Hindered Rotation of the Ammonium Ion in the Solid State

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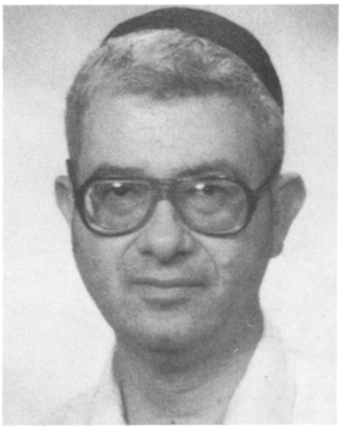
Contents

1. Introduction

Ammonium compounds have been extensively studied by a wide range of experimental techniques because of their unique properties. The tetrahedral ammonium ion is capable of forming four hydrogen bonds, which can point toward the corners of a surrounding tetrahedron. The most favorable hydrogen bonding can take place when the site symmetry of the ammonium ion is tetrahedral. However, there may be more than four hydrogen bond acceptors at nearly equal distances from the nitrogen atom of the ammonium ion. In this situation, it is possible for the ammonium ion to have a number of equivalent or nearly equivalent orientations in the solid. If the energies of the ammonium ions in two or more equivalent positions are the same, there is the possibility of a disordered structure. If the energies are only slightly different, the ammonium ion may undergo hindered rotation with a low barrier. Ammonium compounds with low barriers to rotation show anomalous properties in their heat capacities. The ground librational level of the ammonium ion is 16-fold degenerate (5A, 9T, and 2E states) when the site symmetry of the ammonium ion is tetrahedral or lower and nuclear spin degeneracies are considered. If nuclear spin degeneracies are not considered the degeneracy of the ground librational level is 12-fold degenerate. When the ammonium ion is in an octahedral crystalline field the ground-level degeneracy is 32-fold degenerate, if nuclear spin degeneracies are used. Tunneling splittings have been observed in the ground librational level of a number of ammonium solids at very low temperatures. For an ammonium ion in a tetrahedral crystalline field, the ground librational level splits into three states A ($I = 2$), T ($I = 1$), and E ($I = 0$) symmetry. The nuclear spin is represented by I. When the ammonium ion is in a crystalline field of lower symmetry, the triply



David Smith was born in Fall River, MA, in 1939. He received a B.S. degree in chemistry from Providence College in 1961 and a Ph.D. degree in physical chemistry from MIT in 1965. His doctoral dissertation was under the direction of Professor C. C. Stephenson. He joined the chemistry faculty of Brooklyn College in 1965. In 1968, he was appointed to the chemistry faculty at the Hazleton Campus of the Pennsylvania State University. His main research interest has been the study of the hindered rotation of the ammonium ion in the solid state. Other research interests include the analysis of the heat capacities of inorganic solids and the computation of the tunneling frequencies of small molecules, such as methane and ammonia, adsorbed on the surfaces of solids.

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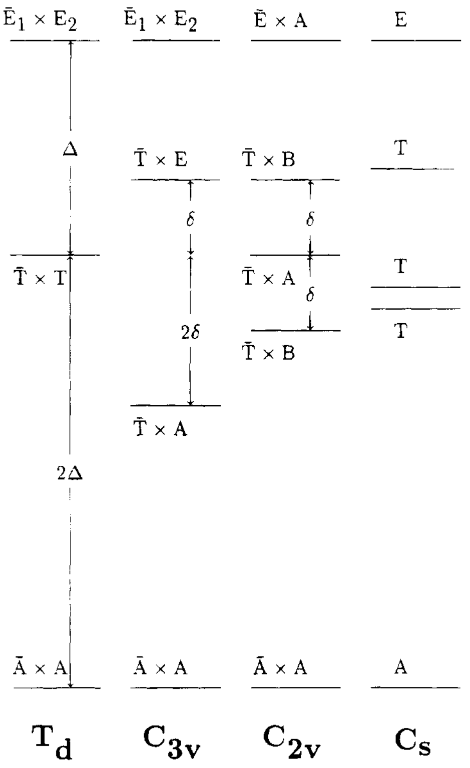

Figure 1. Tunneling states of the ammonium ion in crystalline fields of T_d, C_{3v}, C_{2v}, and C_1 symmetry. The energy levels are classified according to the irreducible representations $\bar{\Gamma} \times \Gamma$, where $\bar{\Gamma}$ is an irreducible representation of the group T and Γ is an irreducible representation of the group the represents the site symmetry of the body. See section 3.2.

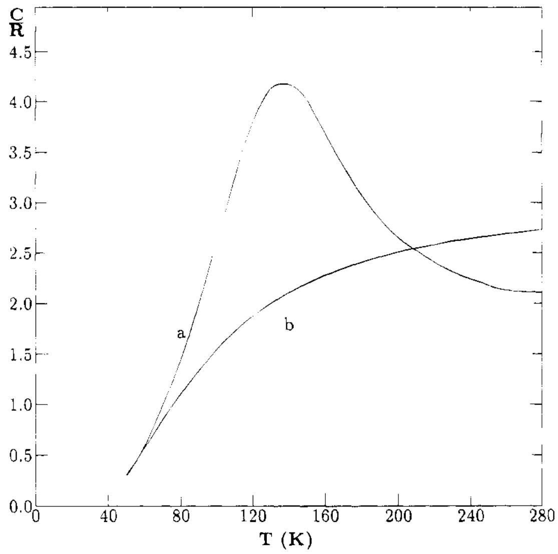

Figure 2. Curve a is the heat capacity due to the motion of the ammonium ion in NH_4BF_4. Curve b is the heat capacity of a three-dimensional harmonic oscillator with a librational frequency of 201 cm^{-1}.

degenerate T state splits into two or three states, as is illustrated in Figure 1.

For a three-dimensional harmonic oscillator, the energy levels are equally spaced. The librational frequency is the difference in the energies of the lowest two harmonic levels. The energy difference for the transition from the 0 → 2 states is exactly twice as large as that for the transition from the 0 → 1 states. If NH_4^+ were a harmonic oscillator, the isotope effect for the librational frequency, i.e. the ratio of the librational frequency of the NH_4^+ to that of ND_4^+, would be $\sqrt{2}$. For NH_4^+ in the solid state with a finite barrier to rotation, the energy difference for the transition from the 0 → 2 states is usually less than twice that for the transition from the from 0 → 1 states. Furthermore, the isotope effect for the librational frequencies is somewhat less than $\sqrt{2}$. For NH_4^+ in its compounds, the higher energy levels eventually change from anharmonic levels to rotational levels. The result of the crossover can be illustrated by considering the heat capacity due to the hindered rotation of NH_4^+. In Figure 2, the heat capacity of a three-dimensional harmonic oscillator with a librational frequency of 201 cm^{-1} is illustrated. At room temperature, C/R, where C is the heat capacity and R is the gas constant, approaches a value of 3. The heat capacity due to the motion of NH_4^+ derived from the observed heat capacity of NH_4BF_4[1] is also illustrated in Figure 2. At low temperatures, the heat capacity due to the motion of NH_4^+ is the same as that of a three-dimensional harmonic oscillator, since the lowest energy levels of NH_4^+ are harmonic oscillator energy levels. As the temperature is increased the population of the higher energy levels increases. There is a gradual transition from anharmonic to rotational energy levels, as higher energy levels are occupied. The effect of this is illustrated in Figure 2, where the heat capacity due to the motion of NH_4^+ in NH_4BF_4 approaches that of a free rotor at room temperature, i.e. C/R approaches $^3/_2$.

For the past 20 years, studies have been undertaken to compute the hindered rotational energy levels of the ammonium ion in many of its compounds in the solid state and to analyze the experimental data on the hindered rotation of the ammonium ion in terms of the computed energy levels. The procedure for computing the energy levels due to the hindered rotation of the ammonium ion was first outlined by King and Hornig for the ammonium ion in an octahedral crystalline field.[2] Since that time, the hindered rotational energy levels have been computed for the ammonium ion in crystalline environments of all possible symmetries.[3,4] The starting point of the computation is to assume single particle rotations, that is the environment of the ammonium ion can be represented by a rotational potential $V(\omega)$, where ω represents the Euler angles. The potential function and wave functions take into account both the tetrahedral symmetry of the ammonium ion and the site symmetry of the ammonium ion. The Hamiltonian matrix is considered a sum of the potential energy matrix and a diagonal kinetic energy matrix. The diagonalization of the Hamiltonian matrices permits the determination of the hindered rotational energy levels. These energy levels have been used to compute the heat capacity, thermal expansion, librational and tunneling frequencies, and activation energies of ammonium ions in the solid state.[5-10]

Two approaches have been used to compute the energy levels due to the hindered rotation of a tetrahedron. The wave functions may be either free rotational wave functions or harmonic oscillator wave functions. The pocket state formalism uses the harmonic oscillator wave functions. However, this method has only been used to computed the rotational energy levels in cubic crystalline fields, while for the procedure using free rotational wave functions the rotational energy levels of a tetrahedron has been computed in crystalline fields of various symmetries.[11] A review of these approaches has been published.[11]

Do any ammonium compounds have coupled ammonium ions? Coupled methyl groups have been studied in lithium acetate dihydrate, dimethyl ether, etc.[12] The number of tunneling states increases and extra terms must be added to the potential function to take into account the coupling of the methyl groups. No such coupling of ammonium ions has been observed.

The theoretical and experimental methods used for investigating the hindered rotation of ammonium compounds may also be used to study solid methane.[13,14] However, the computation of the hindered rotational energy levels in solid methane is far more complex, since the motion of one methane molecule will affect the other methane molecules in the solid.[13] Nevertheless, there are numerous similarities in the procedures that are used.[15] The hindered rotational energy levels have been computed for methane adsorbed on graphite and MgO.[16,17] A review of hindered rotation in matrix isolated materials has appeared.[18]

Tetrahedral ions, *e.g.* BH_4^-, AlH_4^-, and GaH_4^- have also been studied using the procedures that have been found successful for the investigation of ammonium solids.[19-21]

2. Experimental Techniques

2.1. Librational Frequencies

The librational frequency is usually measured for ammonium compounds by use of Raman spectroscopy or inelastic neutron scattering (INS). By taking the Raman spectra of both the NH_4^+ and ND_4^+ compounds, it is possible to pick out the librational frequencies, since the librational frequency of the NH_4^+ compound will be larger than that of the ND_4^+ compound by about a factor of $\sqrt{2}$.

Inelastic neutron scattering has been used successfully to determine the librational frequencies of NH_4^+ compounds, since it is a very sensitive probe of proton motions because of their large scattering cross section and small mass. The measurement of the librational frequencies of ND_4^+, however, are not as easily determined because the scattering cross section of deuterium is much less than hydrogen.

The librational frequencies of a number of ammonium compounds have been determined by observing in the infrared spectra the combination modes $\nu_4 + \nu_6$ and/or $\nu_2 + \nu_6$, where ν_2 and ν_4 are internal vibrations of the ammonium ion and ν_6 is the librational frequency of the ammonium ion. These combination modes give good results for the librational frequencies of the ammonium ion in the ammonium halides and in some other ammonium solids that have high barriers to rotation, but give poor results when the barriers to rotation are low.[22]

For the ammonium ion in a crystalline field of T_d symmetry, there is a single librational frequency that is 3-fold degenerate. In fields of lower symmetry, the librational frequency is split.

2.2. Tunneling Frequencies

High-resolution inelastic neutron scattering has been used to determine the tunneling frequencies of ammonium compounds with tunneling frequencies greater than about 0.5 μeV.[23] Transitions between the A and T states and the E and T states can be observed.[11] The relative intensities of the absorptions help identify which transition the band corresponds to. In a tetrahedral crystalline field the splitting between A and T states is twice as large as between T and E states.[11] Ozaki has derived the relative inelastic scattered intensities in CH_4(II).[24] This theory has been applied to methane embedded in the rare gas solids[25,26] and the ammonium ion in the alkali metal halides.[27]

Nuclear magnetic resonance has been used to determine tunneling frequencies as low as about 0.00002 μeV. Three methods have mainly been used to determine the tunneling frequencies of NH_4^+ solids:[28] NMR line shapes,[29] field cycling techniques,[30] and from the minimum in $T_{1\varrho}$.[31] The analysis of the NMR line shapes can be used to determine the tunneling frequencies of ammonium compounds when the tunneling frequency is about 0.00003 μeV. The tunneling frequencies derived from the minimum in $T_{1\varrho}$ are usually for temperatures between 40–70 K. Since the tunneling frequencies decrease with increasing temperature, the values determined at 4 K cannot be compared to those derived at much higher temperatures. The measurement of the spin–lattice relaxation time T_1 as a function of the proton resonance frequency ν_0, the field cycling technique, can be used to measure tunneling frequencies up to 0.4 μeV at any temperature.

The tunneling frequencies of ND_4^+ may be measured from values of about 0.002 to 0.04 μeV on the basis of calculating the spectra considering a theory which accounts for the quadrupole and dipolar interactions for the four deuterium atoms of ND_4^+.[28,32] Use of deuteron NMR has permitted the determination of the isotope effect in the tunneling frequencies for $(NH_4)SnCl_6$ and NH_4ClO_4.[32-34] The isotope effect in the tunneling frequencies has been computed to vary from 50 for low barriers to rotation to 5000 for high barriers to rotation.[6]

2.3. Low-Temperature Heat Capacity

The low-temperature heat capacity of ammonium compounds can be analyzed by subtracting the heat capacity due to the lattice from the observed heat capacity. The result, the heat capacity due to the motion of the ammonium ion, has been used to derive librational frequencies. For ammonium compounds with high barriers to rotation, the ammonium ion behaves as an harmonic oscillator at low temperatures. Therefore, its heat capacity can be represented by an Einstein function. The librational frequencies of a number of ammonium compounds, as well as compounds of AlH_4^-, BH_4^-, and GaH_4^-, have been

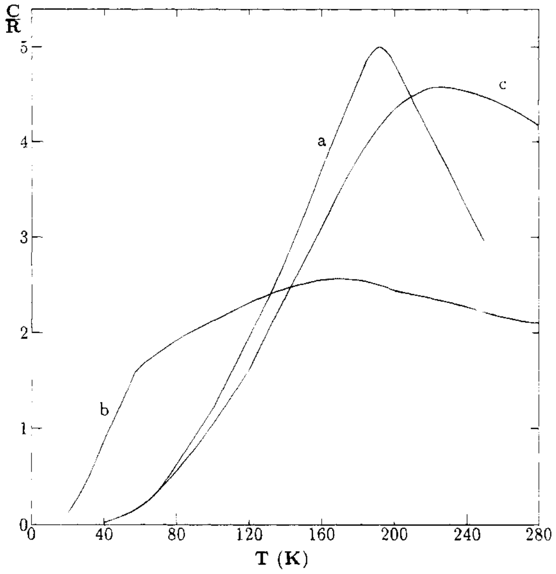

Figure 3. The rotational heat capacity of the ammonium ion in (a) NH_4ReO_4, (b) $(NH_4)_2SnCl_6$, and the borohydride ion in (c) $CsBH_4$.

derived from low-temperature heat capacities.[21] For compounds where the barrier to rotation for the ammonium ion is less than 4 kcal/mol, there is a maximum in the low-temperature heat capacity due to the motion of the ammonium ion. The temperature of the maximum in the rotational heat capacity of the ammonium ion depends both on the barrier to rotation and the environment the ammonium ion is in.[35] The heat capacity due to the motion of the ammonium ion is derived by subtracting the lattice heat capacity and $C_p - C_v$ from the observed heat capacity. Usually the $C_p - C_v$ term is estimated. For NH_4BF_4, NH_4ReO_4, and NH_4IO_4 this is difficult, because of an anomalous thermal expansion.[36] In Figure 3, there is illustrated the rotational heat capacities of $CsBH_4$ (c),[37] NH_4ReO_4 (a),[38] and $(NH_4)_2SnCl_6$ (b),[39] respectively. Since the $C_p - C_v$ term for the rotational heat capacities illustrated in Figure 3 are estimated, there is uncertainty in the values of the rotational heat capacities, particularly at higher temperatures. The rotational properties of the borohydride ion resemble those of the ammonium ion in its compounds. The heat capacities of both $CsBH_4$ and NH_4ReO_4 are about the same at low temperatures, because the librational frequency of the tetrahedral ions are both about 270 cm^{-1}.[19,40] At higher temperatures, they diverge, because of the different environments of the tetrahedral ions.

The librational frequencies of some ammonium compounds have been derived by subtracting the heat capacity of the NH_4^+ solid from the ND_4^+ solid.[35] This difference curve for NH_4BF_4 is illustrated in Figure 4.[1] The first maxima can be reproduced by subtracting from the heat capacity computed from an Einstein function with a frequency of 147 cm^{-1}, the heat capacity computed from an Einstein function with a frequency of 201 cm^{-1}. These frequencies are the librational frequencies of the ND_4^+ and NH_4^+ in ammonium tetrafluoroborate, respectively.[1]

In the difference curves of NH_4BF_4, NH_4ReO_4, and NH_4IO_4,[35,38-43] there are two maxima. The second maxima is due to the fact that these compounds have a high maxima in their rotational heat capacity, as is illustrated for NH_4BF_4 in Figure 2 and for NH_4ReO_4 in Figure 3.

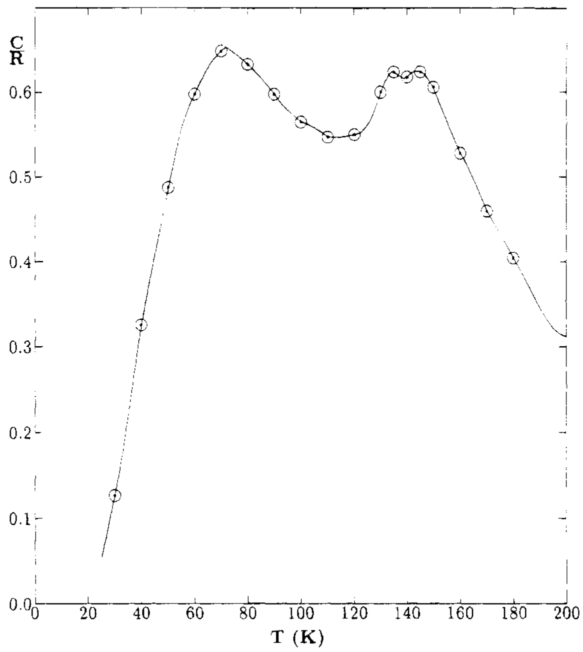

Figure 4. The difference in the heat capacities of ND_4BF_4 and NH_4BF_4 as a function of temperature. The circled points represent the difference in the observed heat capacities of ND_4BF_4 and NH_4BF_4.[1]

2.4. Thermal Expansion

The thermal expansion of ammonium compounds can be analyzed in a way similar to that of the heat capacity, *i.e.* the thermal expansion due to the lattice is subtracted from the observed thermal expansion.[9] Unfortunately, the thermal expansion of only a few ammonium compounds have been measured. Computations from the computed hindered rotational energy levels have predicted that the thermal expansion is negative, when the tunneling frequencies are large.[10] This has been observed for solid methane,[44,45] but has not been observed in ammonium compounds.

2.5. Activation Energies

The activation energy of rotation can be determined from measuring the temperature dependence of the spin–lattice relaxation time T_1. The activation energy corresponds to the energy difference between the ground librational level and the rotational levels above the barrier to rotation. How is the barrier to rotation related to the activation energy? The barrier to rotation is the energy difference between the lowest relative maximum (saddle point) and the minimum. Svare *et al.* suggested that the activation energy is the difference between the zero-point energies at the minimum and at the saddle point at the top of the barrier.[46] So

$$E_a = E_{000} - E^{s}_{00} \tag{1}$$

where E_{000} is the zero-point energy at the minimum in the potential function and E^{s}_{00} is the zero-point energy at the saddle point in the potential function. These terms are illustrated in a simplified diagram

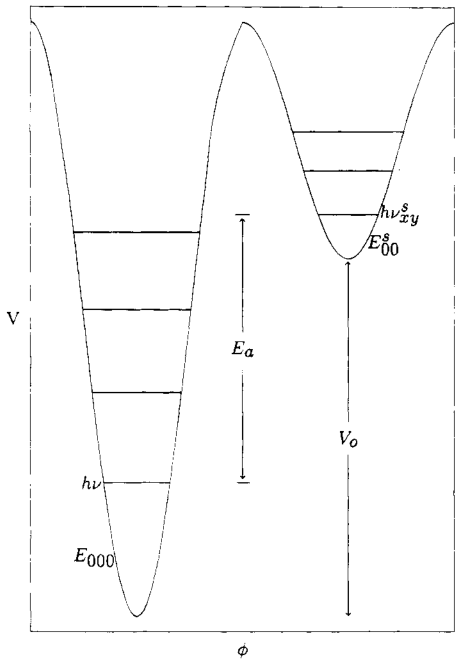

Figure 5. A simplified picture of the minimum and the saddle point of a potential function. See section 2.5.

in Figure 5. In the harmonic approximation, E_a is

$$E_a = V_0 - {}^3/_2 h\nu + h\nu^s_{xy}$$

where V_0 is the barrier to rotation, $h\nu$ is the librational frequency, and $h\nu^s_{xy}$ is the librational frequency at the saddle point. The computation of $h\nu^s_{xy}$ is difficult and has only been accomplished for a crystalline fields of T_d and C_{3v} symmetry.[4,8] For other symmetries, approximations are made. The value of $h\nu^s_{xy}$ may vary from 0 to $h\nu$. Therefore, the activation energy is

$$V_0 - {}^3/_2 h\nu < E_a < V_0 - {}^1/_2 h\nu$$

or

$$E_a = V_0 - h\nu\ (\pm{}^1/_2 h\nu) \qquad (2)$$

Quasielastic neutron scattering studies also permit the determination of the activation energy.[47] From an analysis of the results of these studies, the relative barriers to rotation around 3- and 4-fold axes may also be determined.[48,49]

The measurement of the activation energy is one method of elucidating the dynamics of the ammonium ion.[50] Another method has been to study the infrared spectra of the isotopic probe ion NH_3D^+ in ammonium compounds at low temperatures.[51-55]

3. Theory for a Tetrahedron

3.1. Hamiltonian

The Hamiltonian for a tetrahedral ion or molecule in a crystalline field of G symmetry is invariant under the direct product group $\bar{T}_d \times G$, where $\bar{T}_d$ represents the tetrahedral group of rotations about the body-fixed axes and G represents the group of rotations about the space-fixed axes.[2] The symmetry of the Hamiltonian and the symmetry of the free rotational wave functions take into account both the tetrahedral symmetry of the ion or molecule and the site symmetry of the tetrahedron. For the wave functions however, the point group of the body and the point group that represents the site symmetry must contain only proper rotations in order for the Pauli exclusion principle to be obeyed. So, if the symmetry of the potential function is $\bar{T} \times C_s$, the symmetry of the wave functions is $\bar{T} \times C_1$.

The Hamiltonian operator for a tetrahedron is

$$H = BP^2 + V(\omega) \qquad (3)$$

which satisfies the Schröedinger equation $H\Phi(\omega) = \lambda B\Phi(\omega)$, where P^2 is the total angular momentum operator, λ is the dimensionless energy, and B is the rotational constant.

Single-particle rotations describe the rotational motion of a single molecule or ion in its surroundings. Tunneling excitations are well described by single-particle states. However, librational excitations cannot always be described by single-particle states, because of strong ammonium–ammonium interactions. By observing the tunneling or librational frequencies of ammonium compounds, where some potassium or rubidium ions have been substituted for the ammonium ions, the strength of the ammonium–ammonium interactions can be estimated. The tunneling frequencies of $[K_x(NH_4)_{1-x}]_2SnCl_6$ and the librational frequencies of $K_x(NH_4)_{1-x}H_2PO_4$ have been measured and found that these frequencies do not change significantly as potassium ions are substituted for ammonium ions.[56,57] Therefore, the ammonium–ammonium interactions in these solids must be weak.

3.2. Wave Functions

The wave functions are given in terms of symmetry-adapted basis functions.[2] They take the form

$$\Phi = \sum_{K,M} C(\bar{\Gamma},J,\bar{n},K)C(\Gamma,J,n,M)\psi(J,K,M) \qquad (4)$$

where $\bar{\Gamma}$ represents an irreducible representation of the point group T, Γ represents an irreducible representation of the point group of the site symmetry of the tetrahedron, n is the number of symmetry-adapted basis functions for a given value of the free rotational quantum number J, and K and M run independently from $-J$ to $+J$. The variables with the bar above them refer to the tetrahedron, while those without a bar above them refer to the site symmetry of the tetrahedron. The C coefficients are chosen such that

$$C(\Gamma,J,n,M)Y_{JM}(\theta,\phi)$$

is a basis function for an irreducible representation of group T or G'. The spherical harmonics is represented by $Y_{JM}(\theta,\phi)$. The point group G' is a subgroup of G and includes only the proper rotations of G.

The energy levels for the hindered rotation of the spherical top NH_4^+ are classified according to the irreducible representations $\bar{\Gamma}_i \times \Gamma_j$, where $\bar{\Gamma}_i$ is one of the irreducible representations A, E_1, E_2, or T of the tetrahedral group T and Γ_j is one of the irreducible representations of the group G'. For NH_4^+ in a crystalline field of C_3 symmetry, the energy levels are classified as $\bar{A} \times A$, $\bar{A} \times E$, *etc.*, where the first letter is one of the irreducible representations of the tetrahedral point group (for body symmetry) and the second letter is one of the irreducible representations of the point group C_3 (for site symmetry).

3.3. Potential Functions

The potential function for a tetrahedron in the solid state is

$$V(\omega) = \beta B(8\pi^2)^{1/2}\sum_J \beta_J |J,\bar{A} \times A\rangle$$

$$V(\omega) = \beta B\sum_J \beta_J V_J(\omega) \tag{5}$$

where $\sum_J \beta_J^2 = 1$ and β is a dimensionless field strength parameter related to the barrier to rotation. The values of J in the summation in eq 5 depend on the tetrahedral symmetry of the body and the site symmetry. The values of J are usually set equal to 3, 4, 6, and 7. Higher values of J do not normally affect the energy levels. $V_J(\omega)$ may be written in terms of Wigner rotational functions $D^J_{KM}(\omega)$:

$$V_J(\omega) = \sum_{K,M} a_{JM} c_{JK} D^J_{KM} \tag{6}$$

The values of K and M that are permitted depend on the tetrahedral symmetry of the body and the site symmetry of the tetrahedron, respectively. The parameters a_{JM} and c_{JK} are normalized so

$$c_{J0}^{\ 2} + 2\sum_{K=1}^{J} (c_{JK})^2 = 1 \tag{7}$$

A similar equation can be written for a_{JM}. The values of c_{JK} are given by the cubic harmonics,[58] since the body is a tetrahedron. The values of a_{JM}, which reflect the site symmetry of the tetrahedron, and the value of β are considered parameters to be determined.

3.4. Hindered Rotational Energy Levels

The Hamiltonian matrix is expressed as a sum of a diagonal kinetic energy matrix plus a potential energy matrix, each multiplied by its appropriate $\beta B \beta_J$ coefficient. The diagonal kinetic energy matrix elements are $BJ(J + 1)$. The potential energy matrix elements depend on the site symmetry of the tetrahedron and have previously been given.[2-4] The sizes of the Hamiltonian matrices depend on what value of J the wave functions are expanded using eq 4. The higher the barrier to rotation, the larger the Hamiltonian matrix required for the accurate determination of the librational frequency. For a given value of J, the lower the site symmetry of the tetrahedron, the larger the Hamiltonian matrices. To compute the librational frequencies of NH_4Cl and NH_4Br the wave functions must include terms with $J \leq 20$. To compute the tunneling frequencies of these solids, terms with $J \leq 28$ must be used in the wave functions. Using these terms in the wave function permits the computation of tunneling frequencies as low as 10^{-5} μeV. The Hamiltonian matrices for a tetrahedron in crystalline fields of less than tetrahedral symmetry will be Hermitian. For tetrahedral and octahedral site symmetry, some of the matrices are real and symmetric.

For high barriers to rotation, expressions for the librational frequencies can sometimes be derived from the potential function.[4] The potential function is expressed in terms of trigonometric functions. By making the proper substitutions into the potential function, $V(\omega)$ may be expressed in terms of quadratic and quartic terms of x, y, and z.[59] The energy levels may be derived by using first-order perturbation theory. Expressions for the librational frequencies, barriers to rotation, and activation energies have been derived, when the site symmetry of the tetrahedron is T_d or C_{3v}.[4] These equations are particularly useful in computing the librational frequencies of ammonium compounds with high barriers to rotation, since the size of the Hamiltonian matrices that must be diagonalized in order to determine the librational frequencies are large.

How are the parameters in the rotational potential function to be determined? One method is to match observed librational and tunneling frequencies with values computed for certain values of the parameters. This has been accomplished with the ammonium halides and ammonium hexachlorides.[8,60-63] However, when the site symmetry of the ammonium ion is less than tetrahedral, there are too many parameters that must be determined. Another method is therefore required.

3.5. Derivation of Rotational Potential Function from Atom–Atom Potentials

As the site symmetry of the tetrahedron is lowered, the number of parameters in the rotational potential function increases. Therefore, the only way it is possible to compute the hindered rotational energy levels when the site symmetry of the ammonium ion is less than tetrahedral, is to determine them from atom–atom potentials. Yasuda derived the crystalline field potential for solid methane from atom–atom potentials of the Lennard-Jones type and of the Buckingham (exp-6) type.[64] The interaction between a hydrogen atom of an ammonium ion with any other atom X in the crystal is given by

$$\Phi(R_{ik}) = A_{HX} \exp(-\alpha_{HX} R_{ik}) - C_{HX}/R_{ik}^{\ 6} - D_{HX}/R_{ik}^{\ 8} - q_H q_X/R_{ik} \tag{8}$$

The effective charge on the hydrogen atom of the reference ammonium ion is represented by q_H and the effective charge on an atom X is q_X. The first term on the right-hand side of eq 8 is the repulsive term and the r^{-6} and r^{-8} terms are the leading terms in the van der Waals attraction. The last term on the right-hand side of eq 8 is the electrostatic term. The parameters in the rotational potential function are computed using the equations derived by Yasuda (eqs 9–11).[64]

$$B\beta_J a_{JM} c_{JK} = \sum_X A_{HX} Z_0(R,\alpha_{HX},J) \exp(-\alpha_{HX} R) - \frac{B_{HX} Z(R,6,J)}{4! R^6} - q_H q_X Z(R,1,J)/R \tag{9}$$

where

$$Z_0(R,\alpha_{HX},J) = \sum_p \frac{(\alpha_{HX} r)^p B(p - J,J;-\alpha_{HX}R)}{(p - J)!!(p + J + 1)!!} Y_{JM}(\theta,\phi)\sum_{k=1}^{4} Y_{JK}(\theta_k,\phi_k) \quad (10)$$

$$Z(R,n,J) = \sum_p \frac{(n + p - J - 3)!!(n + p + J - 2)!!}{(p - J)!!(p + J + 1)!!} Y_{JM}(\theta,\phi)(r/R)^p \sum_{k=1}^{4} Y_{JK}(\theta_k,\phi_k) \quad (11)$$

R is the distance between an atom X and the nitrogen atom of the reference ammonium ion, r represents the length of the N—H bond, and $p = J$, $J + 2$, $J + 4$, *etc*. The function $B(p - J,J;\alpha R)$ has previously been defined.[64] The spherical harmonics in eqs 10 and 11 are computed numerically. The angles θ and ϕ are the angles between any atom X and the nitrogen atom of the reference ammonium ion, while θ_k and ϕ_k are the angles made by the N—H bonds of the reference ammonium ion with the z and x axes. A standard orientation is chosen for the reference ammonium ion, so that the summation over "k" in eqs 10 and 11 may be carried out. The standard orientation is that the 2-fold axis of the ammonium ion lies on the z axis and one of the N—H bonds makes a 45° angle with the y axis.

$$\sum_{k=1}^{4} y_K^J(\theta_k,\phi_k) = c_{JK}(2J + 1)^{1/2}\gamma_J \quad (12)$$

The values of γ_J for a tetrahedron have been given by Yasuda.[64] The standard orientation for a tetrahedron in an hexagonal crystal is for one of the N—H bonds to lie on the 3-fold axis and one of the other N—H bonds to lie 60° off the a axis. By using the equations presented in this section, all the parameters in the rotational potential function have been determined for a number of ammonium and borohydride compounds.[21,65–67]

The contributions to the rotational potential function are computed by considering the interactions of all the atoms in the crystal within 7 Å of the reference ammonium ion for the repulsion and the r^{-6} interactions and for the electrostatic interactions all the atoms within 15 Å. There were no problems with convergence.

4. Analysis of the Properties of Ammonium Compounds

Ammonium compounds have been classified according to which atom is the nearest neighbors to the ammonium ion. The rotational potential functions have been derived from atom—atom potentials for solids, where the nearest neighbor to the ammonium ion is chlorine, fluorine, and oxygen.[21,65,66] For these studies the strongest interaction is between the ammonium ion and its nearest neighbors. For a compound NH_4MX_n, the partial charge on M and X must be set. For many compounds, these values have previously been derived. However, the partial charge on the atoms depends on the method used for deriving the charges. For example, the charge of the oxygen atom in NH_4ClO_4 has been assigned values from −0.21 to −0.78 electron units.[68] The charge on the hydrogen atoms of the ammonium ion have been set at 0.19 electron units for all the ammonium compounds studied.[21,65,66] The parameters in the atom—atom potential, eq 8, must be set, because these parameters have not been determined for the interaction of the hydrogen atom of an ammonium ion and an atom X. The parameters in the atom—atom potentials are set by matching the computed and observed librational and tunneling frequencies of a number of ammonium compounds that have the same nearest-neighbor atom. There are three parameters that must be determined for the interaction between the hydrogen atom of the ammonium ion and X (in the case of ammonium—chlorine compounds there are four parameters because of the r^{-8} term). Likewise, there are three parameters for the interaction of the reference ammonium ion with the other ammonium ions in the crystal. Finally, only one term, the r^{-6} term, is used to describe the interaction between the ammonium ion and M. Although there are a number of parameters in the atom—atom potentials that must be determined, a number of these parameters affect only the $J = 3$ term in the potential function, e.g. the charge on X, the parameter for the interaction between the ammonium ion and M, and the interactions between the reference ammonium ion and the other ammonium ions in the crystal.

The electrostatic interactions make an important contribution to the first term in the potential function, anywhere from 20% to 80% of the $J = 3$ term. However, for higher terms in the potential function, the electrostatic interaction plays a less important role. So, for the $J = 6$ term, the electrostatic interaction makes only a small contribution to the overall value of $\beta_6\beta$. The r^{-6} and the repulsive interactions make the major contributions to the $J = 6$ and $J = 7$ terms in the potential function.

The crystal structure of ammonium compounds to be studied must be known. The positions of the hydrogen atoms must have been determined. Furthermore, usually the librational and/or tunneling frequencies have also been observed. Solids with two or more inequivalent ammonium ions have not been analyzed. Although, it is possible to derive the rotational potential function of each of the inequivalent ammonium ions in such solids, the results have not been good. Solids, such as these, usually have a strong interaction between ammonium ions and this leads to poor results when the computed and observed properties are compared.

The ammonium—chlorine compounds studied were NH_4Cl and the ammonium hexachlorides.[65] Since the tunneling frequencies of the ammonium ion in the hexachlorides were observed at liquid helium temperatures, it was necessary to compute the hindered rotational energy levels at low temperatures. This presented a problem for a number of the hexachlorides, since there are no low-temperature crystal structure determinations. The position of chlorine atoms in the solid depends on a parameter

u that is close to $^1/_4$. Unfortunately, the $J = 3$ term in the potential function is a very sensitive function of this parameter. The parameter u for $(NH_4)_2SnCl_6$ has been measured at liquid He temperatures.[69] Therefore, for the other ammonium hexachlorides either the same temperature dependence of u was assumed or the value of the computed tunneling frequency was made to match the observed tunneling frequency.[65]

The rotational potential function of a number of ammonium–fluorine compounds have been studied: [21] the ammonium perovskites, cubic and hexagonal $(NH_4)_2MF_6$, NH_4F, NH_4HF_2, NH_4SnF_3, and NH_4AlF_4. The site symmetries for the ammonium ions vary from C_2 to O_h. A comparison of the results of the computations with the observed rotational properties yielded good results. The only compound studied where the observed and computed librational frequencies does not match is NH_4AlF_4. In the original paper, a comparison of the librational frequencies appears to be good,[21] but a recent inelastic neutron scattering study indicates that the librational frequencies are significantly higher than first thought.[70,71] Of the various ammonium compounds studied, the ammonium–fluorine compounds give the best results in light of the fact that the large number of solids that were studied had a range of crystal structures.

The study of ammonium–oxygen compounds was the least successful of the groups of ammonium solids studied.[66] The solids studied included NH_4ReO_4, NH_4IO_4, NH_4ClO_4, NH_4OOCCH_3, $(NH_4)_2H_3IO_6$, and $(NH_4)_2C_2O_4{\cdot}H_2O$. The site symmetry of these solids range from C_1 to C_3. The low site symmetry of the ammonium ion makes the analysis of these solids more difficult than the previous groups of ammonium compounds studied. A number of compounds gave poor results when the computed and observed librational frequencies were compared, e.g. $NH_4H_2PO_4$ and NH_4VO_3. Despite the difficulties in the analysis of these solids, a comparison of a number of the computed and observed rotational properties of NH_4ClO_4 gave good results. This solid will be discussed in the next section.

In the sections below, the rotational properties of families of ammonium compounds are discussed. When the ammonium ion can form strong hydrogen bonds in a crystal, the barrier will be high and each term, $\beta\beta_J$, in the potential function will be negative. When one or more of the terms in the rotational function are positive and reasonably large, the ammonium compound will have anomalous properties.

The derivation of the parameters in the rotational potential function depend on the N–H distance. From neutron diffraction studies, this distance is usually between 1.02 and 1.05 Å. Although, this is only a small range, this distance can have a significant effect on the computed librational and tunneling frequencies, if all the $\beta\beta_J$ values are negative. If one of the terms is positive and has a significant value, the dependence of the librational and tunneling frequencies on the N–H distance will be small, *e.g.* ammonium hexahalides.

4.1. Ammonium Halides

There is an order–disorder transition below room temperature in NH_4Cl, NH_4Br, and NH_4I. For NH_4Cl, the ordered low-temperature phase is body-centered cubic with the site symmetry of the ammonium ion being T_d. The disordered room temperature phase is also body-centered cubic, but the site symmetry of the ammonium ion is O_h. Both in the ordered and disordered phases, the ammonium ion has a high barrier to rotation. All the terms in the potential function are negative, as expected when four hydrogen bonds can be formed. There have been a number of analyses of the rotational properties of the ammonium halides in terms of the computed hindered rotational energy levels.[10,60,61,65,72]

The high-temperature phase of the ammonium halides is face-centered cubic. The ammonium ion cannot form four hydrogen bonds, but rather only one of the N–H bonds points toward a halide ion. For this structure, the $\beta\beta_4$ term in the potential function is positive, while the $\beta\beta_6$ term is negative. This phase has been studied at low temperatures by embedding less than a few percent of ammonium ions in alkali halides. This leads to large tunneling frequencies,[73,74] even though the librational frequencies are high.[75] Using atom–atom potentials derived for ammonium–chlorine compounds, the parameters in the rotational potential function are too small to reproduce the librational and tunneling frequencies.[76] The derived rotational potential is too weak. Even by setting values of β_4 and β_6, it has not been possible to adequately reproduce the tunneling and librational frequencies.

4.2. Ammonium Hexahalides

The ammonium hexachlorides have a cubic crystal structure at room temperature, with the site symmetry for the ammonium ion being T_d. At low temperatures, some of the hexachlorides have phase changes to other crystal structures. A number of the ammonium hexafluorides have a hexagonal crystal structure, with the site symmetry of the ammonium ion being C_{3v}. All of the ammonium hexahalides have a positive $\beta\beta_6$ term in the potential function, which is reasonably large. This leads to a boxlike potential. The two lowest librational frequencies of some of the hexachlorides have been measured.[77] The second librational frequency is more than twice as large as the first librational frequency. With the ammonium halides, the second librational frequency is less than twice as large as the first librational frequency.[78] The reason why the ammonium hexachlorides are different than the ammonium halides is because of the boxlike potential for these solids. There are other anomalous effects due to the positive value of $\beta\beta_6$,[21] *e.g.* anomalous isotope effects. Unfortunately, there are phase transitions in a number of the deuterioammonium hexachlorides that do not appear in the ammonium analogs, so it is not possible to compare the low-temperature properties of the ND_4^+ with NH_4^+, because of the different crystal structures at low temperatures.

The barrier to rotation for the ammonium ion in the ammonium hexachlorides increases with increasing size of the crystal lattice. Usually, if the size of the lattice increases, the barrier to rotation decreases, since the atoms are farther apart. However, in the ammonium hexachlorides, as the lattice decreases in size, each of the terms in the potential function (J = 3, 4, and 6) increase. The $J = 6$ term in the potential function changes by percentage more than the other two terms. Since $\beta_6\beta$ is positive, an increase in this term decreases the barrier to rotation and the librational frequency. Since $(NH_4)_2PtCl_6$ and $(NH_4)_2PdCl_6$ have the smallest lattice dimensions of the ammonium hexachlorides, they have the largest values of β_6. Therefore, they have the lowest librational frequencies and the second librational frequency is about 2.5 times as large as the first librational frequency, rather than twice as large.[77] Another reason the barrier to rotation increases with decreasing lattice parameter is because the parameter u, which sets the position of the chlorine atoms, increases with decreasing lattice size. The closer u is to 0.25, the smaller the value of β_3 in the potential function.

The parameters in the rotational potential function for $(NH_4)_2SnCl_6$, $(NH_4)PtCl_6$, and $(NH_4)TeCl_6$ have been determined from an analysis of the Bragg scattering from neutron diffraction.[69,79] The parameters determined in this way are in qualitative agreement with those determined from atom–atom potentials.

4.3. Ammonium Perovskites

The rotational motion of the ammonium ion in solids with the formula NH_4MF_3 have been studied by a number of experimental techniques. At room temperature these solids are cubic, with the site symmetry for the ammonium ion being O_h. All of these solids undergo phase changes to a low-temperature structure. The first derivation of the parameters in the rotational potential function was accomplished for NH_4ZnF_3 using only electrostatic interactions.[80] The parameters in the rotational potential function of the Zn, Mn, Co, and Mg perovskites have been determined using the interaction in eq 8.[21] Only the first two terms in the potential function must be considered. The value of the β_6 is larger than β_4 and $\beta\beta_6$ is positive. There is good agreement between the computed and observed rotational properties.[21]

The activation energy of NH_4CdF_3 has been measured and been found to be significantly larger than the other ammonium perovskites, despite the fact that the lattice parameter for the cubic phase of NH_4CdF_3 is larger than the other ammonium perovskites.[81] The phase transition to the cubic phase for NH_4CdF_3 is above room temperature, unlike the other perovskites. The activation energy was measured in the noncubic phase. However, the activation energies of NH_4ZnF_3 and NH_4MgF_3 above and below the phase transition are similar. Therefore, it had been concluded that deriving the parameters of the rotational potential function from atom–atom potentials is inappropriate.[81,82] However, recent X-ray powder diffraction studies of NH_4MnF_3 and NH_4CdF_3 indicate that it is possible to explain the large barrier to rotation in NH_4CdF_3.[83,84] In the low-temperature phase, the lattice parameters of NH_4CdF_3 are larger than NH_4MnF_3, yet the two shortest distances between the nitrogen atom and fluoride ions are 2.76 Å in NH_4CdF_3 and 2.82 Å in NH_4MnF_3. The 2.76 Å distance is even shorter than the 2.91 Å distance in NH_4ZnF_3 (cubic phase). There is yet another reason why NH_4CdF_3 has a larger barrier. The V_3 term (see eq 5) appears in the noncubic phase, but is missing when the site symmetry is O_h. In fact, for the low temperature phase of NH_4CdF_3, the largest term in the potential function is the $J = 3$ term. Since the inclusion of the V_3 term in the rotational potential function significantly increases the strength of the potential, this explains why even though NH_4CdF_3 has a larger lattice parameter than the other perovskites, it also has a larger activation energy.

4.4. Ammonium Scheelites

The ammonium scheelites, NH_4ReO_4 and NH_4IO_4, have a number of anomalous properties. The thermal expansion along the tetragonal a axis is negative over a wide temperature range.[36,85] The rotational heat capacity has hump that is much higher than found in other ammonium compounds. This anomaly in the heat capacity and thermal expansion has been explained in terms of a model of Ising pseudospins.[86] The anomaly in the heat capacity is believed to be due to the anomalous thermal expansion.[36] Unfortunately, the elastic constants of these ammonium solids have not been measured. These elastic constants are necessary to test the theory.

4.5. Ammonium Perchlorate

Ammonium perchlorate has been one of the more extensively studied ammonium solids, because its barrier to rotation is only about 0.5 kcal/mol. The site symmetry of the ammonium ion is C_s.[87] The tunneling frequencies of NH_4^+ and ND_4^+ in ammonium perchlorate have been measured.[34,88] They follow the scheme in Figure 1 for a tetrahedron in a field of C_s symmetry. The low site symmetry of the ammonium ion causes there to be three T tunneling states, with the lower two having similar energies. The librational frequencies, heat capacity, and activation energies have also been measured.[87,89-92] By using atom–atom potentials for ammonium–oxygen compounds,[66] the computed librational frequencies of both NH_4ClO_4 and ND_4ClO_4 agree with the observed values.[87,93] The overall tunneling splitting of the ammonium ion in NH_4ClO_4 is used to help determine the empirical parameters. The computed splitting of the T states does not match the observed splitting in ammonium perchlorate. The hindered rotational energy levels of ND_4^+ are computed by halving the value of the rotational constant and doubling the value of β in eq 5. There are no additional empirical parameters. The computed overall splitting of the tunneling states (A → E) for ND_4^+ in ammonium perchlorate matches the observed value.[34] The difference in the heat capacities of the ND_4^+ and the NH_4^+ compounds at low temperatures is also correctly reproduced.[90,92]

5. Other Tetrahedral Hindered Rotors

The methods used to compute the hindered rotational energy levels of the ammonium ion in its solids can also be used to compute the tunneling and librational frequencies of the methane molecule in solid methane and of the methane molecule adsorbed on solid surfaces. The hindered rotational energy levels of the borohydride ion in its compounds can also be computed by the methods employed for ammonium solids.

5.1. Alkali Metal Borohydrides

There is a lambda (λ) point transition in the observed heat capacities of the alkali metal borohydrides.[94-97] The entropy of transition is about R ln 2 in $NaBH_4$, but about half that value in the other alkali metal borohydrides.[98] The lower entropy of transition in the heavier alkali metal borohydrides is probably due to the partial disordering of the borohydride ion, while in $NaBH_4$ the borohydride ion is totally disordered above the transition temperature.[99] In the alkali metal borohydrides the important interaction is the repulsion between the borohydride ions and the alkali metal ions.[100] The parameters in the rotational potential function have been derived from atom–atom potentials.[67] The computed and observed librational frequencies of the borohydride ion in the alkali metal borohydrides and embedded in alkali metal halides are compared.[19,101,102] The results are good for the borohydride ion in the alkali metal halides, but the computed frequencies are higher than the observed values in the alkali metal borohydrides.[67]

5.2. Methane

Solid methane has two phases at atmospheric pressure; the high-temperature face-centered cubic (fcc) orientationally disordered phase (I) and a low-temperature fcc partially ordered phase (II). This latter phase consists of eight sublattices, two of which are orientationally disordered with O_h site symmetry and six sites are ordered with D_{2d} site symmetry.[13,103] In addition, solid CD_4 has a tetragonal orientationally ordered phase (III). The potential function for the methane molecules on the ordered sites of phase II has been presented by Yamamoto *et al.* in their classical paper on the theory of solid methane[13]

$$V(\omega) = V_c(\omega) + V_m(\omega) \tag{13}$$

where $V_m(\omega)$ is the potential function due to the molecular field and $V_c(\omega)$ is the potential function due to the crystalline field. In phase I and on the disordered sites of phase II, $V_m(\omega) = 0$. The crystalline field potential has been derived from atom–atom potentials. The derivation of the molecular field arising from the electrostatic octupole–octupole interactions between methane molecules is complex.[13] A simplified method has been used to compute the rotational properties of solid methane in phase II and for methane adsorbed on graphite and MgO.[15-17] The molecular field strength is taken as an empirical parameter. The crystalline potential function was derived using atom–atom potentials of Bartell and those of Williams.[104,105] With the use of only one empirical parameter, the librational and tunneling frequencies of methane in phase II have been computed and found to be in good agreement with the observed values.[15,106,107]

The tunneling frequencies of CH_4 adsorbed on graphite has been analyzed using set IV of the atom–atom potentials suggested by Williams.[108] The atom–atom potentials of Bartell and Williams gave potential function that were too strong.[104,105] If the atom–atom potentials[108] used in this problem were used for solid methane in phase II, results similar to using the potentials of Bartell and Williams are found. By using an Hamiltonian with $\tilde{T} \times C_3$ symmetry, the computed tunneling frequencies are found to agree with the observed frequencies.[17,109] Steele has reviewed the molecular interaction of molecular gases on surfaces.[110]

The tunneling frequencies of CH_4 adsorbed on the (100) surfaces of MgO have been analyzed using the atom–atom potential of Williams for the C–H interactions and those of Lakhlifi for the Mg–H and O–H interactions.[108,111] The potential function has $\tilde{T} \times C_{2v}$ symmetry. The computed tunneling frequencies reproduced the observed INS spectra.[16,17] The tunneling frequencies of CH_4 adsorbed on NaCl and LiF have been computed.[112] The strength of the crystalline potential is much stronger for CH_4 adsorbed on NaCl than for it adsorbed on MgO. The crystalline field potential is somewhat weaker for CH_4 adsorbed on LiF than for it adsorbed on MgO.

The tunneling frequencies of methane have been measured by high-resolution inelastic scattering in a number of different environments. Tunneling frequencies of CD_4(III) and CH_4(III) at high pressures have been observed.[113,114] The tunneling frequencies of solid solutions of CD_4 and CH_4 have been measured.[115] Tunneling frequencies of methane embedded in Ne,[116] Ar,[117] Kr,[118] Xe,[119] and Ar–N_2 mixtures[120] have been measured. Measurement of the tunneling frequencies of methane sorbed by second-stage graphite–cesium, $C_{28}Cs(CH_4)$ has also been accomplished.[121]

6. *Theory for Symmetric Tops*

The hindered rotational energy levels of NH_3D^+ and NHD_3^+ have been computed in crystalline environment of O_h, T_d, C_3, C_2, and C_1 symmetry.[17,122-124]

6.1. Hamiltonian

The Hamiltonian for a symmetric top is

$$H = \frac{p_x^2}{2I_x} + \frac{p_y^2}{2I_y} + \frac{p_z^2}{2I_z} + V(\omega) \tag{14}$$

where the moments in inertia $I_x = I_y \neq I_z$. The diagonal kinetic energy matrix elements are $BJ(J + 1) + (A - B)K^2$. The rotational constants for a symmetric top are A and B.

6.2. Potential Functions

The potential function of a symmetric top in a crystalline field is given by eqs 5 and 6. The values of J used in eq 5 can run from 1 to 7, if the site symmetry is less than tetrahedral. However, the values of c_{JK} are no longer the cubic harmonics, as they were for spherical tops. Therefore, the values of c_{JK} and a_{JM} both must be determined from atom–atom potentials.

6.3. Derivation of Rotational Potential from Atom–Atom Potentials

The parameters in the rotational potential function of a spherical top in a crystalline field are determined using eqs 9–11. For a symmetric top, such as NH_3D^+, eqs 10 and 11 must be changed, because the distance from the center of mass to the hydrogen atom is not the same as the distance from the center of mass to the deuterium atom. So, eq 10 becomes for a symmetric top

$$Z_0(R,\alpha_{HX},J) = \sum_p \frac{(\alpha_{HX})^p B(p - J,J;-\alpha_{HX}R)}{(p - J)!!(p + J + 1)!!} Y_{JM}(\theta,\phi)\sum_{k=1}^{4} r_k^p Y_{JK}(\theta_k,\phi_k) \quad (15)$$

$$Z(R,n,J) = \sum_p \frac{(n + p - J - 3)!!(n + p + J - 2)!!}{(p - J)!!(p + J + 1)!!} Y_{JM}(\theta,\phi)(1/R)^p \sum_{k=1}^{4} r_k^p Y_{JK}(\theta_k,\phi_k) \quad (16)$$

The procedure followed for determining the parameters in the rotational potential function is to first determine the values of a_{JM} for the NH_4^+ compound and assume that the values of a_{JM} are the same for the NH_3D^+ compound as the NH_4^+ compound. Then, by using eq 5, 6, and 9, the values of c_{JK} are determined for the NH_3D^+ compound. If only electrostatic terms are included in the eq 8, then

$$c_{JK} = \frac{X_{JK}}{(\sum_K X_{JK}^2)^{1/2}} \quad (17)$$

where

$$X_{JK} = \sum_{k=1}^{4} r_k^J Y_{JK}(\theta_k,\phi_k)$$

The values of c_{JK} computed using eq 17 are usually close to the values found when the values of c_{JK} are determined using eq 9.[17,123] For $J = 3$ or $J = 6$, the c_{JK} values are about the same for NH_4^+ and NH_3D^+, but when $J = 4$ there is a significant difference. For NH_4^+, $c_{40} = 0.509$ and $c_{43} = 0.609$, while for NH_3D^+ $c_{40} = 0.269$ and $c_{43} = 0.681$, if eq 17 is used.[123]

The computation of the parameters in the rotational potential function are computed as with a spherical top, except for the $J = 1$ term in the potential function. For a symmetric top in a crystalline field of symmetry less than T_d, there are additional terms in the potential function; the $J = 1$, 2, and 5 terms. The convergence of the $J = 1$ term, when electrostatic interactions are considered is very slow. The computation had to be carried out using the Evjen method,[125] i.e. by summing up a converging series of electrically neutral shells surrounding the reference symmetric top. In some cases, it was necessary to include all the atoms in 40 unit cells surrounding the unit cell containing the reference symmetric top.

A complication not present in the study of spherical tops is that the nitrogen atom of NH_3D^+ will also contribute to the rotational potential function. The contribution is only significant to the $J = 1$ and $J = 2$ terms in the potential function. It only contributes to the a_{JM} terms, where $M = 0$.

7. Librational and Tunneling Frequencies of Symmetric Tops

7.1. NH_3D^+ and CH_3D

There have only been a few experiments performed that have measured the librational and/or tunneling frequencies of the symmetric tops of the isotopic forms of NH_4^+ or CH_4. The tunneling frequencies of NH_3D^+ in solid KBr have been observed.[126] The tunneling frequencies of CH_3D have been observed when it is embedded in CH_4(II) and in solid argon and when it is adsorbed on graphite.[26,127,128] As mentioned earlier, the derivation of the parameters in the rotational potential function for NH_4^+ in the alkali metal halides do not lead to satisfactory results when the computed and observed tunneling and librational are compared. Therefore, there are no studies available for the comparison of computed and observed properties of NH_3D^+. Only the tunneling frequencies of CH_3D are available for comparison with computed results.

Two questions must be resolved before the parameters in the rotational potential function can be determined. For a symmetric top, such as NH_3D^+, is the nitrogen atom or the center of mass situated on the lattice site? Is the center of interaction the nitrogen atom or the center of mass? For the many molecules that have been studied, the assumption has been made that the center of interaction is situated on the lattice site.[17,122–124] The center of interaction is used in the definition of R in eq 9. For the spherical top NH_4^+, the center of interaction is the center of mass, which is located at the nitrogen atom. However, for a symmetric top, such as NH_3D^+, the center of mass is not at the nitrogen atom. For the isotopic forms of NH_4^+ and CH_4, the center of interaction is set at the nitrogen and carbon atoms, respectively. If this were not the case, the site symmetry of NH_3D^+ in a compound would be different than that of NH_4^+. For symmetric tops, such as CH_3F, the center of interaction is the center of mass.

The tunneling frequencies of CH_4 and CH_3D have been computed for these molecules in phase II of solid methane, when these molecules are embedded in the rare gas solids, and when they are adsorbed on graphite and MgO.[16,17,123,130] A similar computation has recently been done for CHD_3 and CD_4.[112] From a study of CH_3D embedded in solid argon, it is clear that the parameters c_{JK} take on the values of the cubic harmonics and not the expected values of a symmetric top. The computed tunneling frequencies of CH_3D in solid argon could only reproduce the observed tunneling frequencies,[26] if the fact that the center of mass of CH_3D is not at the carbon atom is disregarded when the potential function is derived. The tunneling frequencies of CH_3D in CH_4(II) have been computed for the molecules on the O_h and on the D_{2d} sites and compared to the observed results.[17,127] Only if the values of c_{JK} are taken to be the cubic harmonics will the computed tunneling frequencies on the O_h sites reproduce the observed values. The methane molecules with D_{2d} site symmetry have a crystalline field symmetry of O_h, so there are no extra terms in the potential function. For the molecules on the D_{2d} sites, it makes no difference which set of values are chosen for c_{JK}. However, if the crystal field symmetry of CH_3D is less than tetrahedral, the potential function must reflect the fact the center of mass is not at the carbon atom. This was determined from a comparison of the computed and observed tunneling frequencies of CH_3D adsorbed on graphite.[17,128] In addition to the J = 3, 4, 6, and 7 terms in the potential function, there are terms with J = 1, 2, and 5, if the site symmetry of the symmetric top is less than tetrahedral. These extra terms lead to two sets of tunneling levels separated by the energy Δ. This observed tunneling scheme could only be reproduced, if the center of mass of CH_3D is taken to along the C–D bond. The observed tunneling levels of CH_3D adsorbed on graphite are very interesting, because the separation between the lower five states and the upper two states is about $\Delta = 380$ μeV (see Figure 6a), while the overall splitting of the tunneling states of CH_4 adsorbed on graphite is only about 150 μeV. The tunneling frequencies of CH_3D should be less than CH_4, because of its smaller rotational constants. This unusual behavior has led to the computation of the tunneling frequencies of NH_3D^+ and NHD_3^+ in ammonium compounds to see if these solids also exhibit this anomaly.

The librational frequencies of NH_3D^+ in a number of ammonium compounds have been computed by both neglecting and considering the fact that the center of mass of NH_3D^+ is not at the nitrogen atom.[17,123] A single librational frequency for NH_4^+ in a crystalline field of T_d or O_h symmetry is split into two frequencies for NH_3D^+ and NHD_3^+, one with A symmetry another with E symmetry. This splitting is due both to the kinetic energy term and the potential energy term in the Hamiltonian. The splitting due to the potential energy term arises from the fact that the values of c_{JK} change when the center of mass is not at the nitrogen atom. So the largest splittings should be for ammonium compounds which have a large β_4 term in the potential function, since the values of c_{4K} are the most sensitive to where the center of mass is. Such a solid is NH_4Cl in its room temperature phase. If we take the center of mass not to be at the nitrogen atom, the librational frequencies are 305 (E) and 380 cm^{-1} (A). However, if we assume that for cubic crystalline fields we disregard the fact that the center of mass is not at the nitrogen atom, the librational frequencies are 313 (E) and 360 cm^{-1} (A).[17,123] Similar results are obtained for NHD_3^+ in NH_4Cl. Librational frequencies have also been computed for NH_3D^+ and NHD_3^+ in $(NH_4)_2SnCl_6$ and in cubic $(NH_4)_2SiF_6$.[17,123] Unfortunately, there are no experimental studies of the librational frequencies of NH_3D^+ and NHD_3^+ in their compounds.

The tunneling frequencies of NH_3D^+ and NHD_3^+ have been computed in a number of ammonium compounds, where the site symmetry of the ion is less than tetrahedral.[131] In these cases, large tunneling frequencies result, because of the addition of the J = 1, 2, and 5 terms to the potential function and due to the fact that neither c_{JK} nor a_{JM} take on values of the cubic harmonics. In Figure 6, the tunneling level schemes of these symmetric top ions are illustrated for crystalline fields of low symmetry. In Figure 6a, there are five lower levels and two upper levels. The five lower and two upper levels are not degenerate, but the splitting within the five lower levels is much less than the spitting between the upper and lower levels. This is true for all the diagrams in Figure 6. If nuclear spin degeneracies are not considered, the total degeneracy of each of the diagrams in Figure 6 is 12. In Figure 6a, the total degeneracy of the lower five states is 9 and the upper two states have a degeneracy of 3.

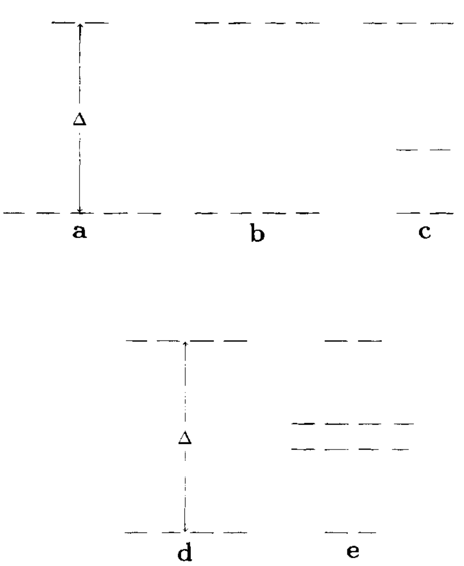

Figure 6. The tunneling states of NH_3D^+ in crystalline fields of (a) C_{3v}, (b) C_2, and (c) C_s symmetry and the tunneling states of $NH_2D_2^+$ in crystalline fields of (d) C_{3v}, and (e) S_4, C_2, and C_s symmetry. The energy states, within a group in these schemes that are shown to be degenerate, have in fact small energy differences. However, these energy differences are very small compared to the difference in energy between the groups of energy states.

The tunneling frequencies of NH_3D^+ and NHD_3^+ have been computed in NH_4F, NH_4HF_2, $(NH_4)_2SiF_6$, $(NH_4)_2GeF_6$, $(NH_4)_2TiF_6$, NH_4ReO_4, NH_4IO_4, and NH_4ClO_4.[131] For each of these solids, rather large values of Δ were computed. For NH_3D^+ in NH_4F, the computed value of Δ is 196 cm^{-1}. The tunneling frequency of the ammonium ion in NH_4F is probably less than 1×10^{-7} cm^{-1}. Unfortunately, it will be difficult to experimentally confirm this computation, since the spectroscopic absorptions are forbidden. The measurement of the low temperature heat capacity of NH_3DF would permit the derivation of the value of Δ. The computed values of Δ are very sensitive to the value of $\beta_1\beta$, so the computed values of Δ must be considered as quantitative guesses.

The computed tunneling states for NH_3D^+ and NHD_3^+ in the solids listed above follow the tunneling splittings illustrated in Figure 6, part a, b, or c.[131] The tunneling splittings followed the same scheme for NH_3D^+ and NHD_3^+, except for these ions in NH_4ClO_4. For this compound, NH_3D^+ followed the tunneling splitting scheme illustrated in Figure 6c, but for NHD_3^+ the scheme was inverted.[131] The analysis of the infrared spectrum in the N–D stretching region of NH_3D^+ and NHD_3^+ doped NH_4ClO_4 at low temperatures confirm that the tunneling states of NH_3D^+ follow the scheme illustrated in Figure 6c, while the tunneling states of NHD_3^+ in NH_4ClO_4 follow a scheme the requires the tunneling states in Figure 6c to be inverted.[54] The low-temperature infrared spectrum of NH_3D^+ in other ammonium solids have also been analyzed.[52-55]

7.2. Other Symmetric Top Molecules

The hindered rotation of ammonia molecules in solid ammonia has been studied.[129] Since the distance from the center of mass to the hydrogen atoms are all the same, eqs 10 and 11 can be used to compute the parameters in the rotational potential function. The values of c_{JK} are computed using eq 12. The computed and observed librational frequencies are in reasonable agreement.[129]

The hindered rotational energy levels of the methyl halides embedded in solid argon have been computed.[122] Energy levels computed for the hindered rotation of the methyl halide molecules do not resemble the hindered rotational energy levels of other molecules or ions studied. The librational frequency of CH_3I embedded in solid argon has been found to be 90 cm^{-1}.[132] The computed librational frequency is close the observed value.[122]

The tunneling frequencies of ammonia in $KC_{24}(NH_3)_{4.2}$[133] and in $CsC_{28}(NH_3)_x$[134] have been measured.

8. Theory for Asymmetric Tops

The hindered rotational energy levels of $NH_2D_2^+$ have been computed in a crystalline field of T_d symmetry.[123] Work has been completed on computing the rotational energy levels in crystalline fields of C_3, C_2, and C_1 symmetry.[135]

8.1. Hamiltonian

To compute the moments of inertia of $NH_2D_2^+$, the hydrogen atoms must be aligned along the x axis and the deuterium atoms along the y axis. The 2-fold axis of $NH_2D_2^+$ must lie on the x axis for the three different rotational constant $A > B > C$.[123] However, in the standard orientation of the ammonium ion, the 2-fold axis lies on the z axis and one of the hydrogen (or deuterium) atoms lies 45° off of the y axis. If the moments of inertia are computed for this standard orientation, there are off-diagonal elements. Since the Hamiltonian is somewhat complex, it will not be given here.[123]

8.2. Potential Function

The potential function for asymmetric tops, such as $NH_2D_2^+$ and CH_2D_2, is given by eqs 5 and 6. As with the symmetric tops, if the site symmetry is less than tetrahedral, the values of J kept in eq 5 run from 1 to 7. Due to the decrease on symmetry on going from NH_4^+ to $NH_2D_2^+$, there are extra c_{JK} terms, unlike the symmetric top case. The parameters c_{JK} may be derived from atom–atom potentials using the same equations as are used for symmetric tops, eqs 15 and 16.

8.3. Computation of Librational Frequencies

The only experimental studies on asymmetric tops of the type considered in this section is the unpublished study of the tunneling frequencies of CH_2D_2 embedded in solid argon[26] and the tunneling frequencies of solid CH_2D_2(III).[136] The structure of phase III is uncertain, so the computations on this phase is not possible. The computed tunneling frequencies of CH_2D_2 embedded in solid argon are able to reproduce the observed values, if the values of c_{JK} are the cubic harmonics.

The librational frequencies of $NH_2D_2^+$ in ammonium compounds have been computed.[17,123] For $NH_2D_2^+$ in solids, where the site symmetry of the ion is less than tetrahedral, the tunneling frequencies have been computed.[135] Large values of Δ have been found. In Figure 6, parts c and d, the tunneling level scheme for $NH_2D_2^+$ or CH_2D_2 in various crystalline symmetries are illustrated.

9. Future Studies

The ammonium scheelites have both an anomalous thermal expansion and low-temperature heat capacity. The measurement of the elastic constants below room temperature of either NH_4ReO_4 or NH_4IO_4 would help elucidate the dynamics of the ammonium ion in these solids. A study of the heat capacity and/or thermal expansion of the solid solutions of the potassium and ammonium solids would also shed light on this problem.

Neither the librational nor tunneling frequencies of hexagonal $(NH_4)_2SiF_6$, $(NH_4)_2GeF_6$, and $(NH_4)_2TiF_6$ have been measured. The measurement of the librational and tunneling frequencies of $(NH_4)_2SiF_6$ at low temperatures would permit a comparison of the computed and observed values. Of the three ammonium compounds listed above, hexagonal $(NH_4)_2SiF_6$ has the largest positive $\beta_6\beta$ term in the potential function and therefore is the most interesting of these three solids.

As mentioned earlier, the ammonium hexahalides have a significant positive $\beta_6\beta$ term in the potential. This leads to a number of anomalous effects.[21] For $(NH_4)_2PtCl_6$ and $(NH_4)PdCl_6$, the librational frequency might well increase as the temperature increases, even though usually the librational frequency of the ammonium ion will decrease as the temperature increases since the lattice volume increases. These two ammonium solids have the largest values of β_6 of the ammonium hexahalides.

There are few experimental studies of the librational and/or tunneling frequencies of NH_3D^+ and NHD_3^+ in ammonium compounds. The study of these symmetric top ions in ammonium compounds would help elucidate the assumptions that should be made in the theoretical approached to the problem. The study of these ions in crystalline fields of low symmetry would permit the determination of the energy-separating groups of tunneling states, Δ.

The computed rotational energy levels have not been able to predict both the librational and tunneling frequencies of the ammonium ion in the alkali metal halides. The measurement of the tunneling frequencies of ND_4^+ might help elucidate this problem.

The computation of the librational and tunneling frequencies of ammonium–chlorine compounds is made difficult by the lack of low-temperature diffraction studies of the ammonium hexachlorides. Crystal structure studies at liquid He temperatures of $(ND_4)_2SnCl_6$, $(NH_4)_2PtCl_6$, and $(NH_4)_2PdCl_6$ would help in the analysis of these solids. The crystal structure determination of other ammonium solids at low temperatures would be of great interest: NH_4BF_4, NH_4PF_6, NH_4CN, and $(NH_4)_3AlF_6$.

Solids that have tunneling frequencies of about 1 cm^{-1}, should have a negative thermal expansion at very low temperatures.[10] This has been observed in solid methane.[44,45] In a solid solution of ammonium and potassium halides, the thermal expansion should be negative at very low temperatures, due to the large tunneling frequencies, if about 50% ammonium ion is present in the solid solution.

In the low-temperature phase of the ammonium halides and in the partially ordered phase of the alkali metal borohydrides, the first term in the potential function, the $\beta_3 V_3$ term, is very small. If the $\beta_3 = 0$, the ground librational level is composed of five states with a total degeneracy of 32. However, when $\beta_3 \neq 0$, the ground librational level is composed of three states with a total degeneracy of 16. For a very small value of β_3, the five degenerate states will start to split.[67] This splitting has never been observed. It might be observed in solid solutions of ammonium chloride and potassium chloride, if the percentage of potassium ion is small.

Small molecules, such as CH_4 and NH_3, show interesting properties when adsorbed on surfaces.[16,109,128] The measurement of the tunneling and/or librational frequencies of CH_4 adsorbed on NaCl and LiF would compliment the studies of CH_4 on graphite and MgO. The observation of the tunneling frequencies of CH_3D on these surfaces would also be of interest. The adsorption of NH_3 on MgO, NaCl, or LiF would compliment the studies carried out on methane on these surfaces, since the electrostatic interactions will play an important role when NH_3 is adsorbed on these surfaces.[137] The electrostatic interactions are not particularly important for methane on these surfaces, because of the small charge on each hydrogen atom of the methane molecule.

10. Acknowledgments

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11. Appendix

A review of the experimental results on the hindered rotation of ammonium compounds is given in this section in Table 1. The values and references of the librational frequencies, tunneling frequencies, and activation energy are given. The references to the low-temperature heat capacity of the ammonium solids are also presented. For solids with a number of phases, only the data for the low-temperature (LT) phase and room-temperature (RT) phase is presented. The site symmetry of the ammonium ion in the solid is given from either X-ray or neutron diffraction studies. Only one reference is usually given for the librational frequencies. For solids that

Table 1. Properties of Ammonium Solids

	site symmetry	$h\nu$, cm^{-1}	E_a, kcal/mol	ω_t, μeV	C_p ref(s)
NH_4Cl (LT)	T_d	389[138,139]	4.7[140,141]	<0.00002[142]	143,144
NH_4Cl (RT)	O_h	355[145]	4.6[140,141]		
NH_4Br (LT)	D_{2d}	348[145,146]	4.0[141,147]	0.000037[29]	148,149
NH_4Br (RT)	O_h	320[145,150]	3.6[11,151]		
NH_4I (LT)	D_{2d}	294[150,152]	2.4[141,153]	0.00024[154]	144
NH_4I (RT)	O_h	277[150,155]			
$(NH_4)_{0.026}K_{0.974}Cl$	O_h	328[156]	0.15[157]		
$(NH_4)_{0.031}K_{0.969}Cl$	O_h			480[74]	
$(NH_4)_{0.021}K_{0.979}Br$	O_h	289[156]			
$(NH_4)_{0.033}K_{0.967}Br$	O_h			516[74]	
$(NH_4)_{0.02}K_{0.98}I$	O_h			600[158]	
$(NH_4)_{0.045}K_{0.955}I$	O_h	230[156]		599[74]	
$(NH_4)_{0.08}K_{0.92}I$	O_h	59,262[75†]			
$(NH_4)_{0.468}K_{0.534}I$	O_h	78,250[75]			144
$(NH_4)_{0.024}Rb_{0.976}Cl$	O_h	330[156]	0.15[157]		
$(NH_4)_{0.034}Rb_{0.966}Br$	O_h	292[156]			
$(NH_4)_{0.021}Rb_{0.979}I$	O_h	225[156]			
$(NH_4)_{0.024}Cs_{0.976}I$	O_h	373,356[156,159]			
$(NH_4)_{0.062}Cs_{0.938}I$	O_h	323,314[156,159]			
$(NH_4)_{0.039}Cs_{0.961}I$	O_h	289,268[156,159]			
$(NH_4)_2SnCl_6$	T_d	108[48]	1.2[31]	3.0[48]	39
$(ND_4)_2SnCl_6$ (LT)	T_d	83[160]	1.5[32]	0.03[32]	161
$[(NH_4)_{0.19}K_{0.81}]_2SnCl_6$	T_d			2.7[56†]	
$(NH34)_2PdCl_6$	T_d	49[162]	0.6[163]	56[162]	164,165
$(NH_4)_2PtCl_6$	T_d	65[77]	0.7[163]	29[166]	167,168
$(NH_4)_2SeCl_6$ (RT)	T_d				169
$(NH_4)_2TeCl_6$ (LT)	C_{3v}	145[77]	1.3[170]	0.099[166]	171,172
$(NH_4)_2TeCl_6$ (RT)	T_d				
$(ND_4)_2TeCl_6$ (LT)			1.6[170]	0.006[170]	173
$(NH_4)_2PbCl_6$	T_d	125[77]	1.4[163]	0.20[30]	
$(NH_4)_2RuCl_6$	T_d		1.9[163]	0.02[*163]	
$(NH_4)_2ReCl_6$	T_d			8.3[166]	
$(NH_4)_2IrCl_6$	T_d			20[166]	
$(NH_4)_2OsCl_6$	T_d			12[166]	

Table 1. (Continued)

	site symmetry	$h\nu$, cm^{-1}	E_a, kcal/mol	ω_t, μeV	C_p ref(s)
$(NH_4)_2SiF_6$	T_d	168[174]	2.2[175,176]	0.02[177]	178,179
$(NH_4)_2SiF_6$ (hex)	C_{3v}		1.1[180]	1.0[177]	178
$(NH_4)_2GeF_6$	C_{3v}		1.3[181]	0.07*[181]	182
$(NH_4)_2TiF_6$	C_{3v}		1.8[181]	0.02*[181]	
$(NH_4)_2PtBr_6$ (LT)			.41[183]	2.8,3.8[184]	
$(NH_4)_2SnBr_6$ (LT)			1.4[176]	0.13,.15[185]	39
NH_4PF_6 (LT)			.90[181]	3.6,4.2,4.8[186]	187,188
NH_4ZnF_3 (LT)		315[189]	1.6[190]	0.006*[81]	191
NH_4ZnF_3 (RT)	O_h	266[177]	1.3[190]		
NH_4MgF_3 (LT)			1.5[81]	0.007*[81]	192
NH_4MgF_3 (RT)	O_h		1.7[193]		
NH_4MnF_3 (LT)	C_s	342,354,384[83]			194
NH_4CoF_3 (RT)	O_h				194
NH_4CdF_3 (LT)	C_s		3.9[81]	0.00003*[81]	192
NH_4MnCl_3 (LT)	C_s		1.4[195]		196
$(NH_4)_2PdCl_4$ (LT)		298[197]	2.6[198]	0.083[197]	
$(NH_4)_2PdCl_4$ (RT)	D_{2h}	281[197]	2.3[198]		
$(NH_4)_2PtCl_4$ (LT)		290[197]		0.095[197]	
$(NH_4)_2ZnCl_4$ (LT)	C_1		2.2[199]	0.10,0.15[200]	
α-NH_4HgCl_3 (LT)	D_{4h}	281[201]			202
α-NH_4HgCl_3 (RT)	D_{4h}	280[203]	2.2[202]		
NH_4AlF_4 (LT)	S_4	382,460[70]	3.6[204]		205
NH34AlF_4 (RT)	D_{2d}	373,453[70]	4.3[204]		
NH_4SnF_3	C_3	375,455[206]	5.3[207]		
NH_4F	C_{3v}	555[208]	9.4[46]		209
NH_4HF_2	C_2		6.1[210]		211
NH_4BF_4	C_s		1.4[181]	0.08*[181]	212,213
$(NH_4)_2CuCl_4\cdot 2H_2O$ (LT)		302,346[214]			215
$(NH_4)_2CuCl_4\cdot 2H_2O$ (RT)	S_4				215
NH_4ClO_4	C_s	113,157[93]	0.7[91]	7.2,11.3[88]	90
ND_4ClO_4	C_s	85,131[93,87]	0.8[89]	0.048,0.050,0.078[34]	92
NH_4BrO_4	C_s				216
NH_4ReO_4	S_4	266,276[40]	2.2[217]	0.003*[218]	38,41
NH_4IO_4	S_4	241,259[219]	2.1[220]	0.006*[218]	42,43
NH_4VO_3	C_s	311,353[221]	3.8[222]		
NH_4NO_3 (LT)	C_1	336[78,152,223]	3.2[224]	0.00027[225]	226
$NH_4H_2PO_4$ (LT)	C_1	290[227]	4.2[228]		229
$NH_4H_2PO_4$ (RT)	S_4	310[227]	4.0[228]		
$(NH_4)_{0.5}K_{0.5}H_2PO_4$	S_4	294[230]			
$(NH_4)_{0.35}Rb_{0.65}H_2PO_4$	S_4	294,308[231]	3.2[232]		
$NH_4H_2AsO_4$ (LT)	C_1	420[227]	3.8[233]		234
$NH_4H_2AsO_4$ (RT)	S_4	440[227]	2.5[233]		
$(NH_4)_2H_3IO_6$ (LT)		360[227]			
$(NH_4)_2H_3IO_6$ (RT)	C_3	405[227]			
$(NH_4)_2Cr_2O_7$ (LT)	C_1	320[152]	1.8[235]	0.04*[31]	
$(NH_4)_2Cr_2O_7$ (RT)	C_1	320[152]	1.1[224]		
$(NH_4)_2CrO_4$	C_1	339[236]	3.0[222]	0.00006[142]	
$(NH_4)_2Ce(NO_3)_6$	C_1	250[46]	1.5[224]	0.1[177]	
NH_4OOCCH_3	C_1	490[237,238]	8.0[46]		
$NH_4H(CH_2ClCOO)_2$ (LT)	C_1	330[239]	4.6[240]	0.00006*[241]	242
$(NH_4)_2SO_4$ (LT)	C_1	350,390,430[243]	2.7,3.9[244]	0.0004[153]	245,246
$(NH_4)_2SO_4$ (RT)	C_s	350[243]	4.1[244]		
$[(NH_4)_{0.16}K_{0.84}]_2SO_4$	C_s	350[243]	1.3[247]		
$[(NH_4)_{0.97}K_{0.03}]_2SO_4$ (RT)	C_s	358,375[248†]			
$(NH_4)_2S_2O_8$	C_1	286[152]	1.8[224]	1.1[249]	
NH_4HSO_4 (LT)	C_1	290[250]	2.0[251]		
NH_4HSO_4 (RT)	C_1	260,290[252]	1.7[251]		
$(NH_4)_3H(SO_4)_2$ (LT)	C_2, C_1	330[253]	2.0[251]		254
$(NH_4)_2Cd_2(SO_4)_3$ (LT)		294,318,337[255]		0.026[256]	257,258
$NH_4NH_2SO_3$	C_1	174,198,228[259]	.99[260]		
$NH_4CF_3SO_3$	D_{2d}	290[261]			
NH_4LiSO_4 (LT)	C_1		2.3[253]	0.03*[262]	263
NH_4LiSO_4 (RT)	C_1	262,369[264]			
$NH_4NaSO_4\cdot 2H_2O$	C_1	255,310[264]	5.2[265]		
$(NH_4)_2Mg(SO_4)_2\cdot 6H_2O$	C_1	330,366[266]			
$(NH_4)_2Zn(SO_4)_2\cdot 6H_2O$	C_1	364[267]			
$(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$	C_1	364[267]			
$(NH_4)_2(COO)_2\cdot H_2O$	C_1	450[46]	6.8[46]		
$(NH_4HC_2O_4)_2\cdot H_2O$ (RT)	C_s				268
NH_4SCN	C_1	343[152]	4.0[224]	0.00007[225]	269
NH_4N_3	C_2	400[270]			
NH_4CN	D_{2d}	410[271]			
NH_4HS	D_{2d}	226[272]			
$NH_4B(C_6H_5)_4$	D_{2d}	35,61[273]		53[273]	274

have many studies, usually the reference to the most recent study is given. If more than one librational frequency is listed, it signifies that there is more than one librational frequency. When there is more than one study and the values of the librational frequencies are different, the results of only one of the studies is listed, although on occasion more than one reference is given. The same is true for activation energies and tunneling frequencies. Tunneling frequencies refer to the A → T transition. If the T states are split, more than one tunneling frequency may be given. Tunneling frequencies that are followed by an asterisk are measured at temperatures higher than 20 K by the method developed by Svare *et al.*[31] The reference to the heat capacity results is given only for the low-temperature phase, even though the studies cover the room temperature phase as well. If the heat capacity of the deuterium compound has also been measured, it is given under the NH_4^+ compound, if there is no entry for the ND_4^+ compound.

A dagger (†) following a number indicates that the reference contains information on other compositions of the solid solutions.

References

(1) Stephenson, C. C.; Orehotsky, R. S.; Smith, D. *Thermodynamic Symposium in Heidelberg/Deutschl*; Schafer, K., Ed.; AZ-Werbung-Weber Druck: Heidelberg, 1967.
(2) King, H. F.; Hornig, D. F. *J. Chem. Phys.* **1966**, *44*, 4520.
(3) Smith, D. *J. Chem. Phys.* **1983**, *79*, 2989; *J. Chem. Phys.* **1976**, *65*, 2568; *J. Chem. Phys.* **1979**, *71*, 2498; *J. Chem. Phys.* **1977**, *66*, 4587; *J. Chem. Phys.* **1973**, *58*, 3833.
(4) Smith, D. *J. Chem. Phys.* **1987**, *86*, 4046.
(5) Smith, D. *J. Chem. Phys.* **1975**, *62*, 4497.
(6) Smith, D. *J. Chem. Phys.* **1978**, *68*, 619; *J. Chem. Phys.* **1975**, *63*, 5003; *J. Chem. Phys.* **1976**, *65*, 1226.
(7) Smith, D. *Chem. Phys. Lett.* **1979**, *66*, 84.
(8) Smith, D. *J. Chem. Phys.* **1981**, *74*, 6480.
(9) Smith, D. *J. Chem. Phys.* **1983**, *78*, 6238.
(10) Smith, D. *J. Chem. Phys.* **1983**, *79*, 2995.
(11) Press, W. *Single-Particle Rotations in Molecular Crystals*; Springer-Verlag: Berlin, 1981.
(12) Aibout, A.; Carlile, C. J.; Horsewill, A. J. *J. Phys. C* **1992**, *4*, 8903. Heidemann, A. *Quantum Aspects of Molecular Motion in Solids*; Heidemann, A., Magerl, A., Prager, M.; Richter, D.; Springer, T., Eds.; Springer-Verlag: Heidelberg, 1986; p 44. Barker, G. J.; Clough, S.; Horsewill, A. J. *Quantum Aspects of Molecular Motion in Solids*; Heidemann, A., Magerl, A., Prager, M., Richter, D., Springer, T., Eds.; Springer-Verlag: Heidelburg, 1986; p 65. Smith, D. *Chem. Phys. Lett.* **1992**, *188*, 349.
(13) Yamamoto, T.; Katapka, Y.; Okada, K. *J. Chem. Phys.* **1977**, *66*, 2701.
(14) Morrison, J. A. *J. Chem. Thermodyn.* **1988**, *20*, 641.
(15) Smith, D. *J. Chem. Phys.* **1990**, *93*, 10.
(16) Larese, J. Z.; Hastings, J. M.; Passel, L.; Smith, D.; Richter, D. *J. Chem. Phys.* **1991**, *95*, 6997.
(17) Smith, D. *Chem. Phys.* **1992**, *164*, 407.
(18) Langel, W. *Spectrochim. Acta* **1992**, *48 A*, 405.
(19) Tomkinson, J.; Waddington, T. C. *J. Chem. Soc., Faraday Trans. 2* **1975**, *72*, 528.
(20) Temme, F. P.; Waddington, T. C. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 783.
(21) Smith, D. *J. Chem. Phys.* **1987**, *86*, 4055.
(22) Dunsmuir, J. T. R.; Lane, A. P. *Spectrochim. Acta* **1972**, *28A*, 45.
(23) Carlile, C. J.; Prager, M. *Int. J. Mod. Phys.* **1993**, *7B*, 3113.
(24) Ozaki, Y.; Katapka, Y.; Yamamoto, T. *J. Chem. Phys.* **1980**, *73*, 3442.
(25) Asmussen, B.; Prager, M.; Press, W.; Blank, H.; Carlile, C. J. *J. Chem. Phys.* **1992**, *97*, 1332.
(26) Asmussen, B. Ph.D. Thesis, Universität Kiel, 1991.
(27) Ozaki, Y. *J. Phys. Soc. Jpn.* **1987**, *56*, 4190; *J. Phys. Soc. Jpn.* **1987**, *56*, 1017.
(28) Ingman, L. P.; Koivula, E.; Lalowicz, Z. T.; Punkkinen, M.; Ylinen, E. E. *Z. Phys. B* **1987**, *66*, 363.
(29) Ikeda, R. I.; McDowell, C. A.; Nakamura, D. *J. Magn. Reson.* **1979**, *35*, 193.
(30) Punkkinen, M.; Tuohi, J. E.; Ylinen, E. E. *Chem. Phys. Lett.* **1975**, *36*, 393.
(31) Svare, I. *J. Phys. C* **1977**, *10*, 4137.
(32) Ingman, L. P.; Koivula, E.; Lalowicz, Z. T.; Punkkinen, M.; Ylinen, E. E. *Z. Phys. B* **1990**, *81*, 175.
(33) Ingman, L. P.; Koivula, E.; Lalowicz, Z. T.; Punkkinen, M.; Ylinen, E. E. *J. Chem. Phys.* **1988**, *88*, 58.
(34) Birczyński, A.; Lalowicz, Z. T.; Ingman, L. P.; Punkkinen, M.; Ylinen, E. E. *Solid State NMR* **1992**, *1*, 329.
(35) Smith, D. *J. Chem. Phys.* **1988**, *89*, 2324.
(36) Brown, R. J. C.; Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Phys.* **1986**, *85*, 5963; *J. Chem. Phys.* **1987**, *86*, 3759.
(37) Gorbunov, V. E.; Gavrichev, K. S.; Totrova, G. A.; Bakum, S. I. *Russ. J. Phys. Chem.* **1986**, *60*, 496.
(38) Weir, R. D.; Staveley, L. A. K. *J. Chem. Phys.* **1980**, *73*, 1386.
(39) Morphee, R. G.; Staveley, L. A. K.; Walters, S. T.; Wigley, D. L. *J. Phys. Chem. Solids* **1960**, *13*, 132.
(40) Park, Y. S.; Shurvell, H. F.; Brown, R. J. C. *J. Raman Spectrosc.* **1986**, *17*, 351.
(41) Brown, R. J. C.; Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1986**, *18*, 787.
(42) Brown, R. J. C.; Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1987**, *19*, 711.
(43) Brown, R. J. C.; Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1987**, *19*, 1111.
(44) Heberlein, D. C.; Adams, E. D. *J. Low Temp. Phys.* **1970**, *3*, 115.
(45) Aaleksandrovskii, A. N.; Kokshenev, V. B.; Manzhelli, V. G.; Tolkachev, A. M. *Sov. J. Low Temp. Phys.* **1978**, *4*, 435.
(46) Svare, I.; Thorkildsen, G.; Otnes, K. *J. Phys. C* **1979**, *12*, 2177.
(47) Bee, M. *Quasielastic Neutron Scattering*; Adam Hilger: Bristol, 1988.
(48) Prager, M.; Press, W.; Alefeld, B.; Hüller, A. *J. Chem. Phys.* **1977**, *67*, 5126.
(49) Mukhopadhyay, R.; Goyal, P. S.; Carlile, C. J. *Phys. Rev. B* **1993**, *48*, 2880. Töpler, J.; Richter, D. R.; Springer, T. *J. Chem. Phys.* **1978**, *69*, 3170. Goyal, P. S.; Dasannacharya, B. A. *J. Chem. Phys.* **1978**, *68*, 2430. Prask, H. J.; Trevino, S. F. *J. Chem. Phys.* **1975**, *62*, 4156. Livingston, R. C.; Rowe, J. M.; Rush, J. J. *J. Chem. Phys.* **1974**, *60*, 4541. Steenbergen, Chr.; de Graaf, L. A.; Bevaart, L.; Bartolomé, J.; de Jongh, L. J. *J. Chem. Phys.* **1979**, *70*, 1450.
(50) Parsonage, N. E.; Staveley, L. A. K. *Disorder in Crystals*; Clarendon: Oxford, 1978.
(51) Knop, O.; Oxton, I. A. *Can. J. Chem.* **1979**, *57*, 404. Kearley, G. J.; Oxton, I. A. *Adv. Infrared Raman Spectrosc.* **1983**, *10*, 111. Knop, O.; Westerhaus, W. J.; Falk, M.; Massa, W. *Can. J. Chem.* **1985**, *63*, 3328.
(52) Burrows, W.; Strauss, H. L. *J. Chem. Phys.* **1993**, *99*, 5668.
(53) Roberts, M. P.; Strauss, H. L. *J. Phys. Chem.* **1987**, *91*, 4241.
(54) Weier, J. E.; Strauss, H. L. *J. Chem. Phys.* **1993**, *98*, 4437.
(55) Weier, J. E.; Strauss, H. L. *J. Chem. Phys.* **1992**, *96*, 8799.
(56) Prager, M.; Press, W.; Roessler, K. *J. Mol. Struct.* **1980**, *60*, 173.
(57) Belushkin, A. V.; Tomkinson, J.; Shuvalov, L. A.; Fedosyuk, R. M. *Z. Phys. B* **1993**, *90*, 135. Kim, J.-J.; Shin, H.-K. *Ferroelectrics* **1992**, *135*, 319.
(58) Bradley, C. J.; Cracknell, A. P. *The Mathematical Theory of Symmetry in Solids*; Clarendon: Oxford, 1972.
(59) Gutowsky, H. S.; Pake, G. E.; Bersohn, R. *J. Chem. Phys.* **1954**, *22*, 643.
(60) Smith, D. *Chem. Phys. Lett.* **1988**, *145*, 372.
(61) Hüller, A.; Kane, J. W. *J. Chem. Phys.* **1974**, *61*, 3599.
(62) Hüller, A.; Raich, J. *J. Chem. Phys.* **1979**, *71*, 3851.
(63) Voll, G.; Hüller, A. *Can. J. Chem.* **1988**, *66*, 925.
(64) Yasuda, H. *Prog. Theor. Phys.* **1971**, *45*, 1361; *J. Chem. Phys.* **1980**, *73*, 3722; **1981**, *74*, 6531.
(65) Smith, D. *J. Chem. Phys.* **1985**, *82*, 5133.
(66) Smith, D. *Low Temp. Phys.* **1993**, *19*, 394.
(67) Smith, D. *Can. J. Chem.* **1988**, *66*, 791.
(68) Jenkins, H. D. B.; Pratt, K. F. *J. Phys. Chem.* **1978**, *74*, 968.
(69) Brückel, Th.; Prandl, W.; Vogt, K.; Zeyen, M. E. *J. Phys. C* **1984**, *17*, 4071.
(70) Rubín, J.; Palacios, E.; Bartolomé, J.; Tomkinson, J.; Fourquet, J. L. *Phys. B* **1992**, *180*, 723.
(71) Couzi, M.; Rocquet, P.; Fourquet, J. L. *J. Phys. (Paris)* **1985**, *46*, 435.
(72) Smith, D. *Chem. Phys. Lett.* **1974**, *25*, 268.
(73) Inaba, A.; Chihara, H.; Morrison, J. A.; Blank, H.; Heidemann, A.; Tomkinson, J. *J. Phys. Soc. Jpn.* **1990**, *59*, 522.
(74) Mukhopadhyay, R.; Tomkinson, J.; Carlile, C. J. *Europhys. Lett.* **1992**, *17*, 201.
(75) Tomkinson, J.; Dasannacharya, B. A.; Goyal, P. S.; Chakravarthy, R. *J. Chem. Soc. Faraday Trans. 2* **1991**, *87*, 3431.
(76) Ozaki, Y.; Maki, K.; Okada, K.; Morrison, J. A. *J. Phys. Soc. Jpn.* **1985**, *54*, 2595.
(77) Otnes, K.; Svare, I. *J. Phys. C* **1979**, *12*, 3899.
(78) Tomkinson, J.; Kearley, G. J. *J. Chem. Phys.* **1989**, *91*, 5164.
(79) Vogt, K.; Prandl, W. *J. Phys. C* **1983**, *16*, 4753. Hoser, A.; Prandl, W.; Heger, G. *Quantum Aspects of Molecular Motion in Solids*; Heidemann, A., Magerl, A., Prager, M., Richter, D.,

Springer, T., Eds.; Springer-Verlag: Heidelburg, 1986; p 19. Prandl, W.; Hoser, A.; Brückel, T. *Mater. Res. Forum* **1988**, *27/28*, 35.

(80) Bartolomé, J.; Navarro, R.; González, D.; de Jongh, L. J. *Physica B* **1977**, *92*, 23.

(81) Palacios, E.; Bartolomé, J.; Burriel, R.; Brom, H. B. *J. Phys. C* **1989**, *1*, 1119.

(82) Navarro, R.; Palacious, E.; Bartolomé, J.; Burriel, R.; González, D. *Quantum Aspects of Molecular Motion in Solids*; Heidemann, A., Magerl, A., Prager, M., Richter, D., Springer, T., Eds.; Springer-Verlag: Heidelburg, 1986; p 33.

(83) Laguna, M. A.; Sanjúan, M. L.; Orera, V. M.; Rubín, J.; Palacious, E.; Piqué, M. C.; Bartolomé, J.; Berar, J. F. *J. Phys. C* **1993**, *5*, 283.

(84) Le Bail, A.; Fourquet, J. L.; Rubín, J.; Palacious, E.; Bartolomé, J. *Physica B* **1990**, *162*, 231.

(85) Powell, B. M.; Brown, R. J. C.; Harnden, A. M. C.; Reid, J. K. *Acta Crystallogr.* **1993**, *B49*, 463.

(86) Taylor, D. R. *Phys. Rev. B* **1989**, *40*, 493.

(87) Prask, H. J.; Choi, C. S.; Chesser, N. J. *J. Chem. Phys.* **1988**, *88*, 5106.

(88) Prager, M.; Alefeld, B.; Heidemann, A. In *Proc. of XIX-th Congress Ampere*, Brunner, H., Hausser, K. H., Schweitzer, D., Eds.; Heidelberg: 1976; p 389. Dorn, B. *J. Glaciol.* **1978**, *21*, 231. Prager, M.; Alefeld, B. *J. Chem. Phys.* **1976**, *65*, 4927.

(89) Lalowicz, Z. T.; Punkkinen, M.; Ylinen, E. E. *J. Phys. C* **1979**, *12*, 4051.

(90) Westrum, E. F.; Justice, B. H. *J. Chem. Phys.* **1969**, *50*, 5083.

(91) Guttler, W.; von Schutz, J. U. *Chem. Phys. Lett.* **1973**, *20*, 133.

(92) Brown, R. J. C.; Weir, R. D.; Westrum, E. F. *J. Chem. Phys.* **1989**, *91*, 399.

(93) Chakraborty, T.; Verma, A. L. *Phys. Rev. B* **1989**, *39*, 3835.

(94) Johnston, H. L.; Hallet, N. C. *J. Am. Chem. Soc.* **1953**, *75*, 1467.

(95) Furukawa, G. T.; Reilly, M. L.; Piccirelly, J. M. *J. Res. Natl. Bur. Stand. Sect. A* **1964**, *68*, 651.

(96) Gorbunov, V. E.; Gavrichev, K. S.; Bakum, S. I. *Russ. J. Phys. Chem.* **1986**, *60*, 296.

(97) Gorbunov, V. E.; Gavrichev, K. S.; Totrova, G. A.; Bakum, S. I. *Russ. J. Phys. Chem.* **1985**, *59*, 1754.

(98) Gorbunov, V. E.; Gavrichev, K. S.; Lazarev, V. B. *Russ. J. Phys. Chem.* **1986**, *60*, 1240.

(99) Smith, D. *J. Chem. Phys.* **1974**, *60*, 958.

(100) Stockmayer, W. H.; Stephenson, C. C. *J. Chem. Phys.* **1953**, *21*, 1311.

(101) Memon, M. I.; Sherman, W. F.; Wilkinson, G. R. *Spectrochim. Acta* **1981**, *37A*, 461.

(102) Brierley, K. P.; Howard, J.; Waddington, T. C. *J. Chem.* Soc., *Faraday Trans. 2* **1981**, *77*, 1075.

(103) Press, W. *J. Chem. Phys.* **1972**, *56*, 2597.

(104) Bartell, L. S. *J. Chem. Phys.* **1960**, *32*, 827.

(105) Williams, D. E.; Cox, S. R. *Acta Crystallog.* **1984**, *B40*, 404.

(106) Heidemann, A.; Lushington, K. J.; Morrison, J. A.; Neumaier, K.; Press, W. *J. Chem. Phys.* **1984**, *81*, 5799.

(107) Heidemann, A.; Press, W.; Lushington, K. J.; Morrison, J. A. *J. Chem. Phys.* **1981**, *75*, 4003.

(108) Williams, D. E. *J. Chem. Phys.* **1967**, *47*, 4680.

(109) Smalley, M. V.; Hüller, A. *Mol. Phys.* **1981**, *44*, 533.

(110) Steele, W. *Chem. Rev.* **1993**, *93*, 2355.

(111) Lakhifi, A.; Girardet, C. *Surf. Sci.* **1991**, *241*, 400.

(112) Smith, D. Manuscript in preparation.

(113) Prager, M.; Press, W.; Heidemann, A. *J. Chem. Phys.* **1981**, *75*, 1442.

(114) Prager, M.; Press, W.; Heidemann, A.; Vettier, C. *J. Chem. Phys.* **1982**, *77*, 2577.

(115) Prager, M.; Press, W. *J. Chem. Phys.* **1990**, *92*, 5517.

(116) Prager, M.; Asmussen, B.; Carlile, C. J. *J. Chem. Phys.* **1994**, *100*, 247.

(117) Prager, M.; Asmussen, B.; Press, W.; Blank, H.; Carlile, C. J. *J. Chem. Phys.* **1991**, *95*, 569.

(118) Asmussen, B.; Press, W. *J. Chem. Phys.* **1993**, *98*, 158.

(119) Prager, M.; Asmussen, B.; Langel, W.; Carlile, C. J.; Blank, H. *J. Chem. Phys.* **1993**, *99*, 2052.

(120) Langel, W.; Prager, M.; Lauter, H.-J.; Blank, H.; Carlile, C. J. *J. Chem. Phys.* **1993**, *98*, 4838.

(121) Trouw, F. R.; White, J. W. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 861.

(122) Smith, D. *Low Temp. Phys.* **1993**, *19*, 390.

(123) Smith, D. *J. Chem. Phys.* **1990**, *92*, 4660.

(124) Smith, D. *J. Chem. Phys.* **1990**, *92*, 4669.

(125) Tosi, M. P. *Solid State Phys.* **1964**, *16*, 23.

(126) Ozaki, Y. *J. Phys. Soc. Jpn.* **1987**, *56*, 825.

(127) Lushington, K. J.; Morrison, J. A.; Make, K.; Heidemann, A.; Press, W. *J. Chem. Phys.* **1983**, *78*, 383.

(128) Ball, P. C.; Inaba, A.; Morrison, J. A.; Smalley, M. V.; Thomas, R. K. *J. Chem. Phys.* **1990**, *92*, 1372.

(129) Smith, D. *J. Chem. Phys.* **1990**, *92*, 4674.

(130) Smalley, M. V.; Ball, P. C. *Mol. Phys.* **1990**, *71*, 1233.

(131) Smith, D. *J. Chem. Phys.* **1994**, *100*, 301.

(132) Langel, W.; Kollhoff, H.; Knözinger, E.; Prager, M. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 1257.

(133) Newmann, D. A.; Zabel, H.; Magerl, A.; Fan, Y. B.; Solin, S. A. *Graphite Intercalation Compounds: Science Applications*; Endo, M.; Dresselhaus, M. S.; Dresselhaus, G., Eds.; Materials Research Society: 1988; p 9.

(134) Carlile, C. J.; McL. Jamie, I.; Lockhart, G.; White, J. W. *Mol. Phys.* **1992**, *76*, 173.

(135) Smith, D. *J. Chem. Phys.*, in press.

(136) Lushington, K. J.; Maki, K.; Morrison, J. A.; Heidemann, A.; Press, W. *J. Chem. Phys.* **1981**, *75*, 4010.

(137) Picaud, S.; Lakhlifi, A.; Girardet, C. *J. Chem. Phys.* **1993**, *98*, 3488.

(138) Fritz, I. J. *Sol. State Comm.* **1973**, *12*, 271.

(139) Goyal, P. S.; Boland, B. C.; Penfold, J.; Taylor, A. D.; Tomkinson, J. *Dynamics of molecular crystals*; Lascombe, Elservier: Amsterdam: 1987; p 429.

(140) Woessner, D. E.; Snowden, B. S. *J. Chem. Phys.* **1967**, *71*, 952.

(141) Sharp, A. R.; Pintar, M. M. *Chem. Phys.* **1976**, *15*, 431.

(142) Lalowicz, Z. T. *Acta Phys. Pol.* **1979**, *a56*, 243.

(143) Chihara, H.; Nakumura, N. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 133.

(144) Stephenson, C. C. Unpublished results.

(145) Schumaker, N. E.; Garl, C. W. *J. Chem. Phys.* **1970**, *53*, 392. Ebisuzaki, Y. *J. Chem. Phys.* **1974**, *61*, 3170.

(146) Goyal, P. S.; Penfold, J.; Tomkinson, J. *Chem. Phys. Lett.* **1986**, *127*, 483. Adams, M. A.; Tomkinson, J. *Physica B* **1992**, *180/181*, 694.

(147) Mema, W.; Trappeniers, N. J. *Physica B* **1976**, *81*, 285.

(148) Sorai, M.; Suga, H.; Seki, S. *Bull. Chem. Soc. Jpn.* **1968**, *38*, 1125.

(149) Stephenson, C. C.; Karo, A. M. *J. Chem. Phys.* **1969**, *48*, 104.

(150) Hochheimer, H. D.; Shand, M. L.; Walker, C. T.; Hüller, A. *J. Chem. Phys.* **1979**, *71*, 5008.

(151) Woessner, D. E.; Snowden, B. S. *J. Chem. Phys.* **1967**, *47*, 378.

(152) Bajorek, A.; Machekhina, T. A.; Parlinski, K. IAEA, Proc. Conf. on Neutron Scattering, Bombay, 1964; p 355.

(153) Niemela, L.; Ylinen, E. E. *Ann. Acad. Sci. Fenn. A6* **1969**, No. 307.

(154) Pintar, M. M. *NMR Basic Princ. Prog.* **1976**, *13*, 125.

(155) Venkataraman, G.; Usha Deniz, K.; Iyengar, P. K.; Roy, A. P.; Vijayaraghavan, P. R. *J. Phys. Chem. Solids* **1966**, *27*, 1103. Heyns, A. M.; Hirsch, K. R.; Holzapfel, W. B. *J. Chem. Phys.* **1980**, *73*, 105.

(156) Gardner, A. B.; Waddington, T. C. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1191.

(157) ElSaffar, Z. M.; Erhard, J. *J. Chem. Phys.* **1977**, *67*, 5335.

(158) Bostoen, C.; Coddens, G.; Wegener, W. *J. Chem. Phys.* **1989**, *91*, 6337.

(159) Price, W. C.; Sherman, W. F.; Wilkinson, G. R. *Proc. R. Soc.* **1960**, *255A*, 5.

(160) Powell, B. M.; Press, W.; Dolling, G. *Phys. Rev. B* **1985**, *32*, 3118.

(161) Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1990**, *22*, 140.

(162) Prager, M.; Press, W.; Heidemann, A.; Vettier, C. *J. Chem. Phys.* **1984**, *80*, 2777.

(163) Svare, I.; Raaen, A. M.; Thorkildsen, G. *J. Phys. C* **1978**, *11*, 4069.

(164) Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1992**, *24*, 1001.

(165) Callanan, J. E.; Weir, R. D.; Westrum, E. F. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1585.

(166) Prager, M.; Raaen, A. M.; Svare, I. *J. Phys. C* **1983**, *16*, L181.

(167) Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1990**, *22*, 1097.

(168) Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1991**, *23*, 653.

(169) Kume, Y.; Muraoka, H.; Matsuo, T.; Suga, H. *J. Chem. Thermodyn.* **1994**, *26*, 211.

(170) Dimitropoulos, C.; Pelzl, J.; Borsa, F. *Phys. Rev. B* **1990**, *41*, 3914.

(171) Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1992**, *24*, 567.

(172) Kume, Y.; Miyazaki, Y.; Matsuo, T.; Suga, H. *J. Phys. Chem. Solids* **1992**, *53*, 1297.

(173) Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1992**, *24*, 661.

(174) Schlemper, E. O.; Hamilton, W. C.; Rush, J. J. *J. Chem. Phys.* **1966**, *44*, 2499.

(175) Blinc, R.; Lahajnar, G. *J. Chem. Phys.* **1967**, *47*, 4146.

(176) Strange, J. H.; Terenzi, M. *J. Phys. Chem. Solids* **1972**, *33*, 923.

(177) Svare, I.; Thorkildsen, G.; Andersson, H. I.; Skjaevel, S. M.; Trivijitkasem, P. *J. Phys. C* **1978**, *11*, 997.

(178) Stephenson, C. C.; Wulff, C. A.; Lundell, O. R. *J. Chem. Phys.* **1967**, *40*, 967.

(179) Smith, D.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1990**, *22*, 421.

(180) Svare, I. *J. Phys. C* **1977**, *10*, 2679.

(181) Svare, I.; Abd el Haleem, A. *Phys. Scr.* **1979**, *19*, 351.

(182) Gorev, M. V.; Gordienko, P. S.; Zhigalov, V. P.; Bulanova, S. B. *Russ. J. Phys. Chem.* **1983**, *57*, 908.

(183) Armstrong, R. L.; van Driel, H. M.; Sharp, A. R. *Can. J. Phys.* **1974**, *52*, 369.

(184) Kearley, G. J.; Blank, H. *J. Chem. Phys.* **1988**, *89*, 1199.

(185) Ingman, L. P.; Punkkinen, M.; Ylinen, E. E.; Dimitropoulos, C. *Chem. Phys. Lett.* **1986**, *125*, 170.

(186) Kearley, G. J.; Cookcroft, J. K.; Fitch, A. M.; Fender, B. E. F. *J. Chem. Soc., Chem. Commun.* **1986**, 1738.
(187) Staveley, L. A. K.; Grey, N. R.; Layzell, M. J. Z. *Z. Naturforsch.* **1963**, *18a*, 148.
(188) Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1990**, *22*, 979.
(189) Steenbergen Chr.; de Graff, L. A.; Bevaart, L.; Bartolomé, J.; de Jong, J. L. *J. Chem. Phys.* **1979**, *70*, 1450.
(190) Raaen, A. M.; Svare, I.; Febich, M. *Phys. Scr.* **1982**, *25*, 957.
(191) Navarro, R.; Burriel, R.; Bartolomé, J.; González, D. *J. Chem. Thermodyn.* **1986**, *18*, 1135.
(192) Palacios, E.; Navarro, R.; Burriel, R.; Bartolomé, J.; González, D. *J. Chem. Thermodyn.* **1986**, *18*, 1089.
(193) Palacios, E.; Bartolomé, J.; Navarro, R.; Garcia, J.; González, D.; Brom, H. B. *Ferroelectrics* **1984**, *55*, 287.
(194) Navarro, R.; Burriel, R.; Bartolomé, J.; González, D. *J. Chem. Thermodyn.* **1987**, *19*, 579.
(195) Rubín, J.; Bartolomé, J.; Magerl, A.; Visser, D.; Kearley, G. J.; de Graaf, L. A. *Physica B* **1989**, *156*, 353.
(196) Pique, C.; Palacios, E.; Burriel, R.; Rubín, J.; González, D.; Navarro, R.; Bartolomé, J. *Ferroelectrics* **1990**, *109*, 27.
(197) Prager, M.; Badurek, G. *J. Phys. C* **1986**, *19*, 6105.
(198) Asai, T.; Kiriyama, H. *Chem. Lett.* **1979**, 397.
(199) Sundaram, C. S.; Ramakrishna, J. *Curr. Sci.* **1981**, *50*, 1064.
(200) Ingman, L. P.; Punkkinen, M.; Vuorimäki, A. H.; Ylinen, E. E. *J. Phys. C* **1985**, *18*, 5033.
(201) Poulet, H.; Mathieu, J. P. *J. Phys.* **1979**, *40*, 1079.
(202) Chihara, H.; Negeta, K.; Yoshioka, Y.; Nakamura, N. *J. Mol. Struct.* **1980**, *58*, 155.
(203) Barr, R. M.; Goldstein, M. *J. Chem. Soc., Dalton Trans.* **1976**, 1180.
(204) Hirokawa, K.; Furukawa, Y.; Nakamura, D. *Z. Naturforsch.* **1987**, *42a*, 1410.
(205) White, M. A.; Wagner, B. D. *J. Chem. Phys.* **1985**, *83*, 5844.
(206) Knopp, O.; Westerhaus, M. J.; Falk, M. *Can. J. Chem.* **1980**, *58*, 270.
(207) Hirokawa, K.; Furukawa, Y. *Z. Naturforsch.* **1988**, *43a*, 187.
(208) Mikke, K.; Kroh, A. *Inelastic Neutron Scattering of Neutrons in Solids Liquids*; IAEA: Vienna, 1962; p 237.
(209) Westrum, E. F.; Benjamins, E. *J. Am. Chem. Soc.* **1957**, *79*, 287.
(210) Reynhardt, E. C.; Watton, A.; Petch, H. E. *J. Chem. Phys.* **1979**, *71*, 4421.
(211) Burney, G. A.; Westrum, E. F. *J. Chem. Thermodyn.* **1976**, *8*, 21.
(212) White, M. A.; Green, N. H.; Staveley, L. A. K. *J. Chem. Thermodyn.* **1981**, *13*, 283.
(213) Callanan, J. E.; Weir, R. D.; Westrum, E. F. *J. Chem. Thermodyn.* **1990**, *22*, 957.
(214) Roy, A. P. *Curr. Trends Lattice Dyn.* **1978**, 531.
(215) Suga, H.; Sorai, M.; Yamanaka, I.; Seki, S. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1007.
(216) Gorbunov, V. E.; Gavrichev, K. S.; Totrova, G. A.; Tarasov, V. P.; Gusev, Yu, K. *Russ. J. Phys. Chem.* **1990**, *64*, 434.
(217) Petch, H. E.; Reynhardt, E. C.; Watton, A. *J. Magn. Reson.* **1978**, *29*, 1.
(218) Morimoto, K. *J. Phys. C* **1982**, *15*, 3789.
(219) Shurvell, H. F.; Brown, R. J. C.; Korppi-Tommola, J. *J. Raman Spect.* **1980**, *9*, 28.
(220) Brown, R. J. C. *J. Magn. Reson.* **1981**, *42*, 1.
(221) Park, Y. S.; Shurvell, H. F. *J. Raman Spect.* **1989**, *20*, 673.
(222) Köksal, F. *Z. Naturforsch.* **1981**, *36a*, 205.
(223) Jayasooriya, U. A.; Kearley, G. J.; Kettle, S. F. A.; Lauter, H. J. *Phys. Stat. Sol.* **1981**, *a63*, 169.
(224) Köksal, F.; Baçheli, S. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1844.
(225) Ikeda, R.; McDowell, C. A. *Mol. Phys.* **1973**, *25*, 1217.
(226) Stephenson, C. C.; Bentz, C. C.; Stevenson, D. A. *J. Am. Chem. Soc.* **1955**, *77*, 2161.
(227) Dimic, V.; Osredkar, M.; Slak, J.; Kandusar, A. *Phys. Stat. Sol.* **1973**, *b59*, 471.
(228) Ripmeester, J. A.; Dalal, N. S. *Phys. Rev. B* **1978**, *18*, 3739.
(229) Stephenson, C. C.; Zettlemoyer, A. C. *J. Am. Chem. Soc.* **1944**, *66*, 1405.
(230) Kim, J. J.; Sherman, W. F. *Phys. Rev. B* **1987**, *36*, 5651.
(231) Goyal, P. S.; Chakravarthy, R.; Dasannacharya, R. A.; Kulshresha, S. K.; Sastry, M. S.; Tomkinson, J. *Phys. Stat. Sol.* **1990**, *b157*, 547.
(232) Slak, J.; Kind, R.; Blinc, R.; Courtens, E.; Zm̌er, S. *Phys. Rev. B* **1984**, *30*, 85.
(233) Grosescu, R. *Chem. Phys. Lett.* **1973**, *21*, 80.
(234) Stephenson, C. C.; Adams, H. E. *J. Am. Chem. Soc.* **1944**, *66*, 1409.
(235) Morimoto, K. *Solid State Commun.* **1984**, *49*, 1169.
(236) Leung, P. S.; Rush, J. J.; Taylor, T. I. *J. Chem. Phys.* **1972**, *57*, 175.
(237) Myers, V. M. *J. Chem. Phys.* **1967**, *46*, 4034.
(238) Kanesaka, I.; Taneko, H.; Kawahara, H.; Kawai, K. *J. Raman Spect.* **1985**, *16*, 297.
(239) Chihara, H.; Nakamurs, N.; Inaba, A. *J. Phys. Soc. Jpn.* **1974**, *36*, 1710.
(240) Sundaram, C. S.; Shenoy, R. K.; Ramakrishna, J. *Ferroelectrics* **1984**, *61*, 233.
(241) Yamamoto, T.; Soda, G.; Nakamurs, N.; Chihara, H. *J. Phys. Soc. Jpn.* **1981**, *50*, 2014.
(242) Chihara, H.; Inaba, A. *J. Phys. Chem. Solids* **1976**, *40*, 1383.
(243) Chandra, P. P.; Dasannacharya, B. A.; Goyal, P. S.; Iyenger, P. K.; Rao, K. R.; Thaper, C. L.; Venkatesh, A. N. *Phys. Lett.* **1976**, *57A*, 463.
(244) O'Reilly, D. E.; Tsang, T. *J. Chem. Phys.* **1967**, *46*, 1291.
(245) Schomate, C. H. *J. Am. Chem. Soc.* **1945**, *67*, 1096.
(246) Higashigaki, Y.; Chihara, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 901.
(247) Goyal, P. S.; Dasannacharya, B. A. *J. Chem. Phys.* **1978**, *68*, 2430.
(248) Srinivasan, V.; Subramanian, C. K.; Narayranan, D. S. *Pranama* **1983**, *21*, 41.
(249) Clough, S.; Horsewill, A. J.; Johnson, M. R.; Mohammed, M. A.; Newton, T. *Chem. Phys.* **1991**, *152*, 343.
(250) Rush, J. J.; Taylor, T. I IAEA Proc. Conf. on Neutron Scattering, Bombay, 1964; p 333.
(251) Watton, A.; Reynhardt, E. C.; Petch, H. E. *J. Chem. Phys.* **1976**, *65*, 4370.
(252) Acharya, P. K.; Narayanan, P. S. *Indian J. Pure Appl. Phys.* **1973**, *11*, 519.
(253) Rajagopal, P.; Aruldhas, G.; Ramakrishnan, V. *J. Phys. Chem. Solids* **1989**, *50*, 675.
(254) Kamoren, M.; Chhor, K.; Pommier, C. *Mol. Cryst.* **1988**, *154*, 165.
(255) Galzerami, J. C.; Kitiyai, R. S. *J. Raman Spect.* **1988**, *19*, 225.
(256) McDowell, C. A.; Raghunathan, P.; Srinivasan, R. *Mol. Phys.* **1975**, *29*, 815.
(257) Stephenson, C. C.; Lundell, O. R. *J. Phys. Chem.* **1962**, *66*, 787.
(258) Artman, J.; Boerio-Goates, J. *Ferroelectrics* **1992**, *132*, 141.
(259) Sundara Raj, A.; Muthusubramanian, P. *J. Raman Spectrosc.* **1982**, *12*, 24.
(260) Köksal, F. *Z. Naturforsch.* **1979**, *34a*, 239.
(261) Varetti, E. L.; Fernez, E. L.; Altabef, A. B. *Spectrochim. Acta* **1991**, *47a*, 1767.
(262) Reynhardt, E. C.; Watton, A.; Petch, H. E. *J. Chem. Phys.* **1982**, *76*, 5761.
(263) Chhor, K.; Abello, L.; Pommier, C. *J. Phys. Chem. Solids* **1989**, *50*, 423.
(264) Acharya, P. K.; Narayanan, P. S. *Ind. J. Pure Appl. Phys.* **1973**, *11*, 514.
(265) Köksal, F. *J. Phys. Chem. Solids* **1984**, *45*, 1201.
(266) Jayakumar, V. S.; Sekar, G.; Rajagogopal, P.; Aruldhas, G. *Phys. Stat. Sol.* **1988**, *a109*, 635.
(267) Sekar, G.; Ramakrishnan, V.; Aruldhas, G. *J. Solid State Chem.* **1988**, *74*, 424.
(268) Fukai, M.; Matsuo, T.; Suga, J. *Phys. Chem. Solids* **1989**, *50*, 743.
(269) Verzee, C. E.; Westrum, E. F. *J. Chem. Thermodyn.* **1970**, *2*, 417.
(270) Iqbal, Z.; Malhotia, M. L. *Spectrochim. Acta* **1971**, *27a*, 441.
(271) Kanesaka, I.; Kawakara, H.; Kiyokawa, Y.; Tsukamoto, M.; Kawai, K. *J. Raman Spectrosc.* **1984**, *15*, 327.
(272) Bragin, J.; Diem, M.; Guthals, D.; Chang, S. *J. Chem. Phys.* **1977**, *67*, 1247.
(273) Roberts, M. P.; Lucazeau, G.; Kearley, G. J.; Dianoux, A. J. *J. Chem. Phys.* **1990**, *93*, 8963.
(274) Davies, T.; Staveley, L. A. K. *Trans. Faraday Soc.* **1957**, *53*, 19.