

## Structure Determination of the High-Pressure Phases RbNO<sub>3</sub> V, CsNO<sub>3</sub> III, and CsNO<sub>3</sub> IV

BY MARTTI S. KALLIOMÄKI AND V. P. J. MEISALO\*

Department of Physics, University of Helsinki, Siltavuorenpenger 20 D, SF-00170 Helsinki 17, Finland

(Received 28 February 1979; accepted 13 August 1979)

### Abstract

Structural data have been collected by *in situ* X-ray diffraction analysis using a diamond-anvil high-pressure camera. The number of measured reflexions was 26 for RbNO<sub>3</sub> V, and up to 27 and 20 for CsNO<sub>3</sub> phases III and IV, respectively. The unit cells have dimensions: RbNO<sub>3</sub> V:  $a = 5.667$ ,  $b = 5.181$ ,  $c = 4.798$  Å at 2.8 GPa, space group *Pmnm*; CsNO<sub>3</sub> III:  $a = 5.837$ ,  $b = 5.143$ ,  $c = 4.978$  Å at 4.5 GPa, space group *Pmnm*; CsNO<sub>3</sub> IV:  $a = 5.562$ ,  $b = 4.857$ ,  $c = 4.957$  Å at 12.5 GPa, also with space group *Pmnm* but with rather different axial ratios from the other phases. All three phases have been shown to be structurally related to the NH<sub>4</sub>NO<sub>3</sub> type of structure. The metal atoms are in the special positions 2(*b*) of *Pmnm* and have the following parameter values:  $z = 0.60$  for Rb in RbNO<sub>3</sub> V, 0.59 for Cs in CsNO<sub>3</sub> III, and 0.58 for Cs in CsNO<sub>3</sub> IV. The N and O(1) atoms, respectively, have positions 2(*a*) with parameters:  $z' = 0.00$  for N and  $z'' = 0.26$  for O(1) in RbNO<sub>3</sub> V; in CsNO<sub>3</sub> III  $z' = 0.00$ ,  $z'' = 0.24$ ; in CsNO<sub>3</sub> IV  $z' = 0.00$ ,  $z'' = 0.23$ . The other O atoms are at 4(*f*) positions with the following parameter values: in RbNO<sub>3</sub> V  $x''' = 0.19$ ,  $z''' = -0.13$ ; in CsNO<sub>3</sub> III  $x''' = 0.18$ ,  $z''' = -0.12$ ; in CsNO<sub>3</sub> IV  $x''' = 0.18$ ,  $z''' = -0.12$ . The reliability of the indexing of the X-ray data is discussed with reference to calculated figures of merit. Difficulties in structure determination are analysed from the general viewpoint of high-pressure X-ray diffraction studies.

### 1. Introduction

The polymorphism of RbNO<sub>3</sub> and of CsNO<sub>3</sub>, as well as the structures of their different phases, has been extensively studied [see, for example, Pistorius (1978), Fujimoto *et al.* (1977), and Rao, Prakash & Natarajan (1975)]. The phase RbNO<sub>3</sub> I, which is stable at ambient pressure above 564 K to the melting point, has

a cubic disordered structure derivable from the halite type, and RbNO<sub>3</sub> II is rhombohedral (between 492 and 564 K). Phase III is stable between 437 and 492 K, and its structure has been commonly considered to be of the CsCl type, although Korhonen (1951) showed the need for a larger ( $Z = 8$ ) cubic unit cell for it. According to Strømme (1971) the proper space group from Korhonen's data is *Pm3m*. Phase IV is stable at lower temperatures and has the space group *P3<sub>1</sub>12* or *P3<sub>2</sub>12* with  $a_0 = 6.54$  Å,  $\alpha = 106^\circ 81'$  (Brown & McLaren, 1962; *cf.* Delacy & Kennard, 1971). However, a detailed structural analysis has not yet been published (*cf.* Brooker, 1973). The high-pressure phase RbNO<sub>3</sub> V was discovered by Bridgman (1937) in connexion with his volume compressibility measurements.

The structure of CsNO<sub>3</sub> I, which is stable above 434 K, is similar to that of RbNO<sub>3</sub> III (Korhonen, 1953; Strømme, 1971). Similarly, the room-temperature phase CsNO<sub>3</sub> II appears to be isostructural with RbNO<sub>3</sub> IV: the phase is rhombohedral (Delacy & Kennard, 1971) and it has been suggested, on different occasions, that both phases have the same structure, although no detailed structural analysis is available for either phase. The dimensions for the unit cell of CsNO<sub>3</sub> II are, according to Brown & McLaren (1962),  $a_0 = 6.69$  Å,  $\alpha = 106^\circ 65'$ . In the high-pressure study referred to above, Bridgman also reported an anomaly in his volumetric data on CsNO<sub>3</sub> indicating a possible high-pressure transformation. However, he was not able to locate the transformation to the assumed new phase CsNO<sub>3</sub> III at room temperature, but only at about 400 K and above. We have found in our preliminary study (Kalliomäki & Meisalo, 1978) another sluggish transformation to a hitherto unknown high-pressure phase CsNO<sub>3</sub> IV.

There have been numerous suggestions as to possible structures for the previously known high-pressure phases of rubidium and caesium nitrates. Bridgman (1916) pointed out in one of his early papers similarities in the phase diagrams of RbNO<sub>3</sub>, KNO<sub>3</sub>, and CsNO<sub>3</sub> [see also Bridgman (1949), p. 240]. General arguments have led Rapoport & Kennedy (1965), Rapoport (1966), as well as Cleaver & Williams (1968) to

\* Present address: Department of Teacher Education, University of Helsinki, Ratakatu 2, SF-00170 Helsinki 17, Finland.

suggest that certain phases of KNO<sub>3</sub>, RbNO<sub>3</sub>, CsNO<sub>3</sub>, and TlNO<sub>3</sub> are isostructural. The phase relations of these interesting nitrates have also been recently reviewed by Pistorius (1978). However, no direct information has so far been available on the structures of the relevant high-pressure phases. Thus it was decided to perform an X-ray diffraction study of these materials under high-pressure conditions. In a conference report (Meisalo & Kalliomäki, 1974) we have suggested an orthorhombic symmetry for the high-pressure phase RbNO<sub>3</sub> V and for the expected, but previously unreported, phase TlNO<sub>3</sub> IV, which we discovered in our optical studies. On the basis of our X-ray diffraction diagrams we found that these phases may have at least qualitatively similar structures.

In the present paper we report our results on the structures of the high-pressure phases RbNO<sub>3</sub> V, CsNO<sub>3</sub> III, and CsNO<sub>3</sub> IV. We discuss the reliability of structure determinations by high-pressure X-ray diffraction methods, as well as structural relations between the phases studied. Phase diagrams and high-pressure transformations of RbNO<sub>3</sub>, CsNO<sub>3</sub>, and TlNO<sub>3</sub> will be subjected to a wider discussion in a different context.

## 2. Experimental

We have obtained powder X-ray diffraction data up to about 15 GPa utilizing a Bassett-type high-pressure camera. Its high-pressure cell is of the opposite diamond-anvil-press type and we use an Inconel support ring to contain the powder sample in a methanol-ethanol mixture under hydrostatic or quasi-hydrostatic conditions between the anvil faces. Above pressures around 10 GPa we used the powder sample as such (dry), the internal standard acting possibly also as a high-pressure medium. We used standard nitrate powders of 'Extra Pure' quality supplied by Merck. No impurity lines were detectable in our X-ray diffraction diagrams. A microfocus generator provided a brilliant source of Mo K $\alpha$  X-rays ( $\lambda = 0.71073$  Å); the K $\beta$  component was eliminated by Nb filters both in the primary beam and in the film-cassette window. The exposure times were of the order of 20–60 h. The X-ray films were analysed using a microdensitometer, but the intensities are reported here in terms of qualitative attributes only, as we want to emphasize the difficulties inherent in intensity measurements when the specimen is subjected to high-pressure conditions. Internal standards, mainly sodium chloride, and the Decker NaCl scale were used for the calibration of the pressure scale. The calibration was performed by similar methods to our earlier work (Meisalo & Kalliomäki, 1973), whose transformation pressures are supported by later independent data. The pressure scale is also discussed in detail by Kalliomäki (1979).

Several diffraction diagrams were obtained for rubidium nitrate above the transformation pressure of about 1.3 GPa at room temperature. Due to the sluggish nature of this transformation, however, single-phase patterns were obtained only at substantially higher pressures. The sluggishness of the transformations is even more problematic in caesium nitrate, where we found it very difficult to obtain a single-phase pattern for the first high-pressure phase. Because of the slowness of the X-ray diffraction studies a more prolonged exposure to a constant high pressure did not offer any advance in this respect.

## 3. Results

### 3.1. High-pressure phase RbNO<sub>3</sub> V

X-ray diffraction data for RbNO<sub>3</sub> V based on one of our typical diagrams obtained at 2.8 GPa pressure are presented in Table 1. The accuracy of the first few experimental  $d$  values is estimated to be of the order of some 0.01 Å, while for sharp reflexions at higher diffraction angles we obtain an accuracy of about 0.001 Å. We may note that there are in our data some broad or diffuse diffraction lines (marked  $d$  in the tables), which could be separated into two or more lines only exceptionally. The indexing was found with the aid of an indexing routine (Taupin, 1973). The differences between experimental and calculated  $d$  values are in agreement with the accuracy estimated above. For the primitive orthorhombic unit cell the dimensions (at 2.8 GPa) are  $a = 5.667$ ,  $b = 5.181$ , and  $c = 4.798$  Å. The volume of the unit cell is  $V = 140.9$  Å<sup>3</sup> allowing two molecular units of RbNO<sub>3</sub>. The axial ratios are 1:0.914:0.847 and the space group assignment is  $Pm\bar{m}n$ . The intensities  $I_{\text{obs}}(hkl)$  of the measured reflexions are reported on the qualitative scale ( $vs/s/ms/m/mw/w/vw/vvw$ ). The symmetry and shape of the unit cell suggest that the structure of RbNO<sub>3</sub> V may be of the NH<sub>4</sub>NO<sub>3</sub> type, and the theoretical intensities  $I_{\text{calc}}(hkl)$  calculated on the basis of this assumption are in fairly good agreement with the experimental ones. In this structure we use the following special positions available in the space group  $Pm\bar{m}n$  for locating the atoms:

Rb	2(b)	$0, \frac{1}{2}, z; \frac{1}{2}, 0, \bar{z}$
N	2(a)	$0, 0, z'; \frac{1}{2}, \frac{1}{2}, \bar{z}'$
O(1)	2(a)	$0, 0, z''; \frac{1}{2}, \frac{1}{2}, \bar{z}''$
O(2)	4(f)	$x''', 0, z'''; \bar{x}''', 0, z'''$ $x''' + \frac{1}{2}, \frac{1}{2}, \bar{z}'''; \bar{x}''' + \frac{1}{2}, \frac{1}{2}, \bar{z}'''$ .

The positional parameters based on our measured intensities are  $z = 0.60$ ,  $z' = 0.00$ ,  $z'' = 0.26$ ,  $x''' = 0.19$ , and  $z''' = -0.13$  in our final calculation. The origins of several broad diffraction lines can be shown in doublets or triplets and of some not exactly located

Table 1. X-ray diffraction data for RbNO<sub>3</sub> V at 2.8 GPa

The lattice spacings are given in Å; the unit cell is orthorhombic with  $a = 5.667$ ,  $b = 5.181$ , and  $c = 4.798$  Å. The calculated intensities are based on the 'NH<sub>4</sub>NO<sub>3</sub> type' of structure and include a qualitative temperature factor. See text for further details (structural parameters *etc.*).

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$
4.790	4.798	0 0 1	w+	8.8					
3.835	3.824	1 1 0	w+	17.9	1.487	1.495 2 2 2	w	0.9	
3.651	3.662	1 0 1	mw	18.2		1.484 3 0 2	w	7.1	
3.524	3.520	0 1 1	mw	16.5	1.417	1.427 3 1 2	w	0.9	
2.998	2.990	1 1 1	us	100.0		1.417 4 0 0	w	3.4	
2.828	2.834	2 0 0	mw	21.9	1.396	1.410 2 3 1	w	6.5	
2.589	2.590	0 2 0	mw	44.9		1.402 0 3 2	w	6.3	
2.433	2.440	2 0 1	mw	18.3	1.353	1.393 2 0 3	w	1.5	
2.206	2.209 1 0 2			11.7		1.361 0 2 3	w	0.2	
	2.206 2 1 1	m		34.7		1.359 1 3 2	w	0.8	
2.178	2.176 0 1 2	m		31.8		1.345 4 0 1	w	1.7	
2.113	2.115 1 2 1	w		8.3	1.322	1.323 2 1 3	w	6.1	
2.039	2.032 1 1 2	vw		3.6		1.323 1 2 3	w	8.6	
1.829	1.831 2 0 2	vw		0.9	1.294	1.314 4 1 1	w	3.2	
	1.776 2 2 1			13.5		1.295 0 4 0	w	3.4	
1.775	1.775 3 1 0	mw		9.3	1.251	1.288 3 2 2	w	8.0	
	1.760 0 2 2			0.6		1.256 2 3 2	w	3.0	
1.725	1.726 2 1 2	w		9.0		1.250 0 4 1	vw	0.7	
	1.681 1 2 2			11.7	1.221	1.243 4 2 0	w	3.9	
1.666	1.665 3 1 1	mw		7.8		1.227 2 2 3	w	1.6	
	1.652 1 3 0			2.6		1.221 1 4 1	vw	1.3	
1.598	1.599 0 0 3	vw		0.2	1.221	1.221 3 0 3	w	2.0	
1.539	1.539 1 0 3			7.7		1.220 4 0 2	w	0.2	
	1.528 0 1 3	mw		2.0					

Table 2. X-ray diffraction data for CsNO<sub>3</sub> III at 4.5 GPa

The calculated  $d$  values and intensities are based on the 'NH<sub>4</sub>NO<sub>3</sub> type' of structure with an orthorhombic unit cell having  $a = 5.837$ ,  $b = 5.143$ , and  $c = 4.978$  Å.

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$
4.994	4.978	0 0 1	mw	19.4	1.319	1.317 3 2 2	w	7.6	
3.786	3.859 1 1 0	mw		32.4		1.286 3 3 0	w	2.9	
	3.788 1 0 1			18.1	1.278	1.286 0 4 0	vw	2.6	
3.578	3.577 0 1 1	w+		16.2		1.271 2 3 2	w	3.3	
3.053	3.050 1 1 1	us		100.0		1.269 4 2 0	w	3.5	
2.920	2.919 2 0 0	m		23.3	1.259	1.263 3 0 3	w	2.4	
2.514	2.518 2 0 1	m		19.5		1.259 4 0 2	w	0.4	
2.290	2.290 1 0 2			13.5	1.259	1.258 2 2 3	vw	0.4	
	2.285 0 2 1	s(d)		6.3		1.245 0 4 1	w	1.0	
2.241	2.261 2 1 1			23.1		1.245 0 0 4	w	0.6	
	2.240 0 1 2			24.6	1.217	1.223 4 1 2	w	3.5	
2.093	2.092 1 1 2	w		6.0		1.218 1 4 1	vw	1.1	
1.894	1.894 2 0 2	w+		1.7		1.217 1 0 4	w	1.3	
1.823	1.820 3 1 0	w		10.3	1.182	1.210 0 4 1	w	1.5	
	1.799 2 2 1			13.9		1.192 0 3 3	w	1.2	
1.788	1.788 0 2 2	w+		1.7	1.182	1.184 1 1 4	vw	2.1	
	1.777 2 1 2			10.3		1.177 2 4 0	w	2.2	
1.712	1.710 1 2 2	mw		11.0	1.139	1.145 2 4 1	w	2.6	
	1.709 3 1 1			9.8		1.145 2 0 4	vw	0.3	
1.592	1.596 1 0 3	w		8.6		1.142 0 4 2	w	0.3	
	1.579 0 1 3			3.2		1.131 4 2 2	w	0.6	
1.531	1.533 3 0 2	w+		6.9	1.114	1.121 1 4 2	w	2.3	
1.467	1.469 3 1 2	vw		2.0		1.120 0 2 4	w	0.7	
	1.459 4 0 0			3.0		1.117 2 1 4	w	1.9	
	1.417 2 3 1			4.3	1.074	1.110 5 1 1	w	3.2	
1.411	1.412 0 3 2	w		4.8		1.100 1 2 4	w	1.7	
	1.400 4 0 1			2.5		1.096 4 0 3	w	0.1	
1.394	1.394 0 2 3	w		0.0		1.085 4 3 1	vw	1.1	
	1.389 2 1 3			7.6		1.072 4 1 3	w	2.3	
1.359	1.356 1 2 3	w+		9.3		1.064 2 4 2	w	0.4	
	1.351 4 1 1			3.0					

traces in very weak reflexions in the calculated spectrum. The low reliability of the intensity data does not justify further refinement of our structural parameters. However, we may note that the parameters are close to those values that were originally suggested for ammonium nitrate, and the atomic packing is apparently rather similar to that in NH<sub>4</sub>NO<sub>3</sub>. Structural details are analysed more closely in the discussion below (§ 4.2).

### 3.2. High-pressure phases of caesium nitrate

In Table 2 we present our X-ray data for CsNO<sub>3</sub> III obtained at 4.5 GPa. The scatter in these data is somewhat larger than in the previous case indicating our experimental difficulties, but the overall accuracy is estimated to be of the same order as above. When a single phase pattern of this phase was finally obtained after several less successful preliminary experiments, all lines were indexed again to a primitive orthorhombic unit cell. The data in Table 2 are from a diffraction pattern where we were able to record a larger number of reflexions, but where we had remnants of strongest lines of the ambient pressure phase. The cell dimensions at 4.5 GPa are  $a = 5.837$ ,  $b = 5.143$ ,  $c = 4.978$  Å. The volume of the unit cell is  $V = 149.4$  Å<sup>3</sup> indicating a bimolecular cell with axial ratios 1:0.881:0.853, not too far from those in RbNO<sub>3</sub> V. The space-group assignment is again *Pmmn* supporting the assumption of a close relationship between the structures of these phases. The calculated intensities in Table 2 are based on the same special positions for the atoms as in RbNO<sub>3</sub> V, the parameter values being  $z = 0.59$ ,  $z' = 0.00$ ,  $z'' = 0.24$ ,  $x''' = 0.18$ , and  $z''' = -0.12$ . It may be noted that the above numerical values give perhaps a too optimistic impression of the actual accuracy of the data. Considering the general quality of our diffraction spectra, we think it only natural that we could have missed a number of weak reflexions found in the calculated pattern. There are also several groups of unresolved reflexions, where we have been able to record only the peak value for the diffuse maximum of the experimental intensity distribution. Due to texture effects some lines have been visible at a rather limited portion of the diffraction cone. Thus it has been extremely difficult to measure intensity data reliably. Even with these reservations in mind, it is obvious that CsNO<sub>3</sub> III and RbNO<sub>3</sub> V may be considered as isostructural phases in the light of the available information.

If pressures of the order of 10 GPa are applied to a specimen of caesium nitrate, definite changes are again consistently observed in the X-ray diffraction pattern. Several sets of diffraction data were obtained both below and above the transformation pressure located at 8.8 GPa. At this pressure there are such abrupt changes in the quality of the diffraction spectrum that it

Table 3. *X-ray diffraction data for CsNO<sub>3</sub> IV at 12.5 GPa*

The calculated values are based on the 'NH<sub>4</sub>NO<sub>3</sub> type' of structure with the unit-cell dimensions  $a = 5.562$ ,  $b = 4.857$ , and  $c = 4.957$  Å.

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$
4.958	4.957	0 0 1	$mw$	21.6	1.658	1.656	1 2 2	$w$	9.0
3.701	3.701	1 0 1	$m$	13.9		1.652	0 0 3	$w$	0.1
3.460	3.469	0 1 1	$w$	11.9	1.583	1.584	1 0 3	$w(d)$	8.6
2.943	2.944	1 1 1	$vs$	100.0	1.482	1.485	3 0 2		5.7
2.780	2.781	2 0 0	$m$	20.8		1.483	1 3 1	$w+$	10.7
2.425	2.429	0 2 0		27.2	1.419	1.472	2 2 2		2.5
	2.425	2 0 1	$m$	18.8		1.421	2 0 3		0.0
2.269	2.264	1 0 2	$m(d)$	11.9	1.362	1.420	3 1 2	$w(d)$	2.8
	2.208	0 1 2		20.9		1.413	3 2 1		0.5
2.189	2.181	0 2 1	$m(d)$	6.1	1.327	1.366	0 2 3		0.1
	2.170	2 1 1		17.7		1.363	2 1 3	$w(d)$	7.4
2.054	2.052	1 1 2	$w$	9.0	1.268	1.355	0 3 2		3.7
2.032	2.030	1 2 1	$w$	5.4		1.327	1 2 3	$vw$	8.7
1.844	1.850	2 0 2	$w$	2.8	1.267	1.267	3 2 2	$vw$	6.0
	1.829	2 2 0		11.6					
1.731	1.737	3 0 1		0.4					
	1.735	0 2 2	$mw$	2.4					
	1.732	3 1 0		8.9					
	1.729	2 1 2		7.9					

was not considered possible to avoid the assignment of these phenomena to some kind of a phase transformation. Although the information concerning the high-pressure transformations will be discussed elsewhere, we may note here that at the transformation pressure there appears to be a negative compressibility along one of the crystallographic axes. See also the discussion in § 4.2.

It can be seen in Table 3 that the new pattern can be indexed on the basis of a primitive orthorhombic unit cell rather similar to those above, the lattice dimensions being  $a = 5.562$ ,  $b = 4.857$ ,  $c = 4.957$  Å. The axial ratios are now 1:0.873:0.891 indicating a substantial change from the previous cases. The space group for even this phase is also  $Pm\bar{m}n$ , but now the special symmetry axis is not along the shortest axis of the unit cell. The volume of the unit cell at 12.5 GPa is 133.9 Å<sup>3</sup>. If we compare our data for CsNO<sub>3</sub> IV with those for RbNO<sub>3</sub> V and CsNO<sub>3</sub> III, it is obvious that the structures of these three phases are closely related. A reasonably good fit to the intensity data was obtained with the same special positions as above and the following parameter values: Cs:  $z = 0.58$ , N:  $z' = 0.00$ , O(1):  $z'' = 0.23$ , O(2):  $x''' = 0.18$ ,  $z''' = -0.12$ .

## 4. Discussion

### 4.1. Reliability of the high-pressure X-ray data

It is important that the reliability of all structural information on high-pressure phases be scrutinized since there are in the literature several examples of

inaccurate or conflicting high-pressure X-ray diffraction data [see, for example, Dandekar & Jamieson (1969), or Schaufelberger & Merx (1974)]. It may be of general interest to analyse here the sources of misinterpretation of high-pressure X-ray diffraction data relevant to this work. We have strived to minimize the effects of the problems in the list below:

(1) There is usually only a small number of measured X-ray reflexions in the data and they cover a rather limited range of  $\sin \theta/\lambda$ .

(2) Sluggish transformations and incompletely annealed strains *etc.*, yield diffuse diffraction maxima and inaccurate angular and intensity data.

(3) Preferred orientation effects are present in most powder samples, a problem which is enhanced by the sometimes unavoidably non-hydrostatic pressure environment and the usually extremely small effective sample volume.

(4) It is difficult to obtain one-phase diagrams especially after sluggish transformations and under non-hydrostatic or inhomogeneous high-pressure conditions.

(5) Non-hydrostatic pressure components or impurities (including moisture) may stabilize crystalline forms that are not found in the phase diagram of the pure material.

(6) Decomposition or other chemical reactions under high pressure may remain undetected or misinterpreted.

(7) Spurious lines from different parts of the high-pressure apparatus itself, outside of the specimen, may be mixed in with the data.

(8) Absorption within the specimen or in the X-ray window of the high-pressure cell may distort the intensity data.

(9) Major errors in the pressure scale may lead to serious misinterpretations.

In the present study we have been able to measure 26, 27, and 20 reflexions respectively for the different phases. The reliability of indexing of powder patterns has been discussed by de Wolff (1968), who suggested a simple indicator, the figure of merit  $M_n$ , to indicate the probability of correctness of an indexing:  $M_n = 1/(2d_n^2 \bar{\epsilon} N_n)$ , where  $d_n$  is the lattice spacing for the  $n$ th observed and indexed line,  $\bar{\epsilon}$  is the average value of the discrepancies in  $1/(d^2)$  up to the  $n$ th line, and  $N_n$  is the total number of possible distinct reflexions up to the same line. According to de Wolff,  $M_{20} \gtrsim 10$  is a guarantee for essential correctness of an indexing, provided that there are only a few spurious lines. Schaufelberger & Merx (1974) compared  $M_{10}$  rather than  $M_{20}$  for different indexings of high-pressure X-ray data since 20 or more observed lines are not often available for high-pressure phases. However,  $M_n$  decreases with higher values of  $n$  and, as they note, the criterion  $M_{10} \gtrsim 10$  is very optimistic. In our own experience,  $M_{20}$  may be less than one half of  $M_{10}$  for an

indexing of typical high-pressure data. Thus for non-cubic phases people have actually compared figures of merit for suspicious indexings.

For the orthorhombic indexing of  $\text{RbNO}_3$  V our calculations give  $M_{20} = 14$ ,  $M_{10} = 32$ . According to de Wolff's criterion we may thus consider our indexing as at least essentially correct. For  $\text{CsNO}_3$  III  $M_{20} = 8$  and  $M_{10} = 55$ . The former value is not high but, although it reflects our experimental difficulties, we consider some further analysis of the suggested structure worthwhile. For  $\text{CsNO}_3$  IV we were able to reach well above the transformation pressure and obtain a sharp, high quality X-ray pattern yielding  $M_{20} = 15$  and  $M_{10}$  as high as 71. Altogether, we regard our indexings with confidence and find some support for the indexing of  $\text{CsNO}_3$  III through reasons of analogy with the other phases.

While the above considerations may convince us that the unit cells of the studied phases have been determined correctly as to their shape and size, it is far more difficult to determine the atomic positions in the unit cells on the basis of the intensity data. We consider here the specific orientation of crystallites in the powder sample under high pressure as our main problem. In spite of our efforts to maintain hydrostatic pressure upon the specimen to as high pressures as possible, relative intensities of different X-ray reflexions have varied considerably from specimen to specimen. There are also large variations in intensities at different points along the Debye ring, although the visual appearance of the diffraction lines has never been spotty, which indicates a rather small crystallite size in the specimens.

There are several indications that in the phases studied as in many other orthorhombic crystals the shortest crystalline axis tends to be aligned along the direction of applied pressure in a simple squeezer type of apparatus. To obtain qualitative evidence on the favoured alignments, positions of high-intensity parts apparent on some of the low-angle reflexions were measured on the X-ray films. Several specimens were prepared to provide different qualities of quasihydrostatic pressure at the specimen by varying construction details and the relative amount of the immersion liquid and the powder. Comparison of X-ray diffraction data from these specimens gave information on the trend of intensity variations with typically somewhat non-hydrostatic and inhomogeneous pressure. It was not possible to obtain quantitative data, but a number of larger differences in observed and calculated intensities in Tables 1 to 3 could be assigned qualitatively to specific orientation effects. For example, we may mention the low intensities of 020 reflexions in all recorded diffraction patterns. As a favourable effect of the specific orientation we have observed that it has often been easier to resolve a tight diffraction-line doublet or triplet into its components, if the intensity distribution along the Debye line has been uneven and different for the separate components.

Where X-ray patterns of higher- and lower-pressure phases have lines at the same angle, one must be particularly careful to make certain that the low-pressure phase does not contribute to the pattern above the transformation. This problem may sometimes be solved simply by going sufficiently high above the transformation pressure, but this is not possible if the stability range of the phase is narrow and the transformation is sluggish.  $\text{CsNO}_3$  III proved to be a very difficult phase in this respect and we followed both the lattice spacings and the intensity variations within the available pressure range to convince ourselves of the purity of the pattern. No spurious lines from outside the specimen and no impurity or decomposition effects were observed in these studies. Chemical impurities may change to a minor extent the position of phase boundaries, but in these kinds of studies such effects are of minor importance.

Absorption in the specimen and in the anvil diamonds reduces the intensities of high-angle reflexions. A correction for this effect was not considered necessary in the present cases, as systematic errors of this kind are 'absorbed' in qualitative temperature factors (Kalliomäki, 1979). In this work we have avoided detailed discussion of topics that are critically dependent on the accuracy of the pressure determination. However, every effort was made to be sure that the pressure scale would be identical with that in our previous studies and that the possible error would be within a few tenths of a GPa in the whole pressure range studied.

Finally, we may note that in view of the serious problems of high-pressure X-ray diffraction studies discussed above, we have not found it advisable to perform further refinements of the structures or numerical error analysis of reported parameters. However, to make easier eventual comparison with the accuracy of other studies under similar conditions we calculated straightforward estimates of the standard errors in the lattice parameters and obtained  $\delta_a = \pm 0.004$ ,  $\delta_b = \pm 0.004$  and  $\delta_c = 0.004$  Å for  $\text{RbNO}_3$  V, and closely similar values for the high-pressure phases of  $\text{CsNO}_3$ . We calculated also the  $R$  value from our original numerical intensity data of  $\text{RbNO}_3$  V and obtained  $R = 0.14$ . This indicates that the structure can be regarded as at least essentially correct.

#### 4.2. Structural aspects of the high-pressure phases studied

The structure of  $\text{RbNO}_3$  V, according to our analysis, is of the  $\text{NH}_4\text{NO}_3$  type. This structure was originally suggested for  $\text{NH}_4\text{NO}_3$  IV, ammonium ions being considered as spherical, with no fixed positions for the hydrogens. If we take also the  $\text{NO}_3$  groups as 'atomic' entities within the crystal, we may find for this type of structure a unimolecular pseudocell revealing the packing to be related to a distorted CsCl type. The

effect of this pseudocell can be visualized in the general pattern of the stronger diffraction lines. This can give in the preliminary studies a hint for indexing the pattern. The nearly tetragonal pseudocell has  $a' = b' = \frac{1}{2}(a^2 + b^2)^{1/2}$ ,  $c' = c$ . The elongation in the direction of the  $c$  axis is obviously due to the coincidence of N—O bonds with this direction. In Fig. 1 the pseudocell has been indicated with dotted lines.

The above view of the atomic packing is rather simplified. An alternative would be to consider these structures as planar arrangements, where the special planes would be those with the planar NO<sub>3</sub> groups. The short N—O distances make possible the relatively dense packing in the planes concerned, but the other interatomic distances within these planes and from one plane to another are not too different. In these respects all three phases studied are rather similar to NH<sub>4</sub>NO<sub>3</sub> IV. Some of the shortest atomic distances are reported in Table 4 referring to the notations introduced in Fig. 1. All atomic distances included here can be found acceptable when they are compared with atomic radii and atomic distances in similar crystals and if we take into account the observed compressibilities of the materials studied. One may also consider qualitatively the distances of, for example, the Cs atoms from the nearest neighbours and find that the variations from the mean Cs—O distance can be assigned to the forces from nearest atoms in the different environments of the two types of O sites. The experimental densities of these phases are: RbNO<sub>3</sub> V:  $\rho = 3.477 \text{ Mg m}^{-3}$  at 2.8 GPa, CsNO<sub>3</sub> III:  $\rho = 4.332 \text{ Mg m}^{-3}$  at 4.5 GPa, CsNO<sub>3</sub> IV:  $\rho = 4.834 \text{ Mg m}^{-3}$  at 12.5 GPa. These values are in agreement with the qualitative compressibilities of the different phases estimated on the basis of several X-ray diagrams, and we note that the density data do not allow large volume discontinuities at phase boundaries.

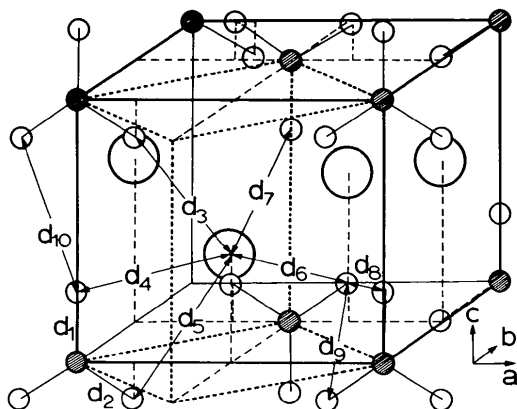


Fig. 1. The unit cell of RbNO<sub>3</sub> V drawn with the origin at the centre of a nitrogen group. The unit cells of the high-pressure phases of CsNO<sub>3</sub> are closely similar. The unimolecular, nearly tetragonal pseudocell is indicated by dotted lines. The metal atoms have been drawn as larger circles, while in the nitrate groups the nitrogens are represented by shaded circles and oxygens by open smaller circles. The interatomic distances  $d_1$ – $d_{10}$  are reported in Table 4.

Table 4. *Interatomic distances in high-pressure structures RbNO<sub>3</sub> III, CsNO<sub>3</sub> III, and CsNO<sub>3</sub> IV*

The distances  $d_1$  and  $d_2$  are the N—O distances within the nitrate groups, etc., as indicated in Fig. 1.

$d$ (Å)	RbNO <sub>3</sub> V	CsNO <sub>3</sub> III	CsNO <sub>3</sub> IV
$d_1$	1.23	1.19	1.14
$d_2$	1.24	1.21	1.15
$d_3$	2.88	2.99	2.91
$d_4$	2.92	3.04	2.94
$d_5$	3.07	3.23	3.19
$d_6$	3.10	3.13	3.03
$d_7$	3.07	3.11	2.98
$d_8$	3.19	3.23	3.06
$d_9$	2.93	2.95	2.79
$d_{10}$	3.16	3.35	3.40

All three phases studied have the same space group  $Pm\bar{m}n$  and even the structural parameter values are rather similar. These structures are also closely related to that of NH<sub>4</sub>NO<sub>3</sub>, which possibility was never brought up in speculations based on similarities in phase diagrams etc. The compressibilities of these phases along the  $c$  axis are very low according to our X-ray data. Thus the axial ratios are changing with

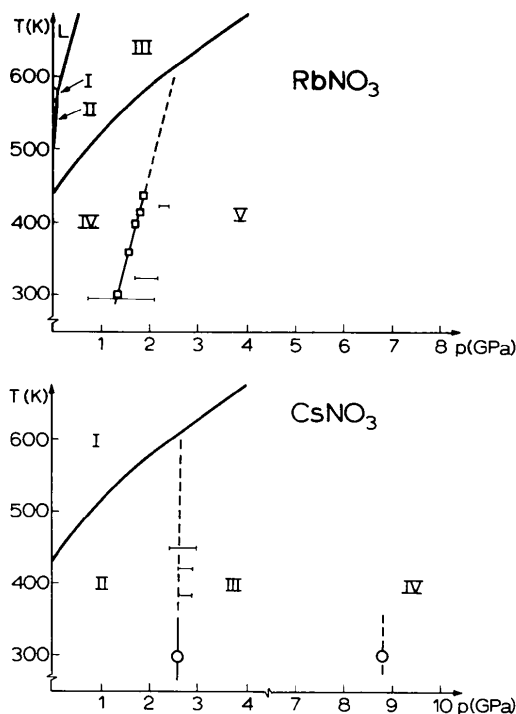


Fig. 2. The  $p$ – $T$  phase diagrams of RbNO<sub>3</sub> and CsNO<sub>3</sub>. They are based on those presented by Pistorius (1978) and revised by the information collected in the course of this work. The squares indicate the data included in our preliminary report (Meisalo & Kalliomäki, 1974) while the circles refer to our unpublished transformation points. Bridgman's (1937) data are indicated by the error bars.

pressure. At the  $\text{CsNO}_3$  III–IV phase boundary our data show also that there is an abrupt compression along the direction of the  $b$  axis and the compressibility along the  $c$  axis appears to be negative. It is interesting that rather large variations in the shape of the unit cell do not have major effects in the values of the structural parameters.

The above considerations give us information on the nature of the  $\text{CsNO}_3$  III–IV transformation. However, this or other transformations in the relevant phase fields will not be discussed in this context. Referring to the *Introduction*, we only note that although we have not been able to resolve the X-ray diffraction pattern of  $\text{TlNO}_3$  IV in detail, the qualitative results reported in our preliminary study (Meisalo & Kalliomäki, 1974) remain valid. Schematic  $p$ – $T$  phase diagrams of  $\text{RbNO}_3$  and  $\text{CsNO}_3$  are presented in Fig. 2 to illustrate the phase relations. The diagrams are based on those presented by Pistorius (1978), who summarized the available information from different high-pressure studies up to 1975. [However, *cf.* Fujimoto *et al.* (1977).] The lines of transformation to the high-pressure phases have been drawn according to the data collected in the course of this work.

### 5. Summary

The structures of the high-pressure phases  $\text{RbNO}_3$  V,  $\text{CsNO}_3$  III, and  $\text{CsNO}_3$  IV have been determined by powder X-ray diffraction analysis. The results show a close relationship between the structures of all these phases and the structure of  $\text{NH}_4\text{NO}_3$  IV. Actually, it appears that the phases presently studied are the only known examples of the so-called ‘ $\text{NH}_4\text{NO}_3$  type’ of structure. The accuracy and reliability of high-pressure X-ray diffraction data have been discussed in detail and it has been shown that the indexings found can be considered reliable. The intensity data have several sources of systematic errors and the values of the structural parameters should be considered with a certain degree of caution. However, we feel that analysis of the structural details and the analogy with the well established structure of  $\text{NH}_4\text{NO}_3$  IV give strong support to the suggested structures.

There have been in the literature several speculations about phase relations on the basis of qualitative aspects, such as similarities in the phase diagrams of related substances, but they have given us little guidance in the course of this study. In spite of the

serious difficulties discussed above, it has been found most necessary to approach even these kinds of problems with powder X-ray diffraction analysis.

This work has been partially supported by the Research Council for Natural Sciences, the Academy of Finland.

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