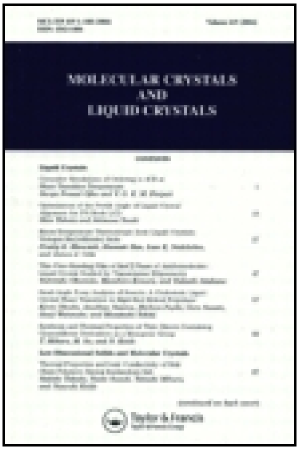

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Low Temperature Thermodynamic and Spectroscopic Study of Triammonium Hydrogen Disulfate $(NH_4)_3H(SO_4)_2$

M. Kamoun [a] , K. Chhor [b] , C. Pommier [b] , F. Romain [c] & A. Lautie [c]

[a] Ecole Nationale d'Ingénieurs, 3038 Sfax, Tunisie

[b] Laboratoire de Chimie-Physique du Solide, C.S.P., U.A. 453, Université Paris Nord, Avenue J. B. Clément, 93430, Villetaneuse, France

[c] LASIR, CNRS, 2 rue Henri Dunant, 94320, Thiais, France

To cite this article: M. Kamoun , K. Chhor , C. Pommier , F. Romain & A. Lautie (1988): Low Temperature Thermodynamic and Spectroscopic Study of Triammonium Hydrogen Disulfate $(NH_4)_3H(SO_4)_2$, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 154:1, 165-177

To link to this article: http://dx.doi.org/10.1080/00268948808078730

Mol. Cryst. Liq. Cryst., 1988, Vol. 154, pp. 165–177
Photocopying permitted by license only

Printed in the United States of America

Low Temperature Thermodynamic and Spectroscopic Study of Triammonium Hydrogen Disulfate $(NH_4)_3H(SO_4)_2$

M. KAMOUN

Ecole Nationale d'Ingénieurs, 3038 Sfax (Tunisie)

K. CHHOR and C. POMMIER

Laboratoire de Chimie-Physique du Solide, C.S.P., U.A. 453, Université Paris Nord, Avenue J. B. Clément, 93430 Villetaneuse (France)

and

F. ROMAIN and A. LAUTIE†

LASIR, CNRS, 2 rue Henri Dunant, 94320 Thiais (France)

(*Received August 5, 1987*)

Heat capacity measurements and Raman spectra analysis of $(NH_4)_3H(SO_4)_2$ were performed between 10 and 130 K. Thermodynamics functions as well as structural and dynamic behaviour of the VII → V phase transition at 81.5 K have been specified. This phase transition is confirmed to be of the first order with $\Delta H = 444$ J mol^{-1} and $\Delta S = 5.5$ J K^{-1} mol^{-1}. The mechanism appears as a reorientational ordering of ammonium ions which are the main responsible for the ferroelectricity rather than the proton engaged in the OH . . . O hydrogen bond.

Keywords: phase transition, thermodynamic function, Raman spectra

I. INTRODUCTION

Triammonium hydrogen disulphate (NHS) has been extensively studied because it exhibits many phase transitions below room temper-

---

†To whom correspondence should be addressed.

ature and on account of the influence of various parameters (temperature, pressure, deuteration) on the appearance of ferroelectricity in the solid.

First dielectric,[1] dilatometric[2] and calorimetric[3] studies above 90 K evidenced four successive phase transitions at 413, 265, 137 and 133 K between phases noted I to V in decreasing temperature order. The transitions at 413 and 133 K are reported as first order. However, none of these phases exhibits ferroelectricity although the deuterated derivative $(ND_4)_3D(SO_4)_2$ is ferroelectric in two temperature ranges (between 208 and 249 K and below 173 K).[4] Furthermore, a large anomaly on the dielectric constant plot was not attributed to a phase transition.[1] This anomaly becomes larger and sharper when a hydrostatic pressure is applied and, above 5 kbars, it splits into two well defined peaks between which a ferroelectric phase appears.[5] More recently Osaka *et al.*,[6] when studying the behaviour of partially deuterated compounds have shown that the isotopic effect is similar to a pressure increase and concluded that $(NH_4)_3H(SO_4)_2$ must be ferroelectric below 63 K at atmospheric pressure. Such a phase (phase VII) was indeed found by dielectric measurement:[7] a first order transition was reported at 46 and 78 K on cooling and heating, respectively. A further small anomaly on ϵ curve at 23 K was also mentioned, however, its nature was not explained.

The electric conductivity curve[8] shows anomalies at 133, 141, 413 K and 247 K. This last phase transition is associated with the broad maximum reported in dielectric studies. However, the II → III transitions at 265 K was not observed.

Structural studies on hydrogenated[9] and deuterated[10] compounds at room temperature (phase II) show similar monoclinic structures (A2/*a*) with four entities per unit cell. The ammonium ions occupy two sets of non equivalent sites one of which at least is claimed ordered.[3,9] SO_4^{2-} ions are linked in dimers by strong crystallographically centrosymmetric hydrogen bonds of 2.54 Å. Spectroscopic data have shown that the phase II is strongly disordered: NH_4^+ ions present a dynamical orientational disorder responsible for serious band broadening of lattice modes whereas the proton in $(SO_4HSO_4)^{3-}$ dimer is statistically disordered.[11,12] There are no structural data about the low temperature phase.

We report here the results of spectroscopic and thermodynamic low temperature study in order to check various phase transitions reported previously and the structural modifications associated with the VII → V phase transition.

II. EXPERIMENTAL

The NHS single crystals were obtained as transparent hexagonal platelets by slow evaporation method from an aqueous solution containing 40 wt % of $(NH_4)_2SO_4$ and 24 wt % of H_2SO_4.[9] The purity of samples was checked by X-ray diffraction and vibrational spectra.

The heat capacity measurements were performed on an automated low temperature adiabatic calorimeter described elsewhere.[13] The temperature measurements were obtained from two miniature germanium and platinium sensors in the 10 to 25 K and 25 to 300 K range respectively. A microcomputer controlled the temperature and the energy input into the sample and realized the data acquisition via a programmable voltmeter. The sample cell had an internal volume of 7 cm^3 and the sample mass was 11,4430 g. The accuracy of measurements was better than 0.5% between 100 and 280 K, increase to 1% at 40 K and to about 5% below 20 K.

Raman spectra of NHS single crystal sealed in glass tube were recorded with a RTI30 Dilor triple monochromator spectrometer linked to a Digital PDP11-34 computer using the 488 and 514.5 nm lines of a Spectra Physics Ar^+ laser operating at about 400 mW. The low temperature measurements were obtained using a conventional liquid helium cryostat (Meric). The spectra slit width was about 2 cm^{-1} and the wavenumber repeatability better than 0.3 cm^{-1}.

III. RESULTS AND DISCUSSION

Raman spectra

Infrared and Raman spectra of various crystal phases of NHS are different and we have been able to characterize each phase spectroscopically. The NH stretching region (ν_1 and ν_3 NH_4^+ ion modes) and Raman low frequency range (lattice modes) are particularly useful for that.[11,12] In the latter, bands are very broad at room temperature indicating that the NHS crystal is strongly disordered in phase II (Figure 1). A progressive narrowing, associated to a relative ordering, occurs with decreasing temperature; but only the low temperature phase VII presents numerous narrow bands and appears as fully ordered. On the other hand, high frequency spectral modifications show that the ammonium ions are involved in the four phase transitions occurring between 10 and 300 K.[12]

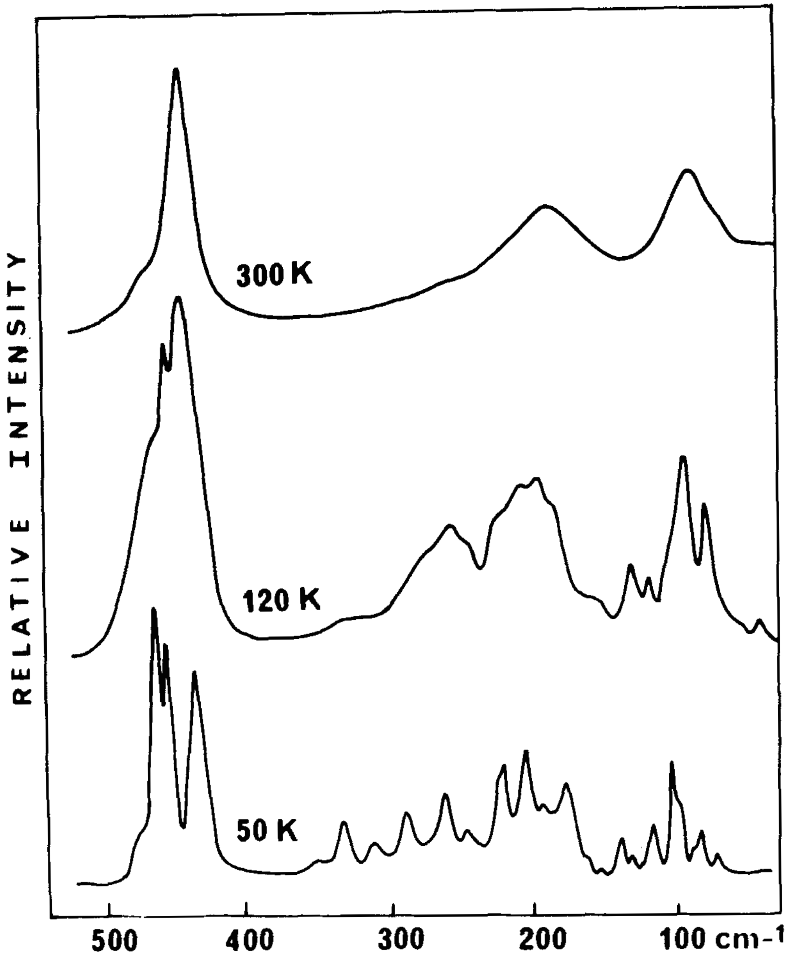

FIGURE 1 Low frequency Raman spectra of NHS at different temperatures.

We have pointed out that the crystallographically centrosymmetric $(SO_4HSO_4)^{3-}$ dimers of the room temperature phase are in fact asymmetric.[11] Indeed the symmetric stretching vibration $\nu_1(SO_4^{2-})$ gives rise to two strong Raman bands at 966 and 1078 cm^{-1} assigned to the proton donor HSO_4^- and acceptor SO_4^{2-} groups respectively. This large splitting is not significantly modified with temperature decreasing and the dimer structure thus does not change in various phases, particularly during the VII → V phase transition (Figure 2) where the proton of the strong OH . . . O hydrogen bond is practically not involved.

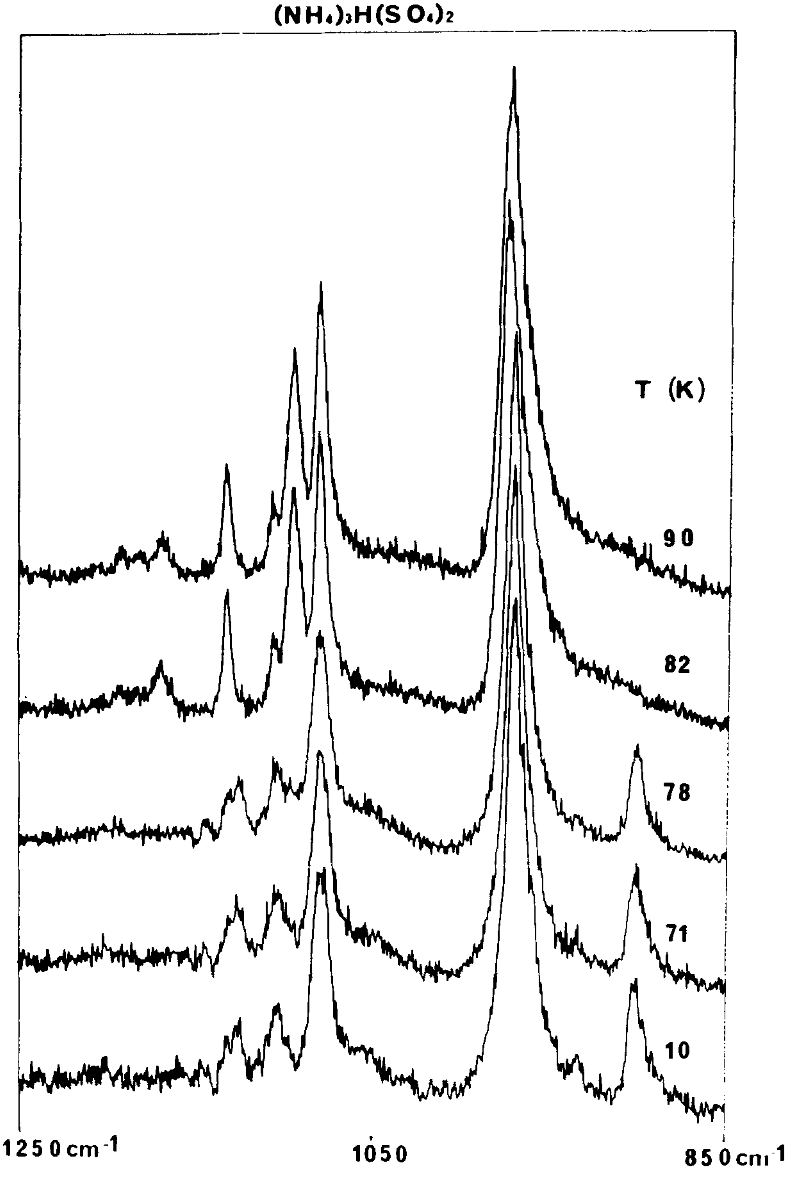

FIGURE 2 Raman spectra of NHS at different temperature about VII → V phase transition.

However, important Raman and infrared spectral changes are observed at about 80 K (Figures 1 and 2). The main effect concern the lattice modes below 400 cm^{-1}: the Raman spectrum becomes more structured while five narrow bands appear at 351, 331, 308, 286 and 257 cm^{-1} instead of a broad envelope about 250 cm^{-1}. These new bands are assigned unambiguously to librational motions of ammonium ions because they shift appropriately, about 200 cm^{-1}, in the spectrum of the deuterated compound (NDS).

This drastic change of the $R'(NH_4^+)$ modes shows that the NH_4^+ ions are strongly involved in the VII → V phase transition and that their orientational ordering with decreasing of temperature appears to be the principal mechanism determining the transition. The rotational barrier height can be estimated from librational frequency of NH_4^+ ions[14] and the average of experimental values lead to about 15 kJ mol^{-1} for the phase VII instead of 10 kJ mol^{-1} in phase V. Although this energies are only approximate, the above large variation confirms that an important ordering of ammonium ions during the transition takes place. Only the spectra of the phase VII are characteristic of a fully ordered crystal while the ammonium ions are dynamically disordered in all other phases. Like in ammonium sulphate,[15] the orientational ordering of the latter can be considered as a major contribution to the ferroelectricity of the NHS crystal. This ordering of NH_4^+ ions in ferroelectric phase is also manifested in the NH stretching region where important modifications with appearance of numerous subbands occur below 78 K.[12]

In order to obtain more information, we have studied the behaviour of other vibrational frequencies as a function of temperature between 10 and 120 K. It can be seen from Figure 3, for instance, that several Raman components of the SO_4^{2-} bending modes (ν_2 and ν_4) show a frequency discontinuity at the transition temperature T_c while the variations are weak and progressive at higher or lower temperature. This fact confirms that the VII → V phase transition is of the first order. The SO_4^{2-} frequency shifts observed are small and the structure of the sulphate tetrahedra does not appear seriously modified by the phase transition.

Heat capacity measurements

Heat capacity measurements have been performed between 11 and 300 K. Above 100 K, our results are in very good agreement with those reported previously.[3] So, we will precise to hereafter the experimental values obtained at lower temperature. These Cp values

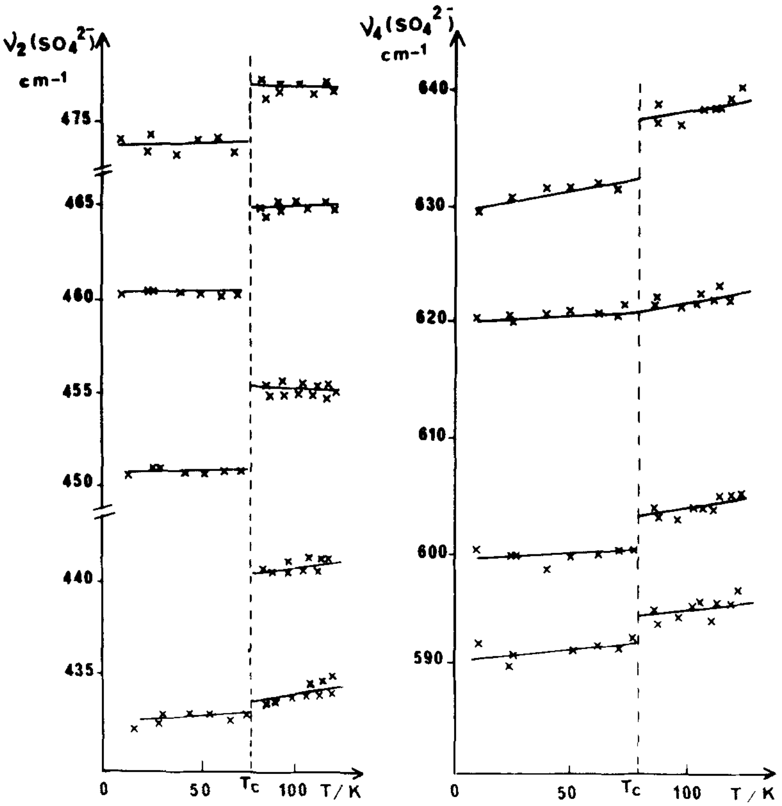

FIGURE 3 Frequencies of SO_4^{2-} ν_2 and ν_4 Raman components as function of temperature; T_C = temperature of the VII → V phase transition.

are reported in Table I and the corresponding heat capacity curve is shown in Figure 4. Beside the anomalies already reported,[3] a λ peak is observed with a maximum Cp value at 81.5 K and an important tail on the low temperature side down to around 30 K. This transition is in agreement with the anomaly on the dielectric constant reported at 78 K on heating,[7] but no evidence of latent heat related with a supposed first order transition was observed. No anomaly on the heat capacity curve was observed around 23 K (slight anomaly on ϵ^3) and around 247 K (anomaly on the electrical conductivity).[8]

In order to calculate the thermodynamic functions of $(NH_4)_3H(SO_4)_2$, the heat capacity below 11 K has been estimated by a T^3 Debye function. Assuming that $Cp - Cv$ is negligible in this temperature range, Cp can be expressed as:

$$Cp = aT^3 \text{ with } a = \frac{12}{5} NR \frac{\pi^4}{\vartheta_D^3} \qquad (1)$$

where N is the number of independent atoms or groups of atoms in a molecular unit, ϑ_D is the Debye temperature.

TABLE I

Experimental molar heat capacities Cp,m of $(NH_4)_3H(SO_4)_2$

T (K)	Cp,m [J K^{-1} mol^{-1}]	T (K)	Cp,m [J K^{-1} mol^{-1}]	T (K)	Cp,m [J K^{-1} mol^{-1}]
11.41	2.51	50.32	64.71	74.54	114.1
11.71	2.77	50.84	66.23	75.13	118.8
15.58	5.34	51.71	67.96	76.22	123.9
17.60	8.08	52.86	68.59	77.66	133.9
18.79	9.53	53.02	69.43	77.97	136.6
21.09	13.18	53.64	71.61	78.30	139.3
23.48	17.04	55.13	74.23	79.29	142.9
25.35	19.23	55.47	74.78	80.09	157.3
26.97	21.99	55.55	74.97	80.22	162.4
27.70	23.16	56.32	77.39	81.18	165.3
27.93	23.53	57.22	78.44	81.55	175.6
31.21	29.28	58.06	79.07	82.10	141.9
31.83	31.64	58.90	81.43	82.45	137.1
32.86	33.69	59.06	82.25	83.09	134.1
33.71	35.24	59.11	82.39	83.13	129.1
33.79	35.54	59.44	83.16	84.06	125.9
36.01	38.63	60.39	84.05	89.14	129.2
36.08	38.70	60.52	84.27	91.10	131.9
37.00	40.19	61.86	87.72	93.01	134.5
37.94	41.13	62.61	88.45	94.88	139.3
37.96	41.25	62.63	89.05	96.73	140.5
39.53	44.58	63.57	91.30	98.53	142.4
40.37	45.52	64.49	91.80	100.3	146.2
41.41	46.76	65.03	93.73	101.1	146.6
41.43	47.01	65.13	94.74	103.8	151.1
42.51	49.63	65.47	95.09	105.5	153.2
42.93	50.01	66.00	96.78	106.7	157.1
43.27	50.49	66.01	97.74	107.2	157.8
45.08	55.39	67.73	99.85	108.8	159.2
45.12	56.00	69.14	101.9	110.5	162.7
45.84	56.98	69.35	102.5	112.1	164.1
45.87	57.18	70.25	103.5	115.2	170.5
47.01	58.93	71.43	109.1	116.8	172.8
47.49	60.36	71.69	109.5	118.3	177.2
48.17	61.41	72.08	109.9	122.2	183.5
48.79	62.14	73.00	111.8	127.1	193.1
49.67	64.02	74.01	113.5	131.7	202.0

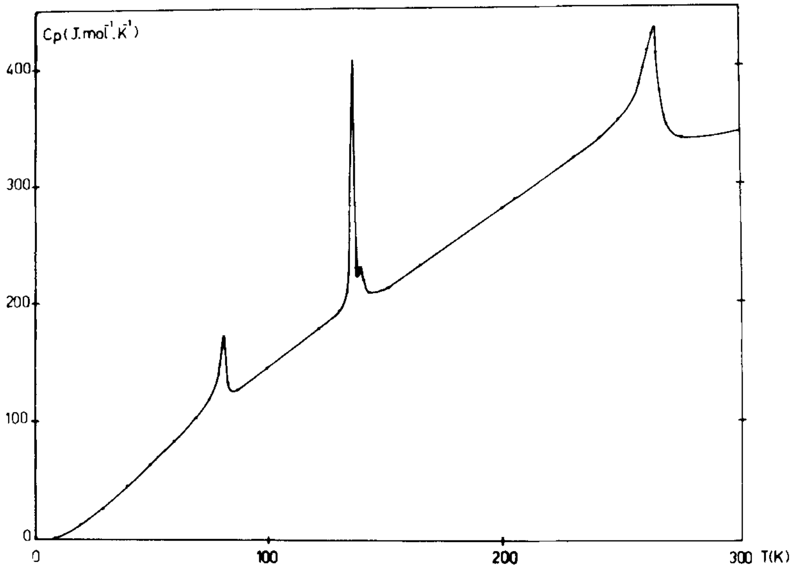

FIGURE 4 Specific heat of NHS in the temperature range 10 to 300 K (see text).

Two extreme values of N could be considered in the case of $(NH_4)_3H(SO_4)_2$: $N = 1$ for a fully molecular crystal, $N = 6$ assuming that the interactions between ionics moieties NH_4^+, H^+, SO_4^{2-} are much weaker than the interatomic forces inside each entity. However, a strong OH . . . O and numerous weak NH . . . O hydrogen bonds occur in NHS[9,10] and this compound can be written as $(NH_4)_3(SO_4HSO_4)$. On this basis, we have taken an intermediate value, N = 4, for which the experimental heat capacities below 20 K lead to a Debye temperature $\vartheta_D = 167$ K. However, the calculated Debye heat capacities above 30 K become higher than the experimental data. So, for further calculations of the lattice contribution, we have considered the value N = 3 corresponding to $\vartheta_D = 152$ K. This implies that the NH . . . O hydrogen bonds would be strong enough to be taken into account.

The thermodynamic functions were calculated and reported in Table II as well as the smoothed heat capacities, for selected temperatures. A rough estimation of a normal base line in the transition range namely between 30 and 90 K allows to evaluate the enthalpy and entropy changes: $\Delta H = 420$ J mol^{-1}, $\Delta S = 5.2$ J K^{-1} mol^{-1} (assuming isothermal transition).

TABLE II

Standard (p^0 = 101.325 kPa) molar thermodynamic function of $(\mathrm{NH_4})_3\mathrm{H}(\mathrm{SO_4})_2$

$\frac{T}{K}$	$\frac{C_{p,m}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{S^0_m(T) - S^0_m(O)}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{H^0_m(T) - H^0_m(O)}{\mathrm{J\,mol^{-1}}}$	$\frac{-[G^0_m(T) - G^0_m(O)]/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$
5	0.207	0.07	0.26	0.02
10	1.66	0.55	4.15	0.14
15	5.47	1.80	21.00	0.40
20	11.57	4.02	60.32	1.01
25	19.06	7.40	135.9	1.96
30	27.65	11.60	252.4	3.19
35	36.64	16.53	413.5	4.72
40	45.61	22.01	618.7	6.54
45	54.68	27.91	869.3	8.59
50	64.20	34.16	1166.2	10.92
55	74.23	40.74	1512.2	13.25
60	84.11	47.63	1908.3	15.82
65	92.67	54.71	2351.1	18.34
70	102.16	61.65	2826.5	21.27
90	130.22	94.36	5437.7	33.94
95	138.26	101.61	6109.7	37.30
100	145.03	108.88	6817.8	40.70
150	212	186	16386	77
200	281	256	28795	112
250	350.41	326	44530	148
300	345	365	54355	184

With the aim to get more accurate values of ΔH an ΔS changes associated with the transition, we have estimated the "normal" heat capacity from spectroscopic data. The following equation is used

$$Cp = (Cp - Cv) + C_{\mathrm{lat}} + C_{\mathrm{int}} + C_{\mathrm{lib}} + C_{\mathrm{tr}} \tag{2}$$

where the difference $Cp - Cv$ can be neglected in the investigated temperature range (T < 90 K). The "lattice" heat capacity C_{lat} is estimated from acoustic modes and some low frequency dispersive optic modes. The others terms are respectively the contributions from internal vibrations of the ions (C_{int}), the librational term of $\mathrm{SO_4^{2-}}$ and $\mathrm{NH_4^+}$ groups (C_{lib}) and the translational high frequency optic modes (C_{tr}).

As stated above, the C_{lat} term can be approximated by a Debye function with three degrees of freedom for each of the three different entities. This 9 $\mathbb{N}$ ($\mathbb{N}$ is the Avogadro number) degrees of lattice freedom can be divided into 3 $\mathbb{N}$ acoustic modes and 6 $\mathbb{N}$ translational optic modes whose frequencies are lower than the Debye cut off frequency (ν_D) (in so far as these last modes are generally dispersive). The Debye temperature ϑ_D so obtained was $\vartheta_D = 152$ K which corresponds to ν_D equal to 105.5 cm^{-1}. The three other terms in equation (2) are expressed using Einstein functions. The mean frequencies used in the estimation of C_{int} are those observed on Raman spectra at $T = 50$ K. However, for NH_4^+ and SO_4^{2-} librational modes the low frequency Raman spectrum at 50 K is very complex (Figure 1) and it is not possible to obtain the experimental values of all frequencies. Under these conditions, the fitting experimental heat capacities obtained below 25 K and between 90 and 120 K from equation (2) used three parameters: two librational frequencies ν_R (NH_4^+) and ν_R (SO_4^{2-}) and a mean translational high frequency ν_T.

The best fit is obtained with $\nu_R(SO_4^{2-}) = 180\ cm^{-1}$, $\nu_R(NH_4^+) = 305\ cm^{-1}$ and ν_T, $= 247\ cm^{-1}$. These frequencies are in accordance with those observed in other compounds containing SO_4^{2-} and NH_4^+ ions[16,17] and mean value of NHS lattice modes assigned to ammonium librations. Table III compares the calculated and experimental heat capacities in the temperature range 10 to 120 K. At 300 K, the difference is about 10% due to the term $Cp - Cv$ which can no more be neglected.

TABLE III

Comparison of experimental and calculated Cp values in the temperature range 0 to 120 K

T (K)	C_p (exp) [J K^{-1} mol^{-1}]	C_v (cal) [J K^{-1} mol^{-1}]	
10	1.66	1.66	
15	5.47	5.47	
20	11.57	11.77	
25	19.06	19.53	
30	27.65	27.74	
35	36.64	35.95	Transition range
40	45.61	44.11	
50	64.20	60.69	
60	84.11	77.94	
70	102.16	95.63	
90	130.22	130.33	
100	145.76	146.55	
110	162.26	161.75	
120	178.76	175.87	

The relative importances of the contributions of the various terms in *Cp* value (equation 2) are shown in Figure 5. Taking into account the new calculated base line in the transition temperature range we can determine the limits of the transition at about 35 and 90 K and the values of the enthalpy and entropy changes:

$$\Delta H = 444 \text{ J mol}^{-1} \qquad \Delta S = 5.5 \text{ J K}^{-1} \text{mol}^{-1}$$

This last value is very close to RLn2 = 5.76 J K^{-1} mol^{-1} and VII → V transition could be attributed to a disordering process of the proton engaged in the strong OH . . . O hydrogen bond. Indeed, such a disorder has been reported in the room temperature crystal structure[9] and shown to be of statistical nature.[11] However, our spectroscopic results show that the ammonium ions are principally involved in this phase transition, in any case much more than the possible ordering of proton in the sulphate dimers which occurs certainly during the II → III transition.[12] The above value of entropy change must correspond therefore to a disordering of NH_4^+ ions between two orientational positions. The rotational barrier being high,

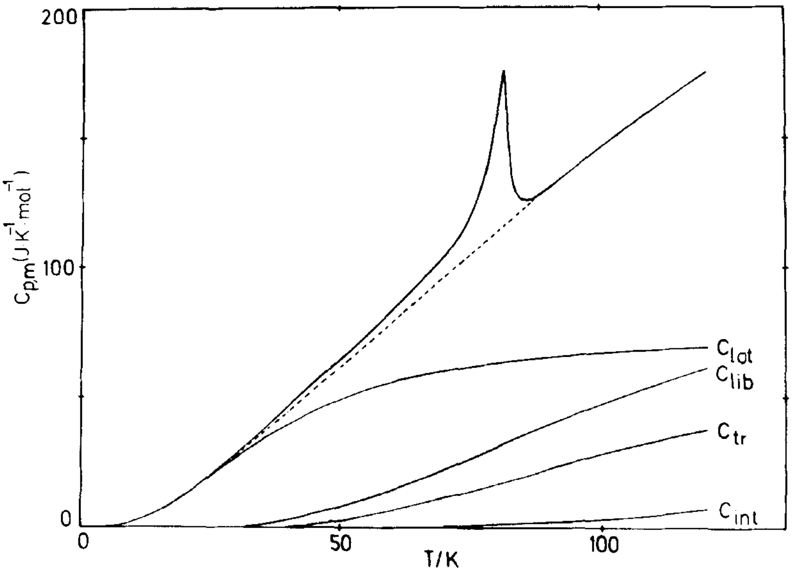

FIGURE 5 Calculated "normal" heat capacity (---) and contributions from different terms. The experimental Cp values between 10 and 120 K (——) are also displayed for comparison.

a tunneling process is probably implicated.[18] The large isotope effect on the phase VII temperature range[7] is consistent with an ordered state of the OH . . . O and NH_4^+ protons in the low temperature ferroelectric phase.

References

1. K. Gesi, *Phys. Status Solidi* (*A*), **33**, 479 (1976).
2. S. Suzuki, *J. Phys. Soc. Japan*, **47**, 1205 (1979).
3. S. Suzuki, Y. Oshimo, K. Gesi and Y. Makita, *J. Phys. Soc. Japan*, **47**, 874 (1979).
4. T. Osaka, Y. Makita and K. Gesi, *J. Phys. Soc. Japan*, **43**, 933 (1977).
5. K. Gesi, *J. Phys. Soc. Japan*, **41**, 1437 (1976).
6. T. Osaka, Y. Makita and K. Gesi, *J. Phys. Soc. Japan*, **49**, 593 (1980).
7. K. Gesi, *Jap. J. Appl. Phys.*, **19**, 1051 (1980).
8. U. Syamaprasad and C. P. G. Vallabhan, *J. Phys. C*, **14**, L571 (1981).
9. S. Suzuki and Y. Makita, *Acta Cryst.*, **B34**, 732 (1978).
10. M. Tanaka and Y. Shiozaki, *Acta Cryst.*, **B37**, 1171 (1981).
11. M. Damak, M. Kamoun, A. Daoud, F. Romain, A. Lautie and A. Novak, *J. Mol. Struct.*, **130**, 245 (1985).
12. M. Kamoun, A. Lautie, F. Romain, A. Daoud and A. Novak, 41st International Meeting of Physical Chemistry, Dynamic of Molecular Crystal, Grenoble (France), J. Lascombe (Editor) (Elsevier, Amsterdam, 1987) pp. 219–224.
13. K. Chhor, J. F. Bocquet and C. Pommier, *J. Chem. Thermodyn.*, **17**, 379 (1985).
14. Y. Sato, *J. Phys. Soc. Japan*, **20**, 275 (1965).
15. E. O. Schempler and W. C. Hamilton, *J. Chem. Phys.*, **44**, 4498 (1966).
16. Z. Iqbal and C. W. Christoe, *Solid. State Com.*, **18**, 269 (1976).
17. B. H. Torrie, C. C. Lin, D. S. Binbrek and A. Anderson, *J. Phys. Chem. Solids*, **33**, 697 (1972).
18. H. L. Strauss, *J. Mol. Struct.*, **126**, 177 (1985).