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Ferroelasticity and Phase Transformation in $Rb_2Hg(CN)_4$ Spinel

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(*Received* 27 *February* 1978; *accepted* 9 *June* 1978)

The low-temperature form of $Rb_2Hg(CN)_4$ [space group $R\bar{3}c$, $Z = 12$, $a_1 = 9{\cdot}076$, $a_3 = 46{\cdot}050$ Å (273 K)] possesses a slightly distorted spinel structure with parameters similar to those of cubic cyanospinels. It transforms into a cubic spinel modification at *ca* 398 K ($a = 13{\cdot}140$ Å at 399 K). Below the transition temperature the crystals exhibit ferroelastic properties, which allow the switching of the distortion directions into any one of four equivalent states. The critical stress is less than 1×10^{-3} kp mm^{-2}. The resulting deformations do not exceed 2×10^{-2}. Larger twinned crystals return to their primary state after the release of stress. They behave like extremely soft elastic springs. The crystals belong to the ferroelastic Aizu species $m3mF\bar{3}m$. The transition shows a constant hysteresis of *ca* 12 K in all crystals investigated. The pressure derivatives of the upper and lower transition temperatures are observed to be almost equal and constant over a wide temperature range ($dT/dP \approx 0{\cdot}245$ K bar^{-1}). The observed enthalpy of transformation is $1{\cdot}03$ J g^{-1} in fair agreement with the prediction of the Clapeyron–Clausius relation. Crystals of $K_2Hg(CN)_4$ exhibit similar properties; their transition temperature, hysteresis, enthalpy of transformation, and dT/dP are considerably less.

Crystallographic characterization; ferroelastic behaviour

Following an earlier investigation on cyanospinels of the type $K_2M(CN)_4$ [with M = Zn, Cd, and Hg (Haussühl, 1976)] crystals of $Rb_2Hg(CN)_4$ with dimensions of *ca* 20 mm were grown from aqueous solutions at *ca* 310 K by the controlled lowering of temperature. The crystals exhibit trigonal symmetry, though their morphology is almost identical to that observed in cubic cyanospinels, namely octahedron {111}, icositetrahedron {311}, and cube {100}. The existence of a

Table 1. *Properties of trigonal* $Rb_2Hg(CN)_4$

Observed forms (trigonal–hexagonal setting)	{001} basal pinacoid	{102} rhombohedron	{$\bar{1}$04} rhombohedron	{$\bar{1}$0.10} rhombohedron	{$\bar{2}$16} scalenohedron	{$\bar{2}$02} rhombohedron
Corresponding cubic faces	(111), ($\bar{1}\bar{1}\bar{1}$) octahedron (partly)	($\bar{1}$11), (1$\bar{1}$1), *etc.* octahedron (partly)	{100} cube	(311) *etc.* icositetrahedron (partly)	(3$\bar{1}$1) *etc.* icositetrahedron (partly)	(3$\bar{1}\bar{1}$) *etc.* icositetrahedron (partly)

Density (experimental) (293 K)	2·881 g cm^{-3}
Thermal expansion coefficients (340 K)	$\alpha_1 = 114 \times 10^{-6}\ K^{-1}$ $\alpha_3 = -38 \times 10^{-6}$
Thermal expansion coefficient above transition temperature (440 K)	$\alpha = 18 \times 10^{-6}$

Indices of refraction (293 K)

λ (nm)	436	546	578	633
n_1	1·476	1·466	1·464	1·461
n_3	1·480	1·470	1·468	1·465

non-cubic phase of $Rb_2Hg(CN)_4$ has been reported previously by Bok & Basson (1966) (who, however, gave no further structural details). The crystals show macroscopic twinning, mainly as simple bicrystals. The twinning mirror planes correspond to cubic {110} planes. The crystals are optically uniaxial positive. The optical extinction in the twin domains occurs in accordance with the existence of four equivalent directions of the threefold axis corresponding to the cubic directions [111], [$\bar{1}$11], [1$\bar{1}$1], and [11$\bar{1}$]. In Table 1 some properties of the crystals are listed.

With the aid of Laue photographs, rotation photographs, and a series of reflexions collected by an automatic diffractometer (CAD-4, Enraf–Nonius) the existence of a rhombohedral lattice with space-group symmetry $R\bar{3}c$ or $R3c$ was established. As no piezoelectric or nonlinear optical effects could be detected, the correct space group is assumed to be $R\bar{3}c$. The morphological symmetry also exhibits a centre of inversion. From Bragg reflexions, obtained on large single crystals, the dimensions of a trigonal–hexagonal unit cell with $Z = 12$ were found to be $a_1 = 9{\cdot}076$ and $a_3 = 46{\cdot}050$ Å (273 K). All strong reflexions correspond to a cubic spinel structure of $K_2Hg(CN)_4$ type; they are split into groups in accordance with the deviation from cubic symmetry, resulting from the given lattice constants. The lattice spacing parallel to the threefold axis, compared with a cubic cyanospinel, is doubled. The metrical deviation of the trigonal lattice from the cubic cyanospinel lattice may be described by a distortion factor D. The basic vectors $\mathbf{A}'_i$ of an undistorted trigonal–hexagonal cell of the cubic spinel lattice are related to the axes $\mathbf{a}'_i$ of the primitive rhombohedral cell of that lattice by the transformation

$$(\mathbf{A}'_i) = \begin{pmatrix} 1 & \bar{1} & 0 \\ 0 & 1 & \bar{1} \\ 1 & 1 & 1 \end{pmatrix} . (\mathbf{a}'_j),$$

with $\mathbf{a}'_j = (\mathbf{b}_k + \mathbf{b}_l)/2$ ($\mathbf{b}_i$ are the basic vectors of the f.c.c. cell). The deviation of the observed ratio $a_3/2a_1$ from the ideal value $A'_3/A'_1 = 2\sqrt{(\frac{3}{2})}$ is significant for the distortion. The observed distortion $D = a_3/2a_1 : 2\sqrt{(\frac{3}{2})} = 1{\cdot}0357$ indicates a dilatation parallel to and a contraction perpendicular to the threefold axis. This distortion can be observed directly by an angle of 2° 10′ which is formed by adjacent pseudo-octahedron faces in twinned crystals. A structure determination, both by X-ray and neutron diffraction methods, is in progress, by which further details of the differences between cubic and trigonal cyanospinel structures are expected to be obtained.

During the preparation of specimens an unusual mechanical instability was observed. The slightest mechanical stresses, occurring during grinding or already introduced by soft touching, produced twinned areas in originally untwinned crystals. All new twin domains belong to one of the four states described above. By a soft uniaxial pressure parallel to the threefold axis untwinned crystals of smaller size can be transformed into single domains of one of the other orientations. The macroscopic deformation observed consists of a longitudinal and a transverse movement in accordance with the above-mentioned twin law which requires a dilatation parallel to and a contraction perpendicular to the new direction of the threefold axis. In twinned crystals with larger dimensions (several mm) the deformation achieved by uniaxial stress is not preserved after the release of stress. Such a crystal immediately returns to its initial state. The deformation operation can be repeated indefinitely. The crystals behave like elastic springs with a very weak restoring force within a deformation range of *ca* 2×10^{-2}.

The critical uniaxial stress for initiating such deformations is less than 10^{-3} kp mm^{-2}. The resulting deformations are generated in small steps with slightly different elastic resistances. A certain acoustic noise accompanies the movement of a system of parallel twinning mirror planes which are easily observable by optical reflexion. This behaviour might arise from internal stresses introduced in multiply twinned crystals, which forbid homogeneous deformations. Such crystals exhibit unusually large piezo-optic effects – several orders of magnitude larger than those in comparable crystals like cubic $K_2Hg(CN)_4$. According to Aizu's (1969) definition the crystals are ferroelastic.

The cubic cyanospinel should be considered to be the appropriate prototype. The observed ferroelastic properties are consistent with Aizu species $m3mF\bar{3}m$ with four equivalent states, in which no ferroelectric effects are possible. Apparently, $Rb_2Hg(CN)_4$ is the first material known to belong to this species. In order to confirm the suggested prototype the crystals were investigated over a wider temperature range.

Phase transformation

It is already known that the cubic high-temperature phase of $K_2Hg(CN)_4$ undergoes a phase transformation into a trigonal phase at *ca* 100 K (Ikeda, Nakamura & Kubo, 1968; Saruwatari, Ikeda, Nakamura & Kubo, 1973; Haussühl, 1976). Further experiments on mixed crystals of the type $(Rb,K)_2Hg(CN)_4$ revealed a strong increase in transition temperature with higher Rb content (Gross & Haussühl, 1977). This suggested that trigonal $Rb_2Hg(CN)_4$ would possess the low-temperature structure type of $K_2Hg(CN)_4$, and that a phase transition into the cubic spinel phase would occur at elevated temperature. The latter was confirmed by X-ray, optical, thermoanalytical, thermal-expansion, elastic and high-pressure measurements. Thin single crystals undergo a reversible transformation into the cubic spinel structure at *ca* 398 K, approaching the transition from lower temperatures. The transition back into the trigonal form takes place with a considerable but almost constant hysteresis at *ca* 386 K. The domains within a specimen often show differences in transition temperatures of up to several degrees. During the transition into the high-temperature form the crystals occasionally break into smaller pieces.

X-ray work both on single crystals (Bragg method) and powders confirmed the spinel structure of the high-temperature form. The lattice spacing of the cubic-face-centered cell at 399 K is $a = 13{\cdot}140$ Å; the trigonal cell immediately below the transition has dimensions $a_1 = 9{\cdot}1845$ and $a_3 = 45{\cdot}866$ Å. This corresponds to a volume change of *ca* 1·55%, which may be responsible for the observed shattering of the crystals. An example for the temperature dependence of 2θ for the reflexion $110_{\text{trig.-hex.}}$ and its corresponding reflexion 220_{cubic} is given in Fig. 1.

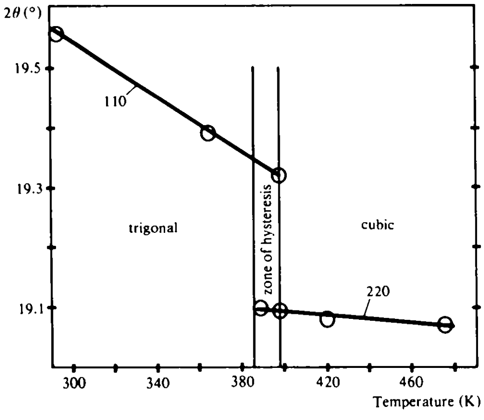

Fig. 1. Temperature dependence of 2θ (Cu $K\alpha$) of reflexion $110_{\text{trig.-hex.}}$ of the low-temperature form of $Rb_2Hg(CN)_4$ and 220_{cubic} of the high-temperature form at normal pressure.

Furthermore, the ferroelastic deformations were observed approaching the transition temperature. The ferroelastic response to uniaxial stress decreases continuously with increasing temperature, reaching a negligible value at *ca* 400 K in accordance with the other observations reported.

The influence of hydrostatic pressure on both transition temperatures was studied with the aid of an optical pressure cell between 380 and 470 K with pressures up to 350 bar. Both the upper transition temperature T_1 (trigonal → cubic), and the lower transition temperature T_2 (cubic → trigonal) exhibit a linear dependence on hydrostatic pressure with almost equal derivatives $dT_1/dP \approx dT_2/dP \approx 0{\cdot}245$ K bar^{-1}. The temperature difference $T_1 - T_2 \approx 12$ K remains nearly constant over the whole pressure range applied. This pressure shift is one of the strongest effects ever observed in solids. An almost constant pressure difference between both transitions of *ca* 40 bar was observed over the whole temperature range. This pressure hysteresis is consistent with the temperature hysteresis. A graph of this behaviour is shown in Fig. 2.

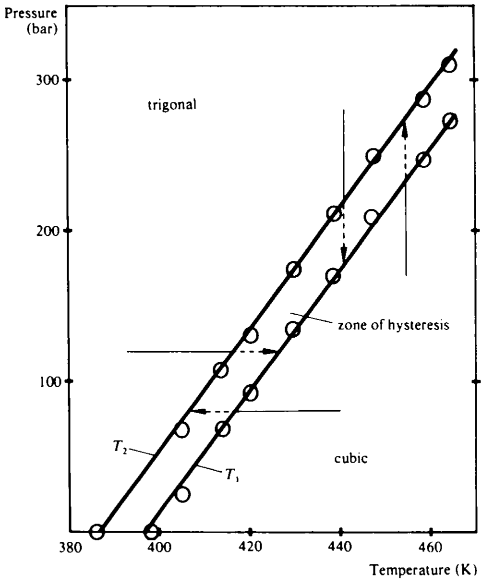

Fig. 2. P–T diagram of $Rb_2Hg(CN)_4$. Starting from any point outside the zone of hysteresis, the transition to the other phase takes place as soon as the opposite border line of the hysteresis zone is passed by a change of temperature or pressure.

A thermoanalytical investigation, carried out on a Perkin Elmer BSG2 differential scanning calorimeter in the range between 380 and 405 K, yielded endothermic signals with an enthalpy of transformation of 1·03 J g^{-1} (±3%). With the Clapeyron–Clausius relation $dP/dT = \Delta H/T\Delta V$, the experimental values for T, dP/dT, and ΔV lead to an enthalpy $\Delta H = 0{\cdot}88$ J g^{-1} in fair agreement with the calorimetric measurement.

It has been suggested that for $K_2Hg(CN)_4$ also the dependence of transition temperature on hydrostatic pressure would be marked; this was confirmed. With the application of pressures up to 1560 bar the temperature for the cubic → trigonal transition could be shifted from *ca* 110 to 306 K. As with the behaviour of $Rb_2Hg(CN)_4$ the derivative $dT/dP = 0{\cdot}122$ K bar^{-1} remains almost constant over the whole pressure range. A much smaller hysteresis in temperature at constant pressure and also in pressure at constant temperature was observed (*ca* 2 K and 7 bar respectively). Under comparable conditions, the transition in $Rb_2Hg(CN)_4$ develops almost spontaneously, contrary to the slow propagation of the transition frontier in $K_2Hg(CN)_4$. The latter crystals are retained without cracks after several cycles of transitions. This is not possible with crystals of $Rb_2Hg(CN)_4$ of larger dimensions. The different behaviour may originate from the much smaller values for the enthalpy of transformation $\Delta H = 0{\cdot}18$ J g^{-1} (at *ca* 113 K) and the relative change in volume $\Delta V/V \approx 0{\cdot}8\%$ in $K_2Hg(CN)_4$ (Haussühl, 1976). Despite this difference there is no doubt that the low-temperature form of $K_2Hg(CN)_4$ is isotypic with trigonal $Rb_2Hg(CN)_4$. This was confirmed by X-ray powder patterns of $K_2Hg(CN)_4$ at *ca* 100 K.

The much higher transition temperature of $Rb_2Hg(CN)_4$ may be qualitatively interpreted by the well known structural properties of normal spinels. Replacing K by Rb, the interstices of the $(CN)_6$ octahedra are enlarged. The anion parameter u is thereby reduced and additional compressive forces on the $Hg(CN)_4$ tetrahedra are expected. Such forces stabilize the low-temperature structure of higher density. Therefore the activation energy for a degeneracy of the trigonal states must be considerably higher in $Rb_2Hg(CN)_4$. The negative coefficient of thermal expansion α_3 confirms the existence of dynamical fluctuations of states in the trigonal phase.

Transitions of this type have not previously been observed with other pairs of cyanospinels in which Hg is replaced by Zn or Cd. It is suggested that such transitions will occur at higher pressures. Further investigations in this field are in progress.

Finally it should be emphasized that the transition temperatures in other simple systems like NaCN–KCN–RbCN show the opposite order [T(NaCN) > T(KCN) > T(RbCN)].

Further investigations are necessary to elucidate the dynamical interactions which are involved in the phase transition of $(K,Rb)_2Hg(CN)_4$ crystals, and which are also responsible for the unique thermoelastic anomalies of the high-temperature form (Haussühl, 1976).

The author is indebted to P. Klüfers and G. Trafara of the Chemical Department of the University of Köln, for performing the measurements on the automatic diffractometer and the differential calorimeter respectively.

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