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Dielectric, Electromechanical and Elastic Properties of $K_{1-x}(NH_4)_xH_2PO_4$ Compounds

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We describe the available experimental data for the dielectric, piezoelectric, and elastic characteristics of the $NH_4H_2PO_4$ antiferroelectric crystals, using the proposed microscopic theory. Within the framework of the thermodynamic theory and using the obtained experimental data we calculate the dielectric, piezoelectric, and elastic characteristics of the $K_{1-x}(NH_4)_xH_2PO_4$ compounds at $x > 0.32$.

Keywords: ferroelectrics, cluster approximation, dielectric permittivity, piezoelectric coefficients, elastic constant.

Стаття постуила до редакції 17.11.2014; прийнята до друку 15.12.2014.

Introduction

Since the 1990-ies, large attention has been paid to investigations of the $K_{1-x}(NH_4)_xH_2PO_4$ type systems, undergoing the phase transitions to the proton glass phase at low temperatures. Theoretical description of the thermodynamic and dielectric properties of these compounds is a complicated and unsolved problem of statistical physics. Description of their dynamic properties within a microscopic approach is particularly interesting. Experimental studies and theoretical description of the temperature curves of real and imaginary parts of the dynamic dielectric permittivity tensor at different frequencies, especially the low-temperature curves of the imaginary parts at low frequencies, are very important.

In earlier theories of the $Rb_{1-x}(NH_4)_xH_2PO_4$ type mixtures either short-range [1] or long-range [2, 3] interactions were taken into account. However, in these crystals the $PO_4(AsO_4)$ tetrahedra and their random surrounding by the Rb or NH_4 ions play a dominant role in the formation of the system energy levels and give rise to a random internal field. At the same time, a crucial role in formation of the ferroelectric and antiferroelectric structures is played by the long-range interactions.

Two types of random interactions for simple Ising systems with pair interactions have

been taken into account in [4, 5] in the cluster approach. In [6 - 9] using the four-particle cluster

approximation a satisfactory quantitative description of experimental data for the temperature curves of polarization, Edwards-Anderson parameter, longitudinal and transverse permittivities of the $Rb_{1-x}(NH_4)_xH_2PO_4$ type systems has been obtained. However, in the intermediate composition range, as well as near the transition temperatures some qualitative and quantitative discrepancies between the theory and experiment do take place.

The ferroelectric crystals of the KD_2PO_4 family are piezoelectric in both phases, which essentially affects the behavior of their physical characteristics. Description of the dielectric properties of the MD_2PO_4 type ferroelectrics within the framework of the conventional proton ordering model (see [10, 11]) was restricted to the static limit and to the high-frequency relaxation. Attempts to explore the piezoelectric resonance phenomenon within a model that does not take into account the piezoelectric coupling are pointless.

In [12, 13] within the framework of the modified proton ordering model with piezoelectric coupling, the static and dynamic dielectric, piezoelectric, and elastic characteristics of the KH_2PO_4 family crystals were calculated. A numeral analysis of the obtained results was performed; optimum sets of the model parameters were found, providing a good quantitative description of experimental data.

The $K_{1-x}(NH_4)_xH_2PO_4$ type crystals, according

to [14], are of the KH_2PO_4 type and have a tetragonal structure ($I\bar{4}2d$) at room temperature.

They are a great example of structural glasses. In these solid solutions a dipole glass state (DG) exists at low temperature and at certain compositions. The T-x phase diagram of these compounds was explored in [15-17]. It is known that the FE or AFE phase transitions are present in systems with ammonium content $0.0 < x < 0.2$ and $0.7 < x < 1.0$, respectively. At $0.2 < x < 0.7$ the glass-like behavior is observed at low temperatures. At boundary compositions, the ferroelectric, paraelectric, and dipole glass state coexist in a wide temperature range [16].

Even though the mixed crystals $K_{1-x}(NH_4)_xH_2PO_4$ are well studied, their electromechanical properties are practically not explored. In [18, 19] a possible role of the piezoelectric coupling for the $K_{1-x}(NH_4)_xH_2PO_4$ systems has been reported. Later, in [20] a necessity for a thorough investigation of the effects caused by the piezoelectric coupling in these systems was underlined. In [21 - 23] a detailed experimental study of the dielectric, piezoelectric, and elastic properties characteristics of these materials is reported.

In the present paper, using the results of the thermodynamic theory and experimental data, we calculate the dielectric, piezoelectric, and elastic characteristics of the $K_{1-x}(NH_4)_xH_2PO_4$ systems at $x \gg 0.32$.

I. Model Hamiltonian of the $NH_4H_2PO_4$ crystals

We shall consider a system of protons moving on the O-H...O bonds in $NH_4H_2PO_4$ (ADP) crystals. The 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 four surrounding it structural elements (fig. 1).

Calculations of the physical characteristics of the ADP crystals are performed in the four-particle cluster

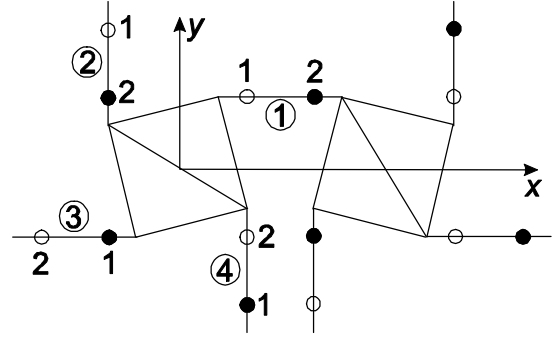


Fig. 1. A primitive cell of the ADP crystals. The numbers ①, ②, ③, ④ indicate the hydrogen bonds: 1, 2 are possible equilibrium positions of the protons.

approximation for the short-range interactions and in the mean field approximation for the long-range interactions, as well as in presence of external electric field E_3 along the crystallographic c axis and mechanical stress $s_6 = s_{xy}$. In absence of tunneling the system Hamiltonian reads

$$H = NH^0 + \frac{1}{2} \sum_{qf} J_{ff'}(qq') \frac{\langle s_{qf} \rangle}{2} \frac{\langle s_{q'f'} \rangle}{2} + \sum_q H_{q,a}^{(4)}, \quad (1)$$

where N is the total number of primitive cells; s_{qf} is the operator of the z-component of the pseudospin, which two eigenvalues $s_{qf} = \pm 1$ correspond to the two equilibrium proton position in the q-th cell on the f-th bond. The "seed" energy corresponds to the sublattice of heavy ions and does not depend explicitly on the deuteron subsystem configuration. It is expressed in terms of the strain e_6 and electric field E_3 and includes the elastic, piezoelectric, and dielectric contributions

$$H^0 = \frac{u}{2} c_{66}^0 e_6^2 - u e_{36}^0 e_6 E_3 - \frac{u}{2} c_{33}^0 E_3^2, \quad (2)$$

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

The four-particle proton Hamiltonians $H_{q,s,a}^{(4)}$ read

$$H_{q,a}^{(4)} = H_q^{(4)a} - \frac{1}{b} x_q \left(-\frac{s_{q1}}{2} + \frac{s_{q2}}{2} + \frac{s_{q3}}{2} - \frac{s_{q4}}{2} \right) - \sum_{f=1}^4 \frac{z_6}{b} \frac{s_{qf}}{2}, \quad (3)$$

$$H_q^{(4),a} = (-d_{s6} e_6 - 2d_{16} e_6) \left(\frac{s_{q1} s_{q2} s_{q3}}{2} + \frac{s_{q1} s_{q2} s_{q4}}{2} + \frac{s_{q1} s_{q3} s_{q4}}{2} + \frac{s_{q2} s_{q3} s_{q4}}{2} \right) +$$

$$+ (V_a + d_{a6} e_6) \left(\frac{s_{q1} s_{q2}}{2} + \frac{s_{q3} s_{q4}}{2} \right) + (V_a - d_{a6} e_6) \left(\frac{s_{q2} s_{q3}}{2} + \frac{s_{q4} s_{q1}}{2} \right) +$$

$$+U_a \left(\frac{s_{q1} s_{q3}}{2} + \frac{s_{q2} s_{q4}}{2} \right) + \Phi_a \frac{s_{q1} s_{q2} s_{q3} s_{q4}}{2}, \quad (4)$$

$$x_q = b(-\Delta_a e^{ik^z a_q} + 2n_a(k^z) h^{(1)} e^{ik^z a_q}),$$

$$z_6 = b(-\Delta_c + 2n_c(0) h^{(1)z} - 2y_6 e_6 + m_3 E_3),$$

$$\text{where } 4n_c(0) = J_{11}(0) + 2J_{12}(0) + J_{13}(0),$$

$$4n_a^0(k^z) = J_{11}(k^z) - J_{13}(k^z),$$

$$J_{ff'}(k^z) = \sum_{a_q^{-a} q'} J_{ff'}(qq') e^{-ik^z(a_q - a_q')}, \quad \text{and}$$

$$k^z = 1/2(b_1 + b_2 + b_3), \quad b_1, b_2, b_3 \text{ are the vectors of}$$

the reciprocal lattice; $e^{ik^z a_q} = \pm 1$; y_6 is the deformation potential; Δ_a and Δ_c are the effective fields exerted by the neighboring hydrogen bonds from outside the cluster. m_3 is the effective dipole moment.

Δ_s^c is determined from the self-consistency condition: the mean values $\langle s_{qf} \rangle$ calculated within the four-particle and one-particle cluster approximations should coincide.

In Eq. (4)

$$V_a = \frac{1}{2} e' - \frac{1}{2} w_1', \quad U_a = \frac{1}{2} e' + \frac{1}{2} w_1', \quad \Phi_a = 2e' - 8w' + 2w_1', \quad a$$

$e = e_a - e_s$, $w = e_1 - e_s$, $w_1 = e_0 - e_s$, $e' = e_s - e_a$, $w' = e_1 - e_a$, $w_1' = e_0 - e_a$, where e_s , e_a , e_1 , e_0 are the configurational energies of protons near the PO₄ tetrahedra.

In absence of the external electric field or stress, we have the following equation for

$$h_a^{(1)} = -\langle s_{q1} \rangle = \langle s_{q2} \rangle = \langle s_{q3} \rangle = -\langle s_{q4} \rangle = \frac{1}{D_a} (2x + 2b'x), \quad (5)$$

$$c_{66a}^E = c_{66a}^{E0} + \frac{8y_6}{u} \frac{b(-y_6 k_a + f_a)}{D_a - 2k_a j_a} - \frac{4bj_a}{uD_a} \frac{h_a^2 f_a^2}{(D_a - 2k_a j_a)} - \frac{2b}{uD_a} (d_{16}^2 4b'x + d_{s6}^2 a' + d_{a6}^2 2^2 x).$$

Using the known relations between elastic, dielectric, and piezoelectric characteristics, we find isothermal elastic constants at constant polarization $c_{66}^P = c_{66}^E + e_{36}^2/c_{33}^e$; isothermal piezoelectric

coefficient $d_{36} = \frac{e_{36}}{E}$; isothermal dielectric

$$D_a = a' + 2x + d' + 4b'x + 1,$$

$$x = \frac{1}{2} \ln \frac{1 + h_a^{(1)}}{1 - h_a^{(1)}} + bn_a(k^z) h_a^{(1)}.$$

$$a' = e^{-be'}, \quad b' = e^{-bw'}, \quad d' = e^{-bw_1'}.$$

II. Dielectric, piezoelectric and elastic characteristics of the NH₄H₂PO₄ crystals

Within the four-particle cluster approximation, we calculate the thermodynamic potential. From the equations of state we find equations for the strain e_6 and polarization P_1 . From these equations we find analytical expressions for the

isothermal static dielectric susceptibility of a clamped NH₄H₂PO₄ crystal:

$$c_{33a}^e = c_{33a}^0 + \frac{m^2}{u} b \frac{2k_a}{D_a - 2k_a j_a} \frac{h_a}{a},$$

$$\text{where } k_a = a + bx, \quad j_a = \frac{1}{1 - h_a^{(1)2}} + bn_c(0),$$

isothermal piezoelectric coefficient

$$e_{36a} = e_{36a}^0 + 2 \frac{m_3}{v} b \frac{-2k_a + f_a}{D_a - 2k_a j_a} \frac{h_a}{a},$$

where

$$f_a = d_{s6} a - d_{16} 2bx;$$

isothermal elastic constant at constant field

susceptibilities of a mechanically free crystal

$$c_{33}^S = c_{33}^e + e_{36} d_{36} = c_{33}^e + \frac{d_{36}^2}{c_{66}^e}.$$

III. Experimental measurements of the thermodynamic characteristics

To find the elastic constants and piezoelectric coefficients one should induce crystal vibrations of as simple form as possible and measure the resonant frequencies (f_r) of a metallized plate of the 45° Z-cut, the antiresonant frequencies (f_a) of a non-metallized plate, as well as the crystal capacity at low frequencies. The coefficient of electromechanical coupling represent part of the electric energy transferred to the crystal at zero frequency, which is transformed to the mechanical energy, and is determined by the frequencies f_r and f_a :

$$k_{36}^2 = \frac{f_a^2 - f_r^2}{f_r^2}.$$

The resonant frequency f_r is given by the expression [24]:

$$f_r = \frac{1}{2l} \sqrt{\frac{1}{r} s_{22}^E},$$

where r is the crystal density, and

$$s_{22}^E = \frac{1}{4}(s_{66}^E + s_{11} + s_{22} + 2s_{12}), \quad \text{where}$$

$s_{11} + s_{33} + 2s_{13}$ are the elastic compliances, calculated in [24]. Using expressions (5.2) and (5.3) we find the elastic compliance at constant field s_{66}^E

$$s_{66}^E = \frac{1}{rl^2 f_r^2} - (s_{11} + s_{22} + 2s_{12}).$$

Respectively, the elastic constant at constant field is

$$c_{66}^E = \frac{1}{\frac{1}{rl^2 f_r^2} - (s_{11} + s_{22} + 2s_{12})}.$$

The compliance at constant polarization is $s_{66}^P = s_{66}^E(1 - k_{36}^2)$.

The elastic compliances and densities for $K_{1-x}(NH_4)_xH_2PO_4$ are calculated in the mean crystal approximation $s_{ij}(x) = s_{ijKDP}(1-x) + s_{ijADP}x$,

$$r(x) = r_{KDP}(1-x) + r_{ADP}x.$$

The experimental values of s_{ijKDP} , s_{ijADP} , r_{KDP} , r_{ADP} are taken from [24].

The dielectric susceptibility of a mechanically free crystal is determined from the measured capacity at low frequency $e_{33}^S = \frac{0.113h}{S_e} C$, where h is the distance

between the electrodes; S_e is the electrode area. The dielectric permittivity of mechanically clamped crystal is calculated as $e_{33}^e = e_{33}^S(1 - k_{36}^2)$.

The temperature dependences of the measured

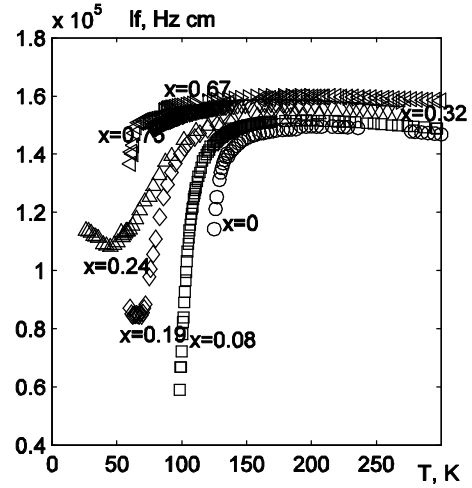


Fig. 2. The temperature dependences of the measured resonance frequencies f_r multiplied by the sample length l for different x .

resonance frequencies f_r multiplied by the sample length l for different x , via which one can determine the elastic constant c_{66}^E and piezoelectric coefficient d_{36} , are presented in fig. 2.

IV. Comparison of the numerical results to experimental data. Discussion

Let us analyze the results of the numerical calculations of the dielectric, piezoelectric, elastic characteristics of the ADP crystals and compare them with the corresponding experimental data. It should be noted that the developed in the previous sections theory, strictly speaking, is valid for the DADP crystals only. In view of the suppression of tunneling by the short-range interactions [67-69], we shall assume that the presented in the previous sections results are valid for ADP as well.

For these calculations we use the values of the model parameters, which were found in [60] by fitting the theory to the experimental temperature dependences of the physical characteristics of ADP. The used optimum set of the model parameters is given in Table 1.

The energy w_1 of two proton configurations with four or zero protons near the given oxygen tetrahedron should be much higher than e and w . Therefore we take $w_1' = \infty$ ($d' = 0$).

The primitive cell volume, containing two PO_4 groups is taken to be equal $u = 0.2110 \cdot 10^{-21} \text{ cm}^3$ for ADP.

In figure 2 we show the temperature dependences of the calculated isothermal static dielectric permittivities e_{33}^S of a free ADP crystal, along with the experimental data [24, 25], as well as the obtained temperature

Table 1

The optimum sets of the model parameters for ADP

T_N	$\frac{e^0}{k_B}$	$\frac{w^0}{k_B}$	$\frac{n_c^0}{k_B}$	$m_3, 10^{-18}$	C_{33}^{0e}	$\frac{Y_6}{k_B}$	$\frac{d_{s6}}{k_B}$	$\frac{d_{a6}}{k_B}$	$\frac{d_{16}}{k_B}$	$c_{66}^0 \cdot 10^{-10}$
(K)	(K)	(K)	(K)	(esu·cm)		(K)	(K)	(K)	(K)	(dyn/cm ²)
148	20	490	-10,0	2,10	0,23	-160	1400	100	-300	7.9

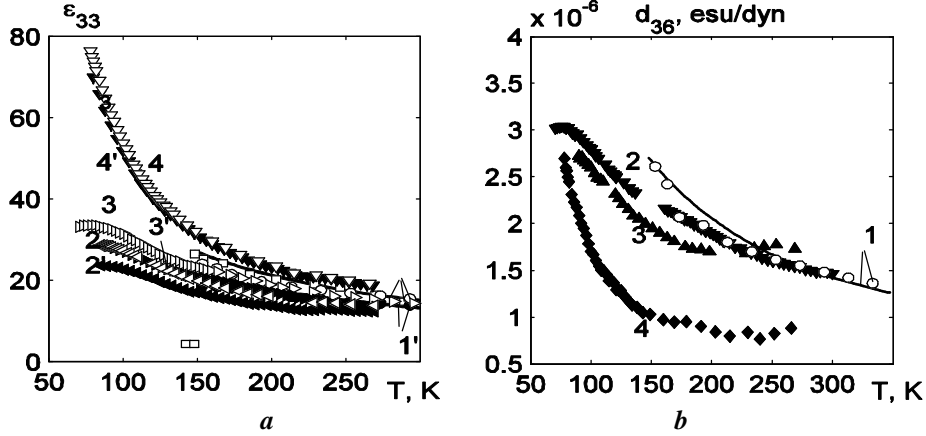


Fig. 3. The temperature dependences of the dielectric permittivity ϵ_{33}^S and coefficient of piezoelectric strain d_{36} of the mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals at the following values of x : 1,00 - 1; 0,75 - 2; 0,67 - 3; 0,32 - 4. The data marked as 1-4 and 1'-4' correspond to the permittivities of free and clamped samples, respectively. Solid line: the theory. Symbols: experimental data taken from [24] (\circ) and [25] (\square)

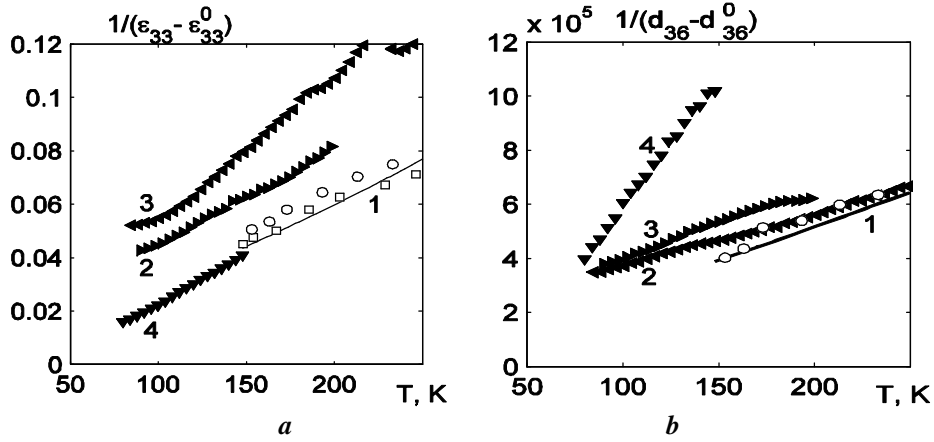


Fig. 4. The temperature dependences of $1/(\epsilon_{33}^S - \epsilon_{33}^0)$ and $1/(d_{36}^S - d_{36}^0)$ of the mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals at the following values of x : 1,00 - 1; 0,75 - 2; 0,67 - 3; 0,32 - 4. Solid line: the theory. Symbols: experimental data taken from [24] (\circ) and [25] (\square)

dependences of the static dielectric permittivities ϵ_{33}^S of free mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals at large x , and the temperature dependences of the piezoelectric coefficient d_{36} also at large x .

The permittivity ϵ_{33}^S of ADP is by $\sim 18\%$ larger than ϵ_{33}^e , and this difference is practically temperature independent.

The temperature dependences of the quantities

$1/(\epsilon_{33}^S - \epsilon_{33}^0)$ and $1/(d_{36}^S - d_{36}^0)$ of mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals at large x are shown in fig. 4.

The temperature curves of $(\epsilon_{33}^S)^{-1}$ and $1/(d_{36}^S - d_{36}^0)$ of the $K_{1-x}(NH_4)_xH_2PO_4$ crystals obey the Curie-Weiss laws $\epsilon_{33}(T) = \epsilon_{33}^0 + C_{CW}/(T - q_c)$ and $d_{36}(T) = d_{36}^0 + D/(T - q_d)$. Here C_{CW}, D are the

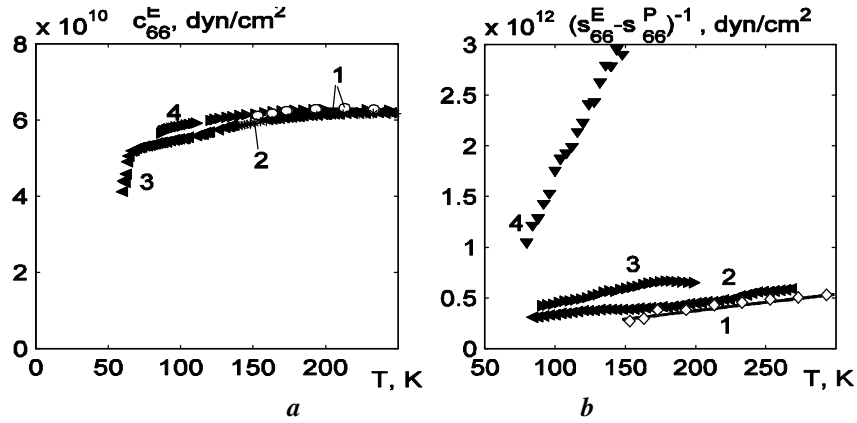


Fig. 5. The temperature dependences of the elastic constant c_{66}^E (a) and $1/(s_{66}^E - s_{66}^P)^{-1}$ (b) of the mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals at the following values of x : 1,00 - 1; 0,75 - 2; 0,67 - 3; 0,32 - 4. Solid line: the theory. Symbols: experimental data taken from [24] (\diamond)

corresponding Curie-Weiss constants, and q_c, q_d are the Curie-Weiss temperatures.

The temperature dependences of c_{66}^E of ADP are shown in fig. 5, (a). The temperature dependence of the difference

$e_{33}^S - e_{33}^e = 4pe_{36}d_{36} = 4pe_{36}^2/c_{66}^E = 4pd_{36}^2/c_{66}^E$ in ADP is plotted in fig. 5, (b).

The elastic constant c_{66}^E of ADP, in contrast to KDP, is finite at $T = T_N$ and hardly temperature dependent.

Conclusions

Within the thermodynamic theory and using the obtained experimental data we calculate the coefficient of piezoelectric coupling, longitudinal dielectric permittivities of free and clamped crystals, piezoelectric

coefficients d_{36} , elastic constant at constant field c_{66}^E of $K_{1-x}(NH_4)_xH_2PO_4$ mixed crystals. A typical for piezoelectrics behavior of the mentioned characteristics is revealed.

The same characteristics are also calculated for pure $NH_4H_2PO_4$ within the framework of a microscopic model that takes into account the piezoelectric coupling.

The piezoelectric properties of these disordered compounds are shown for the first time.

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Діелектричні, електромеханічні і пружні властивості матеріалів $K_{1-x}(NH_4)_xH_2PO_4$

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Обговорюються наявні експериментальні дані для діелектричних, п'єзоелектричних та пружних характеристик сегнетоелектрика $NH_4H_2PO_4$ на основі запропонованої мікроскопічної теорії цього кристалів. В рамках термодинамічної теорії з використанням отриманих експериментальних результатів розраховано діелектричні, п'єзоелектричні та пружні характеристики матеріалів $K_{1-x}(NH_4)_xH_2PO_4$ при $x \geq 0.32$.

Ключові слова: сегнетоелектрики, кластерне наближення, діелектрична проникність, п'єзомодулі, пружна стала.