

The Thermal Transformations in Solid Rubidium Nitrate

By R. N. BROWN AND A. C. MCLAREN*

Central Research Laboratories, Imperial Chemical Industries of Australia and New Zealand Limited,
Ascot Vale, Victoria, Australia

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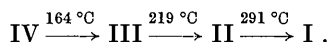
The thermal transformations in solid rubidium nitrate have been studied by optical microscopy, X-ray diffraction and measurements of electrical conductance.

It has been found that forms IV, III and probably II are structurally related. No simple structural relationship between II and I has been found.

The transformations between IV, III and II appear to involve changes of positional randomization of the rubidium ions. There is no evidence for changes of positional randomization at the $II \rightleftharpoons I$ transformations.

Introduction

Plyushev *et al.* (1956) have shown by differential thermal analysis that rubidium nitrate has four stable forms between room temperature and the melting point at ca. 314 °C. They give the transformation temperatures as:



We have made a study of these forms, and of the transformations between them, by means of optical microscopy, X-ray diffraction and measurements of the electrical conductance as a function of temperature.

This paper is part of a general programme of research on the solid state transformations in the nitrates of univalent cations.

Experimental and results

Optical microscopy and X-ray diffraction

Rubidium nitrate IV crystallizes from aqueous solution at room temperature as needles with a triangular cross-section. Single crystals were examined with a polarizing microscope fitted with a conventional hot stage, and by X-ray diffraction. X-ray photographs show that IV is not orthorhombic as given in the ASTM Index Powder Data File, but trigonal with

$$a = 10.48, c = 7.45 \text{ \AA}.$$

The needle axis corresponds to the c -axis and the sides of the triangular cross-section are parallel to the a -axes.

The systematic absences are $00l$ for $l \neq 3n$, the diad axis being normal to $(10\cdot0)$, indicating space group $P3_112$ or $P3_212$. $d_c = 3.11 \text{ g.cm.}^{-3}$ for $Z = 9$. $d_o = 3.11 \text{ g.cm.}^{-3}$. (*Handbook of Chemistry and Physics*, 1957).

* Present address: Physics Department, Monash University, Clayton, Victoria, Australia.

The IV \rightarrow III transformation was observed under the microscope at ca. 160 °C., the crystals becoming isotropic. X-ray photographs at 180 °C. confirm that III is cubic, with $a = 4.36 \text{ \AA}$. $d_c = 2.96 \text{ g.cm.}^{-3}$ for $Z = 1$. Korhonen (1951), on the basis of powder photographs, suggests that the true unit cell consists of 8 of these smaller cells, i.e., with $a = 8.72 \text{ \AA}$.

X-ray photographs of single crystals heated through the IV \rightarrow III transformation, show that the trigonal triad $[00\cdot1]$ of IV transforms to the cubic triad $[111]$ of III with the trigonal $[10\cdot1]$ direction becoming the cube edge direction $[100]$. This relationship between forms IV and III is illustrated in Fig. 1.

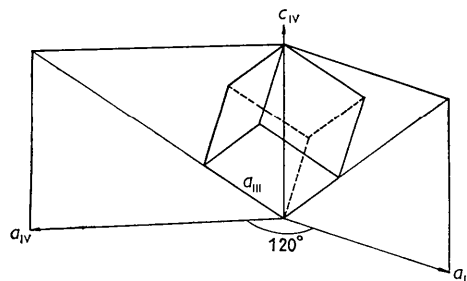


Fig. 1. Structural relationship between the unit cells of forms IV and III of rubidium nitrate.

It will be seen that, at the III \rightarrow IV transformation, any one of the four equivalent cube diagonals can give rise to the trigonal c -axis. Therefore in the transformation cycle IV \rightarrow III \rightarrow IV, the crystals may come back to form IV in any one of four orientations. For a needle crystal of triangular cross-section lying on a microscope slide, it is possible to calculate the angle between the needle axis and the crystallographic c -axis corresponding to each of the four possible orientations. These angles are 0° , 70.5° , 55° and 55° (two cube diagonals are indistinguishable). All these orientations have been observed under the polarizing

microscope. Usually a crystal returns to a single orientation. In a total of 60 transformation cycles in 6 crystals observed under the microscope, the crystal returned to its original orientation in 35 cycles. This is a larger number than would be expected if the new orientation were determined simply by chance. However, if the III \rightarrow IV transformation initiated at more than one point, then the crystal often showed more than one of the possible orientations.

The III \rightarrow II transformation was observed at 220 °C. under the microscope. The crystals cracked and bent and became anisotropic. On cooling, the transformation was observed at a slightly lower temperature, and some further distortion of the crystals took place. Since this distortion made it impossible to study these (and the II \rightleftharpoons I) transformations in single crystals with X-rays, they were therefore investigated by powder diffractometry, using the specimen-heating apparatus previously described by Brown & McLaren (1962a).

Finbak, Hassel & Stromme (1937) have given the unit cell of II as hexagonal with

$$a = 5.48, c = 10.71 \text{ \AA}.$$

Our diffractometer results suggest that there are possible alternative cells. These are given in Table 1, and are listed in order of decreasing goodness of fit.

Table 1

Cell	System	a (Å)	c (Å)	Z	d_c (g.cm. ⁻³)
1	Tetragonal	6.19 ₃	8.74 ₀	4	2.92
2(FHS)	Hexagonal	5.54 ₀	10.72	3	2.58
3	Tetragonal	7.14 ₀	13.12	8	2.93
4	Hexagonal	15.15	4.05 ₈	9	2.73
5	Hexagonal	15.15	5.15 ₂	12	2.87

The II \rightarrow I transformation was observed under the microscope at ca. 290 °C., the crystals becoming isotropic without any extra distortion being evident. A diffractometer pattern at ca. 295 °C. showed that the unit cell was cubic with $a = 7.320$ Å. $d_c = 2.50$ g.cm.⁻³ for $Z = 4$.

Electrical conductance

Measurements of the electrical conductance of compressed powder pellets of rubidium nitrate were made as a function of temperature with apparatus similar to that previously described by Brown & McLaren (1962a). For temperatures up to ca. 250 °C., the measurements were made with direct current. In order to reduce any error due to polarization effects, the electric field was applied for only one second. The reading was then repeated with the current flow in the opposite direction. Above 250 °C., the measurements were made at 1000 c./s. with a Cambridge conductivity bridge.

The results are shown in Fig. 3. It will be seen that the IV \rightarrow III transformation took place at 164 °C.

and that the conductance increased by a factor of 100. The III \rightarrow IV transformation took place at 161 °C. with a corresponding decrease in conductance. This behaviour was repeatable.

The first III \rightarrow II transformation took place at 230 °C. and the conductance decreased by a factor of 3. However, on cooling, the II \rightarrow III transformation took place at 218 °C. and the conductance increased by a factor of 30. The III \rightleftharpoons II cycle was then repeated and the conductance changed by a factor of 30 both on heating and cooling.

On further cooling, the conductance decreased by a factor of 1000 at the III \rightarrow IV transformation to its original value. The sample was then reheated: the conductance increased by a factor of 1000 at the IV \rightarrow III transformation and decreased by a factor of 30 at the III \rightarrow II transformation. This behaviour was confirmed on a second sample.

The II \rightleftharpoons I transformations were observed at ca. 282 °C. only as a change of slope in the graph of log (conductance) against reciprocal absolute temperature.

Discussion

Structural relationships between the forms

It has been shown that the unit cells of IV and III are simply related.

Although there are several possible unit cells for II, it has been found that the dimensions of the unit cell of III and the most probable unit cell of II (No. 1) are also simply related, namely,

$$\begin{aligned} \sqrt{2}a_{\text{III}} &= 6.16 \text{ \AA} & a_{\text{II}} &= 6.19 \text{ \AA} \\ 2a_{\text{III}} &= 8.72 \text{ \AA} & c_{\text{II}} &= 8.74 \text{ \AA} \end{aligned}$$

This suggests that II (No. 1) is the true unit cell of II and that its structural relationship to the unit cell of III is as shown in Fig. 2. Therefore, at the III \rightarrow II transformation, the crystal has a choice of three possible orientations, corresponding to three

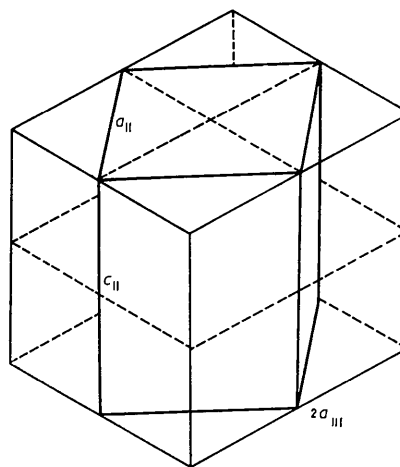


Fig. 2. Structural relationship between the unit cells of forms III and II of rubidium nitrate.

mutually perpendicular directions for the c_{II} -axis. It is suggested that this choice of orientations is responsible for the fragmentation which occurs at the transformation.

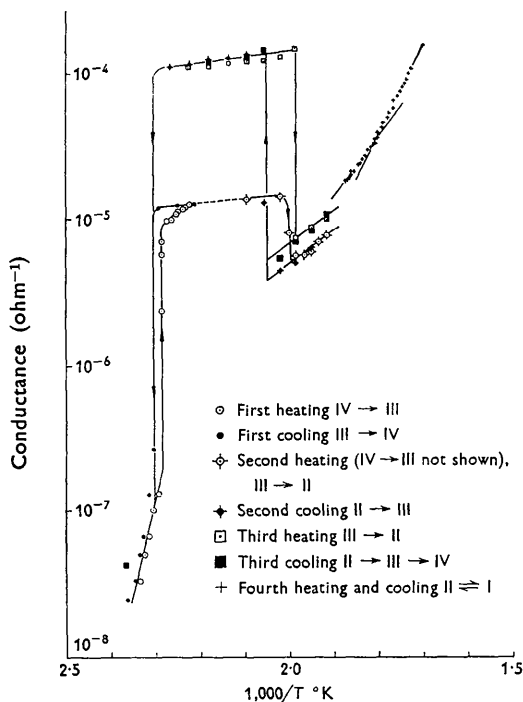


Fig. 3. The electrical conductance of rubidium nitrate as a function of temperature.

No simple relationship between the cell dimensions of II and I has been found. However, it is observed under the microscope that single crystals can undergo the II \rightarrow I transformation without fragmentation. Since the temperature of this transformation is only ca. 20 °C. below the melting point, it is possible that the crystals are sufficiently plastic to withstand a structural change in which a_{II} and c_{II} expand and contract respectively, to become equal (to a_I).

Positional randomization

The measurements of electrical conductance as a function of temperature were undertaken to provide information on the degree of ionic movement taking place during the transformations and in the stable forms.

The conductance changes observed at the II \rightleftharpoons I transformations we take as good evidence that these transformations do not involve any sudden change in positional randomization of the ions.

More-or-less large changes in conductance are observed at the other transformations. It will be seen that when the transformation involves an increase in crystallographic symmetry, the electrical conductance increases, and vice versa. This has also been observed in KNO_3 , $TlNO_3$, $CsNO_3$ and NH_4NO_3 . Brown &

McLaren (1962a) used proton magnetic resonance to show that the increase in conductance at the II \rightarrow I transformation in NH_4NO_3 was due to positional randomization of the NH_4^+ ions. There is evidence that a similar situation exists in $TlNO_3$ (see Brown & McLaren, 1962b). It is therefore suggested that the increase in conductance at the IV \rightarrow III transformation is due to some positional randomization of the Rb^+ ions, and that the decrease at the III \rightarrow II transformation corresponds to an ordering process.

It is not understood why, after the first II \rightarrow III transformation, the conductance of III should show a permanent increase in conductance over its original value.

APPENDIX

Diffractometer powder patterns for forms I, II, III and IV of rubidium nitrate

(Cu $K\alpha$ radiation)

Form I			Form IV		
d (Å)	I/I_0	Index	d (Å)	I/I_0	Index
4.23	19	111	5.25	1	110
3.67	100	200	4.29	16	111
2.585	52	220	3.45	1	102
2.206	14	311	3.43	1	210
2.113	8	222	3.03	100	300
1.827	1	400	2.878	2	202
			2.617	1	220
			2.519	1	212/310
Form II (No. 1)			2.472	16	221
d (Å)	I/I_0	Index	2.386	1	311
4.36	17	002	2.348	1	302
3.57	100	102	2.171	1	401
2.766	40	210	2.144	13	222
2.338	22	212	1.920	8	303
2.187	24	004	1.914	12	411
1.957	2	222	1.747	13	330
1.787	5	312	1.518	1	224
1.717	3	320	1.513	2	600
1.598	1	322	1.426	3	521
1.503	2	410	1.356	1	414
1.460	1	330	1.354	3	522
Form III					
d (Å)	I/I_0	Index			
4.35	8	100			
3.09	100	110			
2.517	12	111			
2.179	7	200			
1.951	9	210			
1.780	7	211			
1.541	1	220			
1.454	2	300/221			

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