2

- The negative expansion in solids is influenced by self-ordering in the interior structure, which is common in polar and magnetic crystals.

- The effect is associated with the nature of **non-centrosymmetric** crystals which is caused by the difference in electroneutrality of atoms forming polar crystals.

- The negative expansion is specified by the **configurational entropy** due to the structural ordering in the pyroelectrics and ferroelectrics.

- The effect can be applied in thermal compensators as well as in the technology for controlling thin films with certain characteristics.

3

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Volume thermal expansion coefficient, defining as $\alpha_V = (1/V)\cdot(\partial V/\partial T)_p$, is sum of diagonal components of expansion tensor: $\alpha_V = \alpha_1 + \alpha_2 + \alpha_3$.

$$\boxed{\alpha_V = (1/V)\cdot(\partial V/\partial T)_p} \qquad \boxed{\rightarrow} \qquad \boxed{\alpha_V = \alpha_1 + \alpha_2 + \alpha_3}$$

– The obvious reason of solids thermal expansion can be justified microscopically, for example, by the model of ionic crystal.
– On the image You can see 2D depiction of the electric charge distribution in an ionic crystal (a); partial overlap of electron shells minimizes the attraction energy of ions (b); speckled curves signify interatomic forcefulness.
– The dependence of energy versus inter-atomic distance U(r) always is characterized by the asymmetric minimum, Fig. 1b. At lowest temperature, the bottom of potential well looks like symmetric parabola, so that, when temperature changes near absolute zero, r = a (lattice parameter). This interprets the reason of coefficient of thermal expansion of totally different solids tends to zero in the area of absolute zero, Fig. 2a. The negative energy of attraction forces of ions changes with distance rather slowly $(r^{-1} - r^{-4})$, while the positive energy of repulsion of ions electronic shells overlap changes very rapidly $(r^{-8} - r^{-12})$. The forming total energy minimum is sharply asymmetric, which leads to the anharmonicity of thermal vibrations of ions and to thermal expansion. Thus, thermal expansion is due to the anisotropy of inter-atomic potential relief.

4

· ① In this model, the average atom shift is ¡x¿ $= (b/c^2)\cdot k_B T$, as a result, the thermal expansion coefficient is defined as the ratio of the average shift $< x >$ to the equilibrium inter-atomic distance a: $\alpha = k_B b/ac$.

② The stronger the inter-atomic connections in a crystal, the more difficult it is to modify and destroy them. hence the higher the melting point, the smaller the thermal expansion: $\alpha_V \sim 1/T_{melt}$ [1] in this case, again, the positive value of α_V is expected

③ The Debye temperature θ_D characterizes the binding energy between atoms, so $T_{melt} \sim \theta_D^2$. Comparing with (2), we have: $\alpha_V \sim \theta_D^{-2}$, it leads to the conclusion that coefficient is expected to be a positive amount [2].

④ The Grüneisen law defines a state of equation for solids, considering inter-atomic forces anharmonicity and establishing the similarity of temperature dependence for α and specific heat $C_V : \alpha = \gamma \cdot C_V/3K$, where K is the bulk modulus (i.e., the modulus of compression), and γ is the Grüneisen constant.

· ⑤ Microscopic analysis reveals that α is a reciprocal of the slope of the curve expressing the dependence of binding energy on interatomic distance (a+x) at a location corresponding to an atom's time-average position: $dU(a+x)/d(a+x) \sim 1/\alpha$. Thus, the $\alpha(T)$ dependence is determined by the middle profile of U(r) dependence of a crystal, where U(r) is the sum of inter-atomic attraction and repulsion energies,

⑥ With increasing temperature, the shift of oscillating atoms to the left becomes smaller than the shift to the right. The time-average equilibrium location of an atom (a+x), as illustrated by the dotted line, changes to the right, and this effect grows larger as the energy of the atoms oscillations increases. All previous reasoning (1)-(6) testifies to a positive α. Next task is to explain the possibility of negative α(T).
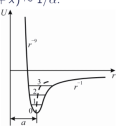
MAIN FEATURES OF THERMAL EXPANSION

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Negative Thermal Expansion in Polar Crystals   4/14

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– Negative alpha ¡ 0 senn in polar crystals corresponds to peculiar case, when entropy increases with pressure rise and it is possible only for configurational entropy.
– The reasons for "negative temperature expansion" are considered mainly on the example of polar crystals, due to the our own experimental data. Insofar as in certain temperature range $\alpha(T)$ takes negative value, so $\alpha(T)$ dependency double goes by through zero line, previously the transition to the usual for most crystals growth $\alpha(T)$ according to the law: α T^3, Fig. 2a.
– The explanation of negative α(T) is given in Fig. 3b. This behavior requires a particular nature of the attraction of ions in polar crystals, which happens due to merger of ionic and covalent bonds; as a result of which they become polar. It is this that leads to specific profile of the attraction energy, which in the polar crystal decreases much more slowly with inter-atomic distance r than usual for the ionic crystals law ($U \sim r^{-1}$). Thus, at low enough temperature, the polar

NEGATIVE THERMAL EXPANSION MODELING

Negative thermal expansion: [a] - minimum and saturation on $\alpha(T)$ dependence;
[b] - symbolic explanation of negative α: 1 – repulsion energy, 2 – polar bonds attraction energy, 3 – non-polar attraction energy, 4 – average dynamic position oscillating particles

$$\alpha \sim T^3$$

Negative Thermal Expansion in Polar Crystals   5/14

crystal is characterized by an additional attraction of dipole-dipole type, which expands the bottom of total energy minimum (recall that fundamentally the polarity of crystal is due to a different electronegativity of neighboring atoms).
– Therefore, the inter-ionic distance (curve 4 in Fig). At that, with increasing temperature, the energy increases in accordance with the climbing steps of horizontal lines, Fig. First it a little increases in the aria, where the dipole-type attraction prevails, so $dr/dT > 0$ and $\alpha > 0$, Fig. Then, as the dipole-type attraction weakens (due to the increase of inter-ionic distance), thermal deformation, shown by curve 4, changes its sign to the negative: $dr/dT > 0$, because the attraction becomes weakened (usual for ionic crystal) so $\alpha < 0$ only in the aria of such transition.
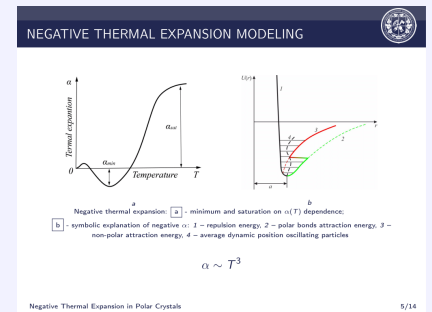
.
In the ideal case, theoretical explanation of negative $\alpha(T)$ needs justify the following reasons:

- physical substantiation of polar non-centrosymmetric crystals existence;

- matching negative $\alpha(T)$ with thermodynamic theory;

- explanation of special $\alpha(T)$ dependence, which twice changing its sign when crossing temperature axis.

NEGATIVE THERMAL EXPANSION EXPLANATION

In the ideal case
○ physical substantiation of polar non-centrosymmetric crystals existence;
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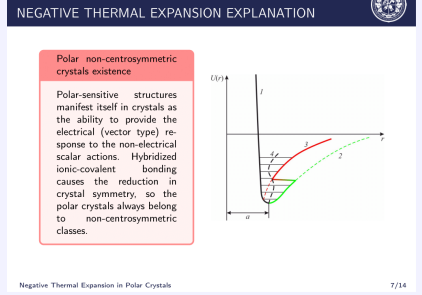
Negative Thermal Expansion in Polar Crystals   6/14

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– Polar-sensitive structures manifest itself in crystals as the ability to provide the electrical (vector type) response to the non-electrical scalar actions. Hybridized ionic-covalent bonding causes the reduction in crystal symmetry, so the polar crystals always belong to non-centrosymmetric classes.

– Moreover, exactly presence of such bonds determines the non-centrosymmetric structure of crystals. Hybridized ionic-covalent bonding is a main cause of the pyroelectric and piezoelectric properties.

– Used in Fig. 3b model is based on the asymmetry in electronic density distribution along the atomic bonds that ensures the ability of a crystal to its polar (electrical) response onto the non-electrical action.

NEGATIVE THERMAL EXPANSION EXPLANATION

Polar non-centrosymmetric crystals existence

Polar-sensitive structures manifest itself in crystals as the ability to provide the electrical (vector type) response to the non-electrical scalar actions. Hybridized ionic-covalent bonding causes the reduction in crystal symmetry, so the polar crystals always belong to non-centrosymmetric classes.

Negative Thermal Expansion in Polar Crystals 7/14

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– The configurational entropy arises as the part of total entropy of a system, which, in addition to kinetic energy of particles, is characterized by the different positions of the groups of particles. – Such contribution to the entropy corresponds to the number of ways of particles mutual arrangement, maintaining some overall set of specified system properties. In this case, the change in the configurational entropy corresponds to the same change in total entropy. To explain the negative $\alpha(T)$ seen in certain temperature range, use the Gibbs function, which is isobaric-isothermal thermodynamic potential eq.(1). – which shows what part of total internal energy of system can be used in the transformations under given conditions.

$$G = U + pV - TS \tag{1}$$

where U is internal energy, p is pressure and S is entropy.
In studied case of a system with constant number of particles, Gibbs energy differential is expressed as:

$$dG = -SdT + Vdp \tag{2}$$

Parameter

$$\alpha = (\partial V/\partial T)_p/V$$

is defined at constant pressure, so the change in volume of a system defined through Gibbs potential at constant temperature, is:

$$V = (\partial G/\partial p)_T \tag{3}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial(\partial G/\partial T)}{\partial p}\right) = \frac{-1}{V}\left(\frac{\partial S}{\partial p}\right)_T \tag{4}$$

– Obtained expression means that entropy is the less the greater is pressure, and this correlation corresponds to the thermal expansion, normally observed in the most of solids where $\alpha > 0$.
– On the contrary, in the dynamically ordering systems, for example, in the polar crystals, there is a certain temperature interval, where the coefficient $\alpha < 0$. This means the increase in entropy with increasing pressure. Such unusual characteristic of polar crystals requires the concept of configurational entropy due to a number of microscopic configurations.

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– Explanation of special $\alpha(T)$ dependence, which twice changing its sign when crossing temperature axis.
–Anomalous dependence of temperature deformation, although it has similar cause, in different crystals manifests itself in different ways. but it is too comlicated to explain it all in once, so it will be explained in the next few sections.

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– In solids, the discussion about negative $\alpha(T)$ should be started with thermal deformation of the ferroelectrics and antiferroelectrics, which show the opposite $\alpha(T)$ anomalies in the vicinity of phase transitions T_c, Fig. (left) The volume of lower-temperature partly ordered phase increases in ferroelectrics as compared to the volume of higher-temperature mostly disordered paraelectric phase.
– The application of hydrostatic pressure on, for example, Ferroelectrics such as BaTiO3(Barium titanate), below its Curie point (i.e., in the polar phase) converts it to the paraelectric (non-polar) phase, which has a higher configuration entropy. The rate of a decrease in T_c, with increasing pressure is - 5 K/kbar , so that at the pressure of 3 GPa at room temperature the polar phase in BaTiO3(Barium titanate) already disappears - it is "squeezed out" by pressure Figure(on the right side) which explains symbolically these processes, that are fully consistent with the concept of configurational entropy.

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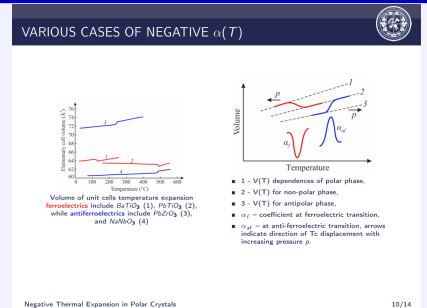
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In the semiconductors, the negative $\alpha(T)$ are observed among crystals, which have the chain and layered structures [3]. Chain crystals include rhombohedral tellurium and selenium, both of which belong to the class 32 polar-neutral piezo-electrics (same as quartz).

In a Te crystal, for example, the coefficient of transverse thermal expansion is positive: $\alpha_1 = \alpha_2 = +27 \cdot 10^{-16} K^{-1}$, but along the chains it is negative: $\alpha_3 = -1.6 \cdot 10^{-6} K^{-1}$. In Te and Se crystals, the Te–Te (or Se–Se) helical chains are elongated along the broad axis 3. Because of the significant anisotropy a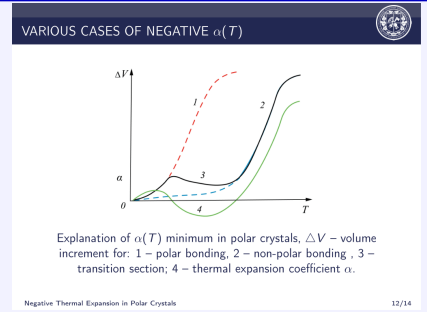nd the negative value of α_3, the interatomic bonds between the chains are considerably stronger than the interaction between the chains. When heated, the crystal compresses in three directions but swells in the transverse directions.

VARIOUS CASES OF NEGATIVE $\alpha(T)$

Typical for ferroelectric $\alpha(T)$ dependence: 1 – $KD2P04$; 2 – TGS ($NH_2CH_2COOH)_3 \cdot H_2SO_4$; 3 – $BaTiO_3$ ceramics.

In a Te crystal, the coefficient of transverse thermal expansion is positive: $\alpha_1 = \alpha_2 = +27 \cdot 10^{-16} K^{-1}$, but along the chains it is negative: $\alpha_3 = -1.6 \cdot 10^{-6} K^{-1}$. In Te and Se crystals, the Te–Te (or Se–Se) helical chains are elongated along the broad axis 3.

Negative Thermal Expansion in Polar Crystals   11/14

13

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– Many semiconductors are the polar crystals: sphalerite, (which is piezoelectric) structure have $A^{III}B^V$ compounds, while to the wurtzite (pyroelectric) symmetry belong $A^{II}B^{VI}$ crystals. So in these crystals the presence of $\alpha(T)$ low-temperature minimum is unsurprising. When the temperature drops, the thermal chaotic motion freezes, allowing some ordering of polar bonds to exist. As a result, the volume of a crystal gradually grows with decreasing temperature.

– At that, the configurational entropy decreases, demonstrating $\alpha(T)$ minimum, Fig. 9 (but a very shallow, not as deep as in the ferroelectrics). When several data points with polar crystal temperature characteristics are compared, there is reason a to think that when temperature falls below a specific threshold, the intensity of thermal oscillations becomes so weak that self-ordering of polar bonds begins, gradually leading to their strengthening. As a result, when the temperature drops, the volume of a crystal increases somewhat, resulting in the negative sign of $\alpha(T)$. The above evidence allows us to conclude that the negative value of thermal expansion coefficient at low temperatures in polar crystals is caused by a partial ordering of polar-sensitive bonds.

VARIOUS CASES OF NEGATIVE $\alpha(T)$

Explanation of $\alpha(T)$ minimum in polar crystals, $\triangle V$ – volume increment for: 1 – polar bonding, 2 – non-polar bonding , 3 – transition section; 4 – thermal expansion coefficient α.

Negative Thermal Expansion in Polar Crystals   12/14

13

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 ☆ It is demonstrated that $\alpha(T)$ is the reciprocal of the slope of the curve expressing the dependence of binding energy on inter-atomic distance at the point corresponding to an atom's time-average location.

 ☆ It is thought that polarity in some crystals is caused by structural compensation for the differing electronegativity of surrounding atoms.

 ☆ It is shown that the negative value of $\alpha(T)$ corresponds to such a circumstance in which the entropy increases with rising pressure: this is a feature of configurational entropy.

 ☆ It is suggested that the area of negative $\alpha(T)$ is caused by polar bond self-ordering, which results in an increase in crystal volume.

 ☆ In ferroelectrics, the volume of polar phase increases in comparison with paraelectric phase, so $\alpha(T)$ shows a deep minimum while phase transition shifts to low temperature when pressure rises.

VARIOUS CASES OF NEGATIVE $\alpha(T)$

Explanation of $\alpha(T)$ minimum in polar crystals, $\triangle V$ – volume increment for: 1 – polar bonding, 2 – non-polar bonding , 3 – transition section; 4 – thermal expansion coefficient α.

Negative Thermal Expansion in Polar Crystals   12/14

And also

 ☆ I would like to add that, On the contrary, in antiferroelectrics the volume of antipolar phase decreases as to paraelectric phase, so $\alpha(T)$ shows big maximum, and the phase transition shifts to higher temperature.

 ☆ The suggested notion is extended to semiconductors with $\alpha(T)$ minimums: it may be assumed that polar inclinations, which fluctuate in the structure, become stable at lower temperatures.