

# Structural Investigation of Lithium-Ammonia Intercalation Compounds of $\text{TiS}_2$ \*

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The structures of two lithium-ammonia intercalation compounds of  $\text{TiS}_2$  have been determined by Rietveld refinement of time-of-flight neutron powder diffraction data taken at 300 and 12 K.  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  and  $\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  are best described as 3R polytypes in the  $R\bar{3}m$  space group throughout the temperature range investigated. The former compound has  $a = 3.4234$  (1) Å and  $c = 26.8235$  (13) Å at 300 K and  $a = 3.412$  (8) Å and  $c = 26.4921$  (11) Å at 12 K, whereas the latter material has  $a = 3.42064$  (9) Å and  $c = 26.7754$  (12) Å at 300 K and  $a = 3.40928$  (9) Å and  $c = 26.4471$  (13) Å at 12 K. Available evidence strongly suggests lithium is coordinated to three ammonia molecules in the van der Waals gap of the former compound. The ammonia molecules are distorted from their normal pyramidal geometry in trigonal prismatic sites and have their pseudo- $C_3$  axes parallel to the  $\text{TiS}_2$  sheets. The distance from nitrogen to the deuterium plane for ammonia increases with increasing  $\text{Li}^{+}$  concentration. The ammonium cation is spherically disordered in trigonal prismatic sites. The substitution of  $\text{ND}_4^{+}$  for  $\text{Li}^{+}$  results in a contraction of the  $\text{TiS}_2$  octahedra parallel to the host layers and an elongation of the octahedra perpendicular to the host layers. These compounds exhibit an anisotropic strain of  $\sim 0.18\%$  along the [001] direction and essentially no strain perpendicular to [001].

## Introduction

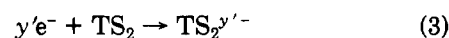
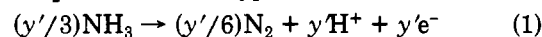
The intercalation of Lewis bases into lamellar transition metal dichalcogenide ( $\text{TX}_2$ ) hosts is of considerable interest in materials chemistry. The resulting compounds exhibit intriguing properties, such as unusual redox chemistry, charge density waves, and anisotropic superconductivity,<sup>1-13</sup> which has provided strong motivation for research in this field. However, very few detailed structural studies of these intercalation compounds have been undertaken.<sup>14,15</sup>

Ammoniated transition metal disulfide compounds have been the subject of numerous chemical and physical studies.<sup>1,4,7,9,10,16-29</sup> It has been demonstrated that the intercalation of ammonia into  $\text{TS}_2$  ( $T = \text{Ti, Ta, Nb}$ ) is accompanied by the co-intercalation of the ammonium cation.<sup>1,4,7</sup> The materials prepared by this reaction are best described by the ionic formulation  $(\text{NH}_4^{+})_x(\text{NH}_3)_y\text{TS}_2^{y-}$ .

Recently, the structure of  $(\text{ND}_4^{+})_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$  has been determined by Rietveld analysis of time-of-flight neutron powder diffraction data ( $R_{\text{wp}} = 0.0285$ ,  $R_p = 0.0196$ , and  $R_e = 0.0233$ ).<sup>14</sup> The space group was found to be  $R\bar{3}m$ , with both  $\text{ND}_3$  and  $\text{ND}_4^{+}$  randomly occupying available trigonal prismatic sites in the van der Waals gap. The nitrogen atoms of both  $\text{ND}_3$  and  $\text{ND}_4^{+}$  are located at the center of the trigonal prismatic sites, as found by a previous X-ray powder diffraction study.<sup>18</sup> The pseudo- $C_3$  axis of  $\text{ND}_3$  is parallel to the host layers, which is consistent with NMR spin-lattice relaxation studies<sup>21,27</sup> and the location of nitrogen determined by X-ray powder diffraction. However, the  $\text{ND}_3$  adopts a distorted planar geometry, with two deuterium atoms hydrogen bonded to the sulfur atoms of opposing  $\text{TiS}_2$  sheets within a trigonal prismatic site and the remaining deuterium atom located in the interlayer midplane, as shown in Figure 1.

Previous research has demonstrated that the extent of ammonia oxidation in  $\text{TS}_2$  hosts can be reduced by intercalation of an alkali metal prior to the intercalation of

ammonium.<sup>29,30</sup> Ammonia oxidation is achieved by eqs 1-3, where  $\text{N}_2$  is formed as a byproduct with the electrons



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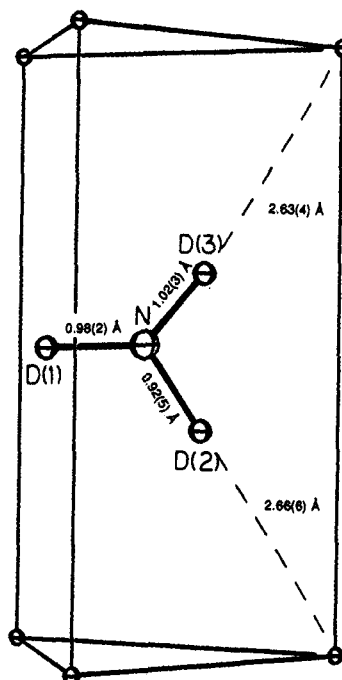


Figure 1. Orientation of planar intercalated  $\text{ND}_3$  in an interlayer trigonal prism of sulfur atoms in  $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$ .

generated reducing the  $\text{TiS}_2$  host layers, while  $\text{H}^+$  combines with  $\text{NH}_3$  and cointercalates as  $\text{NH}_4^+$ .<sup>4</sup> Ammonia oxidation in the absence of such metals proceeds to the composition  $(\text{NH}_4^+)_{x'}(\text{NH}_3)_{y'}\text{TiS}_2^{y'-}$ , where  $y' = 0.22$  after exposure of  $\text{TiS}_2$  to liquid ammonia for 2 days.<sup>29</sup> If an alkali metal is dissolved in ammonia prior to exposure to the host material and the resulting solution is poured onto the host, the metal intercalates rapidly relative to ammonium. The much slower oxidation of ammonia by  $\text{TiS}_2$  ceases at a charge transfer of approximately 0.22 mol of  $e^-/\text{mol}$  of  $\text{TiS}_2$ ,<sup>30,31</sup> which allows a wide variety of mixed cationic intercalation compounds to be prepared by intercalating alkali metal-ammonia solutions into  $\text{TiS}_2$ .

Many members of the  $\text{Li}_x(\text{NH}_4^+)_{y'}(\text{NH}_3)_{y'}\text{TiS}_2^{(x+y')-}$  series,  $x + y' = 0.22 \pm 0.02$ , have been thoroughly characterized in our laboratories.<sup>30,31</sup> The availability of these well-characterized materials has set the stage for structural refinements of selected compositions of this series. In this investigation, we report the results of Rietveld refinements of time-of-flight neutron powder diffraction data for two separate compounds. The first,  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$ , has been intercalated with sufficient Li to prevent ammonium formation. The second,  $\text{Li}^{+}_{0.11}(\text{ND}_4^+)_{0.11-}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$ , is a mixed-cation intercalation compound with lithium and ammonium in equal concentrations. The results of this study provide structural evidence for the formation of discrete lithium-ammonia complexes in the former intercalate as well as the existence of distorted ammonia molecules in both materials.

### Experimental Section

Highly stoichiometric  $\text{TiS}_2$  was prepared by direct reaction of the elements using 40 mg/cm<sup>3</sup> of excess sulfur at 913 K, as de-

scribed previously.<sup>31,32</sup> Thermogravimetric analysis (TGA) indicated a stoichiometry of  $\text{Ti}_{1.002(1)}\text{S}_2$ . The deuterated ammonia (99.5%, Cambridge Isotope Laboratories) was distilled from its sodium-ammonia solution to prevent water contamination. The  $\text{ND}_3$  purity (in deuterium) was confirmed by mass spectrometric analysis. Lithium (99.84%  $^7\text{Li}$ , Oak Ridge) was cut and weighed as needed. Both the host and intercalated materials were handled exclusively in a helium-filled Vacuum Atmospheres Model MO-40-1H drybox (<1 ppm  $\text{H}_2\text{O}$  and  $\text{O}_2$ ) and were removed from the drybox only in leak-checked, sealed containers. All vacuum-line work was done in vessels previously flamed and evacuated to  $10^{-5}$  Torr.

The preparation of the  $\text{Li}-\text{NH}_3$  intercalation compounds of  $\text{TiS}_2$  has been described elsewhere.<sup>30,31</sup>  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  was prepared by dissolving 70.2 mg of  $^7\text{Li}$  in an excess of  $\text{ND}_3$  and then pouring this solution, with vigorous shaking, onto 4.993 g of  $\text{TiS}_2$ .  $\text{Li}^{+}_{0.11}(\text{ND}_4^+)_{0.11-}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  was prepared in a similar fashion by using 31.05 mg of  $^7\text{Li}$  and 4.601 g of  $\text{TiS}_2$ . The reactions were allowed to go to completion, and the products were sealed at  $-196^\circ\text{C}$  under vacuum and annealed for several days at ambient temperature to achieve equilibrium stage-I intercalates.<sup>14,29</sup> TGA<sup>4,14,30,31</sup> was used to quantify the ammonia and ammonium compositions.

X-ray powder diffraction (XPD) patterns were obtained by using a Debye-Scherrer camera, as described previously.<sup>14,30,31</sup> Both  $\text{Cu K}\alpha_1$  and  $\text{Cu K}\alpha_2$  reflections were observed below about  $d = 1.00$  Å, and for these reflections the  $d$  spacings were calculated from the  $\text{Cu K}\alpha_1$  reflections.

Neutron powder diffraction (NPD) time-of-flight (TOF) data sets were collected on the general purpose powder diffractometer (GPPD) at the intense pulsed neutron source (IPNS) at Argonne National Laboratory. The samples were loaded into vanadium sample containers in a helium-filled drybox and then sealed by using indium wire. Data sets were collected at 300 and 12 K for about 1 day each.

The data were analyzed by the Rietveld method<sup>33</sup> using the generalized structure analysis system (GSAS) programs.<sup>34</sup> The data collected by the 150° bank of detectors in the range 0.6–3.0 Å were selected for refinement, except for the 12 K collection for  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$ , where the statistics supported the inclusion of data in the range 0.5–3.0 Å. Positions for titanium, sulfur, and nitrogen were obtained from previous XPD<sup>18</sup> and NPD<sup>14</sup> studies. The background was fitted with a refineable 12-term cosine Fourier series, including a leading constant term. Preferred orientation (along [001]), background, scale, and atomic positional and isotropic thermal parameters were refined and converged. Multiple difference Fourier maps revealed the positions of the deuterium and lithium atoms. In the case of  $\text{Li}^{+}_{0.11}(\text{ND}_4^+)_{0.11-}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  no deuterium atoms could be found for the ammonium cation, so it was assumed they were spherically disordered. This disorder was modeled by having the  $\text{ND}_4^+$  deuteriums partially occupy the vertices of a dodecahedron with a fixed N–D length of 1.04 Å. Subsequent refinements did not show an improvement if the nitrogen contributions from  $\text{ND}_3$  and  $\text{ND}_4^+$  were refined separately.

### Results and Discussion

#### Compositional and Structural Characterization.

Figure 2 shows the TGA thermal deintercalation curves of both materials used for structural investigation. Figure 2a displays the deintercalation curve for  $\text{Li}^{+}_{0.23-}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$ . The mass loss as the sample is heated is due to  $\text{ND}_3$  deintercalation.<sup>30</sup> Figure 2b shows the more complex deintercalation curve for  $\text{Li}^{+}_{0.11}(\text{ND}_4^+)_{0.11-}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$ , where  $\text{ND}_3$  is evolved for the low-temperature step and “ $\text{ND}_4^+$ ” deintercalates via decomposition into  $\text{ND}_3$  and  $1/2\text{D}_2$  for the higher temperature step.<sup>30</sup> The experimental error for the composition of  $\text{ND}_3$  and  $\text{ND}_4^+$

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Table I. Neutron Time-of-Flight Parameters for Lithium-Ammonia Intercalation Compounds of  $\text{TiS}_2$ 

	$\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$		$\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$	
	300 K	12 K	300 K	12 K
space group	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$
cell constants, Å				
<i>a</i>	3.4234 (1)	3.41213 (8)	3.42064 (9)	3.40928 (9)
<i>c</i>	26.8235 (13)	26.4921 (11)	26.7754 (12)	26.4471 (13)
detector bank, deg	150	150	150	150
data range, Å	0.6–3.0	0.5–3.0	0.6–3.0	0.6–3.0
no. of contributing rflctns	219	341	218	206
no. of degrees of freedom	4717	4919	4717	4717
$R_{\text{wp}}^a$	0.0232	0.0287	0.0246	0.0290
$R_p^b$	0.0167	0.0213	0.0179	0.0209
$R_e^c$	0.0163	0.0177	0.0180	0.0176
$\chi^2_d$	2.01	2.63	1.87	2.71

<sup>a</sup>  $R_{\text{wp}} = [\sum [w^*|I_{(\text{obsd})} - I_{(\text{calc})}|]^2 / \sum [w^*I_{(\text{obsd})}^2]]^{1/2}$ , where  $w^*$  is the computed weight. <sup>b</sup>  $R_p = \sum [|I_{(\text{obsd})} - I_{(\text{calc})}|] / \sum [I_{(\text{obsd})}]$ . <sup>c</sup>  $R_e = R_{\text{wp}} / [\chi^2]^{1/2}$ . <sup>d</sup>  $\chi^2 = [\sum [w^*|I_{(\text{obsd})} - I_{(\text{calc})}|]^2 / (N_{\text{obs}} - N_{\text{var}})]$ .

Table II. Positional and Thermal Parameters for  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  at 300 and 12 K

atom	x	y	z	Wyckoff site	occupancy	$U_{\text{iso}}$
300 K						
Ti	0	0	0	3a	3	0.0113 (7)
S	$1/3$	$2/3$	0.05291 (8)	6c	6	0.0085 (6)
N	$2/3$	$1/3$	0.1662 (3)	6c	1.89	0.082 (1)
D(1)	$1/3$	0.095 (6)	$1/6$	18g	1.89	0.117 (6)
D(2)	0.883 (4)	0.442	0.1343 (9)	18h	1.89	0.112 (5)
D(3)	0.892 (4)	0.446	0.1965 (7)	18h	1.89	0.107 (4)
Li	$1/3$	$2/3$	$1/6$	3b	0.675	0.069 (7)
12 K						
Ti	0	0	0	3a	3	0.0037 (4)
S	$1/3$	$2/3$	0.05371 (6)	6c	6	0.0022 (3)
N	$2/3$	$1/3$	0.1655 (1)	6c	1.89	0.0191 (5)
D(1)	$1/3$	0.000 (4)	$1/6$	18g	1.89	0.118 (4)
D(2)	0.894 (2)	0.447	0.1367 (3)	18h	1.89	0.042 (2)
D(3)	0.830 (2)	0.415	0.1961 (4)	18h	1.89	0.055 (2)
Li	$1/3$	$2/3$	$1/6$	3b	0.675	0.009 (2)

in both compounds is  $\pm 0.01$ .

XPD results for both of these compounds immediately after opening the reaction vessels in the drybox did not reveal single-phase, 3R-type stage-I compounds. Instead, an admixture of primarily stage-I and secondarily higher staged material was found. Also, all [00 $\ell$ ] reflections were severely broadened. This behavior is due to rapid  $\text{ND}_3$  loss, which occurs initially upon opening reaction ampoules containing freshly prepared compounds and results in substantial intercalate disorder.<sup>29</sup> To allow the intercalates to come to thermodynamic equilibrium, the samples were transferred in the drybox to Pyrex ampoules, sealed off on the vacuum line at  $10^{-5}$  Torr while the samples were kept at 77 K, and then annealed at ambient temperature. This process facilitates the guest species attaining a homogeneous distribution throughout the host. After several days at 300 K, the intercalates were monophasic and adopted their equilibrium stage-I, 3R polytype structures.

**NPD Rietveld Refinement.** The TOF refinement parameters are given in Table I. The refined atomic coordinates ( $x, y, z$ ) and isotropic thermal parameters ( $U_{\text{iso}}$ ) at 300 and 12 K are shown in Tables II and III for  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  and  $\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$ , respectively. The final difference plots for the NPD Rietveld refinements for both intercalates at 300 K are shown in Figure 3. Pertinent bond distances and angles for both compounds at 300 and 12 K are given in Table IV.

From Table I it follows that the  $c$  cell parameters for both intercalates contract on average 0.33 Å, which corresponds to a contraction of 1.2%, upon cooling from ambient temperature to 12 K. This contraction is most likely due to the decreased thermal motion of the guest species at lower temperatures, as indicated in Tables II and III.

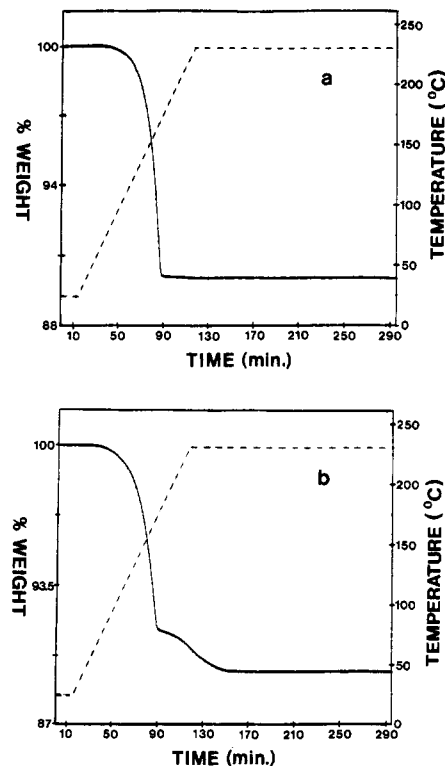


Figure 2. TGA curves for  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  (a) and  $\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  (b). The solid line represents weight as a function of time, while the dashed line represents temperature as a function of time.

A similar effect was observed in the structural study of  $(\text{ND}_4^{+})_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$ .<sup>14</sup> In contrast, the  $a$  cell pa-

Table III. Positional and Thermal Parameters for  $\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  at 300 and 12 K

atom	x	y	z	Wyckoff site	occupancy	$U_{\text{iso}}$
300 K						
Ti	0	0	0	3a	3	0.0143 (6)
S	$\frac{1}{3}$	$\frac{2}{3}$	0.05307 (7)	6c	6	0.0069 (5)
N	$\frac{2}{3}$	$\frac{1}{3}$	0.1661 (5)	6c	1.947	0.125 (2)
D(1)	$\frac{1}{3}$	0.120 (8)	$\frac{1}{6}$	18g	1.6141	0.103 (6)
D(2)	0.880 (6)	0.440	0.136 (1)	18h	1.6141	0.126 (7)
D(3)	0.883 (6)	0.4415	0.1950 (9)	18h	1.6141	0.124 (7)
Li	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{6}$	3b	0.324	0.049 (9)
D(11)	$\frac{2}{3}$	$\frac{1}{3}$	0.12774	6c	0.0666	0.11
D(12)	$\frac{2}{3}$	$\frac{1}{3}$	0.20559	6c	0.0666	0.11
D(13)	0.83788	0.41894	0.13648	18h	0.0666	0.11
D(14)	0.49546	0.24772	0.19687	18h	0.0666	0.11
D(15)	$\frac{2}{3}$	0.62607	0.17966	36i	0.0666	0.11
D(16)	0.37993	$\frac{1}{3}$	0.15369	36i	0.0666	0.11
12 K						
Ti	0	0	0	3a	3	0.0062 (6)
S	$\frac{1}{3}$	$\frac{2}{3}$	0.0535 (7)	6c	6	0.0003 (4)
N	$\frac{2}{3}$	$\frac{1}{3}$	0.1651 (2)	6c	1.947	0.0459 (8)
D(1)	$\frac{1}{3}$	0.114 (4)	$\frac{1}{6}$	18g	1.6141	0.054 (3)
D(2)	0.903 (3)	0.452	0.1343 (5)	18h	1.6141	0.045 (3)
D(3)	0.837 (3)	0.4186	0.1989 (4)	18h	1.6141	0.045 (3)
Li	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{6}$	3b	0.324	-0.009 (3)
D(11)	$\frac{2}{3}$	$\frac{1}{3}$	0.12730	6c	0.0666	0.045
D(12)	$\frac{2}{3}$	$\frac{1}{3}$	0.20603	6c	0.0666	0.045
D(13)	0.83839	0.41919	0.13607	18h	0.0666	0.045
D(14)	0.49494	0.24747	0.19727	18h	0.0666	0.045
D(15)	$\frac{2}{3}$	0.62091	0.17981	36i	0.0666	0.045
D(16)	0.37909	$\frac{1}{3}$	0.15363	36i	0.0666	0.045

Table IV. Interatomic Distances and Bond Angles for Lithium-Ammonia Intercalation Compounds of  $\text{TiS}_2$ 

	$\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$		$\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$	
	300 K	12 K	300 K	12 K
Bond Lengths, Å				
Ti-Ti	3.4234 (1)	3.41213 (8)	3.42064 (9)	3.40935 (9)
Ti-S	2.433 (1)	2.430 (1)	2.433 (1)	2.424 (1)
S-S	3.4234 (1)	3.41213 (8)	3.42064 (9)	3.40935 (9)
S-S	3.459 (4)	3.461 (3)	3.461 (3)	3.446 (3)
N-Li	1.9766 (2)	1.9702 (5)	1.9750 (1)	1.96857 (8)
N-D(1)	1.018 (5)	1.139 (7)	1.001 (5)	1.001 (2)
N-D(2)	1.07 (2)	1.016 (8)	1.02 (2)	1.08 (1)
N-D(3)	1.05 (2)	0.946 (9)	1.00 (2)	1.01 (1)
D(2)...S	2.56 (2)	2.554 (9)	2.60 (3)	2.49 (1)
D(3)...S	2.60 (2)	2.66 (1)	2.65 (2)	2.59 (1)
D(1)-D(2)	1.86 (2)	1.897 (8)	1.82 (2)	1.896 (8)
D(1)-D(3)	1.86 (1)	1.759 (8)	1.80 (2)	1.724 (8)
D(2)-D(3)	1.67 (4)	1.59 (2)	1.57 (4)	1.72 (2)
Bond Angles, deg				
D(1)-N-D(2)	126.3 (10)	126.4 (5)	128 (2)	130.9 (6)
D(1)-N-D(3)	127 (1)	114.8 (4)	128 (2)	117.7 (5)
D(2)-N-D(3)	104 (1)	107.7 (6)	102 (2)	110.1 (7)
N-D(2)...S	175 (1)	169.1 (5)	173 (1)	170.6 (6)
N-D(3)...S	171 (1)	176.9 (5)	171 (2)	175.4 (5)
S-Ti-S	89.41 (6)	89.12 (5)	89.33 (5)	89.38 (5)
Li-N-D(1)	74.0 (11)	90.0 (6)	69.2 (12)	70.3 (6)
Li-N-D(2)	107.8 (4)	110.1 (2)	108.4 (5)	109.4 (3)
Li-N-D(3)	108.2 (5)	104.0 (2)	108.3 (6)	103.7 (3)

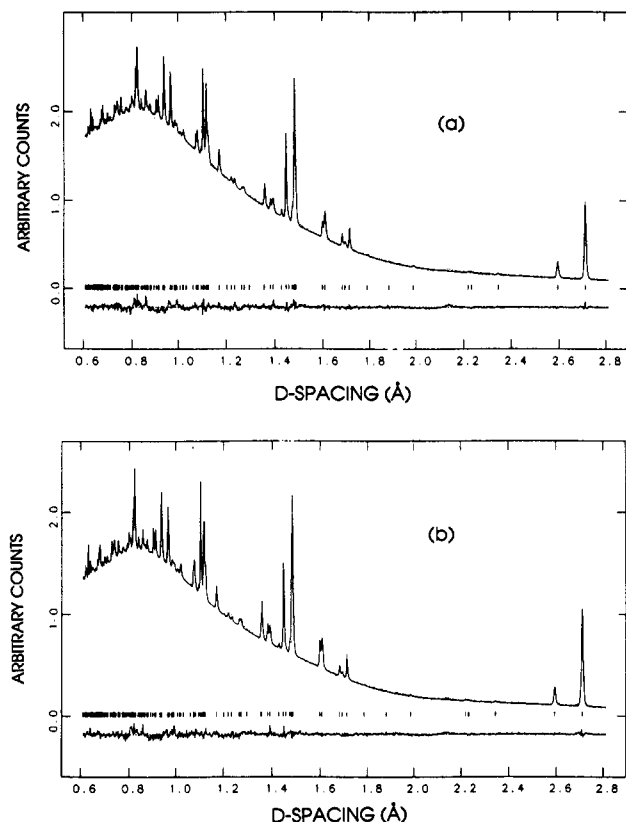
rameters contract very little over the same temperature range, presumably because the  $\text{TiS}_2$  layers are considerably more rigid.

The best refinement of the four data sets considered here was that for  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  at 300 K, with residuals of  $R_w = 0.0232$ ,  $R_p = 0.0167$ , and  $R_e = 0.0163$ . The quality of the refinements at both 300 and 12 K for  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  are better than the corresponding refinements for  $\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$ . Also, both refinements at 300 K are better than those at 12 K. A possible explanation for the former observation is that the deuterium positions for  $\text{ND}_4^{+}$  in  $\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  could not be adequately modeled due to the spherical disorder associated with the orientation of  $\text{ND}_4^{+}$  in trigonal prismatic sites, which is consistent with

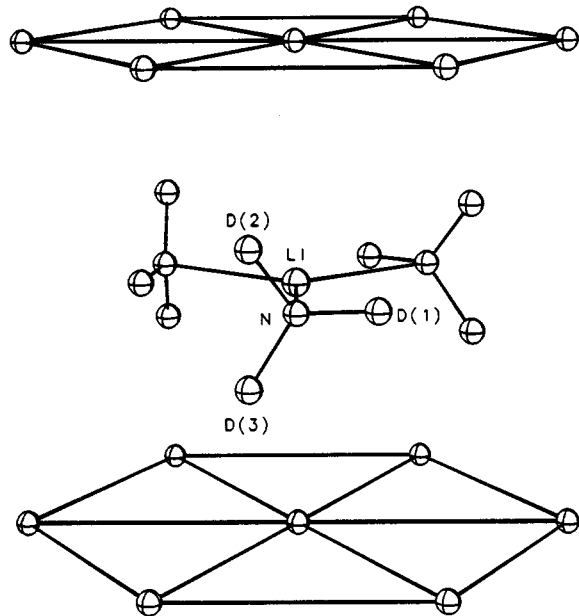
previous NMR and inelastic incoherent neutron-scattering investigations of ammoniated  $\text{TiS}_2$ .<sup>27,35</sup> As for the latter, some unmodeled disorder at 12 K could explain this observation.

An important result of this study is the discovery of substantial structural evidence supporting the presence of discrete lithium-ammonia complexes in the van der Waals gap of  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$ .  $\text{Li}^{+}$  is found on the Wyckoff 3b position situated midway between two sulfur atoms of adjacent  $\text{TiS}_2$  layers.  $\text{ND}_3$  is found at the center of trigonal prismatic sites in the van der Waals gap, with the nitrogen on the Wyckoff 6c position. Both  $\text{Li}^{+}$  and N are located

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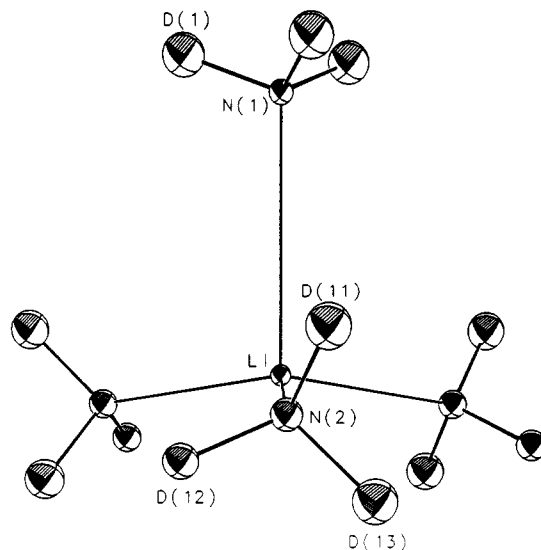


**Figure 3.** Final difference profile plots for  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  (a) and  $\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  (b) at 300 K.



**Figure 4.** Structure of  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  at 300 K showing  $\text{Li}^{+}(\text{ND}_3)_3$  complexes in the van der Waals gap.

on the interlayer midplane, which allows  $\text{Li}^{+}$  to be coordinated by up to three  $\text{ND}_3$  molecules to form complexes with Li-N bond distances of  $\sim 1.97$  Å. The 3-fold coordination of  $\text{Li}^{+}$  by  $\text{ND}_3$  is illustrated in Figure 4. The resemblance of this intercalate structure to that of lithium tetraammine,<sup>36</sup> which is shown in Figure 5, is truly remarkable. All ammonia molecules of an individual  $\text{Li}(\text{ND}_3)_4$  complex are coordinated to lithium, which prevents



**Figure 5.** ORTEP drawing of  $\text{Li}(\text{ND}_3)_4$ . Selected bond distances and angles are as follows: Li-N(1) = 2.488 (16) Å; Li-N(2) = 1.984 (4) Å; N(1)-D(1) = 0.970 (5) Å; N(2)-D(11) = 0.985 (5) Å; N(2)-D(12) = 0.976 (4) Å; N(2)-D(13) = 1.018 (6) Å; N(1)-Li-N(2) = 98.4 (5)°; N(2)-Li-N(2) = 117.9 (2)°; D(1)-N(1)-D(1) = 108.3 (4)°; D(11)-N(2)-D(12) = 109.7 (5)°; D(11)-N(2)-D(13) = 97.4 (6)°; D(12)-N(2)-D(13) = 108.0 (5)°.

intermolecular hydrogen bonding.<sup>36</sup> In both materials lithium is coordinated by three ammonias in a nearly planar arrangement of nearly identical Li-N bond distances. The fourth ammonia in the  $\text{Li}(\text{ND}_3)_4$  structure is coordinated at a much longer Li-N distance (2.488 Å) than the other three (1.984 Å), so that the complex may be better described by the formula  $\text{Li}(\text{ND}_3)_3\text{ND}_3$ . These similarities suggest that discrete lithium-ammonia complexes are likely to form in  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$ . The formation of  $\text{Li}^{+}(\text{ND}_3)_3$  intercalant complexes also follows from TGA, vapor-pressure measurements, and evolved gas analysis, which indicate that freshly prepared Li-NH<sub>3</sub> intercalates of  $\text{TiS}_2$  have  $y''/x = 3.0 \pm 0.1$  for  $x = 0.23 \pm 0.01$ , which further demonstrates the stability of the 3:1 ammonia-to-lithium mole ratio.<sup>29</sup>

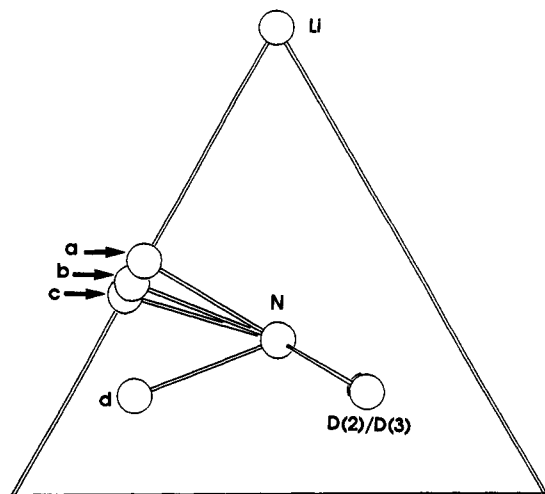
The ammonia N-D bond lengths for both  $\text{Li}^{+}_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  and  $\text{Li}^{+}_{0.11}(\text{ND}_4^{+})_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  at 300 and 12 K range from 0.946 (9) to 1.139 (7) Å, with precise values dependent upon the temperature and composition. Solid  $\text{ND}_3$  has a N-D bond length of 1.012 (2) Å at 2 K.<sup>37,38</sup> The intercalate D-N-D bond angles range from 102 (2) to 130.9 (6)°, again depending on the composition and temperature. Solid  $\text{ND}_3$  exhibits a nearly constant D-N-D bond angle at different temperatures, with an angle of 107.5 (2)° at 2 K. The wide range of bond lengths and angles observed for these intercalation compounds is indicative of distorted ammonia geometries.

In a previous study of  $(\text{ND}_4^{+})_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$ , the  $\text{ND}_3$  molecules were found to be planar. Another interesting feature of the structures of these materials is that the  $\text{ND}_3$  molecules in the lithium-rich compound are further from planarity than those in the lithium-poor compound. This structural investigation of two lithium-ammonia intercalation compounds of  $\text{TiS}_2$  indicates that the  $\text{ND}_3$  geometry is influenced by the intercalant cation, with the  $\text{ND}_3$  structure becoming increasingly nonplanar for increasing  $\text{Li}^{+}$ /decreasing  $\text{ND}_4^{+}$  contents. This progressive distortion of the  $\text{ND}_3$  geometry from planarity for increasing  $x$  may be associated with the repulsion between

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**Figure 6.** [001] projection showing the influence of the  $\text{Li}^+\text{-D}(1)$  repulsion on the molecular geometry of  $\text{ND}_3$  at 300 K in  $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$  (a),  $\text{Li}^+_{0.11}(\text{ND}_4^+)_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  (b), and  $\text{Li}^+_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  (c) compared to the molecular geometry of solid  $(\text{ND}_3)$  superimposed in the same trigonal prismatic lattice site for comparison (d).

$\text{Li}^+$  and  $\text{D}(1)$ , the deuterium atom in the interlayer mid-plane (see Figures 1 and 4). This repulsion results in a  $\text{Li}^+\text{-ND}_3$  ion-dipole attraction, since the  $\text{ND}_3$  distortion from planarity is accomplished by a shift in the  $\text{D}(1)$  position, with the other atomic positions being largely unaffected by variations in  $x/y$ .<sup>29</sup> The influence of cation- $\text{D}(1)$  repulsion on the molecular geometry of  $\text{ND}_3$  at 300 K is illustrated schematically in Figure 6. Qualitatively the same trend is present at 12 K, with  $\text{ND}_3$  being distorted even further from planarity for  $\text{Li}^+_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$ .

As shown in Figure 4 for  $\text{Li}^+_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$ , two of the three deuterium atoms in the intercalant  $\text{ND}_3$  for both Li intercalates participate in hydrogen bonding with the sulfur atoms of the  $\text{TiS}_2$  layers, as found for  $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$ .<sup>14</sup> These hydrogen bond lengths range from 2.49 to 2.66 Å, with  $\text{N-D}\cdots\text{S}$  bond angles ranging from 169 to 177°. Although the lengths of these hydrogen bonds are somewhat longer, and consequently weaker, than those found for  $\text{N}_2\text{H}_5\text{HS}$ , which has hydrogen bond lengths of 2.32–2.49 Å,<sup>30</sup> they are no doubt important to the stability of these materials, as found for  $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$ .<sup>14</sup>

The refined thermal parameters at 300 K for Ti and S are similar to those found for  $1\text{T-TiS}_2$ <sup>40</sup> for both intercalates studied, indicating that the individual sheets of  $\text{TiS}_2$  in the intercalate do not gain much flexibility upon intercalation. This is consistent with the relatively strong covalent bonding within the  $\text{TiS}_2$  layers. However, the much larger thermal parameters for Li and  $\text{ND}_3$  at 300 K are indicative of enhanced thermal motion. NMR studies suggest that both  $\text{NH}_4^+$  and  $\text{NH}_3$  are both undergoing complex molecular motions at ambient temperature.<sup>27,41</sup> As stated previously,  $\text{NH}_4^+$  is undergoing rapid reorientation but not diffusion in ammoniated  $\text{TiS}_2$ .<sup>27</sup> The isotropic thermal parameters for the deuterium atoms in  $\text{ND}_4^+$  were assigned values of 0.11 Å<sup>2</sup> at 300 K and 0.045 Å<sup>2</sup> at 12 K, which are approximately the average of the refined deuterium  $\text{ND}_3$  thermal parameters at 300 and 12

**Table V.** Interatomic Host Layer Distances and Bond Angles for  $\text{Li}^+_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  (1),  $\text{Li}^+_{0.11}(\text{ND}_4^+)_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  (2), and  $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$  (3), and  $\text{TiS}_2$  (4) at 300 K

	1	2	3	4
Bond Lengths, Å				
Ti-Ti	3.4234 (1)	3.42064 (9)	3.4170 (3)	3.4073 (2)
Ti-S	2.433 (1)	2.433 (1)	2.44 (3)	2.4279 (1)
S-S	3.4234 (1)	3.42064 (9)	3.4170 (1)	3.4073 (2)
S-S	3.459 (4)	3.461 (3)	3.476 (2)	3.462 (5)
Bond Angles, deg				
S-Ti-S	89.41 (6)	89.33 (5)	89.05 (5)	89.01 (5)

K, respectively. In contrast to  $\text{NH}_4^+$ ,  $\text{NH}_3$  is executing both  $\text{C}_3$ -axis rotation and diffusion at 300 K for ammoniated  $\text{TiS}_2$ .<sup>27,41</sup> NMR studies have shown that  $\text{NH}_3$  in similar protonated lithium-ammonia intercalation compounds has lower rotational and diffusional activation energies.<sup>27,41</sup> The lower diffusion activation energy may be associated with the two-dimensional diffusion of discrete  $\text{Li}^+(\text{NH}_3)_3$  complexes, which gives the appearance of  $\text{NH}_3$  two-dimensional diffusion in  $^1\text{H}$  NMR. This is currently the subject of a  $^7\text{Li}$  NMR study of  $\text{Li}^+_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$ .

The isotropic thermal parameters for  $\text{Li}^+_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  at 12 K are lower than in the 300 K refinement except for  $\text{D}(1)$ , which does not change within statistical error. The lack of a significant decrease in the value of  $\text{D}(1)$  on cooling may be associated with a lengthening/weakening of the  $\text{N-D}(1)$  bond on cooling (see Table IV) or a small amount of disorder at 12 K. Finally, the thermal parameters for  $\text{Li}^+_{0.11}(\text{ND}_4^+)_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  at 12 K were the most difficult to refine and interpret. Although the thermal parameters for  $\text{ND}_3$  are similar to those found for  $\text{Li}^+_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  at 12 K, S and Li were found to have abnormally small values of 0.0003 (4) and -0.009 (3) Å<sup>2</sup>, (negative thermal parameters are physically impossible), respectively. This may be attributed to the poorer refinement achieved in this study, which is partially due to intercalate disorder. For example, different orientational disorder of  $\text{ND}_4^+$  at 12 K may contribute to the poorer refinement.

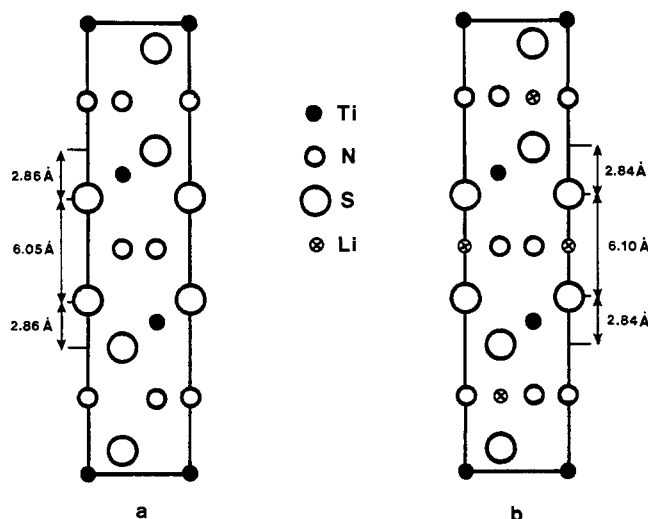
The structural analysis of these intercalation compounds has also provided interesting information regarding the effects of intercalation on the  $\text{TiS}_2$  host. Residual strain in lattice parameters<sup>34</sup> calculated from anisotropic strain-broadening terms indicates essentially no strain perpendicular to [001], even though the host layers must transform upon intercalation from a 1T to a 3R polytype, while there exists a moderate strain component of 0.18 (4)% for all materials studied here parallel to [001].

Intercalation has a subtle effect on the host  $\text{TiS}_2$  layer structure for  $\text{Li}^+_{0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$ ,  $\text{Li}^+_{0.11}(\text{ND}_4^+)_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$ , and  $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$ ,<sup>14</sup> as evidenced by the slight variation in the host lattice interatomic distances and angles shown in Table V. The Ti-Ti and S-S distances associated with the  $a$  lattice parameter for the intercalates are all slightly larger when compared to the same  $\text{TiS}_2$  host distances. This has been explained previously as being due to an increase in the sulfur radius resulting from guest-to-host charge transfer observed for these intercalates.<sup>30</sup> However, this does not explain the decrease in these Ti-Ti and S-S distances parallel to the  $\text{TiS}_2$  layers for increasing  $\text{ND}_4^+$ /decreasing  $\text{Li}^+$  content, since the charge transfer observed for these intercalates is essentially constant. The subtle contraction of these S-S distances, and hence the Ti-Ti distances, with increasing  $\text{ND}_4^+$  content can be attributed to the different lattice sites occupied by  $\text{ND}_4^+$  and  $\text{Li}^+$ . Approximating both ions as

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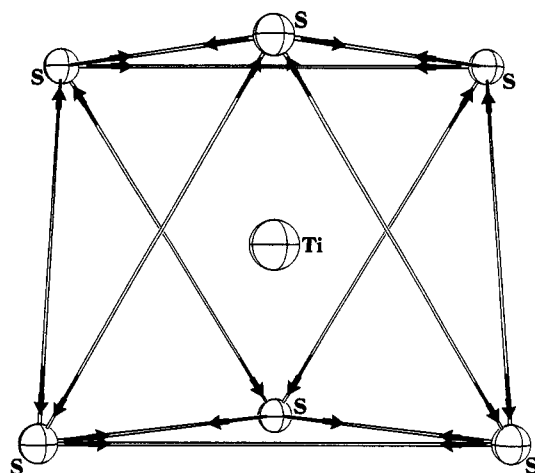
**Figure 7.** (11-20) projections of Ti, S, and N positions in  $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$  (a), and of Ti, S, N, and  $\text{Li}^+$  positions in  $\text{Li}^{+0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  and  $\text{Li}^{+0.11}(\text{ND}_4^+)_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  (b). The 6.10-Å distance shown across the van der Waals gap is for the former lithium intercalate. The distance is 6.08 Å for the latter.

point charges, which is reasonable since  $\text{ND}_4^+$  has been observed to be spherically disordered in these materials,<sup>14,27</sup> the ionic attraction between the negatively charged host-layer sulfur atoms and  $\text{ND}_4^+$  in the  $a_1$ - $a_2$  plane will be greater than will the attraction between the sulfur atoms and  $\text{Li}^+$  in the  $a_1$ - $a_2$  plane (see Figure 4). This follows from both  $\text{ND}_4^+$  and  $\text{Li}^+$  being about the same distance from host-layer sulfur planes, while their nearest displacements in the  $a_1$ - $a_2$  plane from neighboring sulfur positions are about 1.97 and 3.42 Å, respectively. Thus, the attractive component of the ammonium-sulfur interaction within the  $a_1$ - $a_2$  plane should be greater than that for the lithium-sulfur interaction. This stronger  $\text{ND}_4^+$ -S attraction in the  $a_1$ - $a_2$  plane as well as the possibility of S---D---S interactions involving the deuterons of  $\text{ND}_4^+$  may account for the observed contraction of  $a$  with increasing  $\text{ND}_4^+$  concentration.

The S-S distance across the  $\text{TiS}_2$  layer is slightly larger for  $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$  than for the lithium-containing intercalates (see Table V). This can be attributed to ammonium-titanium repulsive interactions along  $c$ , which result in a slight stretching of the S-S distance across the host layers and a slight  $c$  expansion of the host layers. As can be seen in Figure 7, the ammonium cation occupies sites immediately above or below titanium along  $c$ , resulting in stronger intercalant cation-titanium repulsions than for lithium. Also, the slight contraction of S-S distances within a sulfur plane discussed above will allow the sulfur to more effectively screen these ammonium-titanium repulsions. Thus, the substitution of ammonium for lithium in these intercalation compounds slightly distorts the  $\text{TiS}_6$  pseudooctahedra, causing the pseudooctahedra to contract parallel to host layers and elongate perpendicular to them, as illustrated in Figure 8.

### Conclusions

This study has demonstrated that the Rietveld refinement technique for time-of-flight neutron powder diffraction data is an excellent method for determining the structures of these polycrystalline intercalation compounds and for investigating the nature of guest-guest and



**Figure 8.** Distortion of  $\text{TiS}_6$  pseudooctahedra in a  $\text{TiS}_2$  layer associated with the substitution of  $\text{ND}_4^+$  for  $\text{Li}^+$ . The S-S distances in the  $a_1$ - $a_2$  plane decrease from 3.4234 (1) to 3.4170 (1) Å, while the S-S distances across the  $\text{TiS}_6$  octahedra expand from 3.459 (4) to 3.476 (2) Å for increasing  $\text{ND}_4^+/\text{Li}^+$ .

guest-host interactions. This approach has allowed a determination of titanium, sulfur, lithium, nitrogen, and deuterium positions, although the deuterium atoms of  $\text{ND}_4^+$  in  $\text{Li}^{+0.11}(\text{ND}_4^+)_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  could not be located. Since  $\text{Li}^+$  can be surrounded by  $\text{ND}_3$ , with reasonable Li-N bond lengths, in a 1:3 ratio in  $\text{Li}^{+0.23-}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  and TGA, vapor-pressure measurements, and evolved gas analysis indicate this ratio is quite stable for intercalates containing  $0.23 \pm 0.01$  mol %  $\text{Li}^+$ , it appears that discrete  $\text{Li}^+(\text{ND}_3)_3$  complexes do indeed exist in the van der Waals gap. We are currently investigating  $\text{Li}^{+0.23}(\text{NH}_3)_y\text{TiS}_2^{0.23-}$  by differential scanning calorimetry and vapor pressure/Clausius-Clapeyron measurements, with an emphasis on the energetics and stability of intercalated ammonia above and below  $y''/x = 3.0$ . Although the  $\text{ND}_3$  in these intercalates has been shown to be distorted from idealized  $C_3$  symmetry, it does not adopt a planar structure as found in  $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$ . This investigation of  $\text{Li}^{+0.23}(\text{ND}_3)_{0.63}\text{TiS}_2^{0.23-}$  and  $\text{Li}^{+0.11-}(\text{ND}_4^+)_{0.11}(\text{ND}_3)_{0.54}\text{TiS}_2^{0.22-}$  indicates that  $\text{ND}_3$  distorts progressively further from planarity as the Li content increases and the ammonium content decreases. There are also subtle effects on the  $\text{TiS}_2$  host layers accompanying the substitution of  $\text{ND}_4^+$  for  $\text{Li}^+$ . It is apparent from this study that both guest-host interactions (i.e.,  $\text{ND}_3$ -host hydrogen bonding and  $\text{Li}^+/\text{ND}_4^+$ -host electrostatic interactions) and guest-guest interactions (i.e.,  $\text{Li}^+(\text{ND}_3)_3$  complex formation and  $\text{Li}^+/\text{ND}_4^+$ - $\text{ND}_3$  ion-dipole interactions) are important to the stability of this class of intercalation compounds.

**Acknowledgment.** This research has benefited from the use of the intense pulsed neutron source at Argonne National Laboratory, which is funded by the U.S. Department of Energy, BES-Materials Science Division, under contract W-31-109-ENG-38. Additional support was provided by the Los Alamos National Laboratory under U.S. Government contract W-7405-ENG-36. We thank R. L. Hitterman for assistance with data collection. We are grateful to the National Science Foundation for support through grants DMR-841364102 and DMR-8605935, Arizona State University for a generous allocation of computer tie on the VAX-8650, the Center for Solid State Science for use of its Materials Preparation Facility, and M. Wheeler and W. O'Neill for expert glassblowing.