Longitudinal relaxation of mechanically clamped
KH$_2$PO$_4$ type crystals

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Within the framework of a modified proton ordering model of the KH$_2$PO$_4$ family ferroelectric crystals, taking into account a linear over the strain $\varepsilon$ contribution into the proton system energy, we obtain an expression for longitudinal dynamic dielectric permittivity of a mechanically clamped crystal using the four-particle cluster approximation and the dynamic Glauber approach. At a proper choice of the model parameters, we obtain a good quantitative description of available experimental data for these crystals.

Key words: ferroelectric, cluster approximation, dielectric permittivity, relaxation times

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1. Introduction

In the late 1960-ies, most theoretical and experimental studies of ferroelectrics concentrated on various dynamic phenomena. The dispersion of dielectric permittivity of ferroelectrics was explored at low frequencies, which provided an important information on the mechanisms of phase transitions and revealed the peculiarities of the low-frequency dynamics of a system. Ferroelectric dispersion is closely related to the presence of a low-frequency excitation, i.e., a soft mode which can be either resonant or relaxational. Ferroelectric compounds of the KH$_2$PO$_4$ family occupy an intermediate position. The region of fundamental dispersion in these crystals is located in the submillimeter range $\nu \approx 50$ GHz. At deuteration, the ferroelectric dispersion in these crystals is shifted to the millimeter and microwave ranges.

The major task of dielectric spectra studies of ferroelectric crystals is to explore the peculiarities of the soft mode behavior, especially in the phase transition region [1]. As a rule, the soft modes in the KH$_2$PO$_4$ family ferroelectrics are strongly damped. To explore their character is a complicated task. One has to explore the dielectric spectra of these crystals in a wide frequency range that includes several regions requiring specific and unique experimental methods of measurements. There is hardly any experimental group fully equipped for such studies. This fact, along with the principal difficulties in experimental measurements of dielectric spectra, and the dependence of $\hat{\varepsilon}^*(\omega, T)$ on sample quality and surface treatment, causes the situation when the experimental data for dielectric spectra of the KH$_2$PO$_4$ family ferroelectrics turn out to be disembodied and quite conflicting. This should be kept in mind while analysing the experimental data and the theoretical results for dynamic characteristics of ferroelectrics including those of the KH$_2$PO$_4$ family.

In the late 1970-ies, the obtained experimental results for the dynamic characteristics in the KH$_2$PO$_4$ family compounds were interpreted mostly within phenomenological models (see [2-4]). Phenomenological theories do not make it possible to reveal the microscopic nature of the dispersion of dielectric permittivity or to appropriately describe the effect of various factors on the character of its temperature and frequency dependencies. The attempts to solve this problem using the Green’s function method or Bloch kinetic equations method failed [4].

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A vast majority of studies on the theory of relaxation phenomena in the KH2PO4 family ferroelectrics are based on the stochastic Glauber model. For the first time, the relaxation dynamics of the KD2PO4 type ferroelectrics was studied using this method in (2), where, within the four-particle cluster approximation (FPCA), there was initiated a study of the main regularities of longitudinal relaxation in the case of a paraelectrical phase. However, long-range interactions were not taken into account therein, and the corresponding experimental data for the KD2PO4 type ferroelectrics were not discussed. Later on (23), a more consistent model of deuterated KD2PO4 type ferroelectrics and ND2D2O type antiferroelectrics was explored. Within the framework of this model, using the FPCA for short-range interactions and the mean field approximation for long-range interactions, longitudinal dynamic characteristics of these crystals were calculated. It was shown (10, 12) that the theory proposed in (23) provides a satisfactory description of thermodynamic and longitudinal dynamic characteristics of the KH2PO4 type ferroelectrics.

In (13, 15), the authors attempted to develop a more consistent theory of the KH2PO4 family ferroelectrics in the FPCA which takes tunneling (Ω) into account. The results were not good enough to appropriately describe the available experimental data for the dynamic characteristics of these crystals. However, the fact of suppression of the dynamic characteristics of the KH2PO4 type ferroelectrics by short-range interactions was established. An effective tunneling parameter 〈Ω (Ω ≪ Ω) renormalized by the short-range interactions was obtained. It should be noted that the established in (13, 15) suppression of dynamic characteristics of the KH2PO4 type ferroelectrics by short-range correlations is the most probable reason of the Debye type dispersion of electric permittivity observed in these crystals.

In (16–18), thermodynamic and dynamic characteristics of quasi-one-dimensional hydrogen bonded CsH2PO4 ferroelectrics were found using a self-consistent approach to the calculation of thermodynamic and dynamic characteristics of pseudospin systems with essential short-range and long-range interactions, based on the calculation of the free energy functional with short-range interactions taken into account in the reference approach. It was established that an essential suppression of the soft vibration mode by short-range correlations takes place in a wide temperature range. This fact, just like in the case of KH2PO4, is directly related to the Debye type of longitudinal dielectric permittivity dispersion observed in CsH2PO4. It should be mentioned that similar studies of thermodynamic and dynamic characteristics of KH2PO4 can be carried out using the technique developed in (19). Such studies would make it possible to explore the effect of suppression of the soft mode in the KH2PO4 type ferroelectrics more consistently than in (13) and thereby to explain the Debye character of the dielectric permittivity dispersion in these crystals.

It should be noted that the ferroelectric compounds of the KH2PO4 family are piezoelectric. Piezoelectric coupling is observed in external electric fields and mechanical stresses of certain symmetries. Ferroelectric phase transition in the KH2PO4 type crystals is accompanied by the appearance of spontaneous strains, which changes their tetragonal symmetry. So far, the calculations of dielectric characteristics of these crystals within the proton ordering model (1, 2, 7–12) were restricted to a static limit and high-frequency relaxation. The attempts to explore the piezoelectric resonance phenomenon within a model that does not take into account the piezoelectric coupling were vain. The conventional proton ordering model does not permit one to describe the effects associated with the differences of the free and clamped crystal regimes in the static limit or the phenomenon of crystal clamping by a high-frequency field. This leads, in particular, to some qualitative deviations from experiment for the temperature behavior of polarization relaxation time and dynamic dielectric permittivity of the KH2PO4 type ferroelectrics in the phase transition region.

The studies of the piezoelectric coupling effect on the phase transition and on physical characteristics of the KH2PO4 type ferroelectrics were initiated in (20), where the Slater theory (21) was modified by taking into account the splitting of the lowest ferroelectric level due to the strain ɛ6.

The most fundamental results for the KH2PO4 family ferroelectrics were obtained in (22–30). For the deformed crystals of the KH2PO4 type, the Hamiltonian of the proton ordering model was modified for the first time by including ɛ6 into in the shear strain (22, 23), taking into account the deformational mean field and the splitting of the lateral proton configurations. Later on (24, 25), all possible splittings of proton configurational energies by the strain ɛ6 were included into the model. In (24, using this model, the phase transition, thermodynamic and longitudinal dielectric, piezoelectric, and elastic characteristics of K0.7D0.38H2PO4, as well as the effect of the ɛ6 on these quantities were explored. The same characteristics for other K(H1−xDx)2PO4 type ferroelectrics were later on calculated in (26).
The thermodynamic and longitudinal dielectric, piezoelectric, and elastic characteristics of the KH$_2$PO$_4$ type were also calculated in [25, 27] within a model that takes into account the tunneling and piezoelectric coupling. It should be mentioned, however, that taking into account the tunneling within the cluster approximation yields a non-physical behavior of the calculated quantities at low temperatures [31]. In [28–30], the effect of the electric field $E_3$ on the phase transition and on the physical characteristics of KH$_{1.12}$D$_{0.88}$PO$_4$ and KH$_2$PO$_4$ was explored, and a good agreement with experiment was obtained.

In [24–28], where there was used a model with tunneling, the dynamic characteristics of the KH$_2$PO$_4$ family ferroelectrics were not considered. In [32], using a modified proton ordering model proposed in [24], the dynamic dielectric permittivity of a free KH$_2$PO$_4$ type crystals was calculated taking into account the dynamics of $\varepsilon_6$ strain. The experimentally observed effects of crystal clamping by a high-frequency electric field and piezoelectric resonance in KH$_2$PO$_4$ and KD$_2$PO$_4$ crystals were theoretically described for the first time. Peculiarities of the ultrasound attenuation coefficients near the phase transition temperature in these crystals were also described. In [33], we presented a detailed review of the obtained results for longitudinal and transverse static dielectric permittivities, for piezoelectric coefficients, and for elastic constants of several ferroelectric crystals of the KH$_2$PO$_4$ family. Moreover, the typical behavior of longitudinal and transverse characteristics of mechanically free KH$_2$PO$_4$, Rb$_2$PO$_4$, KH$_2$AsO$_4$ crystals was shown and the results for temperature and frequency dependencies of longitudinal and transverse dielectric permittivities of KH$_2$PO$_4$ were presented, along with the corresponding experimental data.

In the present paper, using the model proposed in [24] we calculate the longitudinal dynamic dielectric permittivity of clamped ferroelectrics of the KH$_2$PO$_4$ type and explore its behavior in wide temperature and frequency ranges. Using the obtained results, we perform a detailed analysis of the available experimental data for these crystals.

2. Systems of equations for the time-dependent deuteron distribution functions

We shall consider a system of deuterons moving on the O–D...O bonds in deuterated KD$_2$PO$_4$ type ferroelectrics. A primitive cell of the Bravais lattice of these crystals consists of two neighboring tetrahedra PO$_4$ along with four hydrogen bonds attached to one of them (the “A” type tetrahedron). The hydrogen bonds attached to the other tetrahedron (“B” type) belong to the four structural elements surrounding this tetrahedron (figure 1).

![Figure 1. A primitive cell of the KD$_2$PO$_4$ type crystal. One of the numerous possible ferroelectric deuteron configurations is shown.](image-url)

The dynamic characteristics of these compounds will be calculated within the four-particle cluster approximation that proved to be successful in describing their thermodynamic properties [12, 24, 27].
The Hamiltonian of the deuteron subsystem, taking into account short-range and long-range interactions in the presence of an external electric field $E_3$ along the crystallographic $c$ axis and mechanical stress $\sigma_6 = \sigma_{xy}$, which independently contribute to polarization $P_3$ and strain $\varepsilon_6$, consists of the "seed" and pseudospin parts \[ \hat{H} = N H^{(0)} + \hat{H}_s, \] (2.1)

where $N$ is the total number of primitive cells. The "seed" energy of a primitive cell corresponds to the sublattice of heavy ions and does not explicitly depend on the deuteron subsystem configuration. It is expressed in terms of the strain $\varepsilon_6$ and elastic field $E_3$ and includes the elastic, piezoelectric, and dielectric contributions

\[ H^{(0)} = \nu \left\{ \frac{1}{2} \epsilon_{66}^{0} \varepsilon_6^2 - \epsilon_{36}^{0} \varepsilon_3 \varepsilon_6 - \frac{1}{2} \chi_{33}^{0} E_3^2 \right\}, \]

where $\nu$ is the primitive cell volume; $\epsilon_{66}^{0}$, $\epsilon_{36}^{0}$, $\chi_{33}^{0}$ are the "seed" elastic constant, piezoelectric coefficient, and dielectric susceptibility, respectively. They determine the temperature behavior of the corresponding observable quantities at temperatures far from the phase transition $T_c$.

The pseudospin part of the Hamiltonian reads

\[ \hat{H}_s = \frac{1}{2} \sum_{qf'} \sum_{qf} J_{ff'}(qq') \frac{\sigma_{qf} \sigma_{q'f'}}{2} + \hat{H}_{sh.s}(6) + \sum_{qf} 2 \sigma_{qf} \varepsilon_6 - \frac{1}{2} \sum_{qf} \mu_{f3} E_3 \sigma_{qf}, \] (2.3)

The first term describes effective long-range interactions between deuterons; $\sigma_{qf}$ is the $z$-th component of the pseudospin operator that describes the state of a deuteron in the $q$-th cell on the $f$-th bond. $(f = 1, 2, 3, 4)$. Two eigenvalues of the operator $\sigma_{qf} = \pm 1$ correspond to two possible positions of the deuteron on the bond denoted by "1", "2" in figure in (2.3) $H_{sh.s}(6)$ is a linear over the strain $\varepsilon_6$ Hamiltonian of the short-range interactions between deuterons [26]:

\[ \hat{H}_{sh.s}(6) = \sum_{q} \left[ \left( \frac{\delta_{q6}}{8} \varepsilon_6 - \frac{\delta_{16}}{4} \varepsilon_6 \right) (\sigma_{q1} + \sigma_{q2} + \sigma_{q3} + \sigma_{q4}) - \left( \frac{\delta_{q6}}{8} \varepsilon_6 + \frac{\delta_{16}}{4} \varepsilon_6 \right) (\sigma_{q1} \sigma_{q2} \sigma_{q3} + \sigma_{q1} \sigma_{q2} \sigma_{q4} + \sigma_{q1} \sigma_{q3} \sigma_{q4} + \sigma_{q2} \sigma_{q3} \sigma_{q4}) + \frac{1}{4} (V_s + \delta_{q6} \varepsilon_6) (\sigma_{q1} \sigma_{q2} + \sigma_{q3} \sigma_{q4}) + \frac{1}{4} (V_s - \delta_{q6} \varepsilon_6) (\sigma_{q2} \sigma_{q3} + \sigma_{q4} \sigma_{q1}) + \frac{1}{16} \Phi_s \sigma_{q1} \sigma_{q2} \sigma_{q3} \sigma_{q4} \right]. \] (2.4)

Here

\[ V_s = -\frac{1}{2} \omega_1, \quad U_s = \frac{1}{2} \omega_1 - \epsilon, \quad \Phi_s = 4 \epsilon - 8 \omega + 2 \omega_1 \]

and

\[ \epsilon = \epsilon_a - \epsilon_s, \quad \omega = \epsilon_1 - \epsilon_s, \quad \omega_1 = \epsilon_0 - \epsilon_s, \]

where $\epsilon_s$, $\epsilon_a$, $\epsilon_1$, $\epsilon_0$ are the energies of deuteron configurations near the PO$_4$ group.

The third term in (2.3) is a linear over the shear strain $\varepsilon_6$ mean field Hamiltonian induced by the piezoelectric coupling; $\psi_6$ is the parameter of the deformational mean field.

The last term in (2.3) effectively describes the interactions of deuterons with an external electric field $E_3$. Here $\mu_{f3}$ is the effective dipole moment related to the $f$-th hydrogen bonds, where

\[ \mu_{13} = \mu_{23} = \mu_{33} = \mu_{43} = \mu_3, \]

and $\mu_3$ is the dipole moment of up/down deuteron configurations.

Taking into account the peculiarities of the crystalline structure of the MD$_2$XO$_4$ type ferroelectrics, their dynamic characteristics can be calculated within the four-particle cluster approximation that proved to be effective in describing the thermodynamic characteristics of these crystals [12, 24, 27].

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Long-range interactions are taken into account in the mean field approximation. Within the cluster approach, the thermodynamic potential of MD$_2$XO$_4$ ferroelectrics calculated per one primitive cell reads

\[ g_s(6) = H^{(0)} + 2\nu_c \left( \eta^{(1)z} \right)^2 + \frac{1}{2\beta} \sum_{f=1}^{4} \ln Z_{fs}^{(1)} - \frac{1}{\beta} \ln Z_{os}^{(4)} - \nu_6 \epsilon_6, \tag{2.5} \]

where $4\nu_c = J_{11}(0) + 2J_{12}(0) + J_{13}(0)$, the eigenvalues of Fourier-transform of the long-range interaction matrix $I_{ff'} = \sum_{R_q - R_{q'}} I_{ff'}(q,q')$;

\[ \eta^{(1)z}(\sigma_q) = \langle \sigma_q \rangle = \langle \sigma_{q2} \rangle = \langle \sigma_{q3} \rangle = \langle \sigma_{q4} \rangle \]

is the parameter of deuteron ordering; $Z_{fs}^{(1)} = \text{Sp} e^{-\beta H_{fs}^{(1)}}, Z_{os}^{(4)} = \text{Sp} e^{-\beta H_{os}^{(4)}}$, $\beta = \frac{1}{k_B T}$ are the single-particle and four-particle partition functions. The single-particle $H_{fs}^{(1)}$ and four-particle $H_{qs}^{(4)}$ deuteron Hamiltonians are presented by

\[ H_{fs}^{(1)} = -\frac{\tilde{z}_6}{2} \sigma_{af}, \tag{2.6} \]

\[ H_{qs}^{(4)} = -\frac{4}{\beta} \sum_{f=1}^{4} \frac{\tilde{z}_6}{2} \sigma_{af} + H_{sh,4}(6), \tag{2.7} \]

where

\[ \tilde{z}_6 = \beta \left( -\Delta^z \epsilon + 2\nu_c \eta^{(1)z} - 2\psi_6 \epsilon_6 + \mu_3 E_3 \right), \quad \tilde{z}_6 = \beta \left( -\Delta^z \epsilon + 2\nu_c \eta^{(1)z} - 2\psi_6 \epsilon_6 + \mu_3 E_3 \right). \]

The effective field $\Delta^z$ exerted by the neighboring hydrogen bonds from outside the cluster, is determined from the self-consistency condition: the mean values $\langle \sigma_{af} \rangle$ calculated within the four-particle and one-particle cluster approximations should coincide.

The dynamic characteristics of the MD$_2$XO$_4$ crystals will be explored using the proposed dynamic model based on a stochastic Glauber model [14]. Using the method developed in [10, 12, 32], the system of equations for the time-dependent deuteron distribution functions is obtained in the form

\[ -\frac{a}{d} \left( \prod_f \sigma_{af} \right) = \sum_{f'} \left\{ \left( \prod_f \sigma_{af} \right) \left[ 1 - \sigma_{af'} \tanh \frac{1}{2} \beta \epsilon_{af'}(t) \right] \right\}, \tag{2.8} \]

where $\epsilon_{af'}(t)$ is the local field acting on the $f'$-th deuteron in the $q$-th cell, which can be obtained from the Hamiltonian (2.3). Expanding $\tanh \frac{1}{2} \beta \epsilon_{af'}(t)$ over the pseudospin operators $\sigma_{af}$, occurring in Hamiltonian (2.3), taking into account the fact that $\sigma_{af} = \pm 1$ and the symmetry of the deuteron distribution functions in the MD$_2$XO$_4$ ferroelectrics in the presence of the electric field $E_3$

\[ \eta^{(1)z} = \langle \sigma_q \rangle = \langle \sigma_{q2} \rangle = \langle \sigma_{q3} \rangle = \langle \sigma_{q4} \rangle, \]

\[ \eta^{(3)z} = \langle \sigma_q \sigma_{q2} \sigma_{q3} \rangle = \langle \sigma_q \sigma_{q2} \sigma_{q4} \rangle = \langle \sigma_q \sigma_{q3} \sigma_{q4} \rangle, \]

\[ \eta^{(2)z} = \langle \sigma_q \sigma_{q2} \rangle = \langle \sigma_q \sigma_{q3} \rangle, \quad \eta^{(2)z} = \langle \sigma_q \sigma_{q2} \rangle = \langle \sigma_{q3} \sigma_{q4} \rangle, \quad \eta^{(3)z} = \langle \sigma_q \sigma_{q3} \rangle = \langle \sigma_{q2} \sigma_{q4} \rangle, \tag{2.9} \]

from (2.7), one can obtain a closed system of equations for the time-dependent single-particle, three-particle, and pair distribution functions of deuterons in MD$_2$XO$_4$ within the four-particle cluster approximation and for a single-particle distribution function within the single-particle approximation [32]:

\[ \frac{a}{d} \left( \frac{\eta^{(1)z}}{\eta_{3}^{(1)z}} \right) = \begin{pmatrix} 1 \cdots 1 & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} \tilde{c}_1 \cdots \tilde{c}_4 \cdots \tilde{c}_5 \end{pmatrix}, \tag{2.10} \]
where the following notations are used:

\[
\begin{align*}
\hat{c}_{11} &= -(1 - P_{6}^2 - Q_{61} - Q_{62}), & \hat{c}_{12} &= R_{6}, & \hat{c}_{13} &= M_{61}, & \hat{c}_{14} &= M_{62}, & \hat{c}_{15} &= N_{6}, & \hat{c}_{1} &= L_{6}, \\
\hat{c}_{21} &= (2P_{6}^2 + 2Q_{61} + 2Q_{62} + 3R_{6}), & \hat{c}_{22} &= -(3 - P_{6}^2 - Q_{61} - Q_{62}), & \hat{c}_{23} &= (N_{6}^2 + M_{62} + L_{6}), \\
\hat{c}_{24} &= (N_{6}^2 + M_{61} + L_{6}), & \hat{c}_{25} &= (M_{61} + M_{62} + L_{6}), & \hat{c}_{2} &= (N_{6}^2 + M_{61} + M_{62}), \\
\hat{c}_{31} &= 2(N_{6}^2 + M_{62} + L_{6}), & \hat{c}_{32} &= 2M_{61}, & \hat{c}_{33} &= -(1 - R_{6}), & \hat{c}_{34} &= 2P_{6}, & \hat{c}_{35} &= 2Q_{6}, & \hat{c}_{3} &= 2Q_{6}, \\
\hat{c}_{41} &= 2(N_{6}^2 + M_{62} + L_{6}), & \hat{c}_{42} &= 2M_{62}, & \hat{c}_{43} &= 2P_{6}, & \hat{c}_{44} &= -(1 - R_{6}), & \hat{c}_{45} &= 2Q_{6}, & \hat{c}_{4} &= 2Q_{6}, \\
\hat{c}_{51} &= 2(M_{61} + M_{62} + L_{6}), & \hat{c}_{52} &= 2N_{6}, & \hat{c}_{53} &= 2Q_{6}, & \hat{c}_{54} &= 2Q_{6}, & \hat{c}_{55} &= -(1 - R_{6}), & \hat{c}_{5} &= 2P_{6}, \\
\end{align*}
\]

(2.11)

\[
\alpha \frac{d}{dt} \eta^{(1)} = -\eta^{(1)} + \tanh \frac{1}{2} \hat{c}_{6}. 
\]

(2.12)

3. Relaxational dynamics of mechanically clamped MD\textsubscript{2}XO\textsubscript{4} crystals

Now, using the obtained systems of equations, let us calculate the dynamic characteristics of the MD\textsubscript{2}XO\textsubscript{4} crystals. Let us consider the case of small deviations of the considered system from equilibrium. We can separate the static and dynamic parts in the obtained system of equations. To do so, we present the distribution functions and the effective fields as sums of the equilibrium functions and their fluctuations:

\[
\begin{align*}
\eta_{j}^{(1)} &= \eta_{j}^{(1)} + \eta_{j}^{(1)}
\end{align*}
\]

(3.1)

\[
\begin{align*}
\eta_{j}^{(3)} &= \eta_{j}^{(3)} + \eta_{j}^{(3)}, & \eta_{j}^{(3)(2)} &= \eta_{j}^{(3)} + \eta_{j}^{(3)(2)} (i = 1, 2, 3), \\
\end{align*}
\]

Owing to a piezoelectric coupling, time-dependent electric fields should induce time-dependent strains. However, in the present paper we shall consider the fields with the frequencies of the order of 10\textsuperscript{9} \textasciitilde 10\textsuperscript{12} Hz, which is far above the frequency of piezoelectric resonance. When the frequency is that high, the strains are not capable of following the external fields, which means that the crystal is effectively clamped. Therefore, in the expansions (3.1) we assume the strain \(\varepsilon_{6}\) to be time-independent.

We expand the expressions for the coefficients \(P_{6}, \ldots, L_{6}\) in series in \(\varepsilon_{6}/2\) up to the linear terms. Taking into account these expansions and (3.1), we obtain a system of equations that describes the behavior of fluctuational parts of distribution functions [32, 34]:

\[
\frac{d}{dt} \begin{pmatrix}
\eta_{1}^{(1)} \\
\eta_{2}^{(1)} \\
\eta_{3}^{(1)} \\
\end{pmatrix} = \begin{pmatrix}
c_{11} & c_{12} & c_{13} \\
c_{21} & c_{22} & c_{23} \\
c_{31} & c_{32} & c_{33} \\
\end{pmatrix} \begin{pmatrix}
\eta_{1}^{(1)} \\
\eta_{2}^{(1)} \\
\eta_{3}^{(1)} \\
\end{pmatrix} - \frac{\mu_{3} E_{3}}{2kT} \begin{pmatrix}
c_{4} \\
0 \\
0 \\
\end{pmatrix},
\]

(3.2)

where the coefficients of the system read:

\[
\begin{align*}
c_{11} &= \frac{1}{a} \left( \phi_{11}^{(0)} + \beta \varepsilon_{v} \phi_{11}^{(1)} - k_{11}^{(1)} \varepsilon_{s}^{(1)} \right), & c_{12} &= \frac{1}{a} \left( \phi_{12}^{(0)} - k_{12}^{(1)} \varepsilon_{s}^{(0)} \right), & c_{13} &= \frac{1}{a} \left( \phi_{13}^{(0)} - k_{13}^{(1)} \varepsilon_{s}^{(0)} \right), \\
c_{14} &= \frac{1}{a} \left( \phi_{14}^{(0)} - k_{14}^{(1)} \varepsilon_{s}^{(0)} \right), & c_{15} &= \frac{1}{a} \left( \phi_{15}^{(0)} - k_{15}^{(1)} \varepsilon_{s}^{(0)} \right), & c_{1} &= \frac{1}{a} \left( \phi_{16}^{(0)} - k_{16}^{(1)} \varepsilon_{s}^{(0)} \right), \\
c_{21} &= \frac{1}{a} \left( \phi_{21}^{(0)} + \beta \varepsilon_{v} \phi_{21}^{(1)} - k_{21}^{(1)} \varepsilon_{s}^{(1)} \right), & c_{22} &= \frac{1}{a} \left( \phi_{22}^{(0)} - k_{22}^{(1)} \varepsilon_{s}^{(0)} \right), & c_{23} &= \frac{1}{a} \left( \phi_{23}^{(0)} - k_{23}^{(1)} \varepsilon_{s}^{(0)} \right), \\
c_{24} &= \frac{1}{a} \left( \phi_{24}^{(0)} - k_{24}^{(1)} \varepsilon_{s}^{(0)} \right), & c_{25} &= \frac{1}{a} \left( \phi_{25}^{(0)} - k_{25}^{(1)} \varepsilon_{s}^{(0)} \right), & c_{2} &= \frac{1}{a} \left( \phi_{26}^{(0)} - k_{26}^{(1)} \varepsilon_{s}^{(0)} \right), \\
\end{align*}
\]
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Piezoelectric coupling is neglected, they coincide with the corresponding expressions of [12].

The coefficients for a single-particle distribution function are found from the following system of equations

\[ \eta_i^{(1)z} = \frac{5}{\tau_i} \sum_{i=1}^5 C_i^z \exp \left( -\frac{t}{\tau_i^z} \right) + \frac{\mu_3 E_{3i}}{2} \beta \sum_{k=0}^4 \frac{(i\omega)^k p^{(k)}}{(i\omega)^5 + \sum_{k=0}^4 (i\omega)^k p_k} \]  

(3.3)

where \( p = \left[ (i\omega)^4 p^{(4)} + (i\omega)^3 p^{(3)} + (i\omega)^2 p^{(2)} + (i\omega) p^{(1)} + p^{(0)} \right] \). Expressions for coefficients \( p_4, \ldots, p^{(0)} \) are presented in [12].

Finally, time-dependent single-particle distribution function is obtained in the following form

\[ \eta_i^{(1)z} = \frac{5}{\tau_i} \sum_{i=1}^5 C_i^z \exp \left( -\frac{t}{\tau_i^z} \right) + \frac{\mu_3 E_{3i}^z}{2} \beta \sum_{k=0}^4 \frac{(i\omega)^k p^{(k)}}{(i\omega)^5 + \sum_{k=0}^4 (i\omega)^k p_k} \]  

(3.4)

The dynamic dielectric susceptibility of a clamped crystal is defined as

\[ \chi_{3j}^{(o, T)} = \lim_{E_{3i} \to 0} 2 \mu_3 \frac{d\eta_i^{(1)z}}{dE_{3i}} = \mu_3^2 \beta \sum_{k=0}^4 \frac{(i\omega)^k p^{(k)}}{(i\omega)^5 + \sum_{k=0}^4 (i\omega)^k p_k} \]  

\[ \chi_{3j}^{(o, T)} = \lim_{E_{3i} \to 0} 2 \mu_3 \frac{d\eta_i^{(1)z}}{dE_{3i}} = \mu_3^2 \beta \sum_{k=0}^4 \frac{(i\omega)^k p^{(k)}}{(i\omega)^5 + \sum_{k=0}^4 (i\omega)^k p_k} \]  

(3.6)

The coefficients \( \chi_{3j} \) are found from the following system of equations

\[
\begin{pmatrix}
  n_{11} & n_{12} & n_{13} & n_{14} & n_{15} \\
  n_{21} & n_{22} & n_{23} & n_{24} & n_{25} \\
  n_{31} & n_{32} & n_{33} & n_{34} & n_{35} \\
  n_{41} & n_{42} & n_{43} & n_{44} & n_{45} \\
  n_{51} & n_{52} & n_{53} & n_{54} & n_{55}
\end{pmatrix}
\begin{pmatrix}
  \chi_{31} \\
  \chi_{32} \\
  \chi_{33} \\
  \chi_{34} \\
  \chi_{35}
\end{pmatrix}
= 
\begin{pmatrix}
  n_1 \\
  n_2 \\
  n_3 \\
  n_4 \\
  n_5
\end{pmatrix}.
\]  

(3.7)
Here, the following notations are used

\begin{align*}
n_{11} &= \tau_{1}^{x} + \tau_{2}^{x} + \tau_{3}^{x} + \tau_{4}^{x}; & n_{12} &= \tau_{1}^{x} + \tau_{3}^{x} + \tau_{4}^{x}; & n_{13} &= \tau_{1}^{x} + \tau_{2}^{x} + \tau_{4}^{x}; & n_{14} &= \tau_{1}^{x} + \tau_{2}^{x} + \tau_{3}^{x}; & n_{15} &= \tau_{1}^{x} + \tau_{2}^{x} + \tau_{4}^{x}; \\
n_{21} &= \tau_{1}^{y} + \tau_{2}^{y} + \tau_{3}^{y} + \tau_{4}^{y}; & n_{22} &= \tau_{1}^{y} + \tau_{2}^{y} + \tau_{4}^{y}; & n_{23} &= \tau_{1}^{y} + \tau_{2}^{y} + \tau_{3}^{y}; & n_{24} &= \tau_{1}^{y} + \tau_{2}^{y} + \tau_{3}^{y}; & n_{25} &= \tau_{1}^{y} + \tau_{2}^{y} + \tau_{4}^{y}; \\
n_{31} &= \tau_{1}^{z} + \tau_{2}^{z} + \tau_{3}^{z} + \tau_{4}^{z}; & n_{32} &= \tau_{1}^{z} + \tau_{2}^{z} + \tau_{4}^{z}; & n_{33} &= \tau_{1}^{z} + \tau_{2}^{z} + \tau_{3}^{z}; & n_{34} &= \tau_{1}^{z} + \tau_{2}^{z} + \tau_{4}^{z}; & n_{35} &= \tau_{1}^{z} + \tau_{2}^{z} + \tau_{3}^{z}; \\
n_{41} &= \tau_{2}^{x} + \tau_{4}^{x} + \tau_{5}^{x}; & n_{42} &= \tau_{2}^{x} + \tau_{4}^{x} + \tau_{5}^{x}; & n_{43} &= \tau_{2}^{x} + \tau_{4}^{x} + \tau_{5}^{x}; & n_{44} &= \tau_{1}^{x} + \tau_{2}^{x} + \tau_{3}^{x}; & n_{45} &= \tau_{1}^{x} + \tau_{2}^{x} + \tau_{5}^{x}; \\
n_{51} &= \tau_{2}^{x} + \tau_{4}^{x}; & n_{52} &= \tau_{2}^{x} + \tau_{4}^{x}; & n_{53} &= \tau_{2}^{x} + \tau_{5}^{x}; & n_{54} &= \tau_{2}^{x} + \tau_{5}^{x}; & n_{55} &= 1;
\end{align*}

\[ n_{1} = \frac{\mu_{0}}{\varepsilon_{0}^{v} e_{i}^{p}} \prod_{i=1}^{5} \tau_{i}^{x} p^{(4)}, \quad n_{2} = \frac{\mu_{0}}{\varepsilon_{0}^{v} e_{i}^{p}} \prod_{i=1}^{5} \tau_{i}^{y} p^{(3)}, \quad n_{3} = \frac{\mu_{0}}{\varepsilon_{0}^{v} e_{i}^{p}} \prod_{i=1}^{5} \tau_{i}^{z} p^{(2)}, \]
\[ n_{4} = \frac{\mu_{0}}{\varepsilon_{0}^{v} e_{i}^{p}} \prod_{i=1}^{5} \tau_{i}^{x} p^{(1)}, \quad n_{5} = \frac{\mu_{0}}{\varepsilon_{0}^{v} e_{i}^{p}} \tau_{i}^{x} p^{(0)}. \]

The complex longitudinal dielectric permittivity of the deuteron subsystem of a mechanically clamped MD\textsubscript{2}XO\textsubscript{4} crystal reads

\[ \varepsilon_{33}^{v}(\omega, T) = 1 + 4\pi \chi_{33}^{v}(\omega, T), \quad \varepsilon_{33}^{v}(\omega, T) = 4\pi \chi_{33}^{v}(\omega, T). \]

A numerical analysis shows that the most important contribution to the dispersion of \( \varepsilon_{33}^{v}(\omega, T) \) is made by the first relaxational mode \([\chi(1) \gg \chi(i)]\), while the dispersion of the complex dielectric permittivity of a mechanically clamped crystal is close to the Debye one. If the piezoelectric coupling is omitted, \( \varepsilon_{33}^{v}(\omega, T) \) transforms into the expression corresponding to [12].

4. Comparison of the numerical results with experimental data.

Discussion

Let us analyse the results of numerical calculations performed within the framework of the proposed model for longitudinal dynamic dielectric characteristics of the \( \text{M(H}_{1-x}\text{D}_{x})_{2}\text{XO}_{4} \) crystals and compare them with the corresponding experimental data. It should be noted that the theory developed in the previous sections, strictly speaking, is valid for the MD\textsubscript{2}XO\textsubscript{4} type crystals only. The experimental data are available for the \( \text{M(H}_{1-x}\text{D}_{x})_{2}\text{XO}_{4} \) crystals with different deuterations \( x \) (0 \( \leq x \leq 1 \)). The experimentally established relaxational character of the dielectric dispersion of \( \varepsilon_{33}^{v}(\nu, T) \) [35–38] in these crystals, as has been already mentioned, is associated with suppression of tunneling by short-range interactions. Therefore, we shall neglect the effects of proton tunneling in \( \text{M(H}_{1-x}\text{D}_{x})_{2}\text{XO}_{4} \). We shall assume that the proposed theory for these crystals is also valid if we use the averaged effective values of the model parameters

\[ \varepsilon(x) = \varepsilon_{11}(1 - x) + \varepsilon_{12} x, \quad w(x) = w_{11}(1 - x) + w_{12} x. \]

In [26], we calculated the static longitudinal, piezoelectric, elastic, and thermal characteristics of the \( \text{M(H}_{1-x}\text{D}_{x})_{2}\text{XO}_{4} \) and explored their dependencies on the values of the model parameters. It was shown that at a proper choice of these values, a good quantitative agreement between the theoretical results and the corresponding experimental data was obtained. These sets of the model parameters are used herein in calculating the dynamic characteristics of \( \text{M(H}_{1-x}\text{D}_{x})_{2}\text{XO}_{4} \).

The parameter \( \alpha \) that sets the time scale of the dynamic processes in \( \text{M(H}_{1-x}\text{D}_{x})_{2}\text{XO}_{4} \) is determined from the condition that theoretical results for frequency dependencies of \( \varepsilon_{33}^{v}(\nu, T) \) at different temperatures agree with the experimental data. It is assumed that \( \alpha_{11} \) weakly depends on temperature

\[ \alpha = (P + R|\Delta T|) \cdot 10^{-14}, \quad \Delta T = T - T_c. \]
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Table 1. The obtained optimum values of the model parameters for K(H$_{1-x}$D$_x$)$_2$PO$_4$.

| $x$  | $T_c$ (K) | $T_0$ (K) | $\frac{\nu_0}{\nu}$ (K) | $\frac{\delta_{33}}{\delta}$ (K) | $\frac{\delta_{33}}{\delta}$ (esu cm) | $\mu_{33}$, $10^{-18}$ esu cm | $\mu_{33}$, $10^{-18}$ esu cm | $\chi_0^{33}$ (K) | $P_-$ (s) | $R_-$ (s) | $P_+$ (s) | $R_+$ (s) |
|------|-----------|-----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-----------|-----------|-----------|-----------|
| 0.00 | 122.5     | 122.5     | 50.00                    | 422.0                    | 17.91                    | 1.46                     | 1.71                     | 0.73                     | 0.35      | 0.1000    | 0.43      | 0.0160    |
| 0.21 | 146.0     | 145.9     | 63.78                    | 515.8                    | 23.18                    | 1.54                     | 1.79                     | 0.65                     | 0.85      | 0.0005    | 1.22      | 0.0193    |
| 0.29 | 155.0     | 154.8     | 66.74                    | 551.5                    | 25.21                    | 1.57                     | 1.82                     | 0.62                     | 1.05      | 0.0093    | 1.51      | 0.0217    |
| 0.64 | 191.0     | 190.3     | 79.71                    | 707.8                    | 32.34                    | 1.70                     | 1.96                     | 0.48                     | 1.76      | 0.0385    | 2.44      | 0.0173    |
| 0.79 | 204.0     | 203.1     | 85.27                    | 774.8                    | 34.18                    | 1.76                     | 2.02                     | 0.42                     | 1.92      | 0.0082    | 2.65      | 0.0151    |
| 0.84 | 208.0     | 207.0     | 87.12                    | 797.1                    | 34.63                    | 1.77                     | 2.03                     | 0.41                     | 2.02      | 0.0081    | 2.83      | 0.0167    |
| 0.91 | 213.2     | 212.2     | 89.71                    | 828.4                    | 35.07                    | 1.80                     | 2.06                     | 0.38                     | 2.16      | 0.0079    | 2.88      | 0.0130    |
| 0.93 | 215.0     | 213.9     | 90.45                    | 837.3                    | 35.36                    | 1.81                     | 2.07                     | 0.37                     | 2.20      | 0.0079    | 3.04      | 0.0149    |
| 0.99 | 219.0     | 217.9     | 92.67                    | 864.1                    | 35.52                    | 1.83                     | 2.09                     | 0.35                     | 2.72      | 0.0077    | 4.21      | 0.0189    |
| 1.00 | 220.1     | 219.0     | 93.05                    | 868.6                    | 35.76                    | 1.84                     | 2.10                     | 0.34                     | 2.84      | 0.0077    | 4.54      | 0.0349    |

Table 2. The obtained optimum values of the model parameters for RbH$_2$PO$_4$ and KH$_2$AsO$_4$.

|          | $T_c$ (K) | $T_0$ (K) | $\frac{\nu_0}{\nu}$ (K) | $\frac{\delta_{33}}{\delta}$ (K) | $\frac{\delta_{33}}{\delta}$ (esu cm) | $\mu_{33}$, $10^{-18}$ esu cm | $\mu_{33}$, $10^{-18}$ esu cm | $\chi_0^{33}$ (K) |
|----------|-----------|-----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| RbH$_2$PO$_4$ | 147.6     | 97.0      | 147.6                    | 60.00                    | 440.0                    | 29.13                    | 1.50                     | 2.00                     | 0.40      |
| KH$_2$AsO$_4$ | 95.8      | 35.50     | 385.0                    | 17.43                    | 1.61                     | 1.65                     | 0.70                     |

|          | $\frac{\nu_0}{\nu}$ (K) | $\frac{\delta_{33}}{\delta}$ (K) | $\frac{\delta_{33}}{\delta}$ (esu cm) | $\mu_{33}$, $10^{-18}$ esu cm | $\mu_{33}$, $10^{-18}$ esu cm | $\chi_0^{33}$ (K) |
|----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| RbH$_2$PO$_4$ | 50.00                    | 50.00                    | 50.00                    | 50.00                    | 50.00                    | 7.90                     | 3000.00                  |
| KH$_2$AsO$_4$ | 130.00                   | 130.00                   | 130.00                   | 130.00                   | 130.00                   | 7.50                     | 3000.00                  |

|          | $P_-$ (s) | $R_-$ (s) | $P_+$ (s) | $R_+$ (s) |
|----------|-----------|-----------|-----------|-----------|
| RbH$_2$PO$_4$ | 0.55      | 0.0080    | 0.93      | 0.0140    |
| KH$_2$AsO$_4$ | 0.47      | 0.0160    | 0.61      | 0.0190    |

The obtained optimum values of the model parameters are presented in table 1 for K(H$_{1-x}$D$_x$)$_2$PO$_4$ and in table 2 for RbH$_2$PO$_4$ and KH$_2$AsO$_4$.

Note that $\mu_{33}$, $P_-$, $R_-$, and $\mu_{33}$, $P_+$, $R_+$ correspond to the paraelectric and ferroelectric phases, respectively. The temperature dependencies of the real and imaginary parts of the permittivity $\varepsilon_3''(\nu, T)$ and $\varepsilon_3''(\nu, T)$ at different frequencies for the KH$_2$PO$_4$, KD$_2$PO$_4$, RbH$_2$PO$_4$, and KH$_2$AsO$_4$ crystals are shown in figures 2 and 3. Starting from a certain frequency $\nu_k$, the low-frequency maximum in the temperature curve of $\varepsilon_3''(\nu, T)$ is replaced with a sharp minimum at $\Delta T = 0$ K which widens and deepens with an increasing frequency that reaches $\varepsilon_3''(\nu, T)$ at $\nu = 10^9$ GHz. In KH$_2$PO$_4$, $\nu_k = 33.2$ GHz, in KD$_2$PO$_4$, $\nu_k = 1.4$ GHz, in RbH$_2$PO$_4$, $\nu_k = 20.5$ GHz, in KH$_2$AsO$_4$, $\nu_k = 20.8$ GHz. The maximum of $\varepsilon_3''(\nu, T)$ at $\Delta T = |T_n - T_c|$ decreases and smears out with an increasing frequency, whereas the magnitude of $\Delta T_n$ increases. With increasing fre-
Figure 2. The temperature dependence of $\varepsilon_{33}'$ and $\varepsilon_{33}''$ in KH$_2$PO$_4$ at different frequencies $\nu$ (GHz): 9.2 – 1, $\phi$ [36]; 33.2 – 2; 80 – 3; 154.2 – 4, $\sigma$ [35]; 249 – 5, $\Delta$ [35]; 372 – 6, $\circ$ [35]; 800 – 7. Symbols are experimental points; lines are the theoretical values.

Figure 3. The temperature dependence of $\varepsilon_{33}'$ and $\varepsilon_{33}''$ in KD$_2$PO$_4$ at different frequencies $\nu$ (GHz): 1.93 – 1; 3.0 – 2, $\sigma$ [37]; 10.0 – 3, $\phi$ [37]; 20.0 – 4, $\Delta$ [37]; 40.0 – 5; 80.0 – 6; 154.2 – 7. Symbols are experimental points; lines are the theoretical values.
Figure 4. The temperature dependence of $\varepsilon'_{33}$ and $\varepsilon''_{33}$ in RbH$_2$PO$_4$ at different frequencies $\nu$ (GHz): 0.25 – 1; 10.0 – 2; 27.0 – 3, □ 40; 154.2 – 4, ○ 41; 250.2 – 5, Δ 41; 372.0 – 6, ◊ 41; 700.0 – 7. Symbols are experimental points; lines are the theoretical values.

Figure 5. The temperature dependence of $\varepsilon'_{33}$ and $\varepsilon''_{33}$ in KH$_2$AsO$_4$ at different frequencies $\nu$ (GHz): 9.2 – 1, □ 36; 20.8 – 2; 80.0 – 3, □ 41; 154.2 – 4, ○ 41; 198.9 – 5, Δ 41; 250.2 – 6, △ 41; 372.0 – 7, ◊ 41; 700.0 – 8, ◊ 41; 700.0 – 9. Symbols are experimental points; lines are the theoretical values.
frequency the magnitude of $\varepsilon'_{33}(v)$ decreases at all $\Delta T = |T - T_n|$. The maximal values of $\varepsilon'_{33}(v)$ as well as the values of $\Delta T_n$ are much larger in the paraelectric phase than in the ferroelectric phase. The dispersion of a real part of the permittivity $\varepsilon'_{33}(v, T)$ in the ferroelectric phase is observed in a narrow temperature range $\Delta T = 20$ K, whereas in the paraelectric phase, $\Delta T$ is much larger, being of the order of 200 K.

Let us note that taking into account the piezoelectric coupling, the calculated minimal values of $\varepsilon'_{33}(v)$ at $\Delta T = 0$ at different frequencies are larger than those obtained within the model without the piezoelectric coupling.

At a decreasing $\Delta T$ in the ferroelectric phase, the value of $\varepsilon'_{33}(v)$ increases, has a maximum at $\Delta T = 0$, and decreases with an increasing $\Delta T$ in the paraelectric phase. At an increasing frequency, the maximal value of $\varepsilon'_{33}(v)$ and the rate of its change with an increasing $\Delta T$ diminish.

At $v_g$, the values of $\varepsilon'_{33}(v, T) = \varepsilon''_{33}(v, T)$ are 465 in KH$_2$PO$_4$, 520 in KD$_2$PO$_4$, 562 in RbH$_2$PO$_4$, and 330 in KH$_2$AsO$_4$.

The proposed theory provides a good quantitative agreement with the experiment for KH$_2$PO$_4$ (figure 2) and a little worse agreement for the data of [37] for KD$_2$PO$_4$ (figure 3), especially at $\Delta T < 20$ K for $\varepsilon'_{33}(v, T)$. However, it should be noted that the values of $\varepsilon'_{33}(v, T)$ obtained in [37] at frequencies above 1 GHz have maxima at $\Delta T = 0$ K, rather than minima.

The temperature dependence of $\varepsilon''_{33}(v, T)$ in RbH$_2$PO$_4$ measured in [33] is appropriately and well described by the present theory, except for the values of $\varepsilon''_{33}(v, T)$ at $v = 154.2$ GHz and $\Delta T < 20$ K (figure 4). The theory and experimental data of [40] for $\varepsilon''_{33}(v, T)$ at $v = 27$ GHz are also in a good agreement. The obtained theoretical results for $\varepsilon''_{33}(v, T)$ at 198 and 366 are only in qualitative agreement with the data of [42], which, in their turn, are in disagreement with the results of other measurements of [41].

The calculated temperature dependencies of $\varepsilon'_{33}(v, T)$ and $\varepsilon''_{33}(v, T)$ accord well with the ones measured in [41] for KH$_2$AsO$_4$ at different frequencies starting from the submillimeter range (figure 5). The data for $\varepsilon'_{33}(v, T)$ obtained in [36] at $v = 9.2$ GHz are in a somewhat worse agreement with the theory, especially at $\Delta T < 20$ K.

Figures 6[43] contain the calculated temperature dependencies of the real and imaginary parts of longitudinal dynamic dielectric permittivity $\varepsilon'_{33}(v, T)$ and $\varepsilon''_{33}(v, T)$ of clamped K(H$_{1-x}$D$_x$)$_2$PO$_4$ crystals at different deuterations $x$ and frequencies along with the corresponding experimental data.

**Figure 6.** The temperature dependence of $\varepsilon'_{33}$ and $\varepsilon''_{33}$ in K(H$_{0.70}$D$_{0.30}$)$_2$PO$_4$ at different frequencies $v$ (GHz) [33]: 154.2 – 1, α; 249.0 – 2, Δ; 372.0 – 3, o. Symbols are experimental points; lines are the theoretical values.

With an increasing deuteration $x$ in K(H$_{1-x}$D$_x$)$_2$PO$_4$, the magnitude of $\varepsilon'_{33}(v, T)$ decreases, whereas $\Delta T_n$ increases.

At an isomorphic replacement $K \rightarrow$ Rb, $P \rightarrow$ As, the maximal values of $\varepsilon'_{33}(v, T)$ remain almost unchanged, whereas $\Delta T_n$ slightly increase.

It should be noted that in the MH$_2$XO$_4$, the experimental data of [36, 41, 44, 45] correspond to the region of dielectric permittivity dispersion. At the same time, for KD$_2$PO$_4$ in the measurements of [33], the submillimeter frequencies correspond to a high-frequency “tail” of the dispersion, whereas in the
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Figure 7. The temperature dependence of $\varepsilon_3^{'}$ and $\varepsilon_3^{''}$ in K(H$_{0.36}$D$_{0.64}$)$_2$PO$_4$ at different frequencies $\nu$ (GHz) [35]: 154.2 – 1, o; 249.0 – 2, Δ; 372.0 – 3, c. Symbols are experimental points; lines are the theoretical values.

Figure 8. The temperature dependence of $\varepsilon_3^{'}$ and $\varepsilon_3^{''}$ in K(H$_{0.16}$D$_{0.84}$)$_2$PO$_4$ at different frequencies $\nu$ (GHz) [35]: 154.2 – 1, c; 249.0 – 2, Δ; 372.0 – 3, o. Symbols are experimental points; lines are the theoretical values.

Figure 9. The temperature dependence of $\varepsilon_3^{'}$ and $\varepsilon_3^{''}$ in K(H$_{0.07}$D$_{0.93}$)$_2$PO$_4$ at different frequencies $\nu$ (GHz) [35]: 154.2 – 1, c; 249.0 – 2, Δ; 372.0 – 3, o. Symbols are experimental points; lines are the theoretical values.
Figure 10. The temperature dependence of $\varepsilon_{33}'$ and $\varepsilon_{33}''$ in K(H$_{1-x}$D$_x$)$_2$PO$_4$ at $\nu=9.2$ GHz and for different $x$: 0.0 – 1, 0.29 – 2, 0.99 – 3. Symbols are experimental points; lines are the theoretical values.

Figure 11. The temperature dependence of $\varepsilon_{33}'$ and $\varepsilon_{33}''$ in K(H$_{1-x}$D$_x$)$_2$PO$_4$ at $\nu=138.6$ GHz and for different $x$: 0.63 – 1, 0.91 – 2. Symbols are experimental points; lines are the theoretical values.

Figure 12. The temperature dependence of $\varepsilon_{33}'$ and $\varepsilon_{33}''$ in K(H$_{0.22}$D$_{0.78}$)$_2$PO$_4$ at different frequencies $\nu$ (GHz): 8.6 – 1, 9.7 – 2, 26.5 – 3. Symbols are experimental points; lines are the theoretical values.

data of [37], this is the low-frequency tail. Further experimental measurements of $\varepsilon_{33}^*(\nu, T)$ at $\nu > 10$ are required to evaluate the validity of the calculated $\varepsilon_{33}^*(\nu, T)$.

The most graphic illustration of the dispersion of the real and imaginary parts of the dielectric permit-
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Figure 13. The temperature dependence of $\varepsilon_3^{\prime}$ and $\varepsilon_3^{\prime\prime}$ in RbH$_2$PO$_4$ at different frequencies $\nu$ (GHz) [12]: 198.0 – 1, σ; 366.0 – 2, ◦. Symbols are experimental points; lines are the theoretical values.

Figure 14. The frequency-temperature dependence of $\varepsilon_3^{\prime}$ in K(H$_{0.07}$D$_{0.93}$)$_2$PO$_4$. ■, ▲, ● – [33]. Symbols are experimental points; lines are the theoretical values.

Let us analyse the changes in the real and imaginary parts of $\varepsilon_3^{\prime}(\omega, T)$ in M(H$_{1-x}$D$_x$)$_2$XO$_4$ would be their frequency-temperature plots drawn in wide frequency and temperature ranges. Such plots for theoretical dependencies along with the experimental points are presented in figures [14, 15] for K(H$_{0.07}$D$_{0.93}$)$_2$PO$_4$, in figures [16, 17] for RbH$_2$PO$_4$, and in figures [18, 19] for KH$_2$AsO$_4$.

The temperature dependencies of the inverse relaxation time $(\tau_z^{-1})$ in K(H$_{1-x}$D$_x$)$_2$PO$_4$ along with the values estimated from different experimental measurements are presented in figure [20]. The calculated values of the relaxation times $\tau_z^{2, 3, 4}$, in contrast to $\tau_z^1$, are unlikely to depend on temperature and are much smaller than the value of $\tau_z^1$. The theory provides a satisfactory agreement with the experiment for temperature curves of the relaxation time. A certain difference between the relaxation times estimated from the dielectric permittivity and ultrasound measurements is due to the contributions into attenuation from the mechanisms irrelevant for the permittivity (e.g., scattering by admixtures).
Figure 15. The frequency-temperature dependence of $\varepsilon''_{33}$ in $K(H_{0.07}D_{0.93})_2PO_4$. Symbols are experimental points; lines are the theoretical values.

Figure 16. The frequency-temperature dependence of $\varepsilon'_33$ in $RbH_2PO_4$. Symbols are experimental points; lines are the theoretical values.

Figure 17. The frequency-temperature dependence of $\varepsilon''_{33}$ in $RbH_2PO_4$. Symbols are experimental points; lines are the theoretical values.
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**Figure 18.** The frequency-temperature dependence of $\varepsilon'_{33}$ in KH$_2$AsO$_4$. $\square$ – [36]; ○, Δ, △, ∇, ◊ – [41]. Symbols are experimental points; lines are the theoretical values.

**Figure 19.** The frequency-temperature dependence of $\varepsilon''_{33}$ in KH$_2$AsO$_4$. $\square$ – [36]; ○, Δ, △, ∇, ◊ – [41]. Symbols are experimental points; lines are the theoretical values.

**Figure 20.** The temperature dependence of the inverse polarization relaxation time at different $x$: 0.0 – 1, ▲ [17], ◆ [42]; 0.07 – 2, △ [51]; 0.21 – 3, △ [50]; 0.43 – 4, △ [50]; 0.72 – 5, ■ [50]; 0.805 – 6, ▲ [51]; 0.84 – 7, ◆ [52]; 0.93 – 8, ▼ [48]; 1.0 – 9, ■ [53]. Symbols are experimental points; lines are the theoretical values.
5. Conclusions

Within the framework of the modified proton ordering model, taking into account a linear over the strain $\varepsilon_0$ contribution into the energy of the proton subsystem, and using the four-particle cluster approximation, we calculate the longitudinal dynamic characteristics of mechanically clamped crystals of the KH$_2$PO$_4$ family. For the partially deuterated crystals M(H$_{1-x}$D$_x$)$_2$XO$_4$, these characteristics are obtained within the mean crystal approximation. The data for $\varepsilon_3''(\nu, T)$ and $\varepsilon_3''(\nu, T)$ presented by different groups of experimentalists are analyzed and systematized. At the proper choice of the theory parameters for the M(H$_{1-x}$D$_x$)$_2$XO$_4$ crystals, we obtain a good quantitative description of the available experimental data for $\varepsilon_3''(\nu, T)$ and $\varepsilon_3''(\nu, T)$. For the first time, the dispersion of the longitudinal dynamic dielectric permittivity of clamped crystals of the KH$_2$PO$_4$ family is explored in wide temperature and frequency ranges. It should be noted that the effect of piezoelectric coupling on the dielectric characteristics of these crystals is essential. In the present paper, the observed temperature behavior of $\varepsilon_3''(\nu, T)$ in the phase transition region at different frequencies has been appropriately described for the first time.

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Поздовжня релаксація механічно затиснутих кристалів типу KH$_2$PO$_4$

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У рамках модифікованої моделі протонного впорядкування сегнетоактивних кристалів сім’ї KH$_2$PO$_4$ з врахуванням лінійного за деформацією внеску $c_{66}$ в енергію протонної системи в наближенні чотиричастинкового кластера в межах динамічної моделі Глаубера отримано вираз для поздовжньої динамічної діелектричної проникності механічно затиснотого кристалу. При належному виборі параметрів теорії отримано добрий кількісний опис наявних експериментальних даних для цих кристалів.

Ключові слова: сегнетоелектрики, кластерне наближення, діелектрична проникність, часи релаксації