



NEGATIVE THERMAL EXPANSION IN POLAR CRYSTALS

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Abstract

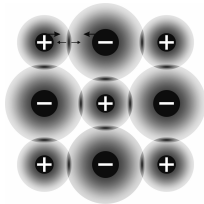
- The negative expansion in solids is influenced by self-ordering in the interior structure, which is common in polar and magnetic crystals.
- The effect is associated with the nature of **non-centrosymmetric** crystals which is caused by the difference in electroneutrality of atoms forming polar crystals.
- 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.

THERMAL EXPANSION

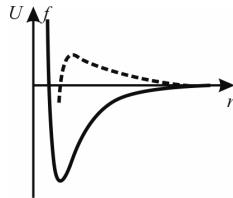
$$\alpha_V = (1/V) \cdot (\partial V / \partial T)_p$$



$$\alpha_V = \alpha_1 + \alpha_2 + \alpha_3$$



a



b

Figure 1: 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.



MAIN FEATURES OF THERMAL EXPANSION

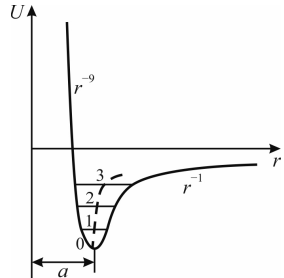
- ① In this model, the average atom shift is $\langle x \rangle = (b/c^2) \cdot k_B T$.
- ② The stronger the inter-atomic connections in a crystal, the more difficult it is to modify and destroy them.
- ③ The Debye temperature θ_D characterizes the binding energy between atoms, so $T_{melt} \sim \theta_D^2$.
- 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 : $\alpha = \gamma \cdot C_V/3K$.



MAIN FEATURES OF THERMAL EXPANSION

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: $dU(a+x)/d(a+x) \sim 1/\alpha$.

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.



NEGATIVE THERMAL EXPANSION MODELING

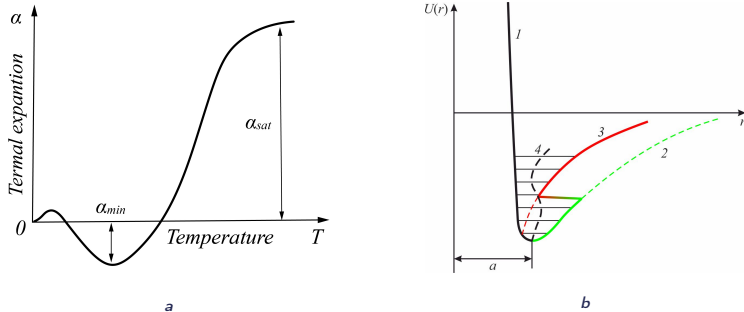


Figure 2: Negative thermal expansion: **a** – minimum and saturation on $\alpha(T)$ dependence; **b** – symbolic explanation of negative α : 1 – repulsion energy, 2 – polar bonds attraction energy, 3 – non-polar attraction energy, 4 – average dynamic position oscillating particles

$$\alpha \sim T^3$$



NEGATIVE THERMAL EXPANSION EXPLANATION

In the ideal case

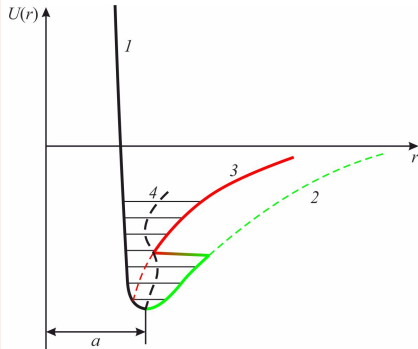
- physical substantiation of polar non-centrosymmetric crystals existence;
- matching negative $\alpha(T)$ with thermodynamic theory;
- explanation of special $\alpha(T)$ dependence, which twice changing its sign when crossing temperature axis.



NEGATIVE THERMAL EXPANSION EXPLANATION

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 EXPLANATION

Matching negative $\alpha(T)$ with thermodynamic theory;

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.

To explain the negative $\alpha(T)$ seen in certain temperature range, use the Gibbs function, which is isobaric-isothermal thermodynamic potential eq.(1).

$$G = U + pV - TS \quad (1)$$

$$dG = -SdT + Vdp \quad (2)$$

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

$$V = (\partial G / \partial p)_T \quad (3)$$

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

