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Piezoelectric Resonance in KH$_2$PO$_4$ Type Crystals Revisited

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Within the framework of proton model with taking into account the piezoelectric interaction with the shear strain e_6, a dynamic dielectric response of KH$_2$PO$_4$ family ferroelectrics and antiferroelectrics is considered. Piezoelectric resonance frequencies of rectangular thin plates of the crystals cut in the (001) plane (0° Z-cut) are calculated, which are found to be in a good agreement with experiment.

Keywords: ferroelectrics, KH$_2$PO$_4$, piezoelectric resonance.

Introduction

In our previous papers [1,2] we explored the dynamic dielectric response of square thin plates cut from the KH$_2$PO$_4$ family crystals in the planes (001), perpendicular to the axis of spontaneous polarization. Using the modification of the proton ordering model [3] that includes the piezoelectric coupling with the shear strain e_6, within the framework of the Glauber approach [4] and the four-particle cluster approximation, we obtained expressions for the dynamic dielectric permittivity of the crystals, which took into account the dynamics of the shear strain e_6. In the low-frequency limit these expressions coincided with the static permittivities of mechanically free crystals, whereas in the microwave region they coincided with the dynamic permittivities of clamped crystals, exhibiting a relaxational dispersion.

In the intermediate region, the obtained permittivities had numerous peaks associated with the piezoelectric resonances. However, while solving the partial differential equations for the strain in [1,2], the boundary conditions were not set correctly. Instead of demanding that the entire edges of the plate were mechanically free, we considered the plate free only at its vertices. It resulted in the underestimated values of the resonant frequencies. In the present paper we shall correct these errors.

We shall not repeat here the details of the previous calculations, which were correct. The system Hamiltonians, most of the used notations, as well as derivation of the dynamic dielectric permittivities of clamped crystal (the pseudospin subsystem dynamics),

can be found in [1,2].

I. Dynamic permittivity of KH$_2$PO$_4$ type crystals

We shall consider shear mode vibrations of a thin $L_x \times L_y$ rectangular plate of a KH$_2$PO$_4$ crystal, cut in the (001) plane, with the edges along [100] and [010] (0° Z-cut). The vibrations are induced by time-dependent electric field $E_{3t} = E_3 e^{iwt}$. In the ferroelectric phase this field, in addition to the shear strain e_6, induces also the diagonal components of the strain tensor e_i, but for the sake of simplicity we shall neglect them.

Dynamics of pseudospin subsystem will be considered in the spirit of the stochastic Glauber model [4], using the four-particle cluster approximation. The system of equations for the time-dependent deuteron (pseudospin) distribution functions is

$$-a\frac{d}{dt}\langle\prod_f s_{qf}\rangle = \sum_{f'}\langle\prod_f s_{qf}\left[1-s_{qf'}\tanh\frac{1}{2}be^z_{qf'}(t)\right]\rangle, \quad (1)$$

where $e^z_{qf'}(t)$ is the local field acting on the f'th deuteron in the qth cell, which can be found from the system Hamiltonian (see [1]); a is the parameter setting the time scale of the dynamic processes in the pseudospin subsystem.

Taking into account the symmetry of the distribution functions

$$h^{(1)} = \langle s_{q1} \rangle = \langle s_{q2} \rangle = \langle s_{q3} \rangle = \langle s_{q4} \rangle,$$
$$h^{(3)} = \langle s_{q1} s_{q2} s_{q3} \rangle = \langle s_{q1} s_{q3} s_{q4} \rangle = \quad (2)$$
$$= \langle s_{q1} s_{q2} s_{q4} \rangle = \langle s_{q2} s_{q3} s_{q4} \rangle,$$
$$h_1^{(2)} = \langle s_{q2} s_{q3} \rangle = \langle s_{q1} s_{q4} \rangle, \quad h_2^{(2)} = \langle s_{q1} s_{q2} \rangle = \langle s_{q3} s_{q4} \rangle,$$
$$h_3^{(2)} = \langle s_{q1} s_{q3} \rangle = \langle s_{q2} s_{q4} \rangle,$$

from (1) we obtain for them a closed system of equations

$$a \frac{d}{dt} \begin{pmatrix} h^{(1)} \\ h^{(3)} \\ h_1^{(2)} \\ h_2^{(2)} \\ h_3^{(2)} \end{pmatrix} = \begin{pmatrix} \bar{c}_{11} & \bar{c}_{12} & \bar{c}_{13} & \bar{c}_{14} & \bar{c}_{15} \\ \bar{c}_{21} & \bar{c}_{22} & \bar{c}_{23} & \bar{c}_{24} & \bar{c}_{25} \\ \bar{c}_{31} & \bar{c}_{32} & \bar{c}_{33} & \bar{c}_{34} & \bar{c}_{35} \\ \bar{c}_{41} & \bar{c}_{42} & \bar{c}_{43} & \bar{c}_{44} & \bar{c}_{45} \\ \bar{c}_{51} & \bar{c}_{52} & \bar{c}_{53} & \bar{c}_{54} & \bar{c}_{55} \end{pmatrix} \begin{pmatrix} h^{(1)} \\ h^{(3)} \\ h_1^{(2)} \\ h_2^{(2)} \\ h_3^{(2)} \end{pmatrix} + \begin{pmatrix} \bar{c}_1 \\ \bar{c}_2 \\ \bar{c}_3 \\ \bar{c}_4 \\ \bar{c}_5 \end{pmatrix} \quad (3)$$

The used here notations can be found in [1]. Dynamics of the deformational processes is described using classical Newtonian equations of motion of an elementary volume, which for the relevant to our system displacements u_1 and u_2 ($e_6 = \frac{\partial u_1}{\partial y} + \frac{\partial u_2}{\partial x}$) read

$$r \frac{\partial^2 u_1}{\partial t^2} = \frac{\partial s_6}{\partial y}, \quad r \frac{\partial^2 u_2}{\partial t^2} = \frac{\partial s_6}{\partial z}. \quad (4)$$

Here r is the crystal density, s_6 is the mechanical shear stress, which, being the function of $h^{(1)}$, E_3, and e_6, is found from the constitutive equations derived in [1].

At small deviations from the equilibrium we can separate in the systems (3) and (4) the static and time-dependent parts, presenting the dynamic variables $h^{(1)}$, $h^{(3)}$, $h_i^{(2)}$, e_6, $u_{1,2}$ as sums of the equilibrium values and of their fluctuational deviations, while the fluctuational parts are assumed to be in the form of harmonic waves

$$h^{(1)} = \mathring{h}^{(1)} + h^{(1)}(x, y) e^{iwt},$$
$$h^{(3)} = \mathring{h}^{(3)} + h^{(3)}(x, y) e^{iwt}.$$

The fluctuational part of (3) is then reduced to the system of linear first-order differential equations with constant coefficients, solving which we get

$$h^{(1)}(x, y) = \frac{b m_3}{2} F^{(1)}(aw) E_3 +$$
$$[-b y_6 F^{(1)}(aw) + b d_{s6} F_s^{(1)}(aw) - \quad (5)$$
$$- b d_{a6} F_a^{(1)}(aw) + b d_{16} F_1^{(1)}(aw)] e_6(x, y),$$

the notations introduced here can be found in [1].

Substituting (5) into Eqs. (4), we obtain

$$\frac{\partial^2 u_1}{\partial y^2} + k_6^2 u_1 = 0, \quad \frac{\partial^2 u_2}{\partial x^2} + k_6^2 u_2 = 0, \quad (6)$$

where k_6 is the wavevector

$$k_6 = \frac{w \sqrt{r}}{\sqrt{c_{66}^E(aw)}}, \quad (7)$$

and

$$c_{66}^E(aw) = c_{66}^{E0} + \frac{4 b y_6}{u D_6} f_6 +$$
$$+ \frac{2b}{u D_6^2} (-d_{s6} M_{s6} + d_{16} M_{16} + d_{a6} M_{a6})^2 +$$
$$+ \frac{4 b y_6}{u} [-y_6 F^{(1)}(aw) + d_{s6} F_s^{(1)}(aw) +$$
$$+ d_{16} F_1^{(1)}(aw) - d_{a6} F_a^{(1)}(aw)] - \quad (8)$$
$$- \frac{4 f_3 f_6}{u D_6} b [-y_6 F^{(1)}(aw) + d_{s6} F_s^{(1)}(aw) +$$
$$+ d_{16} F_1^{(1)}(aw) - d_{a6} F_a^{(1)}(aw)] -$$
$$- \frac{2b}{u D_6} [d_{s6}^2 \cosh(2\mathring{y}_6 + b d_{s6} \mathring{y}_6) +$$
$$+ 4 b d_{16}^2 \cosh(\mathring{y}_6 - b d_{16} \mathring{y}_6) + d_{a6}^2 2a \cosh b d_{a6} \mathring{y}_6].$$

Differentiating the first and second equations of (6) with respect to y and x, correspondingly, remembering that we neglect the diagonal strains $e_1 = \partial u_1 / \partial x$ and $e_2 = \partial u_1 / \partial y$, and adding the two obtained equations, we arrive at the single equation for the strain e_6

$$\frac{\partial^2 e_6(x, y)}{\partial x^2} + \frac{\partial^2 e_6(x, y)}{\partial y^2} + k_6^2 e_6(x, y) = 0. \quad (9)$$

Boundary conditions for $e_6(x, y)$ follow from the assumption that the crystal is simply supported, that is, it is traction free at its edges (at $x = 0$, $x = L_x$, $y = 0$, $y = L_y$, to be denoted as Σ)

$$s_6 |_\Sigma = 0. \quad 10)$$

In our previous consideration [1] this condition was fulfilled at the corners of the crystal plate only, but not along all its edges. Substituting (10) into the constitutive relations, we obtain the explicit boundary conditions for the strains in the following form

$$e_6 |_\Sigma \equiv e_{i0} = \frac{e_{36}(aw)}{c_{66}^E(aw)} E_3, \quad (11)$$

where

$$e_{36}(aw) = e_{36}^0 + \frac{b m_3}{u} [-y_6 F^{(1)}(aw) +$$
$$+ d_{s6} F_s^{(1)}(aw) + d_{16} F_1^{(1)}(aw) - d_{a6} F_a^{(1)}(aw)]. \quad (12)$$

Solution of (7) with the boundary conditions (11) is

$$e_6(x, y) = e_{60} +$$
$$+ e_{60} \sum_{k,l=0}^{\infty} \frac{16}{(2k+1)(2l+1)p^2} \frac{w^2}{(w_{kl}^0)^2 - w^2} \times \quad (13)$$
$$\times \sin \frac{p(2k+1)x}{L_z} \sin \frac{p(2l+1)y}{L_y},$$

with w_{kl}^0 given by

$$w_{kl}^0 = \sqrt{\frac{c_{66}^E(w_{kl}^0) p^2}{r} \left[\frac{(2k+1)^2}{L_x^2} + \frac{(2l+1)^2}{L_y^2} \right]}. \quad (14)$$

Using the expression, relating polarization P_3 to the order parameter $h^{(1)}$ and strain e_6 (see [1]), we find that

$$P_3(x,y,t) = P_3(x,y)e^{iwt},$$
$$P_3(x,y) = e_{36}(aw)e_6(x,y) + c^e_{33}(aw)E_3, \qquad (15)$$

where

$$c^e_{33}(aw) = c^{e0}_{33} + \frac{bm^2_3}{2u}F^{(1)}(aw) \qquad (16)$$

is the dynamic dielectric susceptibility of a clamped crystal.

Now we can calculate the dynamic dielectric susceptibility of a free crystal $c^s_{33}(aw)$ as

$$c^s_{33}(w) = \frac{1}{L_x L_y}\frac{\partial}{\partial E_3}\int_0^{L_x}dx\int_0^{L_y}dy P_3(x,y), \qquad (17)$$

obtaining

$$c^s_{33}(w) = c^e_{33}(aw) + R_6(w)\frac{e^2_{36}(aw)}{c^E_{66}(aw)}, \qquad (18)$$

where

$$R_6(w) = 1 + \sum_{k,l=0}^{\infty}\frac{64}{(2k+1)^2(2l+1)^2 p^4}\frac{w^2}{(w^0_{kl})^2 - w^2}.$$

In the static and the high frequency limits from (18) we obtain the static susceptibility of a free crystal [3] and the dynamic susceptibility of a mechanically clamped crystal, exhibiting relaxational dispersion in the microwave region. Thus, eq. (18) explicitly describes the effect of crystal clamping by high-frequency electric field.

In the intermediate frequency region, the susceptibility has a resonance dispersion with numerous peaks ar frequencies where $Re[R_6(w)] \to \infty$. Frequency variation of $c^E_{66}(aw)$ is perceptible only in the region of the microwave dispersion of the dielectric susceptibility. Below this region it is practically frequency independent and coincides with the static elastic constant c^E_{66}. Since the resonance frequencies are expected to be in the $10^4 - 10^7$ Hz range, depending on temperature and
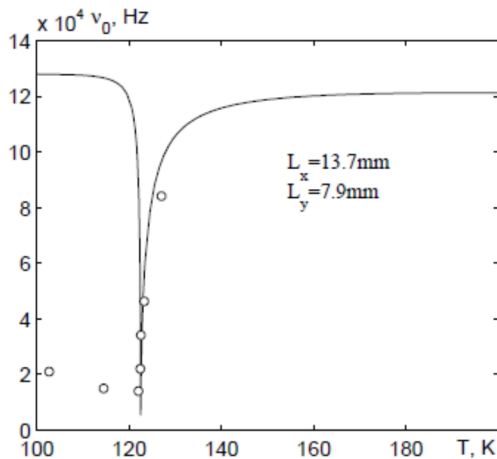

Figure 1. The first resonance frequency $n_0 = w^0_{00}/2p$ of a rectangular $0°$ Z-cut of a KH$_2$PO$_4$ crystal. Symbols are experimental points taken from [6]. Line: the present theory.

sample dimensions, the equation for the resonance frequencies (14) is reduced to an explicit expression by putting in it $c^E_{66}(aw) \to c^E_{66}$.

Comparing (14) to the expression obtained previously [1] for a square $L \times L$ plate cut in the (001) plane

$$w_k = \frac{p(2k+1)}{L}\sqrt{\frac{c^E_{66}(w_k)}{r}},$$

we can see that the incorrectly set boundary conditions [1] led to the first resonance frequency, being $\sqrt{2}$ times smaller than the one given by (14). However, the low and high frequency limits of the susceptibility calculated in [1] (the static value and the clamped values with the relaxational dispersion in the microwave region) were correct.

The used values of the model parameters can be found in [1]. As one can see, in the paraelectric phase the first resonance frequency of a rectangular $0°$ Z-cut of a KH$_2$PO$_4$ crystal, calculated from (14), accords well with experimental data. The discrepancy between the theory and experiment in the ferroelectric phase is obviously caused by the contributions of the domain effects into the elastic constant of the crystal, which are not considered in the present model. Note that the first resonant frequency has a sharp minimum at the transition point, owing to the similar behavior of the elastic constant c^E_{66}.

II. Resonant frequencies of NH$_4$H$_2$PO$_4$ type crystals

We consider vibrations of a $0°$ Z-cut of an antiferroelectric NH$_4$H$_2$PO$_4$ type crystal, produced by an external time-dependent electric field $E_{3t} = E_3 e^{iwt}$. Taking into account the system Hamiltonian, the symmetry of the proton distribution functions for the case of antiferroelectric ordering [2,5], and following the procedure, described in the previous section, we obtain an expression for the dynamic dielectric permittivity of a free crystal, which is formally the same as for the case of ferroelectric ordering (18). However, the elastic constant is different

$$c^E_{66}(aw) = c^{E0}_{66} +$$
$$\frac{4by_6}{uD}[-2y_6 F^{(1)}(aw) + d_{s6}F^{(1)}_s(aw) +$$
$$+ d_{16}F^{(1)}_1(aw) - d_{a6}F^{(1)}_a(aw)] -$$
$$- \frac{4f^h_c f_6}{uD}b[-2y_6 F^{(1)}(aw) + d_{s6}F^{(1)}_s(aw) + \qquad (20)$$
$$+ d_{16}F^{(1)}_1(aw) - d_{a6}F^{(1)}_a(aw)] +$$
$$+ \frac{4by_6}{uD}f_6 -$$
$$- \frac{2b}{uD}[d^2_{s6}a + d^2_{16}4b + d^2_{a6}(1 + \cosh 2\%)].$$
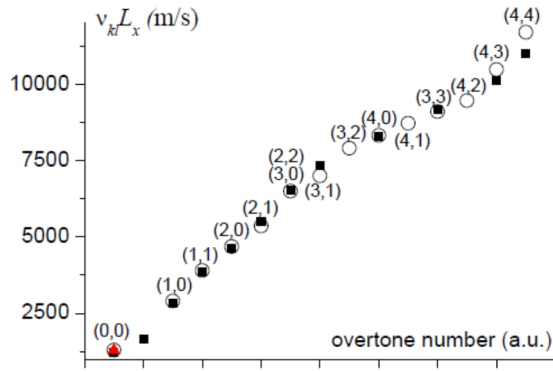
Figure 2. The frequency constants $n_{kl}L_x = L_x w_{kl}^0 / 2p$ of a square 0° Z-cut of a $NH_4H_2PO_4$ crystal. ■,▲: experimental points taken from [7] and [8]. **o**: the present theory. Numbers is parentheses are the (k, l) values.

Just like in the case of KH$_2$PO$_4$ type crystals, it does not have any perceptible frequency variation in the piezoelectric resonance region and coincides with the static constant c_{66}^E. On the other hand, in NH$_4$H$_2$PO$_4$ the elastic constant c_{66}^E does not exhibit any anomalous behavior in the transition region and is about $6 \cdot 10^{11}$ N/m^2 between $T_N = 148$ K and 300 K [5].

The expressions for the piezoelectric coefficient $e_{36}(aw)$, dynamic dielectric susceptibility of a clamped crystal $c_{33}^e(w)$, the function $R_6(w)$, and the equation for the resonant frequencies are the same as in the case of a ferroelectric KH$_2$PO$_4$ type crystals: (12), (16), (19), and (14), respectively. However, the functions $F^{(1)}(w)$ and other auxiliary quantities used in these formulae as well as in (20) differ from those from the previous section and can be found in [2,5].

In fig. 2 we compare the calculated frequency constants (the resonant frequencies multiplied by the sample edge length $L_x w_{kl}^0$; the size-independent quantity) of a square 0° Z-cut of a NH$_4$H$_2$PO$_4$ crystal to the available experimental data. As one can see, a very good agreement is obtained. The fitting procedure and values of the model parameters were given in [2,5].

Conclusions

Within the proton ordering model with taking into

account the shear strain e_6 we explored a dynamic response of ferroelectric and antiferroelectric crystals of the KH$_2$PO$_4$ family to an external harmonic electric field E_3. Dynamics of the pseudospin subsystem is described within the stochastic Glauber approach. Dynamics of the strain e_6 is obtained from the Newtonian equations of motion of an elementary volume, with taking into account the relations between the order parameter of the pseudospin subsystem and the strain. Corrected expressions for the piezoelectric resonance frequencies of simply supported rectangular 0° Z-cuts of these crystals are obtained. They are shown to yield a good quantitative agreement with experimental data for KH$_2$PO$_4$ and NH$_4$H$_2$PO$_4$ crystals.

The ultimate goal of the present studies will be to generalize the obtained expression for the dynamic permittivity to the case of the Rb$_{1-x}$(NH$_4$)$_x$PO$_4$ type proton glasses, in order to explore their dynamic dielectric response. It is known [9,10] that, just like their pure constituents, these mixed systems are piezoelectric, and their dynamic dielectric permittivity has a piezoelectric resonance dispersion. As our preliminary calculations show, the experimentally obtained resonant frequencies of such mixed crystals [11] are well described by the obtained here expression for the resonant frequencies, provided that the corresponding elastic constant c_{66}^E of such a system is known.

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П'єзоелектричний резонанс в сегнетоелектриках типу KH₂PO₄

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В рамках моделі протонного впорядкування з урахуванням п'єзоелектричного зв'язку зі зсувною деформацією e_6 досліджено діелектричний відгук сегнетоелектриків та антисегнетоелектриків сім'ї KH₂PO₄. Розраховані частоти п'єзоелектричного резонансу прямокутних тонких пластин таких кристалів, вирізаних в площині (001) (0°Z-перерізи) добре узгоджуються з експериментальними даними.
Ключові слова: сегнетоелектрики, KH₂PO₄, п'єзоелектричний резонанс.