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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.

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 $Rh_{1-x}(NH_4)_xH_2PO_4$ 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 $Rh$ 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 $Rh_{1-x}(NH_4)_xH_2PO_4$ 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 numerical 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
I. Model Hamiltonian of the NH₄H₂PO₄ crystals

We shall consider a system of protons moving on the O-H...O bonds in NH₄H₂PO₄ (ADP) crystals. The primitive cell of the Bravais lattice of these crystals consists of two neighboring tetrahedra PO₄ 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.

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

\[
H_{q,s,a}^{(4)} = H_{q}^{(4)a} - \frac{1}{\beta} \sum_{q} \left( -\frac{\sigma_{q1}}{2} + \frac{\sigma_{q2}}{2} + \frac{\sigma_{q3}}{2} - \frac{\sigma_{q4}}{2} \right) - \frac{4}{\beta} \sum_{f=1}^{N} \sigma_{qf},
\]

\[
H_{q}^{(4)a} = (-\delta_{q6} \xi_{6} - 2\delta_{16} \xi_{6}) \left( \frac{\xi_{q1}}{2} \xi_{q2} \xi_{q3} \right) + (V_{a} + \delta_{a6} \xi_{6}) \left( \frac{\xi_{q2} \xi_{q3} \xi_{q4}}{2} \right) + (V_{a} - \delta_{a6} \xi_{6}) \left( \frac{\xi_{q2} \xi_{q3} \xi_{q4}}{2} \right).
\]

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.

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 \( 0.32 < x < 1.0 \) 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].

To [14], are of the \( KH_2PO_4 \) type and have a tetragonal structure (\( \text{I} \overline{4}d \)) 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].

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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 \( x \geq 0.32 \).

\( \text{Dielectric, Electromechanical and Elastic Properties…} \)
\[ U_a \left( \frac{\sigma q_1 \sigma q_3 + \sigma q_2 \sigma q_4}{2} \right) + \Phi_a \left( \frac{\sigma q_1 \sigma q_2 + \sigma q_3 \sigma q_4}{2} \right), \quad (4) \]

\[ D_a = a' + 2x + a'' + 4b'x + 1, \]
\[ x = \frac{1}{2} \ln \left( \frac{1 + \eta_a(1)}{1 - \eta_a(1)} \right) + \beta V \left( k^z \eta_a(1) \right). \]
\[ a' = e^{-\beta e'}, b' = e^{-\beta \epsilon'}, d' = e^{-\beta \epsilon'}. \]

**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 \( \varepsilon \) and polarization \( P \). From these equations we find analytical expressions for the isothermal static dielectric susceptibility of a clamped \( NH₄H₂PO₄ \) crystal:

\[ \chi_{33a} = \frac{\mu^2}{\nu} - \frac{2\kappa_a}{D_a - 2\kappa_a\Phi_a}, \]

where \( \kappa_a = a + bx, \Phi_a = \frac{1}{1 - \eta_a(1)^2} - \beta V \left( k^z \eta_a(1) \right) \),

isothermal piezoelectric coefficient

\[ \epsilon_{36a} = \epsilon_{36} + \frac{\mu_3}{\nu} - \frac{2\kappa_a + f_a}{D_a - 2\kappa_a\Phi_a}. \]

where

\[ f_a = \delta_{26a} - \delta_{16}2bx; \]

isothermal elastic constant at constant field

Using the known relations between elastic, dielectric, and piezoelectric characteristics, we find isothermal elastic constants at constant polarization

\[ c_{66}^P = c_{66} + \epsilon_{36}' \chi_{33}' \quad \text{isothermal piezoelectric coefficient} \]

\[ \epsilon_{36} = \frac{\epsilon_{36}}{c_{66}} \quad \text{isothermal dielectric susceptibilities of a mechanically free crystal} \]

\[ \chi_{33} = \frac{\epsilon}{c_{66}} + \epsilon_{36}d_{36} = \chi_{33} + \frac{d_{36}}{c_{66}}. \]
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]:

\[
f_r = \frac{1}{2l} \frac{\sqrt{E}}{\rho}.
\]

where \( \rho \) is the crystal density, and

\[
s^{E}_{22} = \frac{1}{4} (s^{E}_{66} + s_{11} + s_{22} + 2s_{12}),
\]

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 \( s^{E}_{66} \):

\[
s^{E}_{66} = \frac{1}{\rho l f_r^2} - (s_{11} + s_{22} + 2s_{12}).
\]

Respectively, the elastic constant at constant field is

\[
\epsilon^{E}_{66} = \frac{1}{\rho l f_r^2} - (s_{11} + s_{22} + 2s_{12}).
\]

The compliance at constant polarization is

\[
s^{P}_{66} = \sqrt{\frac{E}{\rho l f_r^2}} (1 - k_{36}^2).
\]

The elastic compliances and densities for \( K_{1-x}(NH_4)_x H_2PO_4 \) are calculated in the mean crystal approximation

\[
s_{ij}(x) = s_{ij}^{KDP}(1-x) + s_{ij}^{ADP}x,
\]

\[
\rho(x) = \rho^{KDP}(1-x) + \rho^{ADP}x.
\]

The experimental values of \( s_{ij}^{KDP}, s_{ij}^{ADP}, \rho^{KDP}, \rho^{ADP} \) are taken from [24].

The dielectric susceptibility of a mechanically free crystal is determined from the measured capacity at low frequency

\[
\sigma^{\perp}_{33} = 0.113 \frac{h}{S_{e}},
\]

where \( h \) is the distance between the electrodes; \( S_{e} \) is the electrode area. The dielectric permittivity of mechanically clamped crystal is calculated as

\[
\epsilon^{\parallel}_{33} = \frac{\epsilon^{\perp}_{33}}{(1 - k_{36}^2)}.
\]

The temperature dependences of the measured resonance frequencies \( f_r \) multiplied by the sample length \( l \) for different \( x \), via which one can determine the elastic constant \( \epsilon^{E}_{66} \) 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 \( v = 0.2110 \times 10^{-21} \) cm\(^3\) for ADP.

In figure 2 we show the temperature dependences of the calculated isothermal static dielectric permittivities \( \epsilon^{\parallel}_{33} \) of a free ADP crystal, along with the experimental data [24, 25], as well as the obtained temperature...
L. Korotkov, D. Likhovaja, R. Levitsky and other

The optimum sets of the model parameters for ADP

<table>
<thead>
<tr>
<th>$T_N$ (K)</th>
<th>$\varepsilon^0_e/k_B$</th>
<th>$w^0_e/k_B$</th>
<th>$\gamma^0_e/k_B$</th>
<th>$\chi^0_{33}$ (K)</th>
<th>$\psi_6/k_B$</th>
<th>$\delta_{36}/k_B$</th>
<th>$\delta_{66}/k_B$</th>
<th>$\varepsilon^0_{66} \cdot 10^{-10}$</th>
</tr>
</thead>
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<tr>
<td>148</td>
<td>20</td>
<td>490</td>
<td>-10.0</td>
<td>2.10</td>
<td>0.23</td>
<td>-160</td>
<td>1400</td>
<td>100</td>
</tr>
</tbody>
</table>

The temperature dependences of the static dielectric permittivities $\varepsilon^e_{33}$ 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 $\varepsilon^e_{33}$ of ADP is by ~18% larger than $\varepsilon^0_{33}$, and this difference is practically temperature independent.

The temperature dependences of the quantities $1/(\varepsilon^e_{33} - \varepsilon^0_{33})$ and $1/(d_{36} - d^0_{36})$ of the mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals at large $x$ are shown in fig. 4.

The temperature curves of $(\varepsilon^e_{33})^{-1}$ and $1/(d_{36} - d^0_{36})$ of the $K_{1-x}(NH_4)_xH_2PO_4$ crystals obey the Curie-Weiss laws $\varepsilon_{33}(T) = \varepsilon^0_{33} + C_{CW}/(T - \theta_C)$ and $d_{36}(T) = d^0_{36} + D/(T - \theta_d)$. Here $C_{CW}, D$ are the
corresponding Curie-Weiss constants, and θc, Θd are the Curie-Weiss temperatures.

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

\[ \varepsilon_{33}^0 - \varepsilon_{33}^E = 4\pi d_3^2 c_{36}^E = 4\pi d_3^2 c_{36}^E \]  

in ADP is plotted in fig. 5, (b).

The elastic constant c^E_{66} 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^E_{66} 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 сегнетоелектрики $NH_4H_2PO_4$ 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 $x > 0.32$.

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