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An NMR Study of Ionic Motion in Ammonium Tungsten Bronze

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Ammonium tungsten bronze, $(NH_4)_xWO_3$, has been prepared and studied by X ray, and steady-state and pulsed nuclear magnetic resonance techniques. It has the hexagonal bronze structure. Motional narrowing of the steady-state proton resonance line, corresponding to ionic diffusion, occurs near 200°K. Linewidth vs temperature data yields an Arrhenius activation energy for diffusion of 0.081 eV/ion. A two-pulse technique was used to measure the proton T_1 vs temperature over the range 87–323°K. Evidence for at least two T_1 minima was obtained, one below 85°K due to relaxation presumably caused by ammonium ion rotation with an associated energy barrier of 0.023 eV/ion. Another occurs near 215°K and is due to relaxation related to ionic translation. The motional narrowing experiment infers the presence of another diffusion mechanism, and a related T_1 minimum at temperatures greater than 215°K. Using an adiabatic demagnetization method, the temperature dependence of the correlation time for ionic jumps was also measured. The activation energy for ionic motion obtained from the T_1 data was about 0.075 eV/ion, and from the adiabatic demagnetization experiment was 0.065 eV/ion. With the information at hand it is not possible to identify which of the translational relaxation mechanisms is reflected in the adiabatic demagnetization data. The several possible mechanisms for ionic motion in this crystal structure are discussed, including the feasibility of dissociative equilibrium.

Introduction

Ammonium tungsten bronze, $(NH_4)_xWO_3$, is one of a class of compounds with formula M_xWO_3 in which M, normally a monovalent cation, may be an alkali metal or other ion such as hydrogen (*1*), ammonium (*2*, *3*), thallium (*4*), etc. These compounds exhibit a number of unusual properties (*5–9*). Their structure may be cubic, tetragonal, or hexagonal, depending upon the identity of M and the value of x. Electronic conduction is a function of the stoichiometry, increasing with greater values of x. Superconductivity has also been observed in certain of the tetragonal I and hexagonal tungsten bronzes (*10*).

Some materials in this group are of interest because of their mixed conductor properties, with high ionic mobility due to the existence of atomic-sized tunnels within their crystal structures. This has led to their being used as nonpolarizing electrodes for the measurement of ionic conductivity in solid electrolytes (*11* and *12*).

Diffusion of the mobile monovalent ion in the hexagonal tungsten bronzes is almost certainly anisotropic, with ionic translation normally taking place in the linear channels which lie parallel to the c axis. The results reported here concern the use of NMR techniques to study ionic motion in hexagonal ammonium tungsten bronze. With this particular material, there is a possibility of rotational motion of the NH_4^+ groups as well as translational motion from site to site. In addition, as will be pointed out later, there are several possible mechanisms for the translational motion itself.

NMR spectroscopy is a particularly useful method for the study of ionic motion in solids in cases in which a suitable nucleus can be observed. Ionic self-diffusion can be observed in powder samples and there is no need for radiotracers.

In steady-state NMR measurements of ammonium compounds the proton linewidth collapses from values as high as 15–25 G to 1–5 G at the onset of rotation of the ammonium ion at its crystallographic site. At higher temperatures it is reduced even further, to values less than 0.1 G (the limit imposed by the experimental magnetic field inhomogeneity) due to motion of the hydrogen specie within the lattice, which averages out internal field variations. Related changes occur in the spin–lattice relaxation time. These phenomena can also be observed in adiabatic demagnetization experiments.

From such experimental NMR information, ionic jump frequencies and activation energies for both rotational (or oscillatory) and translational motion can be determined. If one has knowledge of the crystal structure and jump mechanism, the diffusion coefficients can also be calculated. The complete rotational narrowing curve has been observed for NH_4Cl and NH_4Br, and in part for NH_4I (*13*). The present paper discusses a group of nuclear magnetic resonance experiments on hydrogen motion in hexagonal ammonium tungsten bronze, $(NH_4)_xWO_3$.

The Structure of Ammonium Tungsten Bronze

The structure of hexagonal ammonium tungsten bronze has been found (*2*, *3*) to be similar to that of hexagonal rubidium tungsten bronze (*14*), with ammonium groups replacing the rubidium ions. In this structure a nearly planar hexagonal array of WO_3 groups is replicated in the normal direction so that channels are formed perpendicular to the WO_3 basal planes. It is down these channels that the *M* (monovalent) ions are normally most free to migrate. The bronze structure is shown in Figs. 1 and 2. The lattice parameters vary somewhat with the value of x, but remain approximately $a_0 = 7.4$ Å and $c_0 = 7.5$ Å. The tungsten atom positions are slightly skewed from one plane to the next, this displacement being repeated on every other plane. Thus, the unit cell includes two WO_3 planes instead of one, and the ammonium ion sites are separated by a distance $c_0/2$ along the channels. When $x = 1/3$, all the channel sites are filled.

Sample Preparation and Analysis

The $(NH_4)_xWO_3$ sample used in this investigation was prepared by heating ammonium paratungstate, $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$, in a flowing dry ammonia atmosphere, rather than a dry hydrogen atmosphere as has been previously reported (*3*). After 24 hr at about 600°K, the

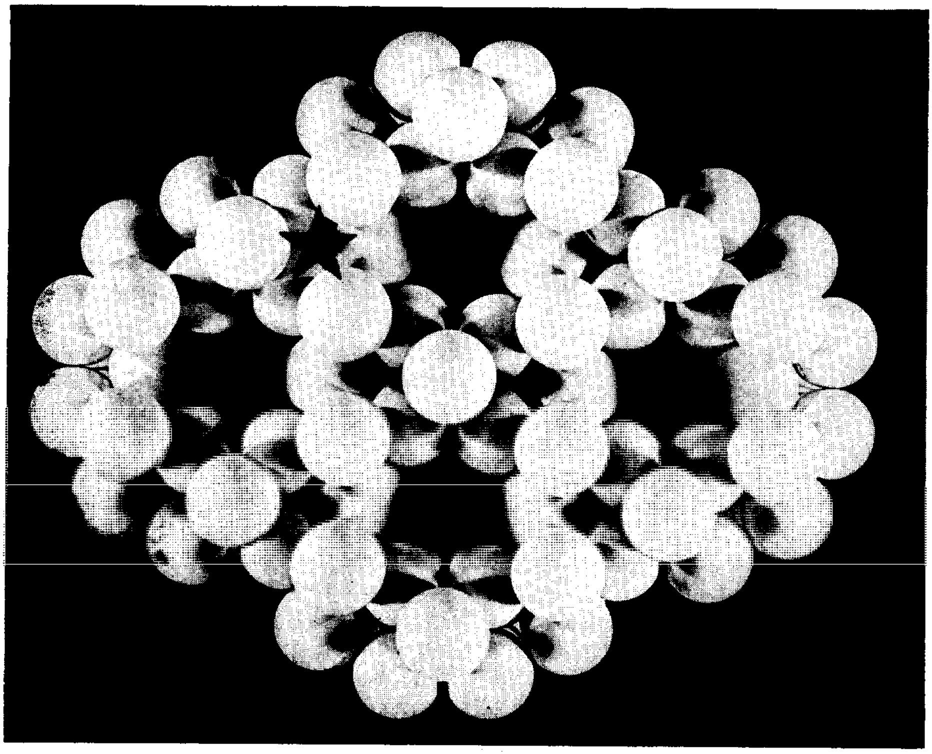

FIG. 1. Hexagonal tungsten bronze structure. View normal to the basal plane showing tunnels parallel to the *c* axis. One example of nonchannel site discussed in text is indicated by star.

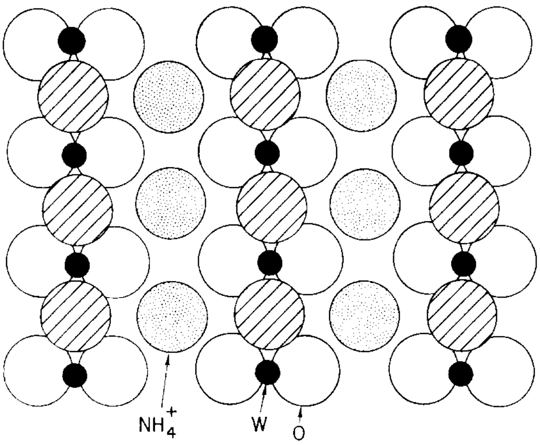

FIG. 2. Hexagonal bronze structure as viewed normal to the *c* axis, showing tunnels.

paratungstate had decomposed to form the bronze. The paratungstate is white and the resulting bronze is dark blue. Several different batches were prepared at different reaction temperatures.

X ray diffraction patterns of the bronze were made for several of the batches. In each case the diffractometer trace was similar to previously published data for both rubidium tungsten bronze (*14*) and ammonium tungsten bronze (*3*), except for minor variations due to slight differences in lattice parameters. The samples were also analyzed chemically. The values of x and y in the formula $(NH_4)_xWO_3 \cdot yH_2O$ were determined for each sample. Only the NH_4^+ groups were desired for the NMR experiment. Thus, the sample with the greatest ratio of $x:y$ was chosen for investigation: $x = 0.33$, $y = 0.0$. The lattice parameters of this sample were measured and found to be $a_0 = 7.390 \pm 0.001$ Å and $c_0 = 7.564 \pm 0.001$ Å.

Since the bronzes have relatively high values of electronic conductivity, the samples were ground to very fine powder in a ball mill in order to reduce rf losses in the NMR experiments.

Experimental Technique

Three different NMR experiments were performed to study ionic motion in the bronze: a wideline, steady-state motional narrowing experiment, a pulse T_1 vs temperature experiment, and a pulse adiabatic demagnetization experiment. Only the proton resonance was studied in each case. In all experiments a frequency of 8.00 MHz (with a corresponding H_0 field of 1.88 kG) was employed. A Varian V-4200 wideline NMR spectrometer system was used to perform the steady-state measurements; the transient measurements were performed using equipment which was constructed at Stanford (*15*). The sample was suspended within a Varian wideline probe adapted (*16*) for use over a wide temperature range.

Motional Narrowing Experiments

The motional narrowing of NMR spectra has been reviewed in several places (*17, 18*). At low temperatures, where the correlation time for atomic motion (the mean time between atomic jumps), τ_c, is much longer than the precession period for the resonant nucleus, ω_0^{-1}, dipolar interaction between neighboring nuclei in a lattice acts to broaden the resonance line. There is a spread in the resonant frequencies of individual nuclei because the local field acting upon each nucleus is the vector sum of the externally applied field, H_0, plus the fields due to all surrounding nuclei. The linewidth in this temperature region is called the "rigid lattice linewidth", δH_{RL}. In this regime the spin–spin relaxation time, T_2, is less than the spin–lattice relaxation time, T_1, so that the observed linewidth is primarily determined by the value of T_2. T_1 decreases to a minimum value where $\omega_0\tau_c \cong 1$. At high temperatures, where the correlation time is much less than the reciprocal of the precession frequency, ω_0, the fluctuations in the local field seen by any given nucleus are sufficiently rapid that the field experienced by all the nuclei averages to H_0, and T_2 becomes considerably larger than it is in the rigid lattice regime. T_2 begins to increase when $\Delta\omega\tau_c$ is of the order of unity. As a result, the resonance linewidth begins to narrow when $\Delta\omega\tau_c \cong 1$ and becomes more narrow with increasing temperature. In the temperature regime in which the line is narrowed to less than half of $\Delta\omega$, it has a Lorentzian shape and the activation energy Q for ionic motion may be found (*19*) from the Arrhenius relationship:

$$\delta H = A \exp(Q/kT) + \delta H_r, \qquad (1)$$

where δH is the linewidth (in G) at a given temperature T, k is Boltzmann's constant, A is a constant dependent upon the gyromagnetic ratio, spin, abundance, diffusion frequency factor D_0, and the jump distance of the resonant species. δH_r is a constant which includes all residual temperature-independent contributions to the linewidth. The temperature dependence of the linewidth for $(NH_4)_{0.33}WO_3$ is shown in Fig. 3. The high-temperature linewidth δH_r (approxi-

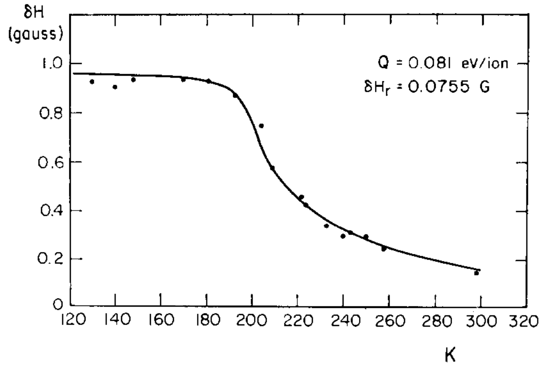

FIG. 3. Steady-state linewidth vs temperature, showing motional narrowing due to translational motion.

mately 75 mG) is attributable to magnet inhomogeneities.

Measurement of the Temperature Dependence of T_1

The well-known "180°–90°" two-pulse technique (*20*) was utilized to measure T_1 from liquid nitrogen temperature to room temperature. The resulting data are shown in Fig. 4. Minima in T_1 occur when $\omega_0 \tau_c = 1$, where τ_c is the correlation time for a given relaxation process. It is seen that the T_1 data indicate the presence of two minima, although the temperature span of the experiment did not extend to sufficiently low values to observe a true minimum in the second case. As will be discussed later, these two minima are attributed to two different types of ionic motion: rotation of the ammonium ions, and translation from one ionic site to another.

Adiabatic Demagnetization Experiments

Ailion and Slichter (*21–24*) have described a method for measuring the mean time between atomic jumps, τ_c, in a material when $T_2 < \tau_c < T_1$. This technique can extend the normally limited range of experimentally accessible jump times to much larger values. In this method, an overall relaxation time τ is measured. One can express $1/\tau$ as a sum of terms, each related to a different relaxation process in the sample. Three contributions to $1/\tau$ are potentially important in this work. Spin relaxation can involve free electrons, ionic translation from site to site, and rotation of the ammonium ions at a given site. Thus we can write

$$\frac{1}{\tau} = \frac{1}{T_1'}\frac{H_1^2 + 2H_L^2}{H_1^2 + H_L^2} + \frac{2(1-p_c)}{\tau_c}\frac{H_L^2}{H_1^2 + H_L^2} + \frac{(1-p_r)}{\tau_r}. \qquad (2)$$

The first term represents the relaxation contribution due to interaction between the nuclear spins and free electrons. T_1' is the spin–lattice relaxation time due to interaction with free electrons. H_1 is the magnitude of the applied radiofrequency field, and H_L is the local field seen by a hydrogen nucleus due to the fields of all its neighbors. The second term represents the relaxation contribution due to ionic translation from crystallographic site to site. τ_c is the mean time between translational jumps, and p_c is a constant which depends upon the geometry of the lattice. The value of p_c has been found (*15*) to be equal to 0.256 for this hexagonal bronze lattice, assuming ionic motion to be in the *c* direction only. The third term represents relaxation due to reorientation of the ammonium ion; p_r and τ_r have similar significance to the corresponding terms in the translational contribution. A semilogarithmic plot of τ vs reciprocal temperature is shown in Fig. 5.

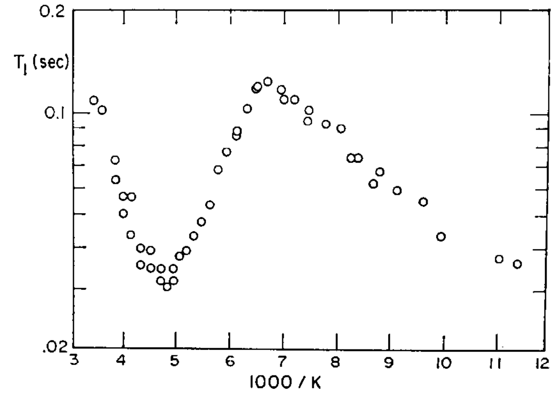

FIG. 4. Temperature dependence of the spin–lattice relaxation time, T_1.

Data Analysis and Interpretation

The activation energies for translational diffusion, obtained from the motional narrowing experiment, the T_1 vs temperature experiment, and the adiabatic demagnetization experiment are presented in Table I.

More than one mechanism can contribute to a change in the steady-state NMR linewidth. This possibility makes the attribution of the observed motional narrowing to a given type of nuclear motion potentially ambiguous. In ammonium tungsten bronze, one expects contributions to the linewidth due to interactions between spins

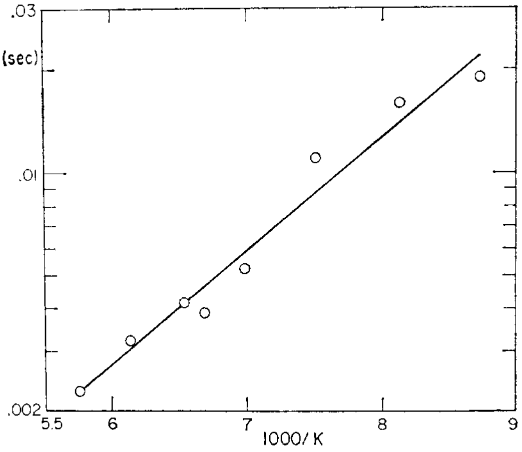

FIG. 5. Temperature dependence of the relaxation time measured by the adiabatic demagnetization method.

within individual ammonium ions (intraionic interactions) as well as interactions between spins on different ions (interionic interactions). Because it is anticipated that the ammonium groups in the bronze will show the type of rotational motion observed (*13*, *25*) in several ammonium salts, which can cause narrowing of the proton resonance line, it was necessary to determine whether the narrowing observed in these experiments was due to ionic translation or to ionic rotation.

As a first approximation, it is reasonable to assume the working hypothesis that rotational motion occurs in this system at temperatures which are comparable to those found (*26*) in materials such as ammonium chloride (~130°K). Hence, there is good reason to believe that the linewidth contribution due to intraionic interactions has already become "motionally narrowed" at the lower temperatures in this work so that the narrowing observed in the vicinity of 200°K is the averaging out (motional narrowing) of the interionic interactions through ionic translation.

Second moment calculations using the method of Van Vleck (*27*) predict that at very low temperatures there will be a "rigid lattice" region (no rotation, no translation) characterized by a second moment of the order of 50 G^2. At higher temperatures, where there is molecular reorientation but no translation, the predicted second moment is of the order of 1.4 G^2. At temperatures between 130 and 190°K, the observed second moment was 0.46 G^2, with a corresponding $T_2 \cong 70$ μsec. Thus even at these temperatures, there is some form of translational motion (which we shall call Type I) in addition to rotation. At higher temperatures (~200°K) there is a further T_2 transition to higher values. Presumably this is the transition to the "completely liquid" state in which $T_1 = T_2$ and corresponds to another type of translational motion (Type II).

Applying Eq. (1) to the data in the region above the narrowing temperature in Fig. 3 using a least-squares curve fitting computer program, yielded an activation energy for the Type II process of 0.081 eV/ion or 7.8 kJ/mole.

The plot of T_1 vs $10^3/T$ in Fig. 4 has a minimum at about 215°K. A second low temperature minimum appears to occur below 100°K. One can infer that the 215°K minimum is related to Type I translational motion, which also causes the second moment transition from 1.4 G^2 to 0.46 G^2. The lower temperature minimum is presumably due to relaxation corresponding to $\omega_0\tau_r = 1$, where τ_r is the rotation period for an ammonium ion, of the order of 10^{-8} sec. This is in accordance with the expectation that in such materials rotational transitions occur at lower temperatures than those due to translational processes.

Torrey (*28*) has shown that on the low temperature side of a translational minimum T_1 is directly proportional to τ_c, while on the high temperature side, T_1 is inversely proportional to τ_c. The activation energy for ionic translation

TABLE I

Experiment	Temperature Range (°K)	Q (eV/ion)	Q (kJ/mole)
(1) High Temperature T_1 slope (translation Type I)	223–323	0.077 ± 0.007	7.4 ± 0.7
(2) Low Temperature T_1 slope (translation Type I)	153–193	0.073 ± 0.003	7.0 ± 0.3
(3) Adiabatic Demagnetization (translational)	114–174	0.065 ± 0.005	6.3 ± 0.5
(4) Motional Narrowing (translation, Type II)	181–298	0.081 ± 0.005	7.8 ± 0.5
(5) Low Temperature T_1 slope (rotation)	87–143	0.023 ± 0.002	2.2 ± 0.2

may be obtained from the Arrhenius relationship: $\tau_c = \tau_0 \exp(Q/kT)$. After subtracting the reciprocal of the extrapolated value of the rotation contribution from the total $1/T_1$, an activation energy of approximately 0.073 eV/ion was obtained from the low temperature slope of the minimum related to Type I motion. The high temperature slope of this minimum yielded an activation energy of approximately 0.077 eV/ion.

The activation energy for ionic rotation was computed in the same way from the low temperature slope of the T_1 curve, assuming that it is the high temperature side of a lower temperature minimum, and again presuming a thermally-activated process. An activation energy of approximately 0.023 eV/ion was obtained from the data in the region from 110 to 133°K. As mentioned earlier, it was not possible to achieve temperatures low enough to examine the low temperature portion of the T_1 minimum because of equipment limitations.

The strong collision theory appropriate to the adiabatic demagnetization experiment applies when $T_2 < \tau_c < T_1$, where τ_c is the correlation time, related to either translational or rotational motion. Both the plot of T_1 versus reciprocal temperature and the motional narrowing results indicate that τ_{rotation} ($<10^{-8}$ sec) is less than T_2 (of the order of milliseconds) at temperatures greater than 100°K. Thus, over the range of temperatures of the adiabatic demagnetization experiment, the contribution to τ from rotational motion will be negligible. The free electron contribution to the relaxation time is proportional to $1/T$ and is also insignificant in this case. Thus, the measured relaxation time should be related to the mean time between translational jumps τ_c by

$$\tau \cong \frac{\tau_c}{2(1-p_c)} \frac{H_1^2 + H_L^2}{H_L^2}. \qquad (3)$$

In this experiment, $H_1 = H_L$. Since p_c is determined by the geometry of the crystal structure and the H values were constant, the slope of a plot of $\log \tau$ vs $1/T$ also gives an activation energy for the translational motion process. In this case it was found to be 0.065 eV/ion which is reasonably close to the values obtained by the use of the other methods. However, it is not now possible to clearly associate this result with either Type I or Type II motion.

It is tempting to assume that one or both of the translational processes involves motion of ammonium ions down the channels in the c direction. There are at least two other possible mechanisms for spin relaxation, however. If some of the ammonium ion positions in the structure were occupied by neutral ammonia (NH_3) groups, the observed motion of the ^1H nuclei could be due to the hopping of an H^+ from a NH_4^+ to an adjacent NH_3 in a manner analogous to electron hopping in wide band compound semiconductors. A similar phenomenon occurs in water and ice, in which H^+ species hop from H_3O^+ to H_2O. Furthermore, as pointed out in the Introduction, this type of motion has been confirmed in the case of NH_4Cl. Another possibility is also present. There is an appropriate site for H^+ ions near the ammonium sites. This type of site, indicated by the star in Fig. 1, would provide the H^+ ion with a large number of nearby oxygen ions, 3 in its own plane, 3 above, and 3 below. Electrostatic energy considerations indicate that this site would be quite favorable for the proton. Indirect evidence that it is a reasonable assumption that a fraction of the NH_4^+ ions dissociate to produce H^+ ions upon these sites was provided by the observation of Banks and Goldstein (*29*) that this site is probably occupied by lithium ions in $Li_yK_xWO_3$, where the channels are completely filled by potassium. The observed translational behavior could then be the motion of the H^+ species between NH_4^+ groups within the linear tunnels parallel to the c axis and this group of isolated sites. There is not yet enough information at hand to clearly distinguish between these various possibilities.

Results similar to these, which also indicate the presence of more than one translational process, have been obtained at York and Oxford (*31*, *32*) in both ammonium and hydrogen tungsten bronze.

A further series of steady-state experiments is underway (*30*) in which it has been found that the stoichiometry has a significant influence upon motional narrowing results. It is hoped that this work will lead to definitive information concerning the actual diffusion mechanisms.

Conclusions

Ionic motion has been studied in hexagonal ammonium tungsten bronze. Bronze samples were prepared and analyzed both by chemical and X ray methods. Lattice parameters for the hexagonal bronze were found to be $a_0 = 7.390 \pm 0.001$ Å and $c_0 = 7.564 \pm 0.001$ Å for $x \cong 0.33$.

Because of its unusual structure, monovalent ions of appropriate size are expected to readily move in channels in the lattice. The channel size is approximately equal to the ammonium ion diameter, while the cavity in which the ammonium ion resides is even larger—about 2.5 Å radius.

Several different NMR techniques have been used to examine the motional behavior of ^1H in this material. The results show three regions of behavior. At very low temperatures motional behavior occurs with an activation energy of about 0.023 eV. Because of analogous findings in other (close-packed) ammonium compounds at such temperatures, it seems reasonable to assume that these observations relate to the rotational motion of ammonium ions, rather than movement of species from site to site.

At higher temperatures two types of motional behavior apparently occur, characterized by activation energies in the range 0.065–0.08 eV. Because of the lattice geometry, it is tempting to ascribe this group of observations to the translational motion of NH_4^+ ions from site to site along the linear tunnels that lie in the *c* direction in this structure. However, it might also be due to H^+ hopping from NH_4^+ to NH_3 species, or motion involving temporary occupation of a site between the main *c* axis channels.

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