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# Anomalous Thermoelastic Properties of the Cyanospinels $K_2Zn(CN)_4$, $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$

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The temperature dependence of the elastic constants of $K_2M(CN)_4$ (M = Zn, Cd, Hg), measured by ultrasonic methods over a wide temperature range, has revealed a new type of anomalous behaviour in $K_2Hg(CN)_4$, different from that observed in KCN and $Ni(NO_3)_2.6NH_3$. In this crystal all elastic constants decrease strongly from about −75 °C to the transition temperature at −162·5 °C. As the temperature is increased from −75 °C the elastic properties of $K_2Hg(CN)_4$ approach those of $K_2Zn(CN)_4$ and $K_2Cd(CN)_4$. These latter crystals do not exhibit any anomalies of this type in the range between −180 and 200 °C.

Anomalous thermoelastic properties of cubic potassium cyanide and nickel nitrate hexaammonia were reported recently (Haussühl, 1973, 1974). Until now it has been possible to interpret the phenomena as due to an increasing overlap of adjacent ions caused by the libration and rotation processes of the asymmetric CN and $NO_3$ ions. In order to provide new data for the discussion a series of other crystals, in which similar effects were expected, have been investigated. In this paper the results obtained in the cyanospinel group, which is structurally and chemically closely related to KCN, are reported.

## Measurements

Single crystals of optical quality of the three cyanospinels with diameters up to 30 mm were grown from aqueous solutions by the method of controlled temperature lowering between 40° and 30 °C with growth velocities of 0·2 mm per day. Only octahedral {111} and icosahedral {211} faces developed.

The velocities of transverse and longitudinal elastic waves propagating in the directions [100] and [110] were measured from −180° to 200 °C in $K_2Zn(CN)_4$ and $K_2Cd(CN)_4$ and from −163° to 200 °C in $K_2Hg(CN)_4$ by ultrasonic techniques. These techniques consisted of diffraction of monochromatic light by ultrasonic waves at about 15 MHz (Schaefer–Bergmann method) and recording the eigenfrequencies of thick plates. The specimens used were of rectangular shape with dimensions of *ca* 10 mm.

The experimental procedures were standard. For the measurements of the velocities of transverse waves at high temperature the crystals were rigidly cemented on Y-cut quartz ultrasonic generators with a synthetic adhesive.

$K_2Hg(CN)_4$ transforms from the cubic high-temperature phase to a phase of lower symmetry at *ca* −162·5 °C. The transition was first postulated by Ikeda, Nakamura & Kubo (1968) and was studied in more detail by Saruwatari, Ikeda, Nakamura & Kubo (1973) who observed a slight splitting of the nuclear quadrupole resonance frequencies of $^{14}N$ at the transition point. The results of our own studies of the phenomena occurring during the transformation of single crystals showed the following additional features: the crystals contract during the transition with a relative volume change $\Delta V/V \simeq -8 \times 10^{-3}$. In the case of a $(001)\times(110)\times(1\bar{1}0)$ cut, the dimensions $l$, which were about 10 mm, changed within a 3° temperature range while passing through the transition point by the following amounts:

$$[001]:\ \Delta l/l = -0{\cdot}1 \times 10^{-3}$$
$$[110]:\ \Delta l/l = -4 \times 10^{-3}$$
$$[1\bar{1}0]:\ \Delta l/l = -3{\cdot}9 \times 10^{-3}.$$

This transformation started at one side of the crystal and spread slowly over the whole specimen under quasi-equilibrium conditions. Thin plates with a thickness up to about 1 mm remained transparent in the low-temperature phase, but inhomogeneous strains induced double refraction and destroyed the optical quality of the crystals. Thicker crystals partly lost their transparency. Ultrasonic waves are strongly damped.

After the reverse transition to the high-temperature phase a coarse system of macroscopic cracks parallel to [100] remained. The hysteresis of the transition, starting from either the higher or the lower temperature, was observed to be about 2 °C in thick single crystals. The original transparency of the high-temperature phase and all other properties are otherwise fully regained. This behaviour is similar to that of potassium cyanide. Preliminary X-ray diffraction studies revealed only a small change in the lattice constants connected with a slight splitting of reflexions. This confirms the suggestion of Saruwatari *et al.* (1973) that the structural differences between both phases are very small. These investigations are being continued. $K_2Zn(CN)_4$ and $K_2Cd(CN)_4$ do not exhibit any sign of a phase transition in the range between −180° and 200 °C. All three substances possess a remarkably high resistance to chemical decomposition below 200 °C.

The values obtained for the elastic constants $c_{ij}$ and the thermoelastic constants $T_{ij} = \mathrm{d} \log c_{ij}/\mathrm{d}T$, $T$ temperature, together with the density and lattice constants, as measured with large single crystals by the buoyancy method and the Bragg method respectively, are presented in Tables 1, 2, and 3. The relative probable errors are within the following limits:

$$c_{11}, c' = (c_{11} + c_{12} + 2c_{44})/2: \quad 0{\cdot}5\,\%$$
$$c_{44}, c'' = (c_{11} - c_{12})/2: \quad 0{\cdot}8\,\%; \quad c_{12}: \quad 1\,\%\,.$$

The errors of the values for 0°C are estimated to be much smaller.

## Discussion

The first crystal structure determination of the cyanospinels was carried out by Dickinson (1922). Cyanide ions, potassium ions, and the bivalent ions M occupy the corresponding sites of oxygen, aluminum and magnesium ions in spinel. The cyanide ions form regular tetrahedra $M(CN)_4$ about the central ion M. With the

Table 1. *Elastic constants* $c_{ij}$, *thermoelastic constants* $T_{ij} = \mathrm{d} \log c_{ij}/\mathrm{d}T$, *and thermal expansion* $\alpha$ *of* $K_2Zn(CN)_4$

Lattice constant $a = 12{\cdot}544$ Å (20°C), density $\varrho = 1{\cdot}667$ g cm$^{-3}$ (20°C). Units: $c_{ij}$ in $10^{11}$ dyn cm$^{-2}$; $T_{ij}$ in $10^{-3}$/°C; $\alpha$ in $10^{-6}$/°C. $c' = (c_{11} + c_{12} + 2c_{44})/2$ . $c'' = (c_{11} - c_{12})/2$.

| Temperature [°C] | $c_{11}$ | $c_{12}$ | $c_{44}$ | $c'$ | $c''$ | $T_{11}$ | $T_{12}$ | $T_{44}$ | $\alpha$ |
|---|---|---|---|---|---|---|---|---|---|
| 200 | 2·055 | 0·973 | 0·329 | 1·843 | 0·541 | −0·525 | −0·82 | 0·015 | 22 |
| 150 | 2·109 | 1·015 | 0·328 | 1·890 | 0·547 | −0·52 | −0·82 | 0·015 | 21 |
| 100 | 2·164 | 1·056 | 0·328 | 1·938 | 0·554 | −0·52 | −0·82 | 0·015 | 19·5 |
| 50 | 2·220 | 1·100 | 0·328 | 1·988 | 0·560 | −0·52 | −0·82 | 0·02 | 17·5 |
| 0 | 2·278 | 1·146 | 0·328 | 2·040 | 0·566 | −0·525 | −0·84 | 0·025 | 16 |
| −50 | 2·337 | 1·197 | 0·327 | 2·094 | 0·570 | −0·53 | −0·87 | 0·030 | 14 |
| −100 | 2·397 | 1·251 | 0·327 | 2·151 | 0·573 | −0·53 | −0·89 | 0·035 | 11·5 |
| −150 | 2·458 | 1·308 | 0·327 | 2·210 | 0·575 | −0·54 | −0·90 | 0·040 | 9 |
| −180 | 2·497 | 1·347 | 0·326 | 2·248 | 0·575 | −0·54 | −0·91 | 0·040 | 8 |

Table 2. *Elastic constants* $c_{ij}$, *thermoelastic constants* $T_{ij} = \mathrm{d} \log c_{ij}/\mathrm{d}T$, *and thermal expansion* $\alpha$ *of* $K_2Cd(CN)_4$

Lattice constant $a = 12{\cdot}848$ Å (20°C), density $\varrho = 1{\cdot}841$ g cm$^{-3}$ (20°C). Units: $c_{ij}$ in $10^{11}$ dyn cm$^{-2}$; $T_{ij}$ in $10^{-3}$/°C; $\alpha$ in $10^{-6}$/°C. $c' = (c_{11} + c_{12} + 2c_{44})/2$ . $c'' = (c_{11} - c_{12})/2$.

| Temperature [°C] | $c_{11}$ | $c_{12}$ | $c_{44}$ | $c'$ | $c''$ | $T_{11}$ | $T_{12}$ | $T_{44}$ | $\alpha$ |
|---|---|---|---|---|---|---|---|---|---|
| 200 | 1·660 | 0·878 | 0·260 | 1·529 | 0·391 | −0·495 | −0·72 | 0·190 | 22 |
| 150 | 1·701 | 0·909 | 0·257 | 1·562 | 0·396 | −0·485 | −0·72 | 0·190 | 21 |
| 100 | 1·742 | 0·940 | 0·255 | 1·596 | 0·401 | −0·475 | −0·73 | 0·190 | 20 |
| 50 | 1·783 | 0·975 | 0·253 | 1·632 | 0·404 | −0·470 | −0·73 | 0·190 | 18·5 |
| 0 | 1·825 | 1·011 | 0·251 | 1·669 | 0·407 | −0·470 | −0·76 | 0·190 | 17·5 |
| −50 | 1·869 | 1·051 | 0·249 | 1·709 | 0·409 | −0·49 | −0·81 | 0·195 | 15·5 |
| −100 | 1·917 | 1·097 | 0·247 | 1·754 | 0·410 | −0·53 | −0·89 | 0·195 | 13 |
| −150 | 1·971 | 1·149 | 0·245 | 1·805 | 0·411 | −0·59 | −0·99 | 0·190 | 9 |
| −180 | 2·008 | 1·186 | 0·243 | 1·840 | 0·411 | −0·64 | −1·08 | 0·180 | 7 |

Table 3. *Elastic constants* $c_{ij}$, *thermoelastic constants* $T_{ij} = \mathrm{d} \log c_{ij}/\mathrm{d}T$, *and thermal expansion* $\alpha$ *of* $K_2Hg(CN)_4$

Lattice constant $a = 12{\cdot}784$ Å (20°C), density $\varrho = 2{\cdot}435$ g cm$^{-3}$ (20°C). Units: $c_{ij}$ in $10^{11}$ dyn cm$^{-2}$; $T_{ij}$ in $10^{-3}$/°C; $\alpha$ in $10^{-6}$/°C. $c' = (c_{11} + c_{12} + 2c_{44})/2$ . $c'' = (c_{11} - c_{12})/2$.

| Temperature [°C] | $c_{11}$ | $c_{12}$ | $c_{44}$ | $c'$ | $c''$ | $T_{11}$ | $T_{12}$ | $T_{44}$ | $\alpha$ |
|---|---|---|---|---|---|---|---|---|---|
| 200 | 1·659 | 0·839 | 0·240 | 1·489 | 0·410 | −0·42 | −0·54 | 0·21 | 22 |
| 150 | 1·693 | 0·861 | 0·238 | 1·515 | 0·416 | −0·39 | −0·51 | 0·22 | 21 |
| 100 | 1·725 | 0·883 | 0·235 | 1·539 | 0·421 | −0·36 | −0·48 | 0·23 | 19·6 |
| 50 | 1·755 | 0·903 | 0·232 | 1·561 | 0·426 | −0·32 | −0·44 | 0·24 | 18·3 |
| 0 | 1·780 | 0·920 | 0·229 | 1·579 | 0·430 | −0·26 | −0·37 | 0·27 | 16·7 |
| −20 | 1·788 | 0·926 | 0·228 | 1·585 | 0·431 | −0·21 | −0·30 | 0·30 | 16 |
| −40 | 1·795 | 0·931 | 0·226 | 1·589 | 0·432 | −0·16 | −0·22 | 0·33 | 15 |
| −60 | 1·799 | 0·935 | 0·225 | 1·592 | 0·432 | −0·09 | −0·11 | 0·36 | 14 |
| −80 | 1·801 | 0·935 | 0·223 | 1·591 | 0·433 | +0·02 | +0·09 | 0·39 | 13 |
| −100 | 1·796 | 0·930 | 0·222 | 1·585 | 0·433 | 0·22 | 0·44 | 0·43 | 12 |
| −110 | 1·789 | 0·923 | 0·221 | 1·577 | 0·433 | 0·40 | 0·81 | 0·48 | 11·5 |
| −120 | 1·780 | 0·914 | 0·220 | 1·567 | 0·433 | 0·63 | 1·31 | 0·55 | 11 |
| −130 | 1·765 | 0·899 | 0·219 | 1·551 | 0·433 | 1·05 | 2·22 | 0·68 | 10·5 |
| −140 | 1·740 | 0·874 | 0·218 | 1·525 | 0·433 | 1·85 | 4·00 | 0·99 | 10 |
| −150 | 1·695 | 0·829 | 0·216 | 1·478 | 0·433 | 3·5 | 7·5 | 1·50 | 9·5 |
| −155 | 1·660 | 0·804 | 0·214 | 1·440 | 0·434 | 4·6 | 10·0 | 2·0 | 9·2 |
| −160 | 1·615 | 0·749 | 0·211 | 1·392 | 0·434 | 6·4 | 15 | 2·85 | 9 |
| −162,5 | 1·586 | 0·720 | 0·209 | 1·361 | 0·434 | 7·9 | 18 | 3·9 | 9 |

aid of Raman and infrared spectra Mathieu & Poulet (1962) and Jones (1961) could not only confirm the existence of these tetrahedra but also decide that the bivalent ion M is bound to the cyanide ion by the carbon and not by the nitrogen atom to form a linear M–C–N configuration. The bond problem was also solved by Sequeira & Chidambaram (1965) in a neutron diffraction study of $K_2Zn(CN)_4$. The best agreement between observed and calculated structure factors was also obtained for the M–C–N bond. This implies that the potassium ions are surrounded by six nitrogen atoms of the adjacent cyanide ions, while in potassium cyanide the potassium ions are randomly coordinated by three carbon and three nitrogen atoms belonging to different cyanide ions.

The room-temperature lattice constants of the zinc, cadmium, and mercury salts are 12·544, 12·848, and 12·784 Å respectively. The small differences result from the different M–C distances. The similar physical behaviour of the three isotypic salts, including the elastic and thermoelastic properties in the high-temperature range, is explained by these nearly identical structural data. $K_2Zn(CN)_4$ possesses slightly higher elastic constants than $K_2Cd(CN)_4$ owing to the difference in the lattice constants. This is in accordance with the behaviour of other isotypic crystal groups like the alkali halides of the rocksalt type. The mercury salt does not obey this rule. But the most surprising feature of the present investigation is the anomalous thermoelastic behaviour of $K_2Hg(CN)_4$ which must be considered in connexion with the phase transition at −162·5°C. Already at room temperature the temperature dependence of the elastic constants is much weaker for the mercury salt than for the other two compounds. Its thermoelastic constants exhibit positive values below *ca* −75°C and steadily grow to very high values such as $10^{-2}$/°C as the transition temperature is approached. The temperature coefficient of the inverse bulk compressibility $K^{-1}=(c_{11}+2c_{12})/3$ behaves similarly. The two other salts show only a slight temperature dependence of their elastic properties, which will be discussed below. The anomalies are different from those observed in potassium cyanide (Haussühl, 1973): in this compound all wave velocities strongly decrease from about 160°C to the transition temperature at *ca* −105°C, but the bulk compressibility and the elastic constant $c_{12}$ behave normally over the whole temperature range studied. The shear resistance $c_{44}$ almost vanishes as the transition temperature is approached. This indicates a direct relation between mechanical lattice stability and the phase transition. Such a strong softening of an acoustic wave is not observed in $K_2Hg(CN)_4$. These differences in the elastic behaviour, the similar properties of the cyanospinels at higher temperatures, and the non-existence of either a phase transition or elastic anomalies in the zinc and cadmium compounds lead to the conclusion that the phase transition and the anomalous elastic behaviour of $K_2Hg(CN)_4$ do not originate from rotational movements of the cyanide ions as in potassium cyanide. This is also in accordance with the above-mentioned fixed bond between the bivalent ion and the carbon atom of the cyanide ion, which is assumed to exist also in the high-temperature range for all cyanospinels. At the moment the forces causing the phase transition in $K_2Hg(CN)_4$ are not yet known. On the basis of nuclear quadrupole resonance measurements Saruwatari *et al.* (1973) pointed out that as they pass through the transition the regular $Hg(CN)_4$ tetrahedra are deformed into tetrahedra with only trigonal symmetry, hence yielding two kinds of cyanide ions with a density ratio of one to three. If this is true, the transition can be explained in terms of a thermally induced equalization of the two different Hg–C bond states above the transition point. This model would also provide a qualitative understanding of the anomalous thermoelastic properties, since the stability of the tetrahedra with cubic symmetry will increase with increasing temperatures. Thus these tetrahedra will give a certain contribution to the average repulsive potential and therefore to the stiffness as the temperature is increased. Yet why the mercury compound alone shows this transition demands a special investigation.

Saruwatari *et al.* (1973) also discussed the influence of the thermal activated librational motions of the cyanide ions on the nuclear quadrupole resonance frequencies which decrease with increasing temperature. These motions indicate an anomalous thermoelastic behaviour different from the one discussed above. The thermoelastic constants of $K_2Zn(CN)_4$ and $K_2Cd(CN)_4$ do not show the usual increase in absolute values with increasing temperature like other isotypic crystal groups, *e.g.* the alkali halides of the rocksalt type. The softening of the elastic resistance with increasing temperature is stronger at low temperatures than at higher temperatures. This indicates that the thermally activated vibrations, which also enhance the effective repulsive potential, have some effect. In $K_2Hg(CN)_4$ this effect is screened by the processes described above.

A further elucidation and explanation of the anomalous properties described here may be possible as a result of investigations on other cyanospinels and on mixed crystals in which potassium is partly replaced by other monovalent ions.

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