

Low-Temperature Behaviour of Ammonium Nitrate by Neutron Diffraction

BY M. AHTEE AND K. J. SMOLANDER

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

B. W. LUCAS

Department of Physics, University of Queensland, St Lucia, Brisbane, Queensland 4067, Australia

AND A. W. HEWAT

Institut Laue–Langevin, avenue des Martyrs, BP 156X, Centre de Tri, 38042 Grenoble CEDEX, France

(Received 26 May 1983; accepted 8 July 1983)

Abstract

The orthorhombic *Pccn* structure of phase V of NH_4NO_3 extends down to 5 K. The nonlinear behaviour of the lattice parameters as a function of temperature and the deformation of the ammonium molecule at 80 K indicate the onset of anharmonic coupling between the vibrational modes of the ammonium and nitrate molecules.

We have recently proposed a new ordered structure for the low-temperature phase V of ammonium nitrate at 233 K (Ahte, Smolander, Lucas & Hewat, 1983). In the literature, there is evidence indicating that there might exist yet another low-temperature phase, phase VII. Volkovich, Rubinchik & Kozhin (1954), relying on DTA and X-ray diffraction measurements, have suggested a new modification below 100 K. Nagatani, Seiyama, Sakiyama, Suga & Seki (1967) detected a small anomaly at 156 K in their heat-capacity data, which they took to indicate the possibility of the existence of phase VII.

In addition to the measurements at 233 K, on which the structure determination of phase V is based (Ahte *et al.*, 1983), neutron powder diffraction patterns have been measured at three more temperatures (5, 80 and 183 K) using the high-resolution diffractometer at the high-flux reactor of the ILL (Grenoble). The diffraction patterns were analyzed by the Rietveld method using isotropic temperature factors.* [For details see Ahte *et al.* (1983).]

In Fig. 1 the high-angle regions of the diffraction patterns at 233 K and 5 K are shown. The pattern at

* Lists of positional parameters, isotropic thermal parameters and structure factors for each temperature have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38709 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

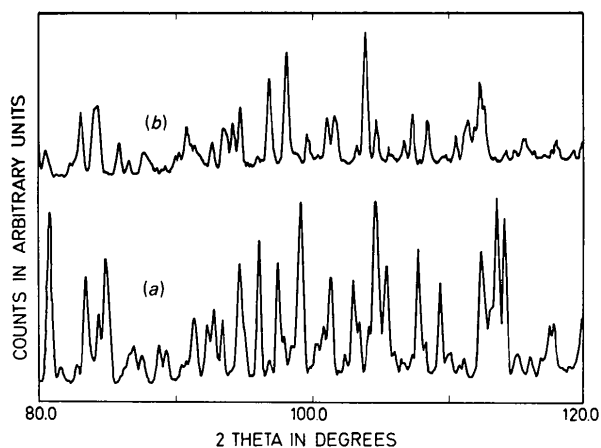


Fig. 1. High-angle region of neutron powder diffraction patterns of ammonium nitrate, phase V: (a) at 5 K; (b) at 233 K, both measured with a neutron wavelength of 1.384 Å.

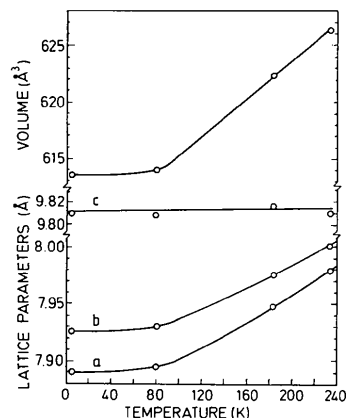


Fig. 2. Temperature variation of lattice parameters and unit-cell volume of ammonium nitrate, phase V. The circles indicate the experimentally determined points.

Table 1. *Interatomic distances (Å) for phase V ammonium nitrate at different temperatures showing the deformation of the two nitrate molecules and the ammonium molecule*

	233 K	183 K	80 K	5 K
NO₃(1)				
Tilt from <i>xz</i> plane	8.6 (0.2) ^o	9.3 (0.2) ^o	7.5 (0.2) ^o	7.2 (0.2) ^o
N(1)—O A(1)	1.230 (10)	1.247 (11)	1.254 (11)	1.282 (9)
N(1)—O B(1)	1.232 (6)	1.238 (6)	1.258 (6)	1.241 (5)
Mean	1.231 (7)	1.241 (8)	1.257 (8)	1.255 (6)
O A(1)—O B(1)	2.127 (9)	2.143 (10)	2.169 (10)	2.179 (8)
O B(1)—O B(1)	2.145 (7)	2.163 (7)	2.190 (7)	2.163 (6)
Mean	2.133 (8)	2.150 (8)	2.176 (9)	2.174 (7)
NO₃(2)				
Tilt from <i>yz</i> plane	11.5 (0.2) ^o	10.3 (0.2) ^o	9.3 (0.2) ^o	8.2 (0.2) ^o
N(2)—O A(2)	1.203 (11)	1.244 (11)	1.277 (8)	1.239 (9)
N(2)—O B(2)	1.234 (6)	1.233 (6)	1.248 (5)	1.242 (5)
Mean	1.224 (8)	1.237 (8)	1.258 (7)	1.241 (6)
O A(2)—O B(2)	2.082 (10)	2.106 (11)	2.166 (8)	2.119 (8)
O B(2)—O B(2)	2.193 (7)	2.205 (7)	2.200 (6)	2.207 (6)
Mean	2.119 (9)	2.139 (10)	2.177 (7)	2.148 (7)
ND₄				
N(3)—D(1)	1.000 (9)	1.023 (10)	1.053 (7)	1.019 (7)
N(3)—D(2)	1.016 (10)	1.015 (10)	1.025 (7)	1.024 (6)
N(3)—D(3)	0.986 (9)	1.012 (9)	1.066 (7)	1.044 (6)
N(3)—D(4)	1.022 (11)	1.011 (9)	1.022 (8)	1.000 (6)
Mean	1.006 (10)	1.015 (10)	1.042 (7)	1.022 (6)
D(1)—D(2)	1.657 (13)	1.659 (14)	1.713 (9)	1.660 (9)
D(1)—D(3)	1.630 (11)	1.619 (12)	1.742 (9)	1.689 (8)
D(1)—D(4)	1.606 (12)	1.666 (12)	1.690 (9)	1.671 (8)
D(2)—D(3)	1.626 (11)	1.641 (12)	1.710 (9)	1.674 (8)
D(2)—D(4)	1.681 (12)	1.694 (11)	1.670 (9)	1.663 (7)
D(3)—D(4)	1.659 (12)	1.661 (10)	1.678 (9)	1.650 (8)
Mean	1.643 (12)	1.657 (12)	1.701 (9)	1.668 (8)

5 K shows much more structure and at first sight the patterns are so different that one would be inclined to consider them as originating from different structures. At each temperature, however, the profile-refinement program gave the same orthorhombic *Pccn* structure as was previously assigned to phase V at 233 K. The simplification of the diffraction patterns, when going to higher temperatures, is due to the smearing action of the increasing thermal motion of the molecules.

In Fig. 2 the lattice parameters and unit-cell volume are plotted as functions of temperature. The curves indicate that the thermal expansion which originates from anharmonic coupling of the molecules starts between 80 and 100 K. As there is virtually no thermal expansion in the *c* direction, the anharmonic coupling of the vibrational modes of the ammonium and nitrate molecules takes place in the *xy* plane.

Jayasooriya, Kearley, Kettle & Lauter (1981) have measured the Raman spectra of ND₄NO₃ at 100 K and identified the frequencies between 47 and 136 cm⁻¹ as being due to translations and librations of the NO₃ molecules and those between 158 and 222 cm⁻¹ as due to NH₄ translations. The occupation number of a mode with angular frequency ω changes rapidly as a function of temperature, *T*, when $\hbar\omega \approx kT$. The temperature 80 K, where significant thermal expansion of the lattice begins and the apparent size of the ND₄⁺ molecule is largest (as seen from Table 1), corresponds to a

wavenumber of about 60 cm⁻¹, which is in the region of the lowest lattice modes of the NO₃ molecules. Thus the motion of the NO₃ molecules is reflected in the positional parameters of the ND₄ molecule. This can tentatively be explained by a strong anharmonic coupling of the lowest NO₃ modes to the lowest ND₄ modes through multiphonon processes. The modes in question here are, of course, optical zone centre modes. The apparent N—O and N—H distances decrease with increasing temperature due to isotropic temperature factors being unable to describe correctly the libration.

The tilt angle of the NO₃(2) molecule increases monotonically with temperature, whereas that of the NO₃(1) molecule has a maximum at 183 K. When the temperature increases, there are two kinds of effects, the excitation of higher and higher modes and the smearing action of increased thermal motion. These effects together give rise to the above-mentioned anomalous behaviour, which can also be seen in the DTA data of Nagatani *et al.* (1967) at 156 K. The frequencies of the intrinsic modes of NO₃ are above 700 cm⁻¹ and those of ND₄ above 1400 cm⁻¹ so that the intrinsic vibrations are not excited at the temperatures studied.

We thank Dr K. Österlund for preparing the deuterated ammonium nitrate, the French Government (BWL) and the Finnish Academy (MA) for their support, and the ILL for making all facilities available to us.

Authors' note: The structure of the low-temperature phase V of ND₄NO₃ has now been proven by two independent studies [Ahtee *et al.* (1983) and Choi & Prask (1983)]. We were informed about the paper by Choi & Prask after the acceptance for publication of our present paper. In their paper, Choi & Prask have measured the diffraction patterns of ND₄NO₃ powder at the temperatures 10 and 78 K and from 130 to 270 K in 20 K steps. The main conclusion, *i.e.* that the orthorhombic *Pccn* structure of phase V extends down to 5 K, has been reached in both papers. In our paper, we pay attention to the change in the slope of the curves of the *a* and *b* parameters *vs* temperature. The same changes are also present in the unit-cell dimensions compiled by Choi & Prask. The differences in the values of the lattice parameters between their and our results arise since the lattice parameters have not been corrected for the errors in the neutron wavelength. When the results of our measurements at 80 K are compared to those of Choi & Prask there is no essential disagreement in the bond lengths. The differences indicated by Choi & Prask in their *Note added in proof* are due to the different measuring temperatures. Since Choi & Prask have not reported the bond lengths as a function of temperature no detailed comparison between their and our results can be made.

References

- AHTEE, M., SMOLANDER, K. J., LUCAS, B. W. & HEWAT, A. W. (1983). *Acta Cryst. C* **39**, 651–655.
- CHOL, C. S. & PRASK, H. J. (1983). *Acta Cryst. B* **39**, 414–420.
- JAYASOORIYA, U. A., KEARLEY, G. J., KETTLE, S. F. A. & LAUTER, H. J. (1981). *Phys. Status Solidi A*, **63**, 169–177.
- NAGATANI, M., SEIYAMA, T., SAKIYAMA, M., SUGA, H. & SEKI, S. (1967). *Bull. Chem. Soc. Jpn*, **40**, 1833–1844.
- VOLFKOVICH, S. I., RUBINCHIK, S. M. & KOZHIN, V. M. (1954). *Bull. Acad. Sci. USSR Div. Chem. Sci.* **209**, 167–174.

Acta Cryst. (1983). **B39**, 687–691

The Structure of LaF₃ – A Single-Crystal Neutron Diffraction Study at Room Temperature

BY D. GREGSON

Institut Laue–Langevin, 156X Centre de Tri, 38042 Grenoble, France

C. R. A. CATLOW

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, England

A. V. CHADWICK

Department of Chemistry, University of Kent, Canterbury CT2 7NR, England

G. H. LANDER

Institut Laue–Langevin, 156X Centre de Tri, 38042 Grenoble, France

A. N. CORMACK

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, England

AND B. E. F. FENDER

Institut Laue–Langevin, 156X Centre de Tri, 38042 Grenoble, France

(Received 30 July 1982; accepted 29 July 1983)

Abstract

A single-crystal neutron diffraction study at room temperature has been carried out to examine the ambiguity in the space group for LaF₃, which cannot be resolved by neutron powder diffraction. With *P*6₃*cm* an *R* factor of 0.042 (249 unique reflections) was obtained compared with a corresponding value of 0.136 for *P*3̄*c*1. Marked anisotropy is observed in the thermal parameters of two of the F atoms, which may be correlated with the positions of near-neighbour atoms.

Introduction

The tysonite structure is still not unambiguously established. There have been a number of reports where various space groups have been proposed; these include

*P*3̄*c*1, suggested by Mansmann (1965) and Zalkin, Templeton & Hopkins (1966), *P*6₃/*mcm* (Ofstedal, 1929, 1931) and *P*6₃*cm* proposed by de Rango, Tsoucaris & Zelwer (1966), where the number of molecular units per unit cell (*Z*) is six. There have also been suggestions for *Z* = 12 in the *P*6₃/*mcm* space group by Sher, Solomon, Lee & Müller (1966) from NMR studies, and for *Z* = 2 in *P*6₃/*mnc* (Schlyter, 1952) from X-ray diffraction. There are several reasons why it is important to establish the correct structure.

LaF₃ is frequently used as a non-magnetic host for spectroscopic investigations of paramagnetic lanthanide ions and LaF₃ itself is a good ionic conductor with interesting high-temperature properties. Above ~1000 K it has an anomalously high heat capacity (Lyon, Osborne, Flotow & Grandjean, 1978) and one of the highest known ionic conductivities (Chadwick, 1982). In a previous powder neutron diffraction study by

0108-7681/83/060687-05\$01.50

© 1983 International Union of Crystallography