

SOLID TRANSFORMATIONS AS A VARIANT OF THREEDIMENSION NANOTECHNOLOGY

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ABSTRACT

The given article discusses a variant of natural nanotechnology in a volume material under solid-phase transformation. The article provides results on acoustic splitting in ammonium oxide NH_4ClO_4 in the low-temperature region. Ammonium oxide NH_4ClO_4 is structurally complex and chemically unstable. It has been stated that splitting of an acoustic wave in ammonium perchlorate under acoustical spectroscopy clearly detects coexistence of centrosymmetrical and noncentrosymmetrical phases. So, by example of ammonium perchlorate we consider possible use of acoustic splitting as a method of onset registration and growth control of a new phase within the parent one.

Key words: solid transformations, nanotechnologies, thermodynamic ambiguity, ammonium perchlorate.

INTRODUCTION

In the recent years words “nanoscience”, “nanotechnology”, “nanomaterials” sound as an overture to innovations. At the same time many previous achievements are being revised from this modern and, in many cases, justified point of view. As an example we can remember soot of the recent past and nanopowder of the present day. The given work can be attributed to the second of the named research areas and its idea is that solid transformations are anomalous properties. Nonequilibrium state of electron, dipole, spin or phonon subsystem of a solid together with the size factor result in lattice lability and practically important, sometimes unique properties which develop in the substance under certain temperature and pressure.

However, we should admit that in solid body technologies there are a lot of “white” spots, for example, we don’t quite understand the mechanisms of onset and consecutive growth of new phases within the parent phase under the phenomenon of “polymorphism”. The most widespread theories about polymorphous transformation going simultaneously in the whole amount of the solid body under elastic deformation have not been confirmed experimentally. The presence of an extended area instead of a line (which is characteristic for usual phase first- and second- order transitions) at the real phase diagram (*fig.1*)

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supposes existence of a complex heterogeneous structure made up of nanoregions with fluctuating or “frozen” order parameter.

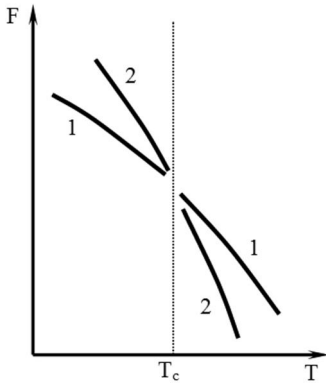


Fig. 1 – “Thermodynamic uncertainty” in the hysteresis area under the phase transition (F – free energy, T – absolute temperature)

electric-antiferroelectric under the polymorphous transformation form non-traditional state of the substance for which the most suitable name will be dipole glass [2]. The characteristic feature of this state is random distribution of nanometer regions with “frozen” local polarization in the crystals.

Obvious interest to the nanocondition of a solid in a natural compact state is limited in diagnostic methods. In work [3] we described the effect of acoustic splitting as an experimental fact of coexistence of two structures of a substance. Potassium nitrate (KNO_3) was used to show that there are two speeds of propagation for a wave of one type under similar ambient conditions. The given report provides results on acoustic splitting in a complex ammonium oxide (ammonium perchlorate, NH_4ClO_4), which structural and chemical instability was described before [4].

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

Fig. 2 shows the low-temperature spectrum of speed and longitudinal waves damping (internal friction Q^{-1}) in the polycrystal of NH_4ClO_4 received by the method of two-part piezoelectric vibrator at the frequencies ≈ 100 kHz.

When cooling ammonium perchlorate samples from room temperature at about $T = 175$ K the derivative changes its sign du/dT . Under the further decrease of temperature $\nu \rightarrow 0$ when approaching the temperature of liquid nitrogen the “secondary” sound is registered twice – near $T \approx 135$ K and $T \approx 95$ K, i.e. two resonances appear instead of one resonance of the acoustic vibrator. Parallel data on the changes of $Q^{-1}(T)$ at the temperature scale show that absorption of one

Almost 80 years ago academician V.D. Kuznetsov stated an idea in his monograph [1] that under polymorphous transformations “there are moments when transition from one phase into another has not yet been completed and the substance is simultaneously (emphasis added) in its two crystalline modifications”. Such structural crystalline states don’t have a generally accepted name yet and are found in literature under the names of diffuse phase transitions, hybrid crystals, fluctuation of symmetry, structurally-mixed phases, spatially heterogeneous condition, phase mixture, coexisting phases, order-in-disorder (or vice versa) and other. Some crystals of mixed composition, for example, ferroelec-

acoustic wave in the sample of ammonium perchlorate increases and absorption of the second wave decreases. Although both forms of NH_4ClO_4 under low temperatures are orthorhombic, they have different space groups – P_{nma} и $P_{n21/a}$ due to the different environment of ammonium ions in ammonium perchlorate lattice. The corresponding ions are denoted as $\text{NH}_4(1)$ and $\text{NH}_4(2)$.

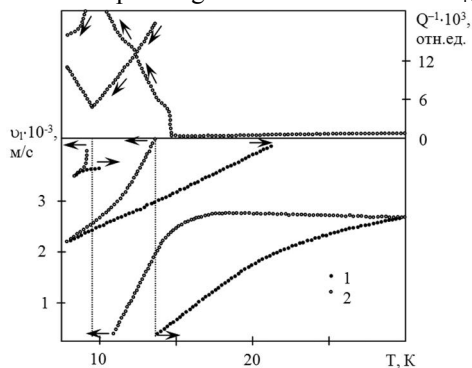


Fig. 2 – Low-temperature changes of ultrasonic speed and internal friction in the polycrystal NH_4ClO_4 . Modes: 1 – heating, 2 – cooling

different speed (one of the cations is less mobile). The sound begins to spread in one as well as in the other group of cations. This is the qualitative interpretation of existence of two sound velocities in one and the same substance under the same conditions. At the reversal of temperature (defrosting) the acoustic diagram is reproduced but it has a significant hysteresis effect – dv/dT sign changes only near the room temperatures (fig. 2 shows the change of $Q^{-1}(T)$ only when cooling).

The observed peculiarities of $v(T)$ and $Q^{-1}(T)$ in NH_4ClO_4 under low temperatures correspond to some results in works [5-13]. Anomalies of some lattice and inner modes of ions ClO_4^- и NH_4^+ near 180 and 40 K in the temperature spectra of Raman scattering in monocrystals of ammonium perchlorate [10]; overlapping of infrared fringes under $T \approx 200$ K [11], appearing of v_1 fringe under 120 K and splitting of forced oscillation fringes v_3 и v_4 of ammonium ion under $T < 50$ K [9]; splitting lines 635 cm^{-1} (oscillation v_4 of ClO_4^- ion) near the temperature of liquid nitrogen [12], abnormal change of quadrupole interaction constant for the atoms of ^{35}Cl in NH_4ClO_4 under the temperatures 200 and 20 K [13] and direct X-ray diffraction study [8] give non-linear temperature dependences of all parameters of ammonium perchlorate lattice.

Fig. 3 shows the parallel results of low temperature X-ray diffraction studies of dimensional changes of elementary ammonium perchlorate lattice in two works [8 and 10].

The first of them has five perchlorate ions and the second has six perchlorate ions (in both phases). Existence of two types of ammonium ions in ammonium perchlorate under low temperatures can be the cause of the observed acoustic splitting. When the ammonium perchlorate crystal is cooled ammonium ions are of the same type until the temperature of 200 K. Below this temperature $\text{NH}_4(1)$ and $\text{NH}_4(2)$ appear. They reorient in the lattice with

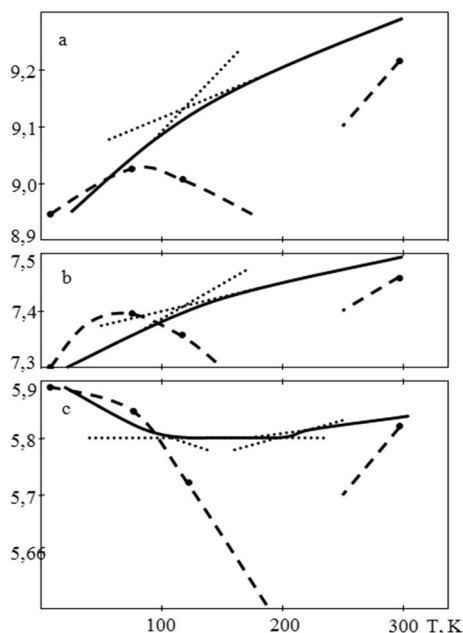


Fig. 3 –Low-temperature changes of lattice parameters a , b and c (in Å) of NH_4ClO_4 monocrystal (full line – the data [8], dashed-dot line – the results [10], averaging and approximation of the data [8] have been done by the authors)

The dynamics of changes in linear dimensions of the ammonium perchlorate lattice appears to be especially impressing as shown by the authors [8] who were completing precise measuring of the lattice parameters in the cooling and heating modes (we provide these data in smoothed form with our own approximation of linear parts of functions $a(T)$, $b(T)$, $c(T)$). Fig. 3 shows that qualitative structural studies of different authors correspond: structural ammonium perchlorate lattice anomalies are grouped near 200 and 100 K. Non-linear change of unit cell parameters near 200 K is caused mainly by parameter c anomaly, and near 100 K all three lattice parameters behave anomalously: at curves $a(T)$ and $b(T)$ we register a knee with a change of quantities da/dT and db/dT (below 120 K the derivatives increase) and derivative dc/dT changes its

sign (below 120 K in direction c (across the layers) the unit cell begins to expand with the decrease of temperature). In the interval $120 \div 298$ K in work [10] the measurements are not completed but the authors note that lattice parameters in similar systems (NH_4IO_4 , NH_4ReO_4) form an arc with an extremum under 200 K and temperature spectra of Raman scattering have pronounced anomalies under 180 K. Comparing our results (fig. 2) and thorough X-ray diffraction and spectroscopic studies of NH_4ClO_4 lattice (fig. 3) we can state coinciding anomalies of acoustic and structural parameters under the temperatures near 100 and 200 K and consider that under the given temperatures we observe transformation corresponding to two isostructural phase transitions.

In ammonium salts structural order or disorder under low temperatures is usually associated with cation reorientation [5]. Orientation ordering (disordering) of some ammonium ions in ammonium perchlorate lattice is represented as follows. In every unit cell with NH_4^+ ion in its middle the connections $\text{N} - \text{H}$ are directed to the neighbouring chlorate ions.

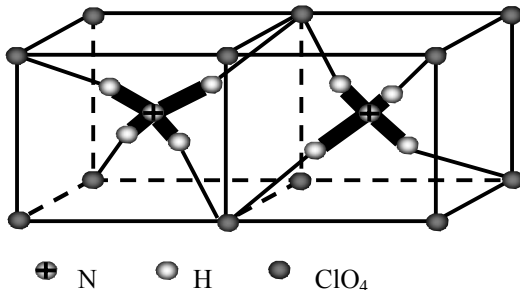


Fig. 4 – Two orientations of ammonium ion NH_4^+ in ammonium perchlorate lattice [14]

In this case every ammonium ion has two possible orientations (fig. 4). In the ordered form under the low temperatures all ions have the same parallel orientation which makes the system an analog of a ferroelectric or a ferromagnetic. With the rise of temperature the ions are disordered along two possible orientations mentioned above which are open for each of them (the collection of unit cells in this phase possesses an effective centre of symmetry) [5].

RESULTS AND DISCUSSION

Splitting of an acoustic wave in ammonium perchlorate under acoustical spectroscopy clearly exposes the coexistence of centrosymmetrical and non-centrosymmetrical phases. Thus, having taken ammonium perchlorate as an example we have considered the possible use of acoustic splitting as a means of onset registration and growth control of a new phase within the parent one. As for the nanoscale we don't exclude that it is the so called secondary structure that is realized under polymorphic transformations ("minimum crystal", "crystal quantum", the minimal size when the crystal keeps its form unchanged: $10^7 \div 10^8$ m). The secondary structure under the usual states of a real crystal is considered to be supplementary to the atom-molecule structure of the substance [15]. In our case it is possible to regulate the dimensions of the secondary structure by changing the time of polymorphic transformation. Another aspect of the problem marked by us is that polymorphic transformation and other solid body reactions where the key role is played by the onset of a new phase can serve as models for studying (yet fragmentary) mechanism of forming bulk materials nanostructures even taking into consideration that the problem of polymorphic transformation itself is far from satisfactory solution. It is appropriate to consider the onset of a new phase on the defects of parent matrix, kinetic and morphological peculiarities, the size factor and other problems of nanosystems physicochemistry in the context of polymorphism.

CONCLUSIONS

Of course, study of the structural forms of a nanometer scale substance in its pre- and posttransition states is not limited by the method of acoustical spec-

trospecty. For example, another classical method of diffuse X-ray scattering in a “classical” object – quartz under the “classical” $\alpha \rightarrow \beta$ -transformation ($T_c \approx 576^\circ\text{C}$) suggests describing the transition from trigonal to hexagonal form in three stages: 1) preparation for the transformation (from 300°C to $540\text{--}560^\circ\text{C}$), 2) transformation itself, so to say, “culmination” ($560\text{--}580^\circ\text{C}$), and 3) completion ($580\text{--}700^\circ\text{C}$) [16]. Meanwhile, it is noted that changes in the Laue maximums ratio are observed in the experiment under the temperature of 100°C , and on the other hand under T_c full symmetry C_6 is not observed yet. Another thing is that acoustical methods allow to register phase transitions of any nature (speed sensitivity is $\Delta v/v \approx 5 \cdot 10^{-7}$).

However, for the natural nanotechnologies in bulk material the first place is probably occupied not by the method but by the object. Mesoscopic materials of a new type with complex molecules ($\text{Sn}(\text{CH}_3)_4$ и $\text{Fe}(\text{CO})_5$) demonstrating nano-effects in bulk are considered with application of Mössbauer effect in work [17].

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