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Third-Order Elastic Constants of Cubic Sodium Cyanide and Potassium Cyanide

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Abstract

The complete third-order elasticity tensors of cubic NaCN and KCN have been determined from stress-shifted resonance frequencies of thick plates at 293 K. The two cyanides exhibit quite similar nonlinear elastic properties which, however, differ strongly from those of comparable alkali halides such as NaCl and KCl. The 'longitudinal' constants c_{111} are *ca* five times smaller and the 'transverse' constants c_{112} and c_{123} *ca* eight times larger than those in NaCl and KCl. The Cauchy relations are strongly violated, as is already known for the second-order elastic constants. The critical shear resistance c_{44}, which is connected with the phase transitions observed at 283 K (NaCN) and 168 K (KCN), exhibits a considerable dependence on hydrostatic pressure only in the case of NaCN: c_{44} drops rapidly with increasing pressure. The absolute change of c_{44} per hydrostatic pressure unit, however, is comparable to that in alkali halides. The nonlinear elastic behaviour of NaCN and KCN is qualitatively interpreted by interactions of volume-conserving type (as existing in fluids).

Introduction

In continuation of earlier investigations on elastic and thermoelastic properties of alkali cyanides (Haussühl, 1957, 1973; Haussühl, Eckstein, Recker & Wallrafen, 1977) we have now determined the third-order elastic constants (TOEC) of cubic NaCN and KCN. These constants are strongly related to other anharmonic properties, such as thermal expansion, thermoelastic constants, and thermal conductivity. The knowledge of

TOEC may provide further critical data for testing the models which have been developed recently to interpret the extremely anomalous thermoelastic properties originating from thermally activated rotational movements of the cyanide ions (Michel & Naudts, 1977).

Furthermore, we expected to obtain additional data for the discussion of the influence of asymmetric ions on nonlinear elastic properties, in particular for crystals of rock salt type.

The experimental method employed has been described in detail in a previous paper (Haussühl & Preu, 1978), where stress-induced shifts of resonance frequencies f of thick plates in the range between 14 and 28 MHz are used for the evaluation of TOEC. The states of resonance are detected by diffraction of monochromatic light by the grating of ultrasonic waves which attain maximum amplitudes at the resonance frequencies. For the generation of longitudinal and transverse waves we used X-cut and Y-cut quartz plates respectively. This method has been proved to be well suited to nonlinear acoustic studies owing to its high accuracy and its simple handling. The basic equations which combine TOEC and observed derivatives $d[\ln(f)]/dP$ have been elaborated by Thurston & Brugger (1964), Brugger (1965a,b), and Wallace (1970). P is the appropriate quantity of uniaxial or hydrostatic mechanical stress.

Experimental

Single crystals of NaCN of optical quality, grown by the Czochralski method (Haussühl, Eckstein, Recker & Wallrafen, 1977), were provided by K. Recker and his group. Crystals of KCN were grown from aqueous

solutions at *ca* 320 K by the method of controlled lowering of temperature. The raw crystals were cut and ground into plane-parallel plates with dimensions of *ca* 10 mm and deviations from plane-parallelism of less than 2 μm. Four preferential orientations were prepared: [100], [011], [111], and [112]. In order to maintain the optical transparency of the hygroscopic crystals, optical glass plates were attached to the polished faces with paraffin oil as immersion fluid. The hydrostatic pressure applied was extended to 1500×10^5 N m^{-2}, whereas the maximum uniaxial stress had to be limited to 10×10^5 N m^{-2} in order to avoid plastic deformations. Such effects would drastically disturb any measurement of resonance frequencies in which the dimensions of the specimens are involved. The frequency shifts as a function of hydrostatic pressure could be measured easily. The shifts produced by uniaxial stress, however, could only be determined with much less accuracy owing to the limited stress range. These measurements were performed on several specimens with different orientations, directions of stress and propagation velocity, until a reproducible set of stress-dependent frequency shifts had been achieved. Only reproducible measurements were selected for the final evaluation of TOEC. They exhibited a linear dependence of frequency shifts on applied stresses. The observed cases of nonlinearity were revealed in further runs not to be reproducible and were therefore rejected.

For crystals of symmetry $m3m$ special equations for the evaluation of the six TOEC c_{111}, c_{112}, c_{123}, c_{144}, c_{166}, and c_{456} are given by Elkin, Alterovitz & Gerlich (1970). Computer programs were written to evaluate these equations numerically for 12 (NaCN) and 14 (KCN) independently measured frequency shifts in different crystal orientations, stress directions, and different combinations of propagation directions and polarization of ultrasonic waves. The overdetermined system of these equations is listed in Table 1. The right-hand sides contain the measured quantities $d[\ln (f)]/dP$ and combinations of second-order elastic constants and coefficients. The weights in the overdetermined system were chosen in inverse proportion to the calculated mean statistical errors (Table 1).

The TOEC and their statistical errors were calculated by means of a least-squares method, and the results are presented in Table 2, which also contains the second-order elastic constants (SOEC) and their pressure derivatives, calculated from the corresponding equations for hydrostatic pressure. The pressure derivatives calculated from the TOEC are in good agreement with the given values for both materials.

Discussion

Recently, the dependences of c_{44} and $c' = (c_{11} + c_{12} + 2c_{44})/2$ on hydrostatic pressure for both NaCN and

KCN were reported by Hochheimer, Love & Walker (1977). These values, which were obtained by Brillouin scattering experiments in a range of hydrostatic pressure up to several kbar, agree fairly well with our results. Raman spectra of NaCN and KCN under hydrostatic pressure have been studied by Dultz, Krause & Winchester (1977) and Dultz & Krause (1978). These authors derived Grüneisen parameters for the transverse-acoustical soft mode connected with c_{44}, without giving further details of nonlinear elastic properties. The TOEC of NaCN and KCN show the following features (see Table 2).

(i) The TOEC of NaCN and KCN possess the same signs and similar magnitudes despite the large difference in transition temperature. In particular, the ratios c_{ijk}/c_{mnl} vary only slightly. Such behaviour, which is also observed in other isotypic crystals, *e.g.* alkali halides of rock salt type, alums or f.c.c. metals, expresses the close structural relationship. The only significant difference between NaCN and KCN occurs in the ratio c_{112}/c_{123}. Furthermore, the pressure coefficient Pc_{44} of NaCN is about 10 times larger than that of KCN. This difference should be considered in connection with the extremely small value of c_{44} in the vicinity of the phase transition of NaCN at *ca* 284 K which is caused by a softening of c_{44}, approaching the transition temperature from higher temperatures. In KCN this transition occurs at *ca* 168 K. The absolute change of c_{44} per hydrostatic pressure unit, however, expressed by $c_{44}Pc_{44}$, differs much less (-0.36 in NaCN and 0.11 in KCN). These values show the same order of magnitude as the corresponding quantities in NaCl and KCl ($+0.37$ and -0.39 respectively).

(ii) The ratios c_{123}/c_{111}, which exhibit typical magnitudes for certain structure types, change from *ca* 1/80 in the regular alkali halides to roughly 1/2 in the cyanides. This results from both a reduction of c_{111} by a factor of *ca* five and an increase of c_{123} by a factor of *ca* eight in the cyanides. We recognize much stronger transverse interactions in the cyanides compared with the regular members of the rock salt group. It should be recalled that the ratio c_{11}/c_{12} is also drastically decreased in alkali halides if Cl is replaced by CN. The ratio Pc_{12}/Pc_{11} of *ca* 2/3 in NaCl and KCl, which is raised to *ca* 2 in the cyanides, confirms this tendency.

(iii) The Cauchy relations, which were believed to be almost fulfilled with the alkali halides, are severely violated by the alkali cyanides in SOEC as well as in TOEC. The relations are $c_{12} = c_{44}$ in SOEC, and $c_{123} = c_{144} = c_{456}$, $c_{112} = c_{166}$ in TOEC. The 'transverse' constants c_{12}, c_{123} and c_{112} are much larger. As has been pointed out earlier, materials with strong deviations from Cauchy relations in the sense of $c_{12} \gg c_{44}$ behave in a certain respect like fluids, where $c_{11} = c_{12}$ and $c_{44} = 0$ (Haussühl, 1967). This is also valid for NaCN and KCN. It might be interesting to compare the TOEC of these cyanides with those of a fluid. The latter obey the

Table 1. *Equations for the evaluation of TOEC*

Each equation should be read horizontally (*e.g.* line 1 for NaCN should read: $c_{111} + 2c_{112} = -36.34 \times 10^{10}$ N m^{-2}). $\mathbf{k}$ and $\mathbf{w}$ are unit vectors in the directions of propagation and polarization of ultrasonic waves; $\mathbf{z}$ is the direction of propagation of the light beam. s^T_{ij} are the isothermal elastic coefficients as derived from the c_{ij} given in Table 2. Units: c_{ijk} in 10^{10} N m^{-2}, s^T_{ij} in 10^{-10} m^2 N^{-1}

Number	Wave type*	Direction of stress	k	w	z	c_{111}	c_{112}	c_{123}	c_{144}	c_{166}	c_{456}	NaCN	KCN
												Left hand side of equation†	Right hand side of equation
1	L	Hydrostatic	[100]	[100]	[010]	1	2	0	0	0	0	-36.34 ± 0.22	-24.12 ± 0.06
2	T	Hydrostatic	[100]	[010]	[001]	0	0	0	1	2	0	-3.00 ± 0.03	-3.80 ± 0.02
3	L	Hydrostatic	$[1\bar{1}0]/\sqrt{2}$	$[110]/\sqrt{2}$	[001]	1	4	1	2	4	0	–	-52.57 ± 0.05
4	T	Hydrostatic	$[1\bar{1}0]/\sqrt{2}$	$[110]/\sqrt{2}$	[001]	1	0	-1	0	0	0	-9.24 ± 0.12	-3.03 ± 0.08
5	T	Hydrostatic	$[1\bar{1}0]/\sqrt{2}$	[001]	[110]	0	0	0	1	2	0	–	-3.75 ± 0.02
6	L	Hydrostatic	$[111]/\sqrt{3}$	$[111]/\sqrt{3}$	$[1\bar{1}0]$	1	6	2	4	8	0	-99.83 ± 0.21	–
7	T	Hydrostatic	$[111]/\sqrt{3}$	$[1\bar{1}0]/\sqrt{2}$	$[11\bar{2}]$	1	0	-1	1	2	0	-12.17 ± 0.21	-6.45 ± 0.11
8	L	[001]	[100]	[100]	[010]	1	b_2/a_2	0	0	0	0	0.92 ± 1.50	-3.41 ± 0.15
9	L	[001]	$[1\bar{1}0]/\sqrt{2}$	$[110]/\sqrt{2}$	[110]	1	b_4/a_2	a_1/a_2	$2a_1/a_2$	4	0	-23.80 ± 0.36	-7.27 ± 0.13
10	T	[001]	$[1\bar{1}0]/\sqrt{2}$	[001]	[110]	0	0	0	1	b_2/a_2	0	–	6.61 ± 0.09
11	L	$[1\bar{1}0]/\sqrt{2}$	[001]	[001]	[110]	1	b_2/a_2	0	0	0	0	0.93 ± 0.35	–
12	L	$[1\bar{1}0]/\sqrt{2}$	$[110]/\sqrt{2}$	$[110]/\sqrt{2}$	[001]	b_2/a_2	b_5/a_2	2	4	$4c_1/a_2$	0	-1128.53 ± 7.31	-15.71 ± 0.09
13	T	$[1\bar{1}0]/\sqrt{2}$	$[110]/\sqrt{2}$	[001]	[110]	0	0	0	1	b_4/b_2	a_3/b_2	-79.01 ± 2.54	-6.74 ± 0.13
14	L	$[1\bar{1}0]/\sqrt{2}$	$[111]/\sqrt{3}$	$[111]/\sqrt{3}$	$[11\bar{2}]$	1	6	2	$2c_3/b_3$	$4c_3/b_3$	$-4a_3/b_3$	–	233.53 ± 8.96
15	T	$[1\bar{1}0]/\sqrt{2}$	$[11\bar{2}]/\sqrt{6}$	$[1\bar{1}0]/\sqrt{2}$	[110]	1	b_1/b_2	$-2a_2/b_2$	4	$4b_4/b_2$	$4a_3/b_2$	–	-40.15 ± 0.90
16	L	$[111]/\sqrt{3}$	$[111]/\sqrt{3}$	$[111]/\sqrt{3}$	$[1\bar{1}0]$	1	6	2	$4c_4/b_3$	$8c_4/b_3$	$8a_3/b_3$	-3635.63 ± 47.4	–
17	L	$[111]/\sqrt{3}$	$[11\bar{2}]/\sqrt{6}$	$[11\bar{2}]/\sqrt{6}$	$[1\bar{1}0]$	1	4	1	2	$4c_2/b_3$	0	–	264.45 ± 2.51
18	L	$[11\bar{2}]/\sqrt{6}$	$[111]/\sqrt{3}$	$[111]/\sqrt{3}$	$[1\bar{1}0]$	1	6	2	$2c_3/b_3$	$4c_3/b_3$	$-4a_3/b_3$	1711.64 ± 15.0	–

* L = longitudinal, T = transverse.

† $a_1 = s^T_{11}, a_2 = s^T_{12}, a_3 = s^T_{44}, b_1 = s^T_{12} - s^T_{11}, b_2 = s^T_{11} + s^T_{12}, b_3 = s^T_{11} + 2s^T_{12}, b_4 = s^T_{11} + 3s^T_{12}, b_5 = 3s^T_{11} + 5s^T_{12}; c_1 = s^T_{12} + s^T_{11} - s^T_{44}, c_2 = s^T_{11} + 2s^T_{12} - s^T_{44}, c_3 = 2s^T_{11} + 4s^T_{12} - s^T_{44}, c_4 = s^T_{11} + 2s^T_{12} + s^T_{44}.$

Table 2. *Third-order elastic constants c_{ijk}, pressure derivatives $Pc_{ij} = d[\ln(c_{ij})]/dP$, and second-order elastic constants c_{ij} of NaCN and KCN at 293 K*

Limits of statistical error are given in parentheses. The corresponding data for NaCl and KCl are literature values. Units: c_{ijk} and c_{ij} in 10^{10} N m^{-2}, Pc_{ij} in 10^{-10} m^2 N^{-1}.

	NaCN	NaCl	KCN	KCl
c_{111}	$-16.22\,(\pm 0.51)$	$-86.36(a)$	$-12.92\,(\pm 0.23)$	$-72.6(b)$
c_{112}	$-9.72\,(\pm 0.24)$	-4.96	$-5.51\,(\pm 0.11)$	-2.4
c_{123}	$-6.76\,(\pm 0.47)$	0.93	$-10.09\,(\pm 0.21)$	1.1
c_{144}	$2.41\,(\pm 0.13)$	0.71	$1.63\,(\pm 0.07)$	2.3
c_{166}	$-2.70\,(\pm 0.05)$	-5.87	$-2.70\,(\pm 0.03)$	-2.6
c_{456}	$-1.44\,(\pm 0.07)$	1.32	$-0.79\,(\pm 0.04)$	1.6
c_{123}/c_{111}	0.42	-0.011	0.78	-0.015
Pc_{11}	$2.19\,(\pm 0.03)$	$2.4(a)$	$2.31\,(\pm 0.04)$	$3.17(c)$
Pc_{12}	$4.14\,(\pm 0.05)$	1.6	$4.93\,(\pm 0.06)$	2.29
Pc_{44}	$-10.87\,(\pm 0.32)$	0.29	$-0.76\,(\pm 0.04)$	-0.61
$c_{44}Pc_{44}$	-0.36	0.37	-0.11	-0.39
Pc_{12}/Pc_{11}	1.89	0.67	2.13	0.72
c_{11}	$2.534(d)$	$4.936(f)$	$1.916(e)$	$4.078(f)$
c_{12}	1.444	1.29	1.197	0.69
c_{44}	0.033	1.265	0.1405	0.633

References: (a) Swartz (1967); (b) Drabble & Strathen (1967); (c) Bartels & Schuele (1965); (d) Haussühl, Eckstein, Recker & Wallrafen (1977); (e) Haussühl (1973); (f) Haussühl (1960).

following relations derived from the conditions of isotropy and vanishing shear stresses: $c_{111} = c_{112} = c_{123}$; $c_{144} = c_{166} = c_{456} = 0$. Our TOEC of NaCN and KCN follow these relations in a surprising manner, in marked contrast to the regular alkali halides. Therefore, the anomalous elastic and the nonlinear elastic behaviour

of NaCN and KCN might be interpreted as partly originating from interactions similar to those dominating in fluid systems. This is also valid for RbCN, which exhibits similar elastic properties, in particular the extreme softening of c_{44} with decreasing temperature. Our statement concerning the fluid-like behaviour is

therefore valid for all alkali cyanides with quasi rock salt structure.

(iv) The differences between cyanides and chlorides observed here again confirm the suggestion, derived from an earlier investigation on alums (Haussühl & Preu, 1978), that the replacement of highly symmetrical ions like chlorine anions by asymmetric ions causes systematic changes in TOEC in the sense that the ratios c_{111}/c_{123} and c_{111}/c_{112} are strongly reduced by lowering c_{111} and increasing c_{112} and c_{123}. This indicates that the 'transverse' interactions, which are connected with the value of Poisson's ratio, are strengthened.

A quantitative interpretation of the nonlinear elastic behaviour of the alkali cyanides of rock salt type is expected to be obtained from a further development of the dynamical models in which the coupling of rotational movements of the cyanide ions with translational modes of the lattice is introduced (Bill, Jex & Müllner, 1976; Michel & Naudts, 1977; Mokross & Pirc, 1978; Rehwald, Sandercock & Rossinelli, 1977). Our results with respect to the fluid-like behaviour might support efforts to establish a simple model for the librational–transverse interactions in fluids.

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SHORT COMMUNICATIONS

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Lindemann's rule and the X-ray Debye temperature of anisotropic Zn and Cd single crystals.

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Abstract

Lindemann's rule was applied to Zn and Cd single crystals and found to be valid for these solids, x_Z being in the range 0·2 to 0·25.

Introduction

As pointed out by Ziman (1965), the basic assumption of Lindemann's rule of melting is that melting occurs if the ratio of the amplitude of atomic vibration to the radius of the space occupied by the atom in the solid reaches a certain value. This fraction seems to be a constant for all monatomic solids.

The mean-square displacement in a particular direction of the atoms in solids is given by (James, 1948, p. 220)

$$\bar{u}^2 = \frac{3\hbar^2 T}{mk\Theta^2}\left[\varphi\left(\frac{\Theta}{T}\right) + \frac{\Theta/T}{4}\right] \tag{1}$$

where $\hbar = h/2\pi$, h = Planck's constant, k = Boltzmann's constant, Θ is the Debye temperature, m the absolute mass of the atom, T the absolute temperature and the function

$$\left[\varphi\left(\frac{\Theta}{T}\right) + \frac{\Theta/T}{4}\right]$$