shell 4^- is that the anion radical stacks have a new electronic transition polarized along the stack direction. This new band is found in the NIR and is characteristic of partially filled band structures in solids containing π-stacks.

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Registry No. 4^-, 135734-25-7; 4^{2-}, 66548-26-3; **4a**, 135710-31-5; **4b**, 129250-11-9; sulfanilic acid sodium salt, 515-74-2; tetrabutylammonium bromide, 1643-19-2; 1,4,5,8-naphthalenetetracarboxylic acid dianhydride, 81-30-1.

Proton Dynamics in $\mathrm{TiS_2}$–$\mathrm{NH_3}$: A New Model for Ammoniated Transition-Metal Dichalcogenides

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The proton dynamics in $\mathrm{TiS_2}$–$\mathrm{NH_3}$ intercalates have been reinvestigated by using high-resolution magic angle spinning and pulsed ^{1}H NMR spectroscopy. A new structural model to describe ammoniated $\mathrm{TiS_2}$ is proposed, consistent with the ensemble of previous structural and chemical studies. Previous discussions of the structure have considered these phases as molecular intercalates, with distorted $\mathrm{NH_3}$ molecules and $\mathrm{NH_4^+}$ ions in the van der Waals gap, and the results of NMR studies have been interpreted in terms of rotational and translational degrees of freedom of these molecular species. In our new interpretation, we suggest that the nitrogen and hydrogen atoms occupy crystallographic sites within the van der Waals gap rather than forming molecular $\mathrm{NH_3}$ and $\mathrm{NH_4^+}$ species, and the dynamic behavior indicated by the NMR data corresponds to protons hopping between sites within the gap. Above approximately 150–200 K, the major relaxation process is proton exchange between sites around different N atoms. Below this temperature range, these diffusive motions are blocked, but it is probable that tunnelling between proton sites around a given N atom continues to occur, down to temperatures of a few kelvin. Within the context of our new model, $\mathrm{TiS_2}$–$\mathrm{NH_3}$ and related intercalated materials should be good proton conductors down to the temperature of the blocking transition for the diffusive motion (150–200 K), and we suggest that they are more appropriately formulated as $\mathrm{TiS_2N_xH_{3x+\delta}}$ to better represent the structural nature of these compounds.

Introduction

The intercalation complexes of layered metal chalcogenides $\mathrm{MX_2}$ (M = Ti, Ta, Nb, Zr; X = S, Se) exhibit a wide range of interesting electrical, chemical, and catalytic properties, and there has been considerable interest in the structural chemistry of these phases.[1] Concerning molecular guest species, two of the most thoroughly studied systems are $\mathrm{TiS_2}$–$\mathrm{NH_3}$ and (2H)$\mathrm{TaS_2}$–$\mathrm{NH_3}$. Most previous studies have focused on the identification and structural characterization of the intercalated ammonia species and investigation of the dynamic behavior of these species. Early studies on these compounds formulated the intercalation complexes as $\mathrm{MS_2}$–$x\mathrm{NH_3}$, with x ranging from 0 to 1.[2-11] More recent work has shown that a redox reaction takes place upon intercalation, and the compounds are now generally formulated as $\mathrm{MS_2}^{x-}(\mathrm{NH_4^+})_x(\mathrm{NH_3})_y$.[1,12-16] These conclusions are based on (a) evolution of $\mathrm{N_2}$ gas during intercalation and (b) observation of evolved excess $\mathrm{H_2}$ on thermal deintercalation, identified by mass spectrometry and chemical methods.

For these compounds, it is well established from X-ray and neutron diffraction studies that the N atoms occupy trigonal prismatic sites within the van der Waals gap.[3,7,17-19] The limiting stoichiometries of the intercalation complexes occur when all gap sites are filled ($x + y = 1$). The positions of the hydrogen atoms are much less well defined.

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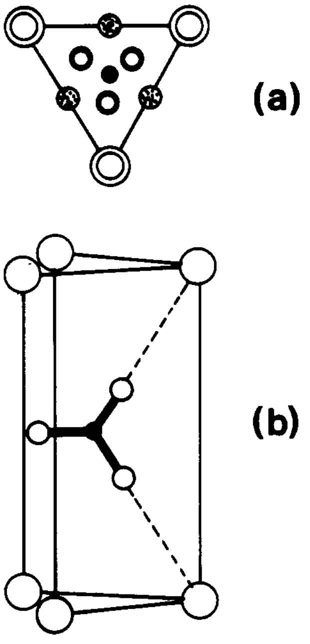

Figure 1. (a) Projection (after ref 19) of the proton 9d (dotted circles) and 18h sites (smaller open circles) along a direction perpendicular to the TiS_2–NH_3 layers upon the interlayer midplane containing nitrogen (filled circles); the 9d positions are on the interlayer midplane. (b) Assumed orientation of the NH_3 molecule in an interlayer trigonal prism of sulfur atoms as suggested by Young et al.[19] The largest circles represent sulfur.

From measurements of the proton NMR spin–lattice relaxation time as a function of orientation for a single crystal of TaS_2–NH_3, Gamble and Silbernagel[20] concluded that the 3-fold axes of the NH_3 molecules were oriented parallel to the disulfide layers. This result is often cited in current discussions of the location of protons associated with the NH_3 molecules in the intercalated phases.[1,12,18,19,21] However, those NMR data were obtained before the identification of redox reactions accompanying the ammonia intercalation, implying the presence of both NH_3 and NH_4^+ as intercalated species. The presence of species other than NH_3 within the van der Waals gap must affect the interpretation of the NMR results.

Bouwmeester and Wiegers[18] carried out a neutron powder diffraction study at room temperature of TiS_2 intercalated with ND_3 and used their data to test various structural models in an attempt to locate the deuterium atoms. Their refinements did not permit any definite conclusions regarding the orientation of the ND_3 molecules and did not indicate any distinction between ND_3 and ND_4^+ species. These authors concluded that either the ND_3 and ND_4^+ species were freely rotating to give spherically symmetric entities on the neutron diffraction timescale or there is a statistical distribution of orientations and occupancies throughout the structure.

Young et al.[19] carried out a similar study, using time-of-flight neutron diffraction techniques, and obtained data for a sample $TiS_2(ND_4)_{0.22}(ND_3)_{0.34}$ at room temperature and 12 K. These authors found a good fit to the diffraction profile for a model with the ND_3 protons on sites 9d ($2/m$) and 18h (m) (Figure 1a) within a structure with space group $R\bar{3}m$. The protons for the ND_4^+ groups were not fit but were simply assumed to be distributed on the vertices of a dodecahedron, to simulate a spherically averaged ion, as deduced from a previous NMR study.[21] From these results, Young et al. concluded that the intercalated ND_3 molecules within $TiS_2(ND_4)_{0.22}(ND_3)_{0.34}$ occupied 6c ($3m$ site symmetry) sites, with a distorted planar geometry, and with the pseudo-3-fold axis lying within the van der Waals planes (Figure 1b). The authors noted that, for the ND_3 groups to occupy $3m$ sites within a structure with space group $R\bar{3}m$, the N and D atoms must be disordered over sets of equivalent sites. This disorder could be static or dynamic in nature. Young et al. considered that the disorder was static, presumably because the same structure was observed at both 300 and 12 K.[19]

We have carried out a high resolution ^1H magic angle spinning (MAS) NMR study at room temperature for a partially intercalated sample $TiS_2(NH_4)_{0.29}(NH_3)_{0.52}$. This showed only a single peak with a chemical shift intermediate between those for NH_3 and NH_4^+, indicating rapid chemical exchange between the two species at 300 K. This result prompted us to reexamine the ^1H NMR line-shape and relaxation time measurements for ammonia-intercalated TiS_2 and TaS_2 in the literature.[8–10,21–23] We found a number of conflicting results in the previously published work, especially regarding the behavior of the ^1H NMR line width with temperature. This led us to repeat the experiments for TiS_2–$x$$NH_3$ samples as a function of temperature (100–500 K). In the present paper, we present the results of the high-resolution room-temperature MAS NMR and variable-temperature pulsed NMR line-shape and T_1 relaxation time studies. In addition, we reconsider the interpretation of the ensemble of the previous chemical, diffraction, and spectroscopic studies on ammoniated TiS_2 and related phases and propose a new structural description of these materials.

Experimental Section

Sample Preparation. The optimal preparation technique for TiS_2 has been the subject of considerable discussion in the literature, as have its composition and intrinsic electrical and magnetic properties.[24–27] These questions have not yet been completely resolved. The starting TiS_2 used in the present study was prepared by reaction of the elements (Ti sponge and powdered sulfur) in stoichiometric proportions at 500 °C in one step, as described by Cajipe et al.[27] The resulting material had composition $Ti_{1.0014}S_2$, determined by complete oxidation to TiO_2, with lattice parameters $a = 3.4058$ Å and $c = 5.693$ Å. This sample was diamagnetic ($\chi = -2 \times 10^{-6}$ emu/mol at room temperature, and decreased with decreasing temperature) and was deep, dull green in color. TEM and optical examination showed the presence of 50–300-μm aggregates of well-crystallized hexagonal platelets <1 μm in dimension.

NH_3-intercalated TiS_2 was prepared by freezing approximately 10 cm^3 of Na-dried ammonia into one leg of a previously dried, Pyrex h-shaped tube containing TiS_2, then sealing the tube under vacuum, and allowing reaction to occur at room temperature for 7–8 days. After reaction, the excess ammonia was removed by freezing into the second leg of the h-tube. Several separate syntheses of fully intercalated TiS_2 were carried out for the NMR experiments described here. Addition NMR experiments were carried out on partially deintercalated materials, prepared by step heating under vacuum to temperatures of 220–370 °C to partially

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remove NH_3 and NH_4^+ components. The samples were at all stages handled in an argon-filled glovebox (<10 ppm H_2O and O_2).

Analysis. The compositions of the intercalates were determined by volumetric (evolved gas pressure) and thermogravimetric analysis (TGA). Previous experiments have shown that deintercalation proceeds in two steps, with evolution of NH_3 at lower temperatures (up to 150 °C), followed by liberation of NH_4^+ component ($NH_3 + {}^1/_2H_2$) at higher temperatures.[14,16,28] The two deintercalation steps are separated by a plateau in the plots of evolved gas pressure or sample weight loss versus time in controlled heating rate experiments. For preparation of partially deintercalated samples, 300–500 mg of fully intercalated $TiS_2(NH_4)_x(NH_3)_y$ was carefully weighed in the drybox and transferred to the vacuum line. Step heating at 3–5 °C/min was carried out, and the volume of evolved gas monitored. Heating was continued until the "target" composition had been reached, identified from the pressure gain (of evolved gas) curve. The samples were weighed after partial or complete deintercalation, and the weight loss coupled with the volume of evolved gas used to define the composition of the starting sample. The fully intercalated samples prepared in this study and analyzed in this way had composition $TiS_2(NH_4)_{0.29\pm0.02}(NH_3)_{0.70\pm0.02}$. Partially deintercalated samples with compositions $TiS_2(NH_4)_{0.29}(NH_3)_{0.11}$, $TiS_2(NH_4)_{0.30}$, $TiS_2(NH_4)_{0.24}$, and $TiS_2(NH_4)_{0.15}$ were also prepared. All these samples were used for the pulsed NMR experiments at low field. The partially deintercalated sample used for the high-resolution MAS NMR experiments was that previously studied by Cajipe et al.[28] and had composition $TiS_2(NH_4)_{0.29}(NH_3)_{0.52}$.

We note that the NH_4^+ content of our samples is significantly higher than that obtained in earlier studies ($x = 0.22 \pm 0.02$).[13-15,21,28] McKelvy and co-workers[29] have recently investigated the variation of NH_4^+ content with intercalation time for TiS_2 and NbS_2 samples. For TiS_2, they found NH_4^+ contents in the range $x = 0.22$–0.24 for intercalation times ranging from 26 h to 12 days, but that the NH_4^+ content increased to $x = 0.25$ for much longer intercalation times (2–5 months). The samples used by McKelvy et al. had a particle size of 180–425 μm, slightly larger than the average particle size used in our syntheses. The individual crystalline sizes were not reported in the earlier study. The intercalation rate and probably also the NH_4^+ content are certainly dependent on individual crystalline size and morphology and perhaps also on the precise stoichiometry of the TiS_2 phase.[30] A combination of these factors is most likely responsible for the differences in NH_4^+ content and intercalation rate between our study and the previous work.

NMR Spectroscopy. For the high-resolution NMR experiments, the samples were loaded into a closed MAS rotor under nitrogen in the drybox. The samples were spun in the MAS NMR experiment using a jet of dry air. Because traces of water are known to affect proton NMR line widths and relaxation times for systems containing NH3,[31-33] care was taken to exclude water from the MAS NMR experiment. The ammoniated TiS_2 samples were transported to Paris in sealed glass tubes and transferred to the NMR rotor in a laboratory glovebox under an atmosphere of dry N_2 gas. After loading the sample into the rotor, the rotor was closed with a Teflon disk, and the rotor lid was screwed shut. The MAS NMR experiment was run as soon as possible after the transfer (approximately 10 min). To evaluate the effect of any reaction with moist air leaking into the rotor during the NMR experiment, NMR spectra were taken for the sample at times up to 20 h after loading. The results of these experiments are described below. For conventional pulsed NMR experiments, the ammoniated TiS_2 samples were loaded into Pyrex tubes under dry argon, then removed from the drybox, and sealed while under gentle negative pressure. The compositions of the various samples studied in these NMR experiments were determined subsequently.

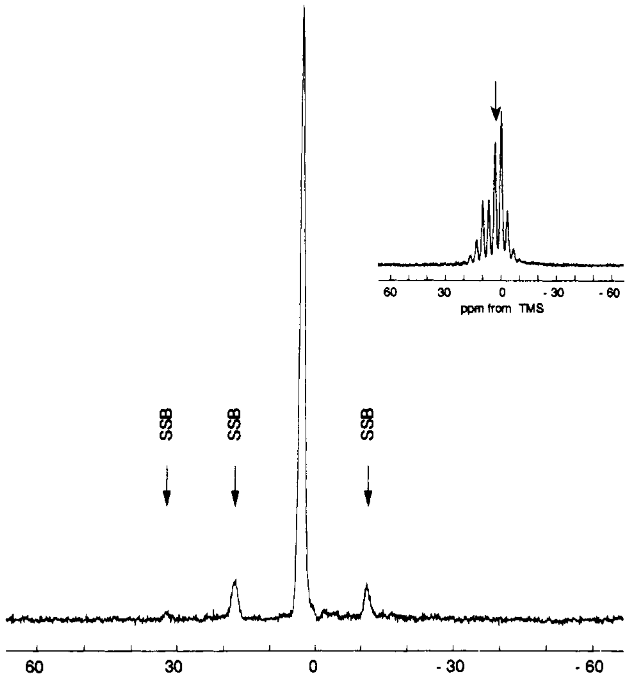

Figure 2. The 7-T ^1H MAS NMR spectra of $TiS_2(NH_4)_{0.29}(NH_3)_{0.52}$ obtained with a spinning speed of 4.34 kHz (SSB = spinning sidebands). The inset shows the intensity distribution of the side bands as obtained for a spinning speed of 0.9 kHz (the arrow indicates the line, the position of which is independent of the spinning speed value, and hence measures the isotropic component of the chemical shift tensor).

The ^1H MAS NMR experiments were carried out usng a Bruker CXP 300 pulse spectrometer operating at 7 T (300 MHz) and equipped with a double bearing Bruker probe for CP-MAS experiments using 5-mm-o.d. sapphire rotors capable of spinning speeds up to 4.5 kHz. The sample was spun at the magic angle (54.74°) at spin speeds of 1–4.5 kHz. Room-temperature proton NMR spectra were obtained following a single $\pi/2$ (5-μs length) pulse with 6-s delay between acquisitions and 100 kHz sweep width. A scan number of 40 was found sufficient to obtain a good single-to-noise ratio. Field homogeneity, optimized using a 5-mm nonspinning tube of acetone, was better than 0.5 ppm. The free induction decays were multiplied by an exponential apodization function, equivalent to a Lorentzian line broadening of 50 Hz (0.2 ppm).

Variable-temperature proton NMR line-width and relaxation time studies were carried out with a modified Bruker multiple pulse instrument operating at a field of 1.36 T (58 MHz). Line shapes were measured by boxcar integration of the free induction decay, and T_1 measurements carried out using a π–τ–$\pi/2$ pulse sequence.

Results

High-Field MAS NMR Study. The room-temperature high-resolution MAS proton NMR spectrum obtained with a spinning speed of 4.34 kHz of $TiS_2(NH_4)_{0.29}(NH_3)_{0.52}$, nominally containing both NH_3 and NH_4^+ groups, is shown in Figure 2. A single narrow central line is observed, flanked by spinning sidebands. The isotropic chemical shift is 3.1 ppm relative to tetramethylsilane (TMS) and the full width at half-maximum (fwhm) of the central line is approximately 1.5 ppm. The intensity distribution of the sidebands is asymmetric, implying anisotropy in the chemical shift tensor (the resonance is spread over ≈20 ppm). This asymmetry was noted by Silbernagel et al.[9] for $TiS_2(NH_3)$ and $TaS_2(NH_3)$ at room temperature in static NMR experients at low field and by Nonte et al.[23] at 7 T for various ammoniated disulfides, including TiS_2.

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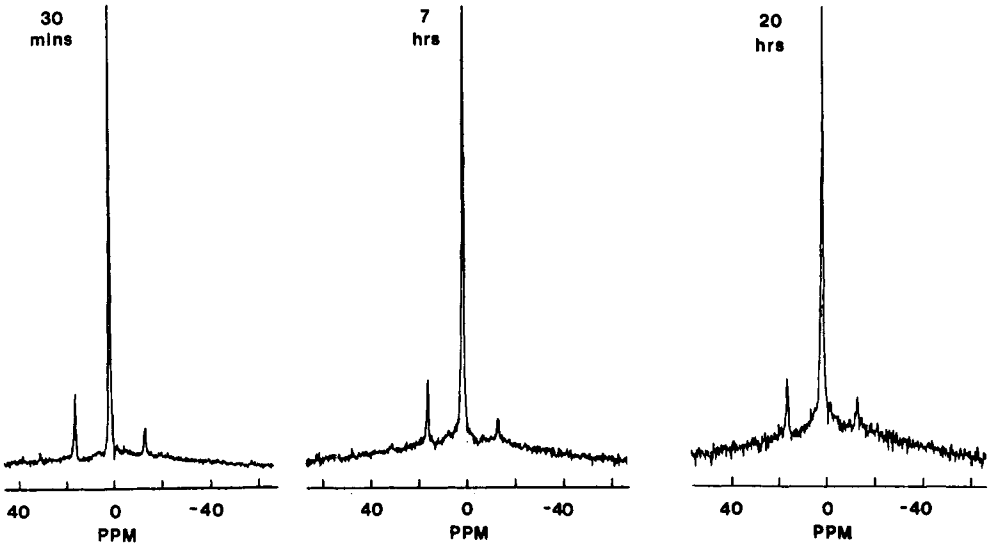

Figure 3. ^1H MAS NMR spectra of $TiS_2(NH_4)_{0.29}(NH_3)_{0.62}$ after exposure to the atmosphere for different periods of time.

This anisotropy is due to the anisotropic magnetic susceptibility of the host materials and the fact that the protons are confined to planes within the van der Waals gap. The fact that a single narrow resonance is observed indicates that if discrete NH_3 and NH_4^+ molecular groups are present within the intercalated TiS_2 structure, these are exchanging protons more rapidly than the proton NMR resonance frequency (300 MHz), at room temperature. Ogg[31,32] has studied the NMR spectra of N–H protons for various species in liquid and gaseous NH_3 and in solution. The resonance for NH_4^+ is deshielded by several (5–7) ppm relative to the isotropic shift of NH_3. If separate lines were present for these two molecular species within our sample, these would have been resolved in our high-resolution MAS NMR experiment.

It has been demonstrated that the presence of trace amounts of water in liquid ammonia result in dramatic changes in the proton exchange rate and NMR relaxation times.[31-33] Because the sample rotor for the MAS NMR experiment could not be sealed hermetically, we carried out our NMR experiments as rapidly as possible after loading the samples into the rotor, to minimize any diffusion of atmospheric water into the sample. To evaluate the possible effects of this, we also obtained MAS NMR spectra for samples exposed to atmospheric water (in the closed NMR rotor) for periods of up to 20 h (Figure 3). The spectrum of the sample run as soon as possible after loading (approximately 10 min) shows a single peak at 3.1 ppm with a flat spectral baseline, as described above (Figure 2). After approximately 30 min, a weak broad baseline feature could just be detected (Figure 3). With continued exposure to the atmosphere, this broad feature continued to increase in relative intensity (Figure 3). The broad feature most probably corresponds to adsorbed molecular H_2O in the rotor assembly, not necessarily on the sample surface. Because no baseline feature could be detected in the 15-min sample spectrum, we consider that this represents a signal representative of a dry ammonia-intercalated TiS_2 sample. Because we did not observe any additional narrowing of the sharp central resonance as the water signal increased in intensity and because we took care to ensure that the starting TiS_2 and intercalated NH_3 were completely dry, we conclude that the single, sharp proton resonance results from a proton-exchange mechanism intrinsic to the ammonia-intercalated TiS_2 sample.

Previous ^1H NMR Line-Width Measurements at Low Field. The result of our high-resolution MAS NMR experiment led us to examine the existing data on proton dynamics within ammonia-intercalated MS_2 phases from wide-line and pulsed NMR experiments.

Silbernagel et al.[9] measured the ^1H NMR spectrum of fully intercalated TaS_2–NH_3 and TiS_2–NH_3 at room temperature and found a motionally narrowed absorption line ($\Delta H' = 0.1$–0.2 G, measured as the splitting between derivative maxima) for both phases. The isotropic chemical shift for TiS_2–NH_3 was measured at 2 ± 1 ppm relative to TMS, in good agreement with our high-resolution MAS result.

On decreasing the temperature, Silbernagel et al. observed changes in the NMR line width and line shape for the two compounds. Below 150 K for TaS_2–NH_3, the line began to broaden and became approximately Lorentzian in shape. Between 140 and 110 K, there was a marked increase in line width to approximately 2.6 G at 110 K. Silbernagel et al. observed no further change in $\Delta H'$ for this compound down to 5 K. The line-width behavior for TiS_2–NH_3 was similar, with an increase to 3.0 G for $\Delta H'$ between 145 and 110 K. In part because the changes in line width were accompanied by line-shape changes, these authors also calculated values of the second moment M_2 from their data. Although the line-width behavior of both fully intercalated compounds was similar, M_2 for TiS_2–NH_3 reached a plateau of approximately 7.5 G^2 at approximately 120 K and showed no further change down to 90 K, whereas M_2 for TaS_2–NH_3 continued to increase, with a value of approximately 20.5 G^2 near 90 K. These differences in the behavior of M_2 reflect differences in the temperature-dependent line shape between the two compounds in the low-temperature region.

Silbernagel et al. recognized that the abrupt increase in line width for the two compounds near 120 K was due to freezing of some thermally activated process involving proton motion within the van der Waals layers of these intercalated compounds and calculated an activation energy of approximately 5 kcal/mol and an attempt frequency on the order of 10^{13} s^{-1} from the line-width data before and after the line-broadening transition. This would result in a relaxation time of approximately 3×10^{-10} s at room temperature (300 K).

In their study, Silbernagel et al.[9] also investigated the temperature dependence of the proton NMR line width for partially intercalated samples with nominal compositions (ignoring the possible presence of NH_4^+ species, which were identified in later work) $TiS_2(NH_3)_{0.5}$ and

$TaS_2(NH_3)_x$ (x = 0.62, 0.50, and 0.16). For the partially ammoniated TiS_2 sample, the NMR line-width behavior was identical with that observed for the fully intercalated sample. The line-width changes for the partially intercalated TaS_2 samples were all similar but different from the fully intercalated TaS_2–NH_3. For these samples, broadening began at approximately the same temperature, near 130 K, but the rate of broadening with decreasing temperature was slower, and no plateau was reached at 90 K.

Silbernagel et al. discussed their results in terms of likely internal and external degrees of freedom of intercalated NH_3 molecules within the van der Waals gaps, expressed as spinning of the molecules about their 3-fold symmetry axes, reorientation of these axes, and diffusion of the NH_3 molecules. They calculated likely values of the second moment constrained by various combinations of these motions. The limiting rigid lattice limit (assuming intercalated NH_3 molecules) was calculated as 50–75 G^2, much larger than any of the measured values of M_2. The authors concluded that the proton motions were never entirely blocked over the temperature range studied, down to 5 K.

An independent investigation of the temperature dependence of proton NMR line widths for two partially intercalated TiS_2 samples, with composition $TiS_2(NH_4)_{0.22}(NH_3)_{0.37}$ and $TiS_2(NH_4)_{0.21}$, was carried out by O'Bannon et al.,[21] with results entirely different from those of Silbernagel et al.[9] For $TiS_2(NH_4)_{0.22}(NH_3)_{0.37}$, these authors found a narrow line (with ΔH (fwhm) approximately equal to 0.3 G) above 270 K, which abruptly broadened to approximately 3.7 G on cooling to below this temperature. A plateau was found between approximately 260 and 120 K, where a second line-broadening transition occurred to give a final line width of 8.3 G, almost 3 times the value observed by Silbernagel et al.[9] No further change in line width was observed down to 4.2 K. O'Bannon et al. interpreted these data in terms of rotation of NH_3 groups about their 3-fold axes in the 120–270 K regime, accompanied by diffusion of NH_3 and NH_4^+ species above 270 K.

Very different behavior was observed by O'Bannon et al. for $TiS_2(NH_4)_{0.21}$. For this compound, the measured line width, ΔH, was measured to be 2.6 ± 0.3 G and was found to be temperature independent over the range 3–540 K. On the basis of this observation, these authors concluded that the NH_4^+ groups are motionally active over the measured temperature range, probably as free rotors. This result was used to construct the assumed model for ND_4^+ positions in the neutron diffraction refinement of Young et al.[19] (see the Introduction).

^1H NMR Line Widths Measured in the Present Study. We have measured ΔH (fwhm) for the ^1H NMR spectrum of a fully ammoniated sample ($TiS_2(NH_4)_{0.29}(NH_3)_{0.70}$) between room temperature and 110 K. The results are shown in Figure 4. Our results are very similar to those of Silbernagel et al.,[9] but different from those of O'Bannon et al.[21] Beginning with the fully narrowed line at room temperature, we observe the onset of a single line-narrowing transition at ≈145 K, i.e., at a temperature closer to that observed by the former group (≈125 K) than the latter (≈270 K). The plateau for ΔH is at 4.0 G, which compares quite well with the 3.0 G found for $\Delta H'$ by Silbernagel et al., considering that ΔH is necessarily slightly larger than $\Delta H'$. Comparing the value found in this work for ΔH and that found by Silbernagel et al. for $\Delta H'$, the ratio $\Delta H/\Delta H' = 1.3$, which is intermediate between the values for Lorentzian and Gaussian lines ($\Delta H/\Delta H' = 3^{1/2}$ and $(2 \ln 2)^{1/2}$, respectively). We see no evidence for a second line-broadening transition at 120 K, as found by O'Bannon et al. We have no explanation for the differences between the results of this study, which are consistent with those of Silbernagel et al., and the observations of O'Bannon et al. We note that, in a later study, O'Bannon et al.[34] investigated the proton NMR line-width behavior for a lithium–ammonia cointercalated sample of TiS_2 ($Li_{0.22}(NH_3)_{0.64}TiS_2$). This showed a single line-broadening transition at 130 K, analogous to those observed in the present study and by Silbernagel et al.[9]

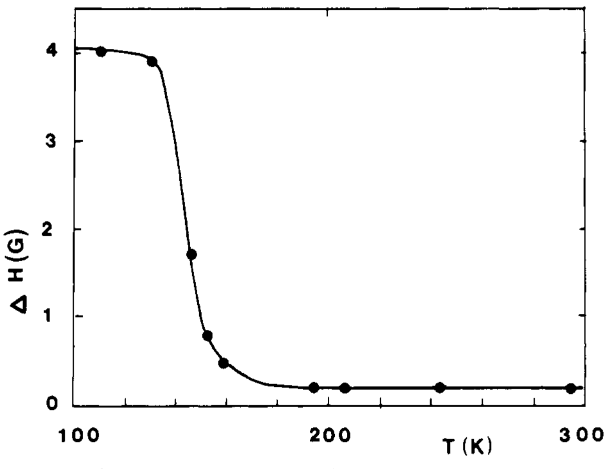

Figure 4. ^1H NMR line width (ΔH) as a function of temperature for fully intercalated $TiS_2(NH_4)_{0.29}(NH_3)_{0.70}$, measured in this study.

O'Bannon et al.[21] had suggested that the earlier study by Silbernagel et al.[9] (there is an apparent error in reference numbering in the paper by O'Bannon et al.) was plagued with problems associated with cryopumping of NH_3 from TiS_2–NH_3, causing the line-broadening transition to be observed at lower temperature due to the presence of solid NH_3 in the sample tube. We do not believe this to be the case for the results presented here, for the following reasons. First, our experiments were carried out beginning from low temperature and then increasing the temperature, reducing the likelihood of ammonia deintercalation, especially for those samples with low ammonia content. In fact, for several samples, we repeated the measurements on the same sample from low to high temperature and then back to low temperature and observed no change in the line-broadening transition. Next, we observed a similar line-broadening transition for all of the samples in this study, including $TiS_2(NH_4)_{0.30}$, $TiS_2(NH_4)_{0.24}$ and $TiS_2(NH_4)_{0.15}$ (Figure 5), which formally contained no NH_3 component and which require much higher temperatures for deintercalation. In addition, the details of the line broadening transition, including the transition temperature and the plateau line width below the transition, were slightly different for all of these samples, suggesting that the line broadening could not be simply due to solid NH_3 within the NMR tube. Finally, the compositions of all samples were determined after the NMR experiments, so that we consider that ammonia remained intercalated in the TiS_2 during the experiment.

We have also obtained ^1H NMR spectra for the partially deintercalated samples $TiS_2(NH_4)_{0.29}(NH_3)_{0.11}$, $TiS_2(NH_4)_{0.30}$, $TiS_2(NH_4)_{0.24}$ and $TiS_2(NH_4)_{0.15}$ (Figure 5). For all samples, the line width (ΔH) shows thermal behavior at first sight similar to that for the fully intercalated samples, with a motionally narrowed line (0.3 G) down to approximately 140–200 K, depending on the composition.

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(34) O'Bannon, G. W.; McKelvy, M. J.; Glaunsinger, W. S.; Marzke, R. F. *Solid State Ionics* **1989**, *32/33*, 167.

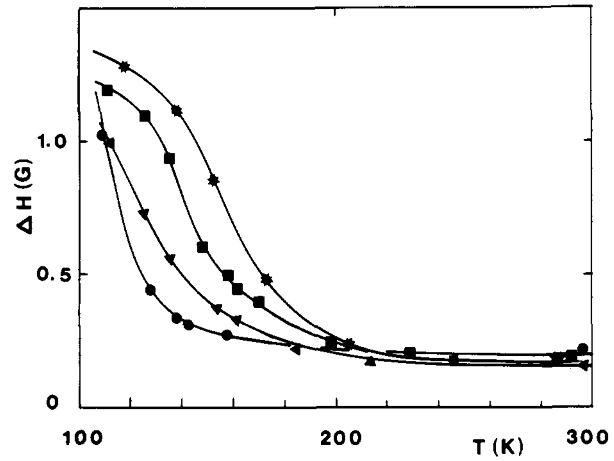

Figure 5. ^1H NMR line width (ΔH) as a function of temperature for $TiS_2(NH_4)_{0.29}(NH_3)_{0.11}$ (dots), $TiS_2(NH_4)_{0.30}$ (squares), $TiS_2(NH_4)_{0.24}$ (stars), and $TiS_2(NH_4)_{0.15}$ (triangles), measured in this study.

Like the fully intercalated sample, the line width then increases to reach a plateau, at least for $TiS_2(NH_4)_{0.24}$ and $TiS_2(NH_4)_{0.30}$. The line width for samples $TiS_2(NH_4)_{0.15}$ and $TiS_2(NH_4)_{0.29}(NH_3)_{0.11}$ had not reached a maximum value at the lowest temperature attained in this study. The line widths for the partially intercalated samples $TiS_2(NH_4)_{0.24}$ and $TiS_2(NH_4)_{0.30}$ at the plateau below the transition are much smaller ($\approx$1.3 G) than that measured for the fully intercalated sample. Similar observations were made by Nonte et al.[23] for ammonia-intercalated samples of TaS_2 and $RuCl_3$. This could be interpreted as being due to a longer average proton–proton distance, as the proton concentration in the van der Waals gap is decreased.

For $TiS_2(NH_4)_{0.29}(NH_3)_{0.11}$, the onset of the transition occurs at significantly lower temperature ($\approx$115 K) than for the fully intercalated sample, suggesting that the proton motions have a lower activation energy in the partially deintercalated sample. However, the onset of the transition occurs at higher temperature for the partially deintercalated samples, nominally containing only NH_4^+ component (Figure 4). For the two samples nominally containing both ammonia and ammonium species, the line-broadening transition occurs over a narrow temperature range (Figures 4 and 5), with an abrupt broadening of the single narrow line present at room temperature (Figure 6). The transition is slightly different for the samples nominally containing only ammonium species (Figure 6). On cooling below the transition temperature, the narrow line is joined by a second, broad component, whose intensity increases with decreasing temperature (Figure 6). Both lines are present simultaneously over the temperature range of the transition. For these samples, neither the line width nor the second moment are sufficient to fully describe the transition, although they give a useful indication of the location of the transition temperature. All of these observations will discussed further below, in the context of our new dynamical model for the intercalation compounds.

T_1 Relaxation Time Measurements. We also found some inconsistencies in the literature concerning measured T_1 relaxation times. For $TiS_2(NH_4)_x(NH_3)_y$, Wein et al.[22] found a double minimum in their T_1 vs T curves at 170 and 230 K, with T_1 values ranging from 50 to 150 ms (at 30 MHz). For $TiS_2(NH_4)_{0.22}(NH_3)_{0.37}$, O'Bannon et al.[21] reported minima at 167 and 336 K, with T_1 values of 15–100 ms (at 25 MHz). Our results for $TiS_2(NH_4)_{0.29}(NH_3)_{0.70}$ at 58 MHz (Figure 7) show only a single minimum at 200 K with T_1 ranging from 40 to 500 ms, confirming the results found by Kleinberg and Silbernagel.[10] The relaxation frequency at the temperature of the T_1 minimum is in excellent agreement with that obtained from the line-width studies of Silbernagel et al.,[9] described above.

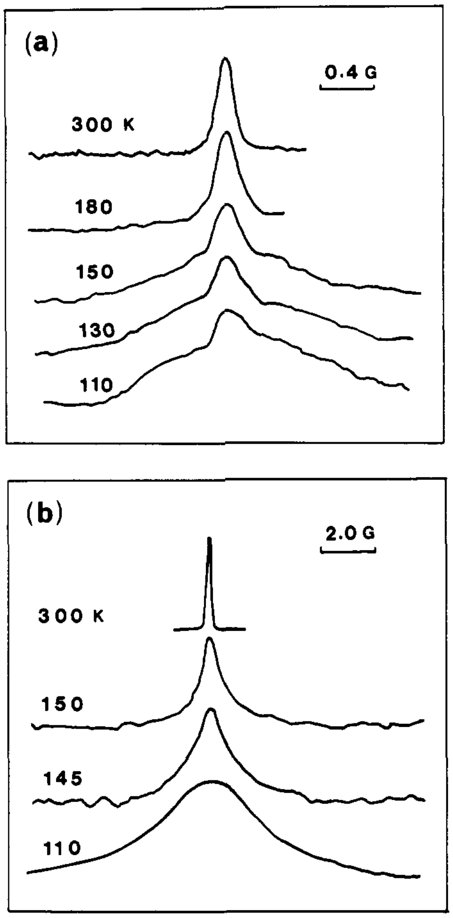

Figure 6. ^1H pulsed NMR spectra (1.36 T = 13.6 kG) of $TiS_2(NH_4)_{0.15}$ (a) and $TiS_2(NH_4)_{0.29}(NH_3)_{0.70}$ (b) recorded at various temperatures.

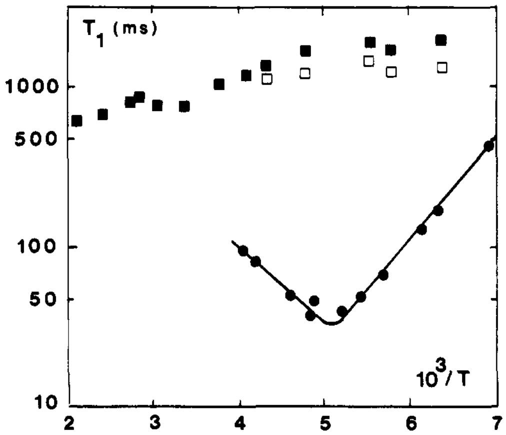

Figure 7. Temperature dependence of the proton spin–lattice relaxation time at 58 MHz for $TiS_2(NH_4)_{0.29}(NH_3)_{0.70}$ (dots) and $TiS_2(NH_4)_{0.30}$ (squares). The two T_1 values for $TiS_2(NH_4)_{0.30}$ at low T are extreme values obtained from the magnetization vs τ curves (see text).

For $TiS_2(NH_4)_{0.21}$, O'Bannon et al.[21] noticed no variation in T_1 over the temperature range 3–500 K (T_1 = 400 ms). In contrast, we observe a slight increase in T_1 with increasing temperature for a similar composition ($TiS_2(NH_4)_{0.30}$, Figure 7). On careful examination of the data for this compound, the magnetization vs τ curves

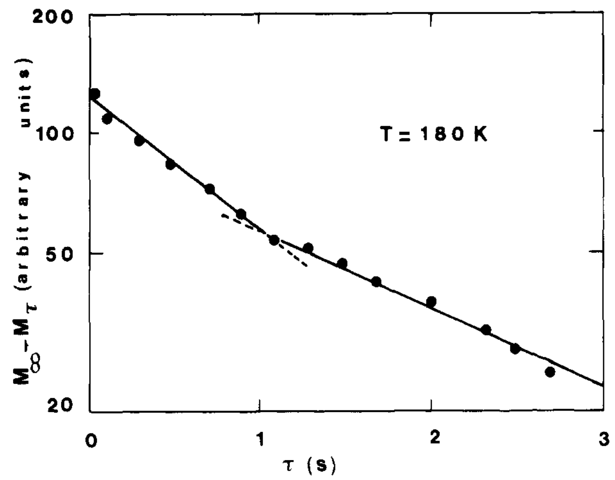

Figure 8. Recovery of the magnetization for the ^1H $^1/_2$–$^{-1}/_2$ transition in $TiS_2(NH_4)_{0.30}$ as a function of the time interval between π saturating RF pulse and the read pulse.

(from which the T_1 values are determined) are not straight lines (Figure 8), which means that there are at least two values of T_1, corresponding to different relaxation mechanisms, both with $T_1 \approx 1$–2 s (Figures 7 and 8). This could contribute to some of the error in determination of T_1 values as a function of temperature for partially deintercalated samples.

Discussion

In the currently accepted structural model for fully intercalated TiS_2–NH_3, both NH_3 and NH_4^+ exist as molecular species intercalated within the van der Waals gap. The statement of the presence of NH_4^+ is based indirectly on the observation of N_2 and H_2 gas evolved during intercalation and deintercalation, respectively.[12–15] There has been no direct observation of NH_4^+ species within the van der Waals gap, by neutron diffraction[18,19] or by high-resolution NMR spectroscopy. Glaunsinger et al.[35] have studied the compounds $TiS_2(NH_3)_{0.36}(NH_4^+)_{0.20}$ and $TiS_2(NH_4^+)_{0.20}$ by incoherent inelastic neutron scattering and assigned bands in the 200–600-cm^{-1} region to internal and external vibrations of NH_3 and NH_4^+ groups. However, these assignments are not unique, and the bands could correspond to other vibrations involving large proton displacements. In addition to the lack of direct verification of the existence of NH_4^+ species, the NH_3 (ND_3) groups observed within the van der Waals gap of TiS_2 have an unusual planar geometry, with unequal N–H (N–D) bond lengths.[19]

We propose an alternative structural model for ammoniate-intercalated TiS_2 and related MX_2 phases, which can rationalize both the unusual geometry of the NH_3 group and the elusive nature of the NH_4^+ groups. In this model, NH_3 and NH_4^+ do not exist as "molecular" species within the van der Waals gap. Instead, the MX_2 layers define sites in the centers of the trigonal prismatic cavities which are filled by N atoms. The N atoms and the MX_2 layers then define the 9d and 18h sites for H atoms within the van der Waals gap of the $R\bar{3}m$ intercalated structures (Figure 1). The N and H site occupancy is determined by local and long-range repulsive and attractive forces, including N–H and S–H attraction, and N···N and N···H repulsion. For a stoichiometry $MX_2 \cdot NH_3$, one-half of the interlayer trigonal prismatic sites are filled symmetrically with N atoms, as observed for the fully intercalated structures.[1] It is most probable (but not necessary) that each N atom is surrounded by three H atoms. The arrangement that provides the least H···H repulsion, by maximizing nonbonded H···H distances about each N atom, is that corresponding to the local site occupancy found by Young et al.[19] (Figure 1).

The redox reaction accompanying ammonia intercalation in most MX_2 phases is usually written

$$NH_3 + TiS_2 \rightarrow x/6\ N_2 + TiS_2^{x-}(NH_4^+)_x(NH_3)_y$$

where $4x/3 + y = 1$. In our model, we propose that the reaction is better written

$$NH_3 + TiS_2 \rightarrow \tfrac{1}{2}(1 - x)N_2 + TiS_2^{\delta-}N_xH_{3x+\delta}^{\delta+}$$

where $^1/_2(1 - x) = \delta/6$. In this way, the redox reaction is expressed not by formation of NH_4^+ molecular species within the van der Waals gap but by intercalation of excess protons in response to the acceptor behavior of the host lattice:

$$\delta/3NH_3 \rightarrow \delta/6N_2 + \delta H^+ + \delta e^-$$

$$TiS_2 + \delta e^- \rightarrow TiS_2^{\delta-}$$

The δ excess protons then occupy previously unfilled 9d or 18h sites about the N atoms within the structure. This model rationalizes the lack of observable NH_4^+ species within the intercalated structures: these simply correspond to additional protons occupying the same set of crystallographic sites defined for the H atoms within the van der Waals gap. Within the context of the model, it seems more useful to describe the "NH_3" (and "NH_4^+") groups as different local site occupancy patterns within the crystals, rather than as perturbed molecular species.

Whatever the chosen structural description for the ammoniated MX_2 phases, any static view of their structure has only limited value, because of the rapid proton exchange and tunnelling motions indicated by the results of NMR spectroscopy. Our high-field ^1H MAS NMR experiment for partially intercalated TiS_2 showed only a single line, indicating that there is rapid (>3 × 10^8 s^{-1}) chemical exchange between any protonated species within the van der Waals gap, at room temperature. The ^1H pulsed NMR experiments at low field showed a single narrow line at room temperature, which undergoes a line-broadening transition below 180 K, for a range of samples with different nominal NH_3 and NH_4^+ contents. The fact that only a single line-broadening transition is observed at approximately the same temperature for all of the samples investigated in this study suggests that a single relaxation mechanism is involved. As discussed above, Silbernagel et al.[9] recognized that the line-broadening transition at ≈120 K for fully intercalated TaS_2–NH_3 and TiS_2–NH_3 was associated with freezing a proton-diffusive motion. We propose that the proton transfer responsible for the observation of a single narrow ^1H MAS NMR peak at room temperature is in fact the same motion and that the line-broadening transition occurring in the 130–180 K range (considering all the samples) in our NMR experiments at lower field corresponds to freezing the proton exchange. Using the activation energy and preexponential attempt frequency calculated by Silbernagel et al. gives a relaxation frequency of approximately 3 × 10^9 s^{-1} at room temperature, consistent with the observation of a single line in the room-temperature MAS NMR experiment at 300 MHz. Silbernagel et al.[9] had rejected the possibility that chemical exchange might be responsible for the fully narrowed lines at room temperature, presumably because work such as that of Ogg[31,32] on pure liquid NH_3 had demonstrated that proton exchange was

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(35) Glaunsinger, W. S.; McKelvy, M. J.; Larson, E. M.; von Dreele, R. B.; Eckert, J.; Ross, N. L. *Solid State Ionics* **1989**, *34*, 281.

slow. However, Ogg[31,32] and O'Reilly et al.[33] showed that addition of traces of H_2O or salts resulted in an increase in the proton-exchange rate by many orders of magnitude, so that there is no reason to discount a rapid proton-exchange reaction between the ammoniated species in the van der Waals gap of MX_2 phases.

At room temperature, the proton NMR line width is fully narrowed, so that all of the protons participate in the diffusive motion. The powder neutron diffraction study of Young et al.[19] indicated that the protons occupy 9d and 18h sites around the N atoms in the van der Waals gap of the $R\bar{3}m$ structure (Figure 1). As noted above, the distorted NH_3 geometry proposed by these workers represents only one possible site occupancy scheme of the 9d and 18h sites. For the crystal to have global $R\bar{3}m$ symmetry, all of these sites must be statistically occupied, via either a static or dynamic disordering mechanism, at room temperature and at 12 K. We suggest that, at all temperatures, the disorder is dynamic in nature, consistent with the results of the NMR experiments. At room temperature, the dynamic disorder is mainly due to proton diffusion within the van der Waals gap, via proton-exchange reactions among the 9d and 18h sites on different N atoms.

In their neutron structure refinement, Young et al.[19] found essentially no difference between the structure of the intercalate at 300 and 12 K. At temperatures below the line-broadening transition, the proton-exchange mechanism occurs on a time scale longer than the NMR time scale, longer than 10^{-5}–10^{-6} s, and is no longer effective in averaging the dipole–dipole broadening interactions. However, the low-temperature line width measured for the fully intercalated samples (approximately 3–4 G) is much smaller (by several gauss) than that expected for a rigid lattice of protons from second moment calculations, indicating that some proton motion persists below 100 K. Silbernagel et al.[9] suggested that this low-temperature motion was due to proton tunnelling, associated with rotation of the NH_3 molecules about their C_3 axes, and that this persisted to temperatures of a few kelvin, because no additional line-broadening transition was observed down to 4 K[9,34] (although Nonte et al.[23] have recently reported the onset of an additional line-broadening transition at 10–30 K for fully ammoniated samples of TaS_2 and $RuCl_3$). Within the context of our model, we suggest that the proton-tunnelling mechanism, which persists to liquid helium temperatures, corresponds to protons tunneling between adjacent 9d and 18h sites about a given N atom, which are separated only by distances on the order of 0.7–0.9 Å. This gives rise to a dynamic disordering mechanism at low temperature, consistent with the space group symmetry determined at 12 K.[19] Also within the context of our new model, the anisotropy in the proton T_1 relaxation time in TaS_2–NH_3 at room temperature observed by Gamble and Silbernagel[20] and ascribed to rotation of rigid NH_3 groups about a preferred orientation (parallel to the layers) of the molecular C_3 axis, is reinterpreted as proton hopping between 9d and 18h sites about the N atoms. This would be equally consistent with the NMR observations.

On cooling to the temperature of the line-broadening transition in the 100–200 K region, the proton diffusive motions between sites around different N atoms are frozen. The number of protons frozen about any given N atom will depend on local bonding (N–H vs S–H) requirements and H···H repulsions, as the sample is cooled through the transition. On the basis of the known stability of NH_3 and NH_4^+ compounds, most nitrogen atoms will probably be surrounded by three or four protons occupying 9d and 18h sites, at least for highly intercalated samples. However, there may be some other, statistical distribution of site occupancies, with some nitrogen atoms being surrounded by more or fewer protons in the frozen configuration.

Finally, we noted above a number of differences in the detailed line-shape changes between samples with different intercalate content, on cooling through the line-broadening transition. These observations raise a number of additional intriguing possibilities for the structure and proton dynamics of these intercalated phases. For the samples nominally containing both "NH_3" and "NH_4^+", the spectra contain a single line (Figure 6b) and the transition is abrupt (Figures 4 and 5). This indicates that all the protons behave in the same way and that all the proton diffusion is frozen out over a narrow temperature range. For the "NH_4^+"-only samples, two lines are present simultaneously over the temperature range of the transition (Figure 6a), and hence two proton diffusion pathways must operate, one that remains active to the lower temperature limit (the narrower line) and one that is frozen out at the onset of the transition (the broader line). The difference in behavior of the two sets of samples can be related to their nitrogen content.

First, we note that a fully narrowed line is observed for $TiS_2(NH_4)_{0.15}$, indicating that proton diffusion occurs down to 180 K. This material has a composition well below the percolation threshold for proton hopping between sites around different N atoms; i.e., there are no continuous pathways between adjacent N atoms for proton diffusion. The fact that the line-broadening transition observed for this sample is similar to those of all the samples studied suggests that the proton dynamics are similar and that the protons are not confined to the environment of a single N atom but diffuse throughout the van der Waals gap. In addition, it was noted in the previous section that the ^1H line width after the blocking transition decreases with decreasing proton concentration. This is consistent with longer average H···H distances for lower intercalate concentrations, which implies that the protons are diluted in the van der Waals gap and that the frozen protons are distributed evenly over sites within the gap and not all localized within the vicinity of N atoms. Accordingly, we suggest that there are two pathways for proton diffusion: one involving 9d and 18h sites around and between adjacent N atom sites (*N-site diffusion pathway*), and a second that connects N sites which are not adjacent and that involves the formation of transients S–H bonds (*S-site pathway*).

Ritter et al.[36] have studied H_xTiS_2 intercalates using ^1H NMR spectroscopy. These hydrogen bronzes exhibit proton diffusion at room temperature due to hopping between S–H bound sites within the van der Waals gap, and a ^1H NMR line-broadening transition (between room temperature and 215 K) is observed due to freezing of this motion at low temperature. The H_xTiS_2 intercalates differ from the ammonia-intercalated compounds in that they exhibit the same ··ABAB·· sulfur stacking as the pristine (1T) TiS_2 structure. One plane of octahedral voids and two planes of tetrahedral voids between the host layers are available for hydrogen. As discussed by Ritter et al.,[36] the smaller tetrahedral sites with four lone-pair orbitals from the sulfur atoms provide a higher electron density to trap the H^+ ion than do the larger octahedral sites. For this reason, they suggested that the protons in H_xTiS_2 are located at the center of the tetrahedral sites, forming four

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(36) Ritter, C.; Müller-Warmuth, W.; Schöllhorn, R. *Solid State Ionics* **1986**, *20*, 283.

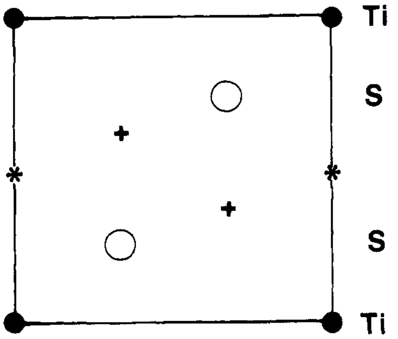

Figure 9. (110) section of the hexagonal cell of TiS_2 showing the tetrahedral (+) and octahedral voids (*) in the van der Waals gap available for protons.

S–H bonds of length ≈2.2 Å. This allows the formation of hydrogen bonds with the sulfur next-nearest neighbours at approximately 3.4 Å (Figure 9), providing a low-energy pathway for proton diffusion via transient formation and switching of S–H···S bonds. Because the sulfur stacking sequence in the fully ammoniated samples is ··AA··, giving large trigonal prismatic sulfur sites within the van der Waals gap, this low-energy pathway for proton diffusion via S–H···S sites is not possible. However, it is possible that as the nitrogen content decreases, a local distortion of the sulfur stacking sequence occurs, rendering proton diffusion via S sites more likely. It has recently been shown that $TiS_2(NH_4)_{\approx 0.2}$ is a six-layer stage-II intercalate with a 6R structure in which half the layers exhibit the (1T) TiS_2 structure with a van der Waals gap assumed to be free of intercalant.[28] These layers could well contain some of the excess protons.

The kinetics of diffusion within these two types of sites must be different. As the N content is decreased, the ratio of N-site to S-site diffusion will also decrease, and the character of the line-shape changes through the transition will vary, as observed. We propose that the sharp line-broadening transition observed for $TiS_2(NH_4)_{0.29}(NH_3)_{0.70}$ and $TiS_2(NH_4)_{0.29}(NH_3)_{0.11}$, with onset at approximately 130 K, corresponds to proton diffusion along N-site pathways. It is of interest that the transition occurs at lower temperature (115 vs 130 K) in $TiS_2(NH_4)_{0.29}(NH_3)_{0.11}$, compared with the fully intercalated sample $TiS_2(NH_4)_{0.29}(NH_3)_{0.70}$, indicating a smaller activation energy. The narrow line component in samples $TiS_2(NH_4)_{0.30}$, $TiS_2(NH_4)_{0.24}$, and $TiS_2(NH_4)_{0.15}$, which persists to approximately 110 K, corresponds to the same diffusion pathway, but the broader component, which begins to appear below approximately 180 K, corresponds to protons diffusing along S-site pathways, which begin to be frozen out at higher temperature. This would be generally consistent with the results of Ritter et al.:[36] the onset of the proton blocking transition in H_xTiS_2 occurs at higher temperature than in the ammonia-intercalated samples and is smeared over a wider temperature range.

For $TiS_2(NH_4)_{0.30}$, no minimum is observed in the T_1 vs $1/T$ plot, because the data are intersected by the deintercalation temperature before a minimum is reached (Figure 7). The slope is shallower than for the fully intercalated sample, indicating a higher activation energy for the proton diffusion process. In addition, the minimum would occur at considerably higher temperature than for the fully intercalated sample, implying a smaller value of the relaxation frequency at a given temperature. These observations suggest a more difficult proton diffusion process in partially intercalated TiS_2, below a threshold $NH_{3+\delta}$ content, consistent with the structural model presented here. For high degrees of intercalation, proton diffusion proceeds via the least energetic N-site pathway, and T_1 is rapid. As the N content decreases, especially below the percolation threshold composition, the higher energy S-site diffusion pathway becomes dominant, and distances between proton dipolar moments become greater, resulting in a smaller contribution to the magnetic relaxation of the proton spins, and T_1 relaxation times increase.

Our new model for ammonia intercalation in TiS_2 and related transition-metal dichalcogenides has several consequences for the chemistry and physical properties of these materials. We propose that these compounds should be good proton conductors, within the plane of the van der Waals gap, at room temperature, down to the temperature of the diffusion blocking transition at 100–200 K. As discussed above, intercalation involves decoupling of the N and H atoms within the crystallographic sites defined in the van der Waals gap. Any redox reaction accompanying intercalation is best described as intercalation of excess protons, which occupy existing vacant crystallographic sites within the van der Waals gap, with donation of electronic charge to the host MX_2 layers (one exciting possibility is that the proton diffusive motions might be coupled to charge density waves in the host layers). If the ammonia is cointercalated with alkali-metal ions, the charge donation is provided by the alkali metal, and there is a corresponding reduction in the excess proton concentration.[14,29,34,37]

During the first stage of deintercalation, some of the N atoms and hydrogen atoms recombine at the crystal edge to reform NH_3 molecules, and the excess protons remain in the lattice. On completing the deintercalation process at higher temperature, the electronic charge balance of the host lattice is restored, the excess protons are reduced to form H_2 molecules, and the rest of the N and H atoms simultaneously recombine to form NH_3 molecules. If the recombination reactions take place atomically close to the crystal surface, this might provide an interesting site for catalytic activity, especially for hydrogenation.

In conclusion, we suggest that in fully intercalated TiS_2–NH_3, N atoms occupy all the available trigonal prismatic sites within the van der Waals gap. Hydrogen atoms are randomly distributed over the 9d and 18h sites shown in Figure 1. There is an excess of protons (δ) over the NH_3 stoichiometry, due to redox reactions with the host material. At room temperature, the protons diffuse freely within the van der Waals gap, the vacant 18h and 9d sites defined by the N sublattice providing low-energy pathways for this diffusive motion. On cooling to below 110 K, the proton diffusion becomes slow, but rapid tunnelling between proton sites continues to occur. As the N content is decreased, the behavior of the protons is similar, but at some critical nitrogen content, itinerant protons at room temperature begin to sample sites determined not by the N atoms but by the S atoms lining the van der Waals gap of the host lattice. This change in diffusion mechanism may be accompanied by a change in the local sulfur stacking sequence forming the van der Waals gap from ··AA·· to ··AB·· as found in the pristine host lattice and H_xTiS_2 hydrogen bronzes.

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(37) Young, V. G.; McKelvy, M. J.; Glaunsinger, W. S.; von Dreele, R. B. *Chem. Mater.* **1990**, 2, 75.