$$\epsilon_x(\infty) = \epsilon_x(\infty) \theta(T_c - T) + \epsilon_x(\infty) \theta(T - T_c),$$
$$\epsilon_x(\infty) = 12.6, \quad \epsilon_x(\infty) = 26.5,$$ (19)

where $\theta(x)$ is theta-function ($\theta(x < 0) = 0; \quad \theta(x \geq 0) = 1$), and $T_c = 122.751 \text{ K}$ is phase transition temperature of the KH$_2$PO$_4$ crystal.

Hitherto there have not been obtained the model theory parameters for KD$_2$PO$_4$ crystal, which could be considered the most appropriate in describing this crystal. This section primarily deals with the setting of model theory parameters for KD$_2$PO$_4$ crystal, with the comparison of the thus calculated thermodynamic characteristics with experimental data and with the comparison of the calculated characteristics with the results of previous works.

Among the other works devoted to the study of KD$_2$PO$_4$ crystal within the proton ordering model in the four-particle cluster approximation for short-range interaction and in the molecular field approximation for long-range interaction the works [12,15,18,23] appear to be worth mentioning.

It was in the work [15], that the study of the dependence of thermodynamic characteristics of KD$_2$PO$_4$ crystal on the model parameters $\epsilon$, $w$, $\nu_z$ within the cluster approximation was carried out for the first time. In this work, based on the intuitively set parameters, the qualitative correspondence of the theoretical calculations of temperature dependencies for spontaneous polarization and entropy of the phase transition for KD$_2$PO$_4$ to the experiment was obtained.

In the work [23] the procedure of setting the parameters for KD$_2$PO$_4$ crystal and other crystals of KH$_2$PO$_4$ family was such that physical characteristics calculated based on these parameters should satisfy the following conditions: 1) the calculated phase transition temperature should correspond to the experimental one; 2) the ordering parameter jump at the point of the phase transition should coincide with the experimental value; 3) the calculated entropy of the phase transition should correspond to the experimental one. However, this work fails to give the comparison of the calculation results for temperature dependencies of polarization and specific heat with the experimental data.
Another careful theoretical study of KD$_2$PO$_4$ crystal was carried out in work [18]. The authors of this work thoroughly studied and systematized the available experimental data, did a meticulous research of the effect of the change of the model parameters upon the temperature dependency of the ordering parameter $P(T)$, entropy $S(T_c + 0)$ and upon the order of the phase transition. The derived theoretical results were compared to the corresponding experimental data. The authors of the work [18] selected the values of the theory parameters basing on the condition of agreement of theoretical calculation results for values $\sqrt{\Delta S(\tau)/S_c}$ ($S_c = S(T_c + 0)$, $\Delta S(\tau) = S_c - S(\tau)$, $\tau = 1 - T/T_c$) with the corresponding results calculated on the grounds of experimental data for the specific heat of the crystals. However, such calculations apart from the error of specific heat measurements also contain the error which occurs while determining the deuteron system contribution to the crystal specific heat as well as while numerically integrating the determined contribution. Two sets of model parameters (set 2 and 3 in table 1) for KD$_2$PO$_4$ crystal were obtained in the work [18]. However, the value 228K [24] was taken as an experimental value of the phase transition temperature which, as work [21] shows, turns out to be erroneous.

**Table 1.** Parameter sets and physical characteristics for KD$_2$PO$_4$ crystal, calculated on their basis. Set 1 — [11], sets 2, 3 — [18], set 4 — the results of this work.

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<td>$\varepsilon_x(\infty)$ ($T &lt; T_c$)</td>
<td>f($T$)</td>
<td>—</td>
<td>—</td>
<td>7.73</td>
</tr>
<tr>
<td>$\varepsilon_x(\infty)$ ($T \geq T_c$)</td>
<td>f($T$)</td>
<td>—</td>
<td>—</td>
<td>21.3</td>
</tr>
<tr>
<td>$C_w$, K</td>
<td>4286</td>
<td>—</td>
<td>—</td>
<td>4020</td>
</tr>
</tbody>
</table>

In the work [11] another set of model parameters (set 1 in table 1) for KD$_2$PO$_4$ crystal was obtained, which gives a correct phase transition temperature $T_c = 219.7$ K, and adequately describes experimental dependencies of polarization and deuteron specific heat on temperature. The work [12] basing on the model parameters, obtained in the work [11], presents the study of transverse dielectric properties of KD$_2$PO$_4$ crystal as well as shows the agreement of theory and experiment. However, the question whether it is possible to achieve a better quantitative fit for KD$_2$PO$_4$ crystal within the proposed model, remains open. Hereinbelow the procedure of a unique setting of model...
The theoretical parameters for KD$_2$PO$_4$ crystal are proposed, which, in our opinion, is the most optimal.

To calculate the physical characteristics, it is necessary to determine the volume of the unit cell of KD$_2$PO$_4$ crystal, which has been approximated in the following way:

$$v_D = \bar{v}_D \theta(T_c - T) + \bar{v}_D \theta(T - T_c),$$

where $T_c$ is phase transition temperature of KD$_2$PO$_4$ crystal, and $\bar{v}_D$ and $\bar{v}_D$ are volumes of the KD$_2$PO$_4$ unit cell in ferroelectric and paraelectric phases, respectively (see table 2). A discontinuous change of the unit cell volume occurs at the first order phase transition, in view whereof the use of theta-functions is sufficiently correct. Besides, this approximation is acceptable due to the minor change of the unit cell volume.

The expressions for thermodynamic characteristics of ferroelectrics of KD$_2$PO$_4$ type include three independent theory parameters $\varepsilon$, $w$, $\nu_z$, which should be set basing on the condition of the best fit between theoretically calculated physical characteristics and experimental data (see table 2). When determining their optimal values it is convenient to use the non-linear equation (17), which provides a unique setting of theory parameters $\varepsilon$, $w$, $\nu_z$, using the experimental data for $T_c$, $T_0$ and $P_c = P_c/P_{sat}$ as the base. Here $P_c = P(T_c)$ is the value of spontaneous polarization jump at the phase transition point, $P_{sat} = P(T \to 0)$ is the value of spontaneous polarization saturation, $P_c = P(T_c)$ is the value of the ordering parameter jump at the phase transition point. Thus the problem of setting the theory parameters $\varepsilon$, $w$, $\nu_z$ comes to the problem of setting physical properties $T_c$, $T_0$ and $P_c$.

The values $T_c$, $T_0$ and $P_c$ were set basing on the following considerations. The value $T_c$, as one of the most important characteristics of phase transition was set equal to its corresponding experimental value. We took the result of the work [26] as an experimental value of $T_c$ for KD$_2$PO$_4$ crystal, namely, $T_c = 219.8$ K.

Experimental values of $T_0$ and $P_c$ are less reliable, that is why they should be set basing on the condition of the agreement of theoretically calculated and experimental characteristics, whose data are quite reliable. For KD$_2$PO$_4$ crystals (KH$_2$PO$_4$ crystals, as well as for partially deuterated crystals) such characteristics are temperature dependencies of spontaneous polarization $P(T)$, and of deuteron (proton, proton-deuteron) specific heat $\Delta C(T)$. Besides, based on this condition, $T_0$ and $P_c$ should be such that they agree with experimental data.

Experimental data for deuteron (as well as for proton-deuteron or proton) specific heat were derived by subtracting the contribution of lattice subsystem to specific heat from the total specific heat experimentally measured. Thus, the lattice specific heat was determined basing on the assumption that at temperatures remote from the phase transition point $T_c$ it coincides with the total specific heat, linearly depends on the temperature $T$ and does not have singularity at the phase transition point.

### Table 2. Experimental data for KD$_2$PO$_4$ crystal.

<table>
<thead>
<tr>
<th>$T_c$, K</th>
<th>219.8 [26], 220.424 [27], 222 [28], 221.1 [21]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$, K</td>
<td>218.2 [29], 218.3 [26], 219.5 [30], 205 [31], 220.4 [21]</td>
</tr>
<tr>
<td>$P_c/P_{sat}$</td>
<td>0.78 [27], 0.46 [26], 0.70 [32]</td>
</tr>
<tr>
<td>$P_{sat}$, 10$^{-2}$ C/m$^2$</td>
<td>6.21 [26], 5.95 [37], 6.15 [33]</td>
</tr>
<tr>
<td>$C_{eu}$, K</td>
<td>4435 [30], 4020 [26], 2860 [31], 3000 [34], 3200 [35], 3930 [21]</td>
</tr>
<tr>
<td>$\bar{v}$, 10$^{-30}$ m$^3$</td>
<td>193.5555 $(T = T_c - 10$ K) [36]</td>
</tr>
<tr>
<td>$\bar{v}$, 10$^{-30}$ m$^3$</td>
<td>193.532 $(T = T_c + 5$ K) [36]</td>
</tr>
</tbody>
</table>
The above described procedure of determining the deuteron subsystem contribution to the specific heat basing on experimental data for total specific heat may be the cause of an additional contribution to the error, that is why more attention was paid to the agreement of theory and experiment for $\Delta C(T)$ than to the agreement for $P(T)$. As an experimental dependency of the specific heat on the temperature for KD$_2$PO$_4$ crystal we took the result of the work [37] and rejected the results of the works [35,38,39] basing on the fact that the phase transition temperature value ($T_c = 214.95$ K [35], $T_c = 202.99$ K [38], $T_c = 203$ K [39]) obtained in these works considerably differed from the value $T_c = 219.8$ K in the work [26], which we accept to be reliable. Hereinafter, deuteron (or proton in case of KH$_2$PO$_4$ crystal or proton-deuteron in case of K(\(\text{H}_1\ldots\text{D}_x\))$_2$PO$_4$ crystal) specific heat will be referred to as specific heat.

At different values of Curie-Weiss temperature $T_0$, the parameter $P_c$ was set basing on the condition of the best agreement of theoretical and experimental dependencies of polarization on the temperature $P(T)$. Except the polarization jump, all the sets of $T_0$ and $P_c$ describe the dependency $P(T)$ similarly well. Theoretical dependencies of specific heat on the temperature were compared to the experimental one and it was perceived that such simultaneous change of values $T_0$ and $P_c$ does not virtually result in an improved agreement of theory and experiment for $\Delta C(T)$.

So, we can take $T_0$ or $P_c$ as experimental values. The precision of measurements $T_0$ is considerably higher than $P_c = P_c/P_{sat}$; the values of $P_c = P_c/P_{sat}$ in different works differ considerably (see table 2). On this basis experimental value was assigned to $T_0$, equal to 218.3 K [26]. The best agreement of theory and experiment for $P(T)$ at $T_0 = 218.3$ K is provided by the value of the ordering parameter at the phase transition point $P_c = 0.78$. By comparison, it was experimentally obtained: $P_c/P_{sat} = 0.46$ [26], $P_c/P_{sat} = 0.78$ [27], $P_c/P_{sat} = 0.70$ [32]. Eventually the values of cluster parameters, which we derived basing on the principles stated above, and their corresponding calculated physical characteristics are set out in the table 1, set 4.

In our opinion, such a procedure of theory parameter setting is the most optimal since any other procedure even if it gives an improved agreement of theory and experiment for some physical characteristics, it inevitably worsens the agreement for other characteristics. Moreover, the procedure proposed by us reconciles the most important physical characteristics, those for which experimental data are the most reliable.

![Figure 1](image1.png)

**Figure 1.** Dependency of spontaneous polarization of KD$_2$PO$_4$ crystal on the temperature. The lines present theoretical results for parameter sets 1, 2, 3, 4, given in table 1. The points present experimental data of the work [26].

![Figure 2](image2.png)

**Figure 2.** Temperature dependency of specific heat of KD$_2$PO$_4$ crystal. The lines present theoretical results for parameter sets 1, 2, 3, 4 given in table 1. The points present experimental data of the work [37].

Figure 1 for KD$_2$PO$_4$ crystal presents experimental and theoretically calculated dependencies $P(T)$. When calculating polarization, an effective dipole moment was determined in such a manner that the calculated value of saturation polarization was equal to the experimental value $P_{sat} = 6.21 \mu$C/cm$^2$ [26]. Effective longitudinal dipole moment derived from this condition is equal to $6.01 \cdot 10^{-30}$ C·m. Figure 2 for KD$_2$PO$_4$ crystal presents experimental and theoretically calculated
dependencies $\Delta C(T)$. The calculations were carried out using the set of parameters obtained in this work: set 4 in table 1, as well as using sets obtained in other works: in table 1 set 1 [11], sets 2, 3 [18]. The calculations results, presented in figures, testify that the best agreement of theory and experiment, jointly for the temperature dependencies of polarization and specific heat, is achieved when using the parameter set obtained in this work.

Now we shall proceed to the discussion of the results obtained for a tensor component of the static dielectric permittivity of KD$_2$PO$_4$. We write the effective dipole moment $\mu_z$ as:

$$\mu_z = \tilde{\mu}_z \theta(T_c - T) + \bar{\mu}_z \theta(T - T_c).$$

The values of parameters $\bar{\mu}_z$ and $\varepsilon_z(\infty)$ were chosen basing on the condition of the best agreement of a theoretically calculated curve $\varepsilon_z^{-1}(T)$ and experimental data. The value of parameter $\bar{\mu}_z$ (set out in table 1) was derived hereinabove basing on the condition of equality of theoretically calculated and experimental values of saturation polarization.

The best agreement with experimental results of the work [26] for inverse static dielectric permittivity $\varepsilon_z^{-1}(T)$ of KD$_2$PO$_4$ is provided by theoretical curve, calculated with parameters $\varepsilon_z(\infty) = 2.5, \bar{\mu}_z = 7.004 \cdot 10^{-30} \text{C} \cdot \text{m}$ (figure 3). It is noteworthy that the value of the effective dipole moment in paraelectric phase derived in this manner is larger than the corresponding value $\bar{\mu}_z$ in ferroelectric phase. From figure 3 one can see that using the appropriate set of parameters $\varepsilon_z(\infty)$ and $\bar{\mu}_z$ one can achieve a virtually perfect agreement of theoretical results based on our parameters $\varepsilon, w, \nu_c$ with experimental data. Besides, theoretical studies show that the same perfect agreement between theory and experiment can be achieved by setting parameters $\bar{\varepsilon}_z(\infty)$ and $\bar{\mu}_z$ and using the other sets of model parameters $\varepsilon, w, \nu_c$. Unfortunately, we do not know the experimental data for $\varepsilon_z^{-1}(T)$ at $T < T_c$ of monodomain sample, so it is difficult to speak about the agreement between theory and experiment in ferroelectric phase.

![Figure 3](image3.png)

**Figure 3.** Temperature dependency of inverse static longitudinal dielectric permittivity of KD$_2$PO$_4$. The line presents theoretical results for the set of parameters obtained in this work (set 4 in table 1). The points are experimental data: $\circ$ — [26], $\blacktriangle$ — [40], $\blacklozenge$ — [30].

There is a further point to be made that concerns a certain peculiarity of setting the parameters $\varepsilon_z(\infty)$ and $\bar{\mu}_z$. Specifically, besides the values chosen in this work for these parameters, one can also choose other values which will provide practically the same good description for experimental data, e.g. $\varepsilon_z(\infty) = 4.9, \bar{\mu}_z = 6.987 \cdot 10^{-30} \text{C} \cdot \text{m}$. But still, the parameters $\bar{\mu}_z$ will differ very little from one another, while $\varepsilon_z(\infty)$ can be twice as different from one another. That is why the value of parameter $\varepsilon_z(\infty)$ for KD$_2$PO$_4$ derived basing on this approach, cannot be considered reliable.

Let us present the results, derived for a static transverse dielectric permittivity $\varepsilon_x(T)$ of KD$_2$PO$_4$. The results of the work [27], in which deuteration level was 98%, were used as ex-
experimental data. High frequency contribution \( \varepsilon_x(\infty) \) was written as:

\[
\varepsilon_x(\infty) = \tilde{\varepsilon}_x(\infty)\theta(T_c - T) + \bar{\varepsilon}_x(\infty)\theta(T - T_c).
\]

The values of parameters \( \mu_x, \varepsilon_x(\infty), \tilde{\varepsilon}_x(\infty) \) were chosen basing on the condition of the best agreement of a theoretically calculated curve \( \varepsilon_x(T) \) and experimental data. The values of these parameters are set out in table 1, and the permittivity \( \varepsilon_x(T) \) together with experimental data calculated on their basis are set out in figure 4.

However, the proposed approach does not provide a dome-shaped behaviour of the value \( \varepsilon_x(T) \) in paraelectric phase near the transition point \( T_c \) (the model with tunnelling used in work [22] for KH\(_2\)PO\(_4\) crystal description also did not provide a dome-shaped behaviour). Figure 4 shows that, as in the case with static longitudinal dielectric permittivity, the set of parameters \( \mu_x, \varepsilon_x(\infty), \tilde{\varepsilon}_x(\infty) \) makes it possible to achieve practically perfect agreement of theoretical results, obtained using our parameters \( \varepsilon, w, \nu_x \) with the corresponding experimental data. Besides, theoretical studies show that the same perfect agreement of theory and experiment for static transverse dielectric permittivity can be achieved by setting the parameters \( \mu_x, \varepsilon_x(\infty), \tilde{\varepsilon}_x(\infty) \) using other sets of model parameters \( \varepsilon, w, \nu_x \) as well.

Our studies of dielectric characteristics of KD\(_2\)PO\(_4\) crystal permit the statement that, as in the case with KH\(_2\)PO\(_4\) crystal (see [22]), the agreement of these characteristics with the experiment cannot be considered as a criterion for setting the model theory parameters \( \varepsilon, w, \nu_x \).

4. Thermodynamic characteristics of the ferroelectric partially deuterated K(H\(_{1-x}\)D\(_x\))\(_2\)PO\(_4\) crystals. Numerical analysis and comparison with the experiment

First we shall briefly review the experimental works in which the phase transition temperature of the K(H\(_{1-x}\)D\(_x\))\(_2\)PO\(_4\) crystals was determined. The dependency of the phase transition temperature on the deuteration level \( x \), determined by different authors, is considerably scattered in the experimental data. In some works (for instance [24,41,42]) the \( T_c(x) \) dependency is considered to be linear. However, the majority of the works show that the dependency \( T_c(x) \) is nonlinear. In the work [21] a thorough research of the phase transition temperature concentration dependency was conducted. The numerous species of the K(H\(_{1-x}\)D\(_x\))\(_2\)PO\(_4\) crystals with different deuteration levels were experimentally studied in this work and the nonlinear behaviour of the \( T_c(x) \), derived in other works, was confirmed. Also, the approximation functions for \( T_c(x) \) were presented:

\[
\begin{align*}
T_c(x) &= (122.9 + 100.9 \cdot x) \text{ K}, \\
T_c(x) &= (122.9 + 117.3 \cdot x - 19.6 \cdot x^2) \text{ K}, \\
T_c(x) &= (122.9 + 124.4 \cdot x - 42.3 \cdot x^2 + 16.1 \cdot x^3) \text{ K}.
\end{align*}
\]  

(21)

In our work we use the results of the work [21] for \( T_c(x) \). The experimental points for \( T_c(x) \) along with the results, derived according to the approximation formulas, are presented in figure 5.

Another issue to be considered before we proceed to the calculations is the value of the deuterium concentration of the partially deuterated crystals. The majority of the experimental works, devoted to the study of the KD\(_2\)PO\(_4\) crystals, in fact, did not deal with the absolutely deuterated crystals but with the partially deuterated ones. Correspondingly the phase transition temperatures \( T_c \) of the KD\(_2\)PO\(_4\) crystals differ considerably in the different works: from 213 K [43] up to 222 K [28]. Such a mismatch was related both to the crystal defects and to different deuteration levels. In the work [21] it was shown that the lattice defects practically did not affect the phase transition temperature, and all the distinctions in \( T_c \) are related to different deuteration levels of the researched crystals. Thus, the information on the \( T_c \) can answer the question about the deuteration level of these crystals. Having the dependency \( T_c(x) \) for the K(H\(_{1-x}\)D\(_x\))\(_2\)PO\(_4\) and having the phase transition temperature of the particular crystal we can unambiguously obtain its deuteration level \( x \). Considering the experimental works, which studied the K(H\(_{1-x}\)D\(_x\))\(_2\)PO\(_4\) crystals,
we accepted their deuteration levels not as they had been assigned by the authors but those ones derived according to the cubic approximation (21) at a known phase transition temperature.

Carrying out the theoretical study of thermodynamic properties of the K(H$_{1-x}$D$_x$)$_2$PO$_4$ ferroelectrics we consider some model theory parameters to be linearly dependent functions of deuteration level.

\[ \varepsilon(x) = \varepsilon_H(1-x) + \varepsilon_{Dx}, \quad w(x) = w_H(1-x) + w_{Dx}, \quad \Omega(x) = \Omega(1-x), \]  \tag{22}

where \( \varepsilon_H, w_H, \Omega \) are the theory parameters for KH$_2$PO$_4$ crystal (19), \( \varepsilon_{Dx}, w_{Dx} \) are the theory parameters for KD$_2$PO$_4$ crystal defined in the present work (set 4 in table 1). Concerning the parameter \( w_1 \), we should note that it is equal to \( 4w - 2\varepsilon \) for KH$_2$PO$_4$. This value is great in magnitude and can be regarded as infinity for particular calculations. Besides, for the KD$_2$PO$_4$ crystal, parameter \( w_1 \) is infinitude and hence we can admit that it is infinitude for partially deuterated crystals too.

We derive the long-range interaction parameter \( \nu_x \) for the K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystal under the condition of the calculated phase transition temperature \( T_c(x) \) coinciding with the experimental one. The calculated values of the spontaneous polarization jump at the phase transition point can differ from the experimental ones. However, experimental values of the spontaneous polarization jump are not reliable, and we can ignore this disagreement.

To carry out particular calculations we also need the value of the primitive cell volume. We approximate it in the following way:

\[ \nu_x(T) = \bar{v}_x(T_c(x) - T) + \bar{v}_x(T - T_c(x)), \]
\[ \bar{v}_x = (1-x)\bar{v}_H + x\bar{v}_D, \tag{23} \]

where the values \( \bar{v}_D(T) \) and \( \bar{v}_H(T) \) are set out in table 2, \( \bar{v}_H, \bar{v}_D \) are the volumes of the primitive cell of KH$_2$PO$_4$ in the ferroelectric and paraelectric phases, respectively: \( \bar{v}_H = 189.635 \cdot 10^{-30}\text{m}^3 \), \( \bar{v}_H = 191.127 \cdot 10^{-30}\text{m}^3 \) \cite{22}; \( T_c(x) \) is phase transition temperature. Such an expression for \( \nu_x(T) \) value can be regarded as valid due to a minor dependency of the unit cell dimensions on the deuteration level and due to a minor temperature change of the unit cell dimensions \cite{25}. As far as K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals undergo the first order ferroelectrics phase transition, the use of theta-functions is sufficiently correct.

We also suppose that the effective dipole moment of the K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals in the ferroelectric phase (we denote it as \( \bar{\mu}_z(x) \)) linearly depends on the deuteration level:

\[ \bar{\mu}_z(x) = \bar{\mu}_z^{(H)}(1-x) + \bar{\mu}_z^{(D)} \cdot x, \tag{24} \]
where $\mu_z^{(H)}$ and $\mu_z^{(D)}$ are the effective dipole moments of KH$_2$PO$_4$ and KD$_2$PO$_4$ (see (19) and set 4 in table 1). The dependencies of polarization on the temperature $P(T)$ calculated under this condition at different deuteration levels along with the experimental data are shown in figure 6. At the deuteration level $x = 0.57$ no experimental values for $P(T)$ are available and the figure shows only the results of theoretical calculations. This figure shows a very good agreement of theory and experiment for the $P(T)$ at all deuteration levels.

Let us consider the dependency of the saturation polarization on the level of deuteration. The study of the current model within the four-particle cluster approximation reveals that under $T_c$ and with a further decrease of temperature the ordering parameter first increases (i.e., approaches 1 but does not reach it) but then begins to decrease. So, the temperature of the saturation point is nonzero and the value of the ordering parameter at this point is less than 1. Hence, the saturation polarization dependency on the deuteration level (see (5)) is nonlinear, even though the effective dipole moment linearly depends on $x$ (the dependency of the primitive cell volume on $x$ is negligible and cannot essentially effect the final result). Regardless of the obtained nonlinear dependency of the saturation polarization on deuteration level, the calculated curve $P_{\text{sat}}(x)$ is in fairly good agreement with the experimental data. The theoretical results along with the experimental data are illustrated in figure 7.

![Figure 6](image_url_6)

**Figure 6.** Temperature dependencies of the spontaneous polarization at different deuteration levels. The lines present theoretical results. The points present experimental data of the work [26]. ○: $x = 0.00$, △: $x = 0.33$, ●: $x = 0.80$, ▲: $x = 1.00$.

![Figure 7](image_url_7)

**Figure 7.** The saturation polarization dependency on the deuteration level (a), on the phase transition temperature (b). The lines present theoretical results. The points present experimental data of the work [26].
In fact, only the model with tunnelling exhibits such a behaviour, whereas within the model without tunnelling the saturation takes place at zero and the ordering parameter is equal to 1 at this point. The figure also illustrates that the theoretically calculated dependency of the saturation polarization on the phase transition temperature is almost linear.

Figure 8 illustrates the temperature dependencies of the specific heat for the K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals at different deuteration levels. The figure shows that the theoretically obtained curves below the phase transition point are in good agreement with the experimental data at every deuteration level.

Figure 9 shows the experimental and theoretical results for the inverse static longitudinal dielectric permittivity. The lines present theoretical results. The points present experimental data: $\triangle$—[35], $\times$—[44], $+$—[38], ($x = 0.00$); $\square$—[35], ($x = 0.11$); $*$—[35], ($x = 0.34$); $\triangledown$—[35], ($x = 0.54$); $\diamond$—[35], ($x = 0.86$); $\partial$—[37], ($x = 1.00$).

Now let us consider the results obtained for the inverse static longitudinal dielectric permittivity $\varepsilon^{-1}_z(x, T)$ of the K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystal. The procedure of deriving the theory model parameters $\varepsilon$, $w$, $\Omega$, $\nu_z$ was described above. We present the effective dipole moment $\mu_z(x)$ as:

$$\mu_z(x) = \tilde{\mu}_z(x)\theta(T_c - T) + \tilde{\mu}_z(x)\theta(T - T_c),$$

where $\tilde{\mu}_z(x)$ is defined according to (24). The parameters $\varepsilon_z(\infty, x)$ (high frequency contribution to the longitudinal dielectric permittivity) and $\tilde{\mu}_z(x)$ are chosen under the condition of the best agreement of the theory results with experiment for $\varepsilon_z^{-1}(x, T)$ in paraelectric phase at every deuteration level $x$.

Figure 9 shows the experimental and theoretical results for the inverse static longitudinal dielectric permittivity of K(H$_{1-x}$D$_x$)$_2$PO$_4$. The figure shows that a good agreement between theory and experiment for all deuteration levels could be achieved using the appropriate set of parameters $\varepsilon_z(\infty, x)$ and $\tilde{\mu}_z(x)$. As a result, the theoretical and experimental values of the Curie-Weiss constants practically coincide at all deuteration levels. We do not know the experimental data for $\varepsilon_z^{-1}(x, T)$ of the monodomain samples in the ferroelectric phase. So, we cannot make any assertion about the agreement between theory and experiment below $T_c$.

Figures 10 and 11 present the derived dependencies of the high frequency contribution to the longitudinal permittivity $\varepsilon_z(\infty, x)$ and of the effective dipole moment along $z$-axis in ferroelectric phase $\tilde{\mu}_z(x)$ on the deuteration level. Both values linearly depend on the deuteration level. The empiric expression $\varepsilon_z(\infty, x) \approx 1 - x$ was derived in the work [21] based on the obtained experimental data. Our results are in reasonable agreement with this empiric expression.
Calculating the statistic transverse dielectric permittivity $\varepsilon_x(x, T)$ of the K(H$_{1-x}$D$_x$)$_2$PO$_4$ we defined the effective dipole moment along $x$-axis $\mu_x(x)$ and high frequency contribution $\varepsilon_x(\infty, x)$ as:

\begin{align*}
\mu_x(x) &= \mu_x^{(H)}(1 - x) + \mu_x^{(D)} \cdot x, \\
\varepsilon_x(\infty, x) &= \bar{\varepsilon}_x^{(H)}(\infty)(1 - x) + \bar{\varepsilon}_x^{(D)}(\infty) \cdot x, \\
\bar{\varepsilon}_x(\infty, x) &= \bar{\varepsilon}_x^{(H)}(\infty)(1 - x) + \bar{\varepsilon}_x^{(D)}(\infty) \cdot x.
\end{align*}

Parameters $\bar{\varepsilon}_x^{(H)}(\infty, x)$, $\bar{\varepsilon}_x^{(H)}(\infty, x)$, $\mu_x^{(H)}$ are outlined in (19). Parameters $\bar{\varepsilon}_x^{(D)}(\infty, x)$, $\bar{\varepsilon}_x^{(D)}(\infty, x)$, $\mu_x^{(D)}$ are set out in table 1 (parameter set 4).

Figure 10. The dependency of the high frequency contribution to the longitudinal dielectric permittivity on the deuteration level.

Figure 11. The dependency of the effective dipole moment along $z$-axis in the paraelectric phase on the deuteration level.

Figure 12. The temperature dependencies of the static transverse dielectric permittivity at different deuteration levels. The lines present theoretical results. The points present experimental data: △ — [21], ($x = 0.00$); ○ — [47], ($x = 0.33$); □ — [46], ($x = 0.84$); × — [32], ($x = 1.00$).

Figure 12 presents the results of calculations for the K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals $\varepsilon_x(T)$ along with the experimental data at different deuteration levels. Due to the weak isotopic effect observed for $\varepsilon_x(T)$ and due to a considerable scatter in the experimental data it is impossible to do any inferences about the degree of agreement between the theory and experiment for $\varepsilon_x(T)$. Thus, it is impossible to do any inferences as to the rightfulness of the assumption (25). This figure only demonstrates the derived results.
Figure 13. Dependency of the long-range interaction parameter on the deuteration level, obtained according to the linear, quadratic and cubic approximations of $T_c(x)$ (21): lines 1, 2, 3 respectively.

Figure 13 presents the dependencies of the long-range interaction parameter on the deuteration level. This parameter was derived under the condition of coincidence of theoretically calculated values $T_c(x)$ with the values defined by the expressions (21). The figure shows that successive approximations yield to the rectification of the dependency $\nu_z(x)$. In case of the cubic approximation of $T_c(x)$, the respective dependency $\nu_z(x)$ is obtained close to linear. Hence, we can admit the approach according to which the theory model parameters are linearly dependent on the deuteration level $x$:

$$
\epsilon(x) = \epsilon^{(H)}(1 - x) + \epsilon^{(D)}x, \quad w(x) = w^{(H)}(1 - x) + w^{(D)}x,
$$

$$
\Omega(x) = \Omega(1 - x), \quad \nu_z(x) = \nu_z^{(H)}(1 - x) + \nu_z^{(D)}x.
$$

(26)

Such an approach to the description of the partially deuterated ferroelectrics will be referred to as the mean crystal approximation.

Figure 14. The dependency of the phase transition temperature on the deuteration level. The points present experimental data of the work [21]. Line 1 presents the result of the mean crystal approximation, line 2 corresponds to the cubic approximation (21).

Figure 15. The dependency of the Curie-Weiss constant on the deuteration level. The points present the experimental data of the work [21]. Line is the result of calculations conducted within the mean crystal approximation (26).

The next important step is to calculate the dependency $T_c(x)$ within this approach. The calculated dependency $T_c(x)$ along with the experimental data [21] and their cubic approximation are presented in figure 14. This figure shows that the derived dependency is very close to the cubic approximation. This result proves the applicability of the mean crystal approximation.
The concentration dependency of the Curie-Weiss constant $C(x)$ calculated within the mean crystal approximation is also worth studying. As long as we revealed that the parameter $\bar{\mu}_z(x)$ linearly depends on the deuteration level $x$, we shall use it in the calculation in the following way:

$$\bar{\mu}_z(x) = \bar{\mu}_z^{(H)} \cdot (1 - x) + \bar{\mu}_z^{(D)} \cdot x,$$

where parameter $\bar{\mu}_z^{(H)}$ is presented in (22), and $\bar{\mu}_z^{(D)}$ is set out in table 1 (set 4). The calculated dependency along with the experimental data are presented in figure 15. The figure illustrates that $C(x)$ is a concavity function just like it is observed in the experiment: $d^2C(x)/dx^2 > 0$.

Conclusions

This paper presents the description of thermodynamic properties of partially deuterated ferroelectric K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals based on the proton ordering model taking into account the tunnelling in four-particle cluster approximation. We use the results obtained in the work [22], in which the model theory parameters for KH$_2$PO$_4$ crystal were obtained and based on these parameters the physical characteristics were calculated. In this work we obtain the model theory parameters for KD$_2$PO$_4$, which are unequivocally determined from the physical characteristics of the crystal $T_c$, $T_0$, $P_c$. Based on the derived theory parameters for KD$_2$PO$_4$ we managed to achieve a better general agreement of theory and experiment in comparison with the previous works [18, 11].

Our study of partially deuterated crystals shows that the proton model with tunnelling in four-particle cluster approximation and in mean-crystal approximation describes thermodynamic characteristics of K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals qualitatively and quantitatively well. Among other results, derived in mean-crystal approximation, the following ones are noteworthy:

1. at all levels of deuteration the model provides a good agreement of theory with experiment for temperature dependencies of polarization and specific heat;

2. there was derived a virtually perfect agreement for the dependency of the phase transition temperature at the deuteration level;

3. theoretical calculations show that $d^2C(x)/dx^2 > 0$, just like it is observed in experiment.

The derived results testify to the applicability of mean-crystal approximation to the description of the partially deuterated K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals. However, it is obvious that mean-crystal approximation cannot be claimed to be a rigorous approach in studying partially deuterated crystals.

To make the study of partially deuterated compounds absolutely correct it is necessary to take into consideration the availability of mixed (HD)-configurations and to accordingly modify the theory as it was done in the work [9]. The study of partially deuterated ferroelectric K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals within a more rigorous theory will be the purpose of our further study.

The study of dynamic characteristics of partially deuterated crystals of K(H$_{1-x}$D$_x$)$_2$PO$_4$ type can provide a further important information related to the applicability of mean-crystal approximation within four-particle cluster approximation.

References

Теоретичне дослідження термодинамічних властивостей частково дейтерованих сегнетоелектриків \( K(H_{1-x}D_x)_{2}PO_4 \)

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Проведено дослідження термодинамічних властивостей частково дейтерованих сегнетоелектричних кристалів \( K(H_{1-x}D_x)_{2}PO_4 \) в рамках протонної моделі з тунелюванням в наближенні чотиричастинкового кластера по близькодіючій взаємодії і в наближенні молекулярного поля по далекодіючій взаємодії. Для кристала \( KD_2PO_4 \) визначено модельні параметри теорії із умови належного опису експериментальних даних для його термодинамічних характеристик. На основі запропонованої процедури визначення модельних параметрів для частково дейтерованих кристалів \( K(H_{1-x}D_x)_{2}PO_4 \) розраховано їх термодинамічні характеристики і проведено порівняння отриманих результатів з відповідними експериментальними даними. Обговорюється питання про застосовність наближення середнього кристалу до описання фізичних характеристик частково дейтерованих кристалів типу \( K(H_{1-x}D_x)_{2}PO_4 \).

Ключові слова: КДП, модель протонного впорядкування, чотиричастинкове кластерне наближення, наближення середнього кристалу

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