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# Longitudinal dielectric relaxation in $KD_2PO_4$ under hydrostatic pressure

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Within the model proposed earlier, we study the effect of hydrostatic pressure on relaxational dynamics of deuterated $KD_2PO_4$ type ferroelectrics. Within the four particle approximation for deuteron ordering model and using the Glauber approach, we calculate the longitudinal dynamic dielectric permittivity of the strained crystal. Possible pressure dependences of the permittivity and relaxation times are discussed.

**Key words:** *KDP, hydrostatic pressure, dielectric relaxation, dynamic dielectric permittivity*

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## 1. Introduction

Lately, much attention has been paid to the investigations of an external pressure effect on static dielectric properties of hydrogen bonded ferroelectrics of $KH_2PO_4$ family. Hydrostatic pressure is known to reduce transition temperature, spontaneous polarization, and Curie constant in these crystals [1]. The pressure derivatives of these characteristics for $KH_2PO_4$ and $KD_2PO_4$ were already successfully described within the proton ordering model by Blinc [2] and Tortsveit [3]. In our recent papers [4–6], we developed a unified approach allowing one to consistently describe pressure effects on transition temperature and on static dielectric properties of several ferroelectrics and antiferroelectrics with general formula $MeD_2XO_4$, where Me $=$ K, Rb, $ND_4$, X $=$ P, As.

Much less attention is attracted by dynamic dielectric properties of strained hydrogen bonded crystals. To our best knowledge, no experimental data for pressure effects on dynamic permittivities of $KH_2PO_4$ family crystals has been reported yet. The aim of the present work is to study within the earlier proposed approach, the dielectric relaxation in deuterated $KH_2PO_4$ type ferroelectric deformed by hydrostatic pressure.

Starting from the pioneering work by Yoshimitsu and Matsubara [8], the relaxation dynamics of deuterated $KD_2PO_4$ type crystals has been studied within the framework of the Glauber approach [7]. The longitudinal relaxation of paraelectric $KD_2PO_4$ was considered, with taking into account only the short-range correlations between quasispins. Later, the proposed approach was elaborated in [9] and in our papers [10–13]. Both ferroelectric and paraelectric phases were considered, and the long-range interactions were taken into account. Expressions for transverse and longitudinal dynamic dielectric permittivities of the crystals, as well as for relaxation times were obtained; the theoretical results were compared with the experimental data, and the set of theory parameters providing the best fit to the experiment was found. Another approach to a description of deuteron dynamics in $KD_2PO_4$ type crystals is based on the usage of Bloch equation [14–16]. However, it gives worse results than Glauber approach, because of the mean field approximation used.

In the present paper, we apply the method developed in [10–13] to the description of longitudinal relaxation in $KD_2PO_4$ type crystals strained by hydrostatic pressure.

## 2. Model of strained $KD_2PO_4$ type crystal

We consider a deuteron subsystem of a ferroelectric crystal of $KD_2PO_4$ type to which hydrostatic pressure and external electric field directed along one of the crystallographic axes are applied. The four-particle cluster Hamiltonian of the system has a conventional form

$$\begin{aligned} H_q \;=\; & V\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2}+\frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2}+\frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2}+\frac{\sigma_{q4}}{2}\frac{\sigma_{q1}}{2}\right] \\ & + U\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q3}}{2}+\frac{\sigma_{q2}}{2}\frac{\sigma_{q4}}{2}\right]+\Phi\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2}-\sum_f\frac{z^i_{qf}}{\beta}\frac{\sigma_{qf}}{2}, \end{aligned} \tag{1}$$

where two eigenvalues of the Ising spin $\sigma_{qf}=\pm1$ are assigned to two equilibrium positions of a deuteron on the $f$-th bond in the $q$-th unit cell, tunnelling being neglected.

Constants $V$, $U$, and $\Phi$ describe the short-range correlations between deuterons. They are given by the following functions of Slater energies $\varepsilon$, $w$, and $w_1$

$$V=-\frac{w_1}{2},\qquad U=-\varepsilon+\frac{w_1}{2},\qquad \Phi=4\varepsilon-8w+2w_1\,. \tag{2}$$

The fields $z^i_{qf}$ include the effective cluster fields $\Delta^i_{qf}$ created by the sites neighboring on the $qf$-th site, external electric field $E_i$ applied along one of the crystallographic axes, and the long-range deuteron-deuteron interactions (dipole-dipole and indirect via lattice vibrations) taken into account in the mean field approximation

$$z^i_{qf}=\beta[-\Delta^i_{qf}+\sum_{q'f'}J_{ff'}(qq')\frac{\langle\sigma_{q'f'}\rangle}{2}+\mu^i_{qf}E_i]. \tag{3}$$

Hydrostatic pressure effects on the system are described within the approach developed in [6]. It is known that the Slater energies $\varepsilon$, $w$, and $w_1$ and the components of the long-range interaction matrix $J_{ff'}(qq')$ are proportional to the square of the separation between two possible positions of a deuteron on a bond – D-site distance $\delta$. According to [17], the variation of the D-site distance $\delta$ with hydrostatic pressure in $KD_2PO_4$ is linear

$$\delta = \delta_0 + \delta_1 p.$$

We expand $\varepsilon$, $w$, $w_1$, and $J_{ff'}(qq')$ in powers of pressure up to the linear terms. Other mechanisms of pressure influence the energy parameters of the model, like, for instance, electrostriction and changes in distances between the dipoles due to the lattice deformation are taken into account by expanding $\varepsilon$, $w$, $w_1$, and $J_{ff'}(qq')$ in powers of the components of the lattice strain tensor $\varepsilon_i$ up to the linear terms, so that

$$\begin{aligned}
\varepsilon &= \varepsilon^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{i=1}^{3}\delta_{1i}\varepsilon_i\,, \\
w &= w^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{i=1}^{3}\delta_{2i}\varepsilon_i\,, \\
w_1 &= w_1^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{i=1}^{3}\delta_{3i}\varepsilon_i
\end{aligned} \qquad (4)$$

and

$$J_{ff'}(qq') = J^{(0)}_{ff'}(qq')\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big] + \sum_{j=1}^{3}\psi^j_{ff'}(qq')\varepsilon_j\,. \qquad (5)$$

Pressure is expressed in terms of the resulting strain $\varepsilon_1+\varepsilon_2+\varepsilon_3$; $S=\sum_{ij}S^{(0)}_{ij}$; $S^{(0)}_{ij}$ is the matrix of elastic compliances. Only diagonal components of the strain tensor are taken into account.

## 3. Relaxational dynamics

The system with Hamiltonian (1) cannot possess its inherent dynamic properties, since all operators in the Hamiltonian commute with it, and, therefore, are time-independent. Therefore, in the spirit of the Glauber approach [7] we assume that the system (1) interacts with a heat reservoir which causes spins of the system to change their states randomly with probability $w_{qf}(\ldots,\sigma_{qf},\ldots)$ per unit time. System behaviour is described in terms of probability functions $P(\ldots,\sigma_{qf},\ldots,t)$, which time dependence is governed by the master equation:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}P\{...,\sigma_{qf},...,t\} &= -\sum_{qf} w_{qf}\{...,\sigma_{qf},...\}P\{...,\sigma_{qf},...,t\} \\
&\quad + \sum_{qf} w_{qf}\{...,-\sigma_{qf},...\}P\{...,-\sigma_{qf},...,t\}
\end{aligned} \qquad (6)$$

probability of the state $\{..., \sigma_{qf}, ...\}$ decreases with time due to the transitions from this state to all others and increases dew to transitions from all other states to this one. From the detailed balancing condition at equilibrium

$$\frac{w_{qf}\{..., \sigma_{qf}, ...\}}{w_{qf}\{..., -\sigma_{qf}, ...\}} = \frac{P_0\{..., -\sigma_{qf}, ...\}}{P_0\{..., \sigma_{qf}, ...\}},$$

(here $P_0\{..., \sigma_{qf}, ...\}$ is the equilibrium distribution function, being proportional to the Maxwell-Boltzmann factor $\exp(-\beta\hat{H})$) the expression for the spin flopping probability $w_{qf}\{..., \sigma_{qf}, ...\}$ follows:

$$w_{qf}\{..., \sigma_{qf}, ...\} = \frac{1}{2\alpha}[1 - \sigma_{qf} \tanh \frac{1}{2}\beta\mathcal{E}_{qf}]. \tag{7}$$

The parameter $\alpha$ describes the time scale in which all transitions in the system take place, $\mathcal{E}_{qf}$ denotes the operator field acting on the $qf$-th spin; this field is given by the system Hamiltonian (1).

To solve the master equation is quite a complicated task. Fortunately, we may considerably simplify it, by taking into account the fact that, usually, we have to know not the explicit expression for the probability function $P(..., \sigma_{qf}, ...)$, but only the expectation values of the products of spins (distribution functions)

$$\langle\prod_f \sigma_{qf}\rangle = \sum_{\{\sigma\}}\prod_f \sigma_{qf} P\{..., \sigma_{qf}, ..., t\}$$

(the sum is carried out over all the $2^N$ system configurations). The equations for such expectation values follow from the master equation and from (7):

$$-\alpha\frac{\mathrm{d}}{\mathrm{d}t}\langle\prod_f \sigma_{qf}\rangle = \sum_f\left\langle\prod_{f'}\sigma_{qf'}\left[1 - \sigma_{qf}\tanh\frac{1}{2}\beta\mathcal{E}_{qf}\right]\right\rangle. \tag{8}$$

The sum here is carried out only over the spins that occur in the product $\prod_{f'}$.

The symmetry of the expectation values of the products of spins in time-varying and static fields are the same. In the longitudinal external field $E = E_3$:

$$\begin{aligned}
\eta^{(3)} &= \langle\sigma_{q1}\sigma_{q2}\sigma_{q3}\rangle = \langle\sigma_{q2}\sigma_{q3}\sigma_{q4}\rangle = \langle\sigma_{q3}\sigma_{q4}\sigma_{q1}\rangle = \langle\sigma_{q4}\sigma_{q1}\sigma_{q2}\rangle,\\
\eta^{(2)} &= \langle\sigma_{q1}\sigma_{q2}\rangle = \langle\sigma_{q2}\sigma_{q3}\rangle = \langle\sigma_{q3}\sigma_{q4}\rangle = \langle\sigma_{q4}\sigma_{q1}\rangle,\\
\eta^{(2)'} &= \langle\sigma_{q1}\sigma_{q3}\rangle = \langle\sigma_{q2}\sigma_{q4}\rangle.
\end{aligned}$$

Substituting the expressions for the local fields $\mathcal{E}_{qf}$, that act on deuterons which are easily determined from (1), into the (8), we get a set of differential equations for the time-dependent distribution functions:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\eta^{(1)}\\ \eta^{(3)}\\ \eta^{(2)}\\ \eta^{(2)'}\end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14}\\ a_{21} & a_{22} & a_{23} & a_{24}\\ a_{31} & a_{32} & a_{33} & a_{34}\\ a_{41} & a_{42} & a_{43} & a_{44}\end{pmatrix}\begin{pmatrix}\eta^{(1)}\\ \eta^{(3)}\\ \eta^{(2)}\\ \eta^{(2)'}\end{pmatrix} + \begin{pmatrix}a_1\\ a_2\\ a_3\\ a_4\end{pmatrix} \tag{9}$$

with somewhat cumbersome coefficients

$$a_{ij} = \begin{pmatrix} P+2Q-1/\alpha & R & 2M & N \\ 2P+4Q+3R & P+2Q-3/\alpha & 2N+2M+2L & 2M+L \\ 2N+2M+2L & 2M & 2P+2Q-2/\alpha & 2Q \\ 4M+2L & 2N & 4Q & 2R-2/\alpha \end{pmatrix},$$

$$a_i = \begin{pmatrix} L \\ N+2M \\ 2Q \\ 2P \end{pmatrix}.$$

Here

$$\begin{aligned}
L &= \frac{\sinh z}{2\alpha}\left[b\gamma_1 + 2ab\gamma_2 + bd\gamma_3\right], \quad M = \frac{\sinh z}{2\alpha}\left[b\gamma_1 - bd\gamma_3\right], \\
N &= \frac{\sinh z}{2\alpha}\left[b\gamma_1 - 2ab\gamma_2 + bd\gamma_3\right], \\
P &= \frac{1}{4\alpha}\left[(1-b^2)\gamma_1 - 2(a^2-b^2)\gamma_2 - (b^2-d^2)\gamma_3\right], \\
Q &= \frac{1}{4\alpha}\left[(1-b^2)\gamma_1 + (b^2-d^2)\gamma_3\right], \\
R &= \frac{1}{4\alpha}\left[(1-b^2)\gamma_1 + 2(a^2-b^2)\gamma_2 - (b^2-d^2)\gamma_3\right], \\
\gamma_1 &= \left[1+b^2+2b\cosh z\right]^{-1}, \\
\gamma_2 &= \left[a^2+b^2+2ab\cosh z\right]^{-1}, \\
\gamma_3 &= \left[b^2+d^2+2bd\cosh z\right]^{-1}.
\end{aligned}$$

The parameter $z$ can be found from the consistency condition, which states that the values of $\eta^{(1)}$ calculated within the four-particle and the single-particle cluster approximations must coincide. In the latter case the equation (8) can be rewritten as

$$\frac{\mathrm{d}}{\mathrm{d}t}\eta^{(1)} = -\frac{\tilde{\eta}^{(1)}}{\alpha} + \frac{1}{\alpha}\tanh\frac{z-\beta\Delta_3}{2}. \tag{10}$$

Equations (9) along with (10) are quite difficult to solve exactly. Fortunately, some reasonable approximations which significantly simplify the problem can be made. Let us assume that

- the time-dependent electric field $E_3(t) = E_0\exp(-\mathrm{i}\omega t)$ is weak and causes only small departures from thermal equilibrium, and
- the strains $\varepsilon_i$ are time independent.

All the quantities involved may be written as static equilibrium values plus time-dependent fluctuations:

$$\begin{aligned}
&\eta^{(j)} = \tilde{\eta}^{(j)} + \eta^{(j)}(t), \quad a_{ij} = a_{ij}^{(0)} + \frac{z(t)}{2}a_{ij}^{(1)}, \\
&z = \tilde{z} + z(t) = \beta[-\tilde{\Delta} + 2\nu_c(0)\tilde{\eta}^{(1)}] + \beta[-\Delta_3(t) + 2\nu_c(0)\eta^{(1)}(t) + \mu_3 E_3(t)]. \quad (11)
\end{aligned}$$

Here we neglected time fluctuations of strains $\varepsilon_i$. Strictly speaking, the strains do depend on time since in piezoelectric crystals such as $KD_2PO_4$, a time-varying external electric field has to cause time-varying strains. However, at frequencies of an external electric field above the piezoelectric resonance frequency ($\sim 10^6$), the strain is not capable of instantly following the periodic changes in the applied electric field [18]. Therefore, due to inertia effects, at the considered here frequencies ($10^9 \div 10^{12}$ Hz), a susceptibility of effectively clamped crystals is measured, and the neglect of time fluctuations of strains is justified.

Substituting (11) into (9) and (10), and neglecting the terms of the second and the higher orders in the fluctuations, we get two systems of equations for the equilibrium distribution functions and for their time-dependent parts. The solutions of the former are as follows:

$$\tilde{\eta}^{(1)} = \frac{\sinh 2\tilde{z} + 2b\sinh\tilde{z}}{D}, \quad \tilde{\eta}^{(3)} = \frac{\sinh 2\tilde{z} - 2b\sinh\tilde{z}}{D},$$
$$\tilde{\eta}^{(2)} = \frac{\cosh 2\tilde{z} - d}{D}, \quad \tilde{\eta}'^{(2)} = \frac{\cosh 2\tilde{z} - 2a + d}{D},$$

where

$$\tilde{z} = \frac{1}{2}\ln\frac{1+\tilde{\eta}^{(1)}}{1-\tilde{\eta}^{(1)}} + \beta\nu_c(0)\tilde{\eta}^{(1)}, \quad D = \cosh 2\tilde{z} + 4b\cosh\tilde{z} + 2a + d,$$
$$a = \exp(-\beta\varepsilon), \quad b = \exp(-\beta w), \quad d = \exp(-\beta w_1).$$

Here we have already excluded the consistency parameter $\Delta$ from $\tilde{z}$.

The time dependence of $\eta^{(1)}(t)$ found from the second set of equations (obtained after the substitution of (11) into (9)) is given by:

$$\eta^{(1)}(t) = \sum_{j=1}^{4} C_j \mathrm{e}^{-t/\tau_j} + \frac{\mu_3 E_3(t)}{2T} n \prod_{j=1}^{4} \frac{\tau_j}{1 + \mathrm{i}\omega\tau_j}; \tag{12}$$

the polarization relaxation times $\tau_j \equiv -1/q_j$ obey the equation:

$$(q_j)^4 - n_3(q_j)^3 + n_2(q_j)^2 - n_1 q_j + n_0 = 0.$$

Expressions for the quantities $n$, $n_j$, and for the relaxation times $\tau_j$ are too cumbersome to be presented here. They can be found in [19]

From the following relation between the field-induced part of polarization and the fluctuation parts of the mean values of quasispins (order parameter)

$$P_3(t) = \frac{4\mu_3}{v}\eta^{(1)}(t), \tag{13}$$

we obtain the expressions for real and imaginary parts of the longitudinal dynamic dielectric permittivity of the system

$$\varepsilon_3'(\omega, T, p) = \varepsilon_{3\infty} + 4\pi\sum_{j=1}^{4}\frac{\chi_j}{1+(\omega\tau_j)^2}, \quad \varepsilon_3''(\omega, T, p) = 4\pi\sum_{j=1}^{4}\frac{\omega\tau_j\chi_j}{1+(\omega\tau_j)^2}.$$

$\varepsilon_{3\infty}$ is a high-frequency contribution to the permittivity; expressions for $\chi_j$, relaxation times $\tau_j$ and coefficients $n$, $n_j$ can be found in [19].

Only two relaxational modes appear in the paraelectric phase:

$$\varepsilon_3'^{+}(\omega,T,p) = \varepsilon_{3\infty} + 4\pi\sum_{i=1}^{2}\frac{\chi_i^+}{1+(\omega\tau_i^+)^2}, \quad \varepsilon_3''^{+}(\omega,T,p) = 4\pi\sum_{i=1}^{2}\frac{\omega\tau_i^+\chi_i^+}{1+(\omega\tau_i^+)^2}. \quad (14)$$

Expressions for relaxation times and quantities $\chi_i^+$ are given in Appendix.

## 4. Discussion

In describing dielectric relaxation, we use the values of the theory parameters which were shown [6] to provide a fair description of pressure dependences of a transition temperature ($\partial T_{\mathrm{C}}/\partial p = -2$ K/kbar [20]) and static dielectric characteristics of $KD_2PO_4$ crystal. The values used are presented in table 1. Details of the fitting procedure are given in [6].

**Table 1.** The theory parameters for the considered crystals.

| $\delta_1/\delta_0$ ($10^{-3}$kbar$^{-1}$) | $\varepsilon^0$ (K) | $w^0$ | $\nu_c^0$ | $\psi_1^-(0)$ | $\psi_2^-(0)$ | $\psi_3^-(0)$ | $\psi_1^+(0)$ | $\psi_3^+(0)$ | $\delta_{ij}$ | $\frac{(\mu_3^0)^2}{v}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $-6.4$ | 92.0 | 830 | 38.0 | 130 | 110 | $-560$ | 120 | $-560$ | 0 | 76 |

| $c_{11}^+$ ($10^2$kbar) | $c_{12}^+$ | $c_{13}^+$ | $c_{33}^+$ | $c_{11}^-$ | $c_{12}^-$ | $c_{13}^-$ | $c_{22}^-$ | $c_{23}^-$ | $c_{33}^-$ |
|---|---|---|---|---|---|---|---|---|---|
| 6.14 | $-0.71$ | 1.05 | 4.82 | 6.14 | $-0.71$ | 1.0 | 6.14 | 1.1 | 4.3 |

To find the lattice strains we use obvious relations

$$-p = \sum_j c_{ij}\varepsilon_j\,, \quad (15)$$

where $c_{ij}$ are the elastic constants of the crystal, also given in table 1.

Pressure dependence of the dipole moment $\partial\mu_3/\partial p$ is determined under the assumption that the effective dipole moment $\mu_3$ is proportional to the separation between two deuteron sites on a bond – D-site distance $\delta$ and to the lattice constant $c$. It yields

$$\left(\frac{\partial}{\partial p}\frac{\mu_3^2}{v}\right)_{p=0} = \frac{(\mu_3^0)^2}{v}\left[2\frac{\delta_1}{\delta_0} + \frac{\varepsilon_3-\varepsilon_1-\varepsilon_2}{p}\right]. \quad (16)$$

Relation (16), which heavily depends on the ratio $\delta_1/\delta_0$, provides a good agreement of theoretical results for the pressure depending variation of static dielectric characteristics of $KD_2PO_4$ with the corresponding experimental data. It shows the

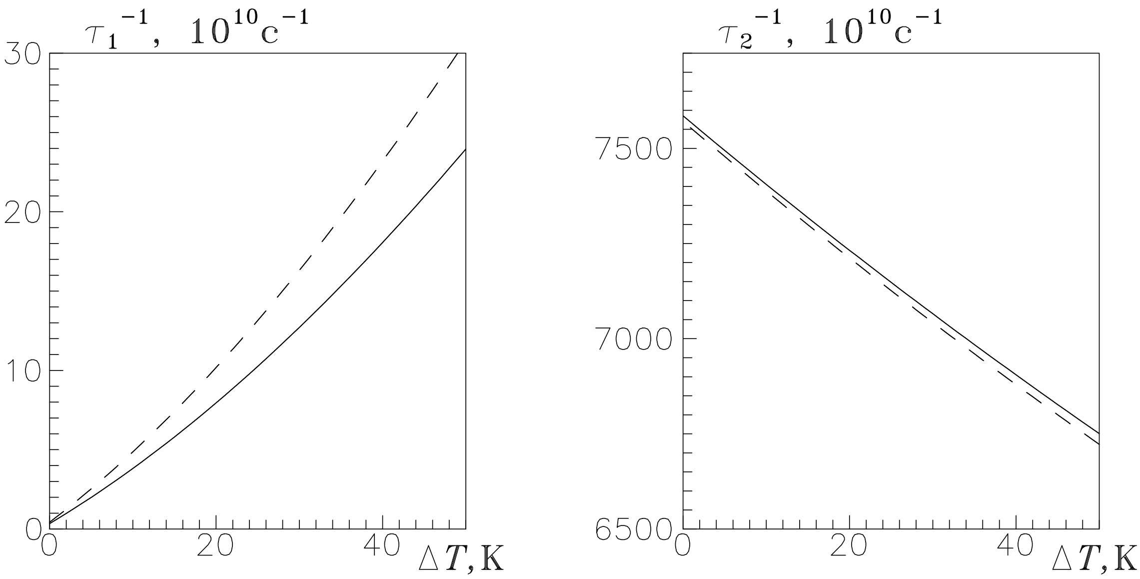


**Figure 1.** Temperature dependence of the longitudinal relaxation times $KD_2PO_4$ at different values of hydrostatic pressure $p$(kbar): solid lines – 0.001; dashed lines – 10.

importance of the D-site distance $\delta$ in the dielectric response of the hydrogen bonded crystal.

A value of the parameter $\alpha$, assumed to be slightly dependent on temperature $\alpha = [1.88 + 0.0609(T - T_{\mathrm{C}} - 1)] \cdot 10^{-14}$c and independent of pressure, was taken from [13].

Figure 1 illustrates the pressure effect on relaxation times (here $\Delta T = T - T_{\mathrm{C}}$). Numerical calculations show that the main contribution into the $\varepsilon_3(\nu, T, p)$ is coming from the first relaxational mode ($\chi_1 \gg \chi_2$), i.e. the dispersion is of Debye type. The relaxation time $\tau_1^+$ is three orders greater than $\tau_2^+$. External pressure does not affect the Debye character of the dielectric relaxation. The relaxation time $\tau_1^+$ decreases with pressure, whereas $\tau_2^+$ hardly depends on pressure.

In figures 2 and 3 we depicted the temperature and frequency dependences of the real the and the imaginary parts of longitudinal dielectric permittivity at different pressures along with the experimental points for $\varepsilon_3(\nu, T, p)$ at an ambient pressure.

Dispersion of the permittivity is observed in the high frequency region ($\nu \sim 10^9 - 10^{10}$ Hz), with the dispersion frequency increasing with temperature. The experimental data for $\varepsilon_3'(\nu, T, p)$, unfortunately available only for the ambient pressure case, are described in the theory rather well. The agreement between the theory and the experiment for $\varepsilon''$ at frequencies lower than the dispersion frequency is much worse, though the character of the dependence is qualitatively reproduced.

Just above the transition point, both real and imaginary parts of the longitudinal permittivity (plotted as functions of $T - T_{\mathrm{C}}$) increase with pressure. As temperature rises, the character of pressure dependence of $\varepsilon_3(\nu, T, p)$ changes to the opposite, and the permittivity starts to decrease with pressure. The higher is the frequency the higher is the temperature at which this change takes place. Similarly, both

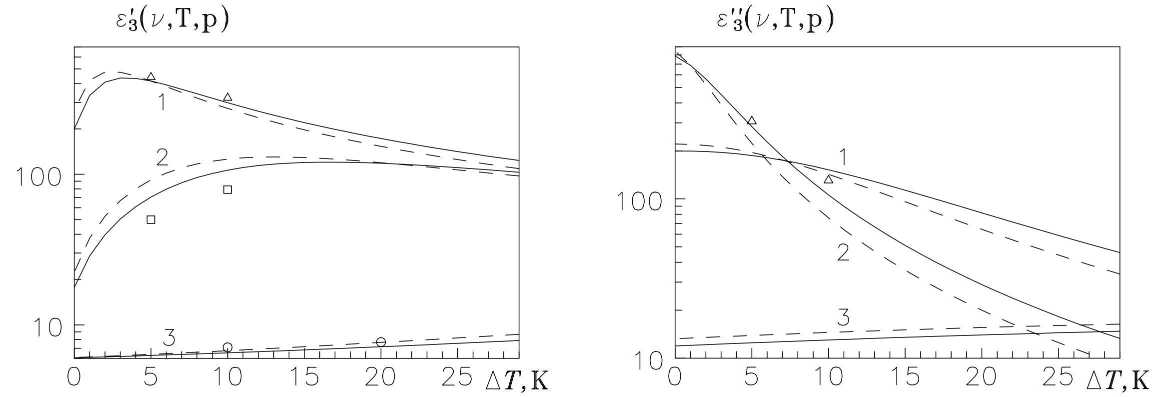


**Figure 2.** Temperature dependence of real and imaginary parts of the longitudinal dynamic dielectric permittivity of $KD_2PO_4$ at different values of frequency $\nu = \omega/2\pi$(GHz): 1, △ [21] – 2.2; 2, □ [22] – 9.2; 3, ○ [23] – 154.2 and hydrostatic pressure $p$(kbar): solid lines – 0.001; dashed lines – 10.

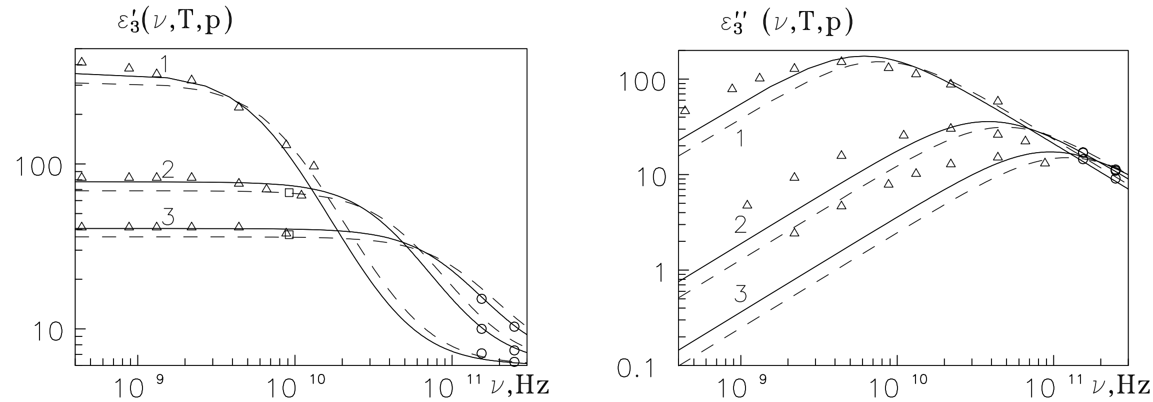


**Figure 3.** The frequency dependence of real and imaginary parts of dynamic dielectric permittivity of $KD_2PO_4$ crystal at different temperatures $\Delta T$(K): 1 – 10; 2 – 50; 3 – 100 and hydrostatic pressures $p$(kbar): solid lines – 0.001; dashed lines – 10. Experimental points are taken from △ – [21], □ – [22], ○ – [23]

$\varepsilon_3'(\nu, T, p)$ and $\varepsilon_3''(\nu, T, p)$ decrease with pressure at frequencies below the dispersion frequency and increase at higher frequencies, with the dispersion frequency raised up by temperature. Overall, the permittivity and relaxation times are raised up by pressure when/if they are raised up by temperature and they are lowered down by pressure when/if they are lowered down by temperature.

## 5. Concluding remarks

Within a Glauber approach and the four-particle approximation for proton-ordering model, we study the longitudinal dielectric relaxation in deuterated ferroelectrics of the $KD_2PO_4$ type deformed by hydrostatic pressure. In our calculations we use the values of the theory parameters and the model dependence of dipole moments which yielded a good agreement with the experimental data for pressure dependences of transition temperature and static dielectric properties of the $KD_2PO_4$ crystal. The longitudinal dynamic dielectric permittivity and relaxation times of strained crystals are calculated under the assumption of time-independent strains. Possible changes in the relaxation times and permittivity are stated. The theory predicts that in the paraelectric phase, pressure does not alter the Debye type of dielectric relaxation, increases one of the relaxation times, leaving the other relaxation time practically unchanged, decreases the magnitude of the real and the imaginary parts of longitudinal permittivity at low frequencies and at high temperatures, and increases them at temperatures just above the transition point and the frequencies above the dispersion frequency. Further dielectric measurements on the crystals under external pressures, which will verify the theory predictions, are required to give us a better insight into the physics of dielectric response of hydrogen bonded crystals.

## Appendix

Coefficients $\chi^{+}_{1,2}$ and relaxation times $\tau^{+}_{1,2}$ occurring in the expressions for the longitudinal dynamic dielectric permittivity of $KD_2PO_4$ type crystal in the paraelectric phase (14) are

$$\chi^{+}_{1,2} = \mp\frac{\mu_3^2}{v}\frac{1}{T}\frac{\tau_1^+\tau_2^+}{\tau_2^+ - \tau_1^+}\left(l_1 - \tau^{+}_{1,2} l_0\right), \quad (\tau^{+}_{1,2})^{-1} = \frac{1}{2}\{-k_1 \mp \sqrt{(k_1)^2 - 4k_0}\},$$

where

$$l_1 = -a', \quad l_0 = -\begin{vmatrix} a_3 & a' \\ b_3 & b' \end{vmatrix}; \quad k_1 = a_1 + b_3, \quad k_0 = \begin{vmatrix} a_1 & a_3 \\ b_1 & b_3 \end{vmatrix}.$$

$$a_1 = a_{11}^{(0)} + \beta\nu_c Y_{(1)} - \xi_a\left[\frac{1}{\alpha} + a_{11}^{(0)} + \beta\nu_c(Y_{(1)} - \frac{1}{\alpha})\right], \quad a_3 = a_{12}^{(0)}(1-\xi_a), \quad a' = \frac{\xi_a}{\alpha},$$

$$b_1 = a_{21}^{(0)} + \beta\nu_c Y_{(3)} - \xi_b\left[\frac{1}{\alpha} + a_{11}^{(0)} + \beta\nu_c(Y_{(1)} - \frac{1}{\alpha})\right], \quad b_3 = a_{22}^{(0)} - \xi_b a_{12}^{(0)}, \quad b' = \frac{\xi_b}{\alpha},$$

$$a_{11}^{(0)} = P_0^+ + 2Q_0^+, \quad a_{12}^{(0)} = R_0^+, \quad a_{21}^{(0)} = 2P_0^+ + 4Q_0^+ + 3R_0^+, \quad a_{22}^{(0)} = P_0^+ + 2Q_0^+,$$

$$\xi_a^z = Y_{(1)}\left[Y_{(1)} - \frac{2}{\alpha}\right]^{-1}, \qquad \xi_b^z = Y_{(3)}\left[Y_{(1)} - \frac{2}{\alpha}\right]^{-1},$$

$$Y_{(1)} = \left[2M_1^+\tilde{\eta}^{(2)} + N_1^+\tilde{\eta}'^{(2)} + L_1^+\right],$$

$$Y_{(3)} = \left[2(L_1^+ + M_1^+ + N_1^+)\tilde{\eta}^{(2)} + (2M_1^+ + L_1^+)\tilde{\eta}'^{(2)} + 2M_1^+ + N_1^+\right],$$

$$P_0^+ = \frac{1}{4\alpha}\left[\frac{1-b^2}{(1+b^2)^2} - 2\frac{a^2-b^2}{(a^2+b^2)^2} - \frac{b^2-d^2}{(b^2+d^2)^2}\right],$$

$$Q_0^+ = \frac{1}{4\alpha}\left[\frac{1-b^2}{(1+b^2)^2} + \frac{b^2-d^2}{(b^2+d^2)^2}\right],$$

$$R_0^+ = \frac{1}{4\alpha}\left[\frac{1-b^2}{(1+b^2)^2} + 2\frac{a^2-b^2}{(a^2+b^2)^2} - \frac{b^2-d^2}{(b^2+d^2)^2}\right],$$

$$L_1^+ = \frac{1}{4\alpha}\left\{4 - \frac{(1-b^2)^{2\,2}}{(1+b^2)^2} - 2\frac{(a^2-b^2)^2}{(a^2+b^2)^2} - \frac{(b^2-d^2)^{2\,2}}{(b^2+d^2)^2}\right\},$$

$$M_1^+ = \frac{1}{4\alpha}\left\{-\frac{(1-b^2)^{2\,2}}{(1+b^2)^2} + \frac{(b^2-d^2)^{2\,2}}{(b^2+d^2)^2}\right\},$$

$$N_1^+ = \frac{1}{4\alpha}\left\{-\frac{(1-b^2)^{2\,2}}{(1+b^2)^2} + 2\frac{(a^2-b^2)^{2\,2}}{(a^2+b^2)^2} - \frac{(b^2-d^2)^{2\,2}}{(b^2+d^2)^2}\right\}.$$

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## Поздовжня діелектрична релаксація в $KD_2PO_4$ під дією зовнішнього гідростатичного тиску

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В рамках запропонованої моделі досліджено вплив гідростатичного тиску на релаксаційну динаміку дейтерованих сегнетоелектриків типу $KD_2PO_4$. В наближенні чотиричастинкового кластера для моделі протонного впорядкування, в глауберівському підході розраховано поздовжню діелектричну динамічну проникність деформованого кристалу. Обговорюються можливі баричні залежності проникності та часів релаксації.

**Ключові слова:** *KDP, гідростатичний тиск, релаксаційна динаміка, динамічна діелектрична проникність*

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