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THE NATURE OF PYROELECTRIC POLARITY

The concept of spontaneous polarization in the pyroelectrics is called into a question, since omnipresent free electric charges make impossible to maintain any equilibrium and time-stable polarized state. We conjecture in this paper that pyroelectricity in polar crystals and piezo-electricity in polar-neutral crystals are due to hybridized ionic-covalent polarity-activating bonds. When they are in non-excited state, these bonds do not produce electric field, yet they are capable of generating the electric response to uniform non-electric influence, e.g., heat, pressure, etc. This response is described by some models of different electric moments. Different contributors to these moments can be measured using partial limitation of crystal thermal strain. In fact, the proposed approach modifies and extends the known concept of spontaneous polarization. In this context, ferroelectrics are distinguished by the fact that, in the electric field, they reorient their polarity-activating inter-atomic bonds with a non-linear response and hysteresis.

K e y w o r d s: polar crystals, piezoelectrics, pyroelectrics, ferroelectrics

1. Introduction

As it is known, electric polarization occurs in any dielectric in the externally applied electric field, but only the polar (i.e., non-centrosymmetric) dielectrics can be polarized in non-electric way [1]. To characterize this phenomenon, the term "spontaneous polarization" (P_S) is traditionally used [2], by analogy to the spontaneous magnetization of ferromagnets. This terminology was motivated by the discovery of dielectric hysteresis in the Rochelle salt crystal about 100 years ago, which was perceived as an analog of magnetic hysteresis. The similarity between these phenomena and the possibility to apply the concept of hysteresis loop has motivated the qualification of the polarization as "spontaneous" in the context of the class of polar crystals called ferroelectrics. Later, with less

solid justification, in our opinion, the term "spontaneous polarization" has been applied to pyroelectrics as well, as they formally resemble permanent magnets. At the same time, the spontaneous polarization in pyroelectrics cannot be measured directly.

Undoubtedly the ferroelectrics are the subclass of the pyroelectrics that break down into domains [3]. All ferroelectrics are characterized by the presence of unique polar axis in their structure. In contrast to other pyroelectrics, they have the property of reversibility of the direction of the activation of their polar bonds.

It should be noted that there is another large family of polar crystals, namely, the piezoelectrics. In many aspects, they exhibit noticeable affinity to pyroelectrics, to the extent that sometimes mutual transformation between them becomes possible, such as the mixed wurtzite ⇔ sphalerite structures in the zinc blende [3, 4].

The above gives grounds to propose generalized models for polar properties seen in the non-centrosymmetric crystals, which, to some extent, can give

different perspective as to the concept of spontaneous polarization. There are many reasons for revising this concept, because the similarity between ferroelectricity and ferromagnetism also looks as purely external.

Firstly, unlike the case of electricity, in the case of magnetism, there are no such elements in the Nature as "magnetic charges". Consequently, the spontaneous magnetization in the absence of external influences can exist in the equilibrium state for an arbitrarily long time. On the contrary, spontaneous polarization must sooner or later be screened by the omnipresent free electric charges, and, thus, it cannot stay in an electrically equilibrium state. It is this circumstance that underlies the fundamental difference between these phenomena.

Secondly, magnetic field H and magnetic induction B (created by closed microscopic or macroscopic electric currents) are axial vectors. In contrast, the electric field E and polarization P are polar vectors, determined by distribution of electric charges. The electric field E is the gradient of electric potential, the lines of this field start and end on electric charges. The macroscopic electric polarization P is induced by electric field, and, in accordance with the Lorentz relation ($E = \beta P$), any polarization should be accompanied by macroscopic electric field E, which necessarily sets free electric charges in motion.

Thirdly, the spontaneous polarization, which was established based on a hysteresis loop observed in the ferroelectrics, was generalized to the pyroelectrics unfoundedly, while ferroelectrics are only a subclass of pyroelectrics. If it were well justified, the pyroelectrics would behave themselves like the electric analog of the permanent magnet, which is surrounded by magnetic field. However, in the equilibrium state, when any external influence is absent, neither pyroelectrics nor ferroelectrics are surrounded by electric field. This particularity could be justified for ferroelectrics, as they are divided into domains. However, the absence of an ambient field around other pyroelectrics is due to free charges screening, and this means that, in the equilibrium state, no macroscopic polarization can be seen.

In this regard, one can remember about the electrets, which really generate external electric field, consistent with their internal field, for considerable time. However, there is a fundamental difference between pyroelectrics and electrets: pyroelectrics can create polarization under non-electric action, being themselves in the equilibrium state. The polarization is naturally acquired during the crystal formation from the liquid or gaseous phase, and it disappears, only when the pyroelectric melts. Moreover, the pyroelectric effect can be reproduced an infinite number of times in the polar crystal. On the contrary, the *residual* polarization of electrets is established artificially by a special technology. As a result, their polarized state is non-equilibrium and temporary: if an electret is exposed to heat, it generates the depolarization current only once, whereupon the electret ceases to be polarized.

The absolute magnitude of spontaneous polarization of pyroelectrics, P_S, cannot be measured directly, one can only measure its derivative, the pyroelectric coefficient $\gamma = dP_S/dT$. One cannot use the method of significant heating to facilitate the direct measurement of the physical quantity of P_S, because pyroelectric effect exists up to crystal melting. Moreover, when pyroelectric is cooled, the coefficient γ sometimes even changes its sign [3]. Note that the spontaneous polarization concept does not fit into other facts described in this paper. Previously, some doubts as to the P_S existence were also expressed in works [5, 6]. As is known, the pyroelectric effect always exists in ten polar classes of crystals, but, as will be shown in this work, the artificial pyroelectric effect can also be obtained in ten classes of polar-neutral "true" piezoelectrics [4]. For this, the method of partial restriction of thermal strains is applied, used in the given work for experimental confirmation of the new proposed concept.

The fact is that, when doing electric measurements of polar structure parameters, such as voltage or current, it is necessary to obtain the vector-type response from a scalar action, as, for example, in the case of uniformly heating pyroelectric. However, in the polar-neutral piezoelectric, such a response, which allows one to measure its polarity, is possible, only if its thermal deformation is partially limited by rigidly fastening polar cut of this crystal on the non-deformable substrate. This method of thermo-piezo-polarization is used to obtain an artificial pyroelectric effect, and a similar method is also possible to obtain the volumetric piezoelectric effect in the polar-neutral crystals such as quartz.

In this paper, we propose an alternative approach to the concept "spontaneous polarization" to explain

the polar properties in the polar and polar-neutral crystals. We conjecture that, in the crystals that have polar properties, the peculiar arrangement of inter-atomic bonds exists and drives an electric response to the non-electric external impact. We will show that the mixed covalent-ionic polarity-sensitive bonds, which form polar or polar-neutral crystals, are a consequence of the structural compensation of dissimilarity of the electronic structure of neighboring ions, giving the opposite contribution to electronegativity. It is this feature that causes many electric, mechanical, thermal, and optical properties in polar crystals, making them quite different from ordinary dielectrics.

2. Main Features of Polar Crystals

The primary cause of the internal polarity in non-centrosymmetric crystals is asymmetry in electronic density distribution along the inter-atomic bonds. In turn, this feature is conditioned by the distinction of adjoining ions in their features of electronic shells, which, in particular, manifests itself as an electronegativity. The ion with increased electronegativity displaces the shared electrons toward itself, so its operating charge becomes more negative, while ion with lower electronegativity acquires, respectively, the increased positive charge. Together these ions create a polar bond with the inhomogeneous distribution of electronic cloud density along the inter-ionic bond. So, it might be concluded that the internal polarity, seen in the non-centrosymmetric crystals, arises due to structural compensation of different structural features of electron shells of neighboring ions [4].

For the further discussion, it should be noted that pyroelectrics and piezoelectrics demonstrate an amazing proximity in the manifestation of completely different properties. At that, the nature of the intrinsic polarity and all the more so, its existence in the polar-neutral piezoelectrics in many respects looks unclear. It will suffice to mention that even the diamond (monoatomic carbon crystal) occasionally could have a form of pyroelectric wurtzite with symmetry class $6mm$, in addition to its principal $m3m$ class cubic diamond structure [1]. Among various piezoelectrics, some others monoatomic crystals exist: the examples are Te and Se crystals, which belong to the piezoelectric quartz-type structure (32 class of symmetry). In mentioned examples of the monoatomic crystals, un-

doubtedly, only the dissymmetry of electronic atomic shells could be responsible for their intrinsic polarity.

There is a lot of experimental evidence of similar manifestation s of electric, mechanical, and thermal properties in different polar crystals. Below, only some evidence of a peculiar "hidden" polarity will be presented for the case of piezoelectrics, which are considered to be polar-neutral crystals.

Firstly, during the crystallization process, the density of polar crystals decreases in comparison to their melt: for example, growing polar crystal GaAs swims in its melt as ice in water [4]. So, it may be deduced that the fixation of polar bonds expands a material, at that, transforming its structure into the non-centrosymmetric one.

Secondly, the chemical properties of polar crystals exhibit the unipolarity of their surface: for instance, in the quartz crystal, its etching occurs more rapidly on the "positive" end of the polar X-axis, while etching occurs more slowly at "negative" end of the X-axis. So, the etched patterns for quartz plates are very different for "+" and "–" surfaces [7]. In just the same way, in a cubic polar GaAs crystal, one can see a considerable distinction in its chemical properties between two surfaces of the polar [111]-plate [3]. By the way, it is the chemical unipolarity of polar crystals that is used in ferroelectric domains study [2, 3].

Thirdly, polar crystals show unique thermal properties: their resistance to heat transfer, Fig. 1, a, far exceeds ones of centrosymmetric crystals due to peculiarities of the phonon dissipation process in polarity-sensitive structure [8]. Moreover, in polar crystals, the thermal expansion coefficient, instead of showing classical dependence $\alpha(T) \sim T^3$, at low temperatures, Fig. 1, b, acquires negative value [9]. This mysterious property is explained by a change, with temperature, of the interatomic attraction close proximity of neighboring ions. For the same reason, due to negative thermal expansion seen at low temperatures, in some polar crystals, their pyroelectric coefficient changes its sign, Fig. 1, c [3].

When describing polar crystals features, it is important that the fundamental high frequency absorption ($\varepsilon'' = \varepsilon' \cdot \tan \delta$) in them vastly superiors this absorption of centrosymmetric crystals [10]. Moreover, dielectric losses $\varepsilon''(\omega)$ in polar crystals show a maximum of absorption Fig. 1, d, due to the interaction between optical and acoustical phonons. Our experimental evidence of this effect is shown in Fig. 1, e
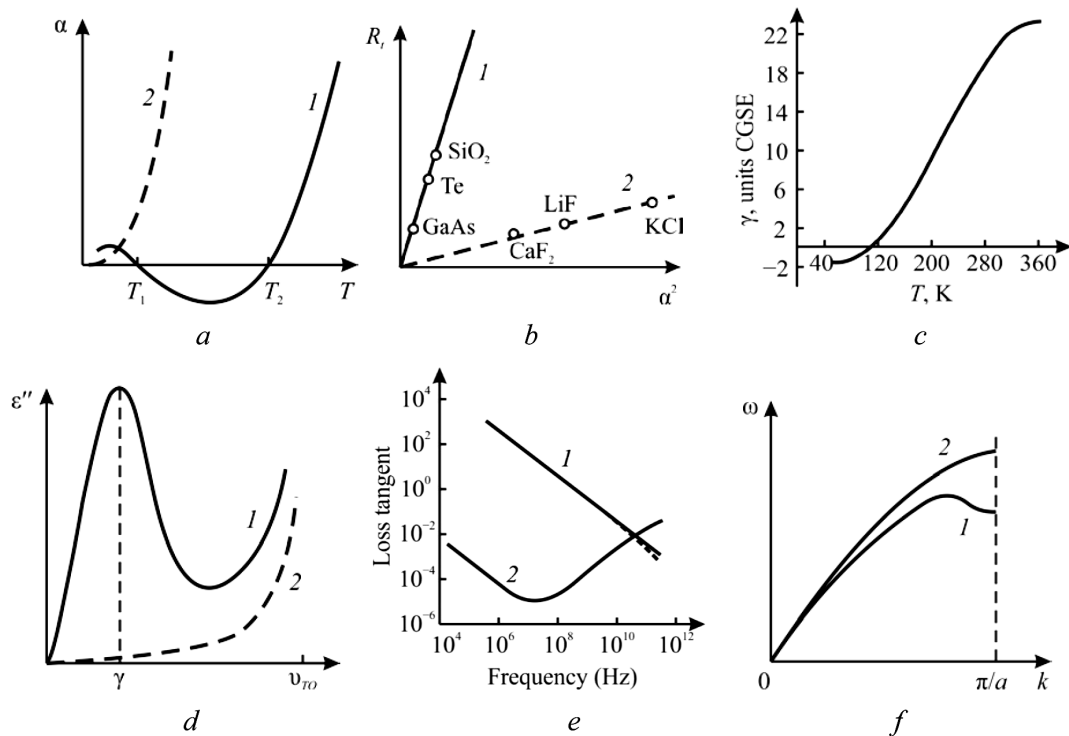
Fig. 1. Fundamental properties of polar crystals: a – thermal expansion coefficient α of polar (1) and non-polar (2) crystals; b – thermal resistively coefficient R_t dependence on α^2 for polar (1) and non-polar (2) crystals; c – pyroelectric coefficient γ in pyroelectric lithium sulfate Li_2SO_4-H_2O [3]; d– quasi-Debye microwave absorption coefficient ε'' in polar crystal (1) and in non-polar crystal (2); e– microwave losses in covalent Si (1) and polar GaAs (2) crystals; f – acoustic branch in Brillouin zone for polar (1) and non-polar (2) crystals

as the comparison of microwave losses in two semiconductors: non-polar Si and polar GaAs. All above-mentioned features of polar crystals correlate with their acoustic phonon spectrum near the boundary of the Brillouin zone, where acoustic mode shows an anomalies decrease, as GaAs in Fig. 1, f. On the contrary, centrosymmetric crystals, such as ionic-bonded crystals NaCl and covalent crystals Si, unlike polar crystals, have no anomalies in the dispersion of acoustic or optical phonon modes.

It goes without saying that electric properties of polar and polar-neutral crystals differ significantly from usual dielectrics. In polar and polar-neutral crystals, their fundamental absorption at very high frequencies $\varepsilon'' = \varepsilon' \tan\delta$ is vastly superior to the absorption of centrosymmetric crystals [10]. Moreover, at microwaves, the dielectric losses $\varepsilon''(\omega)$ of piezoelectrics show an additional maximum of the quasi-Debye-type, due to the interaction between optical and acoustical phonons. The above-mentioned special

features of polar crystals correlate with their acoustic phonon spectrum near the Brillouin zone boundary, where acoustic mode has anomaly, bending down at the very border of the zone, Fig. 1, f [8].

The main property of any dielectric is its electric polarization, i.e., the effect of separation of electric charges, which remain bonded despite their shifting. As a result, the electric moment appears (as the product of magnitudes of charges by their displacement); volumetric density of this moment is polarization P. One peculiar feature of polar dielectrics is that the electric polarization can occur in them not only being induced by the electric field, but also by other influences. A comparison of conventional (non-polar) dielectrics and two categories of polar dielectrics are shown in Table 1. Essential distinction between the active (functional) dielectrics and ordinary dielectrics is obvious.

In many applications, polar dielectrics (sensors, actuators, filters, transformers, motors, *etc.*) are sub-

Table 1. **Electric polarization as a response onto various actions**

Actions	Non-polar crystals	Polar-neutral crystal piezoelectric	Polar crystal – pyroelectric
Scalar action: temperature $\mathrm{d}T$ pressure $\mathrm{d}p$	– –	– –	Pyroelectric effect: $\mathrm{d}P = \gamma \mathrm{d}T$ Volume piezoelectric effect: $\mathrm{d}p = \zeta \mathrm{d}T$
Vector action: electric field E	$P = \varepsilon_0 \varepsilon E$	Electrically induced polarization $P = \varepsilon_0 \chi E + (e^2/c)E$	Electrically induced polarization $P = \varepsilon_0 \chi E + (e^2/c)E + (\gamma^2 T)E(\varepsilon_0 C)$
Tensor action: mechanical stress X	–	Direct piezoelectric effect $P = dX$	Direct piezoelectric effect $P = d'X$

N o t e: parameter γ is pyroelectric coefficient; ζ is volumetric piezoelectric module; d is piezoelectric module; c is elastic stiffness; C is specific heat. For simplicity, this table does not include: (1) flexoelectricity, possible in all dielectrics under non-homogeneous mechanical action; (2) actinoelectricity, which occurs in the piezoelectrics under the grad T action; (3) photopolarization effect in the polar (non-centrosymmetric) dielectrics.

Table 2. **Polar responses in dielectrics including partial limitations of strain**

Piezoelectricity induced by stress	Combined effects at partial clamping	Pyroelectricity induced by heat
Conventional piezoelectric effect in 20 polar classes ("piezoelectric" classes)	Artificial pyroelectric effect in 10 "piezoelectric" classes,	The conventional pyroelectric effect in 10 polar classes ("pyroelectric" classes)
Volumetric piezoelectric effect in 10 "pyroelectric" classes of polar crystals	Artificial volumetric piezoelectric effect in 10 "piezoelectric" classes	Tertiary pyroelectric effect in 20 classes of polar crystals

jected to the external thermal, electric, mechanical, and other influences – scalar, vector, or tensor types. Table 1 shows that conventional dielectric reacts only on the electric field action: $E \Rightarrow P$, while piezoelectric and pyroelectric, besides their usual response $E \Rightarrow P$, are capable of an electric response onto other actions: mechanical $X \Rightarrow P$ and thermal $dT \Rightarrow dP$. At the same time, piezoelectric responds to the electric action not only by ordinary polarization ($P = \varepsilon_0 \chi E$), but also produces electromechanical contribution to the polarization: $P' = (e^2/c)E$, while pyroelectric, in addition, gives electrothermal contribution to the polarization: $P'' = (\gamma^2 T)E/(\varepsilon_0 C)$.

It might be that the most striking features of polar dielectrics are, firstly, interdependence of mechanical, electric, and thermal properties, and, secondly, dependence of these properties on the external conditions, under which polar crystals are studied or applied. The above does not exhausts all possible effects, caused by the intrinsic polarity of polar-neutral non-centrosymmetric crystals. These extended effects are listed by highlighted frames in Table 2.

The point is that some components of the 4-th rank strain tensor in polar crystals can be artificially forbidden by the rigid fastening of thin polar cut onto the non-deformable substrate. As a result, the intrinsic polarity (usually, spatially compensated both in free and clamped crystal) in the *partially* clamped crystal demonstrates the electric response. This allows one, firstly, to measure the components of the compensated polarity, and, secondly, to obtain both artificial pyroelectric effect and volumetric piezoelectric effect, which are impossible in the mechanically free 10 polar-neutral classes of piezoelectrics which are not pyroelectrics, such as, for example, in the quartz.

Such variety of polar crystals features is difficult to explain by the simple idea of spontaneous polarization. So, the purpose of this work is to modify the concept of intrinsic polarization for non-centrosymmetric crystals. The subsequent discussion of the models based on the asymmetry in the electronic density distribution along atomic bonds is free from the assumption of electric field existence (which would
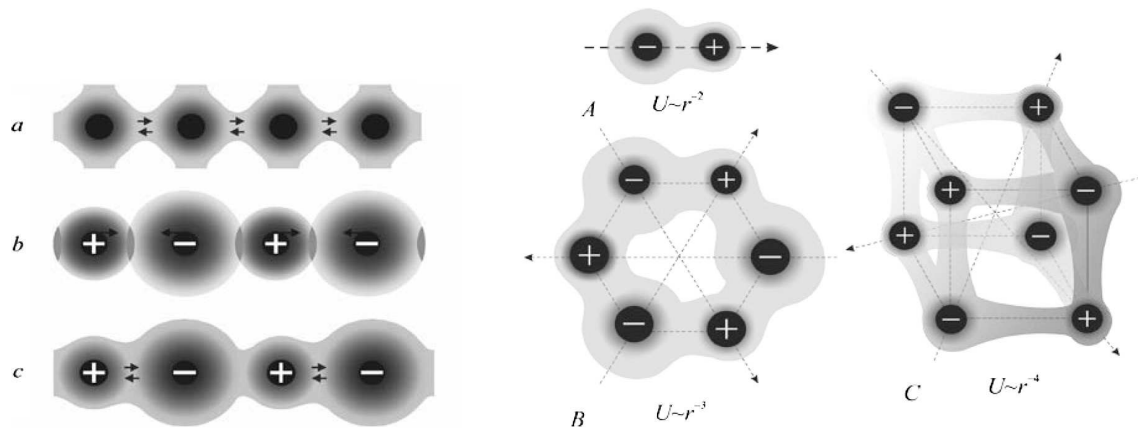
Fig. 2. Simple presentation of polar-sensitive structures. On the left: covalent (*a*), ionic (*b*) and hybridized bonding (*c*) are shown; on the right: A – 1D dipole-like model; B – 2D polarity modeling; C – 3D polar construction; polar directions presented by arrows; specified rates of energy decrease with distance $U(r)$ are shown by power function

need to compensate polarity by free charges). Asymmetric polarity-sensitive bonds do not a result of any internal field present in the crystal, but can provide a polar response onto the non-electric homogeneous external impact (thermal, mechanical) or irradiation, which is impossible in centrosymmetric crystals. It should be noted that the above is not related to the heterogeneous mechanical impact: in such a case, the electric response occurs in any dielectric, as the flexoelectricity [3]. By the same way, the heterogeneous temperature influence (characterized by the temperature gradient) induces, in any piezoelectric, something like the "pyroelectric effect" known as actinoelectricity [7].

3. Simplified Models of Polar Connections

The modeling of the polarity is based on the fact that the electric field can forcedly change a structure of atomic bonds in any crystal, bringing the dielectric into electrically asymmetric (polar) state. In this case, crystal interatomic bonds willy-nilly acquire asymmetry; so, any dielectric demonstrates the electrically induced piezoelectric and pyroelectric properties. The magnitude of the induced effects is dependent on the dielectric permittivity; so that, in relaxor ferroelectrics (in which $\varepsilon \approx 10^4$–10^5), the effects supported by the bias field-induced ones can even surpass the same effects seen in natural polar crystals [4]. Based on the above, one can suppose that the usual piezoelectric effect also can be represented as the "linearized electrostriction". This assumption might be advanced according to the conception that

the fundamental reason for the crystal intrinsic polarity is the asymmetry in the electronic density distribution along bonds between adjacent ions, which have different electronic structures (in particular, due to the electronegativity) that resembles the action of bias field.

In a very simplified form, three models of electronic density distribution (covalent, ionic, and mixed bonding) are shown in Fig. 2, *left*. In covalent crystals, when an external field is applied, the electronic density between atoms increases, by forming displaced clumps. In ionic crystals, attraction of cations and anions is compensated by repulsion of partially overlapping electronic shells, and, in the applied bias field, the inter-ionic clumps shift.

Appropriate to polar crystals, mixed covalent-ionic bonding shown in Fig. 2, *c*, is a distinctive feature of model under discussion, creating the main property of polar crystals. In this way, instead of a bias electric field, which needs to be applied to ionic or covalent crystals and forcing them to be polarized, in the case of mixed covalent-ionic bonds of the crystal, the polarity-activating state is stable without application of any bias field. This state is ensured by the fundamental property of neighboring ions: they have different electronegativities, which produces the polarity-activating structure.

Figure 2, *right*, shows models based on the asymmetry of the electronic density distribution along atomic bonds. These models describe simplistically the spatial orientation of asymmetric hybridized ionic-covalent bonds. The spatial allocations of one-,
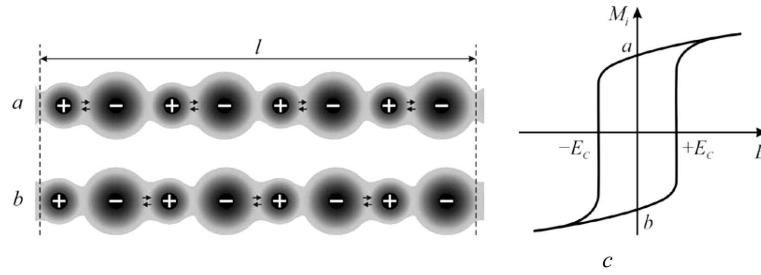
Fig. 3. Model description of two opposite orientations of polar bonds in ferroelectric; directions a and b are indicated on the dielectric hysteresis loop

two- and three- dimensional polar bonds are presented with their directionality (by arrows) and with a spatial decay of the interaction energy: for dipoles, it decreases with distance as r^{-2}, for hexagons as r^{-3}, and, for eight-peaked octupoles, as r^{-4}. These models will be used further to describe various properties of polar dielectrics. Presenting modelling of internal (or "latent", or "hidden") polarity describes the ability of a low-symmetric crystal to make electrical response onto the dynamic (variable in time) external action. If external impact, after its switching on (or changing), afterward remains constant, the polarization induced by this impact does not manifest itself for a long time (since a new equilibrium position is established). The usual energy state of a polar crystal is "able to the electric response onto a non-electric impact" is the entirely equilibrium state at a certain temperature (T_1) and pressure (p_1), and it is stored, in the absence of external influences, as much as one wants. If any external influence acting on the polar crystal is applied (a change in the temperature, mechanical stress, *etc.*), then a new stable state arises, already with T_2 and p_2. At that, a change in the state $(T_1 \rightarrow T_2$ or $p_1 \rightarrow p_2)$ is accompanied by the dynamic appearance of surface electric charges (in other words, the thermally or mechanically induced polarization arises), i.e., the pyroelectric or piezoelectric effect becomes apparent.

The simplified model shown in Fig. 2, *a* corresponds to a pyroelectric crystal, in which the internal polarity-activating bonds are "stable", but they can be deformed by a change in the temperature (giving pyroelectric effect) or by the mechanical stress (giving the usual piezoelectric effect). Such intrinsic polarity-activating property in the linear pyroelectric usually is conserved up to the crystal melting. Under the action of an external *electric* field, in such pyroelectric,

only a linear polarization (as in any dielectric) arises, with a value of permittivity typical of the ordinary ionic crystals.

The dynamics of thermally activating processes are regulated by the chaotic thermal motion. At that, the electric response of polarity-activating bonds can be described by the generalized electric moment M_{ijk}. In the 1D case, this is a simple polarization vector: $M_i = P_i$, in the more complex 2D polar hexagon shown in Fig. 2, *b* the electric response onto an external action is described by the polar moment M_{ij} (tensor of the second rank), and, in the 3D polar octupole, Fig. 2, *c*, this moment is already the tensor of the third rank. The generalized moment temperature dependence is described by the universal law: $M_{ijk}(T) \sim (\theta - T)^n$, meaning that such temperature $(T = \theta)$ exists, at which the electric moment M_{ijk} vanishes. The experimentsescribed described below show that the critical parameter equals $n = 1$, if polarity-activating bonding is arranged in a plane (2D case), while, in the case of a spatial (3D) arrangement of polar bonds, the critical exponent equals $n = 2$. In the dipole-type (1D) polar binding $n = 0.5$, which is the Landau critical index used for $M_i(T) = P_i(T)$ law in the ferroelectrics.

As known, ferroelectrics in the applied electric field demonstrate reorientation of their polarity-activating bonds with a pronounced nonlinear response: exactly this was served to introduce the spontaneous polarization concept and to name the corresponding group of crystals as ferroelectrics. Shown in Fig. 3, a, b, two opposite orientations of internal bonds are quite stable, which is confirmed by the coercive field E_C measured under the hysteresis loop investigation. As known, two stable positions (a and b) of the polar moment orientation are used for ferroelectric memories devices. The switching of two orientations of polarity-
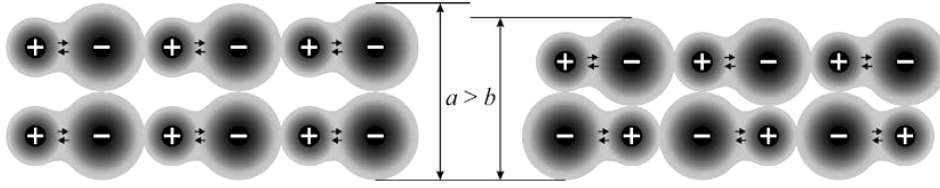
Fig. 4. Comparison of polar ordering (*a*) lattice with antipolar ordering (*b*): it is seen that $a > b$

sensitive bonds occurs, if the applied field exceeds the coercive field, Fig. 3, *c*.

The above modeling makes it possible to describe also the antiferroelectrics, Figure 4, which, in the case of a strong electric field, can be reversibly transformed into ferroelectric state. Stability of an antipolar state is characterized by the value of the electric field capable to switch antipolar phase into polar ones. Notable feature of antiferroelectrics is a decrease in their volume during the phase transition from non-polar to antipolar phase (on the contrary, ferroelectrics volume in their polar state increases). Thus, the applied electric field, converting antiferroelectric into ferroelectric, significantly changes the volume of a matter, that is used to obtain large electromechanical and electrocaloric effects. In general case, when the phase transition is forced by the external electric field from the paraelectric phase to the ferroelectric phase, the jump in volume leads to a change in the crystal temperature (this is clearly seen from relation $PV = RT$: At constant P, a change in V changes T). Usually, this electrocaloric effect produces a temperature change by 1–2 degrees, and this is not enough to be used in technology. However, electrically controlled jump in the volume at the antiferroelectric $\Leftrightarrow$ ferroelectric transition at least doubles this temperature jump which looks good for applications [9].

Shown in Fig. 2, the polarity-activating bonds arrangement explains also a number of other features seen in the polar crystals: the structural proximity of piezoelectrics and pyroelectrics; the chemical anisotropy of polar crystals; the frequency dependence of polar crystals permittivity; the microwave absorption in polar dielectrics; the possibility of electric control over thermal and elastic properties; a heat capacity increase due to fluctuations of polar clusters [8]; the negative thermal expansion coefficient at low temperatures [9]; the reduced thermal conductivity due to the scattering of phonons on polarity-activating bonds [8]; the effect of polar bonds on elec-

tric conductivity [4]; the action of polar bonds on the dielectric losses in microwave dielectrics [10].

Therefore, the existence of polarity-activating bonds in polar crystals can be confirmed by various experiments (some of them were mentioned above in Fig. 1). Next, some methods and results of experimental determination of of compensated components of the hidden polarity in the case of 2D and 3D spatial arrangements will be described in comparison with better studied 1D pyroelectrics.

4. Internal Polarity Correspondent to 1D Model

As known, the pyroelectricity is conditioned by two physical mechanisms: the primary and the secondary effects, which are characterized by pyroelectric coefficients $\gamma^{(1)}$ and $\gamma^{(2)}$ respectively. The first effect is determined by the temperature change of the binding energy for polar bonds (or by dipoles orientation), while the second effect is due to the piezoelectric transformation of the crystal thermal strain. In the case of mechanically free crystal, both of these mechanisms contribute to the thermally induced electric response described by $\gamma = \gamma^{(1)} + \gamma^{(2)}$. In this way, the polarity-actuating internal structure of pyroelectric is able to produce a *vector* response to the external *scalar* impact (in the given case, the homogeneous change of temperature).

The *primary* pyroelectric effect manifests itself regardless of mechanical conditions of a crystal, and simplest description of this phenomenon for 1D-oriented (dipole type) polar bonds is shown in Fig. 5. This effect is described by the coefficient $\gamma^{(1)}$, which is material vector (tensor of the first rank): $\gamma_i^{(1)}(\phi) = \mathrm{d}M_i/\mathrm{d}T = \gamma_{\mathrm{max}} \cos\phi$, where ϕ is the angle between the polar direction and slanting cut of the studied crystal.

The indicatory surface shown in Fig. 5, *a*, consists of two spheres located above and below the symmetry plane m, while coefficient $\gamma_i^{(1)}$ is equivalent for forward and reverse directions of the internal polar-
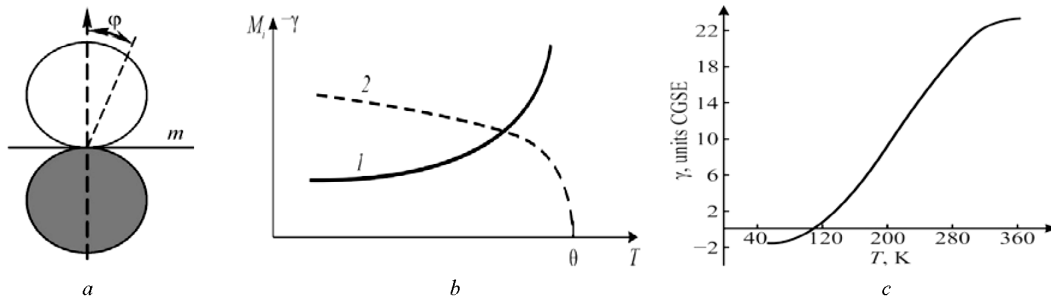
Fig. 5. Pyroelectric characteristics in 1D-type polar structures: *a* – section of indicatory surface; *b* – pyroelectric coefficient (*1*) and internal polarity moment (*2*); *c* – secondary pyroelectric coefficient of a lithium sulfate crystal, Li_2SO_4–H_2O

ity (its maximum is seen at $\phi = 0$ or $\pi/2$). In the case shown in Fig. 5, *b*, the pyroelectric effect appears in a ferroelectric, which might be called as "soft" pyroelectric (in which the direction of the internal polarity can be reversed by a strong electric field). In ferroelectrics, their pyroelectric coefficient sharply increases near the phase transition and then breaks off at the Curie point $T = \theta$. When the temperature increases, the dynamic equilibrium, which keeps polar bonds in the agreed orientation, becomes gradually suppressed by the chaotic thermal motion. The internal polarity moment ($M_i = P_i$) shown in Fig. 5, *b* by curve *2,* can be measured not only thermally, but also independently: through the hysteresis loop studied below the ferroelectric phase transition.

The mechanism of the *secondary* pyroelectric effect can be also explained within the 1D model, if we consider the electric response arising due to the heating of model dipole chain having a length l. An increase in the temperature (dT) leads to the thermal expansion of model chain by dl. At that, the coefficient of the secondary pyroelectric effect $\gamma^{(2)}$ turns out to be dependent on the thermal expansion coefficient α. The elongation or reduction of a modeled dipole chain leads to a change in its electric moment: $dM_i \sim dl/l$, which proportionality to the temperature increment dT is a result of the thermal deformation: $dl \sim \alpha\, dT$. As it follows from the direct piezoelectric effect: $dM_{i2} \sim e\, dl/l$, where e is the piezoelectric strain constant, so the electric moment of the secondary pyroelectric effect can be described as $dM_i = \gamma^{(2)} dT$, where $\gamma^{(2)} = e\,\alpha$ is produced by the piezoelectric conversion of a thermal strain.

Polar crystals, in which the secondary pyroelectric effect predominates, can be classified as the "hard" pyroelectrics, in which the direction of the internal polarization cannot be reversed by an external electric field (unlike ferroelectrics which are the "soft" pyroelectrics). It is worth to note that, in the "hard" pyroelectrics their coefficient $\gamma^{(2)}(T)$ decreases at lower temperatures and even takes negative value (Fig. 5, *c*). A change in the sign of the pyroelectric effect (that is difficult to explain by using the spontaneous polarization concept) is confirmed by many experiments [4, 5]. At that, the largest secondary pyroelectric coefficient is seen in lithium sulfate crystals, which, at the normal temperatures, has technical applications in thermal sensors due to the high stability and low permittivity. In the pyroelectrics-semiconductors of $A^{II}B^{VI}$ group (CdS is representative), as well as in other hexagonal crystals, the secondary pyroelectric effect is much smaller than in lithium sulfate, but also strives for negative value. This feature is associated with the low-temperature minimum of the thermal expansion coefficient $\alpha(T)$, typical of polar crystals. This phenomenon is explained [4] by the negative coefficient $\alpha(T)$ that indicates a change in the nature of interionic attraction forces due to the more close proximity of ions, forming the polar bond.

The secondary pyroelectric coefficient can be measured as a difference between pyroelectric coefficients of mechanically free and clamped crystals. This coefficient can be also calculated from the piezoelectric response equation: $M_i = e_{im}\, x_m$, where e_{im} are the components of the piezoelectric module (third rank tensor), and x_m are the components of the strain (second rank tensor). Under the thermal influence, this effect is excited by thermally induced strains in a polar crystal: $x_m = \alpha_m dT$, where α_m is the component of the thermal expansion coefficient (which is also a second rank tensor). It should be noted that tra-

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ditionally the components of symmetric second-rank tensors (such as strain x_m, stress X_n and others) are denoted by a *single* index, which, however, has six values: $m, n = 1, 2, ..., 6$, while the components of the first-rank tensors (vectors) are usually characterized by the index, which has 3 values: $i = 1, 2, 3$. As a result, the components of the secondary pyroelectric coefficient can be written as follows: $\gamma_i^{(2)} = e_{im}\alpha_m$, which is used in further calculations of a new thermo-polarization effect in piezoelectrics. If, during measurements or calculations, it turns out to be more convenient to use the piezoelectric module d_{in}, then the secondary pyroelectric coefficient $\gamma_i^{(2)} = \alpha_m d_{in} c_{nm}$, where c_{nm} is the elastic stiffness.

The primary pyroelectric effect is most noticeable above the Debye temperature ($T > \theta_D$), where thermal fluctuations in the crystal lattice (phonons) become sufficiently active. The secondary mechanism of pyroelectricity, i.e., the piezo-transformed thermal deformation, is possible at any temperature, but, in mechanically free crystals only. Usually (but not always), this effect prevails at lower temperatures ($T > \theta_D$). Note that the energy of the 1D dipole-to-dipole interaction decreases rather slowly with a distance (as r^{-2}). This has a significant influence on the ordering of polar bonds, which gradually become destroyed, when the temperature rises due to the chaotic thermal movement in the crystal lattice. It should be noted that the ordering of 1D polar bonds looks as relatively stable, since it is much more resistant to the 3D thermal fluctuations. Therefore, most of pyroelectrics (which are not ferroelectrics) maintain their polar sensitivity till the crystal melting. However, if the chaotic 3D-type disordering else can overcome the sustainability of self-ordered quasi-one-dimensional system (as in ferroelectric, Fig. 5, *b*), then its collapse occurs rather rapidly (critically), which leads to the phase transition into a non-polar phase. Firstly gradual, but then accelerated decline of the polarity moment M_i (first-rank tensor, P_S in ferroelectric) obeys Landau's law with critical index "0.5": $M_i \sim (\theta - T)^{0.5}$.

5. Experimental Evidence of 2D and 3D Polarity Models Applicability

In addition to the pyroelectrics (polar crystals), the polar-neutral crystals (piezoelectrics) are also of great importance to understand the nature of polarity, being conditionally attributed to the so-called "verita-ble" piezoelectrics (not pyroelectrics). In this case, a more complex distribution of the polar sensitivity can be modeled by both planar (2D) and bulk (3D) arrangements of interatomic polar bonds, borrowed in Fig. 2, *b, c* from real crystals structures of quartz and sphalerite. The polar-neutral crystals electric response onto external influences can be described by tensors of second and third ranks. In contrast to a 1D dipole-type structure, the 2D and 3D electric moments, describing the arrangement of polar bonds in Fig. 2, *b, c*, are completely self-compensated. In these cases. Any scalar action (i.e., hydrostatic pressure or uniform heating of a crystal) does not cause any vector-type response (electric voltage or current) in such crystals, if they are mechanically fully free or fully clamped. Of course, the vector action (in the form of the electric field applpivation) immediately indicates that these crystals are the polar ones, leading to a linear response in the form of the inverse piezoelectric effect (when non-polar crystals are only capable of the quadratic electrostriction effect).

To reveal the "hidden" polarity in the strain-free polar-neutral crystal without application of an external electric field, either vector or directed tensor actions are necessary. The external influences of a vector type might be the temperature gradient (*grad T*), while the second-rank tensor can act as a directed mechanical stress. Both of them allow one to get the electric response from polar-neutral crystals: these are the tertiary pyroelectric effect or the direct piezoelectric effect (see Table 2). However, these responses only indirectly allow one to conclude about the magnitude of the compensated polarity in polar-neutral crystals. The fact is that, according to the Curie principle, the symmetry of a response contains not only symmetry of the crystal, but also the symmetry of the influence.

Nevertheless, there is a way (and it is used below) to measure the intrinsic polarity using the scalar influence: a uniform change in the temperature or pressure, providing, under conditions when compensation of a polarity is violated: the method of a partial limitation of the thermal strain or piezoelectric strain. In the first case, the polar-neutral crystals show the artificial pyroelectric effect observed by us for the first time in a quartz crystal plate stuck to a non-deformable substrate [3]. In the second case, it is the volumetric piezoelectric effect in the polar
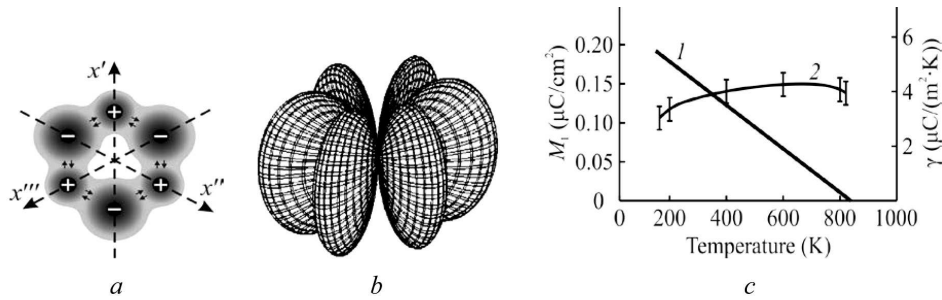
Fig. 6. Internal polarity in 2D structure (quartz): *a* – polar-neutral axes; *b* – indicatory surface; *c* – temperature dependence of internal moment (*1*) and artificial pyroelectric coefficient (*2*)

cut of quartz crystal stuck on a rigid (steel) substrate. Thermodynamic calculations of thermo-mechanically induced pyroelectric effect, as well as measurement technique of the partial clamping method are described in detail in [10]. At that, in any piezoelectric the artificial pyroelectric effect can be obtained, which might be of interest also for practical applications.

The following shows how such thermo-mechanically induced pyroelectric effect is applied to the study of the compensated polarity in 10 classes of the "veritable" piezoelectrics.

Quasi-two-dimensional (2D) systems of self-compensated polarity-actuating bonds is a characteristic of such piezoelectrics as quartz (SiO_2) and other crystals of 32 symmetry classes: berlinite ($AlPO_4$), cinnabar (HgS), and tellurium (Te). In polar coordinates, Fig. 6, *b*, the distribution of the internal polarity in these crystals can be described as $M_{ij}(\beta, \phi) = M_{\max} \sin^3 \theta \cos 3\phi$, where β is the azimuth angle, and ϕ is the in-plane angle. By radius vector directed from center of the figure, one can determine the magnitude of the polar-sensitivity response in any slanting cut of quartz-type crystals. In particular, the maxima of the piezoelectric effect are seen along any one of three polar-neutral axes of X-type, Fig. 6, *a*. At that, no piezoelectric effect is possible along the Y and Z axes.

Since these crystals have the $\alpha - \beta$ phase transition at the temperature $T = \theta$, it is possible to calculate the latent polarity response tensor $M_{ij}(T)$ components, which vanishes at the phase transition, Fig. 6, *c*. For this, we can use the artificial pyroelectric response excited in these crystals as reaction to a homogeneous thermal impact under the conditions of partial limitation of a thermal deformation [10]. In the case of 2D distribution of polar-neutral bonds, the energy of their interaction decreases with distance as $U \sim r^{-3}$, Fig. 2, *b* (i.e., noticeably faster than for the 1D dipole-to-dipole interaction). Therefore, the 2D intrinsic polarity can be more easily destroyed by 3D thermal fluctuations than the 1D polarity: this follows from comparison of inclined straight line *1* in Fig. 6, *c* with the falling dotted line *2* shown in Fig. 5, *b*.

The component of the electric response moment: $M_{[100]} = \Delta M_1 = \int \gamma_1 dT$, being calculated from experimental data of $\gamma_1(T)$, decreases linearly with temperature rise: $\Delta M_1 \sim (\theta - T)$, that is, with a critical index of $n = 1$ (note that the same dependence was observed early in improper ferroelectrics [2], in which their polarity also relates to the piezoelectric effect). The artificial "pyroelectric" coefficient $\gamma_1(T)$, obtained by the method of partially limiting of a thermal deformations, disappears at the $\alpha - \beta$ phase transition (in quartz crystals $\theta = 850$ K).

Spatially distributed (3D) polar sensitivity occurs in many polar-neutral piezoelectric crystals. With a temperature increase, in some crystals, the phase transition to a non polar state can occur earlier than the crystal melting. In this case, the components of the 3D response tensor can be measured by the above-mentioned method of partial limitation of a thermal deformation. One of this case is shown below for piezoelectric KDP = KH_2PO_4 studied in its paraelectric (but non-centrosymmetric) phase. At that, the third-rank tensor $M_{ijk} = dM_{111} \sin \beta \sin 2\beta \cos 2\phi$ is described by the indicatrix shown in Fig. 7, *a*, which corresponds to model shown in Fig. 2, *c*. It is appropriate to note that the same eight-peaked (octupole type) distribution of polar bonds takes place in many polar (sphalerite structures) semiconductors, such as gallium arsenide.
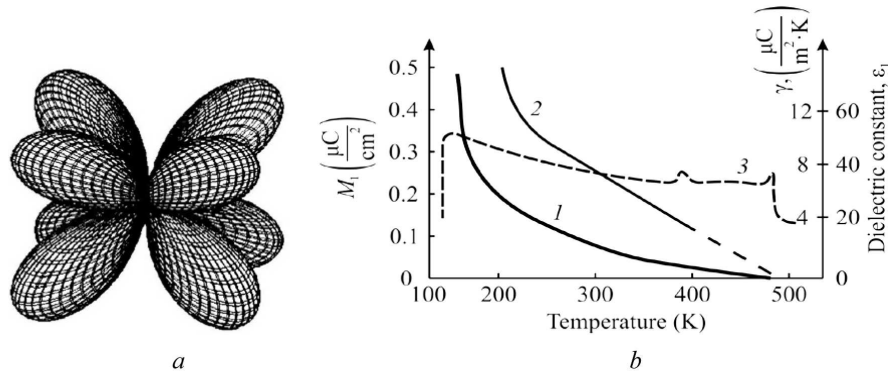
Fig. 7. Intrinsic polarity in paraelectric phase of KDP crystal: *a* – indicatory surface; *b* – some characteristics of crystal: *1* – moment $|M| \sim (\theta - T)^2$; *2* – measured artificial pyroelectric coefficient γ; *3* – permittivity ε_1 measured by us at microwaves at frequency 10 GHz

Some properties of KDP crystals in the temperature range above the ferroelectric phase transition are shown in Fig. 7, *b*, where studied piezoelectric is the polar-neutral crystal of 422 symmetry class. It is noteworthy that the polar moment of polarity-activating bonds decreases in this case very gradually, and next vanishes: $M_{ijk} \sim (\theta - T)^2$, i.e., with critical index $n = 2$. At that, the crystals of KDP type in their paraelectric phase are characterized by high-temperature phase transition, at which the 422-th polar symmetry class of KDP crystals changes its symmetry to the non-polar one. Investigations are provided at microwaves in waveguide, because, at lower frequencies, the high proton conductivity of a KDP crystal hinders any dielectric measurements. As shown in Fig. 7, *b*, curve *3*, a smooth decrease of the permittivity $\varepsilon_1(T)$ is seen. But, at last, it falls down at the temperature $\theta \approx 480$ K just due to the high-temperature phase transition. The presence of this transition was confirmed by the measure of the thermal expansion coefficient, which has a deep minimum at the indicated temperature [11].

Attention might be drawn to the relatively intensive destruction of the steadiness of polarity-activating bonds in the case of their three-dimensional allocation. The point is that the energy of their correlation decreases with distance rather fast ($U \sim r^{-4}$), which indicates the weakened stability of the 3D-ordering in polar-neutral crystals. As a result, the stability of their directional connection can be destroyed much easier by the same 3D-character of thermal fluctuations. The 2D model of the interaction via polar bonds looks as more stable to the thermal 3D
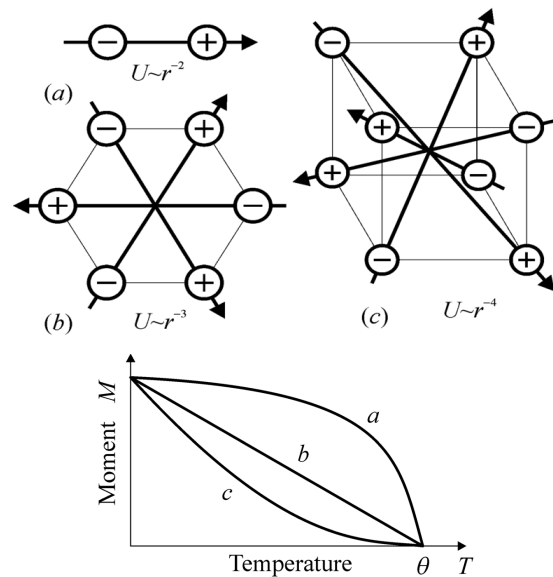

Fig. 8. Modeled 1D (*a*), 2D (*b*) and 3D (*c*) polarity and correspondent temperature dependence of generalized electric moment components, energy interactions power coefficients of dipoles (*a*), hexagons (*b*) and for octupoles (*c*) are calculated by electrostatic methods

chaotic motion, while the1D model is the most stable, (Fig. 8).

Thus, in order to confirm the experimentally proposed models of two- and three-dimensional arrangement of polarity-activating bonds in the polar-neutral piezoelectrics (non-pyroelectrics), a thermo-mechanically induced pyroelectricity is investigated. In those cases, when piezoelectrics experience the phase transition to a non-polar phase, the temperature-depen-

dent value of their own polarity is determined. Otherwise, it is possible to determine only a change in this polarity in studied temperature interval.

6. Conclusions

The likeness of the very diverse physical properties of different polar crystals has been analyzed that indicates the similarity of physical mechanisms of their polarity. Based on comparison with ferromagnetism, it is shown that concept of spontaneous polarization cannot be applied to the pyroelectrics. To explain many unique properties of polar crystals, it is supposed that their features are due to a special type of mixed ionic-covalent bonds, which can generate polar properties. This approach redefines and extends the known concept of spontaneous polarization. The supposed reason for the existence of such bonds in the non-centrosymmetric crystals is different electronegativity of neighboring ions that leads to a well-balanced structure highly sensitive to external influences. The mixed ionic-covalent polarity-generating bonds are the main reason for that the polar crystals show an electric response onto non-electric influences (thermal, mechanical, optical, etc.). Various simple models are proposed to explain the properties of polar and polar-neutral crystals. Effectiveness of suggested models is confirmed experimentally.

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ПРИРОДА ПІРОЕЛЕКТРИЧНОЇ ПОЛЯРНОСТІ

Поняття спонтанної поляризації в піроелектриках ставиться під сумнів, оскільки завжди наявні вільні електричні заряди унеможливлюють будь-який рівноважний і стабільний у часі поляризований стан. Передбачається, що піроелектрика в полярних кристалах і п'єзоелектрика в полярно-нейтральних кристалах зумовлені гібридизованими йоноковалентними зв'язками, що активують полярність та у своєму незбудженому стані не створюють електричного поля, але здатні генерувати електричний відгук на однорідний неелектричний вплив (тепло, тиск тощо). Цей відгук пояснюється моделями різних електричних моментів, компоненти яких вимірюються за допомогою часткового обмеження термічної деформації кристала. Можна вважати, що запропонований підхід модифікує та розширює відому концепцію спонтанної поляризації. При цьому сегнетоелектрики відрізняються тим, що в електричному полі вони переорієнтовують свої міжатомні зв'язки, що активують полярність із нелінійним відгуком і гістерезисом.

К л ю ч о в і   с л о в а: полярні кристали, п'єзоелектрики, піроелектрики, сегнетоелектрики.