

Reduction of longitudinal ultrasonic oscillations in NaClO_3 crystals

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Abstract. The authors study reduction of longitudinal ultrasonic oscillations (internal friction Q^{-1} and logarithmic decrement δ) in NaClO_3 crystals within the temperature range of 78 – 525 K and relative amplitudes of oscillatory deformation of $10^{-7} - 10^{-5}$ according to the method of compound piezoelectric vibrator at the frequencies of $\approx 10^5$ Hz. Q^{-1} maximums under the temperatures of 110 K, 240 K, 260 K, ≈ 400 K and its fast growth under the temperature over 500 K are revealed as well as athermic peak of δ in the region of small deformation amplitudes (near 10^{-7}).

1. Introduction

Elastic waves in solid bodies are characterized by reduction and propagation velocity. Measurements of these parameters allow studying the impact produced upon the elastic waves by any solid properties associated with the lattice of the solid. At present time over a dozen of various types of interactions, influencing elastic waves propagation, have been estimated [1, 2]. If in the process of dynamic testing of an elastic body, as, for example, with ultrasound application, the changes of mechanical stresses and deformations are not co-phased, then, in the inelastic body some amount of the input energy is always spent not on the deformation itself but on other various processes in the lattice and finally turns into (internal friction causing reduction of elastic vibrations). As the measure of internal friction we take the loss tangent $\text{tg}\varphi$ (φ – angle of deformation lagging stress in phase); value Q^{-1} , reciprocal to mechanical Q-factor of the system executing forced oscillations; logarithmic decrement of decaying oscillations δ and decay ratio α_λ of the elastic wave with the length λ , propagating in the solid body. The value of internal friction depends upon the frequency and the amplitude of applied stress and the innumerable measures are related to each other with the ratio [3]:

$$\text{tg}\varphi = Q^{-1} = \delta/\pi = \alpha_\lambda \lambda / \pi. \quad (1)$$

As a rule, various mechanisms causing decay of vibrations are divided into relaxation, resonance and hysteresis [4]. Under the periodic deformation of the solid body all mechanisms reveal themselves to some extent but their contribution to the process of vibration decay is different. When the frequency of oscillations changes from infrasound to hypersound we obtain a number of peaks (maximums) on the curve of internal friction of the real crystal. This kind of Q^{-1} curve with maximums, by analogy with the theory of light, is sometimes called the “mechanical” absorption spectrum. It is impossible to create a method which would allow measuring the internal friction continuously in the interval of



frequencies from 10^{-4} to 10^{11} Hz. That is why the experiments were carried out with the application of a number of methods where the frequencies overlapped each other. The experimental difficulties of Q^{-1} measuring in a wide interval of frequencies are often compensated by an indirect technique, namely – by obtaining the dependence of the internal friction upon the temperature. Curve $Q^{-1}(T)$ is often called “thermal spectrum” for short [4].

At the present moment it is estimated that in ion monocrystals for the frequency range $\sim 10^5$ Hz the basic contribution to the internal friction is made by dislocation mechanisms (for example, decay determined by the thermoelastic effect, for metals makes about 50% of general decay, and for semiconductors and non-conductors its contribution to general decay does not exceed several per cent [1]). Internal friction can be determined by two different phenomena: inelasticity and plastic deformation of the system. Inelasticity is characterized by amplitude-independent parameters of a part of deformation energy input into the system. Plastic deformation, as distinguished from inelasticity, is a function of amplitude of deformation of the studied macroscopic system.

Systematic study of internal friction in the kilohertz range of frequencies in the crystals of A_1B_7 type (alkali halide crystals with ionic bond) was completed by S.P. Nikanorov and B.K. Kardashev [5]. In the course of theoretical analysis of experimental data the given authors studied the role of Peierls barrier and the role of fields of force of point defects of different origin under thermally activated oscillating motion of dislocations near the equilibrium state. According to the results of measurements of the amplitude-dependent absorption of ultrasonic oscillations the authors unambiguously proved that in the stress field of the ultrasonic waves the dislocations dissipate the energy of oscillations at the same obstacles which play an important role in formation of the stress level of the flow. It is of interest to obtain the data on internal friction in crystals with significant covalent component of the interatomic bond. The crystal of sodium chlorate (NaClO_3) is one of such objects.

2. Theory

In the non-conducting crystals for one of extreme cases of interaction in the region $\omega\tau \ll 1$ (ω – circular frequency, τ – time of thermal relaxation of phonons) absorption of ultrasound is determined mainly by phonon-phonon interaction according to Akhiezer mechanism [6]. This mechanism works as follows. When the acoustic wavelength is considerably larger than the free length of thermal phonons ($\omega\tau \ll 1$), the sound wave causes macroscopic deformation which leads to changing frequency $\omega_l(k)$ of the given oscillation mode. In its turn, change of frequency leads to the change of the function of phonon energy distribution. Sound wave dissipation is related to the fact that elastic modulus which the system of thermal phonons contributes to, relaxes, with the absorption ratio described by the formula:

$$\alpha = \frac{\Delta c \tau \omega^2}{2\rho v^3}, \quad (2)$$

where Δc – difference of non-relaxed and relaxed elastic moduli, ρ – density, v – sound velocity.

It is possible to think, as Mason did in his time [6], that phonon contribution into the non-relaxed modulus is determined by changing thermal phonons energy due to changing the boundary Debye frequency in the field of ultrasonic wave deformation. Then, in an isolated situation of longitudinal wave we obtain the following expression for the non-relaxed modulus

$$c_{11}^{\text{np}} = c_{11} + 3 \sum_i \varepsilon_i (\gamma_i^{11})^2, \quad (3)$$

where c_{11} – elastic modulus in harmonic approximation, ε_i – thermal energy of i -th phonon branch. Grüneisen ratio γ_i^{jk} for the i -th phonon branch in Debye approximation is calculated according to Bragger's formula [6]

$$-\gamma_i^{jk} = p_j p_k + \frac{\ell_p \ell_q}{c} (c_{jkpq} + p_r p_s c_{jkprqs}), \quad (4)$$

where p_j – direction cosine of displacement vector, ℓ_p – direction cosine of wavevector (indices p, q, r, s are related to phonons, j, k – to the sound wave), c_{jkpq} – rigidity second-order constants, c_{jkprqs} – rigidity third-order constants, c – elastic modulus actual for phonons.

In the process of equilibration between various phonon branches the elastic modulus relaxes to its equilibrium value which equals

$$c_{11}^p = c_{11} + \bar{\gamma}^2 c_v T, \quad (5)$$

where $\bar{\gamma}$ – Grüneisen constant, T – temperature, c_v – heat capacity of a volume unit. Absorption constant according to (2) under the condition of equality $\Delta c = c_{11}^{hp} - c_{11}^p$ is transformed to

$$\alpha = \frac{\left[3 \sum_i \varepsilon_i (\gamma_i^{11})^2 - \bar{\gamma}^2 c_v T \right] \omega^2 \tau}{2 \rho v^3}. \quad (6)$$

In work [7] Mason formula (6) was analyzed in respect to the calculation of phonon absorption of the ultrasound in the crystals of alkali metals halogenides. To coordinate the calculated and experimental values of α in this case the necessity arises to consider the defect of Δc modulus in quasi-harmonic approximation supposing that the amount of phonons N_i of every type of oscillations remains constant until relaxation and internal energy change is determined only by the changes of ion oscillation frequencies. The difference between the non-relaxed and relaxed elastic moduli appeared to equal

$$\Delta c = T \sum_i c_i \gamma_i^{jk} \gamma_i^{\prime m} - \frac{T}{c_v} \sum_i c_i \gamma_i^{jk} \sum_i c_i \gamma_i^{\prime m}. \quad (7)$$

3. Calculation ratios

Study of inelastic properties of NaClO_3 monocrystal was completed in two variants. Amplitude-independent internal friction within the temperature interval 77 – 525 K at the frequencies of ≈ 100 kHz was studied by the “half-width” of the resonance curve

$$Q^{-1} = \frac{\Delta f}{f_p}, \quad (8)$$

where Δf – interval of frequencies between the resonance curve points, corresponding oscillation amplitudes equaling to 0.707 of the maximum amplitude, and f_p – resonance frequency. Description of the unit and details of the experimental method for this case are provided in monograph [8].

Amplitude-dependent internal friction was studied under the same frequencies and discrete temperatures of 300, 400 and 500 K with application of an electric acoustic unit with load resistance of $R = 1,2$ kilohm, similar to that described in [5]. Logarithmic decrement δ was taken as a measure of internal friction, and it was found as

$$\delta = \left(\frac{2bd_{12}}{s_{22}} \right)^2 \frac{R_3}{f_p m_b}, \quad R_3 = R \left(\frac{U}{U_R} - 1 \right), \quad (9)$$

and amplitude of relative oscillative deformation of the sample was calculated according to the formula

$$\varepsilon = \frac{s_{22}}{2bd_{12}\ell_0 f_p} \cdot \frac{U_R}{R}. \quad (10)$$

Here b , d_{12} , s_{22} and f_p – accordingly thickness, piezoelectric modulus, compliancy constant and resonance frequency of piezoelectric quartz, m_b – mass of vibrator (piezoelectric quartz + sample), R_e – equivalent resistance of vibrator at the moment of resonance, U and U_R accordingly – decrease in current at the section “piezoelectric quartz – resistance R ” and on the resistance at the moment of resonance, ℓ_0 – length of the sample.

NaClO_3 monocrystals were grown from aqueous liquids of a CP preparation by slow evaporation under room temperatures. The best samples had perfect cubic form and their size reached $25 \times 15 \times 10 \text{ mm}^3$. Samples in the form of cores were cut out according to the wet thread technique and their length along the crystallographic direction $\langle 100 \rangle$ corresponded to the condition of resonance excitation of the double compound vibrator at the basic frequency of 100 kHz for the longitudinal standing ultrasonic wave. No new dislocations were introduced into the samples before the measurements started. Maximum amplitude of the relative oscillative deformation in the crest of the standing wave ε changed within two orders (from 10^{-7} to 10^{-5}). Internal friction measurements were completed with an average error of about 10%.

4. Results and their discussion

Thermal dependence of internal friction in NaClO_3 samples practically in the whole region of solid phase existence is presented in Figure 1. Here we also present the changes of Young modulus in direction $\langle 100 \rangle$ of sodium chlorate monocrystal. The fact that at once catches the researcher’s eye that the mechanical spectrum of NaClO_3 sample contains plenty of internal friction maximums (five completely resolved ones under the temperatures 110, 225, 260, 400 and 450 K) and an ascending branch of Q^{-1} maximum under $T > 500 \text{ K}$. Function $E_{\langle 100 \rangle}$, first of all, is considerably non-linear and, second, it has a number of anomalies. The obtained mechanical spectrum is even more surprising as under similar conditions in terms of temperature and frequency $Q^{-1}(T)$ and $E_{\langle 100 \rangle}(T)$ in NaCl crystal have a common linear form – with the growth of the sample temperature internal friction and elastic modulus change monotonously (Q^{-1} increases, $E_{\langle 100 \rangle}$ decreases).

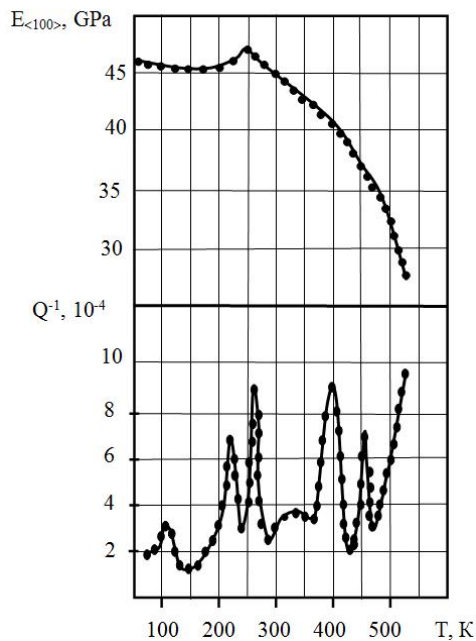


Figure 1. Thermal changes of internal friction and Young modulus of NaClO_3 monocrystal in the cube plane.

The observed peculiarities in the thermal behavior of internal friction and elastic modulus in sodium chlorate crystal are obviously related to the order-disorder processes in its lattice. In simplified form the interpretation of results can be presented as follows. When the crystal of NaClO_3 is heated, its anion sublattice, consisting of pyramidal groups of ClO_3^- with atom of chlorine in the vertex and atoms of oxygen in the base, is destabilized first. Near the temperature of 110 K in the local areas of anion sublattice atoms of chlorine start transitions between two equivalent sites and, by convention, this can be considered the trigger mechanism to the so called isostructural (isomorphous) phase transition in the crystal of sodium chlorate under low temperatures. Maximum Q^{-1} is followed by changing the sign of elastic modulus thermal dependence – $E_{\langle 100 \rangle}$ increases in the interval of 170-260 K. A certain culmination of the described process is achieved under the temperatures of 225 – 260 K when the intensity of chlorine atoms transitions becomes enough to impart the quasi-molecular group ClO_3^- additional degree of freedom – hindered rotation (libration). Separate anions randomly (“in a Brownian way”) change their orientation for two directions. An indirect proof to this is the fact that under the temperature of 260 K NaClO_3 crystal becomes an auxetic (its Poisson’s ratios $\sigma_{\langle 100 \rangle}$ and $\sigma_{\langle 110,001 \rangle}$ become negative). As the temperature of the crystal grows more and more anions become involved into the process of reorientation which finally leads ($T \approx 400$ K) to cation sublattice destabilization. Activation energy of cation vacancy is 0.46 electron-volt and energy of Frenkel pair formation 1.98 electron-volt [8]. Q^{-1} peak under $T = 400$ K in NaClO_3 , this way, is associated with elastic relaxation in the lattice of this crystal due to sodium ions “jumping” between the sites. When the temperature approaches 500 K ($T_{\text{melting}} = 536$ K) the crystal becomes strongly ionized (chlorate ions separate from sodium ions) and, as Curie point in NaClO_3 is taken over the melting temperature ($T_c = 593$ K), then, it is supposed that spontaneous polarization can be caused only by dipoles appearing due to free rotation of ClO_3^- group.

Our studies of internal friction in NaClO_3 monocrystal under the temperature of $T > 300$ K correlate to anomalous behavior of many physical properties of the given material in this temperature region (Fig. 2) [8].

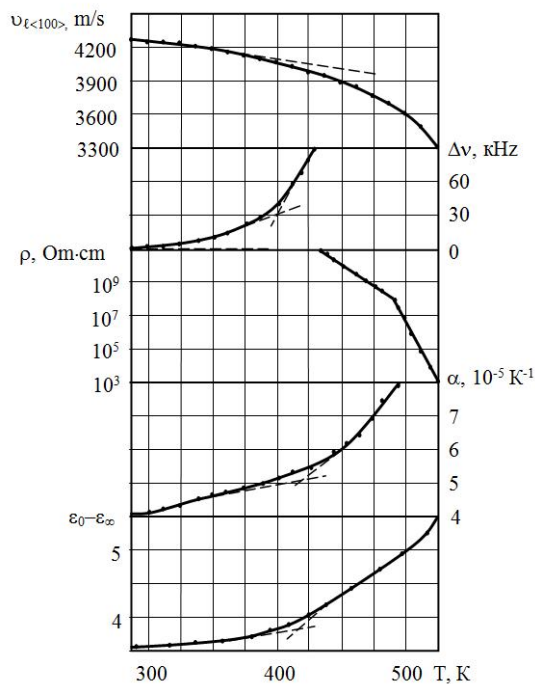


Figure 2. High-temperature changes of longitudinal waves velocity $v_{l\langle 100 \rangle}$, frequency displacement of nuclear quadrupole resonance ^{35}Cl $\Delta\nu$, specific electrical resistance ρ , thermal expansion coefficient α and difference of low- (ϵ_0) and high-frequency (ϵ_∞) transmittivities of NaClO_3 monocrystal.

An unexpected and surprising result was obtained in the experiments on amplitude dependence of internal friction in the studied object (Fig. 3). We mean peak δ under remarkably small amplitudes of oscillative deformation (near 10^{-7}). The plastic properties of NaClO_3 crystal in the ultrasound field of such low intensity are not quite understandable. Results presented in Fig. 3 clearly demonstrate that the view of $\delta(\epsilon)$ curves significantly depends upon the temperature of the samples. The most marked peak of internal friction corresponds to the temperature of sodium chlorate sample of 400 K under which many non-linear properties start (Fig. 2). Let us notice that on dynamic curves of deformation for some materials which have absolutely different chemical nature than our object of study, for example, metals [2, 5, 9], we observe similar “sharp plasticity point”. As an example in Fig. 4 we present a curve of steel deformation in static and dynamic modes taken from the monograph of Bulgarian authors [9]. That’s what they say about the considered phenomenon on page 99 of their book: “... The dynamic curve $\sigma_x(\epsilon_x)$ often has a peculiar “tooth” explained by some structural characteristics of material...” In the piezoelectric (sodium chlorate) and in the ferromagnetic (steel) identical “structural characteristics” caused by such insignificant mechanical effects of elastic pulse advancing, indicate a single mechanism of quasi-microplasticity effect characteristic for various solids being significantly different in nature and physical and mechanical properties [10, 11].

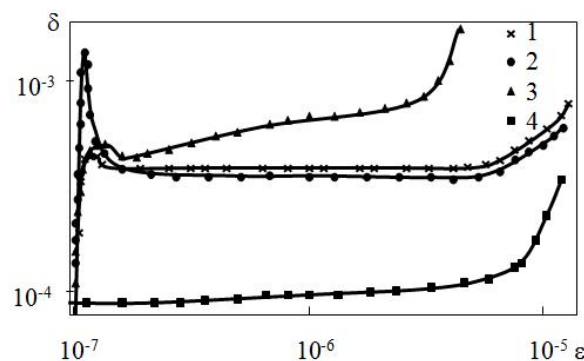


Figure 3. Amplitude dependence of internal friction of NaClO_3 (1, 2, 3) and NaCl (4) crystals. 1, 4 – 300 K, 2 – 400 K, 3 – 500 K.

The developed microplasticity of NaClO_3 under the temperature of 400 K is associated with the beginning of the given crystal transition into the superionic state due to cation sublattice “melting”. Elastic wave modulates the depths of potential wells of quasi-free sodium ions in the conducting sublattice leading to the redistribution of Na^+ due to thermally activated motion. This phenomenon is the phenomenon of inelastic relaxation [12].

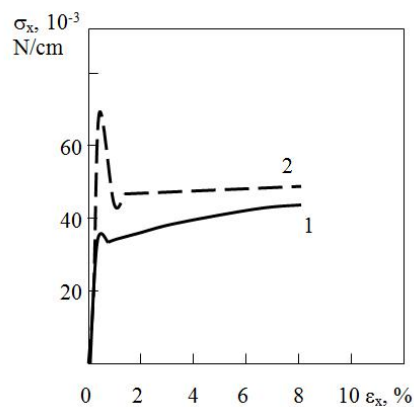


Figure 4. 1 – static curve for steel; 2 – dynamic curve for steel [8].

The test experiment with NaCl crystal (curve 4 in Fig. 3) demonstrates the typical view of function $\delta(\varepsilon)$ with amplitude dependence of internal friction under $\varepsilon \geq 10^{-5}$ determined by motion of dislocations. In NaClO₃ crystal under T = 500 K amplitude independent component of internal friction is practically absent (curve 3 Fig. 3).

5. Findings

1. It is established that mechanical spectrum of NaClO₃ sample contains maximum of internal friction (five completely solved ones under the temperatures of 110, 225, 260, 400 and 450 K) and an ascending branch of Q^{-1} maximum under T > 500 K.
2. A marked peak of internal friction is revealed under T = 400 K when many non-linear properties of sodium chlorate start.
3. The study revealed that the test experiment with NaCl crystal demonstrates the typical view of $\delta(\varepsilon)$ function with amplitude dependence of internal friction under $\varepsilon \geq 10^{-5}$ determined by motion of dislocations. In NaClO₃ crystal under T = 500 K amplitude independent component of internal friction is practically absent.

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