Cubic Sodium Cyanide, Another Crystal with KCN-type Anomalous Thermoelastic Behaviour

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The temperature dependence of all elastic constants of cubic NaCN, measured by ultrasonic methods at *ca* 15 MHz from the transition point at 10·55 to 200 °C, exhibits a similar anomalous thermoelastic behaviour to cubic KCN. Within a wide temperature range all elastic wave velocities increase with higher temperature. The most characteristic feature of the anomalous behaviour is the softening of the shear constant c_{44} approaching the transition temperature. It is given by $c_{44}(T) \simeq 0\cdot2144(T-T_0)/T_0$ (10^{11}dyn cm^{-2}) with $T_0 = 255\cdot4$ K. The extremely small velocity of the elastic transverse wave connected with c_{44} makes NaCN highly suited for acousto-optical deflector devices.

Since the first report of anomalous thermoelastic properties of cubic KCN (Haussühl, 1973) only one other material with similar behaviour has been detected, namely cubic Ni(NO$_3$)$_2$.6NH$_3$ (Haussühl, 1974). Studies on several complex cyanides, such as K$_2$Hg(CN)$_4$, K$_3$Cu(CN)$_4$ and Na$_2$Fe(CN)$_5$NO.2H$_2$O, in which no orientational jumping processes of the cyanide ions occur, revealed no anomalies of that type. In a series of neutron scattering experiments, Price, Rowe, Rush, Prince, Hinks & Susman (1972), Rowe, Hinks, Price, Susman & Rush (1973) and Rowe, Rush, Vagelatos, Price, Hinks & Susman (1975) have shown that KCN and NaCN both possess three phases with similar structural properties. It seems that the transition of the high-temperature cubic phase to an orthorhombic structure, in which the cyanide ions are oriented along **b**, is in both materials mainly caused by the softening of the shear wave, which is connected with the elastic constant c_{44}. In order to provide additional data for the theoretical models recently under consideration we have now determined the elastic constants and their logarithmic temperature derivatives of cubic NaCN over a wide temperature range.

The growth of large single crystals of NaCN has been reported recently by Hinks, Price, Rowe & Susman (1972), who used a Bridgman technique. With this method an extensive procedure of purification of the starting material is necessary. Satisfactory optical quality of the crystals is not easily obtained because of impurities and mechanical deformations introduced by the crucible walls during the cooling process. After several runs with this technique, which yielded only poor results, we tried the Czochralski method. In the first stages we used seed crystals of NaCl and obtained high-quality single crystals of *ca* 2 × 2 × 3 cm from a melt of commercial NaCN *pro analysi* which had not been purified further. Several other crystals were grown with larger seed crystals cleaved from the first boules. The growth velocity ranged between 3 and 6 mm h^{-1}, the seed-crystal rotation between 30 and 50 r.p.m. An argon atmosphere was used. The growth properties are very similar to those of NaCl under the same conditions. Decomposition of the melt is not observed if the atmosphere is kept free from oxygen and carbon dioxide.

In humid air the crystals are slightly more hygroscopic than crystals of KCN. They possess a good cleavage parallel to the cubic faces and are optically fully transparent. The cleaved or ground and polished faces remain stable in dry air for a few minutes. For optical experiments we attached glass plates of optical quality to the polished faces with paraffin oil as immersion fluid. With these precautions the crystals could be kept transparent for several days.

Single crystals of cubic NaCN undergo a phase transition to an orthorhombic phase at *ca* 10 °C, which was first studied in an X-ray investigation by Verweel & Bijvoet (1939). In our own experiments we observed the phase transition in large crystals with very low cooling rates. Passing through the transition temperature, striated milky white areas propagate from the border parts into the interior of the crystal yielding a strong inhomogeneity. The retransition to the high-temperature phase occurs after a hysteresis of several degrees centigrade. The crystals regain their transparency, but not their original optical homogeneity. After heating these crystals for several hours at *ca* 250 °C the optical quality is fully regained. Only a slight double refraction is still present. Similar behaviour is observed in the transition of KCN, with the exception of the inhomogeneity which is much weaker in KCN after retransition. The transition temperature on passing from higher to lower temperatures was measured in several crystals to be 10·55 ± 0·05 °C.

The velocities of transverse and longitudinal elastic waves in the directions [100] and [110] were determined from 10·55 to 208 °C by diffraction of monochromatic light by ultrasonic waves in thick plates at frequencies of about 15 MHz (Schaefer–Bergmann method), and by recording the eigenfrequencies of thick plates. A He–Ne laser with a wavelength of 6328 Å was employed. The specimens were of rectangular shape with dimensions of ca 12 mm.

The values obtained for the elastic constants c_{ij} and the thermoelastic constants $T_{ij} = d \log c_{ij}/dT$, T temperature, together with the thermal expansion, as measured with a Fizeau interferometer and an inductive gauge dilatometer, are given in Tables 1 and 2. The density was determined by the buoyancy method at 20 °C and corrected for all other temperatures with the aid of the known thermal expansion coefficient. The elastic constant c_{12} is the average value derived from the directly measured quantities $c'' = (c_{11} - c_{12})/2$ and $c' = (c_{11} + c_{12} + 2c_{44})/2$, c_{11}, and c_{44}.

The relative probable errors are within the following limits: c_{11}, c' 0·4%; c_{44}, c'' 0·8%; c_{12} 1%. T_{ij} 6% whenever $|T_{ij}| > 0.5 \times 10^{-3}$ deg^{-1}.

Discussion

For comparison the elastic and thermoelastic constants of cubic KCN are listed in Tables 3 and 4. The main features of the elastic behaviour of cubic NaCN may be characterized as follows.

(i) In the near vicinity of the transition temperature all elastic constants of NaCN (10·55 °C) are larger than those of KCN (− 105 °C). An almost quantitative interpretation may be given on the basis of a simple model for the interaction potential of ions of opposite signs in ionic crystals, which leads to the relation (Haussühl, 1958)

Table 1. *Elastic constants, c_{ij}, density, ϱ, and thermal expansion coefficient, α, of sodium cyanide*

$c' = (c_{11} + c_{12} + 2c_{44})/2$, $c'' = (c_{11} - c_{12})/2$. Units: c_{ij} in 10^{11} dyn cm^{-2}, ϱ in g cm^{-3}, α in 10^{-6} deg^{-1}.

$T(°C)$	c_{11}	c'	c_{44}	c''	c_{12}	ϱ	α
10·55	2·521	2·016	0·0238	0·528	1·464	1·602	58
11	2·522	2·016	0·0242	0·529	1·463	1·602	58
12	2·524	2·017	0·025	0·531	1·461	1·602	58
15	2·528	2·019	0·028	0·538	1·453	1·601	58
20	2·534	2·022	0·033	0·545	1·444	1·599	58
30	2·545	2·027	0·0415	0·561	1·424	1·596	59
40	2·554	2·031	0·0495	0·575	1·406	1·593	59
50	2·560	2·035	0·0575	0·587	1·390	1·590	59
60	2·565	2·038	0·066	0·597	1·375	1·587	59
70	2·569	2·041	0·074	0·606	1·361	1·585	59
80	2·571	2·043	0·082	0·614	1·347	1·582	60
90	2·572	2·045	0·0905	0·622	1·333	1·579	60
100	2·572	2·046	0·099	0·628	1·319	1·576	60
120	2·570	2·048	0·116	0·638	1·294	1·570	60
140	2·564	2·049	0·1325	0·646	1·271	1·564	61
160	2·554	2·048	0·1475	0·653	1·248	1·558	62
180	2·540	2·045	0·163	0·658	1·224	1·552	63
200	2·522	2·040	0·178	0·661	1·201	1·546	64

Table 2. *Thermoelastic constants, $T_{ij} = d \log c_{ij}/dT$, of sodium cyanide ($10^{-3}$ deg^{-1})*

$T(°C)$	T_{11}	T'	T_{44}	T''	T_{12}
10·55	+0·59	+0·41	47	3·7	−1·40
20	0·47	0·32	27	3·1	−1·38
30	0·36	0·26	20	2·64	−1·34
40	0·27	0·22	16·2	2·25	−1·21
50	0·205	0·185	14	1·90	−1·12
60	0·155	0·150	12·2	1·60	−1·05
70	0·11	0·120	10·6	1·40	−1·02
80	0·065	0·095	9·8	1·22	−1·04
90	0·03	0·080	9	1·08	−1·05
100	−0·01	0·065	8·3	0·94	−1·01
120	−0·085	0·035	7·2	0·70	−0·93
140	−0·165	0·005	6·1	0·58	−0·90
160	−0·245	−0·04	5·2	0·45	−0·93
180	−0·320	−0·09	4·6	0·31	−0·96
200	−0·38	−0·15	4·1	0·19	−0·97

Table 3. *Elastic constants, c_{ij}, density, ϱ, and thermal expansion coefficient, α, of potassium cyanide*

$c' = (c_{11} + c_{12} + 2c_{44})/2$, $c'' = (c_{11} - c_{12})/2$. Units: c_{ij} in 10^{11} dyn cm^{-2}, ϱ in g cm^{-3}, α in 10^{-6} deg^{-1}.

$T(°C)$	c_{11}	c'	c_{44}	c''	c_{12}	ϱ	α
−105	1·733	1·606	0·0195	0·146	1·441	1·586	62
−100	1·742	1·611	0·0258	0·156	1·429	1·585	62
−80	1·777	1·631	0·052	0·198	1·381	1·579	59
−60	1·810	1·648	0·073	0·235	1·341	1·574	56
−40	1·840	1·664	0·091	0·267	1·305	1·569	54
−20	1·868	1·677	0·1075	0·299	1·271	1·564	52
0	1·893	1·688	0·1235	0·329	1·236	1·558	50
20	1·916	1·697	0·1405	0·360	1·197	1·553	49
40	1·936	1·704	0·1545	0·386	1·164	1·548	49
60	1·952	1·709	0·168	0·411	1·130	1·544	48
80	1·966	1·713	0·180	0·433	1·100	1·539	48
100	1·977	1·715	0·1915	0·453	1·070	1·535	48
120	1·984	1·715	0·2025	0·472	1·041	1·531	48
140	1·988	1·714	0·212	0·486	1·016	1·527	48
160	1·989	1·712	0·221	0·498	0·994	1·522	48
180	1·988	1·710	0·230	0·509	0·971	1·518	48
200	1·986	1·706	–	–	–	1·513	48

Table 4. *Thermoelastic constants, $T_{ij} = d \log c_{ij}/dT$ of potassium cyanide (10^{-3} deg^{-1})*

$T(°C)$	T_{11}	T'	T_{44}	T''	T_{12}
−100	1·03	0·64	51	14	−1·78
−90	0·99	0·60	33	11·7	−1·70
−80	0·95	0·56	23	9·9	−1·63
−70	0·91	0·525	16·5	8·4	−1·57
−60	0·87	0·49	13	7·3	−1·51
−50	0·83	0·46	11	6·5	−1·47
−40	0·79	0·425	9·5	5·9	−1·44
−20	0·71	0·36	7·8	5·2	−1·415
0	0·63	0·30	6·65	4·5	−1·40
20	0·55	0·24	5·6	3·9	−1·40
40	0·47	0·18	4·6	3·40	−1·40
60	0·39	0·13	3·85	2·90	−1·39
80	0·31	0·08	3·3	2·45	−1·37
100	0·23	0·03	2·9	2·05	−1·33
120	0·15	−0·01	2·5	1·65	−1·28
140	0·07	−0·04	2·3	1·35	−1·22
160	0·00	−0·07	2·1	1·10	−1·15
180	−0·05	−0·09	1·9	0·95	−1·07

$$c_{ij} = \bar{F}_{ij} e^2 r^{-4}.$$

e is the charge of an electron, $\bar{F}_{ij}$ is a factor of magnitude 1 and does not depend explicitly on the smallest distances r of opposite charged ions. It contains contributions which are not comprised in the Coulomb component of the potential. Within the isotypic group of the alkali halides of NaCl type the values $\bar{F}_{11}$ range from 0·8 for LiF to 2·0 for RbI. A similar behaviour is observed for the magnitude $\bar{F}_R = (\bar{F}_{11} + 2\bar{F}_{12})/3$ which occurs in the relation $R = 1/K = (c_{11} + 2c_{12})/3 = \bar{F}_R e^2 r^{-4}$, where K is the volume compressibility. Assuming that the ratios $\bar{F}_{11}(\text{NaCN})/\bar{F}_{11}(\text{KCN})$ and $\bar{F}_R(\text{NaCN})/\bar{F}_R(\text{KCN})$ nearly equal $\bar{F}_{11}(\text{NaCl})/\bar{F}_{11}(\text{KCl})$ and $\bar{F}_R(\text{NaCl})/\bar{F}_R(\text{KCl})$ respectively – a relation which is valid for other structurally related crystal groups – one obtains with the known values of NaCl and KCl (Table 5) a satisfactory explanation of the differences in those elastic constants of NaCN and KCN which vary only slightly with temperature, namely c_{11}, c_{12} and c'. The elastic anisotropy, expressed by c_{11}/c', exhibits almost the same magnitude in NaCN and KCN and is of the same type as in NaCl and KCl. Unexplained remains the relatively high value of c'' in NaCN in the vicinity of the transition, compared with that of KCN at $-105\,^\circ$C.

Table 5. *Elastic constants, c_{ij} (22 °C), thermoelastic constants, T_{ij} (0 °C), and lattice constants, a (22 °C), of NaCl and KCL*

Units are given in Tables 1 and 2 (Haussühl, 1960).

	c_{11} T_{11}	c' T'	c_{44} T_{44}	c'' T''	c_{12} T_{12}	a(Å)	F_{11}
NaCl	4·936 −0·80	4·375 −0·492	1·265 −0·266	1·825 −1·10	1·29 +0·17	5·640	1·351
KCL	4·078 −0·835	3·016 −0·545	0·633 −0·212	1·69 −1·10	0·69 +0·56	6·293	1·731

(ii) The logarithmic temperature derivatives T_{ij} exhibit qualitatively the same anomalous behaviour as those of KCN. Even the thermoelastic anisotropy is of the same type. Only T'' varies considerably weaker in NaCN. All wave velocities increase with higher temperature, beginning at the transition temperature, over a wide temperature range. At temperatures above 100 °C a certain trend towards normal behaviour, *i.e.* similar to that of NaCl, is recognized.

(iii) The most anomalous behaviour observed is that of c_{44} in NaCN as well as in KCN. The temperature dependence of c_{44} is described to a sufficient approximation by a linear relation $c_{44}(T) = 0·2144(T - T_0)/T_0$ (10^{11} dyn cm^{-2}) with $T_0 = 255·4$ whereas for KCN a logarithmic plot, $c_{44}(T) = a \log T/T_0$, with $T_0 = 153·7$, $a = 0·219 \times 10^{11}$ dyn cm^{-2} is a better fit to the observed values (T in K). From these relations follow the expressions for the thermoelastic constants $T_{44} = 1/(T - T_0)$ for NaCN and $T_{44} = 1/(T \log TT_0) \simeq T_0/$

$[T(T - T_0)]$ for KCN. For $T \simeq T_0$ the formulae differ only slightly. As the temperature range for the data of NaCN is considerably smaller than for KCN, the deviation from the linear behaviour of c_{44} could not be observed as clearly as in KCN.

The softening of the shear constant c_{44} approaching the transition temperature should be considered as the most characteristic feature of the phase transition observed in cubic NaCN and KCN. The instability of the cubic lattice is connected with the low resistance to mechanical shear deformations. As was already pointed out in the case of KCN and Ni(NO$_3$)$_2$.6NH$_3$ (Haussühl, 1974), the thermal activation energy at the transition temperature, expressed by kT_t, is related to the minimum shear constant c, yielding similar values for c/T_t for both materials. The corresponding value for NaCN and KCN is $c_{44} V/T_t$, where V is the unit-cell volume at the transition temperature T_t. With the lattice constant $a = 5·889$ Å for NaCN at 10·5 °C and $a = 6·482$ Å for KCN at $-105·4$ °C the results are 1·71 and $3·09 \times 10^{-14}$ dyn cm deg^{-1} for NaCN and KCN respectively. The same magnitude of these values indicates that the kinetic processes of the phase transition are of the same type in both crystals. The difference should not be regarded too seriously in view of the high variation of c_{44} in the vicinity of the transition temperature.

Finally we would like to draw attention to the special suitability of NaCN crystals for the construction of acousto-optical deflector devices owing to the extremely small propagation velocity of its elastic shear wave connected with c_{44}, which yields a high figure of merit, though the indices of refraction are relatively small. The easily obtainable optical quality of the crystals and the low cost of their production make them superior to many other materials proposed for such applications. In preliminary experiments intensive diffraction spots were observed indicating also the existence of a reasonably high elasto-optic constant p_{44}.

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