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 of both crystals 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 dynamic permittivity of the crystals obeys the Curie–Weiss law above the transition point, the pressure dependence of the Curie constant accords with the earlier data for a static permittivity. Near the transition point, multiple peaks in the longitudinal permittivity are revealed.

Key words: piezoelectricity, KDP, transverse permittivity, hydrostatic pressure.

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I. 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. A problem is to find the geometric parameter which is crucial here. Katrusiak [1] analyzed a local geometric structure of a separate hydrogen bond, with taking into account the changes in the electron structure of atoms forming the hydrogen bond. He showed that for hydrogen bonds of the C_2 symmetry (as in KH_2PO_4), the primary parameters are distances between a hydrogen and the two oxygens, as well as some of the angles formed by oxygens and groups to which they are attached. The other parameters usually used, like the the O...H–O length and separation δ between equilibrium proton (deuteron) sites on a bond, appear to derive from the primary independent dimensions.

However, it is still not clear what parameter of the H-bond influences most macroscopic properties of a crystal. Ichikawa [2,3], systemizing experimental data for several hydrogen bonded ferroelectric crystals, argued that it is the O...H–O length that determines the transition temperature in them. Structural measurements performed by Nelmes indicated that rather a separation δ is a unique parameter that sets the transition temperature in KH_2PO_4 family crystals. A universality of the linear T_C *vs* δ dependences has been revealed for KH_2PO_4, $NH_4H_2PO_4$, and their deuterated forms [4–7]. The proton ordering model successfully explained this universality [8] and predicted that it holds also for all deuterated ferro- and antiferroelectric crystals of the KH_2PO_4 family with a general formula MeD_2XO_4 (Me = K, Rb, ND_4, X = P, As) having a 3D network of hydrogen bonds.

Model calculations also indicate that the H-site distance is an important parameter in setting the dielectric characteristics of the KH_2PO_4 type crystals: its pressure dependence governs the corresponding dependences of the transition temperature and longitudinal static dielectric characteristics of the crystals [8–10].

High pressure studies are one of the most useful methods of exploring the role of hydrogen subsystem geometry. 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. [9,10] 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. [11] the variation of transverse permittivity ε_{11} of an undeuterated KH_2PO_4 with hydrostatic pressure at room temperature was measured. It was established that ε_{11} decreases with pressure, and the slope $|d\varepsilon_{11}/dp|$ 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 KH_2PO_4 at other temperatures or of deuterated KH_2PO_4 type crystals. Neither is it known in what way external pressure affects the longitudinal or transverse dynamic dielectric characteristics of these crystals.

The aim of the present study is 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 1 MHz, that belongs to the piezoelectric resonance frequency region of these crystals. 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 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. Role of pressure changes in the hydrogen bonds geometry in the pressure dependence of the transverse dielectric response of this crystal is explored.

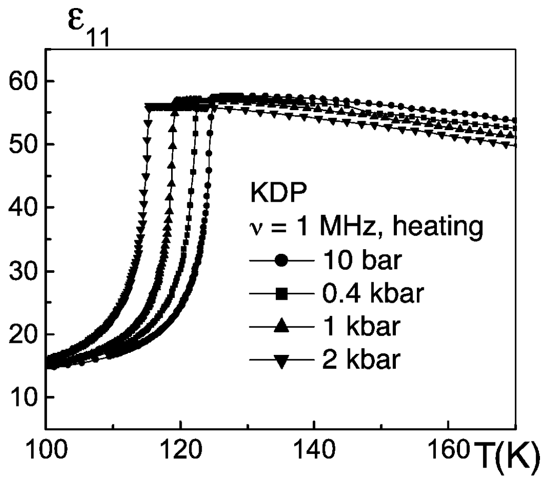
II. EXPERIMENTAL METHODICS

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 [12].

Permittivity was determined from the samples capacity, measured by the conventional bridge method using the ac bridge E7–12 (working frequency 1 MHz). 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. Details and some of experimental data obtained *en route* but not included in the present paper are given in Ref. [13].

III. EXPERIMENTAL RESULTS

Closeness of the measuring frequency to the piezoelectric resonance region, as expected, does not essentially influence the transverse permittivities of the KH_2PO_4 and KD_2PO_4 ferroelectrics. The measured curves (see Fig. 1) have a well-known typical form of the static transverse permittivity in these crystals [14–17]: 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.



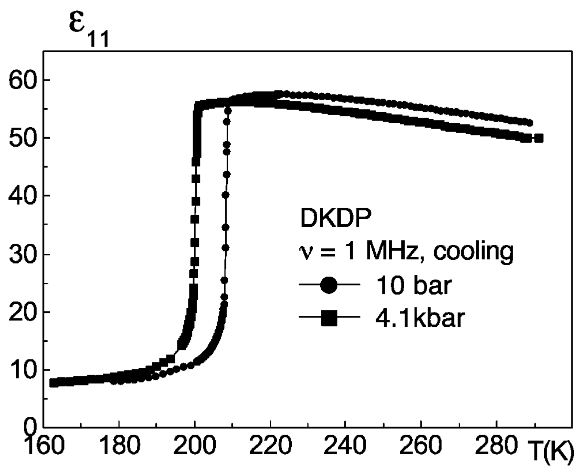


Fig. 1. Transverse dielectric permittivities of KH_2PO_4 and KD_2PO_4 as functions of temperature at different values of hydrostatic pressure. Symbols are experimental points, lines are drawn for clarity.

At temperatures far above the transition points the magnitudes of transverse permittivities of both crystals decrease under hydrostatic pressure ($\partial \ln \varepsilon_{11}/\partial p = -3.6\%\text{kbar}^{-1}$ 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} is not affected. Such pressure behaviour is analogous to the pressure dependence of the transverse permittivity in antiferroelectric crystals $NH_4H_2AsO_4$ and $ND_4D_2AsO_4$ [19].

In Figs. 2 and 3 we present the measured at 1 MHz temperature curves of the longitudinal dielectric permittivity of a pure KH_2PO_4 and undeuterated KD_2PO_4 at different values of hydrostatic pressure.

Near the transition point, we detect multiple clear maxima and/or bends in the permittivity curves of the crystals, reproduced at different values of hydrostatic pressure as well as at heating or cooling [13]. Due to the narrowness of the temperature interval where the permittivity exhibits these peculiarities, in KD_2PO_4 the multipeak structure was detected only at 1.9 kbar (see Fig. 3). For the other pressures, the bends in the curves of ε_{33} were observed in this region (the narrow peaks must have been skipped at measurements). Under hydrostatic pressure this temperature interval becomes even narrower, so that some peaks of ε_{33} may merge.

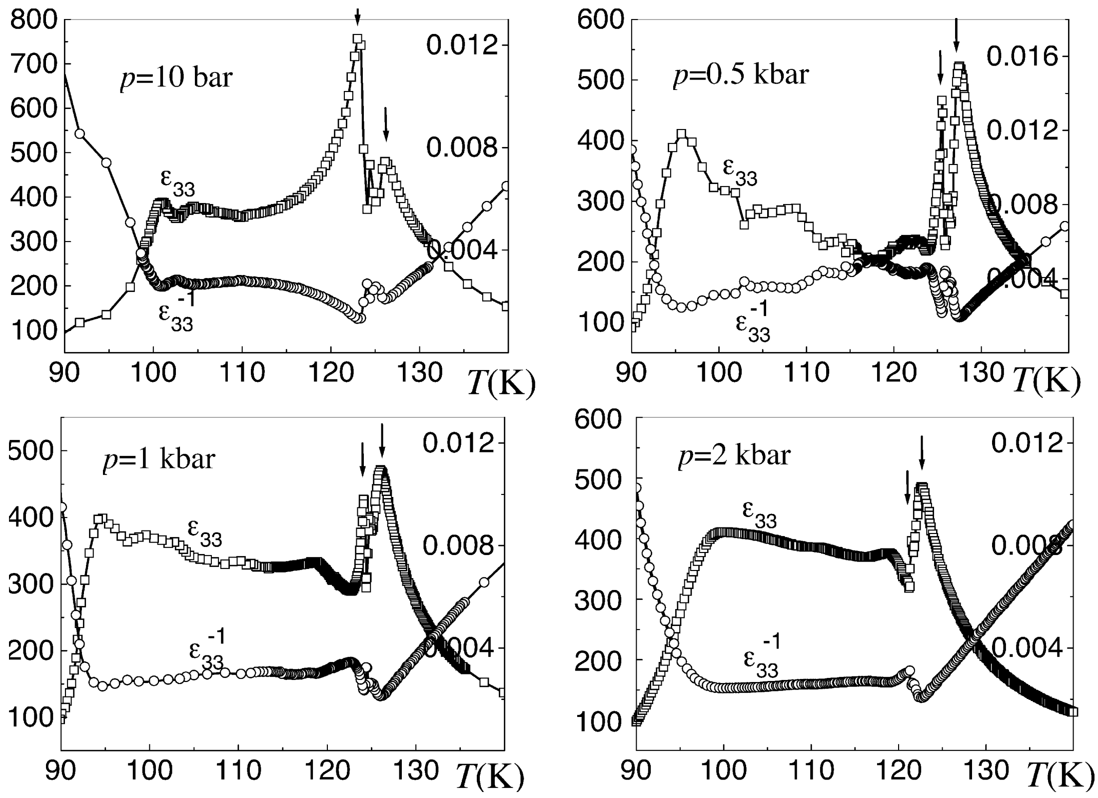


Fig. 2. Longitudinal dielectric permittivity of KH_2PO_4 at $\nu = 1$ MHz (cooling) as a function of temperature at different values of hydrostatic pressure. Symbols are experimental points, lines are drawn for clarity.

The ε_{33}, measured at lower frequencies [13] as well as at frequencies above the piezoelectric resonance but below the dielectric dispersion region [20], has a typical form of the permittivity with one peak at the transition point and the Curie–Weiss behaviour in the paraelectric phase. Apparently, the peaks of the longitudinal permittivity at 1 MHz are a dynamic effect connected with a piezoelectric resonance phenomena. Most likely, they are the peaks at different piezoelectric resonance frequencies (harmonics) or can be attributed to resonances in domains of different sizes. Harmonics frequencies are determined by sample (domain) dimensions and by the appropriate elastic constants (only by c^E_{66} for a 45^o Z cut sample). In KH_2PO_4 and KD_2PO_4, the c^E_{66} has a peculiarity at the phase transition point [18], 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.

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.

Above the transition point (see Figs. 2 and 3, the Curie–Weiss law is obeyed for ε_{33}^{-1} of KH_2PO_4 and KD_2PO_4 in a rather wide temperature range, except for the vicinity of the transition point. The Curie constants at ambient pressure $C = 2949$ K in KH_2PO_4 and $C = 3770$ K in KH_2PO_4 are very close to the corresponding static ones [12] and decrease with pressure linearly with the slopes $\partial \ln C/\partial p = -0.48\%\mathrm{kbar}^{-1}$ in KH_2PO_4 and $-1.5\%\mathrm{kbar}^{-1}$ in KD_2PO_4 (the literature data [12] for the static Curie constants are $C = 2910$ K and $\partial \ln C/\partial p = -0.66\%\mathrm{kbar}^{-1}$ in KH_2PO_4 and 3700 K and $-1.43\%\mathrm{kbar}^{-1}$ in KD_2PO_4).

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 [12] for the transition temperature, saturation polarization and Curie constant of these crystals.

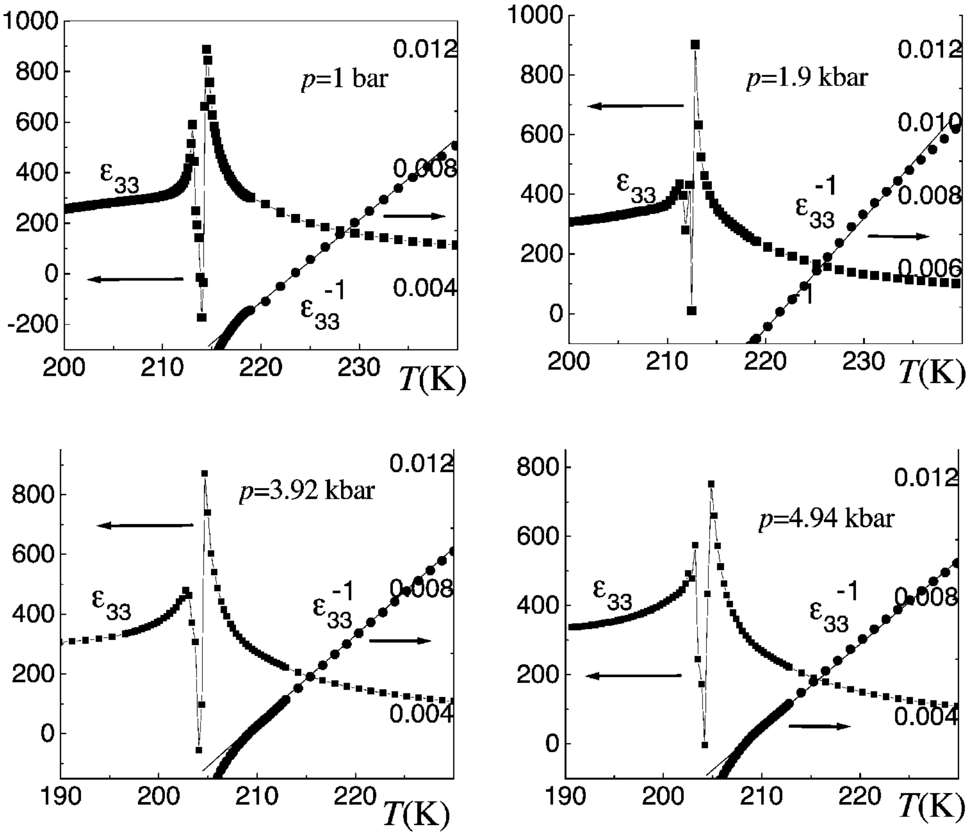


Fig. 3. Longitudinal dielectric permittivity of KD_2PO_4 at $\nu = 1$ MHz (heating) as a function of temperature at different values of hydrostatic pressure. Symbols are experimental points, lines are drawn for clarity. The insets show the permittivity in the vicinity of the transition point.

IV. THEORY

We restrict our theoretical calculations by the case of a highly deuterated KD_2PO_4. The known models of dielectric relaxation in hydrogen-bonded crystals [21,22], based on Glauber's [23] dynamics of pseudospins, are suitable for description of the high-frequency permittivities ($10^9 - 10^{12}$ Hz) only, when a crystal is effectively clamped [24]. 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 [8]. We have already found the transverse dielectric constant of strained KD_2PO_4 [25], but had no experimental data available. Previously, the transverse dielectric constant for these crystals at atmospheric pressure has been calculated by Havlin *et al* [14–16]; our results well accord with theirs.

Calculations are performed with the conventional four-particle cluster Hamiltonian [8]

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

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

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

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. Symmetry of the transverse effective dipole moments μ^1_{qf} is

$$\mu_1 = \mu^1_{q1} = -\mu^1_{q3}, \qquad \mu^1_{q2} = \mu^1_{q4} = 0.$$

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

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

Usually $w_1 \to \infty$. Pressure dependences of the Slater energies and parameters of the long-range interactions are modelled as in Ref. [8]

$$\varepsilon = \varepsilon^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^3 \varepsilon_j\Big], \quad w = w^0\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^3 \varepsilon_j\Big], \quad (4)$$

and

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

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 [26]

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

$S = \sum_{ij=1}^3 S^{(0)}_{ij}$. According to [8,10] 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 $(i = 1, 2, 3)$.

The transverse dielectric permittivity of a KD_2PO_4 crystal calculated with the Hamiltonian (1) reads [25]

$$\varepsilon^\varepsilon_{11}(T,p) = \varepsilon_{1\infty} + 4\pi\frac{\beta\mu_1^2}{v}\frac{2(a + b\cosh z)}{D - 2(a + b\cosh z)\varphi}, \quad (6)$$

where $\varepsilon_{1\infty}$ is a high-frequency contribution, and

$$\varphi = \frac{1}{1-\eta^2} + \beta\nu_a,$$

$$\nu_a = \frac{J_{11} - J_{13}}{4} = \nu^0_a\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^3 \varepsilon_j\Big] + \sum_{i=1}^3 \psi_{ai}\varepsilon_i.$$

J_{ij} is the long-range interaction matrix Fourier transform at $\mathbf{q} = \mathbf{0}$. We also use the following notations

$$D = \cosh 2z + 4b\cosh z + 2a + d,$$

$$z \equiv z_{q1} = z_{q2} = z_{q3} = z_{q4} = \frac{1}{2}\ln\frac{1+\eta}{1-\eta} + \beta\nu_c(0)\eta;$$

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

$$\nu_c = \frac{J_{11} + 2J_{12} + J_{13}}{4} = \nu^0_c\Big[1 - \frac{2}{S}\frac{\delta_1}{\delta_0}\sum_{j=1}^3 \varepsilon_j\Big] + \sum_i \psi_{ci}\varepsilon_i.$$

At zero strains ε_i, the above expression for the transverse permittivity transforms into that of Havlin [14].

The order parameter $\eta \equiv \langle\sigma_{q1}\rangle = \langle\sigma_{q2}\rangle = \langle\sigma_{q3}\rangle = \langle\sigma_{q4}\rangle$ is found by minimization of the free energy

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

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

$$-p = \sum_{j=1}^3 c_{ij}\varepsilon_j, \quad (7)$$

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.

V. 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 I, II. They were found in Ref. [8] 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. [27]. The new parameters ν_a, $f^0_1 = (\mu^0_1)^2/v$, 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}).

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 deuteron configurations with four deuterons close to a given PO_4 group or with none are neglected as well by taking $w_1 \to \infty$.

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

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.

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

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

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. [8] 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. 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 [8].

The slopes $\partial\mu_i/\partial p$ are determined without introducing into the theory any extra fitting parameter by the following simple half-empirical formula, nevertheless yielding a fair agreement with the experiment.

$$\frac{1}{\mu_i^0}\frac{\partial\mu_i}{\partial p} = \frac{\delta_1}{\delta_0} + \frac{\varepsilon_i}{p}. \qquad (8)$$

It follows from that major assumption that the deuteron ordering in the system results in displacements of heavy ions and electron density which contribute to crystal polarization. We suppose [8] that the heavy ions displacements are proportional to a deuteron shift from its central position on a hydrogen bond to the off-central one ($\delta/2$) and to the corresponding lattice constant a_i. The pressure dependence of the effective longitudinal dipole moment μ_3, calculated with (8) 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 [8].

In Fig. 4 we depict the theoretical curves of the transverse static dielectric permittivity of KD_2PO_4 along with the experimental points of Section III.

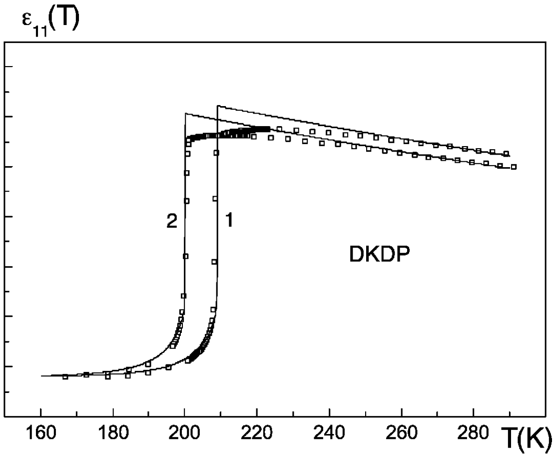


Fig. 4. Transverse dielectric permittivity of KD_2PO_4 as a function of temperature at different values of hydrostatic pressure (kbar) 1 — 0; 2 — 4.1. Lines are calculated theoretically; symbols are experimental points of the present work.

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 [15], 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.

VI. 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 1 MHz, 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 1 MHz are qualitatively different from static ones. The multipeak structure of the permittivity in the vicinity of the transition point is observed. 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 an 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 [8], as well as the previously revealed universality of [8,4] 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.

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ВПЛИВ ГІДРОСТАТИЧНОГО ТИСКУ НА ДІЕЛЕКТРИЧНУ ПРОНИКНІСТЬ KH_2PO_4 І KD_2PO_4 В ДІЛЯНЦІ П'ЄЗОЕЛЕКТРИЧНОГО РЕЗОНАНСУ

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Експериментально досліджено вплив гідростатичного тиску на поперечну та поздовжню діелектричні проникності кристалів KH_2PO_4 і KD_2PO_4 в частотній ділянці п'єзоелектричного резонансу. Поперечна проникність обох кристалів спадає з тиском у параелектричній фазі та зростає в сеґнетоелектричній. Барична залежність поперечної проникности дейтерованого кристала KD_2PO_4 добре описується запропонованою теорією. Поздовжня динамічна проникність кристалів задовольняє закон Кюрі–Вейса вище від точки переходу, а барична залежність константи Кюрі добре узгоджується з даними попередніх вимірювань для статичної проникности. Поблизу точки переходу виявлено численні піки поздовжньої проникности.