PART II - REVIEW
INTRODUCTION AND GENERAL CONSIDERATIONS

NMR has been utilized to provide valuable information on the static and dynamic microscopic phenomena accompanying phase transitions and internal motions present in the crystalline lattice. Study of temperature dependence of the line-width, second moment, \( T_{1P} \) and \( T_{1D} \) enables one to learn about the nature of the low frequency motions, while the SLR relaxation time (\( T_1 \)) studies provide data on the rates of motion over a wide range of frequencies (upto \( 10^{13} \) Hz). Both these studies cover diverse motions like hindered reorientations, free rotations, diffusion, tunnelling etc. They also provide a means of estimating the strength of the barrier, hindering different motions. Phase transitions associated with ordering or disordering of the lattice or with changes in the rotational freedom of reorienting groups, may show up as discontinuities or slope change in \( T_1 \) vs temperature plot. Phase transitions may also show up as line-width or second moment transitions. Hence NMR (both CW and pulsed) serves as a good local probe for investigating the environment of the resonating nuclei, as well as the dynamics and about the nature of phase transitions. As this thesis is concerned with the study of ammonium and substituted ammonium based metal complexes, a survey of the literature dealing with such compounds has been carried out and is presented in this review. This is divided into two sections. Introduction and general considerations of the review are given in section II.1. Section II.2 which is further subdivided into ten subsections gives a classification of these compounds based upon their anions. The Tables at the end of each subsection gives a bird's eye view of the work done along with the main parameters investigated.

Theoretical aspects regarding the spin-lattice relaxation and second moment studies have already been discussed in chapter-1. Earlier it was mentioned that molecules or parts of molecules are known to execute different types of motions in many solids. Symmetric groups like \( \text{CH}_3 \), \( \text{NH}_4 \) etc., have been extensively studied using proton NMR because of its high sensitivity. We outline here the different models proposed to interpret the observed NMR results (\( T_1 \) and \( M_2 \)). \( \text{NH}_4 \) ion motion in a crystal lattice is primarily limited by its surroundings. A free ammonium ion has a tetrahedral symmetry with four protons occupying the four corners of the tetrahedron. The (tetrahedral) ammonium ion has (1) Three 2-fold axes (2) Four 3-fold axes. Replacing a proton of the \( \text{NH}_4 \) ion by a \( \text{CH}_3 \) group would result in a change of symmetry. Methyl ammonium ion and trimethyl ammonium ion have \( C_3 \) symmetry while tetramethylammonium ion has tetrahedral symmetry. Presence of \( \text{CH}_3 \) group leads to an additional degree of freedom viz. the reorientation of the \( \text{CH}_3 \) groups about its 3-fold axis. Extensive NMR studies of ammonium and methyl substituted ammonium compounds and to some extent their double salts have been carried out in the literature and some common features about the potential barriers and phase transition temperatures have been noted. Further it was found that the activation energies for different reorientational motions of the \( \text{NH}_4 \) ion, in \( \text{NH}_4\text{Cl} \) and other metal complexes as given in Table II.2.
shows a gradual decrease in $E_a$ with the introduction of the metal ion indicating a higher degree of freedom. Also, a comparison of activation energies for NH$_4^+$ ion motion in its halides and in its metal halo complexes is interesting because it depends on the size of the cation. It can be easily seen from the tables that NH$_4^+$ ion can rotate more freely in NH$_4$I than in NH$_4$Cl, indicating the effect of the size of the anion. Similar behaviour has been found in substituted ammonium compounds also.

Hydrogen bonds (H-bonds) play an important role in some phase transitions and can be well studied using NMR since it is very sensitive to the isotopic substitution of protons with deuterons. This type of study yields information regarding the nature of the phase transition, the strength of H-bonding etc. Some representative examples of this type of study have been discussed in the text.

Many ammonium compounds having the perovskite (ABX$_3$ A: cation, B: metal ion, X: halogen) structure are known to undergo phase transitions as predicted by a general formula. (see chapter 4 of part I) They possess an ideal cubic structure if the tolerance factor

$$ t = \frac{r_A + r_X}{\sqrt{2} (r_B + r_X)} $$

is unity. Depending upon the relative ionic sizes (t > 1), they show tetragonal, rombohedral, orthorhombic and other distortions. Both A and B play an important role in determining the nature of the distortion. Generally the smaller the A cation, the greater is the tendency for distortion to the orthorhombic symmetry. The high temperature structure of these perovskites is cubic. NH$_4$ZnF$_3$ and NH$_4$MgF$_3$ are two typical examples exhibiting a behaviour as discussed above with phase transitions at 107.5 K and 115.1 K respectively. Comparison of the activation energy of NH$_4$F with the above complexes (Table II.1.) shows a drastic decrease, indicating an increased freedom for the cation motion, due to the introduction of the metal ion. It was also found that the hindering barrier for the cation decreases with increasing metal ion (B) radius.

Proton M$_2$ and T$_1$ studies in antifluorites (NH$_4$)$_2$BX$_6$) has been carried out by many authors. Table II.2, II.3, II.4 give the activation energies for these compounds along with their phase transition temperatures. From their experiments they arrived at a few common conclusions that (1) The activation energy for the cation motion is a function of the unit cell dimensions, (2) The transition temperature is a function of the size of the cation. It shifts to lower temperatures with increasing size of the cations and decreasing size of the anion. (3) $T_c$ also depends upon the d-electron configuration of the central metal atom, described in terms of the ligand field stabilization energy.

Initial part of the review deals with halogen based ammonium complexes in the order flourine to iodine. Later, compounds containing tetrahedral anions, like perchlorates,
sulphates, selenates, arsenates are reviewed. Finally literature on compounds containing nitrates tartarates is presented. Other ammonium salts which do not fall into specific groups are listed in Table II.11 along with motional parameters.
II.1 Fluorides

This section covers a family of compounds with fluoride as the anion. Studies on single salts are very few compared to the studies on double salts. Studies on NH₄ZnF₃ and NH₄MgF₃ (perovskite family) are interesting because of their interesting phase transitions. It was found that T_c in these salts decreases with decreasing metal ion radius. (NH₄)₂BeF₄ is a ferroelectric and has been studied using both ¹H, ¹⁹F NMR. (NH₄)₂SbF₅ has shown superionic conductivity. Studies on antifluorites of the type (NH₄)₂MF₆ (M : Ge, Si, Ti) show that the activation energy for the reorientational motion of the ammonium ion (E_a NH₄) increases with increasing cell volume while that of anion (E_a MF₆) change in the opposite way (i.e. decreases) with unit cell volume. Salient features of NMR studies in these compounds are outlined below.
Ammonium Fluoride NH₄F

NH₄F has a hexagonal structure of the ZnO type, with space group C₆v (C₆mc). Gutowsky et al. were the first to measure the proton second moment in ammonium fluoride, obtaining a value of around 58.5G² at 95 K, the fluorine contribution being 3G². Soutif² investigated the structure using proton NMR. Proton and fluorine NMR study of Drain³ over a range 140-360 K shows that each ammonium ion is surrounded by a tetrahedron of fluoride ions and the tetrahedral ammonium ions form strong N-H ... F bonds. There is no other alternative orientation of the ammonium ions of comparable energy which could lead to an order-disorder transition like in other ammonium halides. Svare et al.⁴ measured proton T₁ and T₁ρ and obtained an activation energy (E_a) of 10 kcal/mole at room temperature for NH₄⁺ ion reorientation.

Ammonium hydrogen Di-Fluoride NH₄HF₂

NH₄HF₂ is orthorhombic (Pnₐm) with four molecules per unit cell and there are two crystallographically inequivalent linear HF₂ ions in the unit cell. Sidel et al.⁵ found a second moment value of 68.7±3.5G² for fluorine and 22.7±3.5G² for protons respectively at room temperature. They noticed a F-H...F type of H-bonding in the solid with the H atom in a double minimum potential well. Alexander et al.⁶ and Grosseau et al.⁷ from their ₁⁹F pulsed NMR studies found that the best fit with the experiment is obtained for a centered hydrogen fluoride ion. Furukawa et al.⁸ have measured T₁, T₁ρ for ¹H and ¹⁹F over a range of 142-345 K. Below 200 K the relaxation rates were accounted for by dipolar interaction modulated via isotropic reorientation of ammonium ions and obtained the activation energy E_a for NH₄ as 6.09±0.24 kcal/mole. (It is also of interest to note that while all the alkali hydrogen difluorides are characterized by a phase transition from tetragonal to cubic phase as reported by Ludman et al.⁹, ammonium bifluoride does not show any such change with temperature). Proton and fluorine second moments over a range of 77-395 K have been measured by Reynhardt et al.¹⁰, who obtained a rigid lattice values (below 130 K) of 76±4G² and 80±1.5G² respectively which agree well with the theoretically calculated second moment values. M₂ is affected by the isotropic reorientation of NH₄⁺ ion at lower temperatures and by the 180° flipping motion of
HF$_2$ ion at higher temperatures. $T_1$ and $T_{1p}$ of $^1$H, $^{19}$F in the range 167-395 K, yielded an activation energy as 6 ± 0.2 kcal/mole for NH$_4$ and 5.9 ± 1 and 15.5 ± 2 kcal/mol for HF$_2$ of type 'a' and type 'b'. The $T_1$ of protons over a range 100-430 K shows a single minimum.

**Ammonium tri Fluoro Zincate NH$_4$ZnF$_3$**

X-ray and neutron diffraction experiments show that NH$_4$ZnF$_3$ is a cubic perovskite with space group (Pm$_{3m}$) and undergoes a structural phase transition at $T_c = 115.1$ K, from cubic to tetragonal with an elongation of the c axis with a $c/a$ ratio of 1.015. The transition was confirmed to be of first order by specific heat measurements. Proton $T_1$ measurements$^{13,14}$ confirmed the presence of a first order phase transition at 115 K with very low activation energy (1.5 kcal/mole) for NH$_4$ motion. Proton and Fluorine CW NMR studies$^{15}$ at different temperatures (down to 4.2 K) and pressures (upto 15 kbars) indicate fast motion even at 77 K and 15 kbars, as well as tunnelling at 4.2 K at atmospheric pressure.

**Ammonium Trifluoro magnesium NH$_4$MgF$_3$**

NH$_4$MgF$_3$ is isostructural with NH$_4$ZnF$_3$ (cubic P$_{m3n}$) and it undergoes a phase transition at 107.5 ± 0.1 K (change in $T_c$ due to change of metal ion). Proton $T_1$ and $T_{1p}$ measurements at 10 MHz by Palacious et al$^{15}$, showed tunnelling effects below 67 K.

**Ammonium Tetrafluoro Aluminate NH$_4$AlF$_4$**

Ammonium tetrafluoro aluminate is tetragonal with D$_4h$ (P$_{4/mmm}$) and undergoes an order-disorder phase transition at 145 K and is related to the ammonium ion orientations. Both wide-line and relaxation measurements$^{16}$ of $^1$H and $^{19}$F show that the ammonium ions are undergoing rapid rotation at 300 K and that the motion is slowed down at 77 K, such that the intra-ionic broadening is significant. This
behaviour is typical of low-barrier ammonium salts. The plot of $T_1$ of $^1H$ and $^{19}F$ with temperature shows a cup-like dip at $T_c$ but no discontinuity indicating that the transition is second order.

**Ammonium Tetra Fluoro Borate NH$_4$BF$_4$**

Pendred et al$^{17}$, using $^1H$ and $^{19}F$ NMR, found that the proton second moment did not reach the rigid lattice value even at 20 K indicating a low potential barrier (for NH$_4^+$ ion reorientation) in NH$_4$BF$_4$ and a weak H-bond if present. $^2H$ NMR in ND$_4$BF$_4$ by Chiba$^{18}$ also does not show any evidence of hydrogen bonds. $T_1$ and $T_2$ of $^{19}F$ were measured by Akhmedov et al$^{19}$ in the range 4.2 K to room temperature. The $T_1$ data shows that above 90 K the F-F interaction modulated by the motion of the BF$_4$ groups dominates while below 90 K the H-F interaction modulated by the rotation of the ammonium groups dominates. Further a jump in $T_2$ of $^{19}F$ above 90 K shows the onset of BF$_4^-$ group motion.

Caron et al$^{20}$ from their $^1H$ and $^{19}F$ NMR ($T_1$ and $M_2$) in NH$_4$BF$_4$ and ND$_4$BF$_4$ observed a phase transition at 472 K from orthorhombic to cubic phase. A proton $T_1$ minimum (260 K) and a proton line-width transition (173 to 223 K) are attributed to the modification of NH$_4^+$ ion motion due to the lattice expansion and to interionic dipolar coupling.

Heuttner et al$^{21}$ have studied the fluorine SLR and line-width in a number of tetrafluoroborates including NH$_4$BF$_4$ and found that the anion activation energy decreases with increasing cation radius. Dautov et al$^{22}$ has studied proton $T_1$ and $T_2$ in the range 4.2-300 K. They observed a $T_1$ minimum at 110 K and low $E_a$ of 1.52 ± 0.3 kcal/mole indicating a weak coupling of NH$_4^+$ ions with the surrounding fluorine atoms. Broad line NMR was studied by Hennel et al$^{23}$ down to 1.2 K. They interpret the observed line shape of NH$_4^+$ ion in this compound as a consequence of rotation around the C$_2$ axis. Lalowicz et al$^{24}$ also made an analysis of the NMR line shape in terms of the rotationally tunnelling NH$_4^+$ ion which also undergoes rapid reorientational jumps around its C$_3$ and or C$_2$ symmetry axes. The proposed composite motion believed to be brought about by coupling of rotor states of the ion with the lattice phonons, leads to the line narrowing and offers an interpretation of experimental second moment data of proton resonance line shape at liquid Helium temperatures. $T_1$ and $T_1D$ of $^1H$ and $^{19}F$ have been studied by Svare et al$^{25}$ in NH$_4$BF$_4$ to determine activation energies $E_a$ for NH$_4^+$ and fluoride ion complex reorientation. In orthorhombic NH$_4$BF$_4$ each NH$_4^+$ ion is surrounded by twelve fluorine neighbours.
at a distance of 2.90 to 3.45 Å. So many near neighbours at so far distances with weak H bonds are likely to mean a low barrier for NH₄ reorientation, as they found and also indicated by X-ray diffraction and with the limited NMR data published. However they were not able to see the slight phase transition at 173 K, as a discontinuity or a change of slope of the proton T₁ or T₁p since the proton relaxation at this temperature is determined by the BF₄ motion, which hardly changes at the phase transition. They found Eₐ (BF₄) = 7.5 kcal/mole in agreement with Heuttner et al²¹. ¹⁹F NMR chemical shift studies in solid NH₄BF₄ were carried out by Sears²⁶ at 14 MHz, by using multiple pulse zero crossing technique. A high value of chemical shift (-34.4 ± 1) ppm relative to C₆F₆ was found and this was explained in terms of the effect of H bonding between nitrogen and fluorine.

Di Ammonium Tetra Fluoroberylate (NH₄)₂BeF₄

(NH₄)₂BeF₄ is orthorhombic (Pnám) at room temperature and becomes ferroelectric below 176 K (Pnám). Blinc and levstek²⁷ observed a narrow line for ¹H even at 93 K and concluded that the potential barrier hindering the motion of the NH₄ ions is very low. Watton et al³⁷ found that the ¹H spectrum at 4.2 K can be approximated very closely to Tomita's spin isomeric spectrum. Burns²⁸ observed a break in M₂ of ¹⁹F at 211 K in a solid solution of the type [(NH₄)₂(BeF₄)ₓSO₄ and it was found to be independent of x. This was attributed to the freezing in of the BeF₄ groups. The proton resonance line show two well-resolved components which were attributed to the presence of two non-equivalent NH₄ groups in the unit cell. ¹⁹F second moment studies at Tc (176 K) by Mikhailov et al²⁹ and Aleksandrova³⁵ show that BeF₄⁻ ions begin to reorient about the a-axis just above Tc (183 K) and that this reorientation is associated with a small distortion of the BeF₄ tetrahedra. The height of the potential barrier hindering the reorientation of BeF₄ group is 9.5 ± 0.4 kcal/mole. Miller et al³⁰ and Blinc et al³¹ studied T₁ of ¹H and ¹⁹F nuclei in both FE and PE phases and found a slope change in proton T₁ vs. 1/T curve in the vicinity of the curie point suggesting that the NH₄ groups are not much affected at Tc which was also confirmed by dielectric and thermal data. In the FE phase, the hindering potential increases from 1.5 ± 0.7 to 5.3 ± 1.2 kcal/mole for NH₄ reorientation. In contrast, the fluorine T₁ vs. 1000/T graph shows an increase from room temperature down to 203 K where it exhibits a maximum and then in the ferroelectric phase it decreases with further decrease of temperature. From their results they conclude that the high temperature relaxation is governed by BeF₄ reorientation whereas the relaxation in the low temperature region is explained in terms of NH₄ reorientation. The study of T₁ and
$T_2$ of $^{19}\text{F}$ over a range 4.2 to 300 K was carried out by Akhmedov et al$^{19}$. Their results are in agreement with that of Burns et al$^{28}$ and Miller et al$^{30}$.

O'Reilly et al$^{32}$ have observed two $T_1$ minima for $^1\text{H}$ due to two inequivalent NH$_4$ ions in the unit cell in agreement with Burns$^{28}$. Above 253 K the $T_1$ of both the $^1\text{H}$ and $^{19}\text{F}$ become strongly nonexponential and are characterized by two relaxation times. $^{19}\text{F}$ NMR chemical shift studies by Aleksandrova et al$^{33,35}$ show that the BeF$_4$ group does not possess an appreciable permanent dipole moment and that the ammonium groups play an important role in the appearance of the spontaneous polarization $P_s$ in (NH$_4$)$_2$BeF$_4$. The temperature dependence of deuteron magnetic resonance studies of Aleksandrova et al$^{34}$ shows that there are two inequivalent ammonium groups with different degrees of distortion and the highly distorted ammonium groups contribute to the macroscopic polarization. They also noticed a small abrupt change in the EFG tensor at $T_c$. The deuteron $T_1$ studies over a range from 85-475 K by Kydon$^{36}$ also show the presence of two inequivalent ND$_4$ groups whose activation energy do not change much. There is an abrupt change in $T_1$ of one of the ND$_4$ groups which suggests that in (NH$_4$)$_2$BeF$_4$ only one ammonium ion is involved in the FE behaviour.

Rutar et al$^{38}$ have carried out quadrupole perturbed NMR of $^9\text{Be}$. The temperature dependence of $T_1$ of $^9\text{Be}$ shows that in the high temperature PE phase far from $T_c$, $T_1$ vs. $1/T$ is determined by slow hindered rotation of the BeF$_4$ groups. The soft mode relaxation mechanism becomes ineffective in the C-phase and $T_1$ is determined by the fast hindered rotation of the ND$_4$ groups. Blinc et al$^{39}$ carried out the temperature dependence of the quadrupole splitting and $T_1$ of $^{14}\text{N}$ NMR lines in the PE and FE and the incommensurate phase of (NH$_4$)$_2$BeF$_4$. The characteristic broadening of the $^{14}\text{N}$ lines in the incommensurate phase and the splitting in the FE phase demonstrate that NH$_4$(2) groups are the main reorientable FE dipoles in the structure though the NH$_4$(1) and BeF$_4$ groups take part as well in the phase transition. The results further show that the incommensurate modulation has a soliton character close to $T_c$ and that the $^{14}\text{N}$ SLR in the I-phase is determined by phasons with a finite energy gap.

Tetramethyl Ammonium Fluoroborate (CH$_3$)$_4$NBF$_4$

Jurga et al$^{41}$ have studied proton and fluorine $T_1$ and found two $T_1$ minima for protons at 256 K and 104 K (which also exhibit non exponential magnetization decay in the range 172-130 K) due to TMA and CH$_3$ reorientation. Fluorine $T_1$ shows a
minimum at 202 K and a maximum at 167 K after which it decreases. The $^{19}$F $T_1$ is non-exponential between 230 and 150 K. They ascribe $^{19}$F $T_1$ minimum to the isotropic rotation of BF$_4$. The fluorine relaxation is dominated by the TMA ion rotation (which is slow compared to BF$_4$) modulating the H-F dipolar interaction in the range 333 to 247 K. Similarly proton relaxation is dominated by BF$_4$ rotation in the region 172-130 K.

**Ammonium Fluoro Antimonate (NH$_4$)$_2$SbF$_5$**

This is a superionic conductor, the room temperature structure is known to be Orthorhombic with space group $C_{mcm}$ and $Z = 4$. It has two phase transitions, a second order one at 145 K from antiferroelectric to ferroelastic and the other at 257 K is of first order in nature. Two inequivalent fluorine atoms were identified in the crystal. I) Axial II) equatorial, the axial fluorine atom being more ionic and giving rise to the observed superionic conductivity. Single crystal $^{19}$F NMR spectra also confirm the above observation. The temperature dependence of $^1$H and $^{19}$F NMR by Avkhutskii et al\textsuperscript{42} over a range 116 to 353 K shows a substantial narrowing of peak to peak line width of $^1$H and $^{19}$F NMR spectra at 220 and 350 K. The activation energy for SbF$_5$ rotation is $8.0 \pm 0.5$ kcal/mole. The ammonium group motion is characterized by a rather low activation barrier ($2$ kcal/mole). Two inequivalent ammonium ions are observed with different distances from the fluorine atom. One of the ammonium ions has more freedom to rotate compared to the other one. Chihara et al\textsuperscript{43} have carried out $^1$H and $^{19}$F $T_1$ measurements and have discussed the reorientation of ammonium cations.

**Ammonium Pentafluoro Stannate (NH$_4$)$_2$Sn$_2$F$_5$**

Protons and fluorine $T_1$ study over a range 100-400 K was carried out by Battut et al\textsuperscript{44}. They find that the temperature and the frequency dependence of $T_1$ of protons and fluorines are quite similar. Cross relaxation measurements clearly show a strong coupling between proton and fluorine atoms. Below 250 K on the low temperature side ammonium reorientation plays a dominant role in relaxation whereas on the high temperature side (above 250 K) the diffusion of Fluorine atoms is responsible for the relaxation. The $E_a$ of ammonium ions for the diffusion process is $0.48$ ev.
Triammonium Hexafluoro Aluminate (NH₄)₃AlF₆

This has cubic structure and belongs to the space group (Fm₃m). Proton and fluorine NMR spectra were recorded at 80-297 K by Guido et al. Theoretical second moments for the two nuclear species were calculated for different models of motions of the ionic groups and were compared with experiment.

Triammonium HexaFlouro Chromate (NH₄)₃CrF₆

This compound is isomorphous with triammonium hexafluoroaluminate. NMR line-width and second moments of the protons and fluorine were studied over the temperature range 130-400 K by Belaya et al. and the results were discussed in terms of exchange interaction and structural features of the material.

Diammonium HexaFlouro Germanate (NH₄)₂GeF₆

This is one of the substances widely studied by NMR and it belongs to the family of the compound with general formula A₂MX₅ where A is alkali or ammonium, M is a tetravalent metal and X is a halogen. These compounds in general have a cubic structure with space group (Fm₃m). Leane et al. have carried out wide line NMR studies of both Proton and Fluorine nuclei from 20 K to room temperature and found that there is no H bonding or it is very weak if it exists. The activation energy Eₐ calculated from line width measurements is very small and less than 0.74 kcal/mole. Proton, deuteron and fluorine relaxation measurements have been done on this compound to characterize the motion of cation as well as the anion. Ylinen et al. conclude from their proton T₁ results over a temperature range 4-310 K that the relaxation above 50 K is mainly due to the classical reorientational motion of ammonium ions with Eₐ 5.4 ± 0.1kJ/mole (1.29 kcal/ mole). No discontinuity was observed in T₁ over the entire temperature range studied except for a slight anomaly at 42 K which was thought to be caused because of anisotropic reorientation of ammonium ions. At 15 K another low temperature minimum of T₁ was observed and this was interpreted in terms of quantum mechanical tunneling rotation of ammonium ions. Deuteron and ¹⁹F T₁ studies in polycrystalline samples by Tuohi et al. over
a temperature range from 40-300 K and 4-400 K respectively show that below 70 K, the recovery of deuteron magnetization was non-exponential. The FID signal disappeared around 38 K indicating a line width transition whereas no such observation was found in protonated compound except a small anomaly around 42 K. The fluorine relaxation is mainly dominated by random reorientation of ND$_4^+$ ion in the low temperature region (100 -250 K) whereas above 300 K it is the reorientation of the GeF$_6$ groups which dominates the relaxation.

$T_1$, $T_{1P}$ studies of Svare et al$^{25}$ yielded an activation energy of 1.3kcal/mole and 11.5kcal/mole for (GeF$_6$)$^2$- which compare well with the values reported$^{48,49,50}$. From the comparison of the data on (NH$_4$)$_2$MF$_6$ they arrived at the conclusion that $E_a$(NH$_4$) for isostructural (NH$_4$)$_2$MF$_6$ salts increases with increasing cell volume, whereas $E_a$(MF$_6$) changes in the opposite way with unit cell volume.

Punkkinen et al$^{51}$ have measured $T_{1D}$ for $^1$H and $^{19}$F at 33 and 38 MHz respectively, in the temperature region 4.2 to 300 K and found two minima at temperatures below 40 K. Above 200 K $T_{1D}$ decreases with increasing temperature. This cannot be related to the NH$_4^+$ reorientation because the proton resonance line narrows owing to the ammonium group motion around 35 K and therefore the corresponding contribution to $1/T_{1D}$ should decrease with increasing temperature. The reorientation of the GeF$_6$ starts to shorten the fluorine Zeeman relaxation time in (ND$_4$)$_2$GeF$_6$ above 200 K.

**Diammonium Hexa Fluoro Silicate (NH$_4$)$_2$SiF$_6$**

This crystallizes either in the cubic form (stable at room temperature) or in the trigonal form (stable below 278 K) depending upon the conditions of crystal growth and both the phases can exist as metastable forms for very long times. No phase transition was observed in the cubic form down to 25 K whereas the trigonal form is known to undergo an order-disorder transition at 38 K with a thermal hysteresis. Guido et al$^{52}$ and Blinc et al$^{53}$ have theoretically calculated $M_2$ of $^1$H and $^{19}$F for different motions of the ionic groups and compared with experimentally observed $M_2$ at room temperature and at 120 K showing that there is no transition in this temperature region and the ammonium groups are rotating with almost spherical symmetry and the $^{19}$F results are consistent with a model in which (SiF$_6$) groups are rigid. Studies of Blinc et al$^{53}$ over a range of 103-373 K reveal complete averaging of intra NH$_4^+$ contribution to second moment occurs. The deuteron NMR results also confirm the above result that the frequency of reorientation motion of NH$_4$ ion is
Svare et al. have carried out PMR absorption studies over a range 103-373 K. Their results have shown that the 3-fold proton disorder in ammonium groups is dynamic.

Proton and fluorine relaxation time studies in cubic and trigonal form have been extensively carried out. Blinc et al. studied proton T_1 at three different frequencies. Their experiments at 23.1 MHz show that T_1 vs. temperature graph can be distinguished into three regions. At lowest temperature, for 1/T a broad dipolar minimum characteristic of NH4 reorientation is found and in the region between 4/T it was independent of frequency and also increases with increasing temperature. In this region NH4 dominates the relaxation. At still higher temperatures a broad maximum was found to occur at 1000/T = 4 and the proton relaxation became non-exponential and is characterized by a pair of relaxation times.

The proton SLR times T_1 and T_{1p} in cubic (NH4)2SiF6 have been measured by Norris et al. at 14.3 and 21.5 MHz at fields of 5 and 3.8G respectively. The T_1 vs reciprocal temperature plot was found to have three distinct regions where T_1 vs. 1/T shows a definite minimum in the region 2.7/T. Strange et al. have carried out proton SLR times T_1 and T_{1p} in cubic (NH4)2SiF6 over a temperature range 60-500 K and evaluated the activation energy for ammonium ion as 2.2 kcal/mole. Svare has carried out proton relaxation studies in trigonal and cubic form down to 30 K and 25 K respectively. He observed a phase transition at 38 K associated with a sudden change in T_1 by a factor of 100 and this phase transition was characterized by a thermal hysteresis from 38.6 to 36.7 K. The phase transition is due to order-disorder in the orientation of NH4 groups. The results yielded an E_a for NH4 reorientation as 1.11 kcal/mole for trigonal modification whereas for cubic form it was 2.06 kcal/mole. The E_a for NH4 reorientation below T_c is 1.7 kcal/mole. The low temperature results show that tunneling reorientation of NH4 ion is responsible for the relaxation and hence the classical minimum was not observed in this case, a tunnel frequency of 50 MHz was estimated at 50 K.

Guido et al. and Svare et al. studied 19F second moment variation from about liquid nitrogen temperature to room temperature and observed that SiF6 groups was rigid up to 303 K above which SiF6 starts reorienting fast resulting in motional averaging. Studies of Blinc et al. and Svare et al. on T_1 of 19F showed no T_1 minimum down to 100 K but yielded a broad maximum around 300 K. Below 250 K the NH4 dynamics and above 300 K the SiF6 dynamics cause the relaxation. Pressure dependence of 19F SLR time T_1 in cubic form of this salt was carried out by
McKowiak et al. The pressure was varied up to 230 MPa. The activation energy for SiF$_2^-$ reorientation was estimated as 71.5 ± 0.4 KJ/Mole (17.081 ± 0.095 kcal/mole.)

Diammonium Hexafluoro titanate (NH$_4$)$_2$TiF$_6$

(NH$_4$)$_2$TiF$_6$ is isomorphous with (NH$_4$)$_2$GeF$_6$ with space group D$_{3d}$-C$_{3m}$. Three protons of NH$_4$ group lie approximately in a plane of six fluorine atoms which are at a distance of 3Å. This leads to one C$_3$ symmetry axis being inequivalent to the other three axes in the NH$_4$ group. Leane and Richards$^{47}$ and Watton et al.$^{61}$ have investigated $^1$H and $^{19}$F NMR and found a rigid fluorine system up to 300 K above which fluorine motion sets in. $M_2$ of $^1$H decreases from 10.2G$^2$ at 4.2 K to a plateau value of 5.5 ± 0.2G$^2$ at 420 K.

$T_1$ of $^1$H and $^2$H have been measured in (NH$_4$)$_2$TiF$_6$ and its deuterated analogue by Niemela et al.$^{60}$ from liquid helium temperatures to room temperature. A proton $T_1$min occurs at 55 K. At liquid helium temperatures the FID signal of proton was intense and relatively slowly decaying which shows that the reorientation of NH$_4$ ion is still rapid may be due to quantum mechanical tunneling about the inequivalent C$_3$ axis. $T_1$ minimum for deuterons occurs at 56 K. A line width transition for deuteron signal was observed at 40 K.

$T_1$ and $T_1^P$ for protons and fluorine are measured from 4.2 to 400 K by Watton et al.$^{61}$. Below 35 K the slope of log $T_1$ vs. 1/T shows progressive decreasing with decreasing temperature for both proton and fluorines indicating the dominance of the effects of paramagnetic impurities on the relaxation in this low temperature region. Below 285 K the SLR of both protons and fluorine spin systems is determined by thermal reorientation of the NH$_4$ ions while the TiF$_6$ ions remain effectively immobile. The unusually small value of proton second moment at 4.2 K suggests that these NH$_4$ ions are undergoing a combination of quantum mechanical tunneling and classical reorientation between equilibrium orientations at low temperatures. It is suggested that this effect is responsible for the observed minimum at 57 K, being somewhat larger than that expected for classical reorientation. The SLR of protons and fluorine is explainable in terms of dipolar coupling between the two spin systems. The ratio of fluorine to proton relaxation times between 60 and 285 K is consistent with the suggestion that three protons of the ammonium ion are nearly coplanar with 6 fluorines. Above 285 K dipolar modulation resulting from thermal reorientation of the TiF$_6$ ions becomes the dominating influence on spin lattice relaxation. Even
though $T_1$ minimum was not achieved in their experimental set up, they estimated the activation energy for the reorientation of the TiF$_6$ octahedra as $8.5 \pm 0.8$ kcal/mol.

Svare et al. from their proton SLR times $T_1$ and $T_1p$ measurements estimated that the activation energy for ammonium reorientation as 1.8 kcal/mol and that of TiF$_6$ as 5 kcal/mol. They also have compared different tunnel frequencies in certain other isomorphous ammonium compounds.

**Ammonium Hexafluoro Phosphate NH$_4$PF$_6$**

This has a cubic structure and belongs to space group $T_h$ with $Z = 4$. Wide line NMR studies and pulsed studies have been done by many workers. Albert et al. carried out both wide line and SLR studies on both spin systems. They found a value of $3.9 \pm 0.3G^2$ and $1.8G^2$ for the proton $M_2$ at 77 and room temperature respectively whereas for $^{19}$F the $M_2$ value was $16 + 1G^2$ at 77 as well as at 300 K respectively which shows that at room temperature the ammonium ion is executing isotropic rotation. Temperature dependence of PMR line shape studies of tunnelling ammonium ions in NH$_4$PF$_6$ has been carried out by Lalowicz et al. The PMR line shapes at liquid helium temperatures are narrower than those usually expected for rapidly tunnelling ammonium ions. The narrowing is temperature dependent suggesting a kinetic process that involves a modulation of the tunnelling states. A possible 'exchange narrowing' mechanism involving fluctuating molecular tortional states brought about by external lattice perturbation is considered and is seen to lead to a satisfactory simulation of the observed low temperature line shapes. Activation energy of $1.7 \pm 0.5$ K governing the exchange process is derived for NH$_4$ motion in NH$_4$PF$_6$. The experimental second moment values are $5G^2$ at 4.2 K and $12.1G^2$ at 1.3 K. Kaliaperumal et al. have carried out pressure and temperature dependence of $^1$H and $^{19}$F NMR absorption spectra. $^1$H second moments at 1kbar at 300 K and 77 K were $3.5G^2$ and $4.6G^2$ respectively while at 14kbar both room temperature and 77 K spectra still remain narrow except for a slight change in the second moment values to $5.7G^2$ and $6.9G^2$, respectively. From this data it was inferred that the application of pressure did not have much effect on the motion of NH$_4$ ions. Pressure variation of $^{19}$F spectra at 5kb, 10kb and 14kb at room temperature and 77 K did not show much variation in the second moment or line width though the second moment transition temperature was shifted towards higher temperature by 15 K. The phase transition at 192 K is not reflected on the line shape of $^{19}$F absorption spectra.
Niemela et al. have studied the $T_1$ of $^2H$ and $^{19}F$ from 20 to 300 K. The phase transition at $194 \pm 1$ K is associated with a change in reorientation rate of PF$_6$ ions whereas the other reported transition at $133 \pm 1$ K has little effect on the reorientational motion of both the ions. The spin-rotation interaction contributes to $T_1$ of $^{19}F$ nuclei at 194 K. Temperature variation of $^1H$ and $^{19}F$ studies have been carried out by Gutowsky et al. According to them at temperatures above 120 K the relaxation of protons as well as $^{19}F$ nuclei is governed by the faster rotation of the fluorine via PF$_6$ rotation. At temperatures below 75 K the relaxation of both the species is dominated by the faster relaxation of protons via NH$_4$ reorientation. At temperatures between 75-120K the spin exchange rate between H and F nuclei is comparable to their SLR rates and both exhibit non-exponential decay of magnetization. However in comparison with ammonium halides this transition is attributed to order-disorder transition to the dynamic state of the NH$_4$ ions similar to ammonium halides. SLR times $T_1, T_1^p$ of $^1H$ and $^{19}F$ nuclear spin system have been carried out by Svare et al. $^{19}F$ chemical shift study in powder NH$_4$PF$_6$ was carried out by Sears. The chemical shift was found to have a larger value in this salt when compared to other alkali hexafluoro phosphate salts.

Tetra Methyl Ammonium hexafluorosilicate [N(CH$_3$)$_4$]$_2$SiF$_6$

Rager et al. studied the $T_1$ of $^1H$ and $^{19}F$ in the range 125 to 460 K and found that in the low temperature region protons and fluorines are coupled by dipole-dipole interactions and both spin systems relax through the motion of methyl groups with increasing temperature. $T_1$ of both are influenced by the reorientation of the cation as a whole. The dynamical behaviour of the compound is mainly determined by the size of the cation.

Trimethyl Ammonium Hexafluorosilicate [N(CH$_3$)$_3$H]$_2$SiF$_6$

Varnek et al. have carried out the temperature dependence of $M_2$ of $^1H$ and $^{19}F$ NMR absorption lines. There is a sharp change in the $M_2$ value at 165 K which can be explained with in the frame work of a model assigning isotropic reorientation of the
Individual groups and a phase transition. The phase transition is supported by Mossbauer spectra.

**Tetraethyl Ammonium Hexafluoro Antimonate** \( [\text{N(C}_2\text{H}_5)_4]\text{SbF}_6 \)

Reynhardt et al.\(^7\) have measured the temperature dependence of proton and fluorine \( M_2 \) and \( T_1 \) which show a \( T_1 \) discontinuity at the previously reported phase transition temperature of 246 K or 272 K and also reveal the existence of two non equivalent methyl groups in the low temperature phase. The fluorine \( T_1 \) results are in good agreement with a model in which the \( \text{SbF}_6 \) octahedron executes a four fold reorientation \( (E_a=5.8 \text{ kcal/mole}) \) at low temperatures and an isotropic reorientation \( (E_a=6.6 \text{ kcal/mole}) \) at higher temperatures. At the phase transition the reorientation frequency of the \( \text{SbF}_6^- \) is drastically increased whereas that of methyl group reorientation is not affected.

**Ammonium Heptafluoro Zirconate** \( (\text{NH}_4)_3\text{ZrF}_7 \)

Lahajnar et al.\(^7\) have studied the proton and fluorine NMR absorption line shape over a range 80-300 K. From the measured value of \( M_2 \) they conclude that ammonium group reorients almost isotropically at room temperature. Fluorine and PMR absorption and relaxation study of this compound over a range of temperature 77-293 K was carried out by Pintar et al.\(^7\). A line width transition due to low activation energy reorientation of two types of ammonium ions was observed. The fluorine absorption data also gave evidence of reorientation of Zirconium Fluorine complex. Two types of motion are found to be effective in relaxing the spin system to the lattice a slower one due to Zirconium fluorine ion reorientation and a faster one due to the reorientation of a weakly hydrogen bonded ammonium ions. The relaxation data exhibit strong F-H and H-F cross relaxations. At higher temperatures fluorine and protons relax essentially through the motion of \( \text{ZrF}_3^- \) complex, while at lower temperatures both spins relax through the reorientation of the ammonium ions.
<table>
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<td>Orthorhombic</td>
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<td>E (NH₄⁺) = 6.09±0.23 kcal/mole See Text [9]</td>
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<td>¹H and ¹⁹F M₂ (77 - 395 K), ¹H M₂ = 76 ± 4 G² &lt; 130 K</td>
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<td>= 1.58 kcal/mole for T &lt; 115 K</td>
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<td>NH₄MgF₃</td>
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<td>¹H T₁ E_a (NH₄⁺) = 1.69 kcal/mole for T &gt; 77 K</td>
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<td>= 0.69±0.04 kcal/mole for T &lt; 67 K [15]</td>
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$\text{NH}_4\text{BF}_4$

Orthorhombic
$\text{D}_{2h} (F \bar{4} \text{mm})$

Phase transition at 472 K

$\text{NH}_4\text{AlF}_4$

Tetragonal
$\text{D}_{4h} (P \bar{4} \text{mm})$

$T_c = 145$ K

$\text{ND}_4\text{BF}_4$

$\text{NH}_4\text{O}_2\text{BF}_4$

Orthorhombic
$\text{D}_{2h} (P \bar{4} \text{mm})$

Ferroelectric below $T_c$

$T_c = 176$ K

$\text{ND}_4\text{O}_2\text{BF}_4$

Orthorhombic
$\text{D}_{2h} (P \bar{4} \text{mm})$

$T_c = 191$ K

$\text{H}^1$ and $\text{F}^1$ $\text{M}_2$ studies (77 - 300 K) [16]

$\text{H}^1$ $\text{M}_2 = 20 \text{ G}^2$ at 77 K and 300 K

$\text{H}^1$ $\text{M}_2 = 22.1 \text{ G}^2$ at 77 K, 6.2 G$^2$ at 300 K

$\text{H}^1$ $\text{F}_1$ $\text{T}_1$ studies (77 - 300 K), cusp-like dip at $T_c$ [16]

$\text{H}^1$ $\text{M}_2 = 14.35 + 1.25 \text{ G}^2$ at 20 K, $4 + 0.16 \text{ G}^2$ at 173 K

$2.9 + 0.1 \text{ G}^2$ at 223 K.

$\text{H}^1$ $\text{M}_2 = 22.26 + 1.6 \text{ G}^2$ at 90 K

$\text{H}^1$ $\text{M}_2 = 19.1 \text{ G}^2$ at 133 K, 2.5 0.5G$^2$ at 180 K

$\text{F}_1$ $\text{T}_1'$, $E_a (\text{BF}_4) = 7.5 \text{ kcal/mole}$ [19,20,21.22,23.24]

$\text{H}^1$ $\text{T}_1$ studies, $E_a (\text{NH}_4^+) = 3.69 + 0.22 \text{ kcal/mole}$ and

$= 1.52 + 0.3 \text{ kcal/mole}$ [20,21]

$T_{1 \text{ min}}$ at 260 K and 110 K

$\text{D}^2$ NMR. Absence of H-bonds [18]

$\text{H}^1$ $\text{M}_2$. spin isomerism [27,28,37]

$\text{H}^1$ $\text{M}_2 = 8 \text{ G}^2$ for $T < 93$ K

$\text{F}_1$ $\text{M}_2$ studies

$\text{F}_1$ $\text{M}_2 = 11.0 + 0.5 \text{ G}^2$ at 90 K ($T < 173$ K

$= 4.2 + 0.2 \text{ G}^2$ at 250 K ($T < 293$ K

$\text{H}^1$ $\text{T}_1$ studies, $\text{F}_1$ $\text{T}_1'$ [30,31]

$\text{F}_1$ chemical shift [33,35]

$\text{H}^2$ NMR (103-293 K). (85-475 K) [34,35]
\((\text{CH}_3)_4\text{BF}_4\)

Orthorhombic at 300 K

Only one \(T_1\) min in \(^{19}F\ T_1\) studies at 202 K

\(E_a\) (BF\(_4\)) = 3.1 kcal/mole

\((\text{NH}_4)_2\text{SbF}_5\)

Two phase transitions

\(V_{\text{h} (C\text{mc})} Z=4\)

\(T_{c1}=257\) K (first order)

\(T_{c2}=145\) K (second order)

\((\text{NH}_4)_2\text{SbF}_5\)

\(E_a\) (SbF\(_5\)) = 8.0±0.5 kcal/mole

\((\text{NH}_4)_2\text{AlF}_6\)

Cubic

\(O_h^c (F_{3m}) Z=4\)

\(E_a\) (NH\(_4\) diffusion) = 11.06 kcal/mole

\((\text{NH}_4)_2\text{CrF}_6\)

Cubic

\(O_h^c (F_{3m}) Z=4\)

\((\text{NH}_4)_2\text{GeF}_6\)

Cubic

\(O_h^c (F_{3m}) Z=4\)

\(^{1}H\ and\ ^{19}F\ T_1\ studies\ [41]\)

Two \(^{1}H\ T_1\) min. at 256 K and 104 K

\(E_a\) (NH\(_4\)) = 4.9 & 4.3 kcal/mole

\(^{1}H\ &\ ^{19}F\ M_2\ studies\ (116-353\ K)\ [42]\)

\(^{1}H\ &\ ^{19}F\ T_1\ studies\ [43]\)

\(E_a\) (NH\(_4\)) = 2 kcal/mole

\(^{1}H\ &\ ^{19}F\ M_2\ studies\ (100-400\ K)\ [44]\)

\(E_a\) (NH\(_4\) diffusion) = 11.06 kcal/mole

\(^{1}H\ &\ ^{19}F\ M_2\) (80-297 K) [45]

\(^{1}H\ &\ ^{19}F\ M_2\) (130-400 K) [46]

\(^{1}H\ &\ ^{19}F\ M_2\) 20-300 K [47]

\(^{1}H\ M_2 = 6.6±0.2\) G\(^2\) at 90 K, \(^{19}F\ M_2 = 11.18±0.5\) G\(^2\) at 90 K

\(^{1}H\ T_1\) \& \(^{19}F\ T_1\) studies [25.48,51]

\(E_a\) (NH\(_4\)) = 1.31 kcal/mole

\(^{19}F\ T_1\) \& \(^{19}T_1\) studies [25.49,51]

\(E_a\) (GeF\(_6\)) = 13.3±1.6 kcal/mole
Phase transition at 18 K

\( C'_{\text{h}} \) \( m^3m \) \( Z=4 \)

Trigonal below 278 K

\[ 1^H \text{ and } 19^F \text{ M}_2 \text{ studies } [52,53] \]

\[ 1^H \text{ M}_2=6.4\pm0.2 \text{G}^2 \text{ for } 103K<311 \text{ K} \]

\[ 19^F \text{ M}_2=14 \text{G}^2 \text{ at } 93 \text{ K} \text{ and } 3 \text{G}^2 \text{ at } 303 \text{ K} \]

\[ 1^H T_1 \text{, T}_1P \text{ studies } [53,54,55,56,57,58] \]

\[ E_a (\text{NH}_4)=2.2 \text{kcal/mole for cubic form} \]

\[ E_a (\text{NH}_4)=1.11\pm0.03 \text{kcal/mole for trigonal form} \]

\[ 19^F T_1 \text{, T}_1P \text{ studies } [54,56] \]

\[ E_a (\text{SiF}_6)=15.1\pm0.5 \text{kcal/mole} [56], 17.0 \text{kcal/mole} [54] \]

\[ 19F T_1 \text{ pressure} \quad [59] \]

Cubic

\( D_{3d} \) \( C_3m \)

\[ \text{Triponal below } 118 \text{ K} \]

\[ 1\text{H M}_2 \text{ studies} \quad [47,61] \]

\[ 1^H \text{ M}_2=6.14\pm0.23 \text{G}^2 \text{ at } 90 \text{ K}, 11.06\pm0.12 \text{G}^2 \text{ at } 20 \text{ K} \]

\[ E_a (\text{NH}_4)=0.74 \text{kcal/mole} \]

\[ 19^F \text{ M}_2 \text{ studies} \quad [47,61] \]

\[ 19^F \text{ M}_2=9.71\pm0.38 \text{G}^2 \text{ at } 90 \text{ K} \]

\[ 1^H T_1 \text{, T}_1P \text{ studies} \quad [25,60,61] \]

\[ T_1 \text{ min. at } 55 \text{ K} [60], 57 \text{ K} [25]. E_a (\text{NH}_4)=1.8 \text{kcal/mole} \]

\[ 19^F T_1 \text{, T}_1P \text{ studies} \quad [61] \]

\[ E_a (\text{SiF}_6)=8.5\pm0.8 \text{kcal/mole} \]

Cubic

\[ T_\text{h} \quad Z=4 \]

\[ 1^H \text{ M}_2 \text{ studies} \quad (77-300 \text{ K}) \quad [63,65,66] \]

\[ 1^H \text{ M}_2=1.8 \text{G}^2 \quad (300 \text{ K}), 3.9\pm0.3 \text{G}^2 \quad (77 \text{ K}) \]

\[ 1^H \text{ M}_2 \text{, no pressure effect upto 14 kbars} \quad [67,68] \]

\[ 19^F \text{ M}_2 \text{ studies} \quad (77-300 \text{ K}) \quad [63,65] \]

\[ 19^F \text{ M}_2=16\pm1 \text{G}^2 \text{ (at } 77 \text{ } \& \text{ 300 K)} \]

\[ 19^F \text{ M}_2 \text{, no pressure effect upto 14 kbars} \quad [67,68] \]

\[ 19^F \text{ Chemical shift studies} \quad [64] \]

\[ ^2H \text{ and } 19^F T_1 \quad (20-300 \text{K}) \quad [62] \]
\([\text{([CH}_3\text{]_4}{\text{N}})_2\text{SbF}_6]\)  

\([\text{([CH}_3\text{]_3}{\text{NH}})_2\text{SmF}_6]\)

\([\text{([C}_2\text{H}_5\text{]_4}{\text{N}})\text{SbF}_6]\)  

Phase transition  

at \(T_{c1}=246\) K and  

\(T_{c2}=272\) K.

\([\text{([NH}_3\text{]_3}{\text{ZrF}}_7]\)

\(^1\text{H}\) and \(^{19}\text{F} T_1\) studies (15-460 K) \([69]\)

\(^1\text{H}\) and \(^{19}\text{F} N_2\) studies \([70]\)

\(^1\text{H}\) and \(^{19}\text{F} T_1\) studies \([71]\)

A discontinuity in \(T_1\) at \(T_c=246\) K

\(E_a((\text{[C}_2\text{H}_5\text{]_4}{\text{N}})=5.8\) kcal/mole (low temp.)

\(E_a((\text{[C}_2\text{H}_5\text{]_4}{\text{N}})=6.6\) kcal/mole (high temp.)

\(^1\text{H}\) and \(^{19}\text{F} N_2\) (80-300 K) \([72]\)

\(^1\text{H}\) and \(^{19}\text{F} T_1\) (77-293 K) \([73]\)
II.2 Chlorides

Single salts have been extensively studied. Step-wise substitution by CH₃ group for each hydrogen atom of the NH₄ ion leads to changes in the cation symmetry and has shown profound effect on their NMR spectra. Studies on double salts like ABX₃ and A₂BX₄ with NH₄ as cation are not many in the literature whereas with TMA ion, probably a much larger number of studies are available. Studies on these complexes are more probably because of easy crystal engineering. Most of the studies are from 77 K to room temperature.

Antiflourites of the type A₂BCl₆ with NH₄ cation are well studied and revealed certain general trends. The activation energy for the reorientation of the cation were found to be a function of the metal ion radius and unit cell edge. The phase transition temperature was found to be a function of the d-electron configuration of the metal atom.

Further studies down to liquid helium temperatures have shown tunnelling effects. (TMA)₂MCIs (M : Pt, Sn, Te) have shown peculiar hysteresis in their Tᵢ with temperature. In this section, an attempt to highlight the salient features of the wide-line and SLR results in chlorides has been made.
Ammonium chloride

Ammonium chloride is one of the most extensively studied compounds. It exhibits a weakly first order phase transition (\(\lambda\)-transition) at 242 K and atmospheric pressure. This order-disorder type transition is associated with the relative orientation of the tetrahedral \(\text{NH}_4^+\) ions in the unit cell which are sterically different as the four protons of ammonium ion are directed towards the four nearest neighbour chlorine ions forming hydrogen bonds. In the room temperature CsCl cubic phase (disordered), \(\text{NH}_4\) tetrahedra are dynamically distributed between these two energetically equivalent orientations. In the ordered phase, below the point the neighbouring tetrahedra point in the same direction, resulting in a microscopic ordering.

The first proton magnetic resonance experiments in \(\text{NH}_4\text{Cl}\) have been carried out by Bitter et al\(^{74}\) at 77 K and Alpert\(^{75}\) from 77 K up to 300 K. From these results they concluded that the phase transition is an order-disorder type and not due to the molecular rotation of ammonium group. The PMR studies of Sach’s and Turner\(^{77}\) and that of Purcell\(^{78}\) are also in agreement with the above conclusion. Gutowsky et al\(^{1,79}\) carried out PMR absorption studies in ammonium chloride and observed a line width transition at 129 K and found that the main contribution to \(M_2\) is intramolecular whereas the contribution due to the chlorine atom is the least. Similar studies by Cook and Drain\(^{78}\) did not show any discontinuity either in the line width or in the relaxation time at the point whereas a decrease in the line width above 128 K was observed revealing that the rate of rotation is too low to contribute to the specific heat at \(\lambda\)-point.

Single crystal PMR studies\(^{80,81}\) along (100), (110) and (111) directions showed a slight but discontinuous change in the \(M_2\) at the \(\lambda\)-point. Watton et al\(^{37}\) have obtained PMR absorption spectra at liquid helium temperature and found a value of 49.3 ± 0.5G\(^2\) at 4.2 K which is the rigid lattice value for ammonium ion and ruled out the possibility of any tunnelling in this salt.

Their \(T_1\) measurements at 4.2 K was 220 sec. with an estimated activation energy of 4.7 kcal/mole for the ammonium rotation in the high temperature. Woessner and Snowden\(^{85,86}\) from their \(^1\)H \(T_1\) studies (140-373 K) found a \(T_1\) change by a factor of approximately 2 at the \(\lambda\)-transition temperature. They estimated an activation energy

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as 4.7 kcal/mole and 6.9 kcal/mole respectively above and below the $\lambda$-transition. $T_1$ does not show any discontinuity with temperature but revealed a slope change at the $\lambda$-transition. Shimomura et al$^{87,95}$ and Sharp et al$^{90}$ have measured proton $T_1$, $T_1\rho$ in the range 1.3 to 500 K and found NH$_4$Cl to be a strongly hindered solid. Shimomura et al$^{95}$ have observed an anisotropy at $\lambda$-point in a $T_1$ vs. temperature plot and the results were explained in terms of the theory given by Bloembergen and Sorkin.

Kodama$^{89}$ has developed theoretical expressions for 4-fold and 3-fold reorientations of NH$_4^+$ ions and treated the phase transition dynamically due to $\pm 90$ flip about the 4-fold axis. He has argued that the broad minimum of $T_1$ and different slopes on either side of the $T_1$ minimum suggest more than one type of motion for NH$_4^+$ ion. The marked deviation from linearity in $T_1$ curve near about $T_C$ is due to the temperature dependence of the barrier heights which have been related to the degree of order in the lattice. The order parameter which is the probability of an ammonium ion taking a favoured orientation varies between 1 and 0.5. Michael$^{91}$ also has given a theoretical model for the SLR behaviour in NH$_4$Cl in terms of molecular reorientation. According to him the reorientation of NH$_4$ tetrahedra around C$_2$ axes in the neighbourhood of $T_C$ are described by a master equation. The theory explains the anomalous behaviour found experimentally for $T_1$ of protons around the phase transition at low pressure and high pressure. Huller and Kane$^{94}$ have proposed an electrostatic model to calculate theoretically the barriers to motion around C$_3$ and C$_2$ axes of NH$_4^+$ ion. Sharp and Pintar$^{101}$ have explained the observed relaxation behaviour as due to 3-fold reorientation of NH$_4^+$ ion. Exponential recovery of magnetization has been observed throughout the temperature range and no hysteresis in $T_1$ has been observed around $T_C$. They have derived the order parameter by assuming that each NH$_4^+$ ion is either in a domain of phase II or of phase III. The order parameter is found to vary between 1 and 0 in contrast to the results of Kodama$^{89}$. Petschek and Halpern$^{104}$ have considered the proton relaxation near $T_C$ theoretically using short distance, short time correlation functions of the kinetic model. They have proposed that due to the symmetry of the system, critically slowed motions of NH$_4$ ions should not have strong effect on the proton relaxation.

Temperature and pressure dependence (at 1 atm, 95 atm and 1920 atm) of proton SLR times were carried out by Trappeniers et al$^{83}$ and Anderson et al$^{84}$. $T_1$ minimum temperature shifts to higher with the application of pressure at a rate of 2/1000 atm. At the $\lambda$-point they found a remarkable change in $T_1$ at 1 atm. contrary to the earlier reports. From the $T_1$ temperature plot they estimated an activation energy as 6.1 kcal/mole and 4.2 kcal/mole respectively below and above the $\lambda$-point. Anderson et al$^{84}$ measurements over a temperature range 169 to 400 K under applied hydrostatic pressure of 1 to 680 atm, showed that the application of pressure had no apparent effect on $T_1$ contrary to the observations$^{83}$ and also there
was no detectable change in \( T_1 \) in passing through the \( \lambda \) - point. Activation energy for \( \text{NH}_4^+ \) rotation above the \( \lambda \) - point is 6 kcal/mole. Mandema and Trappeniers\(^9\) have noticed tricritical effects at a pressure of 2 k bar on the proton \( T_1 \). With pressure, \( T_c \) shifts towards higher temperature at a rate of 9 K/kbar with a gradual flattening of the anomaly in \( T_1 \) at \( T_c \) and the phase transition changes from first order to second order.

\[ ^{14}\text{N} \] and \( ^{35}\text{Cl} \) relaxation studies in \( \text{NH}_4\text{Cl} \) and \( \text{ND}_4\text{Cl} \) have been reported by Speight and Jeffrey\(^9\) and Cook and Jeffrey\(^9\) respectively. They found that \( ^{35}\text{Cl} \) nuclei relax mainly through the quadrupolar interactions where as both the dipolar and quadrupolar interactions contribute to \( ^{14}\text{N} \) relaxation. Kinetic Ising model was used to describe the critical dynamics of \( \text{ND}_4^+ \) ion near \( T_c \). It is found that in \( \text{NH}_4\text{Cl} \), the relaxation measurements are not sensitive to phenomena occurring with a critical wave vector \( q_c = 0 \). \( ^{35}\text{Cl} \) SLR measurements under high pressures up to 6 kbars has been carried out by Ueda\(^9\). Their results in the vicinity of the order-disorder transition temperature revealed that the sharpness of the transition decreases with increasing pressure. In the disordered phase the increase of \( T_1 \) with increasing pressure is explained as due to the increase in activation energy due to the lattice contraction. Itoh et al\(^8\) have measured the proton chemical shift, \( ^{35}\text{Cl} \) SLR time and found that the reorientational motion of the ammonium ion is the origin of the time dependent interaction necessary to relax the nuclear spin orientation. A discontinuity in \( ^{35}\text{Cl} \) \( T_1 \) was observed at the \( \lambda \) -point. Hoch et al\(^9\) from their \( ^{35}\text{Cl} \) relaxation time measurements obtained a value for the critical exponent \( \beta = 0.15 \) from the temperature variation of order parameter using the linearized Ising model.

Sharp and Pintar\(^\) have studied the temperature dependence of \( T_{1D} \) and rotating frame Zeeman energies, \( T_1 \) through cross relaxation dispersion. The results were discussed in the frame work of Blinc-Pirs Zumer theory. The detectable spins in this case were protons and fast relaxation spins are considered as chlorine. Morimoto et al\(^1\) have measured proton \( T_{1D} \) and compared it to \( T_1 \) and found a contradiction to the usual relation that \( T_{1D} \) is larger than \( T_1 \) which was interpreted in terms of the inter molecular interaction among \( \text{NH}_4^+ \) ions. \( T_{1D} \) of protons as a function of temperature in a single crystal of \( \text{NH}_4\text{Cl} \) was studied by Punkkinen\(^1\) and he observed a dip at the transition point in all the three directions.

**Deuterated Ammonium chloride \( \text{ND}_4\text{Cl} \)**

Deuteron magnetic resonance studies in powdered \( \text{ND}_4\text{Cl} \) was carried out by Chiba\(^1\) and Rabideau et al\(^1\) and found a single absorption line through out the temperature range from 213 K to 300 K with a constant line width. Chiba\(^1\) observed
a line width of $1.0 \pm 0.1$ kHz whereas Rabideau evaluated a value of $175.7 \pm 0.7$ kHz for the QCC of at 77 K. They failed to observe any quadrupole split spectrum at 77 K. However the same could be observed after irradiating the sample with γ-rays.

Similar $^2$D NMR in single crystals has been independently carried out by Hovi et al. and Linzer and Foreman. Their measurements were made at only angle and could not provide complete information where as Linzer and Foreman's single crystal work along (100) and (110) directions revealed a single line in the high temperature phase and line splittings in the low temperature phase. However they have not observed $^{14}$N line splittings in NH$_4$Cl as well as in ND$_4$Cl. They observed a QCC of 180 kHz at 77 K in agreement with Rabideau. Woessner et al. have studied the temperature dependence of deuteron $T_1$ at 9.5 MHz. A clear shift in $T_1$ by a factor of two at the $\lambda$-transition point (249.4 K) and the $T_1$ minimum occurred at 192 K. Deuteron $T_1$ studies in a mixture of (ND$_4$)$_2$PbCl$_6$ and ND$_4$Cl were studied by Ylinen et al. and activation energies for ND$_4$ were estimated. High pressure NMR studies of $^{35}$Cl have been done by Ueda and Itoh. Michel et al. have reported $^{14}$N and $^{35}$Cl relaxation in ND$_4$Cl.

Methyl Ammonium Chloride CH$_3$NH$_3$Cl

Mono methyl ammonium chloride exists in three phases, viz. $\alpha$, $\gamma$ and $\beta$. The phase of the sample depends upon the history of the specimen. When cooled slowly from the room temperature $\alpha$-phase, it goes to the $\gamma$-phase and the latter phase does not change into $\beta$-form although it is supercooled into the stability limit of the $\beta$-phase. The $\beta$-phase could be obtained by cooling the $\alpha$-phase rapidly to prevent the $\alpha$-$\gamma$ transition. The $\gamma$-phase is obtained either by slow cooling of the $\alpha$-phase or by warming up the $b$-phase.

CH$_3$NH$_3$Cl $\alpha$ phase $264\text{ K}$ $\gamma$ phase $220\text{ K}$ $\beta$ phase

Both wide line and pulsed NMR investigations have been carried out in different phases of CH$_3$NH$_3$Cl and their deuterated analogues. From the observed second moment transition, Tsau et al. have favoured the uncorrelated motion of the two groups of cation. Andrew and Canepa have shown that the uncorrelated motion of the two ends of CH$_3$NH$_3$ ion in a staggered configuration is energetically more favourable than in an eclipsed configuration from a theoretical calculation of the second moments. Tegenfeldt et al. have examined the PMR spectrum in all the three phases of CH$_3$NH$_3$Cl and its deuterated analogues.
CH$_3$ND$_3$Cl and CH$_3$NH$_3$Cl. The second moment jumps discontinuously at the transition but changes smoothly at the $\gamma$ - $\alpha$ transition.

Greater insight into the reorientational behaviour of the CH$_3$ and NH$_3$ groups in the various phases has come from proton relaxation measurements$^{115,117}$. The proton $T_1$ changes discontinuously by a large magnitude at the phase transition temperatures indicating that the phase transition is associated with the internal motions of CH$_3$ and NH$_3$ groups in the lattice. Tegenfeldt and Odberg$^{115}$ have discussed qualitatively the motion of reorienting groups and derived the motional parameters. Albert and Ripmeester$^{117}$ have carried out extensive $T_1$ and $T_{1P}$ measurements to resolve CH$_3$ and NH$_3$ group motions. In the $\alpha$-phase of CH$_3$NH$_3$Cl, the motions of CH$_3$ and NH$_3$ are relatively free with a low activation energy of 4.45 kcal/mole for CH$_3$. It is inferred that the rotation of CH$_3$NH$_3$ ion as a whole, probably takes place in this phase. But in the $\gamma$ and $\beta$ - phases, both the reorienting groups behave as a coupled one-dimensional rotars. The observed relaxation behaviour and the activation energies have been explained as due to different charge distributions over the cations in the $\beta$ and $\gamma$-phases.

**Dimethyl Ammonium Chloride [(CH$_3$)$_2$NH$_2$]Cl**

In alkyl ammonium salts, the dimethyl ammonium ion has the least symmetry compared to mono, tri and tetramethyl ammonium ions. Of the three dimethyl ammonium halides, only chloride has been investigated by magnetic resonance. It undergoes two structural phase transitions from a high temperature $\alpha$ - phase to $\beta$ - phase around 313 K and then to $\gamma$ - phase at around 260 K. $\beta$ - form has orthorhombic space group Ibam with layers containing (CH$_3$)$_2$NH$_2$ and Cl$^-$ ions. The cations and anions are arranged in a distorted NaCl structure. The $\alpha$-phase has a tetragonal structure.

Wide line NMR studies$^{116,118}$ have been reported by two groups of workers which are in disagreement with each other. Andrew and Canepa$^{116}$ have observed only one second moment transition with limiting values of 14.2 and 3.7 G$^2$ at 4 K and 330 K respectively. The low value of second moment at 4 K has been attributed to tunnelling motion of protons in the CH$_3$ groups and the high temperature value of the second moment has been ascribed to the two fold reorientation of the cation. In contrast to the above studies Sjöblom et al$^{118}$ observed two second moment transitions in the region 110-350K At low temperature it attained a rigid lattice value of 30G$^2$ in contrast to a small value of 14.2G$^2$ reported by Andrew and
Canepa\textsuperscript{116}. The second moment transition at 140 K is attributed to the methyl group reorientation while the other at 330 K was due to the reorientation of CH\textsubscript{3} groups combined with a reorientation motion of the whole ion among the equilibrium positions. From $^2$H NMR in (CH\textsubscript{3})\textsubscript{2}ND\textsubscript{2}Cl at room temperature they\textsuperscript{118} have predicted rapid reorientation of the NH\textsubscript{2} groups.

**Trimethylammoniumchloride** (CH\textsubscript{3})\textsubscript{3}NHCl

Trimethyl ammonium chloride is reported to undergo a structural phase transition from the high temperature $\alpha$-phase to the room temperature $\beta$-phase at 308 K. The structure of $\beta$-phase is monoclinic with a space group P2\textsubscript{1}m. Each cation and anion are joined by a hydrogen bond in a distorted NaCl structure. The structure of $\alpha$-phase is tetragonal with the 4-fold axis along the C-axis of $\beta$-phase. The 4-fold axis is close to or coincident with the N-H--Cl hydrogen bond. From this data it is inferred that the (CH\textsubscript{3})NH\textsuperscript{+} ion is disordered statistically or dynamically.

Both CW\textsuperscript{116,119} and pulsed\textsuperscript{120,121} NMR investigations have been carried out to study the dynamics of (CH\textsubscript{3})NH\textsuperscript{+} ion. At low temperature, methyl groups are slowed down as seen\textsuperscript{116} by the large rigid lattice second moment of 28G\textsuperscript{2}. The reduced second moment at 180 K has been attributed to reorientation of the whole cation about the triad axis combined with C\textsubscript{3} motion of methyl groups. The result of Sjoblom et al\textsuperscript{119} are more or less in agreement with those of Andrew and Canepa\textsuperscript{116}. The $\alpha$-$\beta$ transition has not shown up in $^1$H NMR studies. But the proton T\textsubscript{1} studies\textsuperscript{120,121} have revealed a discontinuity and change of slope at the transition temperature.

**Tetramethyl Ammonium Chloride** (TMACl) (CH\textsubscript{3})\textsubscript{4}NCl

This compound undergoes four structural phase transitions. The transition from phase I to phase II occurs at 536 K and in this phase the crystal is known to be piezo-electric. Further transition from phase II to III occurs at 400 K. It exists in phase III down to 184.9 K below which it undergoes a transition. Finally it undergoes an order-disorder type transition at 75.8 K. When the sample is cooled from phase I, the transition from phase II to III occurs only in the presence of traces of moisture or solvent. If the sample is dry, phase II continues to exist even up to room temperature.
in a supercooled state, without transforming to phase III. At room temperature i.e.,
in the phase III it crystallizes in the tetragonal form with a space group $P4_{21}2_{1}$
with two formula units per unit cell ($Z = 2$) phase I is face centered cubic with $Z = 4$.
Phase II is rhombohedral with $Z = 1$. Phase IV is tetragonal like phase III.

This compound has been the subject of both wide- line$^{116,122,123,126,127}$ and
pulsed$^{124,122,127}$ NMR studies. Dufourcq and Lemanceau$^{122}$ are the first to study the
$^1$H NMR of polycrystalline TMACl. The second moment variation with temperature
has shown two transitions, with three plateau regions. The low temperature (110 K)
plateau value of 33.1G$^2$ is due to rigid structure of N(CH$_3$)$_4$ ion. The high
temperature (270 K) second moment transition with a plateau of 1.53 G$^2$ has been
attributed to the quasi-isotropic reorientation of the whole cation. They have
obtained an activation energy of 6.5 kcal/mole and 8.2 kcal/mole for CH$_3$
reorientation respectively. The activation energies reported by Andrew and
Canepa$^{116}$ have observed only one second moment transition instead of the
expected two. They have reported an activation energy of 6.5 kcal/mole and 8.2
kcal/mole for CH$_3$ and cation reorientation respectively. The activation energies
reported by Andrew and Canepa$^{116}$ and Dufourcq and Lemanceau$^{122}$ agree with
each other for CH$_3$ reorientation but not for N(CH$_3$)$_4$ motion. This is due to the fact
that the investigations of Andrew and Canepa$^{116}$ pertain to phase II while those of
Lemanceau and Dufourcq$^{122}$ have been confirmed to phase III, the results of other
groups of workers$^{123,126,127}$ are in broad agreement with those of Andrew and
Canepa$^{116}$ and Dufourcq and Lemanceau$^{122}$.

Gibson and Raab$^{127}$ have carried out detailed investigations of proton T$_1$ and T$_{1P}$
in all four phases. T$_1$ changes discontinuously at the I-II as well as II-III transitions
and shows a change in the slope with temperature at the transition from phase III-IV.
Phase V, occurring below 75 K has not been investigated. T$_1$ shows a slightly
unresolved double minima at a frequency of 25.9 MHz. The low temperature minimum
has been attributed to the methyl group reorientation while the high temperature
minimum has been attributed to the tetramethyl ammonium group tumbling. Proton
T$_1$ measurements$^{127}$ in phase I have indicated the possibility of infrequent diffusion.
The proton relaxation exhibits an interesting behaviour in phase II which is reported
to be piezo-electric. This has been detected by the presence of a highly structured
spurious signal superimposed upon the FID, even in the absence of an external
magnetic field. The relaxation behaviour in phase II and III is found to depend on the
history of the sample. If the sample is evacuated in phase II ($T > 415 K$) no transition
to phase III occurs even down to room temperature i.e., it remains piezoelectric down
to room temperature. On the otherhand, the samples evaluated and sealed without
heating (in the presence of traces of moisture or solvent) revert to the phase III on
cooling from above (phase II). Phase I seems to be characterized by the methyl
and the isotropic reorientation of the tetramethyl ammonium ion with an activation
energy of 1.1 kcal/mole. Both in the phase II and III, the methyl and the cation reorientation continues. However in the phase IV, the slowing down of these groups are associated with an activation energy of 4.7 kcal/mole. Similar T1 studies have been reported by Albert et al\textsuperscript{124,125} whose results are in good agreement with those of Gibson and Raab\textsuperscript{127}.

The high temperature structural modifications of TMACl which exist between 298 K and 607 K were investigated by Albert et al\textsuperscript{128} from proton SLR T1 and T1p measurements. They found a discontinuity in T1 at the phase transition temperature 536 K, below which it was temperature invariant. T1p data suggest the onset of a very slow self diffusion process of the cations with a activation energy of about 20 ± 3 kcal/mole. Polak\textsuperscript{129} used the NMR second moment values to evaluate the librational amplitudes of the libration of TMA\textsuperscript{+} ion as a whole and librations of the methyl groups. They found that these values agree very well with experimental frequencies calculated using IR data.

\textbf{\textit{α}} -Ammonium Trichloro Mercurate \textit{NH₄HgCl₃ (α-form)}

Proton and \textsuperscript{35}Cl SLR in \textit{α}-ammonium Hg(II) chloride was carried out by Sagisawa et al\textsuperscript{130}. The proton T1 data is explained in terms of C\textsubscript{3} reorientation and S\textsubscript{4} flip of NH\textsubscript{4} ions. A marked change in the proton T1 at 55 K indicates a phase transition as attributed to the ordering of the NH\textsubscript{4} ions.

Ammonium Trichloro Magnesium \textit{NH₄MgCl₃.6H₂O}

Wide line NMR spectra of this compound which is a member of the family (Carnallites) were studied by Schnabel et al\textsuperscript{131}. Temperature variation of PMR spectra shows a stepwise decrease in the second moment with increasing temperature values indicative of rapid reorientation of all water molecules around a fixed axis.

Ammonium Trichloro Stannate \textit{NH₄SnCl₃ / ND₄SnCl₃}

Hallsworth and Pintar\textsuperscript{133} studied the proton spin lattice relaxation of this salt over a temperature range of 300 to 1.4 K. They used Clough model for discussing the low temperature tunnelling relaxation and found this to be a weakly hindered solid. Knispel et al\textsuperscript{132} carried out the deuteron magnetic resonance spectra of...
ND₄SnCl₃ at 4.2 K. The observed spectra were narrow even at 4.2 K with a line width of the order of 4 kHz and this was attributed to tunnelling. No change in the line width was observed even when the temperature is lowered to a value of 1.7 K. Both these salts have shown a wing like structure in the derivative spectra.

**Methyl Ammonium Lead Tri Chloride** CH₃NH₃PbCl₃

This salt belongs to perovskite family with cubic structure at room temperature and is known to undergo a phase transition at 175 K. The ²H and ¹⁴N wide line NMR spectra as well as the spin-lattice relaxation time have been carried out by Wasylishen et al. In the cubic phase the spectra consist of a single and sharp resonance line for both the nuclei and does not show any quadrupole splittings indicating the extremely rapid overall reorientation of the CW axis in a potential of cubic symmetry. Approximate activation energy Eₐ for cation reorientation is around 1.2 kcal/mole at about 300 K. However the temperature dependence of T₁ (²H) do not follow the simple Arrhenius plot. They conclude from the T₁ results that the rotation of the cation about the C₃ axis is less hindered than the rotation of the C₂ axis. Further in phase II the ²H spectra exhibit a characteristic deuterium quadrupole powder pattern with a splitting of ≈ 40 kHz and an asymmetry parameter 'η' less than 0.1. This value of quadrupole splitting corresponds to [3(e²Qq/4h)]/3 where e²Qq/h is the ²H quadrupolar coupling constant (≈ 160 kHz) and is characteristic of n-fold (n > 3) disorder of the N-D bond about a tetrahedral axis (the C-N bond). i.e., at temperatures below 175 K rotation of the N-D bond are restricted to reorientation about the C-N axis.

**Trimethyl Ammonium Cadmium Chloride** (CH₃)₃NHCdCl₃

Trimethyl ammonium cadmium chloride has been studied using proton T₁ studies and CW NMR by Walther et al. This salt is known to undergo three successive phase transitions at 342, 274 and 415 K according to Walther et al. Group theoretical analysis of the structural phase transition sequence in this compound was done by Zuniga et al. The room temperature structure is orthorhombic whereas the other two phases are hexagonal. They conclude that hydrogen bonds exist between the organic group and chlorine atoms. The phase transition sequence can be written as

\[ \text{ORT}(P_{bnn} Z = 4) \rightarrow 342 \text{K, HHT1 (P}_{63/m} Z = 18) \rightarrow 374 \text{K, HHT2 (P}_{63/m} Z = 6) \]
$^1$H $T_1$ as a function of temperature over a range 100-450 K in (CH$_3$)$_3$NH$_2$CdCl$_3$ and (CH$_3$)$_3$NDCl$_3$ is studied by Walther et al. They found a single line which implies that the frequency of hindered molecular motion is much higher than the proton line width which is of the order of 10 KHz. So CH$_3$ group must perform rapid motions. The temperature dependence of PSLR time in both protonated TrmCd and the deuterated compound is exponential in the whole temperature range, thus reflecting again the equivalence of the various protons.

The relaxation below 160 K is attributed to rapid rotation of CH$_3$ group around their C$_3$ axis, Ea value of 0.11ev was estimated for this motion. The phase changes observed around 374 and 415 K are correlated with a decrease of the rate of change of relaxation time which is attributed to an increase in freedom of the molecular motion of the (CH$_3$)$_3$NH group.

Proton absorption experiments carried out by Walther et al. in single crystal of this salt at room temperature, the absorption was a perfect Gaussian where as a triplet structure is clearly identified at 80 K. the triplet structure is interpreted by assuming rapid rotation of the CH$_3$ groups around their symmetry axis. The relaxation data were interpreted in terms of three types of motions: (1) CH$_3$ motion (2) hindered rotation (3) tumbling motion, with the corresponding correlation times $\tau_c$, $\tau_{c1}$, and $\tau_{c2}$ and the activation energies for each one of these motions were evaluated. The deuteron NMR spectra for different orientations of the crystal was carried out. The spectra was independent of temperature between 280 K. Till 342 K which is phase transition temperature each of the three pairs of signals of the low temperature phase is split into a doublet, each signal again with a fine structure.

Tsang and Utton have carried out proton SLR time and second moment ($M_2$) measurements as a function of temperature. Discontinuities in $T_1$ at 104 and 119 K indicate the low temperature phase below 104 K, the correlation time for hindered motion of one of the methyl groups is some what different from that of the other three. Using this model, the calculated $T_1$ and $M_2$ values are in satisfactory agreement with the experimental data. For the low temperature phase, the activation energies of the TMA$^+$ ion, 2.0 ± 0.3 and 1.6± 0.3 kcal/mole (8.4± 0.3 and 6.7± 1.3 kJ/mole) are considerably lower than the values 5.5 - 11 kcals/mole observed for the TMA halides. In the high temperature phase, the activation energy decreases even further to 0.7± 0.2 kcal/mole (2.9±0.8 kJ/mole). This decrease is in accordance with other order-disorder phase transitions involving tetrahedral ions.

The model used was similar to that of Albert et al. There are two types of motions for the TM ion, the overall tumbling of the whole tetrahedral ion, and the reorientation of the CH$_3$ groups about their C-N axis. High temperature crystal
structure is hexagonal $P_{63}m$ and it transforms to monoclinic. The phase transitions are of order-disorder type, driven by the ordering of the TMA ions.

**Tetramethyl Ammonium Trichloro Mercurate $\text{(CH}_3\text{)}_4\text{NHgCl}_3$**

This is one of the trichloro mercurates which is a ferroelectric and belonging to $ABX_3$ system. ($A$ = cation, $B$ = metal ion, $X$ = halogen). TMA trichloromercurate decomposes at 473 K without showing a curie point. The crystal structure of trichloromercurate is reported to be monoclinic with space group $P_2_1$. Ludin and Zeer$^{140,141}$ have studied the proton NMR absorption spectra over a temperature range from 4.3 to 300 K. They observed a second moment transition at 120 K from a value of $23.8 \pm 1.9 \text{ G}^2$ (at 83 K) to $10.0 \text{ G}^2$ above 130 K. At low temperatures the CH$_3$ groups were considered to be rigid. They observed decrease in second moment may not only be due to the rotation of Me groups about the C-N bonds, but also with the subsequent reorientation of (Me$_4$N)$^+$ tetrahedral ions around random ones. It was concluded that H-bonds do not participate in the mechanism of spontaneous polarization as TMAHgCl$_3$ remains FE upto its decomposition temperature. They also found that the potential barrier hindering the reorientation of TMA$^+$ ions is the highest in TMAHgCl$_3$ compared to corresponding Bromide and Iodide compounds, and the signal in this compound at room temperature was very narrow. Sharma$^{142}$, Sharma and Ramakrishna$^{143}$ have carried out proton SLR time $T_1$ studies in this compound over a temperature range from 107 - 425 K. Two minima were observed in $T_1$ vs temperature plot, one at 199.6 K and the other at 166.4 K. The high temperature minimum is attributed to TMA$^+$ ion reorientation whereas the low temperature second minimum was characteristic of random reorientation of the methyl group. The $E_a$, activation energy for the TMA$^+$ ion was more in the case of TMAHgCl$_3$ compared to its isomorphous bromide and iodide compounds. $E_a$ for TMA ion reorientation was estimated as 6.38 kcal/mole.

**Ammonium Tetrachloro Aluminate $\text{NH}_4\text{AlCl}_4$**

Ammonium tetrachloro aluminate crystallizes in the orthorhombic system, space group $Pnma$. Mairessi et al$^{144}$ have carried out proton NMR absorption spectra of single crystals of this compound over a temperature range 80-298 K Second moment of the absorption line remains equal to $4\text{ G}^2$ throughout the range which shows that
the ammonium ion is exhibiting almost free rotation about its axes, resulting in the dipole interactions going to nearly zero.

**Diammonium Tetrachloro Zincate (NH$_4$)$_2$ZnCl$_4$**

Diammonium tetrachloro Zincate is a member of the family of halide ferroelectrics with several successive phase transitions. It transforms from the high temperature normal phase I to a ferroelectric phase II at 406 K and to antiferroelectric phase III at 319 K and finally to ferroelectric phase IV at 270 K. The room temperature structure (phase III) is reported to be monoclinic. This structure consists of NH$_4$ and ZnCl$_4$ tetrahedra which are connected by a network of hydrogen bonds.

Proton M$_2$ and T$_1$ studies carried out by Sundaram et al.$^{145,147,204}$ show that the M$_2$ value is small (2.1G$^2$) and independent of temperature throughout the range of study (140-410 K) indicating the rapid reorientation of NH$_4$ ions. From the T$_1$ measurements two inequivalent NH$_4$ ions in the unit cell are observed. Around 319 K a transition from AFE - FE phase occurs associated with a discontinuous change in the value of T$_1$ by a factor of two.

Ingman et al.$^{146}$ carried out the study of proton spin-lattice relaxation and ammonium rotational tunneling in (NH$_4$)$_2$ZnCl$_4$, as functions of both temperature and resonance frequency. They found the tunnel levels of this compound to be exceptionally sharp, facilitating the study of tunnel frequencies over a wide range of temperatures. Additional insight into NH$_4$ reorientation was obtained from the study of T$_{1D}$.

**Diammonium Tetrachloro Palladate (NH$_4$)$_2$PdCl$_4$**

$^1$H T$_1$ studies$^{148}$ revealed a first order phase transition at 132 K with a thermal hysteresis and the transition was found to be of the order-disorder type.

**Methyl Ammonium Tetrachloro cadmate (CH$_3$NH$_3$)$_2$CdCl$_4$**

This is one of the perovskite type layer compounds having successive structural phase transitions as follows.

$I4/mmm$ 483 K  $Cmca$  279 K  $P4_2$/nmc.  164 K  $P2_1$/C

The transition from the room temperature orthorhombic phase to the tetragonal phase at 279 K as well as the transition to the monoclinic phase at 164 K are known.
to be of first order. However much information is not available about the high temperature phase above 483 K.

Proton M$_2$ and T$_1$ studies by Blinc et al$^{149}$ (in all the three phases except the high temperature phase) show a change in M$_2$ at 164 K ($\Delta$ M$_2$ $\sim$ G$^2$) at TLT to monoclinic transition, but there is no observable change in M$_2$ ($\Delta$ M$_2$ $\sim$ G$^2$) at orthorhombic to TLT transition. Over the whole investigated temperature range the proton spectra are characteristic of rapidly rotating NH$_3$ and CH$_3$ groups. The observed line width transition around 173 K is thus not produced by a freezing in of the CH$_3$ or NH$_3$ rotation but by the disappearance of the flipping motion of the whole CH$_3$NH$_3$ group. Theoretical evaluation of M$_2$ for various possible motions of CH$_3$NH$_3$ allowed by H-bonding schemes in different lattices have been done. In all models the change in M$_2$ at the monoclinic -TLT transition is consistently too large compared to the observed change at the TLT-ORT transition. A possible explanation of this behaviour may be the change in the N-H bond length and H-H distance due to the distortion in the chloride octahedra motion and the resulting change in the N-H..Cl H bonding scheme on going into the monoclinic phase. The temperature dependence of T$_1$ shows that T$_1$ increases with increasing temperature in the whole investigated temperature region demonstrating that the thermally activated motions responsible for the SLR process (NH$_3$ rotation CH$_3$ rotation and the motion of the CH$_3$NH$_3$ group as a whole) are much farther than the proton larmor frequency, whereas there is only a very small change in T$_1$ at the ORT-TLT transition, there is a drastic drop in T$_1$ at the TLT-monoclinic phase change, i.e., at the same temperature as that at which the proton line width transition sets in due to the freezing in of the motion of CH$_3$NH$_3$ groups as a whole.

Methyl Ammonium Tetrachloro Zincate (CH$_3$NH$_3$)$_2$ZnCl$_4$ and its Deuterated Analogues

The room temperature ferroelastic phase of this compound is known to have monoclinic structure with a space group P2$_1$/c and Z = 4. The structure consists of isolated ZnCl$_4$ tetrahedra and CH$_3$NH$_3$ chains, which are bridged by a three dimensional network of hydrogen bonds. This structure has more similarity with the orthorhombic K$_2$SO$_4$ group of compounds than the perovskite group. ZnCl$_4$ tetrahedron appears to be slightly distorted presumably due to hydrogen bonding. Each methyl ammonium ion is surrounded by four Cl$^-$ ions at approximately same distance, and is likely to form four hydrogen bonds. The structure in the high temperature phases II and I are not known. However from group theoretical
consideration, phase II is known to be orthorhombic (Pnma). This compound is known to have the following sequence of phase transitions.

phase I 483K Phase II 426K Phase I (Pnma → P2₁/a)

Specific heat measurements have shown two peaks at 426 K and 483 K and both the peaks are associated with marked thermal hysteresis indicating that the phase transitions are of first order. Proton T₁ studies in the range from 77-305 K revealed a single minimum between 107-113 K for protonated and at 103 K for deuterated salts. The observed T₁ minimum was unambiguously assigned to the CH₃ group reorientation. The discrepancy in observed and calculated T₁ minima in deuterated salt is attributed to the cross correlation effects and that in the protonated salt to a spin diffusion process in which the protons of NH₃ and CH₃ groups are related.

Tetramethyl Ammonium Tetrachloro Mercurate [(CH₃)₄N]₂HgCl₄

[(CH₃)₄N]₂HgCl₄ is orthorhombic with space group Pnma. The proton T₁ studies in the range 77-500 K, showed two well resolved minima, at 202.9 K and at 170.9 K due to the reorientation of TMA ion as a whole and the reorientations of the methyl group alone respectively.

Tetramethyl Ammonium Tetrachloro Zincate [(CH₃)₄N]₂ZnCl₄

This is a ferroelectric below at 279 K and also exhibits many other interesting properties. It undergoes successive phase transitions and has six polymorphic phases at atmospheric pressure as shown below. It transforms from paraelectric phase I to incommensurate phase II at 293 K, to ferroelectric phase III at 279 K and then to paraelectric phase IV at 181 K and 161 respectively. The transition from phase I to II is of second order while that from II to III and from III to IV are first order. At room temperature (phase I) the structure is orthorhombic with space group D₁₆h Pmcn and has four molecules in the unit cell. There are two types of tetramethyl ammonium ions in the unit cell.

Blinc et al have carried out ¹³C line width and chemical shift studies in all the phases. The high temperature measurements show that all the TMA ions are equivalent. Absence of anisotropic broadening reveal the over all tumbling motion of TMA ion as a whole together with the rotation of CH₃ groups. During the transition from paraelectric to the incommensurate phase, there is a considerable increase in the ¹³C line width and a decrease in the ¹³C chemical shift, indicating that N(CH₃)₄ ions are inequivalent. On going to the commensurate FE phase there is another drop in ¹³C chemical shift and a sharp decrease in the resonance line width, which is due to increase in the difference between the occupation probabilities of the different ¹³C
sites. In the paraelectric phases IV and V there is still a single $^{13}$C line. The $^{13}$C chemical shift slowly and monotonically decreases and the line width of the line monotonously increases with decreasing temperature.

Below 161 K in phase VI, the $^{13}$C line in the powdered sample suddenly disappeared demonstrating a huge increase in the line width due to a sudden slowing down or a very strong biasing of the $^{13}$C nuclear exchange between the different $^{13}$C sites and the increased inequivalency between different N(CH$_3$)$_4$ ions.

Proton $M_2$ and $T_1$ are in agreement with that of $^{13}$C data. The proton $M_2$ value was found to be 1.5 G$^2$ at 303 K and increases to 2.5 G$^2$ at the onset of the incommensurate phase at 293 K and remains constant at that value down to 163 K below which it increases to 6G$^2$ at 123 K (phase VI). The high temperature $M_2$ is assigned to TMA ion reorientation whereas at low temperatures CH$_3$ motion still persists. $^1$H $T_1$ studies$^{147,152}$ over a range 77-420 K reveal the following features. They$^{147}$ observed a change in slope of $T_1$ at 293 K which corresponds to the paraelectric to incommensurate phase transition, whereas as at all other phase transitions $T_1$ changes smoothly. Further $T_1$ vs 1000/T exhibits two minima, sharp one at 164 K and another smeared one between 113 to 120 K. The high temperature minimum was attributed to the overall tumbling motion of N(CH$_3$)$_4$ ion as a whole whereas the low temperature minimum suggests the presence of two inequivalent methyl groups; hence two inequivalent TMA ions.

Proton $M_2$ studies by Sundaram et al$^{147}$ over a temperature range 140-380 K revealed a single motionally narrowed line in phase I with a second moment (1G$^2$) characteristic of overall tumbling motion of TMA ion. In phases II and III the spectra have a peculiar line shape consisting of narrow and broad components super imposed on each other and attributed it to CH$_3$ group undergoing fast motion. However the $M_2$ value remains constant down to 180 K below which it broadens. The proton $M_2$ studies at ambient pressures over a range 4.2 K to 300 K and at various pressures (up to 15 kbars) at various temperatures have been carried out by Arumugam et al$^{197}$. They found that the $M_2$ transition temperature (160 K at ambient pressure) shift towards higher temperatures with increasing pressure, a shift of about 40 K was observed at 15 kbars. The room temperature $M_2$ value is attributed to TMA ion tumbling motion.

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Tetramethyl Ammonium Tetrachloro Magnesium \[\text{[(CH}_3\text{)}_4\text{N}]_2\text{MgCl}_4\]

This also belongs to the \(\text{A}_2\text{BX}_4\) family but is not known to be a ferroelectric. Proton \(T_1\) studies \(^{150}\) over a range 100-365 K show that \(T_1\) decreases monotonically with decreasing temperature and reaches a deep but broad minimum around 161.5 K. The results are interpreted in terms of the random motions of methyl groups and TMA ion. This compound did not show any double minima in contrast to the other isomorphous compounds such as \[\text{[(CH}_3\text{)}_4\text{N}]_2\text{ZnCl}_4\] and \[\text{[(CH}_3\text{)}_4\text{N}]_2\text{HgCl}_4\].

Diammonium Hexa Chloro Irridate \((\text{NH}_4)_2\text{IrCl}_6\)

This is one of the few magnetic materials which is studied using NMR as a probe. It has a f.c.c. structure and to a fair approximation is a Heisenberg antiferromagnet, with isotropic interactions. Proton spin-lattice relaxation and line shape measurements by Svare and Raaren \(^{153}\) revealed a narrow line, even below the antiferromagnetic temperature \(T_N\) (2.15 K) which was attributed to rapid \(\text{NH}_4^+\) tunnelling.

Diammonium Hexachloro Osmate \((\text{NH}_4)_2\text{OsCl}_6\)

This has a cubic structure and belongs to the family of antifluorites. Temperature dependence of proton \(T_1\) \(T_{1p}\) measurements were done at different frequencies by Svare et al \(^{154}\) on protonated and partly deuterated samples.

Diammonium Hexachloro Plumbate \((\text{NH}_4)_2\text{PbCl}_6\)

This is another important member of the family of antifluorites having a cubic structure. Proton resonance line shape analysis of \((\text{NH}_4)_2\text{PbCl}_6\) by Lalowicz et al \(^{24}\) shows that experimental line shape is best simulated by assuming tunnelling and rapid reorientational jumps around a \(C_2\) axis. The experiment \(M_2\) is 5.8 ± 0.5\(G^2\) and is in good agreement with the observed value of 6\(G^2\) reported by Punkkinen et al \(^{161}\) from the FID measurements. The composite motion of ammonium ion about \(C_3\) at \(C_2\) axes is believed to be brought about by the coupling of rotor states of the ion with lattice phonons resulting in line narrowing.

Tuohi et al \(^{156,160}\) and Punkkinen et al \(^{157}\) have carried out \(^1\text{H} T_1\) studies at 9, 22 and 42 MHz over a range 4.2 - 300 K. They found three \(T_1\) minima at 69 K, 40 K and 20 K a Larmor frequency of 22 MHz, whereas as at 9 MHz only two minima at 69 K and 44 K were observed. Further the second minimum was found to shift to lower temperatures with increasing Larmor frequency. The high temperature minimum was ascribed to the \(\text{NH}_4\) ion reorientation. Additional \(T_1\) minima can be ascribed to the tunnelling \(\text{NH}_4\) ion with the condition \(\omega_t = n \omega_0 \quad n = 1, 2 \ and \ \omega_0\) is the tunnel
splitting between T and A species of the torsional ground state of NH₄⁺ ion. The tunnel splitting was found to be temperature dependent. The recovery of magnetization was found to be non-exponential below 20 K.

Punkkinen et al. have studied the proton T₁D at 23.8 MHz in the range 4.2 to 90 K and found the relaxation at 4.2 K to be remarkably non-exponential which decreased with increasing temperature until at 60 K, where it shows exponential relaxation. Two minima were observed in T₁D at 70 K and at 30 K which are assigned evidence of tunnelling below 70 K and the other minima occurred at 30 K the temperature at which the FID shape changes. They interpret the results in terms of the possible motions, one fast and the other being slow, which is also supported by M₂ measurements. They conclude that below 30 K 180° tunnel reorientation motion of ammonium is faster than the 120° (3-fold) reorientation.

Punkkinen has proposed a model to explain additional minima and non-exponentiality in T₁ at low temperature by assuming a common Zeeman spin temperature for all nuclear spin isomers. According to him additional minima and non exponentiality are expected to be observable in the region 0.5 ≤ ωe/ωo ≤ 3 where ωo is the zeeman splitting and t is the average separation between the T and A species torsional ground states. For vanishing tunnel splittings the model agrees with the existing theories. The model successfully explains the experimental results in (NH₄)₂PbCl₆.

The magnetic field dependence of proton zeeman relaxation studies at 20 K and 43 K, revealed that T₁ vs. Larmor frequency exhibits tunnelling maxima at 22 MHz and 44 MHz for T = 20 K and at 21 MHz for T = 43 K and the results were explained using Punkkinen's model.

Punkkinen et al. have carried out PSLR time measurements and calculated M₂ from FID signal. Their results suggest that the proton FID consists of the two components with temperature independent second moments 0.7 and 11.5 G². The temperature dependence of the corresponding weights lead to a decrease in the total second moment from 6 G² at 4.2 K to 2G² at 50 K. These results are explained in terms of a model which assumes that the ammonium ion tunnelling splittings are much larger than H w and the rates K₂ and K₃ of the 180° and 120° reorientations of the ammonium ion respectively obey the equations K₂ > > Δω and K₃ < < Δω, where w is the line width.

Proton T₁, T₁D studies below 20 K in pure and partly deuterated salts has been done by Svare et al. and the results are explained in terms of one-phonon relaxation a T and two-phonon relaxation a T². Calculation from Debye. Spectrum of acoustic phonons agree very well with the two-phonon relaxation but fairly completely for the one-phonon relaxation. The one-phonon results can be explained.

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by assuming a fluctuation spectrum independent of up to $10^{10}$ Hz from life time broadened torsional oscillators. Deuteration increases the one-phonon relaxation.

**Diammonium Hexachloro Palladate (NH$_4$)$_2$PdCl$_6$**

Svare et al.$^{154,162,171}$ Proton T$_1$, T$_{1p}$ studies in this complex at different frequencies from 4 to 48 MHz over a range 4.2 to 100 K. The results below 20 K can be explained using the following relation between $\omega_0$ and $\omega_\perp$.

$$T_1^{-1} = 4 \times 10^{-7} \omega T^2 / \omega_0^2 + 10^{-30} (\omega_0)^4 T^5 / \omega_0^2$$

$\omega_1$ is the AA-TT tunnelling frequency in NH$_4$. This is explained as one-phonon relaxation $\alpha_1 T$ and two-phonon relaxation $\alpha_2 T^2$, calculation from Debye spectrum of acoustic phonons agrees very well with the two-phonon relaxation but fails completely for the one-phonon relaxation. The one-phonon results can be explained by assuming a fluctuation spectrum independent of $\omega$ up to $10^{10}$ Hz from life time broadened torsional oscillators. Deuteration increases the one-phonon relaxation. Smith$^{174}$ has computed activation energies for this compound using an expression for the potential function and its parameters were determined from the vibrational frequencies. The tunnelling frequencies are determined using a pocket state formalism using anharmonic effects.

**Diammonium Hexachloro Platinate (NH$_4$)$_2$PtCl$_6$**

This also belongs to the family of antifluorite structure and has been widely studied using NMR technique. Proton M$_2$ and T$_1$, T$_{1p}$ studies$^{163}$ over a range 4.2-296 K show a very low M$_2$ (1.23G$^2$ at 4.2 K and 0.42 G$^2$ at 120 K, and a broad asymmetric minimum for both T$_1$ and T$_{1p}$ and results are explained in terms of Haupt's theory taking into account tunnelling and spin isomerism of NH$_4$ group.

Proton T$_1$, T$_{1p}$ studies by Svare et al.$^{171}$ over a range 40- 300 K agrees well with that of Armstrong et al.$^{163}$ and disagrees with that of Bonorl and Terenzi$^{165}$. Smith$^{174}$ has estimated the activation energy for NH$_4$ using the potential function with anharmonic oscillator wave functions and results agree with the experimental values.

PMR studies$^{24}$ at 4.2 K showed a narrow line which is explained in terms of a composite motion of ammonium ion about C$_3$ and C$_2$ axis and they believe that this motion is brought about by the coupling of rotor states of the ion with the lattice phonons.
Lalowicz et al\textsuperscript{164} from the deuteron T\textsubscript{1} studies over a range 1.7-40 K found a shallow level crossing minima in the frequency dependence. The tunnel splittings between the A and E symmetry levels were estimated as about 10.8 MHz.

**Diammonium Hexachloro Rhenate (NH\textsubscript{4})\textsubscript{2}ReCl\textsubscript{6}**

This is another magnetic material studied by NMR. This has an antiferromagnetic (AFM) transition at 10 K. Svare and Raaben\textsuperscript{153} have carried out proton spin-lattice relaxation below the AFM transition temperature and found an abrupt change in T\textsubscript{1} value at T\textsubscript{c}. Svare et al\textsuperscript{173} have estimated the tunnel frequency \( \omega_t \) as 12 MHz.

**Diammonium Hexachloro Ruthenate (NH\textsubscript{4})\textsubscript{2}RuCl\textsubscript{6}**

Svare et al\textsuperscript{173} from their proton relaxation measurements on this compound concluded that paramagnetic relaxation should be relatively small. Perhaps the short (T\textsubscript{1}) is a result of some paramagnetic contribution to T\textsubscript{1}^{-1} near room temperature. The T\textsubscript{1} minimum around 120 K is clearly caused by NH\textsubscript{4}\textsuperscript{+} motion, but it is only half as deep as expected for isotropic motion. Therefore the NH\textsubscript{4} ion must have more than one mode of motion and part of the relaxation due to motion must be contained in the T\textsubscript{1} minimum below 80 K. This is possible if the lattice is non-cubic so that NH\textsubscript{4}\textsuperscript{+} ion can reorient about different axis with different E\textsubscript{a} or the unit cell may contain inequivalent NH\textsubscript{4} ions. X-ray crystal structure data show that at room temperature, the salt is non-cubic as expected from relaxation results.

**Diammonium Hexachloro Stannate (NH\textsubscript{4})\textsubscript{2}SnCl\textsubscript{6}**

This is another important member of the A\textsubscript{2}MX\textsubscript{6} family having antifluorite structure and extensively studied by NMR due to its diamagnetic nature. PMR line shape studies\textsuperscript{24} at low temperatures (4.2 K) showed a very narrow line which has been explained in terms of the tunnelling reorientational jumps of ammonium ion around C\textsubscript{3} or C\textsubscript{2} axes separately. They also assumed crystal field symmetry to be low enough to remove the three fold degeneracy of the T torsional sublevels. Watton et al\textsuperscript{37} also have carried out proton T\textsubscript{1} and line width studies and their M\textsubscript{2} results are in agreement with earlier studies\textsuperscript{24}. Proton T\textsubscript{1} T\textsubscript{1P} studies\textsuperscript{55,166,167,169} over a range of temperatures have been done. Their studies\textsuperscript{166} over a range 20-125 K show two T\textsubscript{1} minima, the minimum at 57 K is ascribed to the reorientation of NH\textsubscript{4} group while the other at 29 K is explained in terms of tunnelling assisted process. A tunnel splitting of 3 MHz was obtained. The results of Strange and Terenzi\textsuperscript{55} over a temperature range of 60-500 K revealed that reorientation of NH\textsubscript{4} ion is the dominate relaxation which leads to a broad T\textsubscript{1} minimum. However no minimum was observed for T\textsubscript{1}. Vander Klinck et al\textsuperscript{167} observed a peculiar behaviour in \(^{35}\text{Cl}\) NQR of
(NH₄)₂SnCl₆ below 80 K. An unusual ratio of T₁ (Cl³⁷)/T₁(Cl³⁵)=2.4 and was explained as due to the dipolar coupling of ⁳⁵Cl to the tunnelling ammonium protons. Proton T₁ studies as a function of frequency (5.5 to 61.5 MHz) at 20 K show that relaxation is clearly non-exponential at higher frequencies and less so at lower frequencies.

Svare et al⁵⁷,¹⁶² have studied proton T₁, T₁₁₃ at various temperature ranges and found a frequency independent minimum at the transition to classical relaxation at about 40-70 K. Tunnel frequencies were calculated from T₁ and T₁₁₃ data using the relation \( \omega = 4 \times 10^9 \frac{1}{T₁₃} \) min (Hz) and equal to 50 MHz at 57 K. Relaxation of tunnelling NH₄⁺ and NH₃D⁺ ions were explained in terms of one and two phonon transitions.

Similar studies⁵⁸,¹⁶⁸ on partially deuterated salts over 1.5 to 4.2 K show that T₁ depends upon the deuterium content, and true relaxation is a direct process proportional to temperature but T₁ is diffusion limited in some of the more deuterated salts. They have discussed relaxation in terms of the transition probabilities between tunnel-split energy states slightly mixed by the dipolar interaction. First order mixing gives relaxation of symmetric NH₃⁺ but second order mixing is required for relaxation of asymmetric NH₃⁺.

The proton T₁ relaxation dispersion experiments on (NH₄)₂SnCl₆ by Punkkinen et al¹⁵⁷ gave sharp minima for the single crystal sample and only shallow minima for their powder samples. Apart from the orientational dependence of T₁ caused by the variation in orientation of the magnetic field with respect to the ammonium symmetry axis, one might explain this by a distribution of the strains that cause lowering in the crystal field symmetry. Such a distribution would be wider in a powder than in a single crystal there by washing out the T₁ minima and might very well be a sample dependent. At 20 K Punkkinen et al¹⁷¹,¹⁷³ have observed T₁ minima at 6.5, 12.2, 13.0, 18.5, 24.5, 26.0, 32.5 and 37 MHz in an experiment at a Larmor frequency from 6 to 40 MHz. The inter tunnel frequency of 13, 24. and 37 = 13± 24.5 MHz and suppose that the minima at 26.0 & 32.5 are of different origin.

The temperature dependence of PSLR of (NH₄)₂SnCl₆ has been investigated in the range 100-500 K by Koksal¹⁶⁹. The experimental results indicate that intra H-H dipolar interaction modulated by reorientation motion of the ammonium ion is the dominant relaxation mechanism between 100 and 200 K. The activation energy for the reorientation of the ammonium ion was found to be 0.91 kcauls/mole.

Svare et al¹⁶⁸ have carried out ¹H T₁ studies in partly deuterated (NH₄)₂SnCl₆ at 4.2 K and found that relaxation is very much faster than in the non-deuterated salt. They conclude that short T₁ is caused by tunnelling which for a symmetric NH₃D⁺ ¹⁸¹
allows a two-step energy transfer process (spins-tunnel state-lattice). The spin tunnel transfer is resonant at the level crossing \( \omega_0 - \omega_{\text{tunnel}} \) and \( 2\omega_0 - \omega_{\text{tunnel}} \).

Deuteron magnetic resonance spectra have been recorded in \((\text{ND}_4)_2\text{SnCl}_6\) at 4.2 K by Knispel et al\(^{132}\). The spectra were narrow (line width 4 kHz) and it was attributed to tunnelling of ammonium ions.

Svare et al\(^{154}\) have carried out proton \( T_1, T_{1p} \) measurements in pure and deuterated samples at different frequencies. The results for \( \omega_1 \gg \omega_0 \) can be summarized below 20 K as \( 1/T_1 = 4 \times 10^{-7} \omega_T^2 T/(\omega_0)^2 + 10^{-30} (\omega_T)^4 / (\omega_0)^2 \), where \( \omega_T \) is the AA-TT tunnelling frequency in \( \text{NH}_4 \). This is explained as one-phonon relaxation \( \alpha T \) and two phonon relaxation \( \alpha T^5 \).

**Diammonium Hexachloro Tellurate (NH\(_4\))\(_2\)TeCl\(_6\)**

Svare et al\(^{154,171}\) have done \( T_1, T_{1p} \) studies over a range 40-300 K and found an activation energy of 1.6 kcal/mole for \( \text{NH}_4 \) reorientation. From similar studies on other ammonium hexachlorides they concluded that \( E_a \) is a function of lattice dimension. Using non classical minima in \( T_1 \) and \( T_{1p} \), the tunnel frequency for the \( \text{NH}_4 \) was estimated as 30 MHz. Low temperature proton \( T_1, T_{1p} \) studies\(^{154}\) at different frequencies in pure and partly deuterated salts is explained in terms of one phonon and two phonon relaxation.

**Diammonium Hexachloro Titanate (NH\(_4\))\(_2\)TiCl\(_6\)**

Proton \( T_1, T_{1p} \) studies\(^{171}\) over a range 40 to 300 K, showed a clear discontinuity in \( T_1 \) at the phase transition temperature (244 K).

**Methylammonium Hexachloro Platinate \([(\text{CH}_3\text{NH}_3)]_2\text{PtCl}_6\)**

and its deuterated Analogues

These compounds are known to form rhombohedral crystals having a slightly distorted \( K_2\text{PtCl}_6 \) structure. The crystals and the cations form packed layers between the layers. In this structure complex anions lying normal to the three fold axis of the crystal and the cations are situated between these layers. Hydrogen bonds are known to exist between NH groups and neighbouring chlorine atoms.

Proton \( T_1 \) and \( M_2 \) studies\(^{177}\) over a range 4.2 to 400 K show a depression in \( T_1 \) below the transition point (125 K) in addition to a deep minimum at around 57 to 55 K in the case of protonated complex while in other deuterated complexes only a single minimum was observed.
The $T_1$ dependence in $(\text{CH}_3\text{ND}_3)_2\text{PtCl}_6$ on Larmor frequency was found to be larger than that in $(\text{CD}_3\text{NH}_3)_2\text{PtCl}_6$ presumably because of the difference in the extent of deuteration. Both the deuterated compounds showed somewhat nonexponential decay of magnetization at temperatures higher than the respective $T$ minimum which may be due to the cross-correlation of intra molecular dipole-dipole interactions between protons in a CH$_3$ or NH$_3$ group rotating about the triad axis.

**Methyl Ammonium Hexachloro Stannate** $[(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$

This is isomorphous with the platinum complex. The $^1\text{H}$ $T_1$ and $M_2$ studies$^{177}$ over a range 4.2 - 400 K show that the $T_1$ value observed at 20 MHz is smaller than the values observed at 60 MHz. To explain the observed $M_2$ and a shallow $T_1$ minimum, they assumed the relaxation to be caused by independent reorientation of CH$_3$ and NH$_3$ groups (uncorrelated motion) and the reorientation of the cation as a whole about its C-N axis. They also found $T_1$ as a function of Larmor frequency. The proton $M_2$ and $^{35}\text{Cl}$ NQR studies$^{184}$ show an anomaly of NQR frequency at 156 K whereas $^1\text{H}$ does not change indicating that the motion of CH$_3$ and NH$_3$ groups about their C$_3$ axis is not affected by the transition.

**Methyl Ammonium Hexachloro Tellurate** $(\text{MA})_2\text{TeCl}_6$

This compound crystallizes in the hexagonal space group $P_{3m1}$ with $Z = 1$. NQR and DTA studies revealed two phase transitions at 139 K and 230 K. Proton $M_2$ studies$^{178}$ over a range 77 to 300 K show almost a constant $M_2$ (5.5 ± 0.5G$^2$) indicating CH$_3\text{NH}_3$ ion reorientation about its C$_3$ axis. They concluded that the phase transition at 139 K is associated with the motion of complex anions (TeCl$_6$ octahedron) rather than the cations. what they have given (1) the deuteration of methyl group does not alter the temperature dependence of $^{35}\text{Cl}$ NQR frequency. (2) The relaxation time $T_1$ of $^{35}\text{Cl}$ NQR yields a sharp minimum at the transition point whereas the proton $T_1$ exhibits no appreciable anomaly at this temperature. From the Cl$^{35}$ NQR they found that the crystals exist in metastable state below 230 K on cooling and transform to a low-temperature stable phase at 110 K.

The proton $T_1$ studies by Furukawa et al$^{179}$ show different $T_1$ results during heating and cooling cycles. As temperature increases from 4.2 K onwards, no drastic change was observed in $T_1$ plot at both the transition temperatures ($T_{11} = 139$ K, $T_{12} = 230$ K) indicating that the motion of the MA ion is almost unaffected by these transitions. They ascribed the deep minimum near KK/T 15 to the reorientation of the MA$^+$ ion as a whole about its C$_3$ axis while the small depression near KK/T 10 is assignable to the independent reorientation of CH$_3$, NH$_3$ groups. The $T_1$ minimum was broad and asymmetric although all the MA ions are crystallographically equivalent. The rather long $T_1$ minimum compared with the theoretical value is
consistent with such breadth of the T₁ min. Therefore, the activation parameters are evaluated separately from the slopes on the low and high temp. sides of the T₁ minimum and has a value of 7.0 (5.0) for C₃ rotation of MA⁺ ion. The activation energy for the reorientation of MA⁺ ion reflects the intermolecular potential barrier which is detected partly by the NH...Cl hydrogen bonding and partly by the MA⁺...Cl van der walls force. The small value of Eₘ indicates that in this compound the NH...Cl hydrogen bonds are quite weak as compared with that in CH₃NH₃Cl. A deep minimum of proton T₁ was observed in the low temperature phase of this compound, indicating that the methyl ammonium ion perform a rapid reorientation as a whole about its three-fold axis. The activation energy Eₘ for the cation are determined as 1.68 Kcal/mole. For this complex, a shallow T₁ minimum ascribable to the independent rotation of the CH₃ and NH₃ groups in the cation was observed on the high temperature side of T₁ minimum.

During the cooling cycle from room temperature downwards T₁ was found to be shortened by about 1/4th of its room temperature value in the range of 230-222 K, which indicates the abrupt change in the motional state of MA⁺ ion at T₁2. The T₁ value of 4 secs show that the relaxation in the region K/K – 4.5-7.5 shows the presence of a new relaxation process with two correlation times, a small-angle tilting of the C₃ axis of the MA⁺ ion from the original orientation superimposed on the rapid reorientation of CH₃ and NH₃ groups.

Dimethyl Ammonium Hexachloro Stannate [(CH₃)₂NH₂]₂SnCl₆

Proton T₁ and M₂ studies have been carried out by Ishida et al.¹ in this complex and its partially deuterated analogues. The M₂ (10G²) remained constant between 100 to 240 K, after which it decreases with increasing temperature reaching a plateau of 5G² at about 350 K. Similar observations were found in the deuterated salts also. The observed M₂ value in the region 100 to 240 K was attributed to the CH₃ reorientation about C₃ axis while the plateau at 350 K was attributed to the CH₃ reorientation about C₃ axis along with the 180° flip motion (C₃ reorientation) of the whole cation about its two fold pseudo symmetry axis. The proton T₁ exhibits two deep T₁ minima at 69 and 125 K and a maximum at 285 K above which it decreases. The two minima below 200 K were attributed to the the reorientation of two non-equivalent CH₃ groups with different Eₘ and the assignment is in agreement with the crystal structure investigations.

Dimethyl Ammonium Hexachloro Tellurate [(CH₃)₂NH₂]₂TeCl₆

This is isomorphous with the tin complex and is known to have a structural phase transition at 169 K. Ishida et al.¹ have carried out proton T₁ and M₂ studies as a function of temperature in this complex and its partially deuterated analogues. They
found that the $M_2$ value was almost constant ($= 10G^2$) over the range 100-240 K which was interpreted in terms of C$_3$ reorientation of the two CH$_3$ groups about their C-N bond axis. Above 240 K $M_2$ decreases with increasing temperature and has a plateau value of 4 $G^2$ at 350 K and was attributed to the cation performing the C$_3$ reorientation of the CH$_3$ groups as well as the 180° flip motion (C$_2$ reorientation) of the whole cation about its two fold pseudo symmetry axis.

The proton T$_1$ studies show three minima (40, 60 and 90 ms) at 95, 125 and 385 K respectively. The T$_1$ minimum below 200 K are broad and is considered as result of successive overlap of one or more T$_1$ minimum. Further these observed T$_1$ minima are considerably deep and can be attributed to the CH$_3$ reorientation and due to the existence of three or more nonequivalent CH$_3$ groups in the crystal. The low values of activation for CH$_3$ reorientation indicates that cations are more loosely bound in the crystal lattice.

**Trimethyl Ammonium Hexachloro Platinate** [(CH$_3$)$_3$NH)$_2$PtCl$_6$

This compound crystallizes as cubic with space group $Pn_3$ with $Z = 4$. $H$, $M_2$ and T$_1$ studies$^{182}$ over a range 77-300 K show that $M_2$ (1.9G$^2$) remains constant from 300 K down to 180 K which was attributed to the rotation of three CH$_3$ groups about the individual C$_3$ axis and the whole cation about C$_3$ axis. In the region 180 to 150 K the $M_2$ value further increases and corresponds to CH$_3$ motion alone. At 77 K the $M_2$ reaches a rigid lattice value of 28 G$^2$.

The T$_1$ results show two minima, a deep one (12 msecs) at around 160 K which was attributed to the reorientation of the CH$_3$ groups while the other shallower minimum of T$_1$ occurs over a wide temperature (220 to 260 K) and has been assigned to the reorientation of the whole cation about its C$_3$ axis.

**Trimethylammonium Hexachloro Stannate** [(CH$_3$)$_3$NH)$_2$SnCl$_6$

This compound is isomorphous with the corresponding platinum salt. Proton $M_2$ and T$_1$ studies$^{182}$ over a range 77 to 300 K shows a very close resemblance to the Platinum complex in all respects including the values of $M_2$. The interpretation of the results also follows the same basis.

**Trimethyl ammonium Hexachloro Tellurate** [(CH$_3$)$_3$NH)$_2$TeCl$_6$

This is again isomorphous with the corresponding platinum complex and studied by Ikeda et al$^{182}$. The results of $M_2$ and T$_1$ are very similar to that of the platinum complex.
This has a cubic structure and is known to have two structural phase transitions from $\alpha$ to $\beta$ at 181 K and $\beta$ to $\gamma$ at 153 K. Proton $M_2$ and $T_1$ studies over a range of 77-300 K have been carried out by Prabhunirashi et al.\textsuperscript{183} The $M_2$ values were very small from 300 K down to 160 K below which it increases and reaches a value corresponding to rigid lattice at 77 K. Since the line narrowing occurs in a single step, they concluded that the individual $C_3$ reorientation of four CH$_3$ groups in the cation and the overall reorientation of the cation, both occur successively at a very narrow temperature interval. Proton $T_1$ showed different results in warming and cooling cycle. During cooling from 300 K downwards a $T_1$ minimum was found at 210 K. With further decrease of temperature no anomaly was observed at 181 K ($T_c$ for $\alpha$ to $\beta$ transition) whereas an anomaly was observed at 153 K ($T_c$ for $\beta$ to $\gamma$ transition). However the recovery of magnetization was found to be non exponential below this temperature. When the sample was warmed from 77 K upwards the $T_1$ values in the $\gamma$ phase were completely different from those obtained in the cooling run. On further increase in temperature the $T_1$ did not show any anomaly at the lower $T_c$ (153 K). The $T_1$ value approached almost continuously to the $T_1$ values of the $\alpha$ phase, with increasing temperature. Above this temperature the same $T_1$ values were obtained for both the warming cooling runs.

This complex is isomorphous with the platinum salt and is known to have a phase transition at 129 K from DTA studies. The $M_2$ behaviour was very similar to that of platinum salt. A remarkable thermal hysteresis phenomenon was found in the $T_1$ studies of this salt. When the complex was cooled from 300 K downwards two $T_1$ minima were observed at 200 and 130 K. On further cooling, non-exponential recovery of magnetization having two different $T_1$ components begin to appear below 105 K which were clearly pronounced at 100 K. On cooling further the two $T_1$ components approached each other finally a single $T_1$ value was obtained below 90 K. When the sample was warmed from this temperature, the $T_1$ value decreased along the curve having longer $T_1$ values obtained on cooling process and also along the curve obtainable by its extrapolation to the high temperature side. At 129 K, the $T_1$ gradually approached to about one tenth above which temperature it gradually approach to the value obtained on the cooling run.

This salt also is isomorphous with the corresponding platinum salt and is known to undergo a phase transition from DTA studies. Proton $M_2$ results\textsuperscript{183} resemble the
platinum salt in all respects. Proton $T_1$ studies$^{183}$ showed only a single $T_1$ minimum appears around 205 K when cooled from 300 K downwards. On further cooling a small jump of $T_1$ was detected at 157 K which agrees with $T_H$. Below this temperature the magnetization recovery was found to be non-exponential.

The $T_1$ was almost temperature independent below 110 K down to 60 K. During warming up cycle a discontinuity in $T_1$ was observed at 164 K showing that the transition has a characteristic thermal hysteresis of 7 K width in agreement with DTA results.
$\text{NH}_4\text{Cl}$

- transition at 242 K

$\text{ND}_4\text{Cl}$

Cubic

$\text{CH}_3\text{NH}_3\text{Cl}$

P.T. α phase to β phase

Structure of phase is Monoclinic $P2_1/n$

$\text{(CH}_3\text{)}_2\text{NH}_2\text{Cl}$

P.T at 313 K, 260 K

$\text{(CH}_3\text{)}_3\text{NHCl}$

P.T. at 300 K.

$\text{H}_2\text{ studies Temp. dependence } (1.74, 75, 76, 77, 78, 79, 80, 81, 82)$

$\text{H}_2\text{ studies Temp. dependence } (85, 86, 87, 90, 95)$

$E_a (\text{NH}_4)^+ 4.7 \text{ kcal/mole } \left(\text{ point } \left(2 \text{ kcal/mole } \right) \text{ point }ight.$

Theoretical models (89, 91, 94, 101)

$\text{H}_2\text{ studies pressure dependence } (83, 84, 96)$

$\text{H}_2\text{ studies } \left[ \text{T}_1 \right] (97)$

$\text{Cl}_2\text{ studies } \left[ \text{T}_1 \right] (82, 93, 94, 99, 100)$

$\text{H}_2\text{ chemical shift } (82)$

$\text{H}_2\text{ studies } \left[ \text{T}_1D \right] (109, 103, 90A)$

$\text{H}_2\text{ line shape studies } (106, 107, 109, 110)$

and $\text{H}_2\text{Qq values}$

$\text{H}_2\text{ studies } \left[ \text{T}_1 \right] (85, 86, 102)$

$\text{Cl}_2\text{ high pressure studies } (111)$

$\text{H}_2\text{ relaxation studies } (112)$

$\text{H}_2\text{ studies } (113, 114, 116)$

$\text{H}_2\text{ studies } (115, 117)$

observed a discontinuity at $T_c (115, 117)$

$E_a = 4.45 \text{ kcal/mole}$.

$\text{H}_2\text{ studies } (116, 118)$

$I4_1D$ at 4.2 K and 3.7G$^2$ at 330 K.

$\text{H}_2\text{ studies } (116, 119)$

$\text{H}_2\text{ studies } (120, 121)$
Phase transition
at $T_c1 = 184.5$ K
& $T_c2 = 75.8$ K

$\text{NH}_4\text{HgCl}_3$
P.T at 55 K.

$\text{NH}_4\text{MgCl}_3\cdot6\text{H}_2\text{O}$

$\text{NH}_4\text{SnCl}_3$

$\text{ND}_4\text{SnCl}_3$

$\text{CH}_3\text{NH}_2\text{PbCl}_3$
Phase transition at 175 K.

$\text{(CH}_3)_4\text{NHCdCl}_3$
Orthorhombic

$\text{(CH}_3)_4\text{HgCl}_3$
Monoclinic $P_{21}$

$\text{M}_2$ studies [116, 122, 123, 126, 127]
$M_2 = 33.1$ G$^2$ at 110K. and $1.53G^2$ at 270K.
$^1H$ $T_1$ studies $E_a = 6.5$ kcal/mole
$E_a = 8.2$ kcal/mole

$^1H$ $T_1$ studies [130]
A discontinuity in $T_1$ and $^{35}Cl$ studies

$^1H$ $M_2$ studies [131]

$^1H$ $T_1$ studies 1.4 to 300K [133]

$^2H$ line width studies [132]

$^2H$ and $^14H$ line width studies [204]
$E_a$ for $\text{CH}_3\text{NH}_3$ reorientation $1.3$ kcal/mole,

$^1H$ $M_2$ studies [138, 139]
$^1H$ $T_1$ studies [135, 136, 138, 139]
$E_a(\text{CH}_3\text{NH}_3)= 0.11$ ev/mole

$^1H$ $T_1$ studies [139]
$E_a(\text{CH}_3)_4= 2.0\pm0.3$ kcal/m mole

$^1H$ $M_2$ studies [140, 141]
$M_2 = 33.8 \pm 1.9G^2$ at 83K and $10G^2$ at 130K.
$^1H$ $T_1$ studies (142, 143)
\( \text{NH}_4\text{AlCl}_4 \) Orthorhombic
\( P_{\text{nnn}} Z = 4 \)

\( (\text{NH}_4)_2\text{ZnCl}_4 \)
- Normal Phase I \( \rightarrow \) 406 K
  - Paraelectric
- Phase II 319 < \( T \) < 406 K
  - Antiferroelectric
  - Phase III 270 < \( T \) < 319 K
  - Ferroelectric Phase < 270 K

\( [(\text{CH}_3)_4\text{N}]_2\text{ZnCl}_4 \)
- Paraelectric Phase I \( \rightarrow \) 293 K
  - \( P_{\text{nnn}} Z = 4 \)

Incommensurate Phase II
- Orthorhombic
- 279 < \( T \) < 293 K Paraelectric
- Ferroelectric Phase III
  - 276.3 < \( T \) < 279 K
  - Paraelectric IV
  - 181 < \( T \) < 276.3 K
  - Paraelectric V
  - 161 < \( T \) < 181 K
  - Paraelectric VI < 161 K

\( E_a [(\text{CH}_3)_4\text{N}] = 6.38 \text{ kcales/mole} \)
\( 1\text{H} \text{N}_2 \text{ studies } 80-290 \text{K} \) [144]

\( 1\text{H} \text{N}_2 \text{ is } 4 \theta^2 \text{ throughout the temp. range.} \)

\( 1\text{H} \text{N}_2 \) and \( T_1 \) studies [145, 147]

\( M_2 \) is constant throughout the temperature range

Presence of inequivalence \( \text{NH}_4 \) sites

\( E_a (\text{NH}_4)_6 = 2.27 \text{ kcal/mole} \)

Two inequivalent TMA sites

\( E_a [(\text{CH}_3)_4\text{N}]_2 \) = 4.6 kcales/mole
\( E_a [(\text{CH}_3)_4\text{N}]_2 = 3.7 \)

\( E_a [(\text{CH}_3)_4\text{N}]_2 = 4.4 \text{ kcales/mole} \)

\( 1\text{H} \text{N}_2 \text{ studies pressure variation [Armugam]} \)

\( ^{13}C \text{ NMR & chemical shift studies [131]} \)

190
(CH₂NH₂)₂C₆Cl₄

Phase transition

Phase I > 483 K
Phase II 279 < T < 483 K
Phase III 164 < T < 279 K
Phase IV < 164 K

\( T_{4/3} \text{/mm} \)

Orthorhombic \( C_{mca} \)

Tetragonal \( P_{4/nmc} \)

Monoclinic \( E_{2/c} \)

\( ^1H \) studies [149]

\( M_a \) changes by \( 7 \) \( G^2 \) at 164 K

(\( CH₂NH₂ \)₂SnCl₄

Phase I > 483 K
Phase II 426 < T < 483 K
Phase III < 426 K

\( P_{21a} \)

Orthorhombic

\( P_{nna} \)

\( ^1H \) studies [142]

\( E_a (CH₂NH₂) = 2.34 \) kca/s/mole \( E_a (CH₂NH₂) = 1.70 \) kca/s/mole

(\( CH₂NH₂ \)₂MgCl₄

\( \{CH₂NH₂\}₂MgCl₄ \)

\( T_m = 2.15 \) K

\( \{CH₂NH₂\}₂MgCl₄ \)

\( \{CH₂NH₂\}₂MgCl₄ \)

\( \{CH₂NH₂\}₂MgCl₄ \)

Orthorhombic

\( ^1H \) studies [150]

\( E_a (CH₂NH₂) = 2.9 \) kca/s/mole \( E_a (CH₂NH₂) = 5.9 \) kca/s/mole

(\( NN₂O₂SeCl₆ \)

\( NN₂O₂SeCl₆ \)

\( NN₂O₂SeCl₆ \)

Cubic

\( ^1H \) studies [154]

\( E_a (NN₂) = 0.9 \) kca/s/mole

(\( NN₂O₂SeCl₆ \)

\( NN₂O₂SeCl₆ \)

\( NN₂O₂SeCl₆ \)

Cubic

\( ^1H \) line width \& \( M_a \) studies [24]

\( ^1H \) studies [156, 157, 156, 151]

\( E_a (NN₂) = 1.4 - 1.68 \) kca/s/mole

191
\[
\begin{align*}
(NH_4)_2PdCl_6 & \quad \text{Cubic} \\
(NH_4)_2PdCl_6 & \quad \text{Cubic} \\
(NH_4)_2ReCl_6 & \quad \text{Cubic} \\
(NH_4)_2RuCl_6 & \quad \text{Cubic} \\
(NH_4)_2SnCl_6 & \quad \text{Cubic} \\
(NH_4)_2TeCl_6 & \quad \text{Cubic} \\
(NH_4)_2TiCl_6 & \quad \text{Cubic}
\end{align*}
\]

1. \(T_1\) studies [154.162.171]

Tunnelling below 100 K

\(E_a(NH_4)^+ = 0.61\) kcais/mole

2. \(T_1\) studies [24.163]

\(M_2 = 1.23G^2\) at 4.2K & \(0.42G^2\) at 120K.

1. \(T_1\) studies [163.171]

2. \(T_1\) studies [164]

\(E_a(NH_4)^+ < 1.6\) kcais/mole

Tunnelling observed

1. \(T_1\) studies [153]

1. \(N_2\) studies [24.37]

1. \(T_1\) studies [57.154.157.162.166.167.168] [55.169.171.173]

\(E_a(NH_4)^+ = 1.24\) kcais/mole

35Cl \(T_1\) studies in partially deuterated salt [167]

2. \(N_2\) studies [132]

1. \(T_1\) studies [154.171]

\((NH_4)^+ = 4.5\) kcais/mole

1. \(T_1\) studies [171]

\(E_a(NH_4)^+ = 4.5\) kcais/mole
\((\text{CH}_3\text{NH}_3)_2\text{PtCl}_6\)
Phase transition at 55 K

\((\text{CH}_3\text{NH}_3)_2\text{SnCl}_6\)

\((\text{CH}_3\text{NH}_3)_2\text{TeCl}_6\)
Hexagonal
Phase transition at 139 K
\(P_3m1\) \(Z = 1\)

\(((\text{CH}_3\text{NH}_3)_2\text{PtCl}_6)\) \(((\text{CH}_3\text{NH}_3)_2\text{SnCl}_6)\)

\(((\text{CH}_3\text{NH}_3)_2\text{TeCl}_6)\)

\(((\text{CH}_3\text{NH}_3)_2\text{PtCl}_6)\)
Cubic
\(T_h^6 - P_{6x}^3\) \(Z = 4\)

\(((\text{CH}_3\text{NH}_3)_2\text{SnCl}_6)\)
Cubic
\(T_h^6 - P_{6x}^3\) \(Z = 4\)

\(^1H\) \(N_2\) studies [177]
\(^1H\) \(T_1\) studies [177]
\(E_a(\text{CH}_3\text{NH}_3) = 0.52\) kcais/mole

\(^1H\) \(T_1\) & \(N_2\) studies [177,184]
\(^{35}\text{Cl}\) \(T_1\) studies [184]

\(^1H\) \(N_2\) studies [178]

\(N_2\) at 300 K = 5.5 \pm 0.5 G^2 & 6.0 \pm 0.5 G^2 \) at 77 K.

\(^1H\) \(T_1\) studies [179]
\(E_a(\text{CH}_3\text{NH}_3) = 1.7\) kcais/mole

\(^1H\) \(T_1\) & \(N_2\) studies [181]
\(E_a(\text{Clion}) = 1.7\) kcais/mole

\(^1H\) \(T_1\) & \(N_2\) studies [180]

\(^1H\) \(T_1\) & \(N_2\) studies [182]

\(^1H\) \(N_2\) 2.0 G^2 for \(T > 180\) K 10 G^2 for \(150 < T < 180\) K and 28 G^2 at 77 K

\(E_a[(\text{CH}_3\text{NH}_3)\text{ion} \) for \(C_3\) axis rotn. 4.63 \pm 0.23\) kcal/mole

\(^1H\) \(T_1\) & \(N_2\) studies [182]

\(^1H\) \(N_2\) 2.0 G^2 for \(T > 180\) K 10 G^2 for \(150 < T < 180\) K and 28 G^2 at 77 K

\(E_a[(\text{CH}_3\text{NH}_3)\text{ion} \) for \(C_3\) axis rotn. 4.82 \pm 0.23\) kcal/mole
<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase transition</th>
<th>Studies for $T_c$ and $T_m$</th>
<th>Studies for $T_c$</th>
<th>Studies for $T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[CH}_3\text{]}_3\text{NH}_2\text{TeCl}_6$</td>
<td>Cubic</td>
<td>$1^{\text{st}} T_1$ &amp; $M_2$ studies [182]</td>
<td>$1^{\text{st}} T_1$ &amp; $M_2$ studies [182]</td>
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<tr>
<td></td>
<td></td>
<td>$T_c = 153 \pm 1 \text{K}$ (heating cycle)</td>
<td>$T_c = 152 \pm 2 \text{K}$ (heating cycle)</td>
<td>$T_c = 151 \pm 1 \text{K}$ (cooling cycle)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_m = 141 \pm 1 \text{K}$ (cooling cycle)</td>
<td>$T_m = 142 \pm 2 \text{K}$ (cooling cycle)</td>
<td>$T_m = 152 \pm 2 \text{K}$ (heating cycle)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_a = 5.09 \pm 0.23 \text{kcal/mole}$</td>
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<tbody>
<tr>
<td>$\text{[CH}_3\text{]}_4\text{NH}_2\text{TeCl}_6$</td>
<td>Cubic</td>
<td>$1^{\text{st}} T_1$ &amp; $M_2$ studies [183]</td>
<td>$1^{\text{st}} T_1$ &amp; $M_2$ studies [183]</td>
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<tr>
<td></td>
<td></td>
<td>$T_c = 129 \pm 2 \text{K}$ (heating cycle)</td>
<td>$T_c = 127 \pm 2 \text{K}$ (heating cycle)</td>
<td>$T_c = 156 \pm 1 \text{K}$ (cooling cycle)</td>
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<tr>
<td></td>
<td></td>
<td>$T_m = 165 \pm 1 \text{K}$ (heating cycle)</td>
<td>$T_m = 165 \pm 1 \text{K}$ (heating cycle)</td>
<td>$T_m = 156 \pm 1 \text{K}$ (cooling cycle)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_a = 3.05 \pm 0.23 \text{kcal/mole}$</td>
<td>$E_a = 3.05 \pm 0.23 \text{kcal/mole}$</td>
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<th>Studies for $T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[CH}_3\text{]}_4\text{NH}_2\text{SmCl}_6$</td>
<td>Cubic</td>
<td>$1^{\text{st}} T_1$ &amp; $M_2$ studies [183]</td>
<td>$1^{\text{st}} T_1$ &amp; $M_2$ studies [183]</td>
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<tr>
<td></td>
<td></td>
<td>$T_c = 164 \pm 1 \text{K}$ (heating cycle)</td>
<td>$T_c = 165 \pm 1 \text{K}$ (heating cycle)</td>
<td>$T_c = 157 \pm 1 \text{K}$ (cooling cycle)</td>
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<tr>
<td></td>
<td></td>
<td>$T_m = 156 \pm 1 \text{K}$ (cooling cycle)</td>
<td>$T_m = 156 \pm 1 \text{K}$ (cooling cycle)</td>
<td>$T_m = 156 \pm 1 \text{K}$ (cooling cycle)</td>
</tr>
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<td></td>
<td>$E_a = 3.58 \pm 0.23 \text{kcal/mole}$</td>
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<td>$E_a = 3.58 \pm 0.23 \text{kcal/mole}$</td>
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</tbody>
</table>
This section covers NMR studies with bromine as the anion. Compared to chlorides, studies on bromo metal complexes are very few. The available NMR data shows a clear trend of decreasing activation energy with increasing cell volume rendering more freedom for the rotating group. The $T_1$ results closely resemble the results of the corresponding chloride isomorphs.
Ammonium bromide has a cubic structure at room temperature and is known to undergo three structural phase transitions. The transition at 411 K from phase I to II is from disordered NaCl to disordered CsCl structure whereas the other transition from phase II to III at 235 K is an order-disorder type changing from CsCl to tetragonal. Finally it transforms from Phase III to Phase IV at around 108 K and seems to be sluggish and takes place over a range of temperature. Gutowsky et al. [1,80,198] and Cook and Drain [78] have reported a line-width transition at 102 K, without any anomaly at \( T_c \) indicating that phase transition is due to order disorder of \( \text{NH}_4^+ \) ions. Single crystal M2 studies [81] also did not reveal any anomaly at \( T_c \).

Line shape studies [189,37] in the range 1.8 K to 4.2 K, were explained in terms of quantum mechanical tunnelling motion of ammonium ions about their C3 axis. They found a linear relation between the tunnel splittings of the hindered rotational levels and the potential barriers to the motion and concluded that there is less possibility of tunnelling in \( \text{NH}_4 \text{Br} \). A peculiar time dependence [189] of the PMR line shape at 4.2 K was attributed to the spin conversion. A theoretical treatment for the PMR line shape for tetrahedral ammonium ions under the influence of tunnelling has been developed for ammonium ions by Watton and Petch [190] who introduced a splitting parameter 'J' as a measure of the tunnelling splitting of the torsional ground state. Comparison of the theoretical values with the experimental results shows that J = 0.

Ikeda et al. [195] also explained the observed line shape at 4.2 K in terms of tunnelling reorientation of \( \text{NH}_4^+ \) ion.

Proton T1 studies have been carried out over a range of temperature by many workers. [77,78,86,87,185,187] They [185] found a small shift (24%) in T1 at 235 K (\( \lambda \) -point) and a T1 minimum occurred at 165 K whereas Cook et al. [78] did not observe any change in T1. Proton T1 studies [82,194] show that the reorientational motion of ammonium ion is the origin of time dependent interaction necessary to relax the spin orientation. In the case of single crystals of \( \text{NH}_4 \text{Br} \) in the Phase II, which was not observed in the sample, possibly due to the large broadening of the quadrupole split resonance line. They also related the temperature dependence of \( \text{Br} \text{T1} \), to the changing degree of long range order below \( T_c \).

Mondema and Trappeniers [83,193] have studied proton T1 at various pressure up to 2.2 K bar and found a change of 15% in T1 at atmospheric pressure. The \( T_c \) was found to shift towards higher temperatures with increasing pressure, further the sharpness of the transition decreases with increasing pressure.
Ammonium bromide has a cubic structure at room temperature and is known to undergo three structural phase transitions. The transition at 411 K from phase I to II is from disordered NaCl to disordered CsCl structure whereas the other transition from phase II to III at 235 K is an order-disorder type changing from CsCl to tetragonal. Finally it transforms from Phase III to Phase IV at around 108 K and seems to be sluggish and takes place over a range of temperature. Gutowsky et al. and Cook and Drain have reported a line-width transition at 102 K, without any anomaly at T_c indicating that phase transition is due to order disorder of NH_4 ions. Single crystal M_2 studies also did not reveal any anomaly at T_c.

Line shape studies in the range 1.8 K to 4.2 K, were explained in terms of quantum mechanical tunnelling motion of ammonium ions about their C_3 axis. They found a linear relation between the tunnel splittings of the hindered rotational levels and the potential barriers to the motion and concluded that there is less possibility of tunnelling in NH_4Br. A peculiar time dependence of the PMR line shape at 4.2 K was attributed to the spin conversion. A theoretical treatment for the PMR line shape for tetrahedral ammonium ions under the influence of tunnelling has been developed for ammonium ions by Watton and Petch who introduced a splitting parameter 'J' as a measure of the tunnelling splitting of the torsional ground state. Comparison of the theoretical values with the experimental results shows that J = 0. Ikeda et al. also explained the observed line shape at 4.2 K in terms of tunnelling reorientation of NH_4 ion.

Proton T_1 studies have been carried out over a range of temperature by many workers. They found a small shift (24%) in T_1 at 235 K (\lambda^* point) and a T_1 minimum occurred at 165 K whereas Cook et al. did not observe any change in T_1. Proton T_1 studies show that the reorientational motion of ammonium ion is the origin of time dependent interaction necessary to relax the spin orientation. In the case of single crystals of NH_4Br in the Phase II, which was not observed in the sample, possibly due to the large broadening of the quadrupole split resonance line. They also related the temperature dependence of Br T_1, to the changing degree of long range order below T_c.

Mondema and Trappeniers have studied proton T_1 at various pressure upto 2.2 K bar and found a change of 15% in T_1 at atmospheric pressure. The T_c was found to shift towards higher temperatures with increasing pressure, further the sharpness of the transition decreases with increasing pressure.
Proton $T_1$ studies by Sharp et al.\textsuperscript{187} in a single crystal show that $T_1$ is anisotropic and displays critical behaviour near the -transition. This behaviour was explained in terms of dipolar interaction modulated by ammonium ion reorientation and cross relaxation between proton and bromine. Sharp and Pintar\textsuperscript{101,188} have carried out proton and bromine $T_1$, $T_{1\rho}$ studies and found the onset of long-range order at $T_c$ as it is seen in the $T_1$ of $^{79}$Br nuclei. They have proposed that there are critical oscillations associated with the transition from the CsCl phase to the more ordered tetragonal phase, around the 2-fold axis of the ammonium ions. From $^{79}$Br NMR studies by Jeffrey et al.\textsuperscript{191} it was found that bromine Q.C.C. varies as the square of the bromine ion displacement, which is the order parameter of the transition. Proton $T_{1D}$ studies\textsuperscript{192} in a single crystal of NH$_4$Br have shown a strong dependence on the crystal orientation in the magnetic field. Koksal and Bahceli\textsuperscript{194} have reported a discontinuity in PSLR time $T_1$ at 398 K and interpreted it as due to the presence of spin-rotation interaction.

Woessner and Snowden\textsuperscript{196} have reported a small discontinuity in deuteron $T_1$ at the transition in ND$_4$Br. $^{81}$Br NMR in ND$_4$Br has been carried out by Ueda\textsuperscript{93} under high pressures up to 6 K bars. The sharpness of the order-disorder transition observed at 234.5 K decreases with increasing pressure, the increase of $T_1$ with increasing pressure is explained as due to the lattice contraction. Huller and Kane\textsuperscript{94} have proposed an electrostatic model for the calculation of rotational potential in ammonium halides. Theoretically they have worked out the potential barriers in the ordered as well as disordered state of NH$_4^+$ ions in NH$_4$Br and ND$_4$Br. Proton $T_1$, $T_{1\rho}$ measurements in NH$_4$Br by Shimomura et al.\textsuperscript{87} agree well with the earlier reported values. Woessner and Snowden\textsuperscript{86} have studied proton and deuteron PSLR time $T_1$ in NH$_4$Br and ND$_4$. Change in $T_1$ values observed at $\lambda$-point in NH$_4$Br was much less than that observed in NH$_4$Cl. From the temperature dependence of $T_1$, the activation energy was estimated as 4.9 k cal/mole at 185 K and 3.6 k cal/mole at 234.5 K and above Chiba\textsuperscript{106} found a line-width value of 0.8±0.1 kHz from deuteron magnetic resonance experiments. Deuteron NMR studies have been reported by Hovi et al.\textsuperscript{108} without detailed quantitative analysis of the data. Sharp and Pintar\textsuperscript{105} have investigated cross relaxation dispersion and temperature dependence of $T_1$ and $T_{1\rho}$ and found that in both NH$_4$Br and ND$_4$Br the temperature dependence of Bromine spin $T_1$ is parallel to that of the protons and deuteron $T_1$ in the cubic phase II. This indicates that the correlation time for the fluctuation of EFG has the same temperature dependence as that for reorientation of the ammonium ion. This suggests that in phase II the ammonium ion is undergoing either $C_4$ or general reorientation.

**Methyl Ammonium Bromide** \textsuperscript{CH$_3\text{NH}_3\text{Br}$}

Methyl ammonium bromide is known to form tetragonal crystals at room temperature. It is known to exist in four crystalline phases, namely, $\alpha$ above 398 K,
α'at room temperature, and β and δ around 83 K. The δ phase was obtained, only by cooling the sample rapidly from room temperature.

Proton M₂ and T₁ studies have been carried out on this compound as well as its deuterated analogues. They found a M₂ value at 300 K which is characteristic of the reorientation of cations about C-N axis. The results at 77 K indicate that the cations are rigidly fixed in the β-phase whereas the cations are rapidly reorienting in the δ-phase. T₁ measurements for both slowly and rapidly cooled CH₃NH₃Br yield interesting results. On warming the samples in the β-phase, the T₁ curve gives a minimum at 230 K, on the low temperature side of which there is a shoulder and a marked change of T₁ takes place at 281 K in agreement with transition (β-α) detected by DTA. To identify the shoulder, they measured T₁ for CH₃ND₃Br and CD₃NH₃Br, and found only a single T₁ minimum at 192 K where the shoulder appeared, and at 230 K, for the former and the latter respectively. This indicates that the present T₁ curve consists of 2 curves, each of which has a single minimum, and they arise from the C₃-reorientation of CH₃ and NH₃ groups in the cations.

Kalliperuma has studied the pressure dependence of M₂ at various temperatures and found the barrier for NH₃ group motion increases with increasing pressure while the CH₃ group motion was unaffected. The former observation is explained in terms of the changes in cell volume through the changes in the hydrogen bond lengths.

**Trimethyl Ammonium Bromide (CH₃)₃NHBr**

This crystallizes in the space group P₂₁/m, and no phase transition has been reported in this compound. Proton M₂ and T₁ studies have yielded information about the dynamics of the cation.

**Tetramethyl Ammonium Bromide (CH₃)₄NBr**

TMA Bromide does not exhibit any structural phase transitions like the TMA chloride. The motional aspects of the cations have been investigated by both wide-line and pulsed NMR.

Proton M₂ studies at various temperatures show that line narrowing takes place in two steps. The M₂ at 77 K corresponds to rigid lattice which changes to 11.2 G² around 160 K and is attributed to the onset of methyl group rotation, with increase in temperature the M₂ changes to 1.2±0.1 G² at around 300 K, corresponding to the quasiasotropic reorientation of the whole cation. Polak has used proton M₂ data for the calculation of libration amplitudes of the methyl group motion.
Proton T1, T1ρ studies\textsuperscript{124,125,202,203} with temperature revealed double minima, which were attributed to TMA ion reorientation and CH$_3$ group reorientation. Polak and Sheinblatt\textsuperscript{202} have carried out the frequency dispersion studies of proton from 6 to 59 MHz, and found double minima at 6 MHz, which were clearly separated. With increasing larmor frequency they approach each other gradually and collapse to a single minimum at 59 MHz. The observed minima shows a linear variation with larmor frequency.

Tetramethyl Ammonium Tribromo Mercurate (CH$_3$)$_4$NHgBr$_3$

This crystal has a monoclinic structure with space group P2$_1$(C$_2$) and Z = 4. Proton M$_2$ studies\textsuperscript{140,141} over a range 4.2 to 300 K show a first step reduction in M$_2$ from the rigid lattice value due to the CH$_3$ group reorientation and second step reduction in M$_2$ was attributed to the reorientation of TMA$^+$ ion as a whole. The fact that this salt does not have a T$_c$ shows that H-bonds do not participate in the mechanisms of spontaneous polarization. Proton T$_1$ studies\textsuperscript{142,143} over a range 107 to 425 K revealed a single minimum at around 181 K which was attributed to the motion of the methyl group.

Tetramethyl Ammonium Tribromo Cadmate (CH$_3$)$_4$NCdBr$_3$

TMACdBr$_3$ crystallizes in a hexagonal lattice of space group P$\bar{6}$ 3/m with Z = 2. Proton T$_1$ studies\textsuperscript{142} over a range 77-451 K show a maximum at 332.2 K and two T$_1$ minima at 142.9 K and 86.6 K. The observed T$_1$ data is interpreted in terms of Spin-rotation interaction and dipolar interaction. This is the first observation of spin-rotation interaction in TMA compounds. $^1$H NMR at 10, 20 and 30 MHz over a range 77-400 K has been carried out by Venu et al\textsuperscript{204A}. The T$_1$ was independent of frequency and showed a maximum due to spin rotation interaction. In the other region the results can be explained in terms of isotropic tumbling motion of the (CH$_3$)$_4$N$^+$ ion and random reorientation of CH$_3$ group. The CW spectrum remained narrow down to 77 K and develops a wing structure at low temperatures. This observation is attributed to a possible tunnelling motion of the CH$_3$ group which has rather a low activation energy.

Tetramethyl Ammonium Tetra bromo Cadmate [(CH$_3$)$_4$N]$_2$ CdBr$_4$

This crystallizes in orthorhombic system with space group P$\text{nm}$ with Z = 4. Proton T$_1$ studies\textsuperscript{142} over a range 77-478 K show two T$_1$ minima at 138.9 K and 84.4 K and a maximum around 296.7 K. The lower minimum was attributed to the reorientation of the CH$_3$ group and the high temperature minimum to the random reorientations of TMA ion. The maximum was interpreted as due to spin-rotational interactions.
Tetramethyl Ammonium Tetrabromo Mercurate \[ ((CH_3)_4N)_2HgBr_4 \]

This crystallizes as orthorhombic with space group Pnma (D_{2h}^{16}). Proton T_1 studies\(^{205}\) revealed two distinct minima at at 166.7 K and at 80 K, which were attributed to the CH_3 group reorientation and the torsional oscillation of the CH_3 group about the C-N axis respectively. They have also ruled out the presence of any inequivalent TMA ions in the crystal.

### Diammonium Hexabromo Platinate \((NH_4)_2PtBr_6\)

This has a cubic structure and belongs to the family of antifluorites and is known to undergo a structural phase transition at 58.5 K. The Proton M_2 and T_1 studies\(^{163}\) show that the line shape has a central narrow component and broad wings. They observed low M_2 value (5.69 G\(^2\)) at 4.2 K suggest the possibility of tunnelling of NH_4 group. They observed decrease in the line-width with decreasing temperature was attributed to a change of system from a motionally narrowed spectrum to a spin-isomerism spectrum. Proton T_1, T_{1\rho} studies\(^{163}\) over a range 4.2 to 296 K show an abrupt change at the phase transition. In the low temperature phase the PtBr_6 octahedron is known to undergo a tetragonal distortion. However the absence of discontinuity in the slope of the LnT_1 versus 1000/T show that the NH_4 reorientation is not much affected by the transition.

### Diammonium Hexabromo Stannate \((NH_4)_2SnBr_6\)

This is also an antifluorite with cubic structure having a \(\lambda\)-transition at 144.8 K. Proton T_1, T_{1\rho} studies have been carried out by Norris et al\(^{206}\) over a range 60-300 K and Strange and Terenzi\(^{85}\) over 60-500 K. They\(^{206}\) observed a T_1 minimum at 62 K and also a marked slope change in the T_1 at T_c (144.8 K) The T_1 results show that at low temperatures the relaxation is dominated by intramolecular H-H dipolar interactions modulated by the reorientation of ammonium ion and at high temperatures it is the motion of SnBr_6 anions.

Punkkinnen et al\(^{207}\) have studied nuclear spin diffusion in a single crystal and found that structure-spin diffusion between the protons of A and T species. The shape of the induction signal approaches the equilibrium shape during the variable speed time T_2 at a speed characterized by the spin-diffusion time constant T_{SD}. T_{SD} was found to be a function of temperature and the orientation of the crystal.
Methylammonium Hexabromo Tellurate \((\text{CH}_3\text{NH}_3)_2\text{TeBr}_6\)

The room temperature crystal structure is cubic with space group \(R_{3m}\). It is known to undergo a first order phase transition at 289 K and another around 158 K.

Proton \(M_2\) studies\(^{178}\) show that at temperatures above 289 K (\(T_c\)) the overall tumbling motion of the MA cations is occurring, whereas at low temperatures it is the motion of MA ion reorientation about the \(C_3\) axis. Furukawa et al\(^{179}\) have carried out proton T\(_1\) studies and found discontinuities at the two phase transition temperatures (at 289 K and 158 K) Further they observed a shallow T\(_1\) minimum near 100 K and a deep minimum appears at 44 K. The relaxation at high temperatures was ascribed to the reorientation of the whole MA cation together with the independent rotation of \(\text{CH}_3\) and \(\text{NH}_3\) groups whereas at low temperatures the relaxation was due to the tunnelling-assisted \(C_3\) reorientation of the cation. However a possibility of two or more non-equivalent MA\(^+\) ions being in the unit cell is not ruled out. They also conclude that the structural deformation of the complex anion is the cause of the phase transition.

Trimethylammonium Hexabromo Metallate \([\text{(CH}_3)_3\text{NH}]_2\text{MBr}_6\) \((M = \text{Pt, Sn, Te})\)

Proton \(M_2\) and T\(_1\) studies in these complexes over a range 77-300 K were carried out by Ikeda et al.\(^{181,182}\) \(M_2\) remained constant \((= 2G^2)\) from room temperature down to 180 K. On further decrease of temperature, the line broadened and reached a \(M_2\) value of 10 \(G^2\) at around 150 K. Continued cooling of the compounds leads to a progressing line-broadening, with a steep increase of \(M_2\) around 100 K. At 77 K, \(M_2\) is approximately 28 \(G^2\). The \(M_2\) data were explained in terms of the reorientation of all the three \(\text{CH}_3\) groups about their individual \(C_3\) axis and the rotation of the whole cation about the common \(C_3\) axis. The temperature variation of proton T\(_1\) for all the three above complexes are quite similar. In each case a deep minimum in the range 155 to 170 K and a second shallower minimum on the high temperature side of the deep minimum were observed. The deep T\(_1\) minimum was attributable to the reorientation of the \(\text{CH}_3\) groups in the cation whereas the shallow minimum to the reorientation of the whole cation about the \(C_3\) axis.
Tetramethyl Ammonium Tetrabromo metallate \([(\text{CH}_3)_4\text{N}]_2\text{MBr}_6\)

Proton $M_2$ and $T_1$ studies have been carried out by Sato et al\(^{208}\), in all the three complexes and the results are quite similar. They found a very small $M_2$ (0.5 $G^2$) in the range 300 to 170 K which was attributed to the isotropic reorientation of the cation together with the $C_3$ reorientation of the $\text{CH}_3$ groups. With decreasing temperature the line broadens and reaches a value of 23 $G^2$ at 77 K which is lower than the rigid lattice value of 28.9 $G^2$, suggesting that some other dynamical processes being operative even at 77 K.

The proton $T_1$ studies also show lot of similarities in all the three complexes. They observed a deep $T_1$ minimum coexisting with a shoulder on the higher temperature side along with a shallow $T_1$ minimum on the lower temperature side. Further they noticed a peculiar behaviour in $(\text{TMA})_2\text{PtBr}_6$, that when the sample was heated for the first time beyond the transition temperature ($T_{tr} = 386 \pm 2$), the $T_1$ showed a steep increase near the $T_{tr}$, indicating a considerable influence of the phase transition upon the proton relaxation. Above 400 K, the $T_1$ curve of the highest temperature phase yielded a moderate slope. With decreasing temperature from 420 K, approximately the same $T_1$ value was observed down to 400 K as that observed on the heating run. Below 400 K, however, the compound yielded the $T_1$ values about twice that of those obtained on the heating run. It was interesting to note that the sample once being in the highest temperature phase showed the $T_1$ curve of the cooling cycle at all times even when it was heated from room temperature again and again and never yielded the curve traced in the heating cycle. Even after repeating the experiment after a long period of several months, (the sample being kept sealed in a glass ampoule) no changes were observed. It was quite surprising, however, that if the sealed ampoule was once broken and sealed again, the $T_1$ curve observed for the first time was obtained (only in the first heating run). The reproducibility of the above unusual behaviour was checked on different samples and all the samples yielded similar results. The deep $T_1$ minimum and its shoulder observed in these complexes at 150 K are thought to be attributable to the $C_3$ reorientation of the $\text{CH}_3$ groups as well as the overall reorientation of the cation itself.

$(\text{TMA})_2\text{SnBr}_6$ and $(\text{TMA})_2\text{TeBr}_6$ also showed a similar unusual behaviour of $T_1$ as that of the Platinum complex. The same interpretation holds good for these complexes also.
NH₄Br

Phase transitions

T₁ = 411 K
T₂ = 235 K

Cubic

T²⁺(P-43m) Z = 1

1NH₂ studies ...L = 4.6G H₂ = 27G² at 298 K

6 ...L = 23.7G 6 H₂ = 48 + 0.5G² at 78 K [1, 80]

1NH₂ & T₁ studies Eₐ (NH₄⁺) = 3.5 kcal/mole [78]

1NH studies & transition from 3.5 - 5.3G to 20G

from 20 K to 95 K [198]

1NH T₁ studies no anomaly in T₁ [77, 82]

1NH T₁ studies 120 - 390 K

small change in T₁ at 234.5 K [185]

T₁ min = 5.1 ms

Eₐ (NH₄⁺) = 4.95 kcal/mole at 185 K

= 3.6 kcal/mole at 234.5 K

1NH line shape studies at 1.8 K Tunnelling [195]

1NH line shape studies at 4.2 K Spin conversion [189]

1NH T₁ studies Pressure dependence [193]

T₁₀ in single crystal. [192]

1NH T₁ studies discontinuity at 398 K [194]

ND₄Br

2NH T₁ studies small discontinuity [196]

2NH line shape at 4.2 K [37]

Eₐ (ND₄⁺) = 4.00 + 0.16 kcal/mole

2NH T₁, T₁₀ studies [87]

1NH, 2NH T₁, T₁₀ studies

Eₐ (NH₄⁺) = 4.9 kcal/mole at 185 K [86]

= 3.6 kcal/mole at 234.5 K

1NH pressure dependence 15% Change in T₁ at 235 K [83]

2NH NMR studies [108]

T₁₀, T₁ cross relaxation measurements [105]
CH₃NH₃Br

Tetragonal

Phase transition

α phase > 295 K

173 K < β phase at < 295 K

83 K < ρ phase < 173 K

α phase < 83 K

(CH₃)₂NHBr

Monoclinic

P₂₁/m

(CH₃)₄NBr

Monoclinic

P₂(₁)⁻C₂⁻ Z = 4

(CH₃)₄NCdBr₃

Hexagonal

P₆₃/m Z = 2

(CH₃)₂[N(CH₃)₄]₂CdBr₄

Orthorhombic

D₄h (Pnnm) Z = 4

₁H N₂ & T₁ studies (199)

₁H N₂ studies 77-300 K (113)

₁H N₂ studies pressure & temperature dependence (67)

₁H N₂ & T₁ studies (120, 121)

Eₐ [(CH₃)₂NH] = 5.90 kcal/mole (120, 121)

₁H N₂ studies (200)

₁H N₂ studies (120 - 350 K) (122, 126, 201)

₁H T₁ studies T₁ min = 331 K (200, 202, 203)

₁H T₁ T₁P studies Eₐ [CH₃] = 6.4 ± 0.4 kcal/mole

Eₐ [N(CH₃)₄] = 11.5 ± 0.7 kcal/mole (124, 125)

₁H N₂ studies (74 - 200 K) (134, 141)

₁H T₁ studies (107-425 K) (142, 143)

Eₐ [N(CH₃)₄] = 6.34 ± 0.7 kcal/mole

₁H N₂ & T₁ studies frequency dispersion (77-400 K) (142A)

₁H T₁ (77 - 451 K) Maximum of 4.98 sec at 332.2 K

T₁ min = 11.9 m secs & 5.5 m secs at 148.9 K & 86.6 K respectively. Eₐ [(CH₃)₄N] = 4.1 kcal/mole (142)

₁H N₂ & T₁ studies frequency dispersion (77-400 K) (142A)

₁H T₁ (77 - 478 K) (142)

T₁ min = 8.5 m secs at 138.9 K and =5.5 msec. at 84.4 K

Eₐ [(CH₃)₄N] = 4 kcal/mole
\[(\text{CH}_3)_4\text{N}\else_{2}\text{HgBr}_4\]

Orthorhombic

\[D_{2h}^{16} (P_{nma}) Z = 4\]

\[^{\text{1H}} T_1\] studies 77 - 478 K \[205\]

\[T_1\] min = 5.85 ms secs at 166.7 K

= 2.9 ms sec at 80 K

\[E_a \left[\text{(CH}_3)_4\text{N}\right] = 5.2 \text{ kcal/mole}\]

\[^{\text{1H}} \text{ M}_2, T_{1e} \] studies 4.2 - 296 K \[163\]

\[T_1 \& T_2\] Change at \(T_c\) Spin isomerism

\[(\text{NH}_4)_2\text{SnBr}_6\]

Cubic

\[O_h^5 (F_{m3m}) Z = 4\]

\[^{\text{1H}} T_1\] studies 60 - 300 K \[206\]

\[E_a \left[(\text{NH}_4)_2\right] = 0.24 \text{ kcal/mole in phase I}\]

= 1.42 kcal/mole in phase II = 3.6 kcal/mole at 234.5 K

\[^{\text{1H}} \text{ line shape studies spin diffusion} \ [207]\]

\[\text{[(CH}_{3} \text{NH})_2 \text{TeBr}_6\]

Cubic

\[P_{31}\]

\[^{\text{1H}} \text{ M}_2\] studies \[176\]

\[^{\text{1H}} T_1\] studies Discontinuity in \(T_1\) vs. Temp.

\[E_a \left(\text{CH}_3\right) = 3.7 \text{ KJ/mole} \ [179]\]

\[E_a \left(\text{NH}_3\right) = 9 \text{ KJ/mole}\]

\[\text{[(CH}_{3}\text{)}_3\text{NH}]_2\text{HBr}_6\]

K:Ge, Sn, Te

Cubic

\[^{\text{1H}} \text{ M}_2\] studies 77 - 300 K \[181, 182\]

\[^{\text{1H}} T_1\] studies

\[\text{[(CH}_3)_4\text{N}]_2\text{HBr}_6\]

K: Pt, Te, Sn

Cubic

\[^{\text{1H}} T_1\] studies \[208\]

See Text

\[^{\text{1H}} T_1\] studies 77 - 478 K \[205\]

\[T_1\] min = 5.85 ms secs at 166.7 K

= 2.9 ms sec at 80 K

\[E_a \left[\text{(CH}_3)_4\text{N}\right] = 5.2 \text{ kcal/mole}\]

\[^{\text{1H}} \text{ M}_2, T_{1e} \] studies 4.2 - 296 K \[163\]

\[T_1 \& T_2\] Change at \(T_c\) Spin isomerism

\[(\text{NH}_4)_2\text{SnBr}_6\]

P.T. at 144.8 K

\[^{\text{2H}} \text{ line shape studies spin diffusion} \ [207]\]

\[^{\text{1H}} \text{ M}_2\] studies \[176\]

\[^{\text{1H}} T_1\] studies Discontinuity in \(T_1\) vs. Temp.

\[E_a \left(\text{CH}_3\right) = 3.7 \text{ KJ/mole} \ [179]\]

\[E_a \left(\text{NH}_3\right) = 9 \text{ KJ/mole}\]

\[\text{[(CH}_{3}\text{)}_3\text{NH}]_2\text{HBr}_6\]

K:Ge, Sn, Te

Cubic

\[^{\text{1H}} \text{ M}_2\] studies 77 - 300 K \[181, 182\]

\[^{\text{1H}} T_1\] studies

\[\text{[(CH}_3)_4\text{N}]_2\text{HBr}_6\]

K: Pt, Te, Sn

Cubic

\[^{\text{1H}} T_1\] studies \[208\]

See Text

205
II.4 Iodides

The activation energy is low even in single salt due to the increased ionic radius of iodine. However, the activation energy decreases further in double salts and tunnelling effects are found to occur at relatively higher temperatures.
Ammonium Iodide \( \text{NH}_4\text{I} \)

Ammonium iodide is known to have two phase transitions one at 257 K from NaCl to CsCl type and another order-disorder transition at 231 K where it changes form CsCl type to tetragonal. The nature of the transition in NH4I is similar to that observed in NH4Br where the microscopic ordering occurs as a result of antiparallel arrangement of the neighbouring NH4 tetrahedra and is very sluggish in nature.

Proton line shape and M2 studies by Gutowsky et al. show a constant line-width from 90 to 300 K and only a slight broadening below 90 K. Cook and Drain have observed discontinuity in the line width at the first order phase transition temperature of 255 K. Watton and Petch and Richards and Schaeffer have extended the line shape studies down to 20 K and observed peculiar line shape which were interpreted in terms of ammonium ion undergoing tunnelling reorientations. Similar studies by Ikeda and McDowell yielded an empirical relation between the tunnel splitting and the potential barriers hindering the rotation. Hennel and Lalowicz found a strange time dependence of the PMR spectra at liquid helium temperature and explained the results in terms of spin isomers. Pressure dependence studies of proton M2 show that the spectra broaden at 14 k bar indicating the pressure inhibits tunnelling motion. Proton T1 studies show a discontinuity at the phase transition temperature (255 K). Similar studies revealed a T1 maximum due to spin-rotation interaction in the cubic phase. They also noticed a frequency independent relaxation. Pintar et al. have examined the coexistence of cubic and tetragonal phases below \( T_c \) in the ordered phase of NH4I and ND4I, by the proton T1 studies. Further, they found that the replacement of NH4 by ND4 ion does not significantly affect the order in process in the tetragonal phase. Proton T1, T1D studies by Shimomora et al. and Iloth and Yamagata show that in phase I the relaxation is due to free rotation of the ammonium ion. Proton T1D and T1 studies show a very low activation energy in the ordered phase. Cross relaxation dispersion and temperature dependence of nuclear spin dipolar and rotating frame zeeman energies were carried out by Sharp and Pintar.

Their studies showed the less known properties of cross relaxation between detectable spins I and the fast relaxing spin S, such as the two types of \( H_1 \) dispersion and the occurrence of two minima of the rotating frame Zeeman relaxation time \( T_{1x} \) (I) when \( \gamma H_1 T_1(S)_{\text{min}} < 1 \) or the occurrence of two minima of the dipolar relaxation time \( T_{1D}(L) \), when \( \gamma H_1 \text{eff} T_1(S)_{\text{min}} < 1 \) and \( T_1(S)_{\text{min}} < T_2 \) (IS), are briefly discussed in the frame work of the Blink- Puris-Zumer theory.

The temperature dependence of \( T_{1x} \) (H) in polycrystalline NH4I shows that in Phase I, it is independent of temperature and in the vicinity of II-III transition and in phase III, the \( T_{1x} \) (H) depends on the direction in which the temperature was changed.

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prior to the measurements. On warming the sample from 120 K, $T_{1x}(H)$ for all values of rf field $H_1$ increases at first and then goes through a broad maximum before decreasing again in the vicinity of phase transition at 231 K. Throughout phase II, $T_1(H)$ increases exponentially as the temperature increases. At the II-I transition, there is a discontinuity of almost two orders of magnitude in $T_{1x}(H)$. Similar observations were made on $T_1(H)$ of ND$_4$I. $T_1D$ results also show a sharp increase in its value at II to I transition.

Niemella and Solini$^{218}$ have carried out $T_1$ studies of both iodine and proton nuclei over a range 86 to 323 K and found a discontinuity in $T_1$ of both at the phase transition. Blinc et al $^{219}$ have carried out $^{14}$N NMR chemical shift and proton $T_1$ measurements and found a discontinuous change in the chemical shift $\Delta \delta = 20.5$ppm at $\alpha$-$\beta$ transition accompanied by a dramatic drop in the $^{14}$N $T_1$ from 50 seconds to about 1.5 secs. At the $\beta$-$\gamma$ transition, a doublet splitting of the $^{14}$N line was observed.

**Methylammonium Iodide CH$_3$NH$_3$I**

Methylammonium iodide is known to exist in two phases room temperature ($\alpha$-Phase) and at 83 K ($\delta$-Phase). It is bimolecular with a tetragonal structure having a space group $P4/nmm$. Proton $M_2$ studies$^{113,220}$ in this and its deuterated analogues showed very low $M_2$ values around 440 K which are ascribed to the self diffusion of cation (confirmed by the electrical conductivity results) while the results in the region 77 K to 300 K are explainable by the reorientation of both CH$_3$ and NH$_3$ groups about the C-N axis of the cation. In this case the line was narrow ($M_2 = 9.2$ G$^2$) even at 77 K suggesting a strong possibility of proton tunnelling. Kalaparamal$^{67}$ has studied the pressure and temperature dependence of proton $M_2$ and found that application of pressure increases the barrier for rotation of NH$_3$ group motion increases through the changes in the hydrogen bond lengths because of the changes in the cell volume, while that for the CH$_3$ group motion shows no observable change. Proton $T_1$ studies by Sundaram et al$^{221}$ and Ishida et al$^{220}$ over a range 77-420 K in this compound and its deuterated analogues have been carried out. Their studies$^{220}$ show a deep $T_1$ minimum at 67 K which was attributed to the reorientation of the CH$_3$ and NH$_3$ groups about the C$_3$ axis. They did not notice any appreciable change at 167 K, whereas a slope change was observed in the region 133 to 167 K. The $T_1$ value showed a broad maximum at about 270 K and a sudden drop of $T_1$ was observed at 414 K in accordance with $T_{1r}$ detected by DTA. $T_2$ at this temperature was several milli seconds, which is ascribable to the self diffusion of the cations. The observations by Sundaram et al$^{221}$ was quite different from Ishida et al$^{220}$. The $T_1$ results depend very much on the way the sample is cooled. In slow cooling, $T_1$ increases monotonically and reaches a maximum again at 295 K. On the other hand the quenched samples showed only one broad maximum around 200 K. However, both behave similarly from
77 upto 166 K. Again above 295 K, the behaviour is the same independent of the history of the sample. The different T1 behaviour between 166 K and 295 K could be attributed to the phase transitions at 166 K and 295 K.

**Trimethylammonium Iodide  \((\text{CH}_3)_3\text{NI}\)**

This is isomorphous with trimethyl ammonium bromide with space group of \(P2_1/m\). No phase transition has been reported in these compounds. Proton \(M_2\) and \(T_1\) studies\(^{121}\) yielded information about the dynamics of the cation.

**Tetramethylammonium Iodide  \((\text{CH}_3)_4\text{NI}\)**

TMA iodide also like bromide does not undergo any phase transition. Mahajan and Rao\(^{126,201}\) and Dufourcq et al\(^{122}\) have carried out proton \(M_2\) studies over a range 100-400 K. They found the line-width to exhibit motional narrowing in two steps from 100 K upwards. The first narrowing around 170 K was ascribed to the onset of methyl group reorientation and the second around 230 K to the isotropic reorientation of the whole cation.

Albert et al\(^{124,125}\), Koksai\(^{203}\) and Rager and Weiss\(^{222,223}\) have carried out temperature variation of proton \(T_1\) and observed a double minima which were interpreted in terms of CH\(_3\) group rotation and the overall tumbling motion of the cation.

**Methylammonium Triiodo Plumbate  \(\text{CH}_3\text{NH}_3\text{PbI}_3\)**

This has a perovskite structure and is known undergo two successive phase transitions as follows.

Phase I (cubic) 315 K Phase II Phase 164 K Phase III.

The \(^2\text{H}\) and \(^{14}\text{N}\) NMR studies (both \(M_2, T_1\)) was carried out by Wasylischen et al\(^{134}\). They found that in the cubic phase I both \(^2\text{H}\) and \(^{14}\text{N}\) spectra were characterized by a single narrow line and the \(T_1\) (\(^2\text{H}\)) 0.5 seconds, \(T_1\) (\(^{14}\text{N}\)) and increases with temperature. The absence of any \(^2\text{H}\) and \(^{14}\text{N}\) quadrupole splittings indicate extremely rapid overall reorientation of the C-N axis in a potential of cubic symmetry. In Phase II, both \(T_1\) and the small quadrupole splitting show unusual variation with temperature. In the lowest temperature phase rotation of the C-N axis are restricted.
Tetramethylanmonium Triiodo Mercurate \((\text{CH}_3)_4\text{NHgI}_3\)

This has a rhombic structure with space group P\(\text{6}_2\text{1m}\) and is a ferroelectric with out \(T_c\). Proton \(M_2\) studies\(^{140,141}\) over the range 4.2 to 300 K show that even at low temperatures the CH\(_3\) groups are not disoriented. The observed decrease in \(M_2\) was ascribed to the methyl group rotation about the C-N bond and also due to the random reorientations of the TMA ions.

Sarma et al\(^{142,143}\) have carried out proton \(T_1\) over a range 107 to 423 K and observed a single minimum at 174.4 K, indicating that the correlation times corresponding to the motion of TMA ion and methyl group are close to each other and it was predominantly due to the motion of the methyl group.

Diammonium Tetraiodo Cadmate \((\text{NH}_4)_2\text{CdI}_4\)

Proton \(M_2\) and \(T_1\) studies have been done by Venu et al\(^{225}\) over the range 77 to 400 K showing that there is a single line with a constant \(M_2\) down to 160 K, below which it develops wings with a corresponding \(M_2\) of 32 G\(^2\). The proton \(T_1\) data at three different frequencies show that at high temperatures it is independent of frequency and with a change of slope at about 265 K. With further decrease in temperature it revealed a single minimum around 200 K. The slope change at 265 K is due to the phase transition. Below 160 K inequivalent sites for NH\(_4\) groups develop, one corresponding to the rigid lattice limit and the other undergoing a fast reorientation motion. The phase transition may be associated with the appearance of inequivalent groups.

Tetramethylanmonium Tetraiodo Mercurate \((\text{CH}_3)_4\text{NHgI}_4\)

This crystallizes in the orthorhombic space group \(P_{\text{nma}}\) with \(Z = 4\) and is not known to have any phase transitions. Sarma et al\(^{142,205}\) have studied proton \(T_1\) over the range 77 to 467.8 K and found two distinct minima at 163.9 K and 105.3 K which were attributed respectively to the motion of TMA ion together with C\(_3\) rotations of CH\(_3\) groups and to the torsional oscillations of CH\(_3\) groups about the C-N axis.

Tetramethylanmonium Tetraiodo Cadmate \([((\text{CH}_3)_4\text{N})_2\text{CdI}_4\]

This crystallizes in the orthorhombic space group \(P_{\text{nma}}\) with \(Z = 4\). Sarma\(^{142}\) has carried out proton \(T_1\) studies over a range 77 to 470.6 K and found a maximum at 344.8 K and two minima at 152.7 K and 109.9 K. They attributed the high temperature minimum to the TMA ion reorientation and the lower one to the torsional oscillations of the methyl groups. The maximum was interpreted as due to the spin-rotational interaction.

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Diammonium Hexaiodo Platinate \( \text{(NH}_4\text{)}_2\text{PtI}_6 \)

This has a cubic structure. Proton M\textsubscript{2} studies by Watton et al\textsuperscript{37} at 4.2 K show a very small M\textsubscript{2} value and the results are discussed in terms of indistinguishability of NH\textsubscript{4} protons and the formation of spin isomers.

Methylammonium Hexaiodo Tellurate \( \text{(CH}_3\text{NH}_3\text{)}_2\text{TeI}_6 \)

This also has a cubic structure at room temperature and is known to undergo a first order phase transition to a low symmetric phase at 119 K. The proton M\textsubscript{2} studies\textsuperscript{178} show that at high temperature phase I, the overall tumbling motion of the cation is taking place whereas in the low temperature phase the motion is somewhat restricted. The proton T\textsubscript{1} studies\textsuperscript{179} revealed a deep minimum around 66 K and a shallow depression around 100 K. These results are explained in terms of C\textsubscript{3} rotation of CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+} ion and independent rotations of CH\textsubscript{3} and NH\textsubscript{3} groups respectively.

Trimethylammonium Hexaiodo Metallate \( \text{(CH}_3\text{)}_3\text{NH}-\text{MII}_6 \; \text{M:Pt,Sn,Te} \)

Proton M\textsubscript{2} and T\textsubscript{1} studies in these metal complexes by Ikeda et al\textsuperscript{181,182} showed two T\textsubscript{1} minima, a deep one around 160 K was attributed to the reorientation of the CH\textsubscript{3} groups and the other shallow minimum occurring around 220-260 K (depending on the compound) on the high temperature side of the deep one to the reorientation of the whole cation about its C\textsubscript{3} axes.
\[ \text{NH}_4^+ \]

\[ T_{c1} = 257 \text{ K. First order} \]

\[ T_{c2} = 231 \text{ K. Order-disorder} \]

\[ T_{d} \quad (P-43m) \quad Z = 1. \]

\[ \text{Cubic} \]

\[ \text{1H N}_2 \text{ studies} \quad [198, \ 18, \ 209] \]

\[ \text{1H T}_1 \text{ studies} \]

Discontinuity in line width & \[ T_1 \] was observed at 255 K

\[ E_a (\text{NH}_4^+) = 1.7 \text{ to } 2.2 \text{ kcal/mole} \]

\[ \text{1H line shape studies} \quad \text{Tunneling} \quad [198, \ 188] \]

\[ E_a (\text{NH}_4^+ \text{ ion}) = 2.4 \text{ kcal/mole} \]

\[ \text{1H line shape at } 4.2 \text{ K} \quad [213, \ 216, \ 217] \]

\[ \text{1H N}_2 \text{ studies} \quad \text{Pressure dependence} \quad [214] \]

\[ \text{1H T}_1 \text{ studies} \]

\[ \text{1H T}_1 \text{ studies} \quad [211, \ 212, \ 99, \ 210, \ 87, \ 218] \]

\[ \text{1H T}_{1D} \text{ studies} \quad [215] \]

\[ \text{CH}_3\text{NH}_3^+ \]

Two phases

\[ P_4/nnm \quad Z = 2 \]

\[ 83 \text{ K} < \text{phase} < 295 \text{ K} \]

\[ \text{Phase} < 83 \text{ K} \]

\[ \text{Additional phase } \text{l}_{\text{NH}} \]

\[ 414 \text{ K} \quad \text{above} \]

\[ \text{(CH}_3)_2\text{NH} \]

\[ \text{Tetragonal} \]

\[ P_4/nnm \]

\[ 1\text{H N}_2 \text{ studies Proton tunneling} \quad [113] \]

\[ 1\text{H N}_2 \text{ Pressure & Temperature dependence} \quad [67] \]

\[ 1\text{H T}_1 \text{ studies } 77 \quad 420 \text{ K} \quad [221] \]

\[ 1\text{H N}_2 \text{ & } T_1 \text{ studies } (77 \quad 300 \text{ K}) \quad [220] \]

\[ E_a (\text{CH}_3\text{NH})^+ = 1.69 \text{ kcal/mole} \]

\[ 1\text{H N}_2 \text{ & } T_1 \text{ studies} \quad [121] \]

\[ E_a [(\text{CH}_3)_2\text{NH}] = 4.4 \text{ kcal/mole} \]

\[ 1\text{H N}_2 \text{ studies } (100 \quad 400 \text{ K}) \quad [122] \]

\[ E_a (\text{CH}_3) = 5.5 \pm 0.3 \text{ kcal/mole} \quad [126, \ 210] \]

\[ E_a [(\text{CH}_3)_4\text{N}] = 11 \pm 0.7 \text{ kcal/mole} \]

\[ 2\text{H T}_1 \text{ studies} \quad [204] \]

\[ 1\text{H T}_1, T_1 \text{ studies Double minima} \quad \text{was observed} \quad [125, \ 203, \ 222, \ 273, \ 224] \]

\[ \text{CH}_3\text{NH}_2\text{PbI}_3 \]

\[ \text{Cubic} \]

Phase I \[ > 315 \text{ K} \]

\[ 164 \text{ K} < \text{phase} II < 315 \text{ K} \]

\[ \text{Phase} III < 164^\circ \text{C} \]
\[(\text{CH}_3)_4 \text{NHgI}_3\]

Ferroelectric

Orthorhombic

\[P_{621m}\]

\[\text{^1H M}_2\] studies 80 - 300 K [140, 141]

\[\text{^1H T}_1\] studies 107 - 423 K [142, 143]

\[T_{\text{min}} = 5.6 \text{ ms at 174.4 K}\]

\[E_a [\text{M(CH}_3)_4] = 4.07 \text{ kcal/mole}\]

\[(\text{NH}_4)_2 \text{CdI}_4\]

P.T at 265 K

Orthorhombic

\[D_{2h} \quad \text{Pnm} a \quad Z = 4\]

\[\text{^1H T}_1\] studies [77 - 400 K] [225]

\[E_a [\text{CH}_3]_4^+ = 4.1 \text{ kcal/mole}\]

\[(\text{CH}_3)_4 \text{N}_2 \text{HgI}_4\]

Orthorhombic

\[D_{2h} \quad \text{Pnm} a \quad Z = 4\]

\[\text{^1H T}_1\] studies [142, 205]

\[T_{\text{min}} = 5.9 \text{ ms at 163.9 K}\]

\[12 \text{ ms at 105.3 K} \quad E_a [\text{CH}_3]_4 = 4.1 \text{ kcal/mole}\]

\[(\text{CH}_3)_4 \text{N}_2 \text{CdI}_4\]

Orthorhombic

\[D_{2h} \quad \text{Pnm} a \quad Z = 4\]

\[\text{^1H T}_1\] studies 77 - 470.6 K [142]

\[T_{\text{min}} = 7.5 \text{ ms at 152.7 K} \quad [\text{Vani's paper}]\]

\[= 9.5 \text{ ms at 109.9 K}\]

\[E_a [\text{CH}_3]_4 = 3.9 \text{ kcal/mole}\]

\[(\text{NH}_4)_2 \text{PtI}_6\]

Cubic

\[\text{^1H M}_2\] studies \(M_2 = 10 + 1 G^2 \tau \ 4.2 \text{ K}\]

Spin isomerism [37]

\[(\text{CH}_3\text{NH}_3)_2 \text{TeI}_6\]

Cubic

\[\text{^1H M}_2\] studies (77-300 K) [178]

\[\text{^1H T}_1\] studies \(E_a \text{ for CH}_3 \text{ and NH}_3 = 1.19 \text{ kcal/mole}\) [179]

\[E_a [\text{CH}_3]_{\text{NH}_3} = 1.46 \text{ kcal/mole}\]

\[(\text{CH}_3)_3 \text{NH}_2 \text{WI}_6\]

(P = Pt, Sn, Te)

\[\text{^1H T}_1\] studies [181, 182]

\[E_a [\text{CH}_3] = 2.89 \pm 0.12 \text{ kcal/mole}\]

\[E_a [(\text{CH}_3)_3 \text{NH}] = 5.83 \text{ kcal/mole}\]
This section covers NMR studies on NH$_4$ClO$_4$, CH$_3$NH$_3$ClO$_4$, [(CH$_3$)$_3$]$_3$NHClO$_4$, and (CH$_3$)$_4$NCIO$_4$. Changes in the cation symmetry are clearly reflected in the NMR studies. Studies on NH$_4$ClO$_4$ have been carried out over a wide range of temperature by many authors. Studies down to liquid helium temperatures have shown quantum mechanical tunnelling. Line shape and relaxation studies in partially deuterated NH$_4$. $^2$D$_x$ClO$_4$ yield information about tunnelling splitting. Studies at high temperatures have shown interesting cross relaxation with $^{17}$O. CH$_3$NH$_3$ClO$_4$ and (CH$_3$)$_3$NHClO$_4$ have shown interesting phase transitions and proton diffusion at high temperatures.
Ammonium perchlorate crystallizes in the orthorhombic space group $D_{2h}^{16}$. The structural conditions do not permit the formation of strong linear H-bonds of the type N-H-O and hence easy reorientation of NH$_4^+$ ion is possible.

Proton $M^2$ and line shape studies have been carried out in the powder specimen. Richards and Schaefer have reported a very small $M_2$ of 2.42 G$^2$ even at 20 K. However Hennell and Lalowicz have interpreted the complex line shape consisting of the narrow and the broad component with $M_2$ values of 13.5 G$^2$ and 8.9 G$^2$ in terms of isotropic and $C_3$ reorientation of NH$_4^+$ ion respectively. Ibers has investigated proton $M_2$ over the range 70 to 298 K and found that $M_2$ remains constant at (1.18 ± 0.1 G$^2$) throughout the temperature range. He has interpreted the $M_2$ data in terms of the reorientation of ammonium ion about random axis at frequencies greater than about $10^5$ cps. The PMR line shape at low temperatures has been found to be narrower than those expected for rapidly tunnelling ammonium ions. The narrowing was temperature dependent, suggesting a kinetic process that involves modulation of tunnelling states. They considered a possible "exchange narrowing" mechanism involving fluctuating molecular torsional states brought about by external lattice perturbation, which led to a satisfactory simulation of the observed low-temperature line shapes. Theoretical analysis of the NMR line shapes of NH$_4^+$ ion undergoing composite tunnelling and reorientational motion ($C_2$ and $C_3$) has been carried out by Lalowicz et al, which takes into account the coupling of rotor states of the ion with lattice phonons to account for the observed narrow line. Code et al have analyzed the narrow and broad components in the PMR spectra in terms of A type and T type NH$_4^+$ ions where A and T are the irreducible representations of the tetrahedral symmetry of ammonium ion. But Riehl et al have not observed any complicated structure or the broad component in the PMR spectra as reported earlier. They have interpreted their results in terms of possible hindered rotor levels of the NH$_4^+$ ion and spin isomerism.

Proton $T_1$ studies have revealed interesting features. Reil et al have observed a shoulder in $T_1$ vs. temperature plot around 44 K and also non exponential recovery of magnetization below 20 K. The presence of shoulder is due to the fact that tunnel splittings of the torsional ground state of NH$_4^+$ ion are equal to the Zeeman splitting. They have also predicted spin conversion below 4 K. The $T_1$ results of Code et al are in disagreement with that of Riehl et al. Gutter and Van schulz have reported three minima in the temperature dependence of proton relaxation, of which one at 40 K was found to be independent of frequency. These observed minima are explained on the basis of large exchange splittings of the weakly hindered NH$_4^+$ ion. Proton $T_1$ measurements as a function of frequency at various temperatures revealed multiple $T_1$ minima which were explained in terms of the tunnel splittings of
the NH₄ group due to the low symmetry of the crystal field. The temperature dependence of the tunnel splitting was discussed in terms of Allen's model. They also found an unexpected strong anisotropy of T₁ at liquid helium temperature. Morimoto and Shimomora and Ikeda and McDowell have measured proton T₁ between 125 K and 556 K and found two minima at 476 K and 238 K. The high temperature minimum was attributed to the cross relaxation between ¹H and ¹⁷O, while the low temperature minimum to the reorientation of ClO₄ ion which modulate the dipolar interaction. Other study revealed a T₁ maximum at 210 K. They interpreted the T₁ data at low temperatures in terms of dipolar interactions and at high temperatures to the spin-rotational interaction.

Svare and Tungstall from proton T₁ studies in partially deuterated (NH₄₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋之內容

Deuteron NMR spectra of ND₄ClO₄ studied by Chiba did not show any quadrupole splitting even at low temperatures but had a characteristic feature of rapidly reorientating ammonium ions. Deuteron T₁ studies over the range 1.72 to 40 K at different frequencies revealed a shallow level-crossing minimum which were interpreted in terms of tunnel splitting of the NH₄⁺ ion ground state. Deuteron NMR line shape studies at various magnetic fields (0.63 to 1.48 T) and at 4.2 K exhibited a remarkable change in shape and width which was interpreted as due to the level crossing between Zeeman and tunnelling systems.

Svare et al have carried out proton T₁ measurements in partly deuterated NH₄ClO₄ over the range 1.5 to 4.2 K. They found that classical relaxation was same for pure and partly deuterated analogues, whereas the low temperature T₁, T₁ results are reduced by 25% in the deuterated salt, since the relaxation is fast in asymmetric NH₃D⁺ ion.

Shimomura et al have studied proton T₁D and found a large minimum which was interpreted in terms spin-rotation interactions. Morimoto observed temperature dependence of T₁ and T₁D in partially deuterated NH₄₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋之內容

Activation energy Eₐ for reorientation of ClO₄ was estimated as 6.2 kcal/mole.
Methyl Ammonium Perchlorate  \( \text{CH}_3\text{NH}_3\text{ClO}_4 \)

This compound is known to undergo two phase transitions at 321 and 415 K, as detected from DTA studies. Proton \( T_1 \) studies by Ishida et al.\(^{239} \) show a monotonic decrease of \( T_1 \) from 300 K to 77 K which was attributed to the slowing down of the random jumps of the cation about its \( C_3 \) axis. Around room temperature \( T_1 \) showed a broad maximum and did not show any detectable anomaly at the lower \( T_c(321 \text{ K}) \), whereas a discontinuity was observed at 451 K. At the same temperature, \( T_2 \) also increased abruptly from tens of microseconds to 16 milliseconds. These changes in \( T_1 \) and \( T_2 \) were explained in terms of the self-diffusion of the cations.

Trimethyl Ammonium Perchlorate  \((\text{CH}_3)_3\text{NHClO}_4\)

This compound undergoes successive phase transitions as follows.

Phase I 480 K  Phase II 397 K  Phase III

Phase I is tetragonal with \( Z = 2 \), while the crystal structures of phase II and III are not known.

Jurga\(^{240} \) has carried out proton \( M_2 \) and \( T_1 \), \( T_{1p} \) and \( T_{1D} \) studies in this salt. The temperature dependence of the \( M_2 \) shows four plateau values of 29.7, 10.0, 2.1 and 1.0 \( \text{G}^2 \). Above 473 K (i.e. in phase I) a gradual line narrowing appears giving a liquid like line shape. The low temperature plateau of \( M_2 \) in phase III corresponds to rigid-lattice and the intermediate plateau to the reorientation of methyl groups about their \( C_3 \) axis while the high temperature plateau of 2.1 \( \text{G}^2 \) is assigned to the reorientation of methyl groups about their \( C_3 \) axis in combination with reorientation of the whole ion about a triad \( C_3 \) axis lying on the H-N bond direction. The constant value of \( M_2 = 1.0 \text{G}^2 \) in phase II is believed to account for the isotropic or quasi-isotropic reorientation which reduces intra ionic contribution to zero. The observed value of \( M_2 \) corresponds then to interionic interactions in the presence of this motion. Temperature dependence of the proton \( T_1 \), \( T_{1D} \) show two minima at 260 K and 202 K. The phase III to phase II transition does not affect the \( T_1 \) relaxation, however a small discontinuity of \( T_{1p} \) and \( T_{1D} \) was observed. In phase II they observed a \( T_{1p} \) minimum at 444 K. On approaching phase I a jump in \( T_1 \) and \( T_{1p} \) occurs. Spin lattice relaxation in phase III is assumed to be due to \( C_3 \) and \( C_{3i} \) reorientations with different correlation times. In this phase a discrepancy between the calculated and observed \( T_1 \) and \( T_{1D} \) minimum values was found. i.e., the calculated values were less than the experimentally observed values suggesting that an asymmetrical potential barrier exists. The calculation of relaxation times under the assumption of a three fold asymmetrical potential barrier, where two of the minima have equal depths while the third has a higher or lower energy, leads to a
significant elongation of relaxation times, which explains the observed $T_1$ and $T_{1D}$ minimum. He has also suggested that the quasi-isotropic motion in phase II takes place about the $C_3'$ axis (known to lie along the N-H O hydrogen bond) with high frequency and the formation and breaking of these hydrogen bonds is also taking place simultaneously at a frequency much lower than $C_3$ axis rotation, but high enough to narrow the spectrum, hence an effective source of $T_1$ and $T_{1D}$ relaxation. In phase I he observed (1) a liquid like line shape, (2) a decrease in $T_1$ and (3) an increase in $T_{1P}$ with temperature. These results were explained in terms of self diffusion of Trimethyl ammonium ions. The temperature dependence of $T_1$ and $T_{1P}$ implies that the diffusion is slow compared to the spin locking frequency. They have interpreted the $T_1$ results in this phase in terms of Torreys 'Lattice diffusion' model.

Tetramethyl Ammonium Perchlorate TMAClO$_4$

This salt is known to undergo two successive phase transitions at 703 and 613 K. The crystal structure of the high temperature Phase I is not known whereas the Phase II (below 613 K) crystallizes in the space group $P4_1/nma$ with $Z=2$.

The proton $M_2$ and $T_1$ studies$^{240,242}$ show that line narrowing takes place in a single step, suggesting that the motion of CH$_3$ groups about the C-N axis and of the cation as a whole are not separated. Mahajan and Nageswara Rao$^{241,243}$ also carried out proton line width and $M_2$ studies over the range from 140-400 K and their results agree well with the earlier studies$^{240,242}$. The proton $T_1$, $T_{1P}$ studies$^{240}$ show a single $T_1$ minimum at 222 K with slightly different slopes on both sides of this minimum, and a $T_{1P}$ minimum at 153 K. This asymmetrical temperature dependence of $T_1$, $T_{1P}$ made them to conclude that CH$_3$ group reorientation about their $C_3$ axis and and quasi-isotropic (QI) reorientation of the whole cation are taking place with frequencies close to each other. An extended study$^{242}$ by the same workers showed a single $T_1$ minimum at 239 K and they concluded that only isotropic motion of the TMA ion as a whole takes place. Deuteron NMR in N-deuterated salts have been studied by Jurga and Spiess$^{244}$.

Tetramethyl ammonium Chlorate TMAClO$_3$

This compound crystallizes in the tetragonal space group $P4_1/nmm$ with $Z=2$. The DTA studies show that it undergoes Two successive phase transitions at 232 and 256 K.

Proton line width and $M_2$ studies by Mahajan and Rao$^{243}$ show that the line narrowing takes place in a single step in the region 140 and 200 K. They concluded that both, the methyl group reorientation and the overall rotation of the cation are taking
place at very close frequencies and hence can not be separated. However they did not notice any anomalous change in M₂ at phase transition temperatures.

Proton T₁, T₁ρ studies²⁴⁵ show that T₁ exhibits a broad minimum at around 240 K, whereas T₁ρ exhibits a partially resolved shallow minima at about 164 K and 200 K. The results were analyzed in terms of the reorientation of CH₃ groups and the tumbling motion the TMA⁺ ions. Further it was found that neither T₁ nor T₁ρ show any anomalous change at the transition points.
Orthorhombic

$D_{2h}^{16}$ $Z = \frac{1}{3}

$^{1}$H $M_2$ studies & SLR times 70 - 290 K [226]

$E_a (NH_4^+) = 2.0 + 0.6 \text{ kcal/mole}$

$^1$H line shape & $M_2$ studies at 20 K [209]

$^2$H $M_2$ studies [106]

$^1$H $M_2$ studies 1.2 to 4.2 K [227]

$^1$H $T_1$ studies 80 - 400 K [228]

$^1$H $M_2$ & $T_1$ studies 1.5 - 100 K [229]

PMR line shape analysis [66]

Zeeman SLR tunnel splitting studies [230, 231, 232]

$\text{HNR } M_2$ studies $E_a (NH_4^+) = 0.6 \text{ kcal/mole}$ [234]

$^1$H, $T_1$, $T_{1D}$ studies $E_a (NH_4^+) = 0.65 \text{ kcal/mole}$ [57, 58]

$^2$H $^2$H $M_2$ & $T_1$ studies

$E_a (NH_4^+) = 0.76 \text{ kcal/mole}$ [24, 164]

$^1$H $T_{1D}$ studies $E_a (NH_4^+) = 0.65 \text{ kcal/mole}$ [223]

$^2$H HNR. $^1$H $T_1$ studies [236, 237, 238]

$^1$H $T_1$ studies 77 - 300 K

$E_a \left( \text{CH}_3NH_3 \right)^+ = 1.2 \text{ kcal/mole} \text{ about } C_3 \text{-axis}$ [239]

No change in $T_1$ at $T_{C2} = 321$ K

& a discontinuous change in $T_1$ at $T_{C1} = 451$ K

$E_a \left( \text{CH}_3NH_3 \right)^+ SD = 6.93 \text{ kcal/mole}$.

Two phase transition

$T_{C1} = 451$ K, $T_{C2} = 321$ K

$\left(\text{CH}_3\right)_3\text{NHClO}_4$

Phase I tetragonal

480 K < phase I > 548 K

$Z = 2$

397 K < phase II < 480 K

$^1$H $M_2$ & $T_1$, $T_{1F}$ & $T_{1D}$ studies [240]

Anomalies in $T_1$, $T_{1F}$ & $T_{1D}$

$E_a \left( \left( \text{CH}_3 \right)_3 \text{NH} \right)^+ C_3 \text{ reorg} = 5 \text{ kcal/mole}$
$\text{CH}_3\text{ClO}_4$

613 K < phase I < 703 K

Phase II < 613 K

$\text{CH}_3\text{ClO}_3$

Tetragonal

P.T. at

$T_{c1} = 256$ K, $T_{c2} = 232$ K

$\text{IrCl}_3$

P4/nmm $Z = 2$

$^1\text{H} \text{Ir}_2$ & $T_1$, $T_{16}$ studies [240, 242]

$^1\text{H} \text{Ir}_2$ studies [241, 243]

$^2\text{H} \text{Ir}_2$ studies [244]

$^1\text{H} \text{Ir}_2$ studies [243]

$^1\text{H} T_1$, $T_{16}$ studies [245]

$E_a (\text{CH}_3) = 5.06$ kcal/mole

$E_a (\text{Ir}(\text{CH}_3)_4)^n = 7.86$ kcal/mole

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II.6 Nitrates

$^1$H NMR studies of NH$_4$NO$_3$ are interesting because of its successive phase transitions. Moreover, NMR studies on mixed salts like ANO$_3$-NH$_4$NO$_3$ (A: Cs, Rb, Li, K, etc.) reveal the effect of impurity on the $T_c$ of NH$_4$NO$_3$. CH$_3$NH$_3$NO$_3$ and (CH$_3$)$_4$NNO$_3$ show the effect of changes in the cation symmetry on NMR spectra. (NH$_4$)$_2$Ce(NO$_3$)$_6$ is the only double nitrate which has been studied. It shows spin-rotation interaction at high temperatures and tunnelling at low temperatures and is a good example of a weakly hindered salt.
Ammonium Nitrate \( \text{NH}_4\text{NO}_3 \)

Ammonium nitrate exhibits a sequence of six successive phase transitions as follows.

Phase I (cubic) \( 398 \text{ K} \) Phase II (CsCl structure) \( 357.7 \text{ K} \) Phase III \( 305.5 \text{ K} \) Phase IV

Phase IV \( 255.2 \text{ K} \) Phase V \( 103 \text{ K} \) Phase VI

It has been found that in dry \( \text{NH}_4\text{NO}_3 \) only transformations between the phases V, IV, II and I take place. The transitions from the phase IV to III and from III to II take place only in the presence of moisture. The phases I, II, IV and V are structurally similar and the transition between them appear to be of the order-disorder type. On the other hand, the transformations from the phase IV to III and that from phase III to II involve a process of dissolution and recrystallisation. The \( T_C \) in the case of deuterated salt increases very slightly.

Proton line width and \( M_2 \) studies by Brown and Mclaren\(^{246}\) show a marked change at the transition point \( 398 \text{ K} \) from phase I-II. They interpreted the \( M_2 \) results in phase I in terms of the ammonium ion diffusion (in agreement with electrical conductivity results) and to the isotropic reorientation of \( \text{NH}_4^+ \) ions. Watton et al.\(^{37}\) have studied proton line shape at 4.2 K and found a wing structure which was explained in terms of spin isomerism. Ikeda and McDowell\(^{188}\) also analyzed the PMR spectra at 1.8 K and found that the line shape is determined by the energy level scheme of the A, T and E tunnel splitting of the torsional ground state of the \( \text{NH}_4^+ \) ion.

Proton \( T_1 \) studies have been carried out by Hovi et al.\(^{248}\), Niemela et al.\(^{250}\), Riggin et al.\(^{249}\), and Koksal and Bahceli.\(^{194}\) They found a \( T_1 \) minimum in the range 130-170 K, and concluded that the relaxation is due to the translational diffusion of the ammonium ion which is confirmed by electrical conductivity measurements. Riggin et al.\(^{249}\) found that at the plastic to brittle phase transition (at 398 K), the correlation time for translational diffusion of the \( \text{NH}_4^+ \) ion increases by more than 3 orders of magnitude. Otherwise their results are in good agreement with Hovi et al.\(^{248}\). Koksal and Bahceli\(^{194}\) found a \( T_1 \) minimum at 133 K and a maximum around 325 K. Moreover they observed a \( T_1 \) discontinuity at 300 K where it increases 3 times that at 298 K. Above 365 K it decreases rapidly as the temperature is increased. They interpreted the \( T_1 \) data in terms of the ammonium reorientation and spin rotation. Proton \( T_1 \) studies at different pressures (1 to 680 atm) and at various temperatures (169-400 K) did not reveal any change in \( T_1 \) with pressure. However, they noticed an abrupt increase in \( T_1 \) by approximately 14% at the transition point from phase IV to V.
Hovi et al\textsuperscript{247} and Niemela et al\textsuperscript{250} have carried out DMR studies in $\text{ND}_4\text{NO}_3$ over 100-403 K. They\textsuperscript{247} found that in phase I, the observed line width is much smaller than the calculated one and this was explained in terms of diffusion of ammonium ions with an average frequency larger than one kHz. In phase II the observed experimental line width agrees with the calculated one. In phase III-V, the experimental line width is much larger than that caused by dipolar broadening, thus the electric quadrupole interaction of the deuteron is found to be the main source of line broadening in these phases. They also obtained 179 kHz for the deuteron Q.C.C. Hovi et al\textsuperscript{252} observed abrupt line width changes at 255.5±2 K, 308.7±2 K, 366.2±2 K, 400.7±2 K in the deuteron NMR spectra of this compound, below 135 K they observed rapid line broadening.

Richards and Schaeffer\textsuperscript{209} have studied line width and $M_2$ from 20 K to 300 K in $\text{NH}_4\text{NO}_3$ and also in $\text{NH}_4\text{NO}_3$-RbNO$_3$ solid solutions. The $M_2$ at 20 K was about 50 G$^2$ which corresponds to rigid lattice value of ammonium ions. The line shape was little different with minor peaks separated by about 33 gauss, which could not be properly explained. The solid solution with 8 mole% and 15 mole% RbNO$_3$ at 20 K had a $M_2$ value of 31.7 G$^2$ and 29.0 G$^2$ respectively which suggests that the interionic contributions are considerably decreased. At 300 K the $M_2$ values are the same for both pure and solid solutions, and is equal to 2.7 G$^2$. Velkov and Buryak\textsuperscript{251} have studied PMR spectra of $\text{NH}_4\text{NO}_3$-MNO$_3$ (M=Li, Na, K, Cs) systems at different temperatures and found that NO$_3$ ions with Na and Li cation was bidentate whereas that with K, Rb and Cs it was monodentate. They also observed the absence of the fine structure in the PMR spectra of the ammonium ion close to the fusion temperature of $\text{NH}_4\text{NO}_3$.

Methylammonium Nitrate $\text{CH}_3\text{NH}_3\text{NO}_3$

This compound is known to have two successive phase transition at 352 K and 384 K as revealed by DTA studies. The first order phase transition at 352 K is known to show a remarkable hysteresis. Ishida et al\textsuperscript{253} have carried out proton $M_2$ studies over a range 77-300 K. In the region 120 to 150 K $M_2$ of 23 G$^2$ corresponds to the reorientation of $\text{CH}_3$ groups alone ($\text{NH}_3$ being rigid) whereas the second plateau of 8 G$^2$ above 150 K up to room temperature to the reorientation of both $\text{CH}_3$ and $\text{NH}_3$ groups.

The proton $T_1$ and $T_2$ studies\textsuperscript{239,253} show a $T_1$ anomaly at 352 K. At the same temperature the $T_2$ also changed discontinuously from tens of microseconds to 4 milli secs. The observed $T_1$ was interpreted in terms of the dipolar relaxation due to the reorientation of the cation about its C$_3$ axis. In the highest temperature phase (above
384 K), the \( T_1 \) is found to have a negative temperature coefficient, which was interpreted in terms of isotropic reorientation of the cation and also their self-diffusion. Ishida et al.\(^{253} \) observed two well separated minima in \( \text{CH}_3\text{NH}_3\text{NO}_3 \) at 135 K and 198 K. They attributed the low temperature minimum (135 K) to the \( \text{CH}_3 \) reorientation about its \( C_3 \) axis, and the high temperature minimum (198 K) to the \( \text{NH}_3 \) reorientation. A single minimum observed at 137 K in \( \text{CH}_3\text{ND}_3\text{NO}_3 \) was attributed to the \( \text{CH}_3 \) reorientation. On the high temperature side of the \( T_1 \) minimum, \( \text{CH}_3\text{NH}_3\text{NO}_3 \) showed some non-exponential behaviour in the magnetization recovery, which was explained in terms of the theory of symmetry-restricted spin diffusion by Emid et al.\(^{241A} \).

**Tetramethylammonium Nitrate** \( (\text{CH}_3)_4\text{NNO}_3 \)

Proton \( M_2 \) studies\(^{241,243} \) show that the line narrowing takes place in two distinct steps, one in the region 145 to 170 K was ascribed to the \( \text{CH}_3 \) rotation and the other in the range 190 to 206 K to the \( \text{TMA}^+ \) ion reorientation as a whole. Proton \( T_1, T_1\rho \) studies\(^{242} \) over a wide temperature range shows a discontinuity at around 274 K when the solid is cooled and at around 289 K upon heating. DTA studies also show peaks at these points on cooling and heating indicating that it is a first order phase transition. Above these points, the \( T_1 \) exhibits a minimum at 286 K and increases again with increase in temperature, a feature which they ascribe to the \( \text{TMA}^+ \) ion rotation as a whole. Below the phase transition, down to 220 K \( \log T_1 \) vs. \( 1/T \) was found to be nonlinear but below 220 K it showed linearity. Further, they assumed the existence of two different motions in this phase. (1) The rotation of \( \text{CH}_3 \) groups around their \( C_3 \) axis and (2) the tumbling motion of the whole \( \text{TMA}^+ \) ion. The \( T_1 \) measurements show two minima at around 245 K and 200 K, which were attributed to the overall tumbling of \( \text{TMA}^+ \) ion along with \( \text{CH}_3 \) group rotation. The \( M_2 \) data of Mahajan et al.\(^{243} \) was used to calculate \( T_1 \) min. and an excellent agreement was found between the two.

**Diammonium Cerium Nitrate** \( (\text{NH}_4)_2\text{Ce(NO}_3)_6 \)

This salt crystallizes with monoclinic space group. The PMR spectra studied by Watton et al.\(^{37} \) at 4.2 K show a very small \( M_2 \) \((3.0 \pm 0.2 G^2) \) and a line width of \((1.5 \pm 0.1 G) \) which was explained in terms of spin-isomerism.

Morimoto\(^{254} \) has carried out proton \( T_1, T_1\rho \) measurements over the range 4-300 K and found that the relaxation was nonexponential below 20 K. They observed a,\( T_1 \)
$\text{NH}_4\text{NO}_3$

Phase $I < 398$ Cubic

357.7 K $< \text{phase II} < 398$ K CsCl structure

103 K $< \text{phase V} < 255.2$ K

Phase $VI < 103$ K

$1^{1}\text{H M}_2$ studies (20 - 300 K) [289]

$1^{1}\text{H M}_2$ studies [246]

$1^{1}\text{H T}_1$ studies Pressure variation & Temperature variation [84.246]

$2^{1}\text{H NMR}$ studies 100 - 403 K [247]

$1^{1}\text{H T}_1, T_2$ studies 130 - 170 K [248]

$E_a (\text{NH}_4)^+_{\text{TD}} = 12.7$ kcal/mole

$1^{1}\text{H}$ absorption spectra at 4.2 K [37]

$1^{1}\text{H}^2\text{H T}_1$ studies 80 - 430 K [250]

$1^{1}\text{H T}_1$ studies 133-300 K [194]

$2^{1}\text{H PMR}$ studies [252]

$1^{1}\text{H T}_1, T_2$ studies [239]

$T_1$ shows an anomaly at 352 K

$1^{1}\text{H T}_1$ & $M_2$ studies 77 - 300 K [253]

$1^{1}\text{H M}_2$ studies [241, 243]

$1^{1}\text{H T}_1, T_{1F}$ studies [242]

$E_a (\text{Tumb1} (\text{CH}_3)_4\text{N}) = 10.2$ kcal/mole

$E_a (\text{CH}_3)^+ = 6.5$ kcal/mole

$1^{1}\text{H M}_2$ studies [241, 243]

$1^{1}\text{H}^2\text{H T}_1$ studies [242]

$1^{1}\text{H T}_{1F}$ studies & tunnelling studies 1.4 - 300 K [57, 58, 133]

$1^{1}\text{H T}_{1D}$ studies [233]

$1^{1}\text{H T}_{1F}$ studies [6, 254]

$\text{CH}_3\text{NH}_3\text{NO}_3$

P.T. at $T_{c1} = 384$ K

& $T_{c2} = 353$ K

$1^{1}\text{H T}_1, T_2$ studies [239]

$T_1$ shows an anomaly at 352 K

$1^{1}\text{H T}_1$ & $M_2$ studies 77 - 300 K [253]

$1^{1}\text{H M}_2$ studies [241, 243]

$1^{1}\text{H}^2\text{H T}_1$ studies [242]

$E_a (\text{Tumb1} (\text{CH}_3)_4\text{N}) = 10.2$ kcal/mole

$E_a (\text{CH}_3)^+ = 6.5$ kcal/mole

$1^{1}\text{H M}_2$ studies [241, 243]

$1^{1}\text{H}^2\text{H T}_1$ studies [242]

$E_a (\text{Tumb1} (\text{CH}_3)_4\text{N}) = 10.2$ kcal/mole

$E_a (\text{CH}_3)^+ = 6.5$ kcal/mole

$1^{1}\text{H M}_2$ studies $E_a (\text{NH}_4)^+ = 1.6$ kcal/mole [37]

$1^{1}\text{H T}_1, T_{1F}$ studies & tunnelling studies 1.4 - 300 K [57, 58, 133]

$1^{1}\text{H T}_{1D}$ studies [233]

$1^{1}\text{H T}_{1F}$ studies [6, 254]
II.7 Sulphates

Quite a large number of this family of salts are known to be hydrogen bonded ferroelectrics, hence are of interest in view of NMR. \((\text{NH}_4)_2\text{SO}_4\) has been very widely studied. Studies on mixed salts like \((\text{NH}_4)_{1-x}\text{K}_x\text{SO}_4\) and \((\text{NH}_4)_2\text{SO}_4\cdot(\text{NH}_4)\text{BeF}_4\) yield information on the nature and mechanism of phase transitions. Studies on \(\text{ANH}_4\text{SO}_4\) \((\text{A} = \text{H}, \text{Rb}, \text{Li})\) are interesting because of the site substitution. Studies on deuterated salts give information about the extent of H-bonding and its role in the phase transition. Alum and other Ammonium Tutton salts also have shown interesting results. \(\text{TMAHSO}_4\) has shown superionic (proton) conductivity at high temperatures.
Ammonium Sulphate \((\text{NH}_4)_2\text{SO}_4\)

At room temperature, \((\text{NH}_4)_2\text{SO}_4\) is orthorhombic with space group \(P_{n\text{am}}\) and \(Z = 4\), with two inequivalent \(\text{NH}_4^+\) ions in the unit cell. It undergoes a first order ferroelectric phase transition at 223 K to orthorhombic space group \(P_{n\text{a}2}\). The polarization appears along the C axis with the absence of center of inversion and mirror plane.

Proton M\(_2\) studies\(^{27}\) show that the phase transition has very little effect on the NMR spectrum. However, a sharp line-width transition was observed at 163 K, below which the derivative spectrum splits into two well-resolved components. This was explained in terms of the presence of two types of ammonium ions, the broad component arises from frozen ammonium \((\text{NH}_4)_i^+\) ions while the narrow one is due to the rapidly reorienting \((\text{NH}_4)_r^+\) ions. They have also stressed the important role of N-H-O bonds in the FE phase transition. Similar studies of Richards and Schaefer\(^{209}\) over the range 20 to 300 K also led to the same conclusion. Levstek et al\(^{255,263}\) have extended their proton \(M_2\) studies down to liquid helium temperature and found a rather complicated NMR line shape which was interpreted in terms of spin-isomers (tunnelling effects).

Miller et al\(^{30}\) and Blinc et al\(^{31}\) have found abrupt changes in proton \(T_1\) at \(T_c(223\text{ K})\) and in the hindering potential. But their results are not accurate enough to notice the existence of inequivalent \(\text{NH}_4^+\) ions.

Proton \(T_1\) and \(T_{1\rho}\) studies\(^{258}\) have shown minima due to the two inequivalent \(\text{NH}_4^+\) tetrahedra. Above \(T_c\), in the paraelectric phase the ammonium groups, in addition to the usual hindered reorientation, execute oscillations in a double minimum potential, turning out of the ab-plane (mirror plane) by either +30° or -30° and hence there is no net polarization along the C-axis, while below \(T_c\), these torsional oscillations are frozen out, but the reorientations are still present. The \(\text{NH}_4^+\) ions now occupy the equilibrium sites, which are 30° out of the original ab-plane and dipoles add up along the C-axis, canceling out in a and b directions.

Knispel et al\(^{268}\) have carried out proton \(T_1\), \(T_{1D}\) measurements in the range 137-344 K and found the characteristic features of \(T_{1D}\) that (a) it linearly decreases with increasing temperature above 325 K and (b) change in the ratio of \(T_1/T_{1D}\) from 2 to 3 at \(T_c\) \((223\text{ K})\) i.e. a drastic reduction of \(T_{1D}\) above \(T_c\). They attributed this difference to a cross relaxation to \(^{14}\text{N}\), which is comparable to the proton-proton relaxation in the PE phase and negligible in the FE phase. Such cross relaxation is consistent with the distortion and the anisotropic motion of the ammonium group in the non-polar phase. The general reorientation of the ammonium group is responsible for the proton \(T_1\), both above and below \(T_c\), while it does not modulate the components of the EFG tensor at \(^{14}\text{N}\) site, hence \(T_1\) of nitrogen is not affected. The torsional oscillations of \(\text{NH}_4^+\) dipole about the ab-mirror plane as proposed by O'Reilly and Tsang\(^{256,261}\) to account for the
dynamic disorder in PE phase, are capable of modulating the 14N EFG tensor and therefore responsible for the 14N relaxation. This motion is expected to terminate in the FE phase, which would consequently terminate this source of 14N relaxation rate. Thermally activated diffusion of NH₄⁺ ions (with Eₐ = 18±2 kcal/mole) are responsible for strongly temperature dependent reduction of T₁D.

Deuteron magnetic resonance studies have been carried out by many workers ¹⁰⁶,¹⁰⁷,²⁵⁸,²⁶¹. The results reveal a significant alteration of the EFG at the ferroelectric phase transition as revealed by a change in the separation of the lines and the line multiplicity. The results are discussed in terms of the deformation of the ND₄⁺ ions in the crystal. Kydon et al ³⁶,²⁵⁹ have measured deuteron T₁ over a range 77 to 300 K and found two minima in the ferroelectric phase, corresponding to two types of ND₄⁺ ions. The minimum at 165 K was ascribed to (ND₄)⁺ ions and another at 117 K to (ND₁)⁺ ions. There is only a little change in the reorientational freedom of NH₄⁺ ions at Tc.

Blinc et al ²⁶⁴ have determined deuteron and nitrogen quadrupole coupling tensor in the PE phase. Their results show that ammonium ions are highly distorted and there are two chemically non-equivalent ¹⁴N sites in the unit cell with e²Qq of 117 kHz and 91 kHz. High resolution ¹⁵N NMR in solid (NH₄)₂SO₄ using cross polarization technique was done by Gibby et al ²⁶⁶. Knispel et al ²⁶⁷ from their DMR relaxation studies at 4.2 K concluded that type II ammonium ions and type I ions at this temperature are almost decoupled. Their calculated T₁min value agrees with the experimentally observed value of 166±18 kHz indicating that relaxation is due to only type II ND⁺₄ ions. Kasahara et al ²⁶⁹ have studied the effects of K⁺ ion concentration on T₁ in a mixed crystal of (NH₄)₁₋ₓKₓ(SO₄)₂. The crystal is FE for x and Tc decreases with increasing x. The K⁺ ion substitutes only for NH₄⁺ (I) ions and ferroelectricity disappears for x ~ 0.6, where most of NH₄⁺ (I) ions are replaced by K⁺ ions and only a single proton T₁ minimum is observed which is due to NH₄⁺ (II) ions. They have concluded that the motion of NH₄⁺ (I) ion is closely related to the phase transition. Vinogradova and Serylshev ²⁷¹ have carried out Deuteron magnetic resonance spectra at high hydrostatic pressures upto 7.4 k bar over a temperature range 173 to 313 K. The results are interpreted in terms of the changes in orientation and decrease in dipole moment of ND₄⁺ groups and indicate a decrease in Pₘ in the FE phase under pressure. Ramanathan and Srinivasan ²⁷² have carried out CW wide-line proton NMR investigations on ammonium sulphate and Rubidium ammonium sulphate. The results are explained in terms of reorientation of ammonium ions.
Ammonium Hydrogen Sulphate or Ammonium Bisulphate $\text{NH}_4\text{HSO}_4$

This exhibits ferroelectricity between two transition temperatures $T_{c1} \approx 154$ and $T_{c2} \approx 270$ K. The symmetry of the room temperature phase (300 K) is monoclinic $P_{21/c}$. The FE phase is also monoclinic with space group $P_c$ and the low temperature phase which in piezoelectric, has a triclinic symmetry $P_1$. All three phases are pseudo orthorhombic. The temperature dependence of $P_s$ indicates a first order transition at $T_{c1}$ and a second order one at $T_{c2}$. Thermal hysteresis of about $7^\circ$ is observed around $T_{c1}$.

Burns$^{28}$ and Trontelz and Rebic$^{265}$ did not observe any change in the proton and the deuteron line shape from room temperature to 77 K, indicating that the motional parameters of the ammonium ion are not affected at the phase transition. However, Watton et al.$^{256,257}$ determined proton second moment precisely and found minute changes around 140, 250 and 380 K. They concluded that $\text{NH}_4^+$ ions are undergoing rapid general reorientation over the entire range of temperature studied. A small change of 0.5 $G^2$ in the second moment at 250 K is attributed to a decrease in the distortion of the $\text{NH}_4^+$ tetrahedron at high reorientational frequencies. Miller et al.$^{30,31}$ have carried out proton $T_1$ studies over the range 110 to 300 K. There was no change in $T_1$ at $T_{c2}$ but a break in $T_1$ occurs at 173 K instead at $T_{c1}$ (154 K). Proton $T_1$ and $T_{1p}$ studies by Watton et al.$^{256,257}$ show discontinuity of both the quantities at $T_{c1}$ and a slope change in $T_{1p}$ at $T_{c2}$. Also there is no evidence of the previously reported$^{30}$ discrepancy between the $T_1$ discontinuity temperatures and the FE transition temperatures. The observed asymmetric $T_{1\min}$ at 110 K was attributed to an overlap of the $T_1$ minima due to the two-fold and three-fold reorientations (i.e., a general reorientation) and this conclusion is supported by the observed $M_2$ reduction around 110 K. Different activation energies for the two types of motions were evaluated. A change in the $E_a$ was noticed at $T_{c1}$ indicating a decrease in the hindering of the ammonium ion in the FE phase. At $T_{c2}$, $T_{1p}$ undergoes a slope discontinuity with an increase in the potential barrier. The results were interpreted in terms of of distortion of $(\text{NH}_4)^+$ tetrahedron and self-diffusion. However, they$^{256,257}$ were not able to determine whether diffusion of all or just half of the $\text{NH}_4^+$ ions are involved, since the final second moment reduction is incomplete at 388 K.

Trontelz and Rebic$^{265}$ have measured deuteron $T_1$ in $\text{ND}_4\text{DSO}_4$ though the exact transition temperatures of the deuterated salt are not known. $T_1$ and activation energy ($E_a$) changed considerably at both $T_{c1}$ and $T_{c2}$ ($T_{c1} = 174 \pm 5$ K and $T_{c2} = 256 \pm 10$ K). The change in $T_1$ at $T_{c1}$ is small and less abrupt than the changes at $T_{c2}$, while $E_a$ changed considerably. There is a qualitative agreement between $\text{ND}_4\text{DSO}_4$ and $\text{NH}_4\text{HSO}_4$ results$^{30}$ below $T_{c1}$. On the other hand changes in $T_1$ and $E_a$ are much larger for the deuterated salt than for the protonated salt at $T_{c2}$, which indicates a change in the $\text{ND}_4^+$ ion reorientation and in the hindering potential, than some changes in the
deuterons in the O-D--O bonds. These deuterons are already ordered above \(T_{c2}\) and are not likely to experience any rearrangement. At \(T_{c1}\) there is a change in the ND\(_4^+\) ion reorientation as well as in the hindering potential which is also found in the case of the NH\(_4^+\) ion reorientation\(^{30}\).

**Triammonium Hydrogen Sulphate \((\text{NH}_4)_3\text{H(SO}_4\text{)}_2\)**

This is known to be antiferroelectric between 143 and 247 K. Proton \(T_1\), \(T_{1p}\), and \(M_2\) studies have been carried out over the range 77-388 K by Watton et al\(^{257}\). Their results show that line narrowing takes place in two steps, one at about 320 to 340 K and the other around 77 K. The \(M_2\) data reveals that NH\(_4^+\) ions are undergoing rapid reorientation over the entire temperature range. Proton \(T_1\) studies show double minima at 87 K which was attributed to an additional three-fold reorientation superimposed on two two-fold reorientation and did not show any anomaly at the two reported phase transition temperatures. Below 103 K, \(T_1\) shows a slight discontinuous increase with a decrease in activation energy and another sharp discontinuity at 156 K (no change in \(T_1\)) indicating a sudden decrease in the dipolar relaxation rate. This temperature is close to but 13 K higher than the reported transition temperature (143 K). They were unable to explain the discrepancy. \(T_1\) also did not show any anomaly at 247 K. The high temperature \(T_1\) data was interpreted in terms of self-diffusion of ammonium ions.

**Lithium Ammonium Sulphate \(\text{LiNH}_4\text{SO}_4\)**

At room temperature this is hexagonal with space group \(P_{c2n}\) and exhibits ferroelectricity along the b-axis. It is paraelectric (phase I) above 459.5 K and ferroelectric (phase II) between 459.5 K and 283 K. Below 283 K, it is ferroelastic (phase III).

\(^1\text{H}\) NMR studies\(^{276}\) show a narrow line at 300 K and changes a very little with temperature. The line width changes from 2.2 to 5 G with increase in temperature. This behaviour of the line width with temperature is completely anomalous and the corresponding second moment change is only 1.3G\(^2\). The temperature dependence of line width depends somewhat on the rate of temperature change and the thermal pre-history of the sample. Bhat\(^{284}\) has carried out proton \(M_2\) studies over the range 77 to 300 K, and observed a very small \(M_2\) (3.3G\(^2\)) even at 77 K. Similar studies by Watton et al\(^{279}\) over the range 77 to 400 K show that line shape was Gaussian over the entire temperature range. The \(M_2\) value was 1.5±0.1 G\(^2\) from 430 K down to 150 K suggesting that NH\(_4^+\) ions are undergoing rapid reorientation and increases to 5.4±0.1G\(^2\) at 77 K.
Proton $T_1, T_{1\rho}$ studies by Watton et al.\textsuperscript{276} over the range 77 - 400 K show that both ($T_1$ and $T_{1\rho}$) decrease with decreasing temperature and exhibits a discontinuity at 294 K with a decrease in $T_1$ and increase in $T_{1\rho}$ . Below 294 K both decrease with decreasing temperature, down to 133 K, where another small discontinuity occurs accompanied by a relatively large slope change. The activation energy decreases significantly at this point. Below 133 K, $T_{1\rho}$ continues to decrease whereas $T_1$ goes through a minimum at 115 K. The slope change at 133 K suggests another phase transition at this temperature, even though no anomaly was observed from DTA studies. The observed $T_1$ min was ascribed to the simultaneous reorientation around three-fold and two-fold symmetry axes. Proton $T_1$ and $T_2$ studies have been carried out by Vogtsberger et al.\textsuperscript{281} over a range 100- 500 K. They found a single $T_1$ minimum. Data at 60MHz shows a $T_1$ min of 20 msec. at 125 K, whereas the $T_1$ data at 90MHz shows two minima of unequal depth with $T_1$ min = 33 msec. at 133 K and $T_1$ min = 44 msec. at 104 K. The corresponding $E_a = 2.76$ kcal/mole is typical of ammonium groups with almost isotropic reorientation. The existence of double minima is interpreted in terms of presence of two non-equivalent ammonium ions in the unit cell as evidenced from $^2$H NMR studies or may be due to the strong anisotropy of reorientation of a single ammonium group. (A large difference in the activation energy of hindered rotation relative to different axes of local symmetry). In the low temperature transition (283K), no noticeable change is observed in the slope of temperature dependence of $T_1$ and hence no change in $E_a$ for the reorientation process. The angular dependence of proton second moment shows that the hetero-nuclear Li-H dipolar interaction exists.

Wide line NMR studies of $^2$H and $^7$Li in deuterated LAS have been carried out in all three phases.\textsuperscript{276,276,277} Yuzvak et al.\textsuperscript{275} have calculated quadrupole coupling constant and the orientation of the EFG tensor for both $^7$Li and $^2$H in both the phases II and III. They have conjectured that LiO$_4$ and ND$_4^+$ tetrahedra are distorted in both the phases, but the main contribution to the polarization in FE phase comes from the LiO$_4$ tetrahedra rather than from the ND$_4^+$ tetrahedra. Below $T_{CII}$ Li exists in two structurally inequivalent sites (type I and type II) and the distortion of the LiO$_4$(II) tetrahedron is more than that of the LiO$_4$(I) tetrahedron. The phase transition at $T_{CII}$ (283 K) does not affect the orientation of the ND$_4$ groups in the channel.

At the high temperature phase transition, the quadrupole coupling constant and the orientation of EFG tensor at the site of $^7$Li do not change significantly, but a substantial change in the same is brought about ( involving the rotation of the principal axis of the EFG tensor) at the site of $^2$H. The high temperature transition ($T_{C1}$ 459.5 K) takes place from a space group $p4cm$ (rhombic) changing the number of atoms in the unit cell. In phase I, the principal axis of the EFG tensor at the site of $^2$H is parallel to the axis of the rhombic cell. Below $T_{C1}$ (FE phase) one of the principle axes is directed along the C-axis as before and the other two rotate through 45$^o$ about the C-axis. Such a change in the orientation of the EFG tensor at the $^2$H site is accompanied by
the appearance of an uncompensated contribution to the spontaneous polarization. Chekmasova and Aleksandrova have investigated the angular dependence of NMR spectra of $^7$Li and $^2$H in (DLAS) as a function of high hydrostatic pressure and found the existence of a new phase around 9 k bars. From the results it is seen that in the unit cell of the high pressure phase, two non-equivalent $^7$Li and ND4 sites appear where as in phase I and II, there is only one site. They conclude that the high pressure phase has a point group symmetry of $P_2_1$ and is without a change in the unit cell volume. They also confirm that this high pressure phase transition is of the displacive type with considerable structural deformation in contrast to the FE order -disorder transition.

Shenoy and Ramakrishna have carried out $^1$H T1 studies over the range 77-480 K. They have observed a $T_1$ min at 108.6 K and breaks in the curve of $T_1$ versus temperature around 283 and 459.5 K corresponding to the two transitions. The results are interpreted in terms of the reorientation of ammonium ion. The activation energy is 2.6 kcal/mole in phase III (low temperature). They suspect a possibility of ammonium ion tunnelling at low temperatures. A large change in proton $T_1$ at $T_c$ (459.5 K) indicates that the NH4 groups are significantly affected during this transition. The $E_a$ in phase II between 283 and 459 K is 0.8 kcal/mole.

Aleksandrova et al. have carried out NMR studies in LAS. From their structure data they find that at 483 K when phase transition occurs all the SO4 groups rotate about the a axis, in the same direction by 20° and the NH4 groups rotate in the opposite direction by 24° which agrees with the NMR data. As a result of these rotations the mirror symmetry appears along the b axis. The unusual temperature dependence of quadrupole splitting $2\Delta\nu$ in the NMR spectra is noteworthy. For the spectra of the ND4 groups near $T_c$ we observe a sudden jump in the value of $2\Delta\nu$ in accordance with the type of phase transition. Rozanov et al. have carried out the angular and temperature dependence of deuteron and $^7$Li magnetic resonance spectra in LAS. Temperature dependence of the EFG tensor of both the nuclei yield the information for the nature of phase transition as follows. In the high temperature phase $P_{nam}$, the tetrahedral group arrangement is such that it is only averaged by time (the oscillations of these group in respect of the mirror plane takes place). Then in this case the transition mechanism consisting of the ordering of the tetrahedral groups in the extreme positions and the EFG tensors of the PE phase will be the average of the two Fe phase EFG tensors. Measurements of SLR ($T_1$) of protons and the effective relaxation time ($T_2*$) of protons agree well with the model. Below $T_c$, the temperature dependence of the NMR spectra quadrupole splittings are associated with temperature behaviour of the local order parameter, which is the tilting angle of the tetrahedral group. At the low temperature transition, the principal changes of the EFG observed at the Li ion sites. The sublattice formed by structurally non-equivalent Li (I) and Li (II) and NH4 (I) and NH4+ (II) ions appears. However, the AFE dipole motions arise at doubling of the unit cell.
along the a-direction resulting in the compensation of the dipole moments in the volume of the new unit cell.

Reynhardt et al.\textsuperscript{286} have investigated proton and lithium NMR studies at temperatures below 285 K. The proton line shape at 4.2 K has shown that tunnelling rotation of the NH\textsubscript{4} ion around one of its C\textsubscript{2} axis is favoured over the other. Additional tunnelling along three-fold axis is also present. The ground torsional structure of the NH\textsubscript{4}\textsuperscript{+} ion has been determined. The classical reorientation of the two non-equivalent NH\textsubscript{4} group can be described as simultaneous 2 and 3 fold reorientation with estimated activation energies ranging from 1.0 to 1.6 kcal/mole. Slight difference in activation energies have been observed during cooling and heating cycles below 133 K. The 7Li relaxation is determined to a large extent by the reorientation of NH\textsubscript{4} ions. Evidence has been found that the phase transition at 133 K is accompanied by a slight rearrangement of the LiO\textsubscript{4} skeleton. Since the activation energy range from 2.4-0.5 kcal/mole the possibility of quantum mechanical tunnelling was found. PMR absorption studies over 77-400 K show that a narrow plateau of 21.5±1 G\textsuperscript{2}, exists between 4.2 and 30 K and is followed by high temperature plateau of 1.5±0.1G\textsuperscript{2}. The spectrum at 4.2 K consists of a narrow component and a wing, whereas room temperature signal does not have any such structure.
Rubidium Ammonium Sulphate  \( \text{RbNH}_4\text{SO}_4 \)

\(^1\text{H} \) NMR studies have been carried out by Ramanathan et al \(^{289}\). These studies on this salt are significant in view of understanding the peculiar behaviour of many properties of its parent compound i.e. \((\text{NH}_4)_2\text{SO}_4\). For e.g., the CW PMR studies of \(\text{RbNH}_4\text{SO}_4\) showed a narrow spectrum, without any wing structure, while wings were observed in the unsubstituted ammonium sulphate. Absence of the wings indicate that Rubidium ions have substituted preferentially for \((\text{NH}_4)_\uparrow\) ions only. Further it confirmed that \((\text{NH}_4)_\downarrow\) is reorienting at a slower rate than \((\text{NH}_4)_\uparrow\) ion.

The peculiar behaviour of the spontaneous polarization \(P_s\) could be explained on this basis, by removing the contribution to \(P_s\) of \((\text{NH}_4)_\uparrow\) ions by substitution with Rb ions (50% concentration) in ammonium sulphate. Now the polarization is due to only \((\text{NH}_4)_\downarrow\) ions, and hence the \(P_s\) shows a normal temperature dependence. Application of pressure results in an increase in the reorientation rate of ammonium ion hence the Ferroelectric phase transition temperature \(T_c\) which is related to the dynamics of the ammonium ion, shift downwards with increasing pressure. On the other hand substitution of \((\text{NH}_4)_\uparrow\) ions (which are bonded with strong H-bonds) by Rb ions whose ionic radius is slightly larger than the former results in breaking of these H-bonds along with a lattice expansion (i.e. negative pressure) and hence an increase in \(T_c\).

Hydroxyl Ammonium Sulphate  \((\text{NH}_3\text{OH})_2\text{SO}_4\)

Koksal \(^{11}\) has carried out proton \(T_1\) studies over the range 100-430 K and observed two \(T_1\) minima which were attributed to two non-equivalent hydroxyl ammonium ions in the unit cell.

Sodium Ammonium Sulphate Dihydrate  \(\text{NaNH}_4\text{SO}_4.2\text{H}_2\text{O}\)

This salt belongs to the Lecontite family of ferroelectrics, and is known to undergo a ferroelectric phase transition at 101 K and 92 K. The room temperature (PE phase) structure is found to be orthorhombic \(P_2_1_2_1_1\), with \(Z=4\), characterized by three reflection planes (ab,bc, and ca) and a center of inversion. Both the low temperature phases are ferroelectric with a polarization along the C-axis and is known to crystallize either in \(P_2\) or \(P_1\) space groups. The dielectric constant along the C-axis of the crystal also revealed anomalies at these two transitions. The sequence of phase transition can be represented as follows.

\text{PE phase I} \rightarrow \text{101 K} \rightarrow \text{FE phase II} \rightarrow \text{92 K} \rightarrow \text{FE phase III}.

Proton and Deuteron resonance \(^{290,292,293}\) and proton \(T_1\) and \(T_1\) studies \(^{291,293}\) were carried out in this compound over a range of temperature. Both proton and
Deuteron resonance spectra consist of a sharp central line due to rapidly rotating ammonium tetrahedra and two pairs of satellite lines due to the water molecules. There are two types (α and β) of water molecules with non-equivalent proton-proton (P-P) vectors, which are effectively frozen at room temperature. In the deuterated salt, Genin and O'Reilly\(^2\) were able to detect only the β-water molecule, since the flipping rate of α molecules had already slowed down enough and its resonance was too broad to be observed. The observed D-D direction agrees with the corresponding P-P direction. The invariance of the orientation of the P-P vector and the absence of line-width transition\(^2\) in traversing T\(_c\) suggest that the water molecules are not involved directly in bringing about the FE phase transition.

Makita et al\(^2\) have observed a proton second moment transition at T\(_c\) in a poly crystalline sample and again another sudden drop at the dehydration point of 388 K (T\(_d\)), where the doublet line disappears. The value of the line width for the doublet line does not change at T\(_c\), indicating that H\(_2\)O molecules are not involved in the phase transition. This discontinuous change in M\(_2\) at T\(_c\) indicates that the phase transition is of first order. The change in M\(_2\) value at T\(_c\) is attributed to a change in the distance between some magnetic nuclei due to a spontaneous lattice deformation, since the (correlation time associated with) NH\(_4^+\) ion reorientational motion is fast enough (about 3 x 10\(^{-9}\) secs) at T\(_c\), as estimated from the result of Tado and Tatsuzuki\(^2\) to expect any further effect of motion of the NH\(_4^+\) ions at T\(_c\). However, from the estimated value of T\(_c\) 10\(^{-8}\) secs at 80 K, they\(^2\) suggested that in addition to the above contribution (lattice deformation) there might be considerable contribution from the change in reorientational motion of NH\(_4^+\) ions to the second moment below 80 K.

Genin and O'Rielly\(^2\) from their deuteron resonance studies on single crystals of NaND\(_4\)(SO\(_4\))\(_2\)D\(_2\)O from room temperature to 77 K concluded that the ND\(_4^+\) ions did not undergo any distortion at either of the FE phase transitions. However, it may be pointed out here that their results on \(^2\)H resonance are not very clear. \(^{23}\)Na resonance studies showed the presence of two inequivalent sodium sites below T\(_c\) which are equivalent above T\(_c\). The FE transition is attributed to the striking changes in the local EFG at the sodium sites, which is in agreement with Makita's\(^2\) conclusion wherein second moment transition at T\(_c\) is attributed to the changes in distances between some magnetic nuclei, due to spontaneous lattice deformation. PSLR times T\(_1\), T\(_1\rho\) studies\(^2\) in the range 77 to 300 K show double minima, one at 170 K and another at 120 K which are respectively assigned to rotation about two fold and 3-fold axis of the NH\(_4^+\) tetrahedron. The activation energy associated with the C\(_2\) axis reorientation is 4.8 kcal/mole. However this motion does not persist in the FE region. The change in E\(_a\) associated with the three-fold axis of rotation of the NH\(_4^+\) ion (from 2.0 to 3.1 kcal/mole) in going from PE to FE phase at 100 K is indicative of considerable lattice distortion which is correlated by \(^{23}\)Na resonance data. These factors indicated
that the transition at 101 K is displacive type and that at 92 K involves much smaller lattice distortion.

Tado and Tatsuzaki\(^{291}\) have measured PSLR time \(T_1\) from 77-300 K. It is seen that \(T_1\) exhibits the minimum value at \(T_c = 101 \pm 2\) K is rather accidental and \(T_1\) increases sharply with decrease of temperature below \(T_c\). However, no change in \(T_1\) is observed at \(T_{c2} = 92\) K indicating the less violent nature of the phase transition. The activation energies in the PE and FE phases are \(1 \pm 0.5\) and \(3.5 \pm 0.5\) kcal/mole respectively.

**Cadmium Ammonium Sulphate \((\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3\)**

Cadmium ammonium sulphate (CAS) belongs to the lang-beinite family of ferroelectrics. The room temperature structure is cubic \(P_{2_1}3\) and \(Z = 4\). It exhibits ferroelectricity below 95 K and \(P_s\) appears along the [100] direction of the cubic PE phase. It is expected that the low temperature phase is monoclinic.

The proton line-width and \(M_2\) studies\(^{28,294,295}\) did not show any change down to 77 K. The resonance line remains motionally narrowed down to liquid helium temperature\(^{295}\) which shows that the ammonium ions are tunnelling between spin symmetry states. In the deuterated compound, also a single narrow line was obtained at room temperature showing that the deuteron quadruple interaction is averaged out by the reorientation of \(\text{ND}_4^+\) ion\(^{294}\). As the temperature is lowered, the line width increases and around 150 K, the single line splits into two components with a small separation indicating partial restoration of quadrupole interaction due to slowing down of the \(\text{ND}_4^+\) reorientation. This separation reaches a value of 1 kHz at 100 K. At \(T_c\) (90-95 K), the \(^2\text{H}\) spectrum undergoes an abrupt change in to a single broad line due to the unresolved quadrupole splittings of the individual deuterons which have become inequivalent below \(T_c\). This indicates that there is a rearrangement of the \(\text{ND}_4^+\) tetrahedron at \(T_c\).

Proton \(T_1\) measurements\(^{295}\) at 25.85 MHz from 300 to 77 K, showed a discontinuous change in \(T_1\) at \(T_c\) which is identified as due to an abrupt speeding up in the reorientational motion of \(\text{NH}_4\) ion motion at \(T_c\), with the decrease of temperature (which is otherwise slowing down). The calculated activation energy in the PE and FE phase are 2.7 \pm 0.5 and 0.9 \pm 0.5 kcal/mole respectively indicating a low potential barrier in the FE phase. Further they\(^{296}\) concluded that the FE phase transition results from a change in the \([\text{Cd(SO}_4)_3]^2^-\) structure, which alters the hindering potential and not due to the ordering of the \(\text{NH}_4\) ions.

However, proton \(T_1\) measured by McDowell et al\(^{295}\) at 30.8 and 48.2 MHz from room temperature to 77 K has distinctive features different from those of Tado and
Tatsuzaki. The $T_1$ was frequency independent in the range 250 to 125 K (in the PE phase) and was attributed to the ammonium ion reorientations. The observed $T_1$ min was higher than the calculated one, using the BPP formula. Further more, they found a wide distribution of correlation times in the $T_1$ min region which were interpreted in terms of a model, considering the ammonium ion as a quantum rotor. At the FE transition, a sharp break in $T_1$ versus temperature plot occurred for both frequencies studied. A wave vector dependent correlation time associated with the critical fluctuations is introduced to explain the lattice instability at $T_c$. Then experimentally observed relaxation anomaly is expected to result from power spectrum of the critical fluctuations. Qualitatively the $T_1$ anomaly is explained as a manifestation of a magnetic dipolar coupling to the FE lattice mode and the unstable mode (as $q \rightarrow 0$, $1/\tau_0 \rightarrow 0$) results in an 'ordering' transition. Below $T_c$, the spin magnetization recovery was non exponential, which did not become significant with further decrease in temperature. The activation energy below $T_c$ is very small, which is attributed to the changing degree of order in the structure. However the non exponential recovery of magnetization may be due to composite 'three-bath' model involving slow cross relaxation between the protons in different spin symmetric states. The activation energy below $T_c$ is very small which is attributed to the changing degree of order in the structure.

**Ammonium Thiosulphate (NH$_4$)$_2$S$_2$O$_3$**

Proton $T_1$ studies by Svare et al and by Koksai showed a $T_1$ minimum at $13^\circ$K and was attributed to the hindered $C_3$ rotations of the ammonium ion and no spin diffusion was observed. $T_1$ studies by Svare et al, are little different from koksai in terms of interpretation where the reorientation of ammonium ions is by $90^\circ$ around two-fold axis was considered. PMR absorption and line shape analysis of this salt at 4.2 K has been carried out by Watton et al.

**Ammonium Peroxydisulphate (NH$_4$)$_2$S$_2$O$_8$**

Watton et al have carried out proton line width and $M_2$ studies at 4.2 K and the values were $2.9 \pm 0.1$ G. and $19.0 \pm 0.5$ G$^2$ respectively and the results were interpreted in terms of tunnelling of NH$_4^+$ ions. Proton $T_1$, $T_{1P}$ and $T_{1D}$ studies have been carried out by several authors. Koksal and Bahcell found a $T_1$ maximum (20 sec.) at 318 K which was interpreted in terms of spin-rotational interactions and were unable to find any minimum down to 100 K. Morimoto found two $T_1$ minima at 70 K and 42 K, which were attributed to the motion of ammonium ion. Further they observed two $T_1$ minima at 53 K and at 29 K for $H_1 = 17$ Gauss and at 48 K and at 26 K for $H_1 = 9$ Gauss. The observed $T_1$ minimum values are much larger than the calculated ones, indicating that the relaxation in this region is due to the tunnelling motion of NH$_4^+$. 

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ions. A large $T_{1D}$ minimum was observed by Shimomura et al$^{233}$ which was ascribed to the spin-rotational interaction and cross relaxation.

**Tetraammonium Cerium Sulphate Dihydrate** $(NH_4)_4Ce(SO_4)_4\cdot 2H_2O$.

Proton $T_1$, $T_{1p}$ studies$^{254}$ over a range of temperature reveals the following interesting features. The $T_1$ exhibits four minima, the two high temperature minima (at 280 K and 190 K) were attributed to the motion of $H_2O$ molecules while the low temperature minima (at 75 K and 50 K) were attributed to the motion of $NH_4^+$ ions such as random reorientation and reorientation about 2-fold and 3-fold axes. However, they found the observed results could not be explained in terms of classical theory and hence were attributed to the tunnelling motion of $NH_4^+$ ions. The proton FID also shows a line narrowing at 4.2 K, and is in conformation with this result.

$T_{1p}$ also exhibits four minima the two high temperature minima at 294 K and at 136 K (for $H_1 \approx 17$ Gauss) and at 187 K and at 129 K (for $H_1 \approx 9$ Gauss) which were attributed to the motion of $H_2O$ molecules while the low temperature minima at 67 K and at 40 K (for $H_1 \approx 17$ Gauss) and at 62 K and at 37 K (for $H_1 \approx 9$ Gauss) were explained in terms of $NH_4^+$ ion tunnelling.

**Ferrous Ammonium Sulphate Hexahydrate** $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$.

This is a member of the Tutton salts having a monoclinic space group $P2_1$ ($P2_1/a$) with $Z=2$, with an evidence of having hydrogen bonding scheme in the crystal. Angular variation of single crystal proton and deuteron magnetic resonance is carried out by Raj and Murthy$^{297}$. For rotations about the b-axis, six resonance lines were observed symmetrically distributed about a strong central line and show no anisotropic shift which might arise from crystal paramagnetism. The free water molecules (i.e., not $H$-bonded) trapped in the crystal give rise to the central line whose intensity is further increased due to the protons of the rapidly reorienting ammonium molecules. In the case of deuteron each single line was split into two because of the quadrupolar interactions. Following the method of ElSaffar’s, they determined the positions of the hydrogen atoms in the crystal by combining the NMR data with the x-ray crystal structure.

**Diammonium Hydrazinium Disulphate** $(NH_4)_2N_2H_5(SO_4)_2$.

Proton $T_1$ and $T_{1p}$ measurements have been done by Harrel,Jr$^{298}$ over a temperature range from 123 to 491 K. Phase transition have been detected at 330 and 407 K by observing discontinuous changes in the $T_1$ and $T_{1p}$ measurements. The phases have been designated as phase I ($T>407K$), phase II ($407>T>330$ K) and phase III ($T<330$ K). Upon warming through the III to II transition, $T_1$ increases by
about 63% and $T_1$ decreases by about 15% within a 2 K interval centered at 330 K, when warming through the II to I transition $T_1$ increases by about 66% over a 7 K range and $T_1$ decreases by a factor of 2 within 2 K range centered at about 407 K. Both the transitions showed a super cooling effect. The I to II transition was more abrupt and occurred at about 404 K, while II to III transition was less violent and occurred at about 320 K. In the low temperature phase the relaxation is determined by two types of reorienting NH$_4^+$ groups and one type of NH$_3$ group. An additional minimum is evident in the $T_1$ measurement just below the lower phase transition. The lower phase transition is characterized by a discontinuous change in the reorientational rate of the NH$_3$ groups and by the onset of translational diffusion of NH$_4^+$ ions. The upper phase transition is characterized by a rapid increase in the reorientational rate of the NH$_4^+$ groups and by a discontinuous increase in the rate of translational diffusion of the NH$_4^+$ ions. In the high temperature phase, the relaxation is governed by the reorientation and translational diffusion of NH$_4^+$ ions. The activation energy and $T_1$ min associated with different ammonium groups and NH$_3$ groups are as follows: (NH$_4$)$_{II}$ = 2.63 kcal/mole, (NH$_4$)$_{I}$ = 4.48 kcal/mole and -NH$_3$ = 7.16 kcal/mole, with the corresponding $T_1$ min of 18 m.s. at 138 K, 58 m.s. at 187 K and 35 m.s. at 254 K respectively.

Ammonium Aluminium Sulphate Dodeca Hydrate (NH$_4$)$_2$Al(SO$_4$)$_2$ 12H$_2$O.

Proton $T_1$ studies in AASD over a range 100-500 K by Koksal$^{169}$ show that the dominant relaxation between 100 to 200 K is due to the dipolar interaction modulated by reorientational motion of the ammonium ion while above 200 K it is determined by the spin-rotational interaction of the ammonium ions.

Proton $T_1$ and $T_1p$ results by Svare and Holt$^{299}$ and by Grande$^{300}$ agree with each other, whereas the interpretation differs. Svare and Holt$^{299}$ found three $T_1$ minima at 360 K, 200 K and at about 100 K. They have interpreted the $T_1$ results in terms of the crystal structure as follows. They found that out of available twelve water molecules in the structure of (NH$_4$)$_2$Al(SO$_4$)$_2$12H$_2$O, six H$_2$O molecules (type 2) are bound tightly to each Al$^{3+}$, while the other six H$_2$O molecules (type 1) are bound less tightly to each NH$_4^+$. They assigned that the 200 K minimum in $T_1$ to H$_2$O (type 1) flips and the other 360 K minimum to the H$_2$O (type 2) flips. The stronger dipolar coupling of H$_2$O(type 2) to the $^{27}$Al is likely to make the 360 K minimum to be deeper than the former as observed. Further they assigned the lowest $T_1$ minimum observed at 100 K to NH$_4^+$ reorientation. This $T_1$ minimum was 7 times more than that expected for NH$_4^+$ ion. This discrepancy was explained as due to the relaxation of additional six water protons through each ammonium proton. The phase transition associated with a crystal structure change occurs at 70 K and is reflected as a change in $T_1$. 

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Methyl Ammonium Aluminium Sulphate Dodeca Hydrate.

(CH$_3$NH$_3$)Al(SO$_4$)$_2$12H$_2$O.

MASD is known to undergo a first order ferroelectric phase transition at 177 K from room temperature paraelectric phase [cubic space group P$_{m}$3] to ferroelectric [monoclinic space group P$_{ca}$2$_1$]. PMR studies$^{301}$ show that at room temperature the spectra have a complicated line shape with a central narrow peak due to rapidly rotating CH$_3$NH$_3$ group and two broad components on either side due to water molecules. He concluded that the rotation of CH$_3$NH$_3$ groups is closely related to the disappearance of Ferroelectricity in MASD. O'Reilly and Tsang$^{302}$ have carried out both CW and pulsed NMR studies in ordinary as well as deuterated salt and were unable to find any change in the proton spectra at T$_c$. The second moment of polycrystalline deuterated MASD (59 mole% D) was found to be 6.4 G$^2$ at 123 K and 18 G$^2$ at 77 K indicating that the correlation time for the 3-fold axis reorientation of methyl group had increased to (10$^{-5}$ seconds) below 123 K. Results of T$_1$ and T$_{1p}$ in polycrystalline 59 and 84 mole% DMASD show that both T$_1$ and T$_{1p}$ decrease above 250 K and is associated with an increase in vapour pressure of the solid. The T$_1$ data shows a single minimum in the vicinity of 110 K independent of the degree of deuteration and were attributed to the CH$_3$ group rotation about C$_3$ axis. The T$_1$ data also shows a minimum near 210 K but the value of T$_1$ minimum varies strongly with the degree of deuteration. For example, T$_1$ is 2 m.s. for the pure MASD and a factor of ten longer for the 84 mole% of DMASD. At the curie point, T$_1$ undergoes a discontinuity which is partially evident in the 59 mole% sample. As discussed the T$_1$ minimum is ascribed to a 180$^0$ flip motion of the CH$_3$NH$_3$ ion. Below T$_c$, T$_1$ rises to a maximum near 150 K, then decreases with the same slope as T$_1$ at higher temperature. The decrease in T$_1$ in the temperature region below 150 K is assigned to the reorientation of the CH$_3$ group about the triad axis.

The characteristics of the phase transition were studied by an analysis of the NMR spectra of MASD by Vinogradova and Falaleeva$^{303}$. The measurements were carried out at 7.6 kgauss and in the range 138-340 K. They found that in the FE phase the shift of $^{27}$Al from the octahedral center leads to a sharp increase of the dipole contribution to the EFG. The tensor is axially symmetric with its principal axis along the (111) direction in the FE phase. Its magnitude in $^{27}$Al is determined by the ion contribution from the (SO$_4$)$_2$- groups. Dipole contributions are insignificant.

Vinogradova$^{304}$ has carried out PMR studies in the region of FE phase transition. From his earlier studies on Alums he concluded that water molecules do not make any contribution to the spontaneous polarization of the FE alums. The PMR spectra consists of a narrow line (H =3.5G) and a wide line, which were attributed to CH$_3$NH$_3$ and water molecules respectively. Further from the angular variation studies it was found that there is reorientation of CH$_3$ and NH$_3$ groups about the C-N bond which in
turn process about the body diagonals of the unit cell. The FE transition is concluded to be order-disorder type for the CH$_3$NH$_3$ dipole ions and one can link the appearance of spontaneous polarization in the crystal with the ordered arrangement of these ions in the structure. $^{27}$Al NMR serves as a good probe for detecting the phase transitions in Alums. An abrupt increase of the quadrupole bond constant of the $^{27}$Al nuclei and a shift in the principle axis of EFG tensor occurs at the curie point (cubic-Rhombic). An anomaly in PSLR times of protons in FE MASD was noticed by Nakamura et al.$^{305}$. Their $T_1$ studies over a range of temperature from 283 to 103 K agreed very well with that of O'Reilly and Tsang$^{302}$, except near $T_c$ where a dip in $T_1$ was observed. They also suggest that the relaxation rate in the FE phase is mainly dominated by the hindered rotation of the CH$_3$ groups.

**Tetramethyl Ammonium Sulphate** \([\text{(CH}_3\text{)}_4\text{N}]_2\text{SO}_4\)

PMR line-width and $M_2$ studies$^{243}$ over a range 140-400 K showed two distinct steps of line-narrowing with $M_2$ values changing from $29.0 \pm 1.5 \text{ G}^2$ to $10.8 \pm 1.0 \text{ G}^2$ and from $10.8 \pm 1.0 \text{ G}^2$ to $1.2 \pm 0.1 \text{ G}^2$ which were ascribed to methyl group reorientation about the C$_3$ axis and general reorientation of TMA$^+$ ion respectively. Jurga et al.$^{242}$ have studied proton $T_1$ as a function of temperature and found a $T_1$ minimum at 385 K which was assigned to CH$_3$ rotation. $T_1$ at $H_1 = 30 \text{ G}$ exhibits two minima at 347 and 160 K which were attributed to tumbling motion of TMA ion and the rotation of CH$_3$ about its C$_3$ axis respectively.

**Tetramethyl Ammonium Bisulphate** \(\text{N(CH}_3\text{)}_4\text{HSO}_4\)

Tetramethyl ammonium bisulphate exhibits proton superionic conductivity and is known to have a structural phase transition between 320 and 440 K from thermogravimetric and DTA studies. Proton NMR and $T_2$ studies by Blink et al.$^{306}$ show a peak to peak line width of 2.8 G at room temperature, characterizing the rotating N(CH$_3$)$_4$ group and rigid acid protons.

The $T_2$ decay above 373 K was resolved into two components a 'solid-like' one with $T_2 = 200 \text{ m.sec.}$ due to rotating CH$_3$ groups and a 'liquid-like' one with $T_2$ larger than 10 m sec. due to diffusing acid protons. The ratio between the intensities of these two components varies with temperature, at 378 K \((\text{Solid/ Liquid}) \approx (30 \cdot 40) : 1\) and it is 12 above 418 K. This last ratio is equal to the ratio between the number of methyl group and the acid protons in the sample. Thus it was concluded that N(CH$_3$)$_4$ groups are rotating but not diffusing whereas the acid protons are diffusing and hence exhibit a liquid like shape in the Carr- Purcell spin echo envelope.
Methyl Ammonium Sulphate (MAS)  \((\text{CH}_3\text{NH}_3)_2\text{SO}_4\).

MAS is monoclinic at room temperature with space group \(P_2_1/C\) and is known to undergo a first order phase transition at 428 K. Proton \(M_2\) and \(T_1\) studies have been carried out by Ishida et al\(^{307}\) at various temperatures. Proton \(M_2\) above room temperature is 8 \(G^2\) and 6 \(G^2\) for \((\text{MA})_2\text{SO}_4\) and \((\text{MA}-\text{d})_2\text{SO}_4\) respectively and remains unchanged up to the transition temperature \((T_C)\) above which \(M_2\) reduces to 0.5 \(G^2\) for both salts. With further increase in temperature the \(M_2\) values decreased rather rapidly and reached the values less than 0.1 \(G^2\) above 440 K. The observed results are interpreted in terms of 120° reorientation of \(\text{CH}_3\) and \(\text{NH}_3^+\) groups about their \(C_3\) axis for \((\text{MA})_2\text{SO}_4\) and that of \(\text{CH}_3\) groups for \((\text{MA}-\text{d})_2\text{SO}_4\). The extremely small \(M_2\) observed for both salts above \(T_C\) suggests the occurrence of diffusion in addition to the overall rotation of the cations. Proton \(T_1\) in both salts increased gently with increasing temperature and decreased discontinuously at \(T_C\).

The proton \(T_2\) also showed a steep increase at \(T_C\). \(T_1\) and \(T_2\) results in both salts were interpreted in terms of the self-diffusion of the cations. Proton \(T_1\) was measured at two different larmor frequencies (high and low). \(T_1\) increased with increasing temperature at high frequency, while it decreased with increasing temperature at low frequencies. Hence they concluded that self diffusion in this salt is slow compared to other salts of similar type.
Orthorhombic

\[ \text{(NH}_4\text{)}_2\text{SO}_4 \]

Ferroelectric \( \leq 223 \text{ K} \)

\[ P_{\text{nom}} = 4 \]

$^1$H $M_2$ studies [27. 209. 260]

$^2$H $M_2$ studies [106. 107. 258. 261]

$^1$H $T_1$ studies [30. 31]

$E_{\text{a}} (\text{NH}_4\text{)}^+ = 3.9 \text{ kcal/mole for } T < 223 \text{ K}$

$E_{\text{a}} (\text{NH}_4\text{)}^{11} = 2.7 \text{ kcal/mole & } 2.3 \text{ kcal/mole above } 223 \text{ K.}$

$^2$H $T_1$ studies [36. 259. 267. 268]

$^1$H $T_1$ studies $K^+$ ion imprinting effect [269]

$^2$H $M_2$ studies high pressure [271]

$^1$H $M_2$ studies [272]

Monoclinic

\[ \text{(NH}_4\text{)}\text{HSO}_4 \]

\[ T_c = 154 \text{ K. } T = 270 \text{ K}\]

Ferroelectric below 154 K

$^1$H $T_2$ studies [28. 265]

$^1$H $T_1$, TGF studies & anomalies [256. 257]

$^1$H $T_1$ studies 110 – 300 K [30. 31]

$^2$H $T_1$ studies $E_{\text{a}} 2.17 \text{ kcal/mole above } T_c$ [265]

$E_{\text{a}} 2.88 \text{ kcal/mole below } T_c$

$^1$H $T_1$, $T_1$ measurements 77 – 388 K [257]

$E_{\text{a}} (\text{NH}_4\text{)}^+ = 1.7-2.0 \text{ kcal/mole}$

\[ \text{(NH}_4\text{)}_2\text{HSO}_4 \]

\[ \text{Antiferroelectric} \]

between 143 – 247 K

$^2$H & Li $\text{nmr studies}$ [275. 276. 277]

$^1$H $T_1$, $T_1$G studies $E_{\text{a}} (\text{NH}_4\text{)}^+ = 2.76 \text{ kcal/mole}$ [279, 281]

$^1$H $M_2$ studies 77 – 300 K [284, 276]

$^1$H $M_2$ studies Pressure variation [278]

$^1$H $T_1$ studies 77 – 480 K

$E_{\text{a}} (\text{NH}_4\text{)}^+ = 2.6 \text{ kcal/mole}$ [282, 287]

$^2$H & Li angular dependence of NMR spectra [285]

$^1$H & $^7$Li line shape & tunnelling studies [286]

$L\text{iNH}_2\text{SO}_4$

Phase I \( \geq 459.5 \text{ K} \)

FE phase

$283 \text{ K < FE phase II} < 439.5 \text{ K} \quad P_{21m}$

Phase III \( \geq 283 \text{ K} \)

$^1$H $M_2$ studies [284, 276]
$\text{NH}_4\text{SO}_4$

$\text{(NH}_3\text{OH)}_2\text{SO}_4$

$\text{NH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$

Ferroelectric below

$T_{c1} = 101 \text{ K}$

$T_{c2} = 92 \text{ K}$

$\text{(NH}_4\text{)}_2\text{Ca}_2(\text{SO}_4)_3$

Ferroelectric $< 95 \text{ K}$

Cubic

$P_2_3 \quad Z = 4$

$\text{H}_2\text{ studies Pressure & Temperature variation [289]}$

$\text{HT}_2 \text{ studies 190 - 410 } F$ [111]

$\text{H}_2\text{ & }^{15}\text{N}_2 \text{ studies [290, 291, 292, 293]}

E_a(\text{NH}_4^+) = 7 \text{ kcal/mole } > 100 \text{ K}

= 3.1 \text{ kcal/mole } < 100 \text{ K}

$\text{H}_2\text{ studies [292]}

$\text{H}_2\text{ & }^3\text{He \ studies studies [28, 294, 295]}

$\text{H}_2\text{ studies 77 - 300 } K$ [295, 296]

$E_a(\text{NH}_4^+) = 2.7 \pm 0.5 \text{ kcal/mole in the } \text{FE phase}$

$= 0.9 \pm 0.5 \text{ kcal/mole in the } \text{FE phase}$

$\text{H}_2\text{ studies [357, 4]}

E_a(\text{NH}_4^+) = 2.6 \text{ kcal/mole}

$\text{H line shape studies [37]}

$\text{H}_2\text{ & }^3\text{He \ studies [233]}

E_a(\text{NH}_4^+) = 1.7 \pm 0.2 \text{ kcal/mole}$

$\text{H line shape studies [37]}

$\text{H}_2\text{ studies [194, 254]}

$\text{H}_2\text{ studies. Tunneling [254]}$

$\text{H}_2\text{ & }^3\text{He \ studies [233]}

E_a(\text{NH}_4^+) = 1.7 \pm 0.2 \text{ kcal/mole}$

$\text{H line shape studies [37]}

$\text{H}_2\text{ studies [194, 254]}

$\text{H}_2\text{ studies. Tunneling [254]}$
\[(NH_4)_2Fe(\text{SO}_4)_2\text{H}_2\text{O}\] Monoclinic
\[P_{21}/a \ Z = 2\]

\[(NH_4)_2\text{W}_2(\text{SO}_4)_2\]
\[T_{c1} = 407 \ K, \ T_{c2} = 330 \ K\]
Phase I \(T > 407 \ K\)
330 K < phase II < 407 K
Phase III < 330 K

\[(NH_4)_2\text{Al}(\text{SO}_4)_2\text{H}_2\text{O}\]

\[(CH_3NH_3)\text{Al}(\text{SO}_4)_2\text{H}_2\text{O}\]
\[PE > 177 \ K \ Cubic \ P_{\text{m3}}\]
\[FE < 177 \ K \ Monoclinic \ P_{\text{c2a1}}\]

\[(\text{CH}_3)_2\text{W}\text{SO}_4\]
\[H \text{ M}_2 \text{ studies [243]}\]
\[H \text{ T}_1 \text{ studies [242]}\]
\[E_a(\text{CH}_3) = 9.4 \text{ kcal/mole} \ E_a(\text{NH}(\text{CH}_3)_4)^+ = 14.1 \text{ kcal/mole}\]

\[(\text{CH}_3)_4\text{NHSO}_4\]
Superionic conductor

\[(\text{CH}_3)_2\text{NH}_2\text{SO}_4\]
\[T_c = 424 \ K \ Monoclinic \ P_{21/c}\]
\[H \text{ M}_2 \& T_1 \text{ studies [307]}\]
\[T_1 \text{ anomaly at } T_c\]
II.8 Selenates

Compared to sulphates, studies on selenates are not much. There is lot of scope for NMR study on Selenates. Moreover the properties and structure of these compounds resemble their sulphate counterparts in all respects. $\text{NH}_4\text{HSeO}_4$ is a ferroelectric and has been widely studied using NMR of both proton and selenium. $\text{LiNH}_4\text{SeO}_4$ and $\text{NaNH}_4\text{SeO}_4$ are also studied using proton NMR. The latter compound is a ferroelectric and shows a interesting phase transition.
Ammonium Selenate  \((\text{NH}_4)_2\text{SeO}_4\)

Proton line shape studies at 4.2 K by Watton et al.\(^{37}\) show \(M_2\) value of \(50.6 \pm 1.2\) corresponding to the rigid lattice value. Proton \(T_1\) studies\(^{306}\) show that in the region 88 to 128 K the \(\text{NH}_4\) ions are rigid and above 128 K the relaxation is due to the classical hindered rotational motion of the ammonium group.

Ammonium Hydrogen Selenate \((\text{AHSE}) \ \text{NH}_4\text{HSeO}_4\)

AHSE is paraelectric at room temperature having a monoclinic space group with \(Z=6\) and undergoes a first order ferroelectric phase transition at 250 K and again changes to a paraelectric phase at 98 K where the spontaneous polarization disappears. The ferroelectricity is exhibited along \(b\)-axis of the crystal.

Studies of ferroelectric phase transition using proton\(^{309,314}\), Deuteron\(^{312,315}\) and \(^{77}\text{Selenium} \)\(^{309,311,314,315}\) NMR have been carried out by many workers at various temperatures. Aleksandrova et al.\(^{309}\) have investigated high resolution study of selenium using double resonance (proton and selenium) and cross polarization of rare \(^{77}\text{Se} \) nuclei by protons. The angular dependences of the positions of the \(^{77}\text{Se} \) NMR lines were used to find the changes in the magnetic screening tensor parameters of \(^{77}\text{Se} \) in the ferroelectric and paralectric phases. The results indicate the ordering of the Se...O...H hydrogen bonds. Its unusual nature was associated with the fact that out of two types of one-dimensional H-bond chains (\(\alpha\)-type and \(\beta\)-type). Only \(\alpha\)-type became ordered at \(T_c\) while the \(\beta\)-type were already ordered in the paraelectric phase itself. Further they observed changes in the spectra at 263 K, which indicated the occurrence of an additional phase transition (not observed before) and is characterized by unusual properties.

Studies\(^{311}\) of orientational dependence of magnetic screening tensor of \(^{77}\text{Se} \) nuclei showed that in the paraelectric phase all the three structurally inequivalent Se nuclei have similar parameters and similar orientation of the major axis of the tensors relative to the geometry of the SeO\(_4\) group. But after transition to paraelectric phase, tensor parameters change only for those Selenium atoms in SeO\(_4\) group which are bound by \(\alpha\)-bonds, while no change occurs for the other selenium bound by \(\beta\)-bonds. They found that \(\alpha\)-bonds to be symmetric (i.e. localised in the centre of bond) and below \(T_c\), the \(\alpha\)-bond becomes asymmetric whereas protons of \(\beta\)-bonds are ordered even in the PE phase. The presence of an intermediate phase (between PE and FE) is considered.

Studies\(^{314}\) of proton \(M_2\) and \(T_1\) and \(^{77}\text{Se} \) NMR line width showed no significant change in the PMR spectra on going through the ferroelectric to paraelectric phase as expected. The calculation for a rapid motion of the protons between two positions in the \(\alpha\)-bonds lead to a value of \(M_2\) of 0.05 G\(^2\) in confirmation with the observation. It
should be noted that the dynamic ordering of the protons of this bond is the cause of this phase transition. The observed M₂ of 2.55±0.15G² shows that NH₄ ion is undergoing reorientational motion both in the ordered and disordered phases. The significant decrease observed in M₂ at 417 K was attributed to the diffusion of proton and ammonium groups with almost the same activation energies. The proton T₂ and T² measurements also showed a marked change at this transition with a thermal hysteresis indicating it is of first order. The ⁷⁷Se NMR spectra consists of single broad line at high temperatures, contrast to several lines corresponding structurally and magnetically inequivalent ⁷⁷Se nuclei in the low temperature phase indicating that all the ⁷⁷Se nuclei are equivalent in this temperature.

Deuteron NMR studies of highly deuterated AHSe by Moskvich et al.¹² show that phase transition is caused by proton ordering in the hydrogen bonds and its importance of was found when they observed the shift in Tc towards higher temperature after deuteration. The orientational dependences of the DMR line splittings of those deuterons in the hydrogen bonds were measured at room temperature for three orthogonal rotations about the crystallographic a, b and c axis. They found that highly deuterated AHSe has a crystal structure different from the orthorhombic structure of AHSe and in the unit cell of the former there are only four magnetically non equivalent hydrogen bonds connected with each other by two-fold symmetry axis. The EFG tensors were assigned to definite deuterons easily because due to the rather simple geometry of this bond there is a definite orientation of the principal tensor axis relative to the characteristic hydrogen bond directions. Thus the DMR studies in highly deuterated salt, shows that there is one structurally non-equivalent asymmetrical hydrogen bond in which deuteron is ordered. No noticeable changes of DMR line splittings have been found in the study of the temperature dependences of the DMR spectra in the range from 300- 97K, which indicates that in this crystal there is no phase transition in the temperature range studied. Dislocation and time dependent dynamics of the incommensurate phase of AHSe was studied by Aleksandrova et al.¹³. The instability of a modulated structure in time scale was found. The time dependent kinetics of the NMR spectra has been studied under different thermodynamic conditions.

Rosenburger¹⁰ has carried out proton chemical shift studies in AHSe using MAS with a spinning frequency of 2.3 kHz. Two types of H-bonds shorter one (R-O-H = 0.252nm) which contains a symmetry element (a two-fold axis) and two longer H-bonds (R-O-H = 0.256nm) were established by X-rays and were verified with a direct evidence by pmr chemical shifts. The ratio of the sites for the short and the longer H-bond distances is 1:2 (δ = -14.6ppm and -13.3ppm). The obtained data are good agreement with the relation δ = f(R-O-H) according to which a shift was expected of the α values to lower field for the shorter H-bonds. The NH₄ signal of AHSe
at $\delta = -6.8$ppm is split into a triplet probably caused by the indirect nuclear spin-spin interaction of the protons with the $^{14}$N nucleus.

Moskwich et al\textsuperscript{315} has carried out $^2$H, $^{77}$Se NMR and $T_1$ studies at high temperatures in AHSe and its deuterated analogue and found a phase transition temperature as 417 and 446 K respectively and also concluded that high conductivity is due to cationic diffusion.

**Sodium Ammonium Selenate Dihydrate (SASeD) NaNH$_4$SeO$_4$2H$_2$O**

SASeD belongs to family of lecontite and is a ferroelectric like its isomorphous compound sodium ammonium sulphate dihydrate. The room temperature structure is paraelectric with orthorhombic space group $P_{2_1}2_12_1$, with $Z = 4$ and undergoes a ferroelectric phase transition at 180 K, with a change in structure to $P_{2_1}$. The crystal structure studies show that there are two types of SeO$_4$ tetrahedron, two types of sodium ions and two types of ammonium ions below $T_c$.

PMR studies by Aleksandrova et al\textsuperscript{316,318,320,322} reveal the following features. Proton line width corresponding to the protons of water molecules and NH$_4$ ions did not show any change at $T_c$, however the line width corresponding to the NH$_4$ ions broadened around 130 K. The $M_2$ results show that water molecules are rigid at room temperature where as ammonium ions are undergoing orientational motion around more than one axis of symmetry in both the phases. They conclude that the water molecules are not making any contribution to the spontaneous polarization, but, it is due to the distorted ammonium groups. Aleksandrova et al\textsuperscript{322} concluded that the phase transition is of order-disorder trigger type, the ordering one structural unit brings about the displacement and polarization of all other structural elements. Proton $T_1$ studies by Shenoy et al\textsuperscript{288,325} over a range 130 to 300 K showed a continuous change with temperature through $T_c$ (180 K) indicating that phase transition is of second order. No FID due to protons of water was observed and FID due to protons of the ammonium group also decay fast and could not be observed below 130 K showing the freezing of the motion of the ammonium ions on the NMR time scale. A single $T_1$ minimum was observed at around 180 K and the activation energy for ammonium reorientation changes very slightly at the phase transition.

The DMR studies\textsuperscript{317,321,324} have been carried out by many workers. Studies\textsuperscript{317} in 20% deuterated salt showed a sharp change in the spectrum at $T_c$ (176 K) due to the presence of non-equivalent ammonium groups. Studies of Kruglic et al\textsuperscript{321} in 50% deuterated salt exhibit a small splitting due to distorted ammonium groups and two pairs of satellites with large splitting due to D$_2$O molecules are observed. The positions of water molecules in the crystal was determined using the orientation of the principle axis of the EFG tensor. Further they identified two inequivalent water molecules in the
crystal with different activation energies indicating that the water molecules are linked to cations via H-bonds. Similar studies by Aleksandrova et al\textsuperscript{324} shows a good agreement with Kruglic et al\textsuperscript{321}. $^{23}\text{Na}$ NMR studies\textsuperscript{319,324} show a little change in second-order quadrupole effects in both the phases, indicating that there is no appreciable change in the immediate environment of the $^{23}\text{Na}$ nucleus. NMR studies at high pressures up to 10 kbars and temperatures close to $T_c$ (179 K) by Shirokov et al\textsuperscript{323} show that the phase transition is of second order at normal pressures and is transformed to the first order with increasing pressure. $T_c$ is shifted to 171.5 K at a pressure of 1.6 kbars.

**Lithium Ammonium Selenate  LiNH$_4$SeO$_4$**

Proton M$_2$ studies by Bhat\textsuperscript{284} shows that at room temperature the line is narrow ($\delta H = 3.25$ G) with a M$_2$ of 1.75 G$^2$. The line width was found to be 6.4 G with a M$_2$ of 8.75 G$^2$ even at 77 K which is considerably less than rigid lattice values for NH$_4$ group. The results are interpreted in terms of inequivalent NH$_4$ ions in the unit cell, one of them undergoing fast tunnelling reorientations and the motion of the other one being completely frozen. He also concluded that the presence of the Li ion brings down the hindering barrier. The coupling of SeO$_4$ group with NH$_4$ + (with a H- bond) is known to slower the reorientation of NH$_4$ ions.

**Diammonium Selenate  (NH$_4$)$_2$SeO$_3$**

PMR studies at 4.2 K by Watton et al\textsuperscript{37} showed a M$_2$ value of 38±1 G$^2$ and line width of 22.2±0.8 G.

**Ammonium Trihydrogen Selenite  NH$_4$H$_3$(SeO$_3$)$_2$**

This is isomorphous with Rubidium trihydrogen selenite and crystallizes with orthorhombic space group $P2_12_12_1$ with Z = 4. This is a linear dielectric with hydrogen bond location very similar to Rubidium hydrogen selenite. The potentiality of deuteron NMR studies in detecting H- bonds has been exploited by Vonogrodova\textsuperscript{326}, who found an isotopic shift in the curie point and weakening of ferroelectricity with an increase in the deuteron content and concluded that phase transition is due to ordering and disordering of hydrogen atoms involved in H-bonds. The DMR data also suggests that there are three chemically inequivalent deuterons in a unit cell.
Ammonium Diselenite (ND₄)₂Se₂O₅

The crystal structure of this salt at room temperature is orthorhombic space group P₂₁₂₁₂₁ with Z = 4. The structure consists of Se₂O₅ and ammonium ions hydrogen bonded in three dimensional network. Dielectric studies revealed a first order phase transition at around 279 K and 295 K with a thermal hysteresis. Deuteron magnetic resonance in single crystals and proton T₁ studies have been carried out by Vinogradova and Cherkasov. The angular dependence of the first order quadrupole splitting of deuteron NMR in phase I (at 288 K) and phase II (at 248 K), about three mutually orthogonal axis show the orthorhobic symmetry with two non-equivalent ammonium groups ND₄(I) and ND₄(II) in the unit cell. Further it was found that both groups are rapidly reorienting over the entire temperature range (160 to 300 K). The values of $e^2Qq/h$ and $\eta$ are similar for ND₄(I) and ND₄(II) indicating the similarity of their surroundings.

On going through the transition the crystal structure and inequivalence of NH₄⁺ ions still remains only with little changes in the values of the principle components of the EFG tensors. However, the directions of the principle axis change greatly, with $q_{zz}$ direction for ND₄(I) shifted by an angle of 28° and for ND₄(II) by an angle of 47°. Such changes are typical for the order-disorder transitions. Further they found in the high temperature phase, ND₄(I) groups lie on the symmetry element (in the ac plane). The phase transition is associated with the disappearance of this symmetry element which is shown by the splitting of the ND₄(I) spectra. They concluded that ammonium groups play an important role in this transition.

The proton T₁ studies show an anomaly at Tc and a sufficiently broad minimum caused by NH₄⁺ reorientation. Apparently both the non-equivalent ammonium groups have similar activation energies and give closely placed minima and hence explaining the observed temperature dependence of T₁. Only a slight change in the potential barrier and the activation energy occurs at the transition.
\((\text{NH}_4)_2\text{SeO}_4\)

**PE phase**
- Monoclinic
- \(T = 417\) K
- \(250\) K < PE phase < \(90\) K.

**Orthorhombic**
- \(P_{2\alpha}, 2\beta, 2\gamma\)

1. \(\text{H}^+\) studies [306]
2. \(\text{H}^+\) studies [307]

**\(\text{NaNH}_4\text{SeO}_4\cdot 2\text{H}_2\text{O}\)**

**PE phase (RT)**
- Orthorhombic
- \(P_{2\alpha}, 2\beta, 2\gamma, \gamma = 4\)

Ferroelectric < \(180\) K
- \(P_{2\alpha, 2\beta, 2\gamma}\)

1. \(\text{H}$$^+\) studies [316]
2. \(\text{H}^+\) studies [317, 318]
3. \(\text{Na}^+\) studies [319]
4. \(\text{H}^+\) studies [320, 321]
5. \(\text{H}^+\) studies [322]
6. \(\text{H}^+\) studies Pressure dependence [323]
7. \(\text{T}^+\) studies [288, 325]

\(E_{\text{a}}(\text{NH}_4^+) = 4.6\) kcal/mole in the PE phase
= 5.3 kcal/mole in PE phase

1. \(\text{H}^+\) studies \(E_{\text{a}}(\text{NH}_4^+) = 2.36\) kcal/mole [204]

**\(\text{LiNH}_4\text{SeO}_4\)**

**\(\text{NH}_4\text{SeO}_3\)**

**\(\text{NH}_4\text{H}_3(\text{SeO}_3)_2\)**

- Orthorhombic
- \(P_{2\alpha}, 2\beta, 2\gamma, \gamma = 4\)

1. \(\text{H}^+\) studies at \(4.2\) K [37]
2. \(\text{H}^+\) studies [326]
Thermal hysteresis

$\text{(ND}_4\text{)}_2\text{Se}_2\text{O}_5$

Orthorhombic

$T_c = 279 - 295 \text{ K}$

$P_{2,2,2}, Z = 4$

$^2\text{H M}_2\text{ studies [327]}$

$^1\text{H T}_1\text{ studies}$

$E_a (\text{NH}_4^+) = 6 \pm 0.4 \text{ kcal/mole}$
II.9 Arsenates and phosphates

Arsenates and phosphates are interesting in view of their antiferroelectric phase transitions. Further proton and deuteron $T_1$ show interesting results as H-bonds play an important role in the phase transitions. $\text{NH}_4\text{H}_2\text{SO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ have been extensively studied to understand the mechanism of antiferroelectric phase transition. Other salts studied are $(\text{NH}_4)_2\text{AsO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_3\text{PO}_4$ and $\text{NaNH}_4\text{PO}_4\cdot4\text{H}_2\text{O}$. Salient features of the studies are highlighted.
Ammonium Dihydrogen Arsenate (ADA) \((\text{NH}_4)\text{H}_2\text{AsO}_4\)

This is paraelectric at room temperature having a tetragonal structure with space group \((I\overline{4}2d)\) and is known to undergo a phase transition at 216 K to an antiferroelectric phase with an orthorhombic space group \((P\overline{2}22)\).

Proton line shape and \(T_1\) studies over a range 87-293 K by Newman\(^{329}\) show a slight increase in the line width with lowering of temperature. An interesting change occurs at about 103 K, with the appearance of symmetrical shoulders on either side of the central narrow peak, which was explained as a superposition of a broad one arising from the \(\text{NH}_4^+\) protons and the narrow peak arising from the acid hydrogens. The \(T_1\) measurements show two minima, a shallow one at 240 K which was attributed to acid hydrogens and a deep one at 180 K due to the ammonium ion reorientation. He has ruled out the possibility of H-bond formation between \(\text{AsO}_4\cdot 3\) with \(\text{NH}_4^+\) ions.\(^{348}\)

Proton \(T_1\), \(T_{1Z}\) and \(T_{1D}\) studies at various temperatures between 120-385 K. The \(T_1\) studies\(^{331}\) show an anomalous increase at \(T_c\) (216 K). They found hindered reorientation of \(\text{NH}_4^+\) ions as the dominant source of relaxation both below and above \(T_c\), but with different activation energies. They observed two \(T_1\) minima at 180 K and 216 K and their interpretation is in good agreement with Newman\(^{329}\). Further they concluded that the dynamics of acid protons is responsible for triggering the transition. Both \(T_Z\) and \(T_{1D}\) results\(^{332,333}\) have exhibited a discontinuity at \(T_c\) (216 K). A second discontinuity in \(T_{1D}\) occurs in the high temperature region at 314 K, which possibly indicates a new phase transition. The Zeeman relaxation is caused by the reorientation of \(\text{NH}_4^+\) groups around three and two-fold axis. Below \(T_c\), the ratio of \(T_{1Z}/T_{1D}\) is two and it decreases in the vicinity of \(T_{1Z}\) min., which proves that in the AFE phase both Zeeman and dipolar relaxation are due to the fast reorientation of \(\text{NH}_4^+\) groups. However, at high temperatures, a slow motion of \(\text{H}_2\text{AsO}_4\) group was established from these studies.

Proton \(T_1\) studies by Dalal et al\(^{334}\) in ADA and its deuterated analogue show that ammonium ions play a dominant role in the phase transition. At high temperatures well above the critical point (\(T_c\)) the \(\text{NH}_4^+\) ions are thought to be executing fast reorientations and at \(T_c\) a sudden change in \(\text{NH}_4^+\) motion occurs, and each \(\text{NH}_4^+\) ion is thought to make a permanent hydrogen bond with an oxygen atom of an \(\text{AsO}_4\cdot 3\) group, leading to a distortion of the group and hence a phase transition. A sudden discontinuity in \(T_1\) at \(T_c\) confirms this fact. Tokoshima and Tatsuzaki\(^{335}\) have carried out the angular and temperature dependence of \(^{75}\text{As}\) NMR line width along the C-axis in the PE phase of ADA and found a slight but distinct anomaly in the line width from 273 to 217.6 K, which was attributed to the fluctuations of electric dipoles. Results of Adriaenssens\(^{336}\) on \(^{75}\text{As}\)
NMR line width agrees with the earlier studies\textsuperscript{335}. They\textsuperscript{336} attribute the changes to the presence of two low frequency modes.

Deuteron NMR studies by Blinc et al\textsuperscript{330,339} yield the same quadrupole coupling tensor indicating that ND\textsubscript{4}\textsuperscript{+} ions are physically and chemically equivalent above T\textsubscript{c} and also show a little deviation from perfect tetrahedral symmetry (e\textsuperscript{2}Qq\textsuperscript{-}) due to N-H-O hydrogen bonding, while below the phase transition, a discontinuous change in deuteron quadrupole coupling occurs with the appearance of four new sets of NH\textsubscript{4} deuteron tensors indicating that they are chemically equivalent but not physically equivalent. The NMR lines in the PE and AFE phase lines coexist with different relative intensities over a range of about 200 K. The EFG tensors below T\textsubscript{c} are not anymore axially symmetric and the deuteron e\textsuperscript{2}Qq increases with respect to the PE phase. The rapid reorientation of the NH\textsubscript{4}\textsuperscript{+} group is however still present on and an average deuteron spectrum is produced. The distortion of the NH\textsubscript{4} + ion is however larger than in the PE phase and the distorted NH\textsubscript{4}\textsuperscript{+} tetrahedra are in contrast to the PE phase differently oriented at different lattice sites. From these data they conclude that phase transition in ADA is connected not only by an ordering of the O-H-O hydrogens, but also by a significant contribution of the ammonium ion\textsuperscript{8}.

**Ammonium Hydrogen Arsenate (BHA) (NH\textsubscript{4})\textsubscript{2}HAsO\textsubscript{4}**

Proton M\textsubscript{2} and T\textsubscript{1} studies from room temperature down to 213 K by Milia et al\textsuperscript{338} show that the spectrum consists of a single motionally narrowed line with M\textsubscript{2} of 4G\textsuperscript{2}, indicating rapid reorientation of NH\textsubscript{4}\textsuperscript{+} ions around more than one axis. The narrow line persists down to 123 K (lowest temperature covered in this study), but below 213 K a second line appears which rapidly broadens with decreasing temperature. At 123 K the M\textsubscript{2} of the narrow line is still 4 G\textsuperscript{2} whereas the M\textsubscript{2} of the broad line is of the order of 50 G\textsuperscript{2}. They have assigned the broad line to the frozen- in ammonium ion and the narrow line to the acid protons. The temperature dependence of proton T\textsubscript{1} and T\textsubscript{1p} in BHA exhibits minima which are typical for hindered molecular rotation of the NH\textsubscript{4} groups. The 'acid' protons do not seem to influence the T\textsubscript{1} data. The two T\textsubscript{1} minima are close to each other and the values of T\textsubscript{1} minimum observed are twice that expected for NH\textsubscript{4} groups. The results could be explained assuming two inequivalent NH\textsubscript{4} groups in the crystal structure.

**Ammonium Dihydrogen Phosphate (ADP) NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}**

This is known to undergo an antiferroelectric phase transition at 148 K from room temperature paraelectric space group (I\textsubscript{4}2d with Z = 4) to P\textsubscript{2} 2 2 and the volume of the primitive cell is doubled.
Both Proton $M_2$ and $T_1$ studies by Newman over a range 87-293 K show only a slight change in the line width with lowering of temperature. However, he observed an interesting change in the line shape at 113 K, with the appearance of symmetrically placed shoulders on either side of a central narrow peak, which become more and more pronounced with decreasing temperature. The $M_2$ data were interpreted in a similar way to that given for ADA. The $T_1$ data vs. temperature shows two minima, a deep one at 173 K and a shallow one at 217 K. The high temperature minimum was attributed to acid hydrogen and the low temperature minimum for ammonium ion reorientation. However, he ruled out the possibility of H-bonds between cation and anion in this structure.

Proton $T_1$, $T_{1p}$ studies by Kasturi and Moran over a range from 74 to 315 K showed a discontinuity in the relaxation rate ($1/T_1$) at $T_c$ (147 K) and it developed a temperature dependent anisotropy below $T_c$. The relaxation rate in the rotating frame ($1/T_{1p}$) showed a smooth temperature dependence, in addition to some additional sharply temperature dependent structures. Further it exhibited an anomaly at $T_c$. They analysed these data and concluded that (1) the ammonium ions are reorienting about two fold axis both above and below $T_c$. (2) There are severe distortions of the NH$_4^+$ ions and rotational anisotropies in the AFE state, but the phase transition does not involve cooperative rotational ordering of the ammonium ion. (3) There is critical slowing down of some dynamical mechanism at the phase transition. Further they noticed a change in the activation energy at the phase transition along with a considerable anisotropy in the AFE phase. A similar study by Ripmeester and Dalal (T$_1$, T$_{1p}$ and T$_{1D}$) over a range 125 to 265 K agrees with that of Kasturi and Moran. They also found a orientation independent $T_1$ in the paraelectric phase with $T_1$ and $T_{1p}$ being equal. $T_1$ was found to exhibit a minimum at 178 K. All the three parameters change discontinuously at $T_c$ (148 K). $T_1$ becomes longer by a factor of 3 and $T_{1p}$ and $T_{1D}$ become shortened by the same factor on going to the low temperature phase. They further concluded that a critical fluctuation contribution to relaxation near the PE to AFE phase transition (postulated by Kasturi and Moran) was unnecessary to account for the $T_1$ results. PMR studies of single crystals was carried out by Adriaenssens et al who found a good agreement between the theoretically calculated $M_2$ and experimental $M_2$.

Blinc et al have carried out DMR studies and tried to explain the NMR results in terms of Devonshire's long range force model. They determined O-D..O deuteron quadrupole coupling tensors and concluded that the AFE phase transition due to the order-disorder arrangement of the deuterons of the O-D..O bonds in agreement with the Nagamiya model of hydrogen ordering. DMR studies have also been carried out by Chiba and Genimetal. They observed a quadrupole coupling tensor which indicate a greater distortion of the ND$_4^+$ ion in the AFE phase than in the PE phase. Genimetal investigated the principal coordinates of the deuteron EFG...
The discontinuity is accompanied by a change in activation energy for the NH$_4$ ion reorientation. $^1$H and $^{31}$P double resonance experiments using multiple pulse sequences was carried out by Willsch et al.$^{344}$

**Ammonium Hydrogen Phosphate (BHP) (NH$_4$)$_2$HPO$_4$**

This salt crystallizes in the space group $P2_1/C$ with $Z = 4$ and structure consists of O-H..O and N-H..O bonds. Proton M$_2$ and T$_1$ measurements over a range 77 - 430 K by Watton et al.$^{337}$ revealed a M$_2$ of 42.3±0.2 G$^2$ between 77-110 K which was attributed to rigid NH$_4^+$ ions. Further M$_2$ decreases with increasing temperature and reaches a second plateau of 23 G$^2$ in the range 110 to 165 K, which gets further reduced and reaches a constant value of 3.9±0.1 G$^2$ over the range 270 - 430 K. At approximately 215 K a definite change in the slope of the M$_2$ versus temperature curve is observed, which is indicative of two different mechanisms responsible for reducing the second moment between 170 and 270 K. No substantial change in M$_2$ occurs from 77 to 4.2 K. In view of the observed data they propose a possibility of one of the NH$_4^+$ ions having sufficiently low activation energy for 3-fold rotation to allow quantum tunnelling effects to become important at low temperatures. The line shape at 165 K also shows two components, with width 4.8 and 22 G, but the area under the broad curve has dropped to approximately 22% of the total area, implying that 25% of the ammonium groups are stationery. For this they propose a model in which one NH$_4^+$ group in the asymmetric unit is stationary while three others execute C$_3$ reorientations. Reduction in second moment from 42.3 to 23.0 G$^2$ between 110 and 160 K, is therefore the result of three-fold reorientation of two NH$_4^+$ groups. At 215 K the broad (22 G) component has disappeared. Above this temperature all NH$_4^+$ groups are therefore involved in molecular reorientations. They conclude from the theoretical calculations that 50% of the NH$_4$ ions are executing C$_3$ reorientations undergoing general tumbling motion and other half are executing general tumbling motion (M$_2$ =10±0.3 G$^2$) in agreement with experimental M$_2$ value of 9.3±1.0 G$^2$. The experimental M$_2$ values of 3.9±0.1 G$^2$ from 270 to 430 K is attributed to general tumbling motion of all NH$_4^+$ ions.

The proton T$_1$ shows, a non-exponential decay of the FID below 150 K. They isolated two relaxation times, and both of them were found to exhibit the same temperature dependence. In both cases a maximum was reached at approximately 87 K above which T$_1$ decreases and the non-exponentiality was not observable above 150 K. Two T$_1$ minima were observed at 216 K and 313 K. They found a one to one correspondence between T$_1$ and M$_2$ data for all the temperatures.

Milla et al.$^{336}$ also have carried out proton M$_2$ and T$_1$, T$_1\rho$ studies as a function of temperature and found that the results are similar to those of diammonium hydrogen arsenate. They observed a proton line-width transition at 203 K, above which the
spectrum consists of a single, motionally narrowed line while below 203 K two lines were found, one due to the acid protons and the other due to the protons of the ammonium ion. Further the line-width transition was not sharp indicating that the molecular motion is not governed by a single correlation time. They also found two well separated $T_1$ min, one at 303 K and the other at 213 K in agreement with Walton et al$^{337}$. They have interpreted the $T_1$ data in terms of two non-equivalent NH$_4^+$ ions in the unit cell, with the same activation energy. Proton $M_2$ and $T_1$ studies by Shimomura et al$^{357}$ in the range 110 to 420 K also revealed results similar to the earlier studies$^{337,338}$. They found the relaxation to be non-exponential above 167 K and obtained two minima in $T_1$ at 294 K and 215 K which were attributed to the two NH$_4^+$ groups with different rates of motion.

**Triammonium Phosphate (NH$_4$)$_3$PO$_4$**

The PMR studies by Levstek et al$^{255}$ show that the spectrum changes from a single line at room temperature, to one with two components at temperatures below $T_c$ (193 K). These components were attributed to two types of ammonium ions, one frozen and the other rotating.

**Sodium Ammonium Hydrogen Phosphate Tetrahydrate NaNH$_4$HPO$_4$4H$_2$O**

Proton $T_1$ studies by Koksal$^{357}$ revealed a minimum at 270 K, which was interpreted as due to the reorientation motions of NH$_4$ ions around C$_3$ axis along with the spin diffusion of protons other than those in the NH$_4^+$ ions. The activation energy estimated from $T_1$ data is 5.16 kcal/mole.

261
\( \text{NH}_4\text{H}_2\text{AsO}_4 \)  
Tetragonal  
Antiferroelectric < 216 K  
\( T_c = 216 \text{ K} \)

\( \text{NH}_4\text{H}_2\text{PO}_4 \)  
Tetragonal  
Antiferroelectric < 148 K  
\( T_c = 148 \text{ K} \)

\( \text{NH}_4\text{H}_2\text{PO}_4 \)  
\( P_{2_1}/c \)  
\( T_c = 193 \text{ K} \)

\( \text{NaNH}_4\text{PO}_4\text{H}_2\text{O} \)

1. \( \text{H}_2 \text{PO}_4 \) and \( T_1 \) studies 47 - 293 K [329]
2. \( \text{H}_2 \text{PO}_4 \) and \( T_1 \) studies 120 - 365 K [331]
3. \( E_a (\text{NH}_4^+) = 3.3 \text{ kcal/mole < 216 K} \)
   \( = 2.65 \text{ kcal/mole > 216 K} \)
4. \( \text{H} \) and \( T_1 \) studies Discontinuity at \( T_c \) [332, 333]
5. \( \text{As} \) \( \text{H}_2 \) studies [335, 336]
6. \( \text{H} \) \( \text{H}_2 \) studies [334]
7. \( \text{H} \) \( \text{M}_2 \) studies [340]
8. \( \text{H} \) \( \text{M}_2 \) studies [346]
9. \( \text{H} \) \( \text{M}_2 \) studies [339]
10. \( \text{H} \) \( \text{M}_2 \) and \( T_1 \) studies [338]
11. \( \text{H} \) \( \text{M}_2 \) and \( T_1 \) studies 87 - 293 K [329]
12. \( \text{H} \) \( \text{M}_2 \) and \( T_1 \) studies [330]
13. \( \text{H} \) \( \text{M}_2 \) and \( T_1 \) studies [340, 341, 343]
14. \( E_a (\text{NH}_4^+) = 3.7 \text{ kcal/mole } T < T_c \)
   \( = 4.3 \text{ kcal/mole } T > T_c \)
15. \( \text{H} \) \( \text{P} \) \( \text{ENDOR} \) studies [344]
16. \( \text{H} \) \( T_1 \) \( T_1 \) \( \text{studies 74 - 315 K} \) [345, 346]
17. \( \text{H} \) \( \text{M}_2 \) studies [348]
18. \( \text{H} \) \( \text{M}_2 \) and \( T_1 \) studies 77 - 430 K [337, 338]
19. \( \text{H} \) \( \text{M}_2 \) studies [347]
20. \( \text{H} \) \( \text{M}_2 \) studies [255]
21. \( \text{H} \) \( T_1 \) studies [357]
22. \( E_a (\text{NH}_4^+) = 21.4 \text{ KJ/mole} \)
II.10 Tartarates

Ammonium Tartarate is an important member of the Rochelle salt family of ferroelectrics. It undergoes a ferroelectric phase transition at 109 K. NMR results show a possibility of quantum mechanical tunnelling in this salt at low temperatures. The other salts studied under this group include Lithium ammonium tartarate, Ammonium hydrogen tartarate and Diammonium d-tartarate.
Ammonium Rochelle Salt (ARS) \( \text{NaNH}_2\text{C}_4\text{H}_4\text{O}_6\text{H}_2\text{O} \)

Sodium ammonium tartarate tetrahydrate known as ammonium Rochelle salt (ARS) is a member of the Rochelle salt family of ferroelectrics. It is ferroelectric below 109 K with spontaneous polarization along the b-axis, which can be reversed not by an electric field but by a shearing stress. Its PE phase is orthorhombic \( P_{2_1} 2_1 2 \) and is isomorphous with Rochelle salt. The PE phase of this crystal is monoclinic with space group \( P_{2_1} 1 \) and the primitive cell is doubled along the a-axis. The FE phase transition in ARS is known to be improper.

Proton \( T_1 \) was measured by Morimoto\(^{254, 349, 350} \) from 4.2 K to room temperature and by El Saffar and Peterson\(^{353} \) from 77 to 300 K. These two results are in good agreement with each other. \( T_1 \) versus temperature data shows a first \( T_1 \) minimum at 290 K which is attributed to the flip-flop motion of water molecules. Above 233 K, the motion of water molecules is the dominant cause of relaxation, whereas below 250K, \( T_1 \) decreases with decreasing temperature and shows a minimum at about 170 K.

Further it shows a discontinuous change of \( T_c \) which is a characteristic of first order phase transition. Both El Saffar and Peterson\(^{353} \) and Morimoto\(^{349} \) have concluded that in the PE phase (250 < \( T < T_c \)), the dominant relaxation is due to the three-fold axis reorientation accompanied by a fast two-fold axis reorientation of the \( \text{NH}_4 \) ion.

Below \( T_c \) there are two minima at about 75 K and at 45 K, which were explained using BPP theory by Morimoto et al\(^{349} \) in terms of the \( \text{NH}_4^+ \) ion reorientation about two-fold axis at different rates. However, El Saffar and Peterson\(^{353} \) observed small separations in deuteron spectra in ARS and it was completely different from those expected, if \( \text{ND}_4^+ \) ions were reorienting about the two-fold axis. Their \( T_1 \) measurements and that of Morimoto (discussed below) reveal the presence of quantum mechanical tunnelling at low temperatures. Hence, it was concluded that the observed narrow proton resonance line and small deuteron splitting in ARS is due to quantum mechanical tunnelling.

\( T_1 \) studies of Morimoto\(^{254, 351} \) at rf fields \( H_1 = 17 \text{ G} \) and 9 G shows four minima. The \( H_1 \) dependent \( T_1 \) minimum values occurring at 214 K and 204 K respectively are attributed to flip-flop motion of the water molecules. They could successfully explain the observed results of these minima on the basis of BPP theory. The second minimum occurs at 130 K and the \( T_1 \) values are the same for both the rf fields viz., 17 G and 9 G, which could not be accounted for by the BPP theory. The same situation occurs for the third (at 55 K) and fourth (at 35 K) minima. The observed minima appear at higher temperatures and have much larger values than the expected ones. This anomalous behaviour is attributed to the tunnelling of \( \text{NH}_4 \) ions.
Deuteron resonance in ARS was studied by El Saffar and Peterson\textsuperscript{353} (of both D\textsubscript{2}O molecules and ND\textsuperscript{4+} ions). The spectra of D\textsubscript{2}O molecules reveal that all the four chemically inequivalent D\textsubscript{2}O molecules are executing 180° flip motion with different rates. The central portion of the resonance line is due to the slightly distorted ND\textsuperscript{4+} ions undergoing rapid hindered reorientation and the distortion of the ND\textsuperscript{4+} ions persist throughout the temperature range (from room temperature to 77 K) studied. There is only one EFG tensor corresponding to the two chemically inequivalent ND\textsuperscript{4+} ions in ARS and the directions of the principal components of this tensor remain independent of temperature in the PE phase. A radical change in the magnitude and directions of principal components of the EFG tensor take place at T\textsubscript{c} (109 K) indicating the onset of a first order phase transition. A calculation of the dipole moment of the distorted ND\textsuperscript{4+} ions and their contribution to the polarization in the FE phase leads to the conclusion that about 52\% of the polarization is accounted for by the distorted ND\textsuperscript{4+} ions. The remaining contribution to \( P_s \) comes from the dipole moments associated with the water molecule and the hydroxyl groups. Takoshima and Tatsuzaki\textsuperscript{352} have carried out \( ^{23}\text{Na} \) satellite NMR spectrum near the transition temperature. They found that each line in the PE phase splits discontinuously into four lines at the transition temperature. The splitting of lines in the FE phase occurs due to the loss of two fold symmetry along the C-axis and the cell doubling along the a-axis. The temperature dependence study of resonance field for the lowest field satellite line showed a discontinuous jump of resonance field at T\textsubscript{c}, which is indicative of first order phase transition.

Deuteron relaxation studies have been carried out by El Saffar and Peterson\textsuperscript{353} in a single crystal of deuterated ARS in the temperature range 120 - 300 K. They found the magnetization recovery to be non-exponential from 300 to 170 K, with different relaxation times for deuterons of ND\textsuperscript{4+} ions and D\textsubscript{2}O molecules. However below 170 K, the magnetization recovery was exponential. The T\textsubscript{1} associated with the ND\textsuperscript{4+} ions exhibits a minimum and the activation energy is 5.3 \( \pm 0.4 \) kcal/mole, which is understandably higher than 4.5\( \pm 0.2 \) kcal/mole associated with the NH\textsuperscript{4+} ions. The calculated quadrupole coupling constant for \( n = 0 \) is 103 kHz which is rather low compared with the values of 180 kHz obtained for the rigid ND\textsuperscript{4+} ions in other compounds. This may be due to the cross relaxation between the ND\textsuperscript{4+} ions and the other deuterons in the system.

The T\textsubscript{1} behaviour for D\textsubscript{2}O molecules is also quite unusual. The activation energy associated with the 180° flip motion of D\textsubscript{2}O molecules could not be determined because of less accurate measurements in the region of 250 - 300 K. The E\textsubscript{s} below 250 K is 1.5 kcal/mole, which is unlikely to be associated with the 180° flip motion of the D\textsubscript{2}O molecules.
The rise in $T_1$ with the decrease in temperature below 250 K is due to the decrease in the amplitude of the thermal vibration in the lattice. $T_1$ reaches a peak value at about 140 K and then decreases, indicating the possibility of further loosening of the lattice allowing thermal vibrations with greater amplitudes just before the onset of the FE transition. However, $T_1$ could not be measured below $T_c$ because of weak and distorted signal.

**Lithium Ammonium Tartarate (LAT) LiNH$_4$C$_4$H$_4$O$_6$H$_2$O**

The room temperature crystal structure of this compound is $P_{2_1}2_12_1$, with $Z = 4$. It undergoes a ferroelectric phase transition below 98 K with spontaneous polarization along b-axis. The low temperature phase is expected to be monoclinic and the two-fold axis along a and c are no longer present below $T_c$.

$^7$Li, $^1$H and $^2$H resonance studies$^{354,355,356}$ in single crystals both above and below $T_c$ have been carried out. $^7$Li EFG tensor was almost independent of temperature and the changes were less significant at $T_c$ indicating that lithium sites are not much affected at the transition.$^1$H NMR spectra also did not show any change through $T_c$ indicating small significance of hydroxyl protons. $^2$H resonance studies show that the D$_2$O molecules are executing 180$^\circ$ flip motion at room temperature and did not show any appreciable change below $T_c$. However, the spectra due to the ND$_4^+$ ions showed drastic changes in EFG tensor at $T_c$, which is indicative of a first order phase transition. They found a dipole moment associated with the distortion of the ND$_4^+$ ion which simply rotates at $T_c$ with little change in magnitude. However, they did not observe two types of ND$_4^+$ ions as expected. The calculated $P_0$ assuming a rigid body like rotation of the distorted ND$_4^+$ tetrahedra could account for about 60% of the observed one and the remaining contribution coming from the hydroxyl groups of the tartarate ions.

$^1$H $T_1$ studies at 43 and 12 MHz and $T_1$ at rf fields $H_1 = 19.5$ G and 14 G over a range 45 to 385 K have been carried out by ElSaffar et al.$^{355,356}$ They observed $T_1$ minimum at 385 K and the $T_1$ minimum at 225 K were assigned to the motion of the hydroxyl protons and not to the 180$^\circ$ flip motion of the H$_2$O molecules. The $T_1$ data at 43 MHz exhibits 2 minima at 117 K and at 60 K. The first minimum at 117 K was ascribed to the ammonium ion reorientation about the three fold axis accompanied by a fast reorientation about its two fold axis. Considering the cross relaxation of protons not directly involved in relaxation process, the computed value of 52 msec. for the $T_1$ minimum at 117 K is in good agreement with the observed value. However, the other $T_1$ minimum of 50 msec at 60 K does not agree with the calculated ones based on a model of fast reorientation of NH$_4^+$ ion about its C$_3$ axis and a relatively slower one about its C$_3$ axis and this discrepancy is explained as due to the small difference in activation energy for two types of NH$_4^+$ ions. A discontinuity in slope occurs at $T_c$ for $T_c$ versus temperature plot.
The observed $T_1$ value reaches a minimum of 2 msec. near 75 K instead of 0.37 msec. at about 65 K, as expected theoretically and then gradually increases with increasing temperature. This indicates that the reorientation about the three-fold axis cannot be considered as random and that the effective correlation time does not increase with decreasing temperature, but rather levels off. This is also reflected in the $ND_4^+$ deuteron resonance which has a small line separation down to 34 K. However, a completely different resonance spectrum is expected as indicated by the correlation time data extrapolated to 34 K. They have also indicated the possibility of quantum mechanical tunnelling influencing the relaxation behaviour in LAT at low temperatures.

**Diammonium-d-Tartrate (NH$_4$)$_2$C$_4$H$_4$O$_6$**

$^1$H $T_1$ studies by Koksal$^{357}$ over a range of temperature revealed double minima of equal value (33 msec.) at 271 and 227 K, which were ascribed to the presence of two types of inequivalent ammonium ions in the unit cell. They found these minima values to be higher than the calculated ones (11.5 msec.) according to the BPP relation. Hence the observed data were interpreted in terms of two types of inequivalent NH$_4$ ions in the unit cell, along with the spin diffusion occurring among all the protons. Hence the calculated $T_1$ (11.5 msec) should be multiplied by a factor of (24/8), which is the ratio of the total number of protons to the number of magnetically equivalent ammonium protons in the molecule. However, at the $T_1$ minima one of the two types of ammonium ions is dominant in dissipating the spin energy to the lattice which means that the first type of NH$_4^+$ ions becomes dominant at the high temperature $T_1$ minimum and the second type of NH$_4^+$ ions at the low temperature $T_1$ minimum. Taking this multiplication factor of 3, we obtain $T_1\text{min} = 34.5$ msec. in agreement with the experimentally observed $T_1$. Pines et al.$^{358}$ has carried out $^{13}$C NMR Chemical Shielding tensor studies in single crystals of ammonium -d- tartrate using proton enhanced NMR and found that the unit cell contains two molecules and the eight lines of the spectrum correspond to eight magnetically inequivalent carbon nuclei and four correspond to carboxyl group and the other four to aliphatic groups. Gay$^{359}$ has extended the studies on $^{13}$C NMR using proton cross- polarization and magic-angle-spinning. The proton decoupling field was 40 kHz and spinning rate is 2.5 kHz. His results showed that the carboxyl resonance is split into a doublet, indicating that exact equality of the shielding components does not occur. Even though the crystal structure determination shows that both tartrate ions have identical bond length and angles with an experimental error, the NMR experimental results indicate that two carboxyl groups of each tartrate ion are chemically different. This inequivalence is brought about by differences in hydrogen bonding to NH$_4^+$ ions and CHOH groups. It is seen that the oxygens of one carboxyl are involved in four N-H-O hydrogen bond and two O-H-O bonds, while the other has four N-H-O bonds, but only a single O-H-O bond. It is
observed spectrum splitting. Proton $T_1$ studies by El Saffar\textsuperscript{362} revealed two minima of equal value (26 msec.) at 218 K and 270 K, which were attributed to two chemically inequivalent NH$_4^+$ ions NH$_4^+$ (I) and NH$_4^+$ (II). These are hydrogen bonded to carboxyl and hydroxyl oxygen atoms. The ions of the type NH$_4^+$ (I) were found to form a stronger H-bonds than NH$_4^+$ (II) and also they are reorienting at different frequencies and are coupled to each other through the protons of the tartarate group via dipole-dipole interaction.

**Ammonium Hydrogen Tartarate \text{NH}_4\text{HC}_4\text{H}_4\text{O}_6.**

Proton $T_1$, $T_1\rho$ measurements in this compound has been investigated by Morimoto\textsuperscript{254}. $T_1$ has a minimum of 11 msec. at about 54 K which is considered to be due to the motion of NH$_4^+$ ions. At 4.2 K, $T_1$ was longer than ten minutes and proton free decay showed line narrowing. The calculated $T_1$ minimum does not agree with the observed minimum. The first minimum of $T_1\rho$ appears at 45 K for $H_1$ 17 G and at 50 K for $H_1\approx 9$ G. It is difficult to attribute these $T_1$ minima to the motion of ammonium ions. They consider that these minima are due to the protons other than those in NH$_4$ groups. The second minima of $T_1$ appear at almost the same temperature (35 K and take almost same values for $H_1 = 17$ and $9$ G. $T_1\rho$ depends on $H_1$ with decreasing temperature below 35 K.
**NNH₃.C₂H₄.O₄.H₂O**

Ferroelectric < 109 K  
P₂₂₂  
Paraelectric  
P₂₁₁

**LiNH₄.C₂H₄.O₄.H₂O**

Paraelectric  
P₂₂₂  
Ferroelectric < 98 K  
Monoclinic

**NH₄₂.C₂H₄.O₄**

Orthorhombic  

**NH₄₃C₄.H₄.O₆**

Orthorhombic  

$^2$H T₁ & T₂ studies 77 - 300 K [153]

Eₐ(H₂) = 5.3 ± 0.4 kcal/mole

$^{23}$Na M₂ studies [352]

$^1$H T₁ studies 4.2 - 300 K [254, 349, 350, 351]

Eₐ(NH₄⁺) = 4.5 ± 0.2 kcal/mole

$^7$Li. e²Q/h studies [354]

$^7$Li. $^1$H & $^2$H studies 77 - 300 K [35, 356]

$^1$H T₁ results [357]

$^{13}$C nmr Chemical shielding [358]

$^1$H T₁ studies [362]

Eₐ(NH₄⁺) I = 6.9 kcal/mole

Eₐ(NH₄⁺) II = 6.0 kcal/mole

$^1$H T₁, T₂P studies [254]
II.11 Table of Miscellaneous compounds.

This section covers NMR study of the ammonium compounds (which do not fall into any group). Table II.11 gives the important features of the NMR data, along with the motional parameters.
\[ \text{CH}_3\text{COONH}_4 \quad \text{Monoclinic} \quad P_{2_1}/c \quad Z = 4 \]

\[ 1^H \text{N}_2 \text{ studies } 77 - 300 \text{ K} \quad [360] \]
\[ 1^H \text{ T}_1 \text{ studies } E_a = 8 \text{ kcal/mole} \quad [4] \]

\[ (\text{NH}_4)_2\text{CO}_3 \]

\[ 1^H \text{ T}_1 \text{ studies } E_a(\text{NH}_4^+) = 6.1 \text{ kcal/mole} \quad [4] \]

\[ (\text{NH}_4)_2\text{CO}_3\cdot\text{H}_2\text{O} \]

\[ 1^H \text{ T}_1, \text{T}_{2p} \text{ studies } E_a(\text{NH}_4^+) = 4 \text{ kcal/mole} \quad [357] \]

\[ (\text{NH}_4)_2\text{CrO}_4 \quad \text{Monoclinic} \quad C_{2/m} \quad Z = 4 \]

\[ 1^H \text{ N}_2 \text{ studies } 20 \text{ K} - 300 \text{ K} \quad [209] \]
\[ 1^H \text{ N}_2 \text{ studies } 77 - 300 \text{ K} \quad [284, 361] \]
\[ 1^H \text{ line shape studies at } 1.8 \text{ K tunnelling} \quad [388] \]
\[ 1^H \text{ T}_1 \text{ studies } 100 - 430 \text{ K} \quad [11, 12, 4] \]
\[ E_a(\text{NH}_4^+) = 3.7 \text{ kcal/mole} \]

\[ 11 \text{ Al}_2\beta\text{Si}_3 \text{ (NH}_4)_2\text{O} \quad \text{Hexagonal} \quad P_{6_3}/mmc \]

\[ 1^H \text{ N}_2 \text{ studies } 4.2 \text{ K, } 77 - 360 \text{ K} \quad [363] \]
\[ E_a(\text{NH}_4^+) = 0.5 \pm 0.01 \text{ ev} \]
\[ 1^H \text{ T}_1, \text{T}_{2p}, \text{T}_{1p} \text{ studies } 77 \text{ K} < T < 500 \text{ K} \quad [364] \]
\[ E_a(\text{NH}_4^+) = 4.8 \text{ kcal/mole} \]

\[ (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \]

\[ 1^H \text{ N}_2 \text{ studies } 20 \text{ K} - 300 \text{ K} \quad [209] \]
\[ 1^H \text{ N}_2 \& \text{T}_1 \text{ studies } 4.2 \text{ K} - 300 \text{ K} \quad [37] \]
\[ E_a(\text{NH}_4^+) \leq 0.2 \text{ kcal/mole} \]
\[ 1^H \text{ T}_1 \text{ studies} \quad [194, 237] \]
\( (\text{NH}_4)_3 \text{IO}_6 \)
Ferroelectric \( 254 \text{ K} \) \( \text{N}_3 \ Z = 1 \)

\( ^{1}H \text{ N}_2 \) studies \( [380] \)

\( ^{127}I \text{ EFG Tensor study} \) \( [381] \)

\( ^{1}H \text{ T}_1 \text{ T}_2 \) studies \( [382] \)

\( (\text{NH}_4)_2 \text{C}_{2} \text{O}_4 \cdot \text{H}_2 \text{O} \)
Orthorhombic
\( \text{P}_{2} \ 2 \ 2 \ 2 = 1 \)

\( ^{1}H \text{ N}_2 \) studies \( \text{H} - \text{bond} \) \( [383] \)

\( ^{2}H \text{ T}_1 \cdot \text{T}_{1c} \rho_{Q/h} \text{from} \text{N}_2 \) studies \( [384] \)

\( E (\text{NH}_4^+) = 7.27 \text{ kcal/mole} \)

\( ^{13}C \text{ Chemical shift tensor} \) \( [385] \)

\( \text{NH}_4 \text{TeWO}_6 \)
Fast ion Conductor

\( ^{1}H \text{ N}_2 \cdot \text{T}_1 \text{ & T}_{1c} \) measurements \( 77 - 300 \text{ K} \) \( [388] \)

\( \text{NaNH}_4 \text{CrO}_4 \cdot 2\text{H}_2 \text{O} \)
Orthorhombic
\( \text{P}_{2} \ 2 \ 2 \ 2 = 4 \)

\( ^{1}H \text{ N}_2 \) studies \( 77 - 300 \text{ K} \) \( [284] \)

\( (\text{NH}_4)_2 \text{TeO}_4 \)

\( ^{1}H \text{ M}_2 \) \& Line shape studies \( [209] \)

\( ^{1}H \text{ Line shape analysis} \) \( [379] \)

\( \text{NH}_4 \text{BiC}_6 \text{H}_5 \text{O}_7 \)

\( ^{1}HT_1 \) studies \( [357] \)

\( (\text{NH}_4)_2 \text{HC}_6 \text{H}_5 \text{O}_7 \)

\( ^{1}H \text{ T}_1 \) studies \( \rho_{a} (\text{NH}_4^+) = 20 \text{ KJ/mole} \) \( [357] \)

\( \text{NH}_4 \text{VO}_3 \)

\( ^{1}H \text{ N}_2 \) studies \( [209, 37, 379, 389] \)

\( ^{1}H \text{ N}_2 \) \& \( T_1 \) studies \( [391] \)

\( \text{NH}_4 \text{C}_2 \text{O}_4 \cdot 0.5\text{H}_2 \text{O} \)
Orthorhombic
\( \text{P}_{\text{nma}} \ 2 = 8 \)

\( ^{13}C \text{ Chemical shielding tensor} \) \( [385] \)

\( ^{14}N \text{ nmr studies} \) \( [386] \)

273
\((\text{NH}_3\text{OH})\text{Cl}\)  
\(\text{H}^1 \ T_1 \text{ studies} \ [357]\)

\((\text{NH}_3\text{OH})_2\text{SO}_4\)  
\(\text{H}^1 \ T_1 \text{ studies} 100 - 430 \ K \ [11]\)

\((\text{CH}_3\text{O})_3\text{W}_2\text{CO}_3\)  
\(\text{H}^1 \ \text{M}_2 \text{ studies} \ [243]\)

\((\text{NH}_4)_2\text{WO}_3\)  
\(\text{H}^1 \ \text{M}_2 \ & \ T_1 \text{ studies} \ [392, 393]\)

\((\text{CH}_3\text{O})_4\text{W}^\text{+} \text{H}_8\)  
\(11^\text{B} \text{ nmr} \ [395, 396]\)

\(\text{H}^1 \ 11^\text{B} \text{ M}_2 \ & \ T_1 \text{ studies} \ [397]\)

\(E_a(\text{CH}_3) = 2.3 \pm 0.2 \text{ kcal/mole}\)

\(E_a(\text{W}(\text{CH}_3)_4) = 3.3 \pm 0.3 \text{ kcal/mole}\)

\((\text{CH}_3\text{O})_4\text{W}^\text{+} \text{D}_{10}\)  
\(2^\text{H} \text{ M}_2 \text{ studies} \ [398]\)