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The crystal structure of the low-temperature phase of NH_4NO_3 (V) at $-150\,^{\circ}C$*

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With 7 figures

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Auszug

An Kristallen der tetragonalen Tieftemperaturmodifikation von NH_4NO_3–V, die aus der Zimmertemperatur-Form IV durch Abkühlen auf $-150\,^{\circ}C$ entstanden, wurde die Kristallstruktur bestimmt. Die Gitterkonstanten sind $a = 7{,}98$ Å, $c = 9{,}78$ Å, wobei $a_V/[110]_{IV}$; die Raumgruppe ist $P4_2$ mit $Z = 8$. Es wurden Fourierprojektionen auf (001) und $(1\bar{1}0)$ ausgewertet und die Ungenauigkeitsfaktoren $R_{hk0} = 0{,}15$, $R_{hhl} = 0{,}18$ erreicht.

Die NH_4- und NO_3-Gruppen liegen in Säulen längs der c-Achse und bedingen durch die Folge der NO_3-Gruppen den polaren Charakter der Struktur. Die Struktur ist als Ganzes der ebenfalls tetragonalen Hochtemperaturform II sehr ähnlich, von der sie sich nur durch leichte Orientierungsabweichungen sowohl der NO_3- wie der NH_4-Gruppen (bis 9°) und der damit verbundenen Verdoppelung der c-Achse unterscheidet. Es wurde eine Verzwillingungs-Unordnung beobachtet, die davon herrührt, daß die Ausgangsmodifikation IV unpolar ist. Die Atomabstände werden diskutiert.

Abstract

The crystal structure of the tetragonal phase, V, of NH_4NO_3 at $-150\,^{\circ}C$ has been determined by x-ray methods, by cooling single crystals of the room temperature phase. The axes transformations are: $[001]_{IV}$—$[001]_V$; $[100]_{IV}$ and $[010]_{IV}$—$[1\bar{1}0]_V$. The lattice constants are $a = 7.98$ Å, $c = 9{,}78$ Å. The space group is $P4_2$ and $Z = 8$. The structure has been solved from the Fourier projections (001) and $(1\bar{1}0)$. The final values of the discrepancy factor are $R_{hk0} = 0.15$ and $R_{hhl} = 0.18$.

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The NO_3 and NH_4 groups lie on columns along *c* axis, the structure being polar along this axis due to the sequence of the NO_3 groups. The structure as a whole is very similar to that of the high-temperature tetragonal form, differing from phase II in a slight change of orientation (9 degrees) in both the NO_3 and the NH_4 groups, which causes the doubling of the lattice constant *c*. A twin disorder due to the fact that the starting structure is not polar has been found. A discussion of the interatomic distances is given.

Introduction

The polymorphism of NH_4NO_3 is a well known book example of thermal transformations in solids. According Hendricks, Posnjak and Kracek[1], five different low pressure forms are known to exist, namely:

Phase	Transition temperature °C	Symmetry (H., P., K.)
V		hexagonal
	−185	
IV		orthorhombic
	32	
III		orthorhombic
	84	
II		tetragonal
	125	
I		cubic

Hendricks *et al.*[1] studied the I, II and V phases of NH_4NO_3 by x-ray powder photographs. Only some additional Weissenberg photographs were taken of the form III and of the room temperature phase IV, the intensities being measured in only a semiquantitative way. No Fourier methods were applied in the study of the crystal structure of any of these phases.

A systematic study of the single-crystal transformations of NH_4NO_3 was started in our laboratory. As a consequence of such work, disorder of the NO_3 groups in the tetragonal (II) phase was discovered by Amorós, Alonso and Canut[2] on the ground of diffuse scattering, confirmed later by Shinnaka[3], and by Amorós and Banerjee[4] by

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[1] S. B. Hendricks, E. Posnjak and F. Kracek, Molecular rotation in the variation of crystal structure of ammonium nitrate with temperature. J. Am. Chem. Soc. **54** (1932) 2766—2786.

[2] J. L. Amorós, P. Alonso y M. L. Canut, Transformaciones polimorfas en monocristales. II. Transición IV—II (84 °C) del nitrato amónico y forma metaestable II′ (55 °C). Bol. R. Soc. Esp. Hist. Nat. (G) **56** (1958) 77—91.

[3] Y. Shinnaka, X-ray study and molecular rotation in tetragonal ammonium nitrate. J. Physic. Soc. Japan. **14** (1959) 1707—1716.

[4] J. L. Amorós y R. L. Banerjee, El mecanismo de la transición IV → II en el NO_3NH_4. Bol. R. Soc. Hist. Nat. (G) **58** (1960) 165—180.

Fourier methods. In addition, AMORÓS, ALONSO and CANUT[5] found that the low-temperature phase was tetragonal instead of hexagonal, as deduced from the method developed by AMORÓS, VARGAS and CANUT[6] for the determination of the crystal symmetry from a single cylindrical Laue photograph. Comparison between the thermal diffuse scattering of the IV and III phases of ammonium nitrate has also shown that a phase transformation may merely mean a more stable arrangement of ions which is often be marked by an abrupt change of crystal dynamics[7].

All this previous work showed us the need of a careful crystal-structure analysis of the polymorphism of the NH_4NO_3. In this paper, the crystal structure of the V (low temperature) form is given, as well as a general discussion of the mechanism of the single-crystal reversible transformation:

V		IV		II
	$\xleftarrow{-18\,°C}$		$\xrightarrow{55°C}$	
tetragonal		orthorhombic		tetragonal
(low temperature)		(room temperature)		(high temperature)

Low-temperature phase of NH_4NO_3

The phase V of ammonium nitrate is the one stable below −18 °C. HENDRICKS, POSNJAK and KRACEK[1] obtained x-ray powder photographs at −33 °C and at −78 °C, with the intensity distribution of the powder lines corresponding to a hexagonal lattice having $a = 5.72$ Å and $c = 15.9$ Å.

AMORÓS, ALONSO and CANUT[5] have shown that when a single crystal of the NH_4NO_3 room-temperature form is cooled below −18 °C, a single (or twinned) crystal of the V phase is obtained. The symmetry of this phase was found to be tetragonal instead of hexagonal. From comparison between rotation photographs of the room (IV) and low-temperature (V) phases, the following cell transformation was given:

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[5] J. L. AMORÓS, P. ALONSO y M. L. CANUT, Transformaciones polimorfas en monocristales. I. Formación de superestructura en la transición IV—V (—18 °C) del nitrato amónico. Bol. R. Soc. Esp. Hist. Nat. (G) **56** (1958) 65—75.

[6] J. L. AMORÓS, J. VARGAS y M. L. CANUT, Determinación de la simetría Laue de un cristal mediante un solo Laue cilíndrico. Bol. R. Soc. Esp. Hist. Nat. (G) **56** (1958) 363—378.

[7] P. ALONSO, M. L. CANUT y J. L. AMORÓS, Dinámica de redes en cristales iónicos. I. Difración difusa de las formas polimorfas IV (entre —18 °C y 32 °C) y III (entre 32 °C y 84 °C) del nitrato amónico. Bol. R. Soc. Esp. Hist. Nat. (G) **56** (1958) 51—64.

IV phase (room temperature)	V phase (low temperature)
$a = 5.75$ Å ($2a = 11.5$ Å)	$a' = 11.2$ Å
$b = 5.45$ Å ($2b = 10.9$ Å)	$b' = 11.2$ Å
$c = 4.96$ Å ($2c = 9.92$ Å)	$c = 9.8$ Å
$8 \times \mathrm{vol} = 1243$ Å^3	$\mathrm{vol} = 1229$ Å^3

The formation of a superstructure at low temperature was assumed as a consequence of the interlayer lines appearing in the rotation photographs of the low temperature phase.

High-temperature tetragonal phase of NH_4NO_3

The phase II of NH_4NO_3 is the one stable between 84 °C and 125 °C, appearing in a metastable form above 55 °C. A single-crystal transformation is obtained by heating *suddenly* above 55 °C a single crystal of the room-temperature phase[2]

IV	$\xrightarrow{55^\circ\mathrm{C}}$	II
orthorhombic	(suddenly)	tetragonal
(room temperature)		(high temperature)

The appearence of the high-temperature tetragonal structure occurs with formation of disorder as deduced from the observed diffuse scattering extended along [001] except at the origin, with maxima lying in the center of the reciprocal square-reticular planes[2].

The structure of phase II was incompletely determined by Hendricks *et al.*[1]. Shinnaka[3] later confirmed the validity of the structure proposed by the former authors and determined the distribution of the atoms along [001].

The structure of phase II is polar along the c axis. Amorós and Banerjee[4] showed that the transition IV → II, from a non-polar to a polar structure, occurs with packing disorder of the NO_3 groups in two extreme A and B centrosymmetric positions along the polar axis. From the Fourier projections along [001], it was deduced that the structure of this phase is formed by $75^0/_0$ of the A and $20^0/_0$ of the B positions, as well as a small residue of the room-temperature phase.

Cell dimensions and preliminary space group

X-ray Weissenberg photographs of the V phase were taken by cooling single crystals of the room temperature phase. Cu$K\alpha$ (filtered) radiation and a vertical Weissenberg goniometer built in our department[8] were used. The camera is provided with a low-temperature device that blows on the crystal a stream of dried nitrogen gas, which has been cooled previously by passing through two spiral copper tubes, the first one immersed in a mixture of dry ice and alcohol plus acetone, and the second one in liquid nitrogen. With such a device, any temperature down to —185 °C can be reached by controlling the flow of N_2 gas.

Crystals of the IV form, grown in water solution at room temperature and of convenient size ($0.3 \times 0.3 \times 1.5$ mm approximately) were mounted along [100], [010], and [001] as rotation axes, and Weissenberg photographs were obtained at —30°C, —70°C, —150°C and —185 °C. The transformation shows some hysteresis as sometimes —30 °C is reached without obtaining the transformation of the form IV into the form V. The following axial transformation between the IV phase and the reduced cell of the V form was observed:

$$\left.\begin{matrix}[100]_{\mathrm{IV}} \\ {[010]_{\mathrm{IV}}}\end{matrix}\right\rangle [\bar{1}10]_{\mathrm{V}} \text{ or } [1\bar{1}0]_{\mathrm{V}}$$

$$[001]_{\mathrm{IV}} - [001]_{\mathrm{V}}.$$

The cell dimensions of the V phase of NH_4NO_3 at —150 °C were determined from a Weissenberg photograph (diameter, 9 cm) taken with $[\bar{1}10]$ as a rotation axis,

$$a = 7.98 \pm 0.02 \text{ Å}$$

$$c = 9.78 \pm 0.02 \text{ Å},$$

in agreement with the data of Amorós *et al.*[2] when the smallest tetragonal cell is taken ($a = 7.98\sqrt{2} = 11.2$).

For intensity measurements, zero, first- and second-layer Weissenberg photographs at —70 °C and at —150 °C with the crystal mounted along $[\bar{1}10]$ and [001] were taken. A multiple-film technique was used, and the intensities were estimated visually with the aid of a calibration scale obtained from a single reflection of a crystal of NH_4NO_3 at room temperature. The range of intensities was from 685 to 1, and 267 independent reflections in the accesible sphere of reflection were measured.

The intensities were corrected for Lorentz and polarization effects and were correlated. In the preliminary stage, the observed intensities

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[8] J. L. Amorós, M. Guibert, M. L. Canut y F. Arrese, Un goniómetro Weissenberg vertical para altas y bajas temperaturas. R. de Ciencia Aplicada **15** (1961) 289—297.

were reduced to a semiabsolute scale by using Wilson's method[9], giving an isotropic temperature factor at —150 °C of $B = 0.7$ Å^2. The square roots of the corrected intensities yielded a set of structure amplitudes given in Table 2.

The systematic absences as obtained from the Weissenberg photographs were: h = odd for hhl, $h + k$ = odd for $hk0$, and l = odd for $0kl$. The space group determined was $P4_2/ncm$. The complete structure analysis showed, however, that the space group is $P4_2$ and that the extinctions $h + k$ = odd for $hk0$ and l = odd for $0kl$ (apart l = odd for $00l$) were due only to particular positions of the atomic coordinates.

Determination of the structure of phase V

The determination of the structure has been made via Patterson and Fourier methods. Although three-dimensional data were recorded, there was no need of data other than that for projections on (001) and ($\bar{1}10$), as no misleading overlapping of the atoms was observed in these projections.

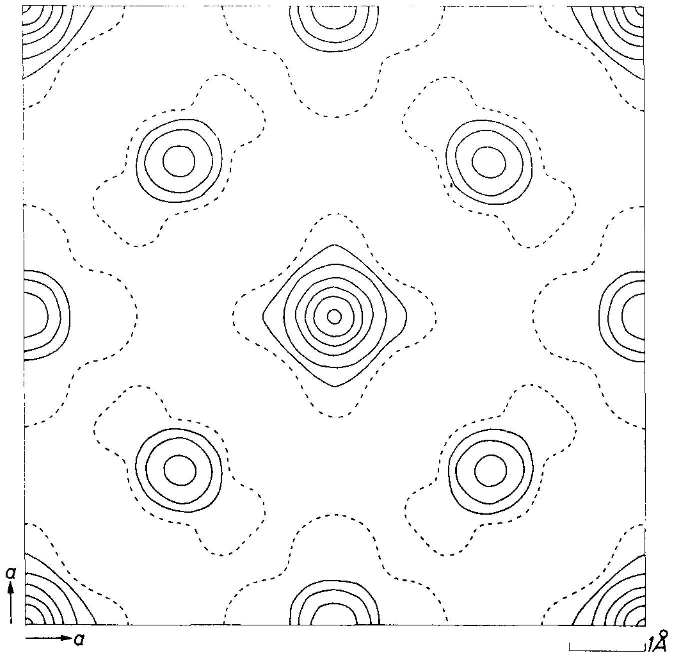

Fig. 1. NH_4NO_3—V. Patterson projection along [001]. Contours are at arbitrary intervals

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[9] A. J. C. Wilson, Determination of absolute from relative x-ray intensity data. Nature [London] **150** (1942) 152.

Patterson synthesis

The Patterson projections using *hk*0 and $\bar{h}hl$ with the general symmetry $P4/nmm$ were computed in the normal manner (Figs. 1 and 2). Both Patterson projections are concordant in the sense that they show all peaks along lines located at intervals $\frac{1}{4}\frac{1}{4}z$, corresponding to linear concentrations not intrinsic of the space groups considered, and showing therefore that structural units, i.e. the NO_3 and NH_4 groups, lie on columns at $00z$ and $\frac{1}{4}\frac{1}{4}z$.

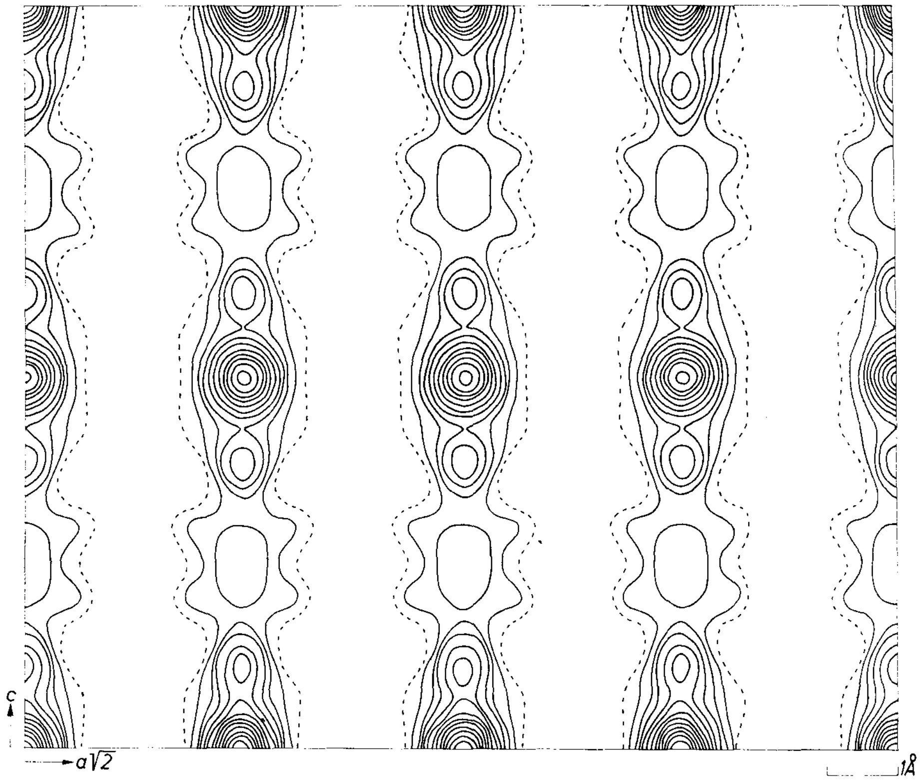

Fig. 2. NH_4NO_3 — V. Patterson projection along [$\bar{1}$10]. Contours are at arbitrary intervals

Because of the extremely high symmetry of the Patterson projections we could find no solution of the crystal structure by using the Buerger's minimum function.

Rejections of the space groups $P4_2/ncm$ and $P4_2/n$

Assuming that the structural units were located at $0\frac{1}{2}z$, $00z$ and $\frac{1}{4}\frac{1}{4}z$, a Fourier projection (001) was computed with all positive signs in terms of space group $P4_2/ncm$. From this projection the NH_4 groups were located at $00z$, $0\frac{1}{2}z$ and the NO_3 groups lying on the mirror planes. Many attempts to refine any trial structure by using this space group failed and, therefore, a change in the space group was considered necessary, in order to eliminate the disturbing mirror planes parallel to the 4_2 axis.

As the extinction condition l = odd for $00l$ is contained in the condition l = odd for $0kl$, trials of the structure were made by using the space group $P4_2/n$, which derives from the $P4_2/ncm$ when the disturbing mirror planes are eliminated. The NO_3 groups were located in this case parallel to (100), preserving the former special distribution, i.e. the NO_3 groups at $\frac{1}{4}\frac{1}{4}z$ and the NH_4 at $00z$, $0\frac{1}{2}z$, the origin taken at $\bar{4}$. The first trial gave for $hk0$ a discrepancy factor $R = 0.20$, justifying the lowering of the symmetry. However, the presence of the n glide in this space group introduces a sequence of NO_3 groups along the c axis, with two non-equivalent crystal-chemical surroundings for the NH_4 groups. The unsuitability of such arrangement was reflected in the calculated $\bar{h}hl$ structure factors, that were zero for l = odd, in spite of the corresponding observed non-zero values. Efforts along this line were not successful, suggesting that the crystal symmetry had to be reduced to $P4_2$.

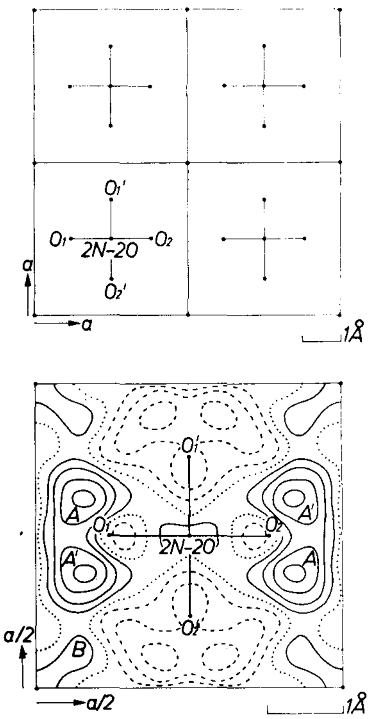

Fig. 3. Above: Trial model (space group $P4_2$) for (001) projection. Below: $(F_o - F_c)$ synthesis down [001]. Contours are at intervals of 1 $e \cdot Å^{-2}$

Determination of the structure projected on (001)

By using the space group $P4_2$, the NH_4 groups were located at the origin on the 4_2 axis and on the two fold axis, and the NO_3 at $\frac{1}{4}\frac{1}{4}z$, as in previous trials. A tentative structure with the hypothesis of the NO_3 groups in crossed positions as in the scheme given in Fig. 3 (upper part) gave for $|F_{hk0}|$ a discrepancy factor $R = 0.30$. The $(F_o - F_c)$

synthesis (Fig. 3, below) showed that the hypothesis at right-angle crosses had to be discarded, as negative maxima appeared in the positions where the oxygen atoms were located (except that on top of N). The existence of two strong positive maxima A and A' suggested that the NO_3 groups had to be located about 9 degrees up and down from the starting position of the line O_1O_2, and O_2' and O_1' had to be dropped out. Furthermore, a low positive maximum B suggested a probable position for the H belonging to the NH_4 group.

Table 1. *Atomic coordinates*

		Point symmetry	x/a	y/b	z/c	Final z/c
NO_3	N	(*d*)	0.250	0.250	0.511	0.518
	O_1	(*d*)	0.120	0.270	0.449	0.456
	O_2	(*d*)	0.330	0.230	0.449	0.456
	O_3	(*d*)	0.250	0.250	0.635	0.642
$NO_3(')$	N′	(*d*)	0.250	0.250	0.011	0.018
	O_1'	(*d*)	0.120	0.230	0.949	0.956
	O_2'	(*d*)	0.380	0.270	0.949	0.956
	O_3'	(*d*)	0.250	0.250	0.135	0.142
NH_4	N	(*a*)	0.000	0.000	0.250	0.250
	H_1	(*d*)	0.076	0.076	0.190	0.190
	H_2	(*d*)	0.076	−0.076	0.310	0.310
$NH_4(')$	N′	(*b*)	0.500	0.000	0.250	0.250
	H_1'	(*d*)	0.576	0.076	0.190	0.190
	H_2'	(*d*)	0.424	0.076	0.310	0.310
$NH_4('')$	H″	(*c*)	0.500	0.500	0.250	0.250
	H_1''	(*d*)	0.424	0.424	0.310	0.310
	H_2''	(*d*)	0.424	0.576	0.190	0.190
$NH_4(''')$	N‴	(*c*)	0.000	0.500	0.250	0.250
	H_1'''	(*d*)	−0.076	0.424	0.310	0.310
	H_2'''	(*d*)	−0.076	0.576	0.190	0.190

Assuming an overall temperature factor $B = 0.7$ Å^2, the structure factors for the $hk0$ reflections, H included, were computed in terms of the x, y atomic coordinates given in Table 1.

It must be pointed out that the reflections $h + k =$ odd, which are absent in the Weissenberg photographs, but are not forbidden for the space group used, $P4_2$, have zero also for calculated F values due to the particular positions of the atoms. The N and the O_3 and O_3' do not contribute to these reflections, and the contributions of the H and those of O_1 and O_1', O_2 and O_2' cancel each other.

The discrepancy factor dropped to $R(hk0) = 0.15$ for observed intensities only, and to $R(hk0) = 0.17$ for all reflections. Comparison between the observed and calculated structure amplitudes is given in Table 2. The electron-density map (Fig. 4) shows very sharp, well resolved peaks corresponding to the atomic groups, with quite satisfactory peak heights. The NH_4 groups appearing at 0,0 and $\frac{1}{2}$,0 are not homologous; however, the Fourier map shows the same heights for the N and H electron-distribution confirming the hypothesis. The electron distribution appearing at ($\frac{1}{4}$, $\frac{1}{4}$) corresponds to two superimposed NO_3 groups crossed 18° one each other. At the central position of this group, two N plus O_3 and O′ project together, and the elongated peaks are the result of the overlap of two pairs of oxygens, O_1, O_1' and O_2, O_2', with atomic centers close together.

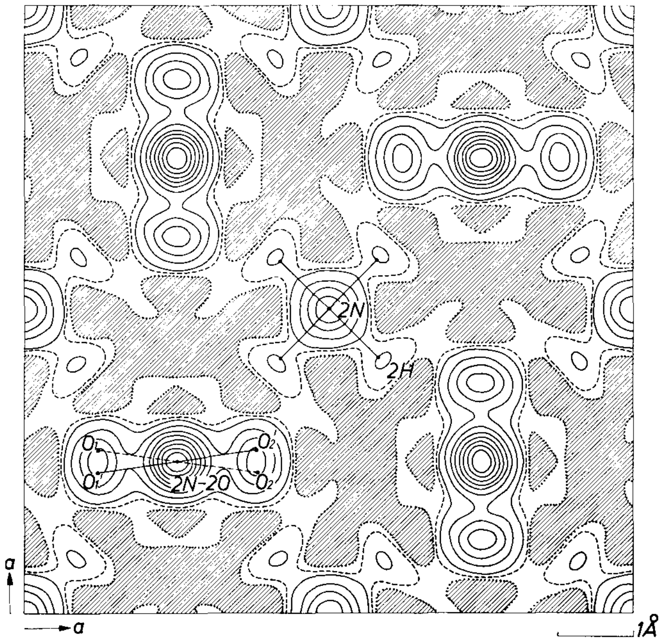

Fig. 4. Final electron-density projection of NH_4NO_3 V at 120°K, along [001]. Contours at intervals of $3e \cdot Å^{-2}$. Regions lower that $1e \cdot Å^{-2}$ (dotted line) are shaded. The broken line corresponds to $2e \cdot Å^{-2}$

The difference Fourier synthesis computed at this stage did not show the need of changing the angle between the two superimposed NO_3 groups.

Table 2. *Observed and calculated structure factors*

h k l	F_o	F_c	h k l	F_o	F_c	α°	h k l	F_o	F_c	α°
0 1 0	0	0	5 5 0	0	0	0	1 1 5	0	0	0
0 2 0	80.3	- 92.9	5 6 0	0	0	0	2 2 5	8.2	7.9	153
0 3 0	0	0	5 7 0	18.4	- 13.5	180	3 3 5	0	0	0
0 4 0	90.6	88.5	5 8 0	0	0	0	4 4 5	0	2.3	206
0 5 0	0	0	5 9 0	0	- 2.2	180	5 5 5	0	0	0
0 6 0	55.9	- 48.1	6 6 0	49.8	41.4	0	6 6 5	0	4.7	70
0 7 0	0	0	6 7 0	0	0	0	0 0 6	17.5	37.4	289
0 8 0	41.6	59.5	6 8 0	15.5	- 19.2	180	1 1 6	0	0	0
0 9 0	0	0	7 7 0	0	0	0	2 2 6	16.5	12.1	348
0 10 0	0	0.1	2 2 0	128.0	126.8	0	3 3 6	0	0	0
1 1 0	0	0	4 4 0	27.4	20.7	0	4 4 6	16.5	14.9	52
1 2 0	0	0	6 6 0	49.8	41.4	0	5 5 6	0	0	0
1 3 0	63.5	62.8	1 1 1	0	0	0	6 6 6	10.8	8.7	214
1 4 0	0	0	2 2 1	31.4	26.3	177	1 1 7	0	0	0
1 5 0	31.8	- 36.5	3 3 1	0	0	0	2 2 7	7.2	3.5	45
1 6 0	0	0	4 4 1	6.2	1.0	340	3 3 7	0	0	0
1 7 0	0	- 9.8	5 5 1	0	0	0	4 4 7	0	0.5	278
1 8 0	0	0	6 6 1	14.4	17.0	8	5 5 7	0	0	0
1 9 0	0	8.7	7 7 1	0	0	0	6 6 7	5.2	5.9	127
2 2 0	129.9	125.1	0 0 2	61.4	67.3	3	0 0 8	17.5	11.9	348
2 3 0	0	0	1 1 2	0	0	0	1 1 8	0	0	0
2 4 0	0	- 1.1	2 2 2	31.9	32.4	124	2 2 8	40.7	38.6	22
2 5 0	0	0	3 3 2	0	0	0	3 3 8	0	0	0
2 6 0	61.0	55.1	4 4 2	38.2	46.6	149	4 4 8	44.4	44.6	24
2 7 0	0	0	5 5 2	0	0	0	5 5 8	0	0	0
2 8 0	31.7	- 26.9	6 6 2	5.2	6.8	99	1 1 9	0	0	0
2 9 0	0	0	7 7 2	0	0	0	2 2 9	6.1	5.6	12
2 10 0	6.0	26.0	1 1 3	0	0	0	3 3 9	0	0	0
3 3 0	0	0	2 2 3	10.8	6.8	122	4 4 9	0	1.3	197
3 4 0	0	0	3 3 3	0	0	0	5 5 9	0	0	0
3 5 0	0	- 1.3	4 4 3	8.7	5.0	349	0 0 10	56.7	44.8	175
3 6 0	0	0	5 5 3	0	0	0	1 1 10	0	0	0
3 7 0	21.4	19.9	6 6 3	9.8	11.7	29	2 2 10	18.0	10.8	153
3 8 0	0	0	7 7 3	0	0	0	3 3 10	0	0	0
3 9 0	0	- 8.7	0 0 4	65.0	79.4	329	4 4 10	0	10.5	78
4 4 0	27.4	20.7	1 1 4	0	0	0	1 1 11	0	0	0
4 5 0	0	0	2 2 4	16.5	19.0	24	2 2 11	5.2	5.0	2
4 6 0	15.0	- 6.7	3 3 4	0	0	0	3 3 11	0	0	0
4 7 0	0	0	4 4 4	0	15.6	101	0 0 12	5.2	12.3	173
4 8 0	42.9	37.9	5 5 4	0	0	0	1 1 12	0	0	0
4 9 0	0	0	6 6 4	12.9	10.9	352	2 2 12	11.3	9.4	358

Determination of the structure projection on $(\bar{1}10)$

The special crystal axis transformation from phase IV into phase V (i.e. $[100]_{\mathrm{IV}} \rightarrow [\bar{1}10]_{\mathrm{V}}$), gave us the possibility of analysing directly the crystal structure projected on $(\bar{1}10)$, that is, the diagonal planes of the cell containing the 4_2 axis. The fact that the groups NH_4 and NO_3 are arranged in columns at $00z$ and $\frac{1}{4}\frac{1}{4}z$ allowed us the study of the structure projected on $(\bar{1}10)$ without heavy overlapping of the atoms and, therefore, a three-dimensional analysis was not needed to solve the whole crystal structure.

Starting from the information given by the (001) projection a model was drawn according with the following ideas. As the NH_4 are located on the 4_2 and 2 axes, they should be at heights differing by $c/2$. As there are no conditions on the heights of the NH_4 groups, z/c was taken as 0.250 and, accordingly, the NO_3 groups were placed between the NH_4 groups.

The $(\bar{h}hl)$ structure factors were calculated with the atomic coordinates given in Table 1 and by using the formula of the space group $P4_2$. The discrepancy factor at this stage was $R = 0.25$ for observed intensities only.

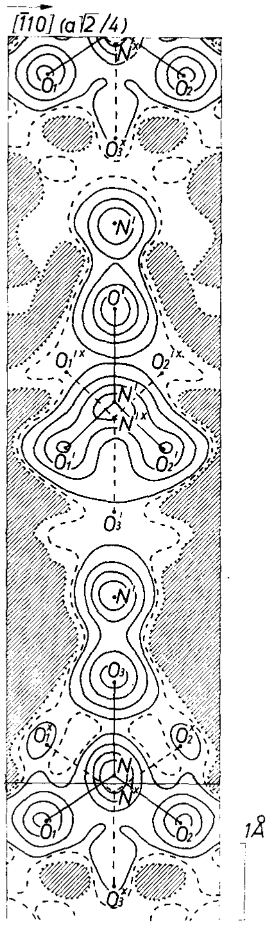

Fig. 5. Electron-density projection of NH_4NO_3 V along $[\bar{1}10]$. Contours at intervals of $3 e \cdot Å^{-2}$. Regions lower that $1 e \cdot Å^{-2}$ (dotted line) are shaded. The broken line corresponds to $2 e \cdot Å^{-2}$

Here again we must point out that the reflections forbidden according to the space group used, $P4_2$, are only $l =$ odd for $00l$, but that in the observed reflections $l =$ odd for $0kl$ were also absent. The corresponding calculated values are zero: all N and the O_3 and O_3' do not contribute to these reflections and the O_1, O_2 and the corresponding O_1', O_2' cancel each other. The same occurs with the contributions of the different H.

On the other hand, in spite that the observed absences $h =$ odd for $\bar{h}hl$ are not proper extinction conditions of any space group, the corresponding calculated values are zero because N, O_3 and O_3' of the NO_3 groups do not contribute to such reflections, and the O_1, O_2 contributions cancel those of O_1', O_2'. The same occurs with the N and H of the NH_4 groups.

Fig. 5 shows the electron-density map plotted from the results of the Fourier synthesis obtained with the observed structure factors at —70 °C and the phases calculated for the atomic arrangement corresponding to the atomic coordinates given in Table 1. The two NO_3 groups do not project in the same way on the plane $(\bar{1}10)$, as can be seen by the location of the O_1, O_2 and O_1', O_2' atom peaks.

The peak heights of the oxygen atoms give about $13 e \cdot Å^{-2}$ instead of the $16 e \cdot Å^{-2}$ that could be expected for two superimposed oxygens. However, the electron density lost here do appear in positions centrosymmetrically corressponding to the position of the NO_3 groups. In the figure, O* correspond to the centrosymmetric positions of O, $O_1^*O_2^*O_3^*$ lying on $3\ e \cdot Å^{-2}$ peaks. The effect seems less pronounced in the group $O_1'O_2'O_3'$, as the corresponding O* lie on $2\ e \cdot Å^{-2}$ peaks. Similar effects were found by Amorós and Banerjee[4] in the tetragonal phase

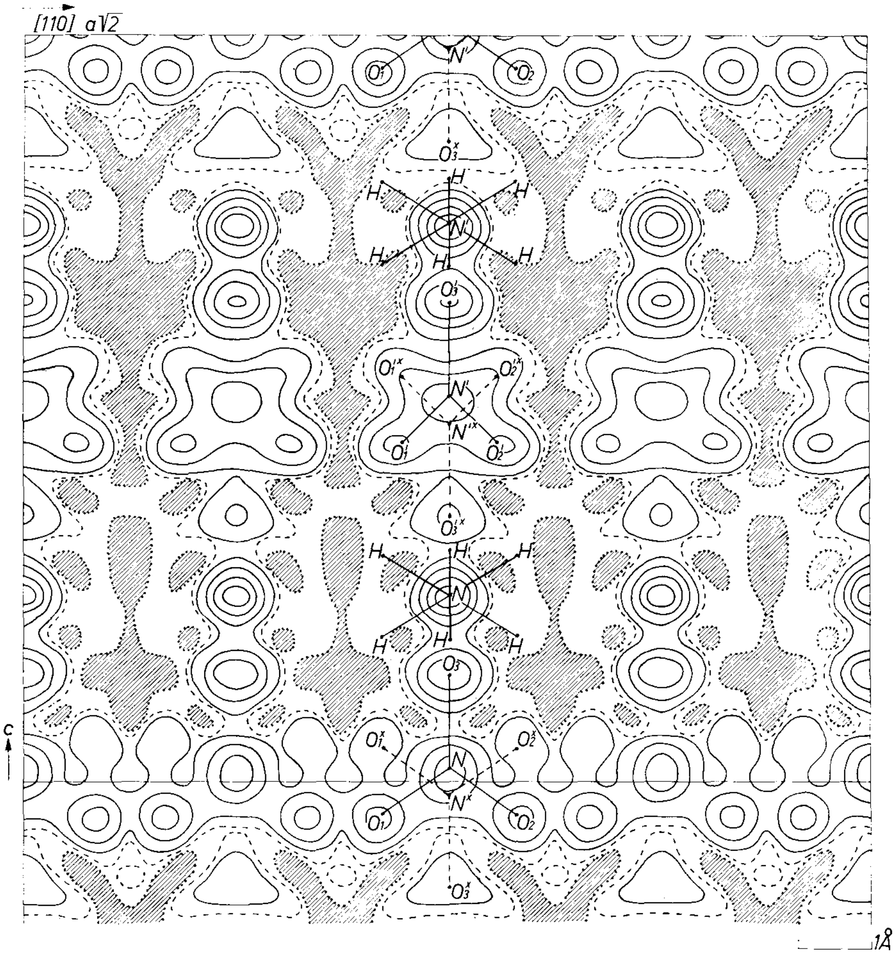

Fig. 6. Final electron-density projection of NH_4NO_3 V at 130 °K, along [$\bar{1}$10]. Contours are at intervals of $3\,e \cdot Å^{-2}$. Regions lower that $1\,e \cdot Å^{-2}$ (dotted line) are shaded. The broken line corresponds to $2\,e \cdot Å^{-2}$

of high temperature. In form II, evidence for some statistical disorder of the NO_3 groups was obtained from the observed diffuse scattering with maxima lying between layers[2]. In the low-temperature tetragonal phase, no evidence for disorder through diffuse scattering analysis has been found, but a possible explanation could be that the transition occurs with the formation of an intimately and interpenetratingly twinned structure.

At this stage, a set of new intensities at —150 °C was taken. An attempt to introduce anisotropic temperature factors did not improve the discrepancy factor. The best final value of z coordinates of the NO_3 groups were determined by trial and error (Table 1). Structure factor calculated with those coordinates and introducing a $25^0/_0$ of disorder, as deduced from the Fourier projection, dropped the discrepancy factor from $R_{hhl} = 0.25$ to $R_{hhl} = 0.18$ for the observed intensities only, and to $R_{hhl} = 0.21$ for all reflections. The final electron-density map plotted from the results of the Fourier synthesis is shown in Fig. 6. The observed structure-factor amplitudes and the corresponding magnitudes and phases calculated from the final structure are presented in Table 2.

The above results refer to the reflections $\bar{h}hl$. It was important also to check the reflections hkl, for $l =$ odd. Computations made with several reflections hkl, by using the atomic coordinates given in Table 1 and space group $P4_2$, showed that, when $h + k =$ odd, the O and the N do not contribute, and only four H atoms were responsable for these intensities. On the other hand, when $h + k =$ even, all atoms contribute. This facts are consistent with the observed extinctions.

Description and discussion of the crystal structure

The crystal structure of NH_4NO_3 V is formed by discrete groups NO_3 and NH_4 that are located in columns along the c axis, the distance between such columns being $(a/4,\ b/4)$, therefore columns NO_3 and NH_4 alternate in the plane (110). In each column there are two groups NO_3 or NH_4 per unit cell (Fig. 7).

The NO_3 groups of each column are not parallel to each other, but are contained in two planes that form 18° between them. Such planes are symmetrical according (100). The dimensions of the NH_4 and NO_3 groups in the starting hypothesis were taken as given in Interatomic Distances[10]:

$$NH_4\ \ N—H = 1.04\ \text{Å}$$

$$NO_3\ \ N—O = 1.24\ \text{Å}$$

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[10] Tables of interatomic distances and configuration in molecules and ions. The Chemical Society (1958) M 47.

The crystal structure can be described in terms of a tetragonal pseudocell of the CsCl type. Each NO_3 or NH_4 group is surrounded by eight NH_4 or NO_3 groups respectively, the O — N distances between adjacent groups being slightly different:

$$O_1 - N = 3.01\ \text{Å}$$
$$O_4 - N = 2.88\ \text{Å}$$
$$O_6 - N = 3.17\ \text{Å};$$

from this follows that each NO_3 group is more strongly bonded to a group NH_4 than to another NO_3, allowing for the slight displacement of the NO_3 from the (100) planes.

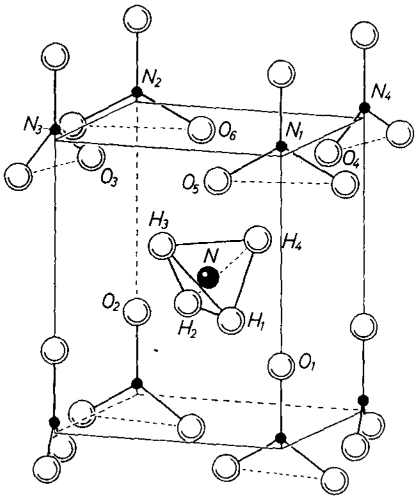

Fig. 7. Three-dimensional scheme of the structure of NH_4NO_3 V

The distances O (NO_3) — H (NH_4) follow the same rule,

$$H_3 - O_3 = 1.91\ \text{Å} \qquad H_4 - O_6 = 2.42\ \text{Å}$$
$$H_1 - O_1 = 2.01\ \text{Å} \qquad H_3 - O_6 = 2.82\ \text{Å},$$

showing one bond stronger than the others. The observed distances are in agreement with those observed in the crystal structures of $NH_4NO_3 \cdot 2NO_3H$ by Duke and Hewellyn[11], HNO_3 and $HNO_3 \cdot H_2O$ by Luzzati[12, 13], as well as in other nitrates.

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[11] J. R. Duke and F. J. Llewellyn, The crystal structure of ammonium trinitrate. Acta Crystallogr. 3 (1950) 305—311.

[12] V. Luzzati, Structure cristalline de l'acide nitrique anhydre. Acta Crystallogr. 4 (1951) 120—131.

[13] V. Luzzati, Structure cristalline de l'acide nitrique á une molecule d'eau. Acta Crystallogr. 4 (1951) 239—244.

In order to compare the interatomic distances in the series of crystal phases of NH_4NO_3, the corresponding ones to the phases II and IV were also calculated. Table 3 gives the values obtained, showing clearly the effect of the temperature in the bonding of such substance.

Table 3. *Interatomic distances in* NH_4NO_3

Distance	NH_4NO_3 — II (high temperature)	NH_4NO_2 — IV (room temperature)	NH_4NO_3 — V (low temperature)
$N(NO_3)$—$N(NH_4)$	5.00 Å	4.96 Å	4.86 Å
$N(NH_4)$—$O(NO_3)$	3.01—4.17 Å	2.95—3.37 Å	2.88—3.17 Å
$O(NO_3)$—$O(NO_3)$	3.45 Å	3.28 Å	3.24 Å

(3.46 Å SHINNAKA[3])

It follows from references [3] and [4], and from this paper, that the crystal structures of both phases II and V are very similar, form II corresponding probably to a vibrational modification of form V. The main difference is found in the fact that the groups NO_3 along [001] of the same column are symmetrically oriented in phase V, and have the same orientation in form II, this orientation corresponding to the mean position of the NO_3 groups in phase V. The columns of NO_3 in both structures are linked by the NH_4 groups. As a consequence, the crystal structure of phase V is only slightly different from that of phase II, the cell dimensions being nearly twice those of form II. Besides, both forms present some disorder of the groups NO_3, as exemplified by the diffuse scattering of form II and the smaller R factor when the twin disorder is introduced in the calculations of form V. The similarity in the crystal-structure types explains the easy single (or twinned) crystal transformations IV → II and IV → V. It is to be expected that at high pressures a direct transformation II → V will be possible.

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