

ON THE NON-STATISTICAL SUBSTITUTION OF POTASSIUM WITH AMMONIUM  
IN THE  $K_2SO_4 - (NH_4)_2SO_4$  SYSTEMV.M. Petruševski<sup>1</sup> and W.F. Sherman<sup>2</sup><sup>1</sup> Institut za hemija, Prirodno-matematički fakultet, Arhimedova 5,  
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The FT-IR spectra of protiated and partly (5 %) deuterated solid solutions of potassium and ammonium sulfate ( $[K_{1-x}(NH_4)_x]_2SO_4$ ) were recorded at temperatures between 295 and 76 K. The number of different N-D stretching bands was used as a criterion for the presence of one or two types of crystallographically different ammonium ions in the mixed crystal. For  $0 < x < 0.2$ , ammonium ions of only one type are present. However, for  $0.2 < x < 0.5$ , the number of the N-D stretching bands and their shape strongly indicate the presence of two types of  $NH_4$  ions. The possible reasons for this peculiar behaviour are discussed.

## 1. INTRODUCTION

The room temperature phases of potassium and ammonium sulfates are known to be isostructural [1,2]. Both compounds crystallize in the space group  $Pnam$  with  $Z = 4$ . One type of sulfate anions and two types of univalent cations exist in the structure. All ions are situated on mirror planes.

At low temperatures a phase transition occurs in ammonium sulfate, followed by a lowering of the crystal symmetry (the space group is  $Pna2_1$ ).

When the crystal passes through the phase transition temperature, the distances and angles of the sulfate and ammonium ions are subject to sudden changes. These have been extensively studied by a variety of spectroscopic techniques [3-7].

Mixed crystals of potassium and

ammonium sulfate have also been studied by IR and Raman [8] as well as by diffraction [9] methods. It was found [8] that the potassium ions are not statistically substituted by the ammonium ones, the latter "preferring" the  $K_{II}$ -site. In solid solutions with up to 50 % ammonium sulfate, only one type of ammonium ions was detected. This finding seemed very interesting since in such a case the  $[K_{0.5}(NH_4)_{0.5}]_2SO_4$  mixed crystal would be perfectly ordered.

It was therefore thought to be worthwhile to check this conclusion and to study the Fourier-transform infrared spectra of the slightly deuterated (5 %)  $[K_{1-x}(NH_4)_x]_2SO_4$  mixed crystals. It should be pointed out that Srinivasan *et al.* [8] have studied the changes in the symmetric  $SO_4$  stretching mode in the protiated compounds, and at room temperature only.

## 2. EXPERIMENTAL

$K_2SO_4$  and  $(NH_4)_2SO_4$  were reagent-grade commercial products. The mixed crystals were prepared by crystallization from aqueous solutions. The deuterated crystals were prepared using a  $H_2O/D_2O$  mixture with 5 % of  $D_2O$  as a solvent.

The IR spectra were recorded from KBr pellets on a Perkin-Elmer 1720 FT-IR spectrophotometer at liquid-nitrogen temperature (LNT). Spectra of both protiated and slightly deuterated samples were recorded. Difference spectra were plotted in order to compensate the background absorption due to the two-phonon bands arising from the sulfate stretching vibrations. Such a compensation is especially important for samples with low ammonium content.

## 3. RESULTS AND DISCUSSION

The LNT infrared spectrum of the slightly deuterated ammonium sulfate is shown in Fig. 1. As seen, the number of the isolated N-D stretching bands and their shape are in a good agreement with the crystallographic results [1] for the ferroelectric  $(NH_4)_2SO_4$  phase. The bands (Table 1) were assigned assuming that higher frequencies of the N-D stretchings correspond to longer  $H \cdots O(S)$  distances. The six resolved bands serve as a clear evidence that two types of ammonium ions are present in the structure.

On the other hand, in the spectra of mixed crystals containing 5 % of ammonium sulfate (*cf.* Fig. 2), only one type of ammonium ions should exist since only four bands attributable to four different N-D stretching vibrations appear in the

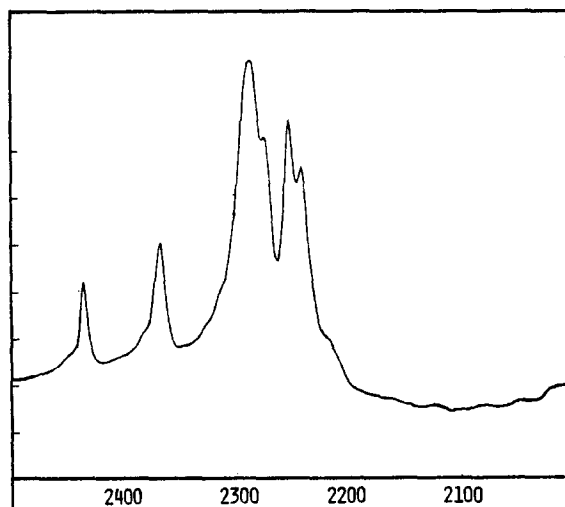


Fig. 1. LNT IR spectrum of slightly deuterated ammonium sulfate.

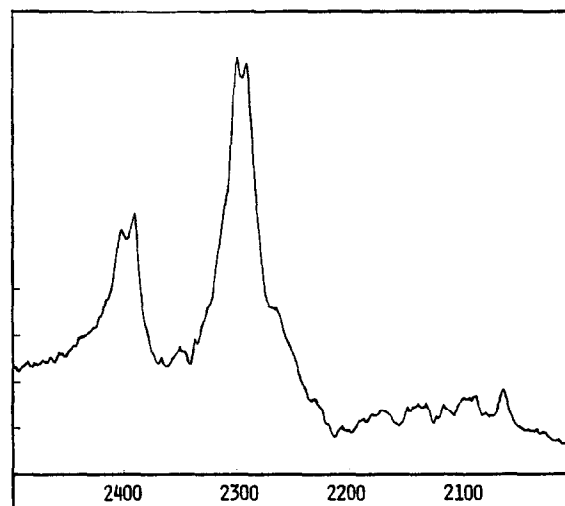


Fig. 2. LNT IR spectrum of slightly deuterated  $[K_{0.95}(NH_4)_{0.05}]_2SO_4$ .

spectrum. The frequency shifts (with respect to pure ammonium sulfate) may be explained by the different environment of the ammonium ions in the mixed crystal and, hence, to presence of hydrogen bonds of strengths different from those in pure ammonium sulfate.

When the content of ammonium ions is increased (*cf.* Figs. 3 and 4),

Table 1. Assignment of the isolated N-D stretching vibrations in the slightly deuterated ferroelectric ammonium sulfate\*

Hydrogen bond	$R(H\cdots O)/\text{pm}$	$R(N\cdots O)/\text{pm}$	ND frequency/ $\text{cm}^{-1}$
N1-H1 $\cdots$ O3	213(3)	301(2)	2366.0
N1-H1 $\cdots$ O1	238(2)	299(1)	
N1-H2 $\cdots$ O3	192(3)	290(1)	2286.0
N1-H3 $\cdots$ O4	182(3)	286(2)	2242.0
N1-H4 $\cdots$ O2	192(4)	290(3)	2286.0
N2-H5 $\cdots$ O2	185(2)	283(1)	2253.0
N2-H6 $\cdots$ O2	228(2)	301(1)	
N2-H6 $\cdots$ O3	239(5)	287(2)	2435.0
N2-H6 $\cdots$ O4	259(4)	311(2)	
N2-H7 $\cdots$ O4	187(3)	285(2)	2274.5
N2-H8 $\cdots$ O1	196(4)	295(3)	2286.0

\* The frequencies are at LNT. The distances and angles in the ferroelectric ammonium sulfate were recalculated from the published [1] fractional coordinates and the proposed hydrogen bonding scheme was carefully reexamined. It was found that the hydrogen bond in which the H1 atom takes part is, most probably, bifurcated.

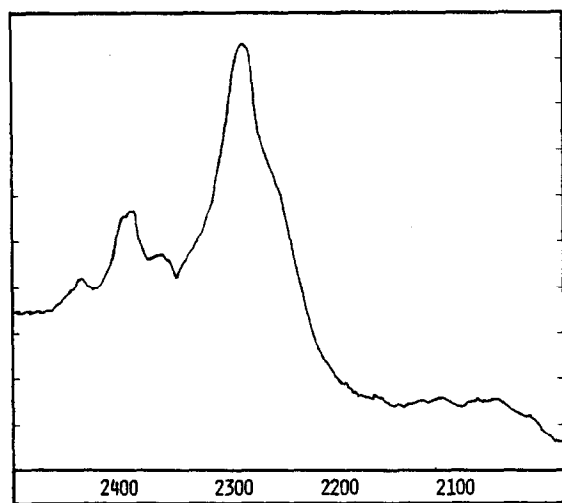


Fig. 3. LNT IR spectrum of slightly deuterated  $[\text{Ko}_{.6}(\text{NH}_4)_{0.4}]_2\text{SO}_4$ .

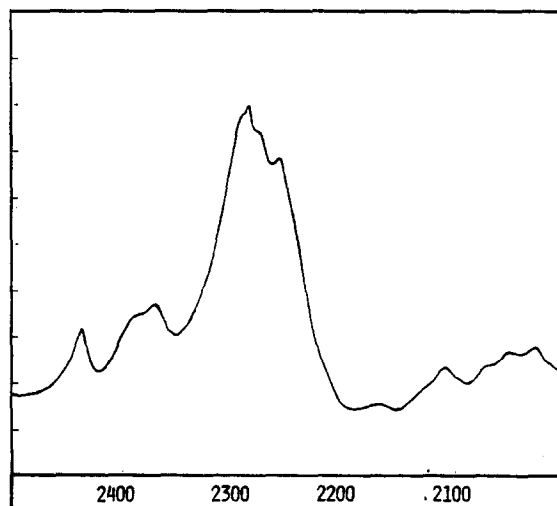


Fig. 4. LNT IR spectrum of slightly deuterated  $[\text{Ko}_{.5}(\text{NH}_4)_{0.5}]_2\text{SO}_4$ .

the spectral picture is gradually changed. The complex band shape strongly indicates the presence of at least two types of ammonium ions

in the  $[\text{Ko}_{.5}(\text{NH}_4)_{0.5}]_2\text{SO}_4$  mixed crystal, a situation which is remarkably different from the one discussed by Srinivasan *et al.* [8].

The explanation which we offer is based on the zero-point energy difference between the two ammonium sites. It might be inferred, namely, that the  $(\text{NH}_4)_{\text{II}}$  site is lower in energy and its occupancy is therefore preferred. Hence, if only few percentage of ammonium are present, only the  $\text{K}_{\text{II}}$  ions would be substituted.

It does not seem, however, that the energy difference is very large, since the hydrogen bonds of the two ammonium ions are of comparable strength. Furthermore, the root-mean-square frequencies (calculated from the thermal parameters [1]) at low temperature are 162 and 158  $\text{cm}^{-1}$  for the two  $\text{NH}_4$  types respectively, indicating sites of similar energy. In such cases, it is important to consider the changes in the Gibbs energy, since at equilibrium this quantity should be at minimum. The entropy of the mixed crystal  $[\text{K}_{0.5}(\text{NH}_4)_{0.5}]_2\text{SO}_4$  would be close to zero if only one type of ammonium ions exist, since the structure would then be fully ordered. This would, of course, increase the Gibbs energy value ( $G = H - TS$ ).

The variation in the distribution of ammonium will cause substantial changes in the  $TS$  term, but only moderate changes to the total energy. Hence ammonium enters in both sites, with a probability dependent on the magnitude of the zero-point energy difference between the  $(\text{NH}_4)_{\text{I}}$  and  $(\text{NH}_4)_{\text{II}}$  sites and on the relative concentration of ammonium to potassium.

Our results appear to be somewhat different from those of Srinivasan *et al.* [8], probably because the conclusions regarding the presence of one or two types of ammonium ions were reached using different criteria.

## ACKNOWLEDGEMENT

This work was sponsored by the British Council (within the framework of an ALIS link) and the Ministry for Science of the Republic of Macedonia. The authors are grateful for the financial support of these two institutions. The authors are also indebted to Prof. B. Soptrajanov for his interest in the work.

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