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# MOLECULAR DYNAMICS STUDY BY THE NEUTRON INELASTIC SCATTERING METHOD. IV. AMMONIUM METAVANADATE



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# MOLECULAR DYNAMICS STUDY BY THE NEUTRON INELASTIC SCATTERING METHOD. IV. AMMONIUM METAVANADATE

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## 1. Introduction

In a crystal composed of a number of structural groups, in which the intramolecular forces are much stronger than the intermolecular ones, there may be a set of modes involving a rotatory type of external vibrations and translational ones in which molecular groups participate as a whole.

Various properties of a solid are in general largely affected by such vibrations because of their relatively low frequencies as compared with these of vibrations of atoms within the groups (internal vibrations). For this reason external motions of the molecular groups in solids are the subject of much experimental and theoretical interest.

The dynamics of the molecular hydrogenous groups (such as $NH_4$, $H_2O$, $OH_3$, OH) in various compounds have been systematically studied in our laboratories by the neutron scattering technique [1-6]. This work is a continuation of these studies.

The experimental material concerning the physical properties of $NH_4VO_3$ is poor.

The crystal structure of this compound has not as yet been determined. The absorption spectrum of $NH_4VO_3$ in the the wave number region 550-6000 $cm^{-1}$ was reported by Miller and Wilkins [7] without assignment of lines. Richard and Schaefer [8] studied the dynamics of $NH_4$ groups in ammonium metavanadate by the NMR method. These authors concluded from their results that at low temperatures (20°K) ammonium ions probably perform torsional vibrations.

In view of this fact it seemed interesting to perform an investigation of the dynamics of $NH_4VO_3$ by the inelastic neutron scattering method.

It should be pointed out that by using the INS method it is possible to obtain direct information about the motions of the ammonium ions owing to the large incoherent proton cross-section and to the lack of selection rules. Since most of the scattering in $NH_4VO_3$ is from the protons, the inelastic scattering will primarily reflect the rotational and translational motions of the hydrogenous groups.

## 2. Experimental technique

The measurements of inelastic neutron scattering on $NH_4VO_3$ were carried out using a time of flight neutron spectrometer with Be-filter and Zn-monocrystal in front of the detector. A detailed description of the spectrometer has been published elsewhere [9,10].

Polycrystalline $NH_4VO_3$ (reagent grade) was packed in a thin walled aluminium sample-holder. The sample thickness was ca 1 mm. The measurements were made at room temperature ($18 \pm 2^{\circ}C$). A separate run was made with an empty sample holder in order to estimate its contribution to the observed spectra.

## 3. Results and discussion

Fig. 1 presents the intensity distribution of neutrons scattered from polycrystalline $NH_4VO_3$ at room temperature as a function of the analyser channel number i.e. as a function of time of flight. The data have been corrected for background, sample-holder contributions, and other instrumental effects.

Fig. 2 presents a function $p(\epsilon)$ (see part 1) calculated from the intensity distribution of scattered neutrons presented in Fig. 1 in the one phonon incoherent approximation wihout taking into account the resolution of the spectrometer and with the assumption that the Debye-Waller factor is equal 1.

Distributions obtained for $NH_4VO_3$ (Figs. 1, 2) are strikingly similar to those obtained for other ammonium salts in which $NH_4$ ions execute torsional oscillations.



There are present three well-defined peaks at energies: 46, 38, and 29 meV corresponding to frequencies 371, 306.5, 234 $cm^{-1}$ respectively and two shoulders at higher energies.

The sharp, intense peak at 371 $cm^{-1}$ is no doubt caused by torsional oscillations of $NH_4$ ions. Its frequency is somewhat higher than in the case of ammonium chloride (359 $cm^{-1}$), which suggests that the rotational freedom of $NH_4$ ions is greater in $NH_4Cl$ than in $NH_4VO_3$.

Owing to the unknown crystal structure of $NH_4VO_3$ as well as to a lack of data concerning temperature dependence of the neutron spectra, it is difficult to give satisfactory interpretation of the second peak at frequency 306.5 $cm^{-1}$ ($\Delta E$ = 38 meV). A possible one is that it is associated with a second torsional band. In this case, sets of ammonium ions with different environments shouls exist in the crystal lattice of $NH_4VO_3$, similarly as in $(NH_4)_2SO_4$ and $NH_4NO_3$.

Another possibility is that it arises from the excitation of the first to the second excited state. However, taking into account the considerable difference between the frequencies of the "ground" torsional peak (0-1) and the "excited" one (1-2) which suggests that the anharmonic effects in $NH_4VO_3$ would be much greater than in $NH_4Cl$, the second possibility seems to be less probable than the first.

The peak at 29 meV (234 $cm^{-1}$) is connected with lattice modes involving translational vibrations of ammonium ions against neighbours.

Shoulders at higher energies are (probably) combinations bands.

The results discussed above provide good evidence that ammonium ions in $NH_4VO_3$ perform, up to room temperature, torsional oscillations with frequencies 371 and probably 308 $cm^{-1}$.

From the known frequencies one may easily estimate the height of the potential barriers for torsional oscillations of molecular groups by means of an empirical relationship given by Yoshito Sato [11]:

$$V = 0.64 - 0.016 \times 10^{-2}\nu + 0.31 \times 10^{-4}\nu^2 \pm 0.27$$

where $V$ – barrier height in kcal/mole,

$\nu$ – frequency in $cm^{-1}$.

The results of the calculation are:

V = 4.7 kcal/mole, from frequency of the main torsional peak,

V = 3.5 kcal/mole, from frequency of the second torsional peak.

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## References

1. A. Bajorek, W.W. Golikov, I. Zukowska, E.L.Shapiro, A.Szkatula, J.A. Janik, Proc. of Symposium "Inelastic Scattering of Neutrons in Solids and Liquids" Vol. I, p. 383, IAEA, Vienna 1963.
2. J.M. Janik, J.A. Janik, J.M. Mellor, H. Palevsky, J. Phys. Chem.Solids, 25, 1091 (1964).
3. A. Bajorek, T.A. Matchekhina, K. Parlinski, Proc. of Symposium "Inelastic Scattering of Neutrons" Vol II, p. 355 IAEA, Vienna 1965.
4. Bajorek, Doctor's thesis, Math. Phys. Chem. Faculty, Jagiellonian University, Cracow 1965.
5. J.M. Janik, J.A. Janik, A. Bajorek, K. Parlinski. Physica Status Solidi, 9, 905 /1965/.
6. K. Parlinski, Doctor's thesis, Math. Phys. Cpem. Faculty, Jagiellonian University, Cracow 1966.
7. F.A. Miller, G.H. Wilkins, Anal. Chem., 29, 1253 (1952).
8. R.E. Richards, T.S. Schaefer, Trans. Faraday Soc., 57, 210. (1961).
9. A. Bajorek, T.A. Matchekhina, K. Parlinski, F. L. Shapiro, Proc. of Symposium "Inelastic Scattering of Neutrons", Vol. II, p. 519, IAEA, Vienna 1965.
10. K. Parlinski, M. Sudnik-Hrynkiewicz, A. Bajorek, J.A. Janik, W. Olejarczyk, Proc. of Panel on Research Applications of Repetively-Pulsed Reactors and Boosters, Dubna, July 1966.
11. Y. Sato, J. Phys. Soc. Japan, 20, 275 (1965).

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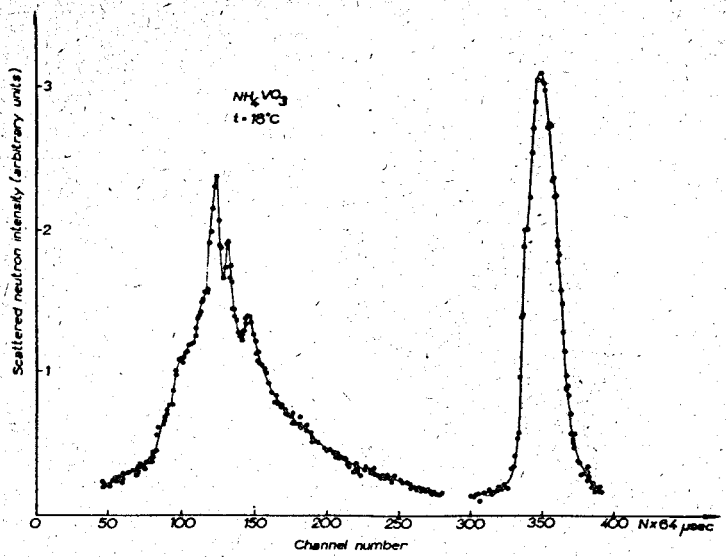


Fig. 1. The intensity of neutrons scattered from crystalline $NH_4VO_3$ at room temperature, as a function of the analyser channel number. Channel width 64 μsec.

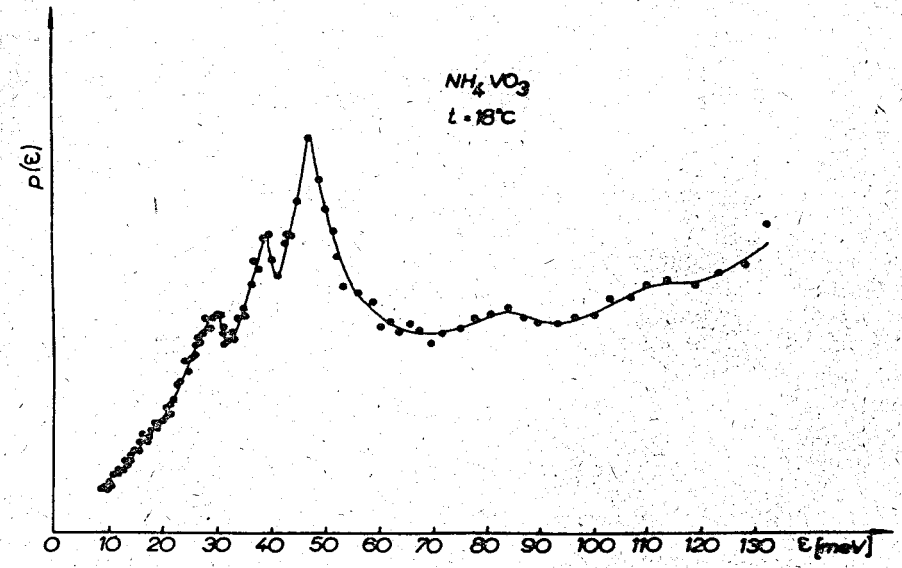


Fig. 2. The p(ε) function for $NH_4VO_3$ at room temperature obtained on the basis of data of Fig. 1.