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Hydrostatic pressure influence on dielectric permittivity of KH_2PO_4 and KD_2PO_4 in the piezoelectric resonance region

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We measured transverse and longitudinal dielectric permittivities of KH_2PO_4 and KD_2PO_4 in the piezoelectric resonance frequency region under the hydrostatic pressure. The transverse permittivity decreases with pressure in the paraelectric phase and increases in the ferroelectric phase. The pressure dependence of the transverse permittivity of deuterated KD_2PO_4 is well described by the presented theory. The longitudinal permittivity of a pure KH_2PO_4 exhibitsseveral peaks in the vicinity of the transition point. Upon increasing hydrostatic pressure, the peaks get closer and may merge.

1 Introduction

An important role in the phase transition and dielectric response of ferroelectrics and antiferroelectrics of the KH_2PO_4 family is played by the geometry of hydrogen bonds in these crystals. Pressure dependence of the separation δ between equilibrium proton (deuteron) sites on a bond governs the corresponding dependences of the transition temperature and longitudinal static dielectric characteristics of the crystals [1, 2, 3]. Moreover, the dependence $T_{\rm C}$ on δ is universal [3, 4] for several crystals of the KH_2PO_4 type having a three dimensional network of hydrogen bonds (MeD_2XO_4, Me = K, Rb, ND_4, X = P, As, KH_2PO_4, and $NH_4H_2PO_4$).

High pressure studies are one of the most useful methods of exploring the role of hydrogen subsystem geometry in the phase transition and dielectric response of these crystals. Influence of hydrostatic pressure on the transition temperature, spontaneous polarization, and Curie constant of the KH_2PO_4 family ferroelectrics is well studied experimentally. This influence for the prototype compounds KH_2PO_4 and KD_2PO_4 was theoretically described yet in Refs. [1, 2] using the four-particle cluster approximation for the proton ordering model. The fact that this model can account for the external pressure effects is considered as one of its experimental evidences.

However, much less is known about pressure effects on the transverse dielectric characteristics of these crystals. Only in Ref.[5] the variation of transverse permittivity ε_a of an undeuterated

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KH_2PO_4 with hydrostatic pressure at room temperature was measured. It was established that ε_a decreases with pressure, and the slope $d\varepsilon_a/dp$ decreases as frequency is increased from 400 Hz up to 25 kHz. As far as we know, there is no experimental data for influence of external pressures on transverse dielectric properties of deuterated KH_2PO_4 type crystals. Neither it is known in what way external pressure affects the longitudinal or transverse dynamical dielectric characteristics of these crystals.

The aim of the present study is to fill this gap, namely, to explore the dependences of transverse and longitudinal dynamic dielectric permittivities of the KH_2PO_4 and KD_2PO_4 on hydrostatic pressure in a wide temperature range. Measurements are carried out at the frequency of 1MHz, that belongs to the piezoelectric resonance frequency region of these crystals [6]. This fact should not affect the behavior of the transverse permittivity, provided the samples are oriented precisely, but the temperature curves of the longitudinal permittivity must be essentially different from the static ($0-10^4$ Hz) and high-frequency (10^9-10^{12} Hz) ones. The pressure dependence of the transverse permittivity of a deuterated KD_2PO_4 is described within a microscopic theory. Thence, we can find out whether the pressure changes in the hydrogen bonds geometry determine the pressure dependence of not only the longitudinal [1, 2, 3], but also of the transverse dielectric response of this crystal.

2 Experimental methodics

We measured the dielectric permittivity of two crystals: a pure KH_2PO_4 (transition temperature at ambient pressure $T_{C0} \sim 123$ K) and a highly deuterated sample with $T_{C0} \sim 210$ K (0.87 nominal deuteration), hereafter abbreviated as KD_2PO_4. The obtained decrease of the transition temperatures with hydrostatic pressure $\partial T_C/\partial p$ is -4.6 K/kbar in KH_2PO_4 and -2.1 K/kbar in KD_2PO_4, that well accords with the literature data [7].

The permittivity ε was determined from the samples capacity using the well-known formula

$$\varepsilon = \frac{d}{\varepsilon_0 S} C,$$

where d is the sample thickness; C is its electric capacity; S is the area of electric contacts; $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m. Capacity was measured by the conventional bridge method using the ac bridges E7-12 (working frequency 1 MHz) and P5016 (10 kHz and 50kHz) within 0.2-0.4%. As electric contacts a silver paste was used.

Optic grade samples were placed in a autonomous hydrostatic pressure chamber, with silicone oil serving as a pressure transmitting medium. Pressure was measured by mechanical and manganin manometers with an accuracy ± 2 MPa. Temperature was measured to ± 0.1 K with a copper-constantan thermocouple. Capacities were obtained in a dynamical regime with a temperature change rate $2 \cdot 10^{-2}$K/c.

3 Experimental results

Closeness of the measuring frequency to the piezoelectric resonance region, as expected, does not essentially influences the transverse permittivities of the KH_2PO_4 and KD_2PO_4 ferroelectrics. The measured curves have a typical form of the static transverse permittivity in these crystals (see fig. 1). In the paraelectric phase ε_{11} slowly increases on lowering temperature, reaching its maximal value at $T \approx T_C + 15$ K, somewhat decreases in the interval $T_C < T < T_C + 15$ K, has a jump at the transition and gradually decreases to a certain limiting value as temperature is lowered down in the ferroelectric phase. This gradual decrease in a deuterated KD_2PO_4 is much faster than in a pure KH_2PO_4, reflecting the fact that in KH_2PO_4 the phase transition is close to the second order, while in KD_2PO_4 a pronounced first order phase transition takes place with a significant jump of spontaneous polarization [8].

The obtained pressure dependences of the transverse permittivities of ferroelectric KH_2PO_4 and KD_2PO_4 are analogous to the corresponding dependences of the transverse permittivity in antiferroelectric $NH_4H_2AsO_4$ and $ND_4D_2AsO_4$ [9]. Under hydrostatic pressure, the magnitudes of transverse permittivities of both crystals at temperatures far above the transition points decrease with $\partial \ln \varepsilon_{11}/\partial p = -3.6\%\text{kbar}^{-1}$ in KH_2PO_4 at $T = 160$ K and $-1.13\%\text{kbar}^{-1}$ in KD_2PO_4 at $T = 260$ K. In the ferroelectric phase ε_{11} increases with pressure, but this effect results from the changes in the distance of a given temperature point from the transition temperature, whereas the low temperature limit of ε_{11} does not depend on pressure.

In figs. 2 and 3 we presented the temperature curves of the longitudinal dielectric permittivity of a pure KH_2PO_4 and undeuterated KD_2PO_4, respectively, at different values of hydrostatic pressure. Note an interesting behavior of the permittivity of KH_2PO_4, which exhibits three clear maxima (correspondingly, two minima) in the vicinity of the transition point. Possibly due to the narrowness of the temperature interval in which the peaks of the longitudinal permittivity occur, in a deuterated KD_2PO_4 the three-maximum structure was detected only at $p = 1.9$ kbar (see fig. 3). For the other pressures, only one minimum of the permittivity was clearly observed. However, the bends in the curves of ε_{33} in the temperature interval between the detected paraelectric and ferroelectric peaks indicate that the second, ferroelectric phase minimum must occur in KD_2PO_4 as well.

As follows from fig. 4a, where the curves of longitudinal and transverse permittivities ε_{33} and ε_{11} are compared, the right maximum occurs at the transition point. The two other maxima and the left minimum, which take place in the ferroelectric phase, are reproduced at different values of hydrostatic pressure as well as at heating or cooling (see fig. 4b). At lower frequencies ($\nu = 10$ kHz and $\nu = 50$ kHz), the ε_{33} of deuterated KD_2PO_4 has a typical form of the static permittivity with one peak at the transition point and the Curie-Weiss behavior in the paraelectric phase (fig. 4c).

Under hydrostatic pressure, the magnitude of the transition point maximum in KH_2PO_4 does not change, while that of the left ferroelectric one is reduced from ~ 770 at 10bar down to ~ 400 at $p = 2$ kbar. Beside, the temperature interval where the extrema of the permittivity occur becomes narrower, so that the two-minimum structure of ε_{33} transforms to a single-minimum one.

At temperatures below the peaks, the longitudinal permittivity of deuterated KD_2PO_4 has a typical shoulder-like form, caused by the multi-domain structure of the samples. Qualitatively similar dependences can be traced in a pure KH_2PO_4 as well, but the “fine structure” of ε_{33} here is fancier. Hydrostatic pressure almost does not affect the shape of the temperature curve $\varepsilon_{33}(T < T_C)$. Width of the plateau is about 30 K in both crystals, with the height of about 400 being practically pressure independent.

As seen in figs. 2 and 3, the Curie-Weiss law is obeyed for ε_{33}^{-1} of KH_2PO_4 and KD_2PO_4 above the transition point in a rather wide temperature range, except for a vicinity of the transition point. The Curie constants are very close to the corresponding static ones [7] and decrease with pressure linearly from $C = 2949$ K in KH_2PO_4 and $C = 3770$ K in KH_2PO_4 at ambient pressure with the slopes $\partial \ln C/\partial p = -0.48\%\text{kbar}^{-1}$ in KH_2PO_4 and $-1.5\%\text{kbar}^{-1}$ in KD_2PO_4 (the literature data for the Curie constants of static permittivities are $C = 2910$ K and $\partial \ln C/\partial p = -0.66\%\text{kbar}^{-1}$ in

KH_2PO_4 and 3700 K and $-1.43\%\mathrm{kbar}^{-1}$ in KD_2PO_4, respectively [7]).

Note a strong dependence of the logarithmic pressure derivatives of the dielectric characteristics of the crystals on deuteration and the fact that this dependence is different for the transverse and longitudinal quantities: $|\partial \ln \varepsilon_{11}/\partial p|$ in KH_2PO_4 is much higher than in KD_2PO_4, whereas for $|\partial \ln C/\partial p|$ the reverse holds. A similar effect has been revealed earlier [7] for the transition temperature, saturation polarization and Curie constant of these crystals.

4 Theory

We restrict our theoretical calculations by the case of highly deuterated KD_2PO_4. The known models of dielectric relaxation in hydrogen-bonded crystals [10, 11], based on Glauber's [13] dynamics of pseudospins, are suitable for description of the high-frequency permittivities ($10^9 - 10^{12}$ Hz) only, when a crystal is effectively clamped [12]. Therefore, in order to describe the above presented pressure dependences of the longitudinal dielectric permittivity one must develop a special model of dielectric relaxation which would take into account dynamics of piezoelectric strain ε_6 as well. However, since this dynamics is not essential for the transverse dielectric response of KD_2PO_4, the latter can be described within static models. We shall do that within the proton ordering model modified to the case of strained crystals [3].

Calculations are performed with the conventional four-particle cluster Hamiltonian

$$H_q = V\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2} + \frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2} + \frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2} + \frac{\sigma_{q4}}{2}\frac{\sigma_{q1}}{2}\right]$$
$$+U\left[\frac{\sigma_{q1}}{2}\frac{\sigma_{q3}}{2} + \frac{\sigma_{q2}}{2}\frac{\sigma_{q4}}{2}\right] + \Phi\frac{\sigma_{q1}}{2}\frac{\sigma_{q2}}{2}\frac{\sigma_{q3}}{2}\frac{\sigma_{q4}}{2} - \sum_{f=1}^{4}\frac{z_{qf}}{\beta}\frac{\sigma_{qf}}{2}. \quad (1)$$

Two eigenvalues of the Ising pseudospin $\sigma_{qf} = \pm 1$ are assigned to two equilibrium deuteron sites on the f-th bond in the q-primitive cell. The internal fields z_{qf} include a long-range interactions between deuterons (dipole-dipole and lattice mediated) taken into account in the mean field approximation, cluster fields Δ_{qf} which describe the short-range interactions with the pseudospin σ_{qf} not explicitly included into the cluster Hamiltonian, and an external electric field applied along the a-axis of the tetragonal unit cell

$$z_{qf} = \beta\left[-\Delta_{qf} + \sum_{q'f'} J_{ff'}(qq')\frac{\langle\sigma_{q'f'}\rangle}{2} + \mu^1_{qf}E_1\right], \quad (2)$$

μ^1_{qf} is the projection on the a-axis of the effective dipole moment created by displacements of heavy ions and redistribution of electron density induced by deuteron ordering. In the case of transverse electric field E_1, the following relations between the mean values of pseudospins and between the effective dipole moments μ^1_{qf} are obeyed

$$\eta^x_{24} = \langle\sigma_{q2}\rangle = \langle\sigma_{q4}\rangle, \qquad z_{24} = z_{q2} = z_{q4};$$
$$\mu_1 = \mu^1_{q1} = -\mu^1_{q3}, \qquad \mu^1_{q2} = \mu^1_{q4} = 0.$$

Parameters of the short-range deuteron correlations U, V, Φ are functions of the so-called Slater energies ε, w, w_1:

$$V = -\frac{w_1}{2}, \qquad U = -\varepsilon + \frac{w_1}{2}, \qquad \Phi = 4\varepsilon - 8w + 2w_1. \quad (3)$$

Pressure dependences of the Slater energies and parameters of the long-range interactions are modelled as [3]

$$\varepsilon = \varepsilon^0 \Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big], \quad w = w^0 \left[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\right], \quad w_1 = w_1^0 \Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\Big]. \tag{4}$$

and

$$J_{ff'}(qq') = J_{ff'}^{(0)}(qq') \left[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\right] + \sum_{j=1}^{3}\psi_{ff'}^{j}(qq')\varepsilon_j. \tag{5}$$

Here we take into account the quadratic dependence of these parameters on the separation δ between two equilibrium deuteron sites on a bond, whereas the pressure dependence of δ is known to be linear [14]

$$\delta = \delta_0 + \delta_1 p = \delta_0 \left(1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\right),$$

$S = \sum_{ij=1}^{3} S_{ij}^{(0)}$. According to [2, 3] we suppose that the only essential mechanism of the pressure influence on the Slater energies is a decrease in the D-site distance δ. However, for the parameters of the long-range interactions there exist other important mechanisms of variation with pressure (for instance, the dipole-dipole interactions increase when the distance between deuterons is reduced), taken into account in (5) via the expansions in the diagonal components of the strain tensor ε_i $(i = 1, 2, 3)$.

Excluding the fields Δ_{qf} from z_{qf} by making use of the condition that the mean values $\eta_{qf}^x \equiv \langle\sigma_{qf}\rangle$ calculated with Hamiltonian (1) and with the one-particle Hamiltonian

$$H_{qf}^{(1)} = -\left(\frac{z_{qf}}{\beta} - \Delta_{qf}\right)\frac{\sigma_{qf}}{2}$$

coincide, we obtain

$$\begin{aligned}
z_{1,3} &= \frac{1}{2}\ln\frac{1+\eta_{1,3}^x}{1-\eta_{1,3}^x} + \beta\left[\nu_1\eta_{1,3}^x + \nu_3\eta_{3,1}^x + 2\nu_2\eta_{24}^x \pm \frac{\mu_1 E_1}{2}\right],\\
z_{24} &= \frac{1}{2}\ln\frac{1+\eta_{24}^x}{1-\eta_{24}^x} + \beta\left[\nu_2[\eta_1^x + \eta_3^x] + [\nu_1 + \nu_3]\eta_{24}^x\right],\\
\eta_{1,3}^x &= \frac{1}{D^x}\left[\sinh A_1 + d\sinh A_2 \pm 2a\sinh A_3 + b(2\sinh A_4 \pm \sinh A_5 \pm \sinh A_6)\right],\\
\eta_{24}^x &= \frac{1}{D^x}\left[\sinh A_1 - d\sinh A_2 + b(\sinh A_5 - \sinh A_6)\right],
\end{aligned}$$

where the following notations are used

$$\begin{aligned}
&D^x = \cosh A_1 + d\cosh A_2 + 2a\cosh A_3 + b(2\cosh A_4 + \cosh A_5 + \cosh A_6),\\
&A_{1,2} = \frac{z_1^x + z_3^x}{2} \pm z_{24}^x, \quad A_{3,4} = \frac{z_1^x \mp z_3^x}{2}, \quad A_{5,6} = \frac{z_1^x - z_3^x}{2} \pm z_{24}^x;\\
&a = \exp(-\beta\varepsilon), \quad b = \exp(-\beta w), \quad d = \exp(-\beta w_1),\\
&\nu_j = \frac{J_{1j}(0)}{4}
\end{aligned}$$

$J_{ij}(0)$ is the long-range interaction matrix Fourier transform.

From the field-induced polarization of the crystal along the a-axis

$$P_1 = \sum_f \frac{\mu^i_{qf}}{v}\frac{\langle\sigma_{qf}\rangle}{2} = \frac{2\mu_1(\eta^x_1 + \eta^x_3)}{v},$$

the transverse static dielectric permittivity $\varepsilon^{\varepsilon}_1(0, T, p)$ of a clamped crystal (at ε_i =const) can be calculated

$$\varepsilon^{\varepsilon}_{11}(0, T, p) = \varepsilon_{1\infty} + 4\pi \left(\frac{\partial P_1}{\partial E_1}\right)_{\varepsilon}\Bigg|_{E_1=0} = \varepsilon_{1\infty} + 4\pi\frac{\beta\mu_1^2}{v}\frac{2(a + b\cosh z)}{D - 2(a + b\cosh z)\varphi}, \tag{6}$$

where

$$\varphi = \frac{1}{1-\eta^2} + \beta\nu_a, \quad \nu_a = \nu_1 - \nu_3 = \nu^0_a\left[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\right] + \sum_{i=1}^{3}\psi_{ai}\varepsilon_i,$$

$\varepsilon_{1\infty}$ is a high-frequency contribution to the permittivity. The dielectric permittivity of a free crystal (at p=const) $\varepsilon^F_i(0, T, p)$ is related to (6) by

$$\varepsilon^F_{11}(0, T, p) = \varepsilon^{\varepsilon}_{11}(0, T, p) + 4\pi d^2_{14}c^E_{44}, \tag{7}$$

where d_{14} is the piezomodule, and c^E_{44} is the elastic constant of a short-circuited crystal.

For the involved quantities, the following relations hold in the zero external field limit

$$\begin{aligned}
&\eta \equiv \langle\sigma_{q1}\rangle = \langle\sigma_{q2}\rangle = \langle\sigma_{q3}\rangle = \langle\sigma_{q4}\rangle;\\
&z \equiv z_{q1} = z_{q2} = z_{q3} = z_{q4} = \frac{1}{2}\ln\frac{1+\eta}{1-\eta} + \beta\nu_c(0)\eta;\\
&D = \cosh 2z + 4b\cosh z + 2a + d,\\
&\nu_c(0) = \frac{1}{4}\left(J_{11}(0) + 2J_{12}(0) + J_{13}(0)\right) = \nu^0_c(0)\left[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^{3}\varepsilon_j\right] + \sum_i\psi_{ci}(0)\varepsilon_i.
\end{aligned}$$

The order parameter η is found by minimization of the free energy

$$f = \frac{\bar{v}}{2}\sum_{ij}c_{ij}\varepsilon_i\varepsilon_j - 2w + 2\nu_c(0)\eta^2 + 2T\ln\frac{2}{(1-\eta^2)\,D}, \tag{8}$$

whereas to find the strains we should solve the system of equations

$$-p = \sum_{j=1}^{3}c_{ij}\varepsilon_j, \tag{9}$$

where c_{ij} are the elastic constants of the whole crystal, being determined from an experiment. Contribution of a deuteron subsystem to pressure or temperature dependences of the elastic constants is neglected.

5 Numerical analysis

The values of the theory parameters for a deuterated crystal KD_2PO_4 with the transition temperature at ambient pressure $T_{C0} = 210$ K are presented in Tables 1,2. They were found in Ref. [3] and used for a description of the uniaxial pressure $p = -\sigma_3$ dependences of the transition temperature, longitudinal dielectric permittivity, and spontaneous polarization of the crystal. The elastic constants of the paraelectric crystals coincide with the experimental data of Ref. [15]. The new parameters ν_a, $f_1^0 = (\mu_1^0)^2/v$, and $\varepsilon_{1\infty}$ are found by fitting the theoretical temperature curve of the transverse permittivity to experimental data (ν_a sets the slope $\partial\varepsilon_{11}/\partial T$, whereas f_1, and $\varepsilon_{1\infty}$ give the magnitude of ε_{11}.

Table 1: The theory parameters for a KD_2PO_4 crystal with $T_{C0} = 210$ K, $\partial T_C/\partial p = -2.1$ K/kbar. Plus and minus indices denote the quantities used in the paraelectric and ferroelectric phases, respectively.

ε^0	w^0	$\nu_c^0(0)$	$\nu_a^0(0)$	f_1^{0+}	f_1^{0-} (K)	ψ_{c1}^-	ψ_{c2}^-	ψ_{c3}^-	ψ_{c1}^+	ψ_{c3}^+	$\delta_1/\delta_0 \cdot 10^3$ (kbar^{-1})
87.6	785	37.05	-32	830	520	120	100	-545	110	-545	-7.5

The so-called deformation potentials ψ_{ai}, which enter only the expression for the transverse permittivity, do not essentially affect the permittivity. Therefore, for the sake of simplicity we put $\psi_{ai} = 0$. Contributions of the double-ionized deuteron configurations (with four deuterons close to a given PO_4 group or with none) are neglected as well by taking $w_1 \to \infty$.

Hence, the only new theory parameter, governing the pressure dependence of the calculated characteristics, is the ratio δ_1/δ_0 – the relative rate of the pressure changes in the D-site separation δ. We choose it so that at all other parameters unchanged, the correct dependence of the transition temperature on the hydrostatic pressure $\partial T_C/\partial p = -2.1$ K/kbar is obtained.

In Ref. [3] we have shown that at the chosen analogously values of δ_1/δ_0, the recalculated dependences $T_C(\delta)$ for six deuterated ferroelectric and antiferroelectric crystals with a three dimensional network of hydrogen bonds MeD_2XO_4 (Me = K, Rb, ND_4, X = P, As) form a single universal linear dependence, while T_C and δ can be altered by either hydrostatic or uniaxial $p = -\sigma_3$ (for KD_2PO_4) pressures. Experimentally this universality has been established by R. Nelmes *et al* [4] for undeuterated KH_2PO_4 and $NH_4H_2PO_4$ and deuterated KD_2PO_4 and $ND_4D_2PO_4$. At the adopted in this paper value of δ_1/δ_0 for KD_2PO_4 with $T_{C0} = 210$ K, the dependence $T_C(p)[\delta(p)]$ for this specific crystal also accords with the universal line [3].

The slopes $\partial\mu_i/\partial p$ can be determined without introducing into the theory any extra fitting parameter on the basis of the following simple half-empirical speculations, nevertheless yielding a fair agreement with the experiment.

It is believed that the deuteron ordering in the system results in displacements of heavy ions and electron density which contribute to crystal polarization. Since, when ordered, a deuteron shifts

Table 2: Elastic constants of the considered crystal (units of 10^5bar).

c_{11}^+	c_{12}^+	c_{13}^+	c_{33}^+	c_{11}^-	c_{12}^-	c_{13}^-	c_{22}^-	c_{23}^-	c_{33}^-
6.93	-0.78	1.22	5.45	6.8	-0.78	1.0	6.99	1.0	5.3

from its central position on a hydrogen bond to the off-central one by a distance $\delta/2$, according to [3] we assume that the heavy ions displacements are also proportional to δ and that μ_i is proportional to the corresponding lattice constant a_i. This yields

$$\frac{1}{\mu_i^0}\frac{\partial \mu_i}{\partial p} = \frac{\delta_1}{\delta_0} + \frac{\varepsilon_i}{p}. \tag{10}$$

The pressure dependence of the effective longitudinal dipole moment μ_3, calculated with (10) provides a fair agreement with the available experimental data for the pressure dependence of spontaneous polarization of KD_2PO_4 and of the static dielectric permittivities of KD_2PO_4 and RbD_2PO_4 [3].

In fig. 5 we depict the theoretical curves of the transverse static dielectric permittivity of KD_2PO_4 along with the experimental points of Section 4. The permittivity is calculated with (6), since due to smallness of the piezomodule d_{14} [16] the difference between transverse permittivities of clamped and free KD_2PO_4 can be neglected; the pressure dependence of the dipole moment μ_1 is given by (10).

The theory qualitatively well reproduces the temperature curve of the permittivity, including a decrease with temperature in the paraelectric phase and the jump at the transition point, but is not able to explain the existence of a small broad maximum of ε_{11} at temperature slightly higher than the transition point. That is a common drawback of all existing calculations of the transverse permittivity, that can be removed by assuming a temperature dependent high-frequency contribution to the permittivity $\varepsilon_{1\infty}$.

As one can see, a satisfactory quantitative agreement with experimental data for the rates of a decrease in the permittivity with pressure in the high-temperature phase and of an increase in the low-temperature phase is obtained. The fact that the value of the ratio δ_1/δ_0, yielding the correct theoretical pressure dependence of transition temperature, provides the correct pressure dependence of the transverse dielectric permittivity, no extra fitting parameters being introduced into the theory, gives one more evidence on the important role played by the hydrogen bonds geometry, namely the separation δ between equilibrium deuteron sites, in the phase transition and dielectric response of the hydrogen bonded crystals.

6 Concluding remarks

We performed experimental studies of hydrostatic pressure influence on transverse and longitudinal dielectric permittivities of ferroelectric KH_2PO_4 and KD_2PO_4 crystals at 1MHz, the frequency that belongs to the piezoelectric resonance region.

The obtained temperature curves of transverse permittivity ε_{11} are similar to the corresponding curves of static permittivity of the crystals, while the pressure dependences of the permittivities are analogous to those in the antiferroelectric crystals $NH_4H_2AsO_4$ and $ND_4D_2AsO_4$.

Unlike ε_{11}, the temperature curves of the longitudinal permittivity ε_{33} at 1MHz are qualitatively different from static ones. The multipeak structure of the permittivity in the vicinity of the transition point is observed. Under hydrostatic pressure, the two minima of the longitudinal permittivity are getting closer, so that its two-minimum structure transforms to a single-minimum one. Above the transition point, the longitudinal permittivities of KH_2PO_4 and KD_2PO_4 obey the Curie-Weiss law; the pressure dependences of the corresponding Curie constants well accord with the data for the Curie constants of static permittivities.

The measured rates of decrease with pressure in the transition temperature and permittivity ε_{11} in the paraelectric phase and of a increase in ε_{11} in the ferroelectric phase in a deuterated KD_2PO_4 are well described within the proton ordering model. Theoretical pressure dependences of T_C and ε_{11} to a great extent are governed by the ratio δ_1/δ_0. This parameter denotes relative pressure changes in the separation δ between equilibrium deuteron sites on a bond. Obtained in the present paper theoretical description of the pressure dependence of ε_{11}, a similar agreement with experimental data for spontaneous polarization and longitudinal static dielectric permittivity [3], as well as the previously revealed universality of [3, 4] of the transition temperature vs H(D)-site distance δ in the MeD_2XO_4 (Me = K, Rb, ND_4, X = P, As), KH_2PO_4 and $NH_4H_2PO_4$ crystals, indicate that an important role in the phase transition and dielectric response of the crystals is played by the geometry of hydrogen bonds, in particular, by the separation δ between hydrogen sites.

So far we have no clear explanation of the multipeak structure of the longitudinal permittivity. Apparently, it is a dynamic effect connected with a piezoelectric resonance phenomena, since at lower frequencies as well as at frequencies above the piezoelectric resonance but below the dielectric dispersion region [17] the ε_{33} has a typical form of the permittivity with one peak at the transition point and the Curie-Weiss behavior in the paraelectric phase.

The maxima of ε_{33} in the ferroelectric phase might be merely the peaks at different piezoelectric resonance frequencies (harmonics). The harmonics frequencies are determined by sample dimensions and by the appropriate elastic constants (only by c_{66}^E for a 45^o Z cut sample). The c_{66}^E has a peculiarity at the phase transition point [6], dropping from about $6 \cdot 10^{10}$ dyn/cm^2 to zero and increasing back to this value in the paraelectric phase. Therefore, at changing temperature in the vicinity of the transition point, the resonant harmonics frequencies span a wide frequency range, so that at certain temperatures they may coincide with the measuring frequency 1 MHz.

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References

[1] R. Blinc and B. Žekš, Helv. Phys. Acta **41**, 701 (1968).

[2] S. Torstveit, Phys. Rev.B **20**, 4431 (1979).

[3] I.V. Stasyuk, R.R. Levitskii, and A.P. Moina, Phys. Rev. B **59**, 8530 (1999).

[4] R.O. Piltz, M.I. McMahon, and R.J. Nelmes, Ferroelectrics **108**, 271 (1990).

[5] Y. Kobayashi, S. Endo, K. Deguchi, O. Shimomura, T. Kikegawa, Phys. Rev. B **55**, 2850 (1997).

[6] W.P. Mason, Phys. Rev. **69**, 173 (1946).

[7] G.A. Samara, Ferroelectrics **22**, 925 (1979).

[8] G.A. Samara, Ferroelectrics **5**, 25 (1973).

[9] K. Gesi and K. Ozawa, J. Phys. Soc. Japan **53**, 4405 (1984).

[10] K. Yoshimitsu, T. Matsubara, Progr. Theor. Phys., Suppl. Extra Number, 109 (1968).

[11] R.R. Levitskii, I.R. Zachek, V.I. Varanitskii, Ukr. Fiz. Zhurn **25**, 1961 (1980) (in Russian).

[12] W. Kanzig. *Ferroelectrics and antiferroelectrics*, Academic Press, New York, 1957.

[13] R.J. Glauber, J. Math. Phys. **4**, 294 (1963).

[14] R.J. Nelmes, Ferroelectrics **71**, 87 (1987).

[15] L.A. Shuvalov and A.V. Mnatsakanyan, Sov. Phys. – Crystallogr. **11**, 210 (1966).

[16] L.A. Shuvalov, I.S. Zheludev et al. Bull. Acad. Sci. USSR. Phys. Ser. **31**, 1919 (1967).

[17] R.M. Hill, S.K. Ichiki, Phys. Rev. **132**, 1603 (1963).

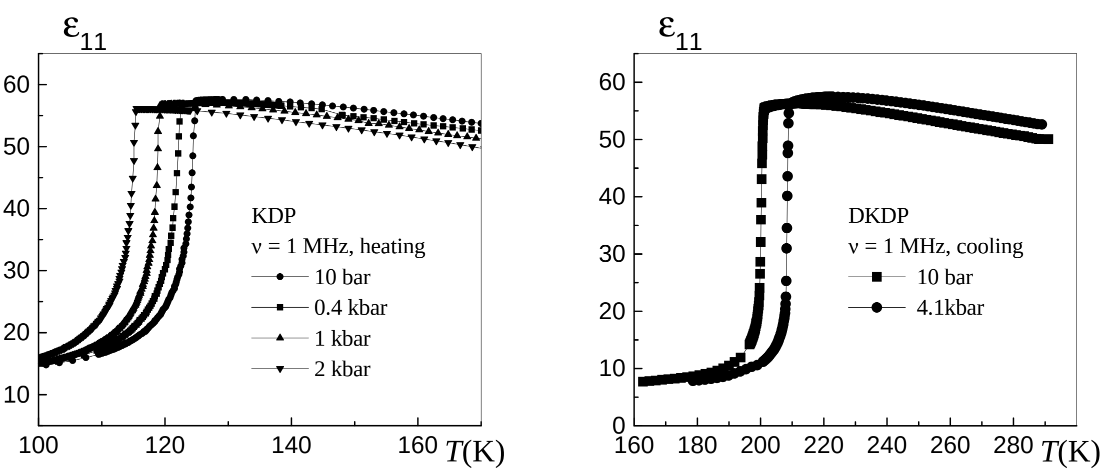

Figure 1: Transverse dielectric permittivities of KH_2PO_4 and KD_2PO_4 as functions of temperature at different values of hydrostatic pressure. The frequency is $\nu = 1$MHz. Symbols are experimental points, lines are drawn for clarity.

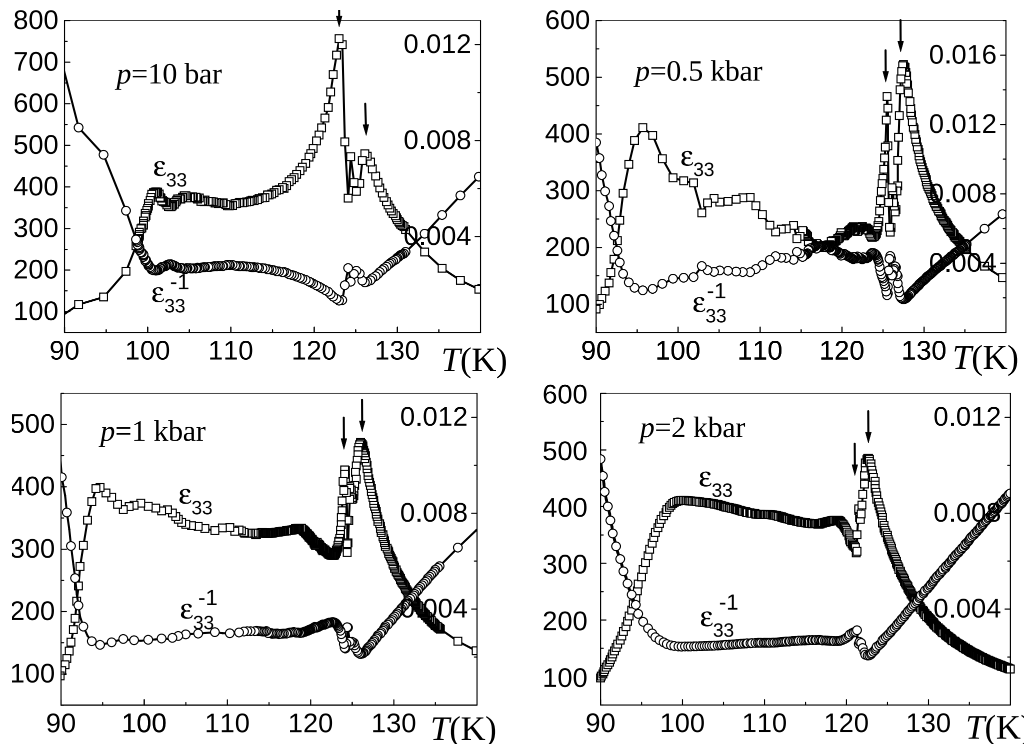

Figure 2: Longitudinal dielectric permittivity of KH_2PO_4 at ν = 1MHz (cooling) as a function of temperature at different values of hydrostatic pressure. Symbols are experimental points, lines are drawn for clarity.

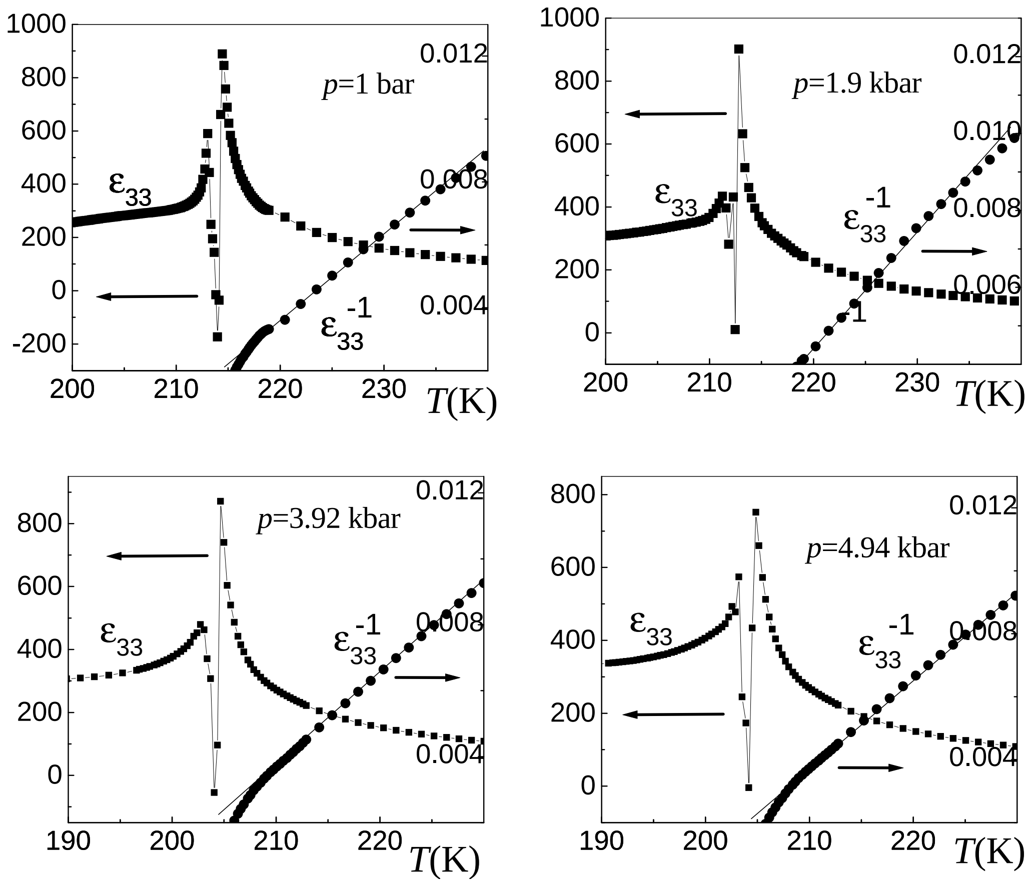

Figure 3: Longitudinal dielectric permittivity of KD_2PO_4 at $\nu = 1$MHz (heating) as a function of temperature at different values of hydrostatic pressure. Symbols are experimental points, lines are drawn for clarity. The insets show the permittivity in the vicinity of the transition point.

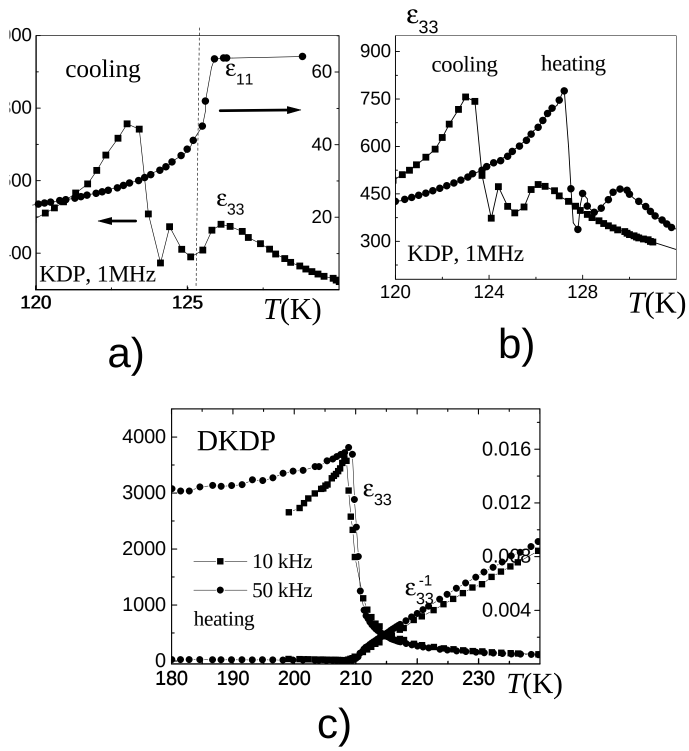

Figure 4: Dielectric permittivities of KH_2PO_4 and KD_2PO_4 as functions of temperature at ambient pressure. Measuring frequencies and direction of temperature changes (heating or cooling) are indicated at figures. Symbols are experimental points, lines are drawn for clarity.

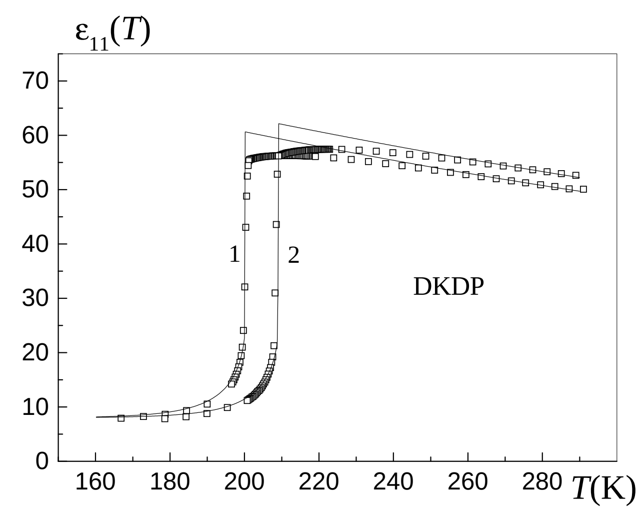

Figure 5: Transverse dielectric permittivity of KD_2PO_4 as a function of temperature at different values of hydrostatic pressure (kbar) 1 – 0; 2 – 4.1. Lines are calculated theoretically; symbols are experimental points of the present work.