The pressure-induced disordering of ammonium metavanadate

David M Adams, Julian Haines and Simon Leonard

Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

Abstract. The structural behaviour of ammonium metavanadate, NH_4VO_3, under high pressures has been studied to 65 kbar using energy-dispersive synchrotron x-ray powder diffraction, and to 106 kbar by FTIR methods, in a diamond anvil cell. A reversible crystalline-to-disordered phase transition was found at 49 kbar. The transition is thought to be due to relative slipping of the vanadate chains parallel to their axes, the product being disordered, possibly amorphous, rather than crystalline because the process is hindered and the solid prevented from attaining periodicity by hydrogen bonding to ammonium ions.

1. Introduction

We have shown recently that the response to high pressure of the potassium, rubidium and caesium vanadates, M^IVO_3, is highly cation-dependent, the structural reaction being different in each case [1, 2]. NH_4VO_3 is isomorphous with these vanadates [3] but from its size, and ability to hydrogen bond, it is not clear which, if any, of these types of structural change it will exhibit under pressure. Accordingly, we have undertaken a combined energy-dispersive synchrotron x-ray powder diffraction (EDXRPD) and infrared spectroscopic study of it.

Ammonium vanadate has been investigated extensively using a variety of experimental techniques. The structure is isomorphous with that of KVO_3 ($Pbcm$, $z = 4$) in which there are anionic chains of (VO_4) tetrahedra separated by cations. The NH_4^+ ion is in sixfold coordination and forms two single and two bifurcated hydrogen bonds, which may have some dynamic character. Several infrared and Raman studies have been performed on NH_4VO_3 [4–11]. These include an investigation of the Raman spectrum to 45 kbar, which indicated that pressure-induced changes are mostly accommodated by changes in the V–O bridging bonds and O–V–O bridging angles [8], and a variable-temperature Raman study, which suggested that an order–disorder transition might be present near 150 K [10].

The dynamics of the ammonium ion in NH_4VO_3 have been investigated by neutron scattering [12] and proton NMR studies at low temperature [13, 14] and high pressure [15]. At room temperature, the ammonium ion is not in free rotation but, rather, performs twofold and threefold reorientations. Upon cooling there is a significant decrease in the rate of reorientation between 150 and 80 K. No further changes in the second moment of the resonance line were observed down to 4 K at 1 bar and up to 14 kbar at 77 K.

2. Experimental details

EDXRPD data were obtained with the sample in a diamond anvil high-pressure cell (DAC) mounted in the x-ray beam on Station 9.7 at the SERC Daresbury Laboratory. The x-ray beam used was 0.1 mm in diameter at the sample. Gaskets of stainless steel AISI 316 with a central hole of 300 μm were used. The pressure calibrant was ruby.

Infrared spectra at high pressure (4 cm^{-1} resolution) were acquired on a Bio-Rad Digilab FTS-40 spectrometer using a DAC. NH_4VO_3 was diluted with KBr and loaded into the 400 μm gasket hole along with 0.34% w/w $NaNO_2$ in NaBr as a pressure calibrant [16]. All IR spectra were obtained at 30 °C.

3. Results and discussion

3.1. EDXRPD results

Data were collected to a maximum pressure of 65 kbar at $2\theta = 9.53°$. The parent *Pbcm* structure was identified up to 47 kbar after which the quality of the spectrum began to decline, figure 1. At 49 kbar new peaks appeared at 16.89, 24.28 and 27.01 keV, indicating a phase change. By 65 kbar the spectrum of the new phase had degraded badly, with very broad lines and a low signal : noise ratio. These effects are fully reversible.

The atmospheric pressure orthorhombic cell was refined using *d*-spacings from experiment, yielding results comparable with those from single-crystal studies, table 1. Plots of the lattice parameter changes with pressure are given in figure 2. The uniaxial and bulk compressibilities for the parent *Pbcm* cell to 50 kbar are

$$a = 1.17 \qquad b = 0.393 \qquad c = 0.516 \qquad \kappa = 1.70 \times 10^{-3}\,\text{kbar}^{-1}.$$

These are in the ratios $a:b:c = 3:1:1.3$.

Data from the high-pressure phase were of too poor a quality to allow an attempt at its identification.

3.2. Infrared results

At ambient pressure, ten bands were observed in the mid-IR spectrum of NH_4VO_3 in the DAC, figure 3. The five higher-frequency modes arise from the internal vibrations of the ammonium ion, whilst the five lower-frequency bands arise from the vanadate chain [4–11]. These five latter vibrations increase in frequency with increasing pressure, figure 4. The magnitude of these shifts, table 2, is very similar to those observed for the corresponding Raman modes [8] and to the corresponding infrared modes of $RbVO_3$ [2].

The behaviour of the internal modes of the ammonium ion is more complex. The frequencies of the N–H stretching vibrations ν_1 and ν_3, originally at 2945 and 3199 cm^{-1}

Table 1. Lattice parameters (Å) for NH_4VO_3.

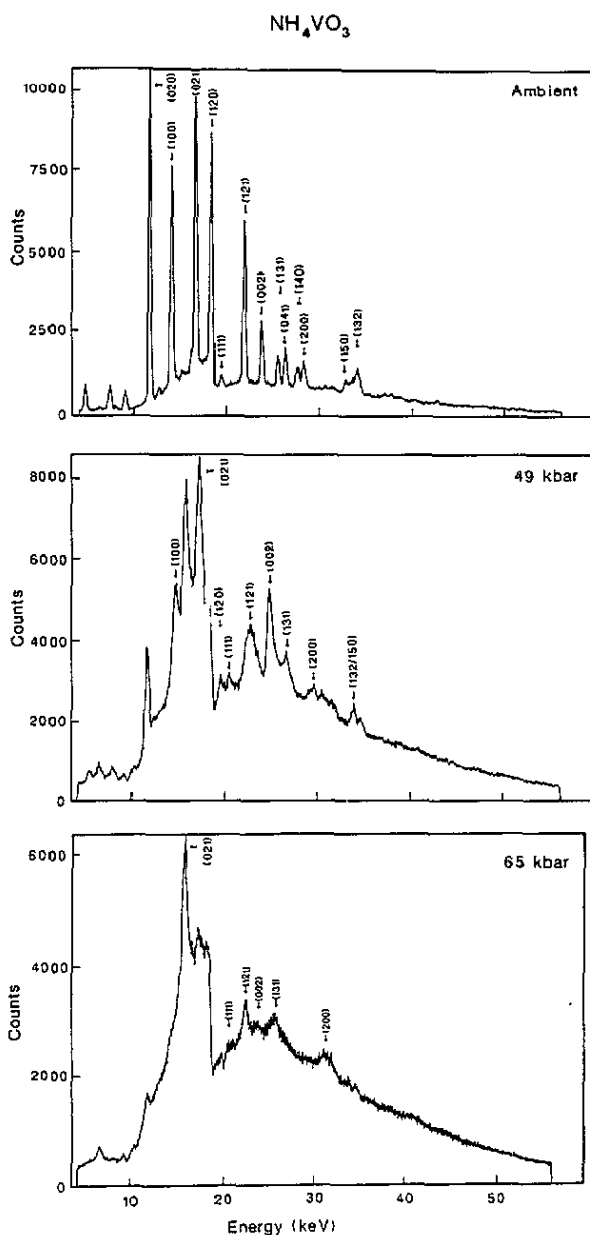|	Single crystal [3]	EDXRPD (this work)
a	4.909	4.920(6)
b	11.786	11.821(6)
c	5.830	5.831(2)

NH₄VO₃

Figure 1. EDXRPD spectra for ammonium metavanadate at ambient pressure, at 49 and 65 kbar.

respectively, increase, while that of the overtone, $2\nu_4$, decreases slightly with pressure. The increase in frequency observed for ν_1 and ν_3 is in contrast to what is normally observed for hydrogen-bonded N–H vibrations, which usually decrease in frequency with pressure as the hydrogen bonds become stronger. In the case of ν_3, this shift to higher frequency has been attributed to pressure-induced asymmetry of the bifurcated H bonds, while for ν_1, which corresponds to the linear H bonds, the situation is com-
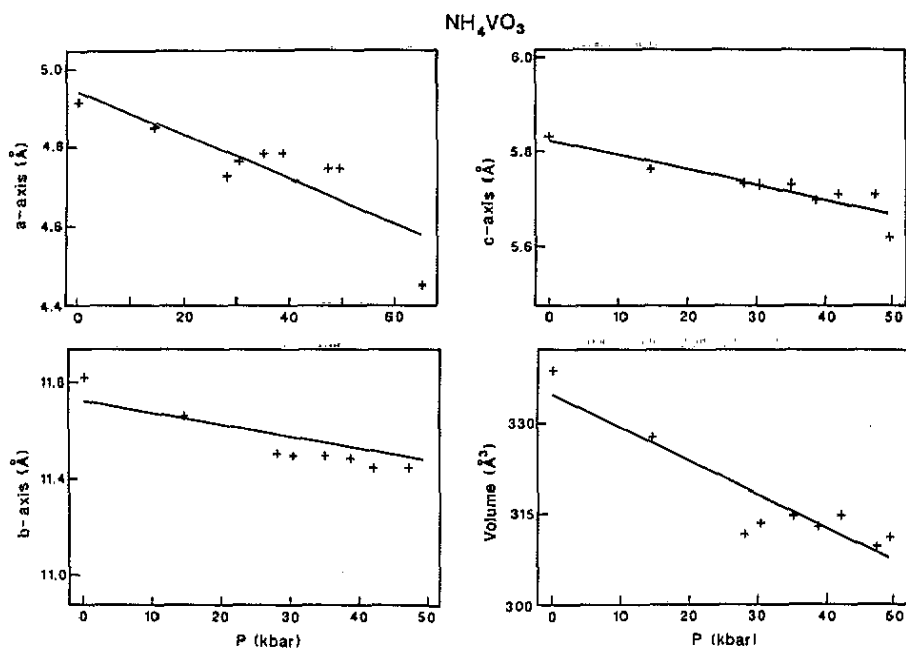
NH$_4$VO$_3$

Figure 2. Variation with pressure of the lattice constants and unit cell volume of ammonium metavanadate.

plicated by strong coupling to other vibrations. These vibrations were also found to shift to higher frequency with decreasing temperature [11]. The HNH bend, ν_4, near 1416 cm^{-1} does not shift with pressure.

Significant changes in this region of the IR spectrum were observed just above 20 kbar. The shoulder near 3130 cm^{-1}, ν_3, and the weak band at 3037 cm^{-1}, $\nu_2 + \nu_4$, increased in intensity, while ν_4 split into two components. Similar changes were observed in the

Table 2. Pressure dependencies of the IR modes of NH$_4$VO$_3$.

ν (cm^{-1})[†]	d ln ν/dP (10^4 kbar^{-1})[‡]	ν_0 (cm^{-1})[§]	
3214	1.6	3198.4	ν_3
3118	−1.0	3129.8	ν_3
3035	−0.55	3041.3	$\nu_2 + \nu_4$
2942	0.90	2942.3	ν_1
2795	−0.99	2801.5	$2\nu_4$
1422 Sh	1.7	1413.4	
1412	0.89	1416.5	ν_4
945	2.3	934.3	
907	2.6	899.6	
879	9.0	850.1	
719	7.7	699.5	
521	6.8	508.9	

† At 34 kbar.
‡ Calculated using ν_0.
§ Intercept of least-squares line.

NH$_4$VO$_3$
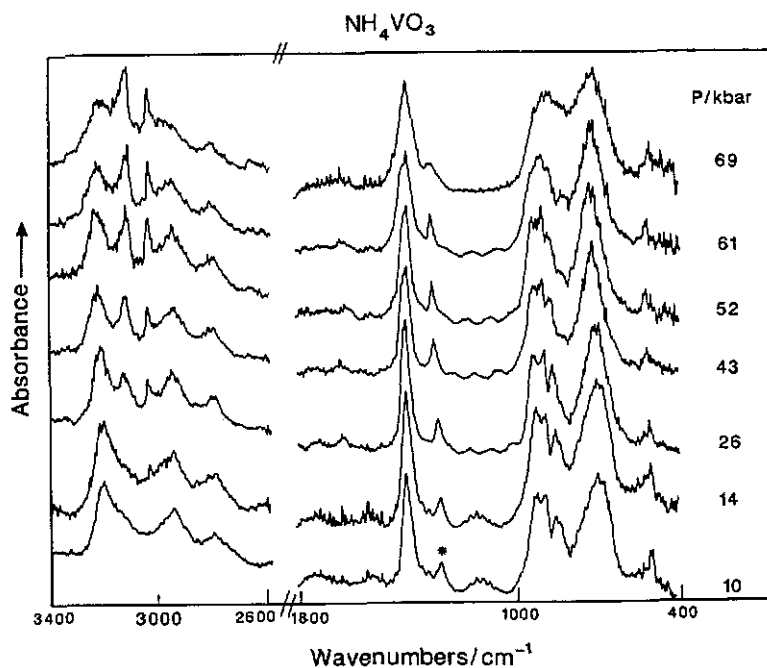
Figure 3. IR spectra of ammonium metavanadate as a function of pressure. $* = \nu_3$ of NO$_2^-$.

(a) NH$_4$VO$_3$

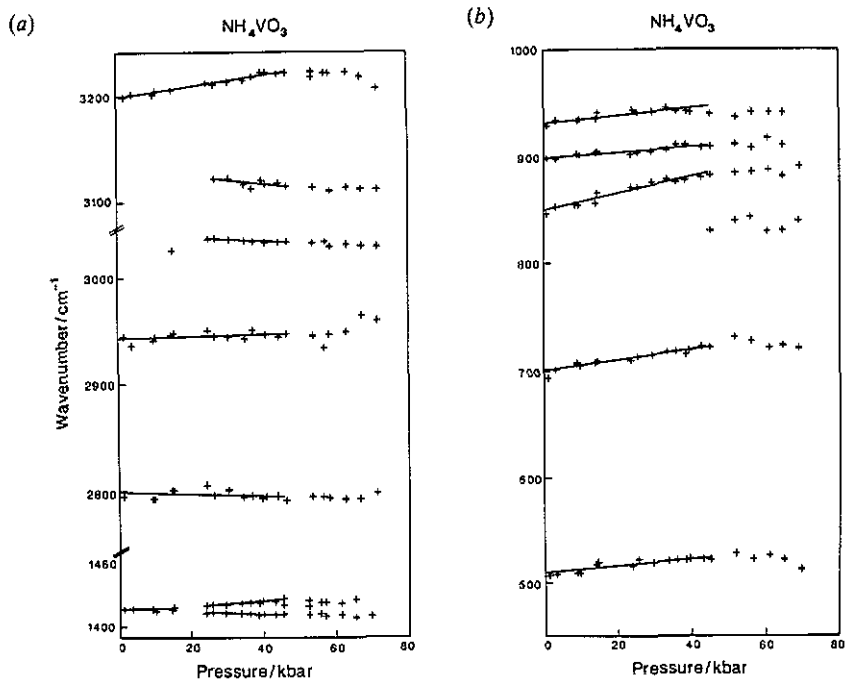(b) NH$_4$VO$_3$

Figure 4. Pressure dependencies of the IR modes of ammonium metavanadate. (a) NH$_4^+$ modes. (b) Vanadate modes.
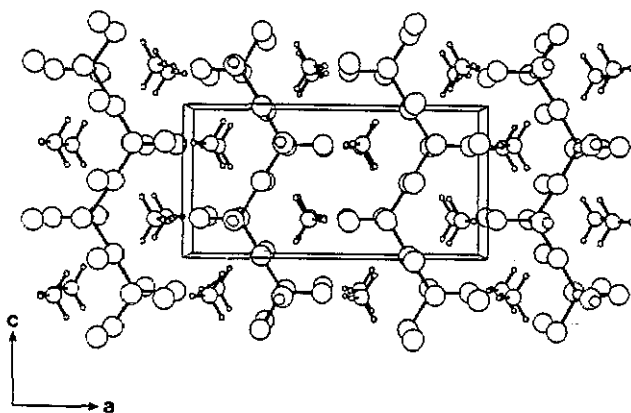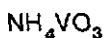
$$NH_4VO_3$$

Figure 5. The crystal structure of ammonium metavanadate.

Raman spectrum of NH_4Cl at high pressure [17]. The splitting of ν_4 in NH_4VO_3 was also observed at low temperature [11].

Above 49 kbar considerable broadening of the internal modes of the vanadate chain and the appearance of a new band at 841 cm^{-1} were observed, indicating the onset of a phase transition. We note that in the case of the transition in KVO_3 [1] a new band was also observed in this region, and hence the transition in NH_4VO_3 could be of the same type, involving slipping of the vanadate chains relative to one another, rather than simply reorientation of ammonium.

The bands in the N–H stretching region were affected to a lesser degree. Changes in relative intensity were observed and a slight broadening of some bands. This could indicate that the ammonium ion plays a minor role in the phase transition process. The bands in the spectrum continue to broaden with increasing pressure until at 69 kbar only two bands are observed in the V–O stretching region, figure 3. This broadening increased up to 106 kbar, the highest pressure reached.

3.3. Structural considerations

This type of spectral behaviour is characteristic of the formation of a highly disordered or amorphous solid, or a glass, and is therefore consistent with the EDXRPD results, which also show loss of long-range order. This change was found to be reversible with the reverse process being complete at approximately 25 kbar. Pressure-induced crystalline-to-amorphous phase transitions have been well documented and a recent study indicated that such a transition occurs in $Ca(OH)_2$ [18]. This too was found to be a reversible process and was attributed to kinetic inaccessibility at 300 K of the stable crystalline high-pressure phase.

A model can be proposed for the phase transition and subsequent formation of a disordered phase in NH_4VO_3. In KVO_3 the pressure-induced phase change is first order and involves slipping of the vanadate chains relative to each other parallel to their chain axes; the process is accompanied by appearance of new features in the EDXRPD spectrum. In contrast, the structural transformation in $RbVO_3$ is not heralded by new diffraction

peaks, but is clearly indicated by changes of slope in lattice parameter plots: the structural modification consistent with these facts requires relative movements of the chains perpendicular to their axes, and is a second-order process.

The transition in NH_4VO_3 is accompanied by new peaks in the EDXRPD spectrum, suggesting that the mechanism is of the chain slipping type proposed for potassium vanadate. That it occurs at essentially the same pressure as in KVO_3 supports this proposal. The presence of strong hydrogen bonding between the vanadate chains and the ammonium ions would hinder the chain slipping process, leading to a breakdown of periodicity in the crystal and the formation of a highly disordered, possibly amorphous solid. A crystalline high-pressure phase might exist but, as in the case of $Ca(OH)_2$, could be kinetically inaccessible at room temperature.

Acknowledgments

References

[1] Adams D M, Christy A G, Haines J and Leonard S 1991 *J. Phys.: Condens. Matter* submitted
[2] Adams D M and Fletcher P A 1988 *Spectrochim. Acta* A **44** 233
[3] Hawthorne F C and Calvo C 1977 *J. Solid State Chem.* **22** 157
[4] Botto I L, Baran E J and Ayomino P J 1976 *Monatsch. Chem.* **107** 1127
[5] Hamann S D 1978 *Aust. J. Chem.* **31** 11
[6] Onodera S and Ikegami Y 1979 *Inorg. Chem.* **18** 466
[7] Onodera S and Ikegami Y 1980 *Inorg. Chem.* **19** 615
[8] Heyns A M, Venter M W and Range K-J 1987 *Z. Naturf.* b **42** 843
[9] Hamann S D 1988 *Aust. J. Chem.* **41** 1935
[10] Park Y S and Shurvell H F 1989 *J. Raman Spectrosc.* **20** 673
[11] De Waal D, Heyns A M, Range K-J and Eglmeier C 1990 *Spectrochim. Acta* A **46** 1639
[12] Bajorek A, Parlinski K and Sudnik-Hrynkiewicz M 1967 *Physica* **35** 465
[13] Richards R E and Schaefer T 1961 *Trans. Faraday Soc.* **57** 210
[14] Peternelj J, Valic M I and Pintar M M 1971 *Physica* **54** 604
[15] Ramanathan K V and Srinavasan R 1976 *Nucl. Phys. Solid State Phys. (India)* **19C** 371
[16] Klug D D and Whalley E 1983 *Rev. Sci. Instrum.* **54** 1205
[17] Jeon S-J, Porter R F and Ruoff A L 1988 *J. Raman Spectrosc.* **19** 179
[18] Kruger M B, Williams Q and Jeanloz R 1989 *J. Chem. Phys.* **91** 5910