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Thermodeformational Behavior of Cubic Crystals of Sodium Cyanide

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Abstract. In the paper the authors provide results of the study of anisotropic and isotropic acoustic (elastic waves propagation velocities), dimensional (elastic moduli) and nondimensional (Poisson's ratios) elastic characteristics of mono- and polycrystals of sodium cyanide within the temperature range 283.7÷473 K.

1. Introduction

For most solids it is considered normal to decrease under temperature growth according to the linear law and small dependence (or no dependence) under low temperatures of elastic waves, elastic constants and elastic moduli propagation rates [1-4]. Any deviation from the given functional changes is to be treated as anomalous. In this context the results of experimental study of temperature dependences of stiffness constants $c_{ij}(T)$ of alkali metals cyanides monocrystals completed by Haussühl and others [5-9] afford ground for such conclusion. The characteristics of thermoelastic behavior of high-temperature disordered cubic phases of cyanides MeCN (Me = Na, K, Rb, Cs) are as follows:

a) Velocities of elastic waves propagation increase with temperature growth within significant temperature ranges.

b) One of two shear constants (in NaCN stiffness constant c_{44}) tends to zero when temperature approaches critical value of T_c (T_c – temperature of structural phase transition NaCN I → NaCN II, $T_c = 283.7$ K [7], 288.1 K [10]) according to dependence $T_{44} = d\left(\log c_{44}\right)/dT = 1/\left(T \log T/T_0\right)$, where T – temperature in K, and T_0 – specific constant (for NaCN $T_0 = 255.4$ K [7]).

c) Volume compressibility and thermal expansion under temperature change demonstrate dependences typical for stable solids.

The theory of emolliating of stiffness constants and phonons in ion molecular crystals on the example of alkali cyanides is considered in [11]. The authors suggest correlations describing renormalization of phononic frequencies due to interaction between translational and rotational degrees of freedom. According to the correlations under some temperatures stiffness constants c_{11}, c_{44} may go to zero. In alkali cyanides, as temperature grows, constant c_{44} is the first to go to zero, in superoxides – c_{11}. This difference is determined by the correlation between the short-range repulsive forces and the interaction force of quadrupole moment of molecule with electric field gradient fluctuating due to phonons. Dependence of c_{11}, c_{44} on temperature is also influenced by anharmonicity and direct interaction of molecules. Due to $c_{44} = 0$ for NaCN the calculated critical temperature of T_0. The difference is associated with application of mean field approximation when calculating.

Information on elastic moduli (Young modulus E, shear modulus G) for three specific crystallographic directions <100>, <110>, <111> of the cubic phase ($T > T_c$) of NaCN monocrystal, values of these moduli of sodium cyanide polycrystals as well as anisotropic ($\sigma_{<hkl>}$) and isotropic (σ) Poisson's ratios of the given compound from the group of cyanic crystals are not found in reference literature. In the given paper the authors determine and discuss the mentioned above elastic characteristics of cubic NaCN and some properties of cyanide associated with its elasticity, particularly anharmonic.

2. Theoretical basis

The lattice of isomorphic sodium, potassium, rubidium cyanides under room temperature is of KCN-type, a distorted type of rock salt lattice (NaCl, type B_1, spatial group Fm-3m) which formally is impossible as the crystal lattice of the given substances is made up of three different atoms (Fig. 1) [12]. But as temperature decreases the structures of their lattices become less symmetrical (Table 1) and then positions of carbon and nitrogen atoms can be distinguished: the distance between them is 0.105 nanometer. In the cubic phases of alkali metals cyanides ion CN^- behaves as if its symmetry was spherical. This is only statistically average due to rotation of completely-bound ("dumbbell") C and N atoms around the common centre of gravity and, thus, imitate spherical symmetry.

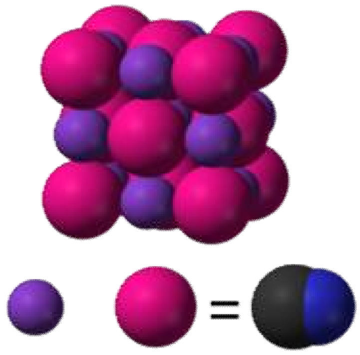

Figure 1. Elementary cell of the cubic phases of KCN-type crystals: large spheres – CN^-, small – Na^+; K^+, Rb^+ [12]

The mechanism which is alternative to the rotational mechanism of disorder in the lattices of cyanides is orientation of CN^- ions in a limited number of positions [13]. Excess entropy $\Delta S \approx R\ln 2$ under III → II transition in salts NaCN and KCN quite evidently show that in orthorhombic forms II of these crystals CN^- ions are randomly distributed between two orientations. From excess entropy under NaCN II → NaCN I transition follows that it results in significant further disorder orientation in high-temperature cubic phase: $\Delta S \approx R\ln 4$ and corresponds to the transition to eight orientations of cyanide ions. Analysis of the results of heat capacity, nuclear magnetic resonance of inelastic spectrum in NaCN I showed that in the cubic phase barriers of CN^- ions reorientation are relatively small (8 12 kJ/mole) [13]. A rather common characteristic of disordered cubic forms of alkali metals cyanides is that motion of ions of one type notably affects orientational motion of ions of another type (cyanide ions).

Table 1. Thermodynamic and structural data on cyanides of alkali metals [13]

Cyanides	III ↔ II T_c (K), $\Delta S_c/R$	II ↔ I T_c (K), $\Delta S_c/R$
NaCN	171.9; 0.61 (λ) monoclinic	288.1; 1.41 (λ) orthorombic NaCl
KCN	 monoclinic	168.3; 1.01 (λ) orthorombic NaCl
RbCN		110.3; 0.695 (F) orthorhombic NaCl
CsCN		193.1; 1.31 rhombohedrical CsCl

Note: T_c – temperature of transition, ΔS_c – entropy change, R – universal gas constant, (λ) – smooth transition, (F) – abrupt transition.

Results and discussion

The given work is based on experimental data on stiffness constants c_{ij} of monocrystal NaCN I in the interval 283.7 – 473 K obtained with ultrasonic resonance at the frequency of 15 mHz with limiting error for c_{11}, c_{44} and c_{12} accordingly of 0.4%, 0,8% and 1.0% [7]. Experiment conducted at higher frequencies (order of units – dozens of gigahertz, method of Brillouin scattering) brings to values of c_{11}, c_{12} which are lower by 6-7% and c_{44} which is by 14% lower for NaCN under 20°C [14]. This fact for c_{44} was checked and discussed in [15]: there is no c_{44} dispersion and loss of stability of NaCN I lattice under $T \to T_c$ continues due to mode frequency of transversal acoustic phonons vanishing. Elasticity of low-temperature forms of pure sodium cyanide was not studied.

Table 2. Anisotropic sound velocities and Gruneisen parameters of NaCN monocrystal

T, K	Crystallographic direction										
	[100]			[110]					[111]		
	υ_L	υ_t	γ	υ_L	υ_{t1}	υ_{t2}	γ_1	γ_2	υ_L	υ_t	γ
1	2	3	4	5	6	7	8	9	10	11	12
283.7	3967	385	4.360	3731	385	1816	4.340	2.089	3396	1500	2.396
293	3981	454	4.310	3556	454	1846	4.263	1.873	3403	1530	2.340
313	4004	557	4.220	3569	557	1898	4.151	1.790	3412	1583	2.243
333	4020	645	4.133	3582	645	1936	4.043	1.733	3423	1624	2.171
353	4031	720	4.050	3592	720	1967	3.942	1.688	3433	1659	2.112
373	4040	793	3.964	3602	793	1994	3.838	1.650	3443	1691	2.060
393	4046	860	3.879	3612	860	2016	3.737	1.621	3455	1719	2.016
413	4049	920	3.797	3620	920	2033	3.641	1.599	3466	1743	1.981
433	4049	973	3.723	3626	973	2047	3.556	1.580	3474	1763	1.949
453	4045	1025	3.647	3630	1025	2059	3.469	1.563	3480	1782	1.920
473	4039	1073	3.572	3632	1073	2067	3.385	1.552	3486	1798	1.896

All calculated ratios used in the given paper are provided in [16, 17]. Results of current research are provided in Tables 2-4 and in Figure 2. Table 2 provides data on anisotropic rates of propagation of longitudinal (υ_L), transverse (υ_t) elastic waves, Gruneisen parameters γ in directions <100>, <110>, <111> of NaCN monocrystal in the interval from 283.7 K to 473 K. Except longitudinal sound velocity along face diagonal <110> all other propagation velocities increase non-linearly with temperature growth. Maximal temperature dependence is demonstrated by transverse wave velocity along cube edge (<100>, increase by 1.79). Anisotropic Gruneisen parameters along three specific directions of NaCN monocrystal significantly decrease with temperature growth, especially $\gamma_{2<110>}$ (by 26%), which is not typical for ion crystals, for example, for NaCl. At the same time, for all studied temperature range Gruneisen parameters maintain the inequation: $\gamma_{<110>} > \gamma_{1<110>} > \gamma_{<111>} > \gamma_{2<110>}$.

Table 3. Elastic anisotropy factor *A*, Couchy relation Δ, bulk moduli *B*, Young *E* and shear *G* of NaCN monocrystal

T, K	*A*	Δ	*B*	$E_{<100>}$	$E_{<110>}$	$E_{<111>}$	$G_{<100>}$	$G_{<110>}$	$G_{<111>}$
				hPa					
283.7	0.045	61.51	18.2	14.45	0.93	0.71	0.24	0.46	0.66
293	0.061	43.76	18.1	14.86	1.28	0.98	0.33	0.62	0.88
313	0.086	28.40	17.9	15.56	1.90	1.47	0.50	0.91	1.27
333	0.111	20.83	17.7	16.05	2.51	1.96	0.66	1.19	1.62
353	0.134	16.43	17.6	16.45	3.08	2.42	0.82	1.45	1.94
373	0.158	13.32	17.4	16.78	3.67	2.91	0.99	1.71	2.26
393	0.182	11.16	17.2	17.03	4.25	3.40	1.16	1.96	2.55
413	0.205	9.59	17.0	17.22	4.81	3.87	1.32	2.20	2.82
433	0.226	8.46	16.8	17.35	5.30	4.30	1.48	2.41	3.05
453	0.248	7.51	16.6	17.44	5.79	4.74	1.63	2.61	3.27
473	0.269	6.75	16.4	17.47	6.26	5.15	1.78	2.80	3.47

Table 4. Density ρ, thermal-expansion coefficient α, sound velocities, elastic moduli, thermodynamic γ_D and acoustic γ_a Gruneisen parameters of NaCN polycrystal

T	ρ, 10^3	α, 10^{-6}	υ_L	υ_t	*E*	*G*	*B/G*	γ_a	γ_D
K	kg/m^3	K^{-1}	m/s		hPa				
283.7	1.602	58	3527	908	3.87	1.32	13.75	3.62	1.10
293	1.599	58	3538	953	4.25	1.45	12.44	3.55	1.31
313	1.593	59	3555	1029	4.91	1.69	10.60	3.42	1.50
333	1.587	59	3572	1094	5.50	1.90	9.33	3.32	1.49
353	1.582	60	3586	1151	6.05	2.10	8.37	3.22	1.51
373	1.576	60	3600	1207	6.60	2.30	7.56	3.12	-
393	1.570	60	3614	1258	7.12	2.49	6.92	3.04	-
413	1.564	61	3627	1305	7.59	2.66	6.39	2.96	-
433	1.558	62	3635	1345	8.01	2.82	5.97	2.89	-
453	1.552	63	3642	1384	8.41	2.97	5.60	2.82	-
473	1.546	64	3647	1419	8.78	3.11	5.27	2.76	-

Elastic anisotropy factor and Cauchy relations (Table 3) are indicative of NaCN crystal being strongly anisotropic where the forces of interaction between the ions are also acentral. For example, for NaCl under normal temperature $A = 0.72$ and $\Delta = 1.02$ (are close to one) [15]. Anisotropic Young $E_{<hkl>}$ and shear $G_{<hkl>}$ moduli as opposed to bulk modulus increase with temperature growth and the following inequations are maintained: $E_{<100>} > E_{<110>} > E_{<111>}$, $G_{<100>} < G_{<110>} < G_{<111>}$.

Elastic and some other characteristics of NaCN polycrystal are presented in Table 4 (note: for cubic lattices *B* of mono- and polycrystals coincide). Here we would like to pay attention to two moments.

1. Relation of *B/G* moduli in NaCN is large especially near T_c. Such values of *B/G* are characteristic of superplastic materials. To compare let us provide typical values of *B/G* for malleable gold (6.03), fragile diamond (0.83) and NaCl which is on the border of fragility-plasticity (1.73).
2. Bad agreement between acoustic and thermodynamic Gruneisen parameters. However heat capacity of NaCN was measured only in low-temperature region (5-345 K [10, 18]) and γ_a and γ_D are compared for small overlapping temperature range bordering with T_c which value differs due to two methods of recording (see Introduction).

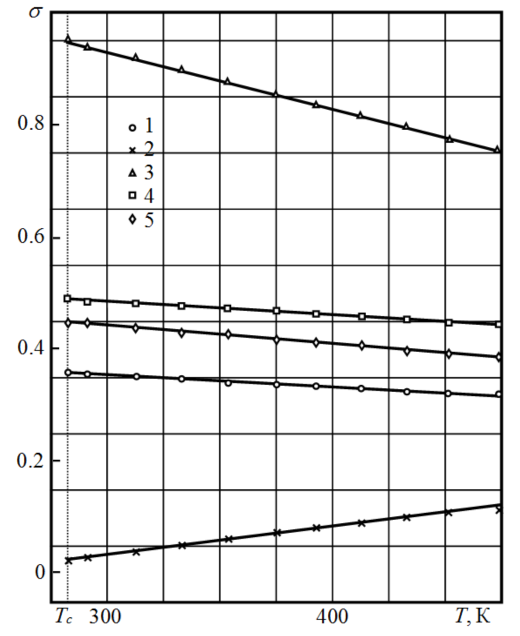

Figure 2. Poisson's ratios of mono- (1, 2, 3, 4) and polycrystals (5) of NaCN dependence on temperature 1 $-\sigma_{<100,001>}$, 2 – $\sigma_{<110,001>}$,3 – $\sigma_{<110,1\bar{1}0>}$,4 – $\sigma_{<111,111>}$

Dependence of Poisson's ratios of sodium cyanide mono- and polycrystals on temperature is presented in Fig. 3. Longitudinal-transverse deformation of NaCN along direction <110> is diametrally opposite: value of $\sigma_{<110,001>}$ is minimal and its function to temperature is positively sloped, $\sigma_{\langle 110,1\bar{1}0\rangle}$ is maximal, near T_c its value tends to one and $d\sigma_{\langle 110,1\bar{1}0\rangle}/dT$ <0. In point of T_c transition into partially ordered orthorhombic phase NaCN II isotropic Poisson's ratio approaches upper limit 0.5 (σ = 0.454) and under further temperature decrease a break is obvious on dependence $\sigma(T)$. All Poisson's ratios of the cubic phase of NaCN I crystal are positive within the studied temperature range and are expected to stay positive until melting (T_{melting} = 835 K). Only Poisson's ratio $\sigma_{<110,001>}$ can reach zero in phase NaCN II near the temperature of 250 K (extrapolation from T_c). This value of temperature well coincides with experimentally found parameter $T_0 = 255.4$ K applied for describing temperature dependence of shear stiffness $c_{44}(T) = 2.144(T - T_0)/T_0$ hPa [7]. If $\sigma_{<110,001>}$ of NaCN II takes negative values under $T < T_c$ and, thus, rhombic sodium cyanide turns into non-axial auxetic still remains open to question.

Conclusion

On the base of data on stiffness constants the authors studied temperature dependences of anisotropic and isotropic acoustic and elastic characteristics of sodium cyanide mono- and polycrystals within the range 283.7÷473 K. It has been established that as temperature grows we observe anomalous increase of sound velocities (except longitudinal velocity along <110>). Uncharacteristic temperature dependence is observed for anisotropic Gruneisen parameters – along three specific directions – with temperature growth they significantly decrease. NaCN crystal is a strongly anisotropic object where forces of interaction between ions are significantly non-central. Relation of *B/G* moduli in NaNC indicates superplasticity of the crystal near T_c. Temperature dependences of anisotropic moduli (Young, shear, bulk) and Poisson’s ratios are linear.

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