Science Discovery Materials
2026, Vol. 1, No. 3, pp. 81–95
https://doi.org/10.11648/j.sdm.20260103.11

SciencePG
Science Publishing Group

Research Article

Intrinsic Polarity of Crystals: Elementary Models, Heat Capacity and Transfer, Negative Thermal Expansion

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Abstract

In all dielectrics, electric polarization is induced by an external electric field, but polar crystals also exhibit intrinsic polarity, forming non-centrosymmetric polar and polar-neutral structures of pyroelectrics and piezoelectrics. It is postulated that intrinsic polarity in crystal structures arising due to the different electronegativities of neighboring ions. The emergence of intrinsic polarity is facilitated by high ionic charge, large Lorentz factor and high anharmonicity of ions vibrations that are the characteristic of mixed covalent-ionic bonds. Polar crystal structures are characterized by reduced symmetry and the ability to electrically respond to mechanical, thermal, optical, and other nonelectrical stimuli. The paper examines the causes of polarity and antipolarity in crystals, assuming that the dynamics of polar cluster formation corresponds to the concept of configurational entropy. Experimental data and explanations for many manifestations of intrinsic polarity in crystals are presented.

Keywords

Polar Crystals, Electronegativity, Configurational Entropy, Specific Heat, Thermal Expansion, Heat Transfer, Piezoelectrics, Pyroelectrics

1. Introduction

Polar materials include non-centrosymmetric crystals, polarized ceramics, thin films, liquid crystals, and other objects [1, 2]. Among polar crystals, most notable are piezoelectrics, pyroelectrics, ferroelectrics and some other ferroics, whose distinctive feature is the pronounced polarity of their interatomic bonds [3, 4]. The unusualness of polar crystals manifests itself in various aspects, for instance, intrinsic polarity is somehow related to the energy spectrum of electrons: polar semiconductors have a direct band gap, while nonpolar semiconductors have an indirect band gap. In addition, intrinsic polarity can influence others electronic properties of crystals, such as electric conductivity [5]. Besides, it is seen structural similarity between piezoelectrics and pyroelectrics: they can interconvert: for example, the piezoelectric structure of sphalerite can transform into the pyroelectric structure of wurtzite, and they even coexist, as in zinc blende crystals. Other transformations are also possible, such as reversible transition from ferroelectric to antiferroelectric when temperature changes or under the influence of an applied electric field [1]. Sometimes polarity can manifest itself only in the thin layers of materials being absent in bulk crystals [6]. Another fact that may be surprising is a weak but reliably observed polar properties in simple cubic covalent semiconductors Ge and Si [7].

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Received: 17 July 2026; **Accepted:** 10 August 2026; **Published:** 27 August 2026

Thus, the physical nature of intrinsic polarity in crystals remains largely unclear, which explains the interest in this problem.

1.1. Polar Crystals Unusual Properties

The article examines the singularities of polar crystals. Most of the following properties of polar crystals differ significantly from those of non-polar crystals:

1) the density of polar crystals decreases during crystallization compared to their melt and density of ferroelectrics also decreases when transition to polar phase from non-polar one;
2) the chemical properties of polar crystals depend on crystal's orientation, for example, when chemical etching of crystal surfaces;
3) the resistance to heat transfer of polar crystals exceeds ones of non-polar crystals;
4) the volumetric thermal expansion coefficient in polar crystals shows minimum near temperature ~ 0.1 qD;
5) the microwave energy absorption of polar crystals exceeds that of non-polar crystals;
6) . the optical properties of polar crystals are characterized by second harmonic generation, double refraction and dichroism;.
7) the electro-thermal properties of polar crystals demonstrate the pyroelectric and electrocaloric effects;
8) the conductivity in some polar crystals can change thousands of times even at small change in temperature or under the influence of electric field;
9) the mutual transformation of mechanical, electrical and thermal energy is characteristic of polar crystals;
10) the electrical parameters of polar crystals depend significantly on their mechanical and thermal conditions, as well as their elastic and thermal parameters noticeably depend on polar crystals electrical conditions.

1.2. Anti-polar Crystals Special Properties

Since this work focuses on the physical causes of intrinsic crystal polarity, the antipolarity of some crystals is also highly informative. This rather hidden property has been most studied in ferroelectric materials, where the transition from an antipolar to a polar crystal occurs when the crystal's temperature changes or an electric field is applied. Antipolar crystals are then compared with polar ones based on the following properties:

1) the maximum of permittivity is seen in the antiferroelectrics at phase transition from their paraelectric phase in which Curie-Weiss law is fulfilled (like in ferroelectrics);
2) the density of the antiferroelectric phase increases at phase transitions from their paraelectric phase (in contrast to the polar phase of ferroelectrics);
3) the coefficient of thermal expansion in the antiferroelectrics at phase transition has a maximum (on the contrary to ferroelectrics which show deep minimum);
4) the heat capacity in antiferroelectric at the Curie point shows minimum while in the ferroelectric it has a maximum;
5) the thermal diffusivity of antiferroelectrics at the Curie point demonstrates maximum due to optical phonons participation of in the heat transfer while ferroelectrics thermal diffusivity shows minimum;
6) the hydrostatic pressure shifts the antiferroelectric phase transition toward higher temperatures, while the ferroelectric phase transition, on the contrary, shifts toward lower temperatures;
7) the microwave energy absorption of intipolar crystals is no different from ordinary ionic crystals (unlike polar crystals, where this absorption is hundreds of times greater);
8) the electro-mechanical properties of antipolar crystals manifest itself only in the electrostriction: the piezoelectric effects in them are absent;
9) the electro-thermal properties of antipolar crystals not show pyroelectric or electrocaloric effects;
10) during electrically induced reversible antiferroelectric/ferroelectric phase transition, a giant electrocaloric effect is observed due to the large change in structure.

When discussing the above and other unique physical phenomena in polar crystals, three key points should be considered. First, the conventional concept of spontaneous polarization, which arose from the formal comparison of ferroelectricity with ferromagnetism, is inapplicable to pyroelectrics [8]. Second, the cause of internal polarity in crystals with mixed covalent-ionic bonds is the different electronegativity of neighboring ions. Third, most of the unique properties of polar crystals are determined by the dynamics of polar clusters, which is described by configurational entropy.

A more detailed explanation of these points is given below.

1) Unlike spontaneous magnetization, which exists stably because magnetic charges are absent in nature, the applicability of spontaneous polarization concept to pyroelectrics is questionable, as the ubiquitous free electric charges make the existence of a stable polarized state impossible. Moreover, magnetization is described by an axial vector being generated by moving electric charges, as opposed to polar vector of polarization created by stationary electric charges. So the analogy between polarization and magnetization is only formal [5].
2) In dielectrics, their molecular, covalent, or ionic bonds are formed due to the distribution of electron density between structural elements. It is generally believed that electrons belonging to the outer (valence) electron shells of atoms play a primary role in the formation of chemical bonds, since their impact usually significantly exceeds the influence of deeper electrons of atoms or ions. These concepts are sufficient for understanding the basic properties of non-polar dielectrics, but to explain the exist-

ence of intrinsic polarity in some ionic crystals it is necessary to consider the action of abyssal electron shells of ions on crystal structure formation—that is, the concept of different electronegativity of neighboring ions, which plays an important role in the formation of a polar crystal structure.

3) Some thermal, mechanical, and electrical properties of polar crystals are so unusual that they can only be explained by the assumption that thermal motion in these crystals leads to the self-organization of polar bonds into dynamic clusters. As is well known, the entropy of a thermodynamic system—a crystal—is defined as a measure of the system's disorder, determined by the number of states that individual particles can occupy. However, entropy is also influenced by the number of bound states in the system; that is, the dynamics of self-organization of microgroups consisting of several combined particles. This is precisely what leads to configurational entropy, which is part of the overall entropy of the system, being determined by the arrangement of its constituent particles, and not by their motion [9]. Thus, configurational entropy is determined by positional disorder, while vibrational (or "kinetic") entropy is due to the disorder of moving particles [10].

The aim of the work is to come closer to explaining the causes and patterns that contribute to the emergence of polar structure in some crystals, as well as to explain their unusual features using simplified modeling and the mentioned concepts.

2. Simplified Concepts of Internal Polarity

The structure of polar crystals can vary greatly, making it difficult to explain the nature of their internal polarity using a single physical mechanism. Therefore, each specific type of polar crystal merits a detailed study of its structural features and physicochemical properties. Nevertheless, some common features can be identified that explain the physical basis for the formation of polar structures.

2.1. Interatomic Bonds in Polar Crystals

The interatomic bonds that ensure the stable spatial structure of a crystal are formed through the restructuring of atoms electron shells. The formation of stable interatomic bonds is always accompanied by a decrease in the total energy of the crystal. At that, the electrons belonging to the outer shells of atoms play a key role in the formation of chemical bonds, as their contribution to the energy of crystal significantly exceeds that of electrons belong to deeper-shells of atoms.

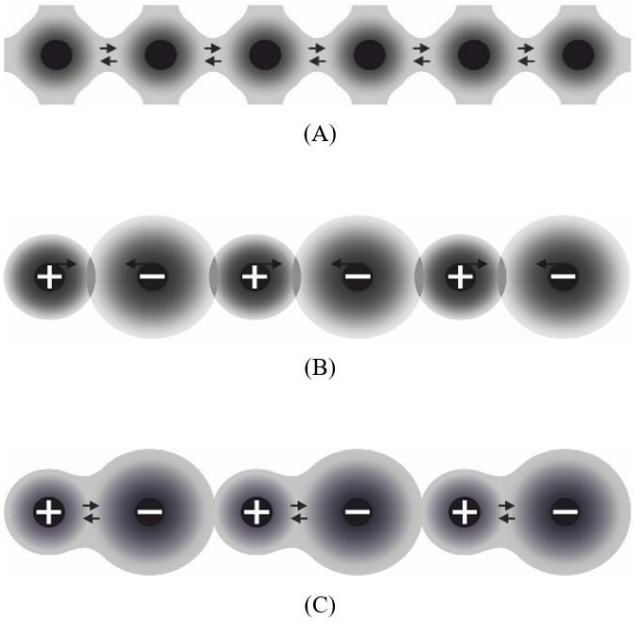


Figure 1. *Modeling of interatomic bonds in dielectrics.*

(A) - covalent crystal; (B) - ionic crystal in which Coulomb ions attraction is balanced by overlapping of electronic shells; (C) - polar-sensitive bonding, where above more simple bonding are mixed (black diffused circles denote atomic cores surrounded by regions with gradually decreasing electronic density).

Figure 1 shows, in a highly simplified form, the three main models of electron density distribution capable of generating polarity in dielectrics: covalent, ionic, and mixed bonds. In covalent crystals, the electron density is distributed only between adjacent atoms, creating a strictly directional bond, Figure 1A. In ionic crystals, the attraction of cations and anions is compensated by the repulsion of partially overlapping electron shells, Figure 1B. Mixed covalent-ionic bonding, shown schematically in Figure 1C, is a distinctive feature of polar crystals and manifests itself in two ways: (1) the ionic nature of this bond determines the crystal's increased susceptibility to external influences; (2) the contribution of the covalent nature to the mixed polar bond is manifested in its strict directionality, which contributes to the asymmetry in the distribution of electron density along this bond.

Polar bonds are energetically supported by substantial difference in the electronegativity of adjacent ions. Indeed, in the nonpolar monatomic covalent crystals, the electronegativity of adjacent atoms is identical; in the nonpolar ionic crystals the difference in electronegativity between adjacent ions is comparatively small, but in the polar crystals, it is precisely this big difference that determines their unique properties.

In connection with the above, it is worth noting that some manifestations of internal polarity can also be observed in the non-ionic crystals, where atoms are linked only by the covalent bonds. Two cases can be distinguished: when covalent crystals can be diatomic (or polyatomic), so the likely cause of their polarity may also be the difference in electronegativity between different atoms. Second, internal polarity can also be noticeable

in the monatomic covalent crystals (the reason for the existence of polarity in these crystals will be explained later.

Thus, polar bonds arise as a structural compensation for the different electronegativity of neighboring ions, which play a decisive role in the formation of polar bonds. Below, we will demonstrate that long-range interactions between the resulting polar bonds facilitate the formation of polar clusters, which is crucial for the manifestation of the crystal's intrinsic polarity. To understand this interaction and explain the dynamics of polar clusters in a polar crystal, it is necessary to introduce the concept of configurational entropy.

2.2. Polar Crystals Lattice Dynamics Peculiarities

One of the theoretical methods used in solid-state physics to study various phenomena is crystal lattice dynamics based on the phonon model. The fundamental energy characteristics of solids are considered to be the Debye energy $\hbar\omega_D$ and the Boltzmann energy k_BT. The Debye temperature is $\theta_D = \hbar\omega_D/k_B$ and the Debye frequency is $\omega_D = 2\pi\nu_D$; they are related by two fundamental constants: the Planck constant $\hbar$ and Boltzmann's constant k_B. When describing the applicability of phonon theory to describing particle motion in solids, as well as many other properties of crystals, the degrees of freedom of particles can be divided into three cases.

First, if the particles interaction energy U_{int} is small compared to the thermal motion energy k_BT, i.e., $U_{int} < k_BT$, then the corresponding degrees of freedom behave like a "nearly ideal gas" of phonons, which is typical of ordinary non-polar dielectrics. Possible nanoscale fluctuations in such a structure, including polarons, are unstable and suppressed by chaotic thermal motion. The phonon model is quite applicable to describing the thermal and electrical properties of non-polar crystals.

Second, in the opposite case, when $U_{int} > k_BT$, the corresponding degrees of freedom are usually sufficiently ordered, so the particle motion can also be described by the phonon model, but this time taking into account the possible interaction of acoustic and optical phonons with noticeable anharmonicity of the crystal lattice vibrations. Most polar dielectrics (piezoelectrics and pyroelectrics) fall into this category because their intrinsic polarity is sufficiently stable, and therefore the application of the phonon concept to them can be considered justified.

Third, a much more complex case can arise, when the interaction energy is $U_{int} \sim k_BT$. In this case, the theoretical description of polar structures becomes very complex, especially when analyzing phase transitions in them, at which a non-polar phase transforms into a polar or antipolar one. In this case, the traditional phonon concept inadequately describes the experimental situation. This is due to the unique nature of interatomic interactions, when the probability of collective particle motion is greater than the probability of their individual motions. Furthermore, in this situation, a real possibility arises for polar clusters formation which dynamically respond to the changes in external influences on a crystal.

Important factors in the emergence of internal polarity

To model the oscillation dynamics of a one-dimensional ionic crystal, oscillations in a long chain of ions are considered. The energy $U(x)$, which characterizes the oscillations of a given ion, can be expanded in a series in terms of the magnitude of the ion's displacement x from its equilibrium state:

$$U(x) = \tfrac{1}{2}\, cx^2 + \tfrac{1}{4}\, bx^4 + \ldots \quad (1)$$

where c characterizes elasticity and b characterizes non-linearity of oscillations. When describing the dynamics of electric polarization, induced by an external electric field in a conventional ("linear") dielectric, a good approximation is to consider only the first term of expansion (1): $U(x) = \tfrac{1}{2}\, cx^2$, where c is the elastic stiffness. This case corresponds to a non-polar crystal of centrosymmetric structure.

The role of anharmonicity (important for understanding the nature of intrinsic polarity) also can be determined from expression (1), in which, in addition to the first (harmonic) term $\tfrac{1}{2}cx^2$, it is necessary to take into account the second term of the series $\tfrac{1}{4}bx^4$ with an anharmonicity coefficient $b > 0$. at the same time, in the absence of subsequent terms of series (1), the resulting two-terms equation is obtained in which anharmonicity coefficient must be certainly positive ($b > 0$) to ensure the stability of studied anharmonic ionic lattice model (even in the case of large fluctuations in the ions vibrations). As for the elastic stiffness, it can, in principle, be either positive: $c > 0$, Figure 2A and C, or negative: $c < 0$, Figure 2A and D. In the second case, the lattice stability is provided by the positive coefficient b.

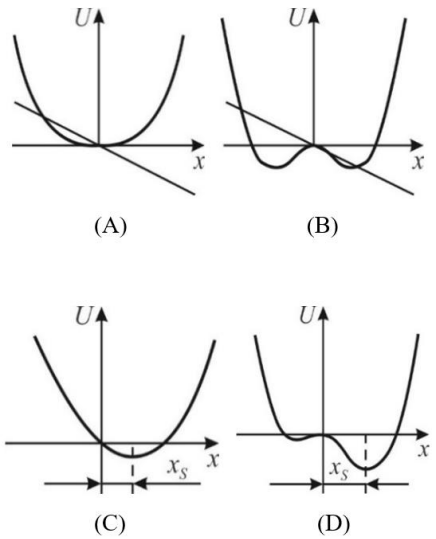


Figure 2. *Dependence of energy U(x) change on displacement x from ion equilibrium position in one-dimensional model.*

(A) - at c > 0 with moderate anharmonicity;
(B) - at c < 0 with high anharmonicity (inclined line characterizes the additional energy from applied electric field);
(C) and (D) - show resulting displacement x_S

In Figure 2A and 2B the $U(x)$ dependences for the two limiting cases $c > 0$ and $c < 0$ are compared in a one-dimensional model: both structures are centrosymmetric, but under the influence of an applied electric field (the energy contribution of which is shown by the inclined line), the energy minimum corresponding to the new equilibrium (polarized) state shifts by an amount x_S. In a three-dimensional structure, there can be six such local minima—as, for example, in barium titanate when a titanium ion is displaced within an oxygen octahedron. It is also relevant to note that such a shift can also occur without the application of an external field in the case of significantly different electronegativity values of neighboring ions forming a polar bond.

To simulate the vibrations of a polar crystal, an artificial method is used, because ions lattice needs to be polarized, let's say, by an electrically induced displacement x_S, Figure 2B and 2D. To describe such a situation, to the polynomial (1) must be added the energy of local electric field F acting on the ion with the energy $-Fqx$ (the field F is related to the externally applied electric field E by the Lorentz relation):

$$U(x) = ½\, cx^2 + ¼\, bx^4 - Fqx, \tag{2}$$

As a result, an the original parabola (1) becomes non-centrosymmetric, corresponding to the polar structure. As a result, a strain x_S arises, at which the energy $U(x)$ has a minimum. Since now the equilibrium state is the polarized ones (with f minimum at $x = x_S$), a total force acting on the system of charges in this state equals zero: $\partial U(x)/\partial x = 0$ which leads to the equation: $cx + bxc^3 - F = 0$. The electric field correspondent to the energy minimum is $F_C = \beta P_S$ where β is the Lorentz factor.

Thus, in a one-dimensional model, represented by a polarized chain of ions, the polarization can be expressed as $P_S = nqx_S$, where n is the ions concentration and q is the ions charge. By substituting this data into equation (2) a cubic equation can be obtained

$$cx_S + bx_S^3 - nq^2\beta x_S = 0, \tag{3}$$

where term cx_S describes the "elasticity" of a system, while term bx_S^3 characterizes its "anharmonicity". This equation has three roots:

$$x_1 = 0;\ x_{2,3} = \pm\,[(nq^2\beta - c)/b]^{1/2} \tag{4}$$

When considering the polarized state of interest to us (only for deformation xS 1 0), the first solution x1 = 0 of equation (4) is a secondary root of the equation, which is not considered in this case. An analysis of the other two solutions of the equation under consideration leads to the following conclusions.

$$nq^2\beta x > cx \tag{5}$$

The right-hand side of this inequality corresponds to the *elastic force* that counteracts polar displacement x_S (the overlap of electronic shells of the neighboring ions seeks to return the non-polar state). The left side of the inequality (5) has also the dimension of a force, and it is the *leading interaction* (that leads to the polar state). Thus, the polarity can occur in such crystals, in which the leading interaction exceeds the returning interaction. Further analysis of inequality (5) indicates that the *large charge* (q^2) of the displaced ions and the enhanced Lorentz factor β make significant contributions to the intrinsic polar state of the crystal.

All the listed factors are in a good agreement with the experimental data.

In common crystals, the closest neighbouring particles are considered as the strongly interacting particles (with $U(x) = ½\, cx^2$), while the interaction of others distant particles might be neglected (i.e., $\beta \to 0$). However, in the polar crystals, in contrast, the interaction of neighbouring particles can compensate one another (parameter "c" might be *small and even negative*). In the latter case, as seen in Figure 2D, the formation of electric dipoles is inevitable. At the same time, both directions of polarity are initially equally probable, which explains the possibility of polarization switching in the ferroelectrics by an externally applied electric field. However, the dipole coupling can also be quite "rigid," as in the pyroelectrics, and it is relatively long-range (its energy $U(r)$ decreases with distance as r^{-2}). On this background, the interaction of those polar formations, which are several removed, may appear as dominant. In this case, the probability of collective interactions exceeds the probability of individual interactions.

The importance of collective interactions is confirmed by experiments: a polar crystal exhibits increased specific heat capacity, reduced elastic stiffness, lowered heat transfer, negative thermal expansion coefficient, increased dielectric permittivity, etc. From the above, it can be concluded that mixed covalent-ionic bonding is a distinctive feature of polar crystals and may underlie simple models discussed below, which approximately explain crystal polarity. Polar bonding is based on the different electronegativity of adjacent ions and also inherits the directional properties of covalent bonds and the long-range interaction of ionic bonds.

2.3. Elementary Models of Polar Structures

To describe the polar properties of crystals, any elementary model must, first, lack a center of symmetry and secondly, to ensure electrical neutrality. Third, the polar model must be capable of translation, forming a macroscopic polar system (one-dimensional, two-dimensional, or three-dimensional), and also describe the polar properties of various polar materials (including micro- and nanostructures). Figures 6-8 present basic elementary models of intrinsic polarity based on the asymmetry of the electron density distribution along atomic bonds. These models describe, in a simplified form, the spatial orientation of asymmetric hybridized ionic-covalent bonds. However, the models presented below do not take into account the hydrogen-bonded and organic polar crystals.

One-dimensional simplest electrically neutral but polar configuration of ions is a dipole, Figure 3. This model is applicable to ten polar classes of crystals possessing *pyroelectric* symmetry. Corresponding to dipole type polarity the pyroelectric coefficient γ_i is a material vector (i.e., a first-rank tensor) with a spatial distribution of polarity $\gamma_i(\varphi) = \gamma_{imax} \cdot \cos\varphi$, where φ is the angle between the polar direction and the oblique cut of the crystal in which the pyroelectric effect is being studied or applied. The same indicatrix as in Figure 3 describes the volume piezoelectric effect as an electrical response to hydrostatic pressure (such an effect is impossible in free crystals of piezoelectrics which are not pyroelectrics).

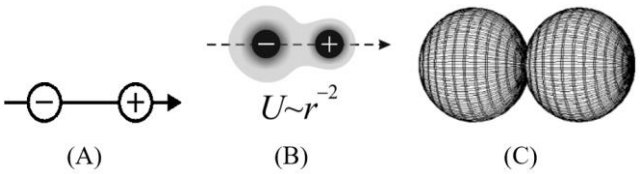


Figure 3. *One-dimensional polar structure is a dipole.*

(A) the polar direction is shown by an arrow;
(B) the change in interaction energy with distance U(r) is a power function;
(C) the indicatrix of the electrical response of the polar bond to an external influence is represented by two spheres for both possible orientations of the dipole

It should be noted that studied in this way the pyroelectric coefficient corresponds only to the *primary* pyroelectric effect, which is observed in a clamped crystal which cannot deform with temperature change. In the case of possible thermal deformation of a pyroelectric, the spatial distribution of a pyroelectric response becomes more complex than shown in Figure 3 due to the additional *secondary* pyroelectric effect (in which supplementary electric response occurs due to thermal deformation of crystal). The magnitude of intrinsic polarity can be determined from the pyroelectric coefficient if a polar crystal undergoes a phase transition to a non-polar phase (and in ferroelectrics from a hysteresis loop).

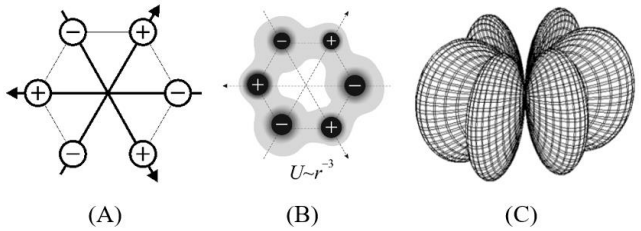


Figure 4. *Two-dimensional model of the polar structure is a hexagon.*

(A) the polar directions are shown by arrows;
(B) the decrease in the interaction energy with distance U(r) is shown by a power function;
(C) the indicatrix of the electrical response to an external stimulus is represented by six almond-shaped figures.

Two-dimensional simplest configuration of ions might be the quadrupole, but this centrosymmetric system of ions is not polar (though note that it provides a basic understanding of the antipolarity). Therefore, we must choose the polar *hexagonal* configuration as a simple polar 2D configuration, Figure 4 (incidentally, this model is suggested by nature itself, as it corresponds to a piezoelectric quartz crystal). This model appears as three dipoles arranged at an angle of 60° to one another, while the spatial distribution of the electrical response to a non-electrical stimulus (for example, in the case of a direct piezoelectric effect) appears as six almond-shaped surfaces connected at the center.

Thus, for two-dimensional polar structure the interaction energy of hexagon model decreases with distance as:

$U(r) \sim r^{-3}$ (faster than in 1D case). Figure 4 in the polar coordinates describes the internal polarity distribution in the piezoelectrics of quartz type, where piezoelectric module is the second rank tensor: $d_{ij}(\beta, \varphi) = d_{max}\sin^3\theta \cdot \cos 3\varphi$, where θ is the azimuth angle and φ is the in-plane angle. By the radius vector, directed from a center of shown figure, one can determine the magnitude of polar-sensitivity response in any slanting cut of quartz-type crystals. Compensated polarity components can be measured by partially constraining thermal deformations [5], which are only possible in the direction of one of the polarities. This creates an artificial pyroelectric effect, allowing polarity determination in the case of a crystal transition to a non-polar phase (for example, in quartz at 300 K, this coefficient is $\gamma_{100} = 2.6\ \mu Cm^{-2}K^{-1}$, corresponding to a polarity of 0.16 $\mu C/cm^2$.

Three-dimensional model shown in Figure 5 can be selected using the same principle. This model represents an octupole, which, incidentally, corresponds to the actual crystal structure of sphalerite. The spatial distribution of interionic electron density in this model can be conditionally described by four dipoles, the three-fold polar axes of which are positioned at an angle of 104° to each other (the direction of these imaginary dipoles is shown in the model by arrows).

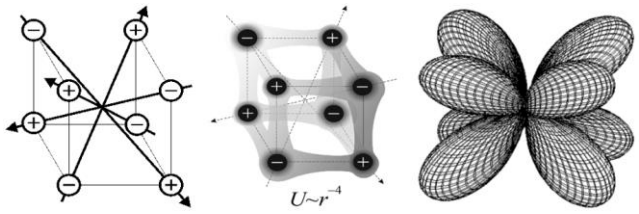


Figure 5. *Three-dimensional model of the polar structure is an octupole; the polar directions are shown by arrows, the decrease in energy with distance U(r) is characterized by a power function, the indicatrix of the electrical response to an external stimulus is represented by eight-vertex pear-shaped figures for all possible orientations of the polar axes.*

The 3D model shown in Figure 5 is adapted to the piezoelectrics-semiconductors of a gallium arsenide type, where one

of possible electric responses is the piezoelectric modulus being a third-rank tensor: is $d_{ijk} = d_{max}$ sinβ·sin2β·cos2φ. It is appropriate to note that same octupole-type orientation of polar bonds takes place in many others polar crystals.

Figures 4 and 5 show a simulation of intrinsic (or "latent" or "hidden") polarity, describing the ability of a low-symmetry crystal to respond to dynamic (time-varying) *heterogeneous* external stimuli, such as a temperature gradient (vector) or mechanical stress (second-rank tensor). Unlike dipole structures (pyroelectric type, as in Figure 3), which respond to *any* external stimuli, including scalar ones, the structures shown in the models in Figures 4 and 5 are polar-neutral and do not respond to scalar stimuli. The fact is that the one-dimensional polar structure shown in Figure 3 is characterized by a *single* polar axis, which corresponds to the main structural motif of 10 classes of pyroelectric crystals; of course, piezoelectricity is also observed in them.

In total, all 21 classes of non-centrosymmetric structures are polar crystals: 10 of them are pyroelectrics corresponding model in Figure 3, while the models presented in Figures 4 and 5 are applicable to 10 polar classes of piezoelectric crystals that are not pyroelectric. In such crystals, scalar effects (uniform changes in temperature or hydrostatic pressure) do not cause an electrical response, which is fully compensated in both planar and bulk structures. Therefore, in contrast to the "special" polar axis characteristic of pyroelectrics (model in Figure 3), double and triple polar axes (model in Figures 4 and 5) can be considered "polar-neutral." Accordingly, the 10 classes of crystals with pyroelectric symmetry can be called "true polar," and the remaining 10 classes of crystals with piezoelectric symmetry are "polar-neutral." The compensated polarity components can be measured by partially limiting the thermal deformation [5]. For example, the artificial pyroelectric effect observed in such case in gallium arsenide has a quasi-pyroelectric coefficient γ_{111} = 1.8 μC·m^{-2}·K^{-1} (comparable in value to the pyroelectric coefficient of tourmaline: γ = 4 μC·m^{-2}·K^{-1}). Thus, a semiconductor with a sphalerite structure acquires pyroelectric properties that can find application in integrated thermal sensors [11].

However, there are 21 classes of noncentrosymmetric crystals, and it would be interesting to determine whether the hidden polarity of this single, unaccounted-for symmetry class is somehow manifested. In fact, in this symmetry class, an odd (though nonlinear) inverse piezoelectric effect is observed in a strong electric field E; i.e., the nonlinear component of the odd inverse piezoelectric effect is proportional to E^3 (but not E^2, as in the case of the even electrostrictive effect). Thus, in terms of their response to an electric field, all noncentrosymmetric dielectrics exhibit an odd electromechanical effect (but in one class, this effect is nonlinear).

It is important to note that described above models can be jointly used to explain properties of various polar crystals. For example, piezoelectricity and pyroelectricity can be observed in the same crystal (these symmetries can even coexist in polymorphic forms); this is observed for crystals with sphalerite and wurtzite structures.

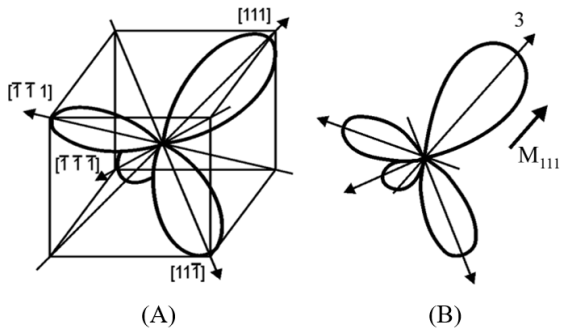


Figure 6. *Internal polarity in two polar cubic crystals (only positive directions of the [111] type polar axes are shown).*

(A) - spatial distribution of piezoelectric sensitivity in a polar-neutral crystal;
(B) - appearance of an additional dipole component, which indicates a pyroelectric structure

Figure 6 shows how simple polarity models can describe this situation. These models can also be applied to explain the coexistence of the polar-neutral sphalerite structure (Figure 6A) with the polar wurtzite structure (Figure 6B), which is seen in the zinc blende-type crystals of ZnS or GaN. In the figure, the polar moment M_{111} represents a "dipole type polarization" along the single threefold polar axis. Thus, in sphalerite, one of the polar-neutral axes becomes a "special polar" axis characterizing wurtzite, while the other three axes remain "polar-neutral." It should be noted that similar distribution of polarity as in Figure 6B exists in the ferroelectrics of $LiNbO_3$.type. These crystals contain not only a pyroelectric polar axis but also three polar-neutral axes. In the crystal sections cut perpendicular to these axes, the limiting thermal deformation leads to an artificial pyroelectric effect with a coefficient of γ = 40 μC·m^{-2}·K^{-1}, which is only slightly inferior to the usual value of the coefficient of the pyroelectric effect of $LiNbO_3$, equal to γ = 50 μC·m^{-2}·K^{-1}.

In conclusion, we note that shown above polar models may coexist in the different combinations in accordance with 20 classes of the piezoelectric symmetry crystals.

3. Heat Capacity and Heat Transfer in Polar Crystals

The special thermal properties of polar crystals include, firstly, heat capacity maximum observed near the phase transition from the non-polar state to polar phase. Secondly, an increase in the volume of crystal polar phase compared to its non-polar phase. Thirdly, the decreased thermal conductivity, which is dozens of times lower than in non-polar crystals. Fourthly, a negative coefficient of volumetric thermal expansion, which is observed not only in the region of ferroelectric phase transition but in all polar crystals in a temperature range near ~ 0.1 θ_D.

3.1. Specific Heat Capacity

Above the Debye temperature, the specific heat capacity of

crystals, $C(T)$, is a very conservative parameter, increasing only gradually with increasing temperature. The heat capacity is determined primarily by the number of thermally excited phonons, so any change in the specific heat capacity from its steady-state value is extremely unusual. However, this phenomenon is still observed in ferromagnets, where magnons dynamics significantly contribute to conventional phonon heat capacity (but this effect disappears above Curie point).

Similar to ferromagnetics, the heat capacity in the polar phase of ferroelectrics increases significantly compared to its normal level due to the dynamic mechanism of polar clusters self-organization. This effect is most pronounced immediately below the phase transition temperature, where an additional contribution to the heat capacity can be even greater than the base average value.

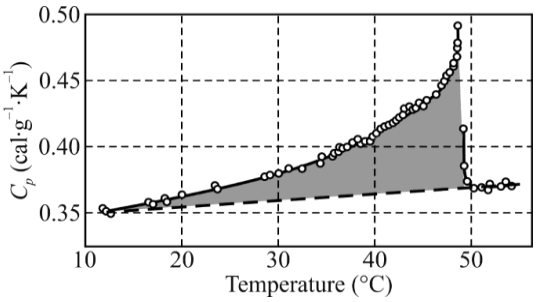


Figure 7. *Specific heat temperature dependence for TGS crystal ($NH_2CH_2(COOH)_3 \cdot H_2SO_4$) in accordance with [12, 13].*

As an example, the ferroelectric triglycine sulfate (TGS) is considered, which is nonpolar above the Curie point T_C and becomes polar below it. The underlying part of the heat capacity is shown in Figure 7 by the dotted line at the base of $C(T)$ peak. The maximum heat capacity in the TGS crystal reaches ~50% of its base value (in some ferroelectrics, it can be even many times greater). This maximum is due to the nature of the phase transition, and corresponds to the latent heat released during the phase transition. The $C(T)$ anomaly discussed here manifests itself over a broad range of excess heat capacity. Above the Curie point, in a disordered phase, the heat capacity anomaly is absent, whereas below the phase transition point it gradually decreases with the decrease of temperature, because the polar bonds become more ordered (condensed). Therefore, as in the case of magnons in a ferromagnet, the asymmetric maximum in the heat capacity observed below the phase-transition temperature indicates a dynamic process of the segregation and disintegration of polar clusters, consistent with the concept of configurational entropy. In connection with the subsequent discussion of this phenomenon, which is important for understanding the nature of electrical polarity in crystals, it is appropriate to note that a *minimum* heat capacity is observed at the temperature of antiferroelectric phase transition that fits into same concept.

To confirm above arguments on the role of dynamic self-ordering of polar regions in the polar phase, an additional experiments were carried out [12]. Firstly, during the measurements the special condition was created when mechanical strain of crystal was limited; in this case, the maximum in $C(T)$ dependence was largely suppressed. Secondly, when heat capacity measuring, the DC electrical bias field was applied to a crystal, which also led to the *decrease* of $C(T)$ maximum, but without shifting $C(T)$ maximum on the temperature scale.

The hear capacity has a significant impact on such important thermal properties of crystals as the thermal conductivity and the thermal expansion.

3.2. Heat Transfer in Polar Crystals

Thermal energy in dielectrics is transferred primarily by the short-wavelength acoustic waves ("thermal phonons"), whose propagation velocity is significantly lower than that of long-wavelength "sound phonons." Two parameters are used to heat transfer describe: thermal conductivity (λ) and thermal diffusivity (ξ). The first parameter is important for assessing the technical properties of the material, while the second parameter is more important for physical mechanisms analyzing. For example, the thermal diffusivity $\xi(T)$ shows a minimum during the ferroelectric phase transition, but, conversely, during the antiferroelectric phase transition, it exhibits $\xi(T)$ maximum. This and many other reasons are sufficient grounds for discussing heat transfer in polar crystals.

In covalent dielectrics, the thermal conductivity is relatively high: λ = 100-200 W/(m·K) and is caused mainly by acoustic phonons. In ionic dielectrics, due to adding acousto-optic interaction, the thermal conductivity is lower: λ = 10-20 W/(m·K). In polar crystals with mixed ionic-covalent bonding, the thermal conductivity is even lower: λ = 1-10 W/(m·K). Near the phase transitions of ferroelectrics, the thermal conductivity can be further reduced to < 0.1 W/(m·K); however, it should be noted that in ferroelectrics a bias electric field can significantly control the heat transfer, which could be of technical interest.

According to kinetic theory, thermal conductivity depends on the specific heat capacity C of the crystal, the mean free path of phonons $<l>$, and the average velocity $<\upsilon>$ of phonons: $\lambda = (1/3) \cdot \upsilon \cdot l = (1/3) C \cdot \upsilon^2 \cdot \tau$, where τ is the mean time of free path determined by the anharmonicity coefficient. Consequently, the thermal conductivity is related to the coefficient of thermal expansion, which is also determined by the anharmonicity coefficient.

The thermal diffusivity ξ is defined as the thermal conductivity divided by the density of substance ρ and its specific heat capacity C_p at constant pressure: $\xi = \lambda/(C_p \cdot \rho)$. Like thermal conductivity, the thermal diffusivity in anisotropic materials can be different in different crystallographic directions. In essence, it characterizes the rate at which a crystal transfers the heat from crystal hot side to its cold side, in other words, the thermal diffusivity is a measure of *thermal inertia*, since

the heat moves faster through a substance with increased thermal diffusivity. When temperature increases, the thermal diffusivity decreases because the probability of phonon collisions becomes greater, being determined by the anharmonicity of lattice vibrations, which is measured by the Grüneisen parameter γ_G. The average free path of phonons is $<l> \sim a/(\alpha \cdot \gamma_G \cdot T)$, where a is the lattice constant and α is the thermal expansion coefficient. In the temperature interval discussed here (when temperature $T > \theta_D$) the decrease of $\xi(T)$ follows the Aiken law: $\xi(T) \sim T^{-1}$.

The thermal diffusion coefficient is a criterion for heat transfer mechanisms: it characterizes not the overall heat flow, but the kinetic properties of the energy carriers. For example, in a non-polar silicon crystal (Si) and a polar quartz crystal (SiO_2), the speed of sound (determined by long-wavelength phonons) is approximately the same: ~5000 m/s. In fact, long sound waves propagate in crystals without significant scattering, since their wavelength significantly exceeds the size of microscopic structural defects.

However, the speed of short-wave thermal phonons in nonpolar (Si) and polar (SiO_2) crystals of these crystals differs sharply: at a temperature of 300 K in silicon it is $\xi = 88$ mm^2/s, and in quartz it is $\xi = 1.4$ mm^2/s. In nonpolar crystals, only dislocations and atomic defects somewhat impede the propagation of short thermal waves. In polar crystals, however, polar clusters with sizes comparable to the wavelengths of these thermal waves are also present and, owing to the piezoelectric effect, are acoustically active. Therefore, polar crystals, which have high transparency for long elastic waves, exhibit strong diffuse scattering for short elastic waves. At the same time, the propagation velocity of short thermal waves decreases, making polar crystals an effectively turbid medium for these waves, despite the high velocity and low attenuation of long-wavelength acoustic waves. Nevertheless, this phenomenon allows the thermal resistance of such a medium to be controlled using an electric bias field [4]. Applying an electric field leads to the ordering of dipole clusters, which dissipate thermal phonons.

The analysis of thermal diffusivity provides more insight into the physical mechanisms of heat transfer than the analysis of thermal conductivity. A comparison between thermal diffusivity and thermal conductivity is presented in Figure 8 using KDP-type crystals as an example.

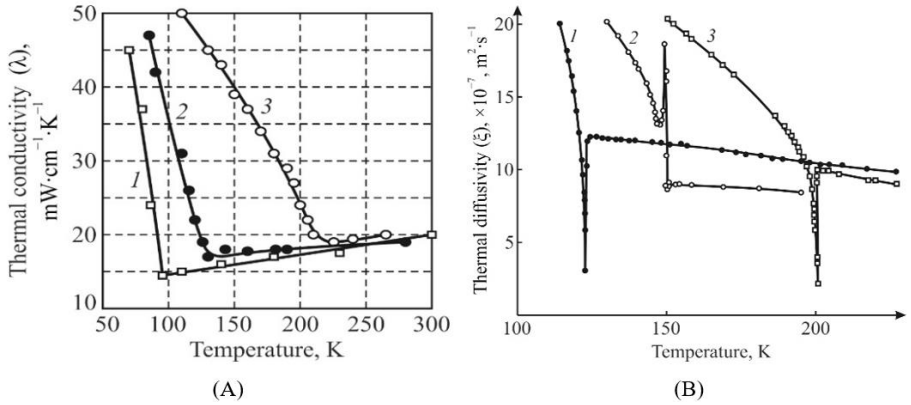


Figure 8. *Heat transfer near ferroelectric phase transitions.*

(A) - thermal conductivity of KH_2PO_4 (Curve 1), KH_2AsO_4 (Curve 2), KD_2PO_4 (Curve 3);
(B) - thermal diffusivity of KH_2PO_4 (Curve 1), KD_2PO_4 (Curve 3) in comparison with antiferroelectric $(NH_3)H_2PO_4$ (Curve 2) [14].

The obvious difference between these temperature dependences of thermal conductivity in the phase transition region is characterized only by a bend, followed by a gradual increase below the Curie point due to increased polar bond ordering (Figure 8A). In contrast, the temperature dependence of the thermal diffusion in KDP group crystals is characterized by a pronounced minimum (Figure 8B), indicating a decrease in the phonon wavelength, which is especially noticeable in the phase transition region.

The difference between the temperature dependences of thermal conductivity and thermal diffusion is due to the fact that the decrease in the phonon wavelength in the case of thermal conductivity is compensated by a maximum in the specific heat capacity. It is especially noteworthy that at the Curie point of the antiferroelectric ammonium dihydrogen phosphate ADP = $(NH_4)H_2PO_4$, a sharp maximum of thermal diffusion is observed (Figure 8B), rather than the deep minimum typical of ferroelectrics [8]. This critical dependence of thermal diffusion indicates that the optical phonons participate in the heat transfer mechanism near the phase transition.

Both above and below the Curie temperature, acoustic phonons in polar crystals are partially mixed with the optical phonons. Consequently, optical phonons also contribute to heat transfer. Heat transfer is enabled by the spatial dispersion of optical modes. The interaction of acoustic phonons with the soft transverse optical mode, characteristic of ferroelectrics, reduces the mean free path of phonons, which reaches its minimum at the phase-transition temperature.

Thus, a distinctive feature of polar crystals, all of which are piezoelectric, is the interaction between acoustic and optical phonons. If the optical phonons exhibit significant spatial dispersion, they can contribute directly to heat transfer. In most cases, however, this contribution is relatively weak, and optical phonons primarily increase phonon scattering, thereby substantially reducing the thermal conductivity. Therefore, in studies of heat transfer near phase transitions, thermal diffusivity is a quite informative parameter, since it provides a deep insight into the role of thermal phonons in the heat-transfer process.

The reason is that, in antiferroelectrics, the frequency of optical vibrations decreases critically not at the center of the Brillouin zone, as in ferroelectrics, but at its boundary. Consequently, the optical phonons mix with short-wavelength (thermal) acoustic phonons, which are responsible for most of the heat transfer. As a result, the thermal diffusivity increases sharply at the Curie temperature (Figure 8B). In ferroelectrics, however, this effect is absent because the critical decrease in the frequency of transverse optical vibrations occurs in the region of long-wavelength phonons, and they do not mix. Consequently, ferroelectric crystals exhibit a much larger maximum dielectric permittivity. For example, at the Curie temperature and a frequency of 10 GHz, the maximum dielectric permittivity is about $\varepsilon_{max} \approx 1000$ in KDP, whereas under the same conditions it is only about $\varepsilon_{max} \approx 90$ in the antiferroelectric crystal ADP [15].

Thus, mixed ionic-covalent polar bonds strongly influence heat transfer in polar crystals, resulting in significantly lower thermal conductivity than in purely ionic or purely covalent crystals. Thermal diffusion anomalies observed near ferroelectric phase transitions can be explained by the transformation of an ordered polar structure into a disordered nonpolar one. In the ordered phase, the thermal diffusivity increases, indicating that it is the disordering of polar-sensitive bonds that impedes heat diffusion.

4. Configurational Entropy

Many of the aforementioned properties of polar crystals can be explained using the concept of configurational entropy [9, 10]. The entropy of a thermodynamic system is defined as a measure of its disorder determined by the number of states that moving particles can occupy. However, entropy is also affected by the number of possible micro-locations in the system, which depends on the self-organization in the micro-groups consisting of several aggregated particles. This leads to the concept of configurational entropy, which represents the fraction of the total entropy of a system that is associated with the arrangement of its constituent particles rather than with their motion. This measure of disorder arising from possible configurations is quantified by the positional disorder, while the vibrational (or "kinetic") entropy characterizes the disorder arising from every particles motion. Therefore, the configurational entropy, determined by the dynamic change in groups of constituent particles, is a part of the total thermodynamic entropy of the system. In this case, the change in configurational entropy corresponds to the same change in total entropy.

As an example, the possibility of a negative volumetric thermal expansion coefficient, α, characteristic of polar crystals at sufficiently low temperatures, is examined below. The Gibbs function G is considered, corresponding to the isobaric-isothermal thermodynamic potential, characterizing the portion of the system's internal energy available to perform useful work under the specified conditions: $G = U + pV - TS$, where U is the internal energy, p is the pressure, V is the volume and S is the entropy. The minimum of the Gibbs potential corresponds to the equilibrium state of the system at a given temperature, pressure, and number of particles. In this case, for a system with a constant number of particles, the differential of the Gibbs energy is expressed as: $dG = -SdT + Vdp$, where $\alpha = (dV/dT)_p/V$ is determined at constant pressure. The change in the volume of the system, determined by the Gibbs potential at a constant temperature, is equal to: $V = (dG/dp)_T$, which allows us to obtain the following expressions:

$$\alpha = \frac{1}{V}\left(\frac{\partial\left(\frac{\partial G}{\partial p}\right)_T}{\partial T}\right) = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T\,\partial p}\right)$$

by replacing variables one can have:

$$\alpha = \frac{1}{V}\left(\frac{\partial\left(\frac{\partial G}{\partial T}\right)}{\partial p}\right) = -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_T$$

This formula implies that, at constant temperature the coefficient α depends on how entropy depends on pressure. In the case of ordinary "kinetic" (thermal) entropy, it follows that the greater the pressure the lower the entropy. Therefore, a crystal should expand with increasing temperature ($\alpha > 0$), which is typically observed in most solids.

However, in polar crystals, which are dynamically self-organizing systems, the coefficient α is negative at relatively low temperatures. This situation in polar crystals corresponds to an increase in the entropy with increasing pressure. This phenomenon can be explained in terms of configurational entropy, which arises from the dynamic change of polar clusters—nanoscale configurations of groups of particles. A specific arrangement of particles characterized by average quantities represents a macrostate, whereas the individual particle configurations consistent with the given macrostate represent its microstates.

Thus, the configurational entropy is determined by the set of different arrangements of certain parts of the system, and this rule can be applied to all possible system configurations. As the hydrostatic pressure increases, the potential for partial ordering of dynamic nanoscale clusters is suppressed, so the mutual chaos intensifies. Therefore, a distinctive feature of configurational entropy is its sensitivity to the pressure changes. The correlation between the coefficient α_V of volume thermal expansion ($\delta V = \alpha_V \delta T$) and the compressibility ζ_V of a crystal that is ($\delta V = \zeta_V \delta p$) is due to the fact that both of these

phenomena characterize: the volume change of crystal under the action of uniform *scalar* quantities (such as the uniformly varying temperature δT or hydrostatic pressure δp). The dependence of relative change in volume δV of a crystal under the hydrostatic pressure change is characterized by the compressibility. Scalar parameter ζ_V is formed as invariant of elastic compliance tensor: $\zeta_V = s_{11} + s_{22} + s_{33} + 2(s_{12} + s_{13} + s_{31})$; in the cubic crystals and other isotropic solids the compressibility equals $\zeta_V = 3(s_{11} + 2s_{12})$.

It should be noted that compressibility is strongly dependent on the energy of interatomic bonds. Consequently, the corresponding response of the crystal when its volume changes on temperature (δT) or on pressure (δp), in both cases is associated with the intrinsic elastic properties of the crystal, reflecting the characteristics of its atomic bonds. It is therefore not surprising that when discussing the physical nature of negative $\alpha_V(T)$, this property is compared with crystal's compressibility ζ_V, which characterizes the response of the crystal to hydrostatic compression-tension (i.e., $\alpha_V \Leftrightarrow \zeta_V$).

The relationship between entropy and pressure can be understood in terms of Le Chatelier's principle. Because the ordering of polar bonds decreases the entropy while increasing the system volume, an increase in pressure, which reduces the volume, favors the disordering of polar bonds and, consequently, an increase in entropy. Conversely, a negative change in volume with increasing temperature indicates the presence of disordering processes in the system. Therefore, when describing the properties of polar crystals, the phenomenon of a negative $\alpha_V(T)$ value requires taking into account configurational entropy.

Below the Debye temperature, when it is necessary to take into account the quantum nature of crystal lattice vibrations, the spectrum of thermal vibrations expands with increasing temperature, and the specific heat capacity increases, with the coefficient of thermal expansion increasing proportionally $\alpha_V(T) \sim C_V(T) \sim T^3$. Such a dependence is indeed observed for most crystals of chemical elements and simple compounds, for example, halide salts and oxides. In all these cases, the increase in the $\alpha_V(T)$ dependence corresponds to the Grüneisen law [16], which establishes the same temperature dependence for the specific heat capacity C_V and the coefficient of thermal expansion: $\alpha_V = (\gamma_G C_V)/3K$. Here γ_G is the Grüneisen constant, which is included in the equation of state of a solid, being a measure of the anharmonicity of the interatomic forces acting in the crystal. The bulk modulus of elasticity K is the reciprocal value of compressibility ζ_V. At that, parameter K is defined as the ratio of the magnitude of mechanical stress to the magnitude of relative compression, and it can be determined through the components of the elastic stiffness tensor: for example, in cubic crystals $K = (c_{11} + 2c_{12})/5$. In other words, the bulk modulus of elasticity describes the ability of a material to resist the changes in solid's volume, i.e., it characterizes the ability of an object to change its volume under the action of hydrostatic pressure δp. The relationship $\alpha_V \leftrightarrow K$ is due to the fact that both effects on the crystal (a uniform change in its temperature and a comprehensive change in pressure) are scalar effects on the crystal, and therefore, the crystal's response—comprehensive deformation—reflects the characteristics of internal atomic bonds under both types of effects. Therefore, it is not surprising that, in further discussion of the nature of the negative coefficient of thermal expansion, it is appropriate to compare this property with the bulk modulus of elasticity of the crystal, which characterizes its response to hydrostatic compression and tension.

The essence is that the scalar influences, such as uniform changes in temperature or gyrostatic pressure, possess higher (spherical) symmetry; this allows for the experimental determination of the internal symmetry of exactly interatomic bonds of a crystal. However, other methods for investigating the nature of these bonds are indirect, as they violate the symmetry of the response of the object being studied. For example, with a vector influence on a crystal (such as a temperature gradient, an electric field, etc.), as well as with a tensor influence on a crystal (for example, directed mechanical stress), the symmetry of these influences is superimposed on the internal symmetry of the crystal. Consequently, the response characteristics may provide distorted information about the crystal's internal properties.

Many physical phenomena point to the significant role of the configurational component of entropy in interpreting the properties of polar substances. A convenient method for this is to track the role of polarity during the ferroelectric phase transition. Specific heat capacity anomalies and suppressed heat transfer in polar crystals have already been discussed; their volume expansion and negative thermal expansion remain to be discussed.

5. Increase in Polar Phase Volume and Negative Thermal Expansion

Dynamic processes of self-organization of polar clusters, activated by thermal vibrations of the crystal lattice, explain not only the above-described anomalies of the thermal properties of polar crystals, but also many features of their electrical and mechanical properties.

The particularity of polar crystals *electrical* properties (except the piezoelectric and pyroelectric effects) include, firstly, the anomalously high microwave absorption of a quasi-Debye type; secondly, the anisotropy of the permittivity in most polar crystals; thirdly, the gigantic value of the permittivity in the relaxor ferroelectrics.

The same concept can be applied to explain the unique *mechanical* properties of polar crystals. This applies, for example, to the reduction in elastic wave velocity in the polar phase of crystals, as indicated by the minimum elastic stiffness in the phase transition region. It is also noteworthy that hydrostatic pressure lowers the temperature of the ferroelectric phase transition, as if "squeezing out" the ordered polar phase, leading to its transformation into a disordered phase. Meanwhile, the temperature of the antiferroelectric phase transition increases under

the influence of hydrostatic pressure, which favors antipolarity.

5.1. Increase in Volume in the Polar State of Crystals

Numerous experiments demonstrate an increase in the volume of a polar crystal during its transformation from a non-polar (disordered) phase. For example, during a first-order phase transition, a polar crystal floats in denser melt. The same effect of decreasing the crystal's density (i.e., increasing its volume) is also observed during a second-order phase transition from a non-polar to a polar state. This effect of volume change is particularly interesting when compared to the antipolar crystals, in which, on the contrary, when transition from initially non-polar phase, the volume of a crystal decreases.

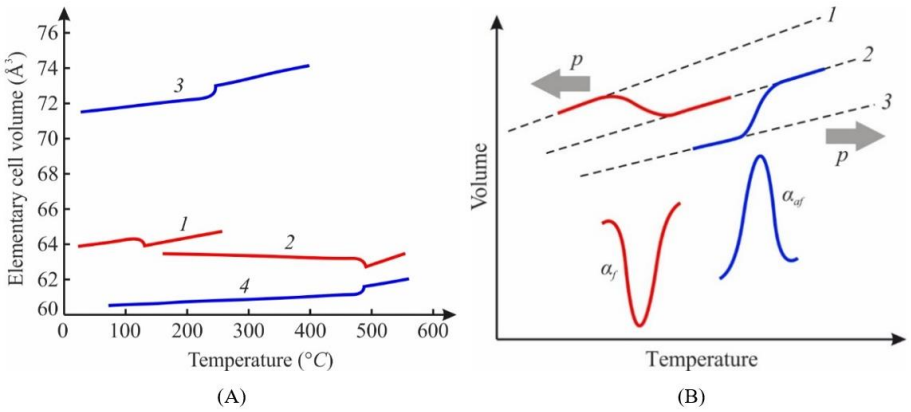


Figure 9. *Temperature expansion in ferroelectric materials.*

(A) - unit cell volume in the ferroelectrics $BaTiO_3$ (1), $PbTiO_3$ (2), antiferroelectrics $PbZrO_3$ (3) and $NaNbO_3$ (4); (B) - schematically represented anomalies in volume V(T) and α(T) during phase transitions: 2 ⇒ 1 - paraelectric-ferroelectric; 2 ⇒ 3 - paraelectric-antiferroelectric. Designations: 1 - V(T) dependence for polar phase, 2 - V(T) dependence for non-polar phase, 3 - V(T) dependence for antipolar phase, α_f - thermal expansion coefficient at ferroelectric phase transition, α_{af} - same coefficient at anti-ferroelectric phase transition, broad arrows indicate the direction of phase transition temperature T_c displacement with increasing pressure.

Figure 9A compares the temperature dependence of the volume in ferroelectric and antiferroelectric crystals, which exhibit opposite thermal expansion anomalies near the phase transition. In ferroelectrics, the volume of the ordered ferroelectric phase increases compared to the volume of the disordered paraelectric phase. In the ferroelectrics $BaTiO_3$ and $PbTiO_3$, the nonpolar phase is cubic, whereas the low-temperature polar phase is tetragonal. The unit cell is elongated along the *c*-axis and contracted along the two *a*-axes; nevertheless, the unit-cell volume increases below the phase-transition temperature in both ferroelectrics. This behavior results from a redistribution of the crystal's electron density such that the development of internal polarity below the phase-transition temperature requires a larger volume. At the same time, the crystal symmetry is lowered.

The hydrostatic pressure, applied to $BaTiO_3$ below its Curie point (i.e., in the polar phase), returns this crystal into the paraelectric non-polar phase, Figure 9B. The temperature of barium titanate phase transition (shown as *2* ⇒ *1* passage) decreases with the rate - 5 K/kbar as the pressure increases [1]. As a result, at the pressure of 30 kbar applied in $BaTiO_3$ at room temperature its polar phase already disappears: it is "squeezed out" by pressure. Similarly, in ferroelectric $PbTiO_3$ the temperature of ferroelectric phase transition under the action of gyrostatic pressure decreases, but with a rate of - 8 K/kbar. Figure 9B explains symbolically this process, which is completely consistent with the concept of configurational entropy.

Naturally, that the increase of volume in the polar phase during ferroelectric phase transition is accompanied by a large minimum of the thermal expansion coefficient, Figure 11B. On the contrary, in the case of antiferroelectrics, the volume of antipolar phase decreases at Curie point T_c; correspondingly, in the phase transition, the $\alpha_V(T)$ dependence shows a big maximum. The density of antiferroelectric increases, so the entropy in the antipolar phase decreases also. Accordingly, the hydrostatic pressure shifts the antiferroelevtric phase transition temperature towards high temperatures: in the case of $PbZrO_3$ with the rate of + 5.5 K/kbar [1].

Thus, the increase of uniform pressure suppresses the polar properties of ferroelectric but, on the contrary, stabilizes the antipolar phase of antiferroelectrics (in agreement with configurational entropy concept).

5.2. Negative Thermal Expansion Coefficient

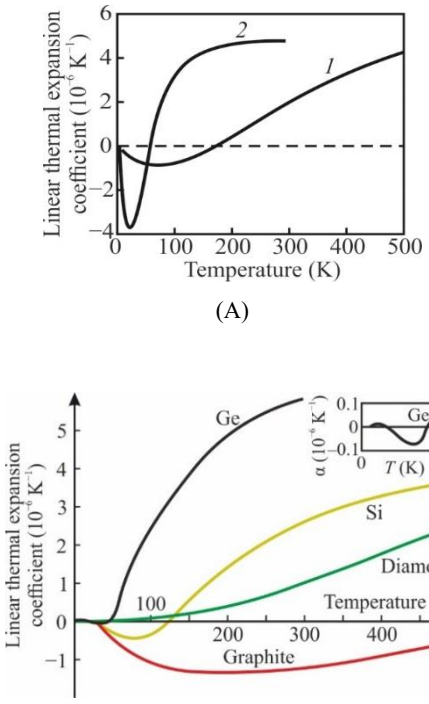
The coefficient of thermal expansion α_{ij} is a second-rank tensor that characterizes the change in the relative dimensions of a crystal with a change in temperature at a constant pressure p and is measured in units of [K^{-1}]. The thermal expansion of polar

crystals can be anisotropic, and the tensor components can have different signs. However, below we will consider a scalar parameter: the volumetric coefficient of thermal expansion α_V, which characterizes the degree of change in the volume of a crystal with temperature: $\alpha_V = (1/V)\cdot(\partial V/\partial T)_p$. It can be calculated from the diagonal components of the thermal expansion tensor, in particular, for crystals of medium symmetry $\alpha_V = \alpha_1 + \alpha_2 + \alpha_3$, so in the crystals of cubic symmetry $\alpha_V = 3\alpha$.

At normal and elevated temperatures (usually above the Debye temperature), the coefficient $\alpha_V(T)$ gradually increases with temperature; at the same time, in the ionic and covalent crystals its value typically does not exceed 10^{-5} K^{-1}. Below the Debye temperature an exponential temperature dependence of the thermal expansion coefficient is generally observed: $\alpha_V \sim T^3$ (similar to the heat capacity). As known, the anharmonic nature of thermal vibrations of the crystal lattice leads to a positive sign of the thermal expansion coefficient: $\alpha_V(T) > 0$. The positive value of this coefficient also follows from other facts. The parameter $\alpha_V(T)$ characterizes the properties of the internal bonds of atoms, in particular, the energy of these bonds, which is determined by the melting temperature of the crystal: $T_m \sim \theta_D^2$. The following empirical relationship is well satisfied in a wide variety of crystals: $\alpha_V T_m = const$ [16], which means that the smaller the coefficient α_V the higher the melting temperature T_m. Both of these important thermodynamic parameters can be expressed in terms of the Debye temperature θ_D of the crystal. This is unconditional proof that the total value of $\alpha_V(T)$ is expected to be positive.

That is why the *negative* value $\alpha_V(T)$ looks quite unusual, however it can be argued that such an anomaly is seen below the Debye temperature (when not all phonons of the crystal lattice are activated, so some circumstances can influence this process). As will be shown below, the phenomenon $\alpha_V(T) < 0$ is typical only for a certain temperature range, specifically in the vicinity of about 0.1 θ_D. Therefore, the negative value of volume thermal expansion coefficient, seen in the polar crystals, is only an episode in the general $\alpha_V(T)$ dependence. However, this peculiarity allows a deeper understanding of the physical nature of a crystal's own polarity.

Figure 10A shows typical examples of strong "negative expansion" effect in polar ionic crystals in comparison with a similar but weakly expressed effect in covalent and layered crystals, Figure 10B. At the same time, this phenomenon is usually observed at temperatures close to 0.1 θ_D and occurs not only in the polar crystals belonging to 21 non-central symmetry classes, but also in some non-polar crystals that nevertheless exhibit a weak manifestation of polarity, for example, in Ge and Si, where a small minimum of $\alpha_V(T)$ is noticeable, as shown in Figure 10B. It is reasonable to assume that, at sufficiently low temperatures, thermal motion becomes weak enough for the self-organization of even very weak polar bonds to become significant. This suggests that even cubic covalent crystals may possess a certain tendency toward polar ordering. Such behavior may originate from a fluctuating polar motif that becomes appreciable only at low temperatures.



(A)

(B)

Figure 10. *Negative thermal expansion in polar ionic and weakly polar covalent crystals.*

(A) - polar crystals ZnO (1) and HgTe (2); (B) - covalent crystals Ge, Si, and C-diamond and layered crystal C-graphite [17].

The thermal expansion coefficient $\alpha(T)$ is an extremely sensitive parameter, which can vary by a factor of dozens in solids. The variability of $\alpha(T)$ depends on the rigidity of interatomic bonds, including the degree of ordering of polar bonds. The probable cause of the $\alpha(T)$ negative value in Si and Ge is the partial ordering of fluctuations in hexagonal (wurtzite) polar clusters formed by triple bonds of the Si≡Si type, sometimes appearing instead of the usual double bonds Si=Si. This assumption is based on the fact that the polar hexagonal form is sometimes found in a carbon crystal alongside the more common *m*3*m* diamond structure. Initially, the hexagonal carbon crystal was discovered in meteorites as "hexagonal diamonds"; later, they were synthesized in the laboratory. However, in diamond (Figure 10B), which has an extremely rigid structure and $\theta_D \sim 1900$ K, a negative $\alpha(T)$ value is not observed, since polar fluctuations are suppressed, while in much less rigid Si ($\theta_D \sim 600$ K) and Ge ($\theta_D \sim 360$ K) crystals weak self-organization polar effects with a negative $\alpha(T)$ value can occur.

It should also be noted that a hexagonal structure with polar fluctuations can be realized in graphite and graphene, the cell plane of which is characterized by negative $\alpha_1 = \alpha_2$ with a minimum at a temperature of ~ 200 K, Figure 10B. The ther-

mal expansion of graphite shows a minimum of $\alpha_1 = \alpha_2$ at approximately 200 K, since the stronger C=C double bond is much stronger than the C-C bond, which is responsible for α_3. In support of this hypothesis, it should be noted that the temperature minimum of thermal expansion in graphene is even deeper than in graphite, and α_{min} is also observed in carbon nanotubes at a temperature of 240 K. There is reason to believe that the negative value of the $\alpha(T)$ dependence in the low-temperature region is a common property of crystals with a low coordination number (i.e., with an open structure), which are characterized by a tetrahedral arrangement of atoms: in them, the ordering of polar-sensitive bonds becomes simpler. Conversely, in structures with close particle packing, the thermal expansion coefficient is usually positive.

Figure 11 illustrates a possible mechanism for "negative volume expansion" in polar crystals, whose structure exhibits a tendency toward self-organization of polar bonds under conditions of thermally chaotic crystal motion. At low temperatures, the crystal volume $V(T)$ initially increases, as usual, with increasing temperature (curve *1* in Figure 11), so the initial portion of the $\alpha(T)$ dependence is positive, as shown in the low-temperature portion of curve 4.

However, with further increases in temperature and the intensity of thermal vibrations, the disorder of the polar bond orientation also increases, so that the increment in $\Delta V(T)$ slows down, since it cannot follow curve *1* in Figure 11, which applies only to the ordered structure. The cessation of the increase in $\Delta V(T)$ affects its temperature derivative: the parameter $\alpha(T)$ decreases until it enters the negative region, curve 4 in Figure 11. In a disordered, more disordered structure, the potential temperature dependence of the volume increment $\Delta V(T)$ is described by curve 2'. Subsequently, as the temperature increases further, the increment in $\Delta V(T)$ changes in accordance with curve *2*, and therefore the usual increase in $\alpha(T)$, proportional to the cube of the temperature, is observed. Thus, transition region *3* in Figure 11 is formed, which corresponds to negative $\alpha(T)$.

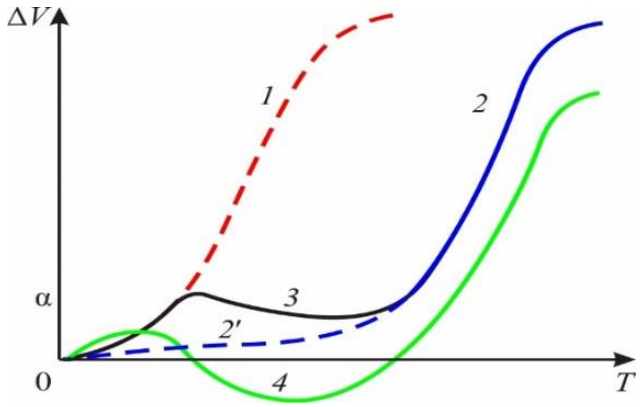


Figure 11. *Negative thermal expansion ΔV(T), 1 - covalent part of mixed bonding, 2 - ionic part of mixed bonding, 3 - transition region; 4 - thermal expansion coefficient;*

Thus, below the Debye temperature, with a further decrease in the intensity of thermal motion ("phonon freezing"), in polar-sensitive crystals the possibility of self-organization of polar bonds opens up (region *3* in Figure 11). As a result, as the temperature decreases, the crystal volume (instead of the usual decrease in correspondence with curve *2* in Figure 11) increases slightly, but not as sharply as in the case of a ferroelectric phase transition, rather very smoothly. Accordingly, a minimum in $\alpha(T)$ is observed in polar crystals, although not as sharply defined as in ferroelectrics.

6. Conclusions

Polar crystals are characterized by their ability to undergo electrical polarization under the influence of non-electrical factors: mechanical, thermal, optical, and others. They are capable of mutually converting mechanical, thermal, and electrical energy. Modeling and calculations show that the formation of a polar structure is facilitated by the anharmonicity of ion interactions, their increased charge, and large Lorentz factor of structure. The internal polarity of non-centrosymmetric crystals arises as a structural compensation for the different electronegativity of neighboring ions. Pronounced anisotropy reduces the coordination number of the polar crystal lattice and leads to its less dense structure. Moreover, the polarity of crystals is manifested in a wide range of their properties, not just in their electrical characteristics. The unique properties of polar and antipolar crystals are analyzed through experiments, modeling, and thermodynamics. These crystals have similar structures but exhibit opposite anomalies in both electrical and thermal and elastic properties due to the specific distribution of electron density in crystal lattice. This contributes to the formation of “soft” phonon modes of crystal lattice, the frequency of which critically decreases at phase transitions either in the center of Brillouin zone (→ creating polarity), or at its boundary or elsewhere in the zone (→ causing antipolarity).

Intrinsic polarity manifests itself as a gentle minimum of thermal expansion coefficient at a temperature of about 0.1 θ_D, but in ferroelectrics the sharp minimum of $\alpha(T)$ corresponds to the Curie point (in contrast, a sharp $\alpha(T)$ maximum is observed in antiferroelectrics). The increase in the volume of the polar phase of the crystal is due to a decrease in its symmetry (in contrast, volume of antiferroelectrics decreases). The heat capacity increase during the phase transition to the ordered polar phase is explained similar to magnons, i.e., by heat transfer dynamics of polar clusters (antiferroelectrics show heat capacity minimum in Curie point). The maximum of thermal diffusion at Curie point of antiferroelectric (instead of its minimum in ferroelectrics) is explained by the participation of optical phonons and the zeroing of the "soft" phonon mode not at the beginning (as in a ferroelectric), but in the middle of the Brillouin zone.

Abbreviations

ADP	Ammonium Dihydrogen Phosphate
DC	Direct Current
KDP	Potassium Dihydrogen Phosphate
NTE	Negative Thermal Expansion
TGS	Triglycine Sulfate

Author Contributions

Yuriy Poplavko: Conceptualization, Formal Analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing

Conflicts of Interest

The author declares no conflicts of interest.

References

[1] Lines, M. E., and Glass, A. M. Principles and application of ferroelectrics and related materials, Oxford, Clarendon Press, 1977.

[2] Burfoot, J. C. and Taylor, G. W. Polar dielectrics and their application, New Jersey, Macmillan Press, 1979.

[3] Uchino, K. Ferroelectric devices. New York, Marcel Dekker, 2000.

[4] Böer, K. W. and Pohl, U. W. Semiconductor Physics, Cham, Springer, 2023.

[5] Poplavko, Y. M. Electronic materials. Principles and applied science, Elsevier, 2019.

[6] Schlom, D. G., Chen, L.-Q., Eom, Ch.-B., Rabe, K. M., Streifer, S. K., and Triscone, J. M. Strain Tuning of Ferroelectric Thin Films. Annu. Rev. Mater. Res. 2007, 37, 589-626. https://doi.org/10.1146/annurev.matsci.37.061206.113016

[7] Liu, Z. K., Wang, Y., and Shang, S. L. Origin of Negative Thermal Expansion Phenomenon in Solids. Scripta Materialia. 2011, 65(8), 664-667. https://doi.org/10.1016/j.scriptamat.2011.07.001

[8] Rabe, K. M., Ahn, C. H., Triscone, J.-M. (Eds.), Physics of Ferroelectrics: A Modern Perspective. Springer, 2007.

[9] Lejček, P., and Školáková, A. Grain Boundary Configurational Entropy: A Challenge. Journal of Materials Science. 2023, 58, 10043–10057. https://doi.org/10.1007/s10853-023-08634-w

[10] Tiwtusthada, S., Saelee, T., Khajondetchairit, P., Rittiruam, M., Praserthdam, P., and Praserthdam, S. The Development of Configurational Entropy Formulation for High-Entropy Oxides: Review and Outlook. Journal of Alloys and Compounds. 2025, 1037, 182599. https://doi.org/10.1016/j.jallcom.2025.182599

[11] Poplavko, Y. M., and Pereverzeva, L. P. Pyroelectricity of Partially Clamped Piezoelectrics. Ferroelectrics. 1992, 130, 361. https://doi.org/10.1080/00150199208221444

[12] Dimarova, E. N., Poplavko, Y. M. Electrical Bias Field Influence on Ferroelectrics Thermal Conductivity. Izvestia AN SSSR, Serial Phys., 1967, 31(11), 1842.

[13] Strukov, B. A. Heat Capacity in TGS Single Crystal. Solid State Physics (Russian). 1963, 6(9), 2862.

[14] Zavorotny, V. F., Poplavko, Y. M., Pasechnik, L. F. Diffusion of Heat in KDP-type Ferro- and Antiferroelectrics. Solid State Physics (Russian, St. Petersburg), 1993, 35, 2832.

[15] Poplavko, Y. M. Dielectric Spectroscopy of Electronic Materials. Applied Physics of Dielectrics. Elsevier, 2021.

[16] Kittel, C. Introduction to Solid State Physics, 5th ed. New York, John Wiley, 1976.

[17] Martienssen, W., and Warlimont, H. (Eds.) Handbook of Condensed Matter and Materials Data. Berlin, Springer, 2005.

Biography

Yuriy Poplavko is a Ukrainian physicist and educator specializing in electronic materials science. Over the course of more than four decades, he has held academic positions in Ukraine, Portugal, and South Korea, with a longstanding affiliation at the National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute". Professor Poplavko is recognized for his contributions to the study of dielectrics, polar crystals, and ferroelectrics. He is particularly noted for pioneering the method of microwave dielectric spectroscopy, which has become a valuable tool in materials research. His scholarly output includes over 200 scientific articles and numerous books. Throughout his career, Poplavko has played a significant role in advancing the understanding of the physical properties of electronic materials, and his work continues to influence both theoretical and applied research in the field.