JOURNAL OF SOLID STATE CHEMISTRY 67, 142–150 (1987)

Deintercalation and Reintercalation Energetics of Ammoniated Titanium Disulfide*

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Received April 4, 1986; in revised form July 21, 1986

The deintercalation and reintercalation processes in ammoniated TiS_2 have been studied by thermogravimetric analysis, differential scanning calorimetry, vapor-pressure measurements, and powder X-ray diffraction. The enthalpies determined calorimetrically for complete NH_3 and NH_4^+ deintercalation of $(NH_4^+)_{0.24}(NH_3)_{0.23}TiS_2^{0.24-}$ are approximately 10.5 and 22 kcal/mole, respectively. These enthalpies are in good agreement with those reevaluated from a previous calorimetric study of ammoniated TaS_2. Ammonia vapor-pressure curves for deintercalation and reintercalation of $(NH_4^+)_{0.24}(NH_3)_{y''}TiS_2^{0.24-}$ exhibit hysteresis, and the enthalpies for these reactions are estimated to be 15.5 and −13 kcal/mole, respectively. The absolute values of these enthalpies decrease progressively as NH_3 is deintercalated and then reintercalated. The structural changes that accompany these processes are relatively complex and involve at least two phases. Further structural studies are necessary to help elucidate the energetics of these intercalation compounds. © 1987 Academic Press, Inc.

Introduction

In 1971, Gamble *et al.* (*1*) reported a wide range of Lewis bases that could be intercalated into lamellar transition metal dichalcogenide hosts. During the past 15 years these intercalation compounds have been studied rather extensively, with the intercalation compounds of the prototypical Lewis base NH_3 in transition metal disulfides (TS_2) receiving the most attention (*1–17*). The most thoroughly characterized intercalation compound of this type is ammoniated TiS_2 (*15–17*). However, the behavior of this simple intercalant in TiS_2 and TaS_2 is complex in the sense that NH_3 is oxidized initially to NH_4^+ (*11, 15, 16*), NH_3, and NH_4^+ may be ordered (*16*), the orientation of NH_3 is unusual (*8, 15*), NH_3 can execute a variety of molecular motions (*4, 9, 10, 18*) and it may be structurally distorted (*18*).

Ammoniated TiS_2 is best formulated as a mixed ionic–molecular intercalation compound $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$, in which NH_4^+ and NH_3 occupy interstitial sites between two-dimensional $[TiS_2]^{y'-}$ macroanionic sheets (*15*). For charge compensation, one electron is donated to the TiS_2 conduction band per NH_4^+ ion (*15*). Intercalation of NH_3 into TiS_2 results in formation of NH_4^+ with $y' = 0.22 \pm 0.02$ and the intercalation of neutral NH_3 as well (*15, 16*). The proposed reaction sequence for NH_4^+ formation upon intercalation of TiS_2 is (*15, 16*)

$$\tfrac{1}{3}y'NH_3 \rightarrow \tfrac{1}{6}y'N_2 + y'H^+ + y'e^- \quad (1)$$

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* This research was supported by NSF Grant DMR 82-15315.

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0022-4596/87 $3.00

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$$y'H^+ + y'NH_3 \rightarrow y'NH_4^+ \qquad (2)$$

$$y'e^- + TiS_2 \rightarrow [TiS_2]^{y'-}, \qquad (3)$$

where presumably the NH_3-cracking reaction given by Eq. (1) is catalyzed by exposed Ti at the crystal edges. The reverse processes, i.e., NH_3 and NH_4^+ deintercalation, occur via the following reactions (*15*):

$$(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-} \rightarrow (NH_4^+)_{y'}TiS_2^{y'-} + y''NH_3 \qquad (4)$$

$$(NH_4^+)_{y'}TiS_2^{y'-} \rightarrow TiS_2 + y'NH_3 + \tfrac{1}{2}y'H_2. \qquad (5)$$

There is a conspicuous lack of information concerning intercalation energetics in the literature. The only previous study was performed by Dines and Levy in 1975 (*7*) on ammoniated TaS_2. However, their work was based on the assumption that the only intercalant present in TaS_2 was NH_3. In 1977, Schöllhorn and Zagefka (*11*) reported the presence of NH_4^+ in ammoniated TaS_2, so that this intercalation compound is best described as $(NH_4^+)_{y'}(NH_3)_{y''}TaS_2^{y'-}$, where $y' \simeq 0.1$. Moreover, the recent detection of NH_4^+ in ammoniated NbS_2 (*19*) strongly suggests that NH_4^+ formation is a general phenomenon for NH_3 intercalation into TS_2.

In this paper we report the results of the first detailed investigation of the reaction energetics of intercalation compounds. Well-characterized ammoniated-TiS_2 intercalation compounds have been selected for this work, and they have been studied both energetically and structurally using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), vapor-pressure measurements, and powder X-ray diffraction.

Experimental

Highly stoichiometric TiS_2 was prepared by direct reaction of the elements at 640°C using 40 mg/cm^3 of excess S, as described previously (*15*). The stoichiometry of the $Ti_{1+x}S_2$ prepared in this fashion is $Ti_{1.002}S_2$, with the maximum error in x being ± 0.001 (*16*). Both the host and ammoniated TiS_2 samples were handled in a helium-filled Vacuum Atmospheres Model MO-40-1H Dry Train dry box (<1 ppm H_2O and O_2) and only removed from the dry box in leak-checked, sealed containers.

Polycrystalline samples of $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$ were prepared by loading TiS_2 into one leg of an h-cell. Ammonia (99.9% from Matheson Gas Products) was dried over Na on a high-vacuum line and cryopumped using liquid nitrogen into the opposite leg of the h-cell. Sufficient NH_3 was cryopumped to be in large excess of its maximum 1 : 1 stoichiometry with TiS_2 (*15*). The h-cell was then sealed to form an n-tube, and the NH_3 was poured onto the TiS_2. The intercalation reaction was complete in about 2 hr at 20°C, which reflects the near stoichiometry of the TiS_2 (*20*). The excess NH_3 was condensed in the opposite branch of the n-tube and sealed off from the intercalate. The tube containing the sample was broken in the dry box, and the intercalate was transferred to a vial which was sealed and stored in the dry box.

$(NH_4^+)_{y'}TiS_2^{y'-}$ was prepared by thermally deintercalating the NH_3 from $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$. Samples of $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$ ($\simeq$100 mg) were loaded in the dry box into the deintercalation vessel shown in Fig. 1, which was attached to a high-vacuum line. The sample was held initially at liquid-nitrogen temperature while the helium from the dry box was removed, after which the vacuum pumps were isolated from the line. The sample was allowed to warm to ambient temperature, after which it was heated slowly to 147°C using a magnetically stirred mineral oil bath to selectively remove NH_3. The temperature and pressure were monitored by a thermometer located in the oil bath as close as possible to the sample and a Model 220B MKS Bara-

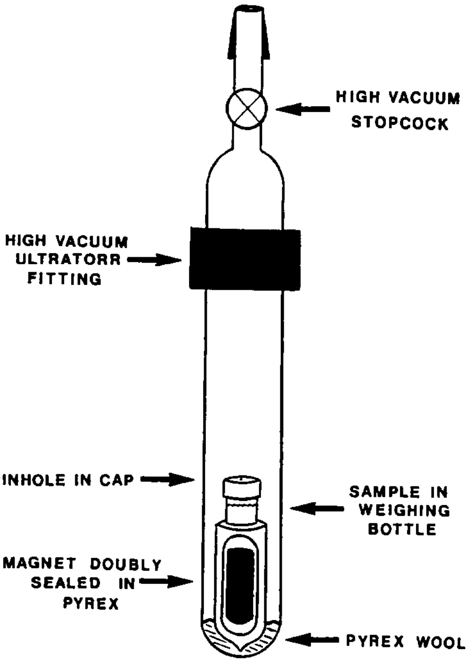

FIG. 1. Schematic diagram of the vessel used for vapor-pressure measurements. The magnet facilitates removal of the sample.

tron gauge, respectively. After the NH_3 pressure stabilized at 147°C, the sample was isolated from the vacuum line. The NH_3 in the line was condensed with liquid nitrogen to make sure no noncondensable gases were present and NH_4^+ decomposition had not occurred (see Eq. (5)). Next, the sample was evacuated to 10^{-3} Torr for a few minutes to remove the deintercalated NH_3. The absence of NH_3 in $(NH_4^+)_{y'}TiS_2^{y'-}$ was verified by TGA.

The stoichiometries of $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$ and $(NH_4^+)_{y'}TiS_2^{y'-}$ were determined by TGA and vapor-pressure measurements as described previously (*15, 16*), with the TGA experiments again performed using a modified Perkin-Elmer TGS-2 system with a 0.1-μg sensitivity and 0.01% weight resolution. The precise NH_3 composition was determined prior to each measurement due to the continuous evolution of NH_3 from these compounds (*15*).

The deintercalation and reintercalation of NH_3 were studied volumetrically using a vacuum line having a volume of 690 cm^3, and the pressure was measured using a Baratron gauge calibrated to 0.01 Torr. Over the pressure range studied (0 to 15 Torr), a negligible quantity of NH_3 ($\leq 1\%$) was adsorbed by the vacuum system. $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$ samples were loaded into the deintercalation vessel, attached to the vacuum line, cooled to liquid-nitrogen temperature, and evacuated to 10^{-5} Torr. The line and sample were then isolated from the vacuum pumps, and the sample was allowed to warm to ambient temperature. Once the pressure stabilized and remained constant for at least 20 min, a pressure-volume-temperature (*PVT*) data point was taken. The sample was then heated at approximately 10°C intervals to 147°C using a mineral oil bath. After each 10°C interval, the temperature was held constant (±0.5°C) until the pressure was stable for at least 20 min prior to recording *PVT* points. After NH_3 deintercalation was complete, as judged by stabilization of the NH_3 pressure at 147°C, the sample was cooled back to ambient temperature at 10°C intervals, thereby reintercalating the NH_3 gas. *PVT* measurements for reintercalation of NH_3 were performed in the same manner as for NH_3 deintercalation.

A Perkin-Elmer Model DSC-4 differential scanning calorimeter was used for the DSC studies. The power was calibrated using an electrical heater which supplies a 10-mcal/sec signal (±1%) to the sample container. The melting transition of In was used to verify the power calibration and to calibrate the temperature (±0.2 K). Argon (99.999% pure from Matheson Gas Products) was passed slowly through a cold trap at −78°C to reduce any residual water to below 1 ppm prior to its use as the DSC carrier gas. The ratio of the carrier-gas flow rate to the sample-gas evolution rate as a function of time was increased progressively until no thermal effect of the evolved gases could be observed, i.e., until the observed deintercalation enthalpies were constant for further increases in this ratio. Samples were weighed ($\approx 5.00 \pm 0.03$ mg), sealed in Al pans in the dry box, and transferred to the DSC-4. Essentially the same procedure was used as for the TGA work (*15, 16*). An argon-purged dry bag attached to the DSC sample-introduction port was used to prevent any sample degradation.

Powder X-ray diffraction patterns were recorded at ambient temperature using Ni-filtered Cu*Kα* radiation. Samples were loaded into 0.3-mm Pyrex capillaries in the dry box and sealed prior to loading them into a Debye-Scherrer camera, which was calibrated using NBS SRM 640 silicon.

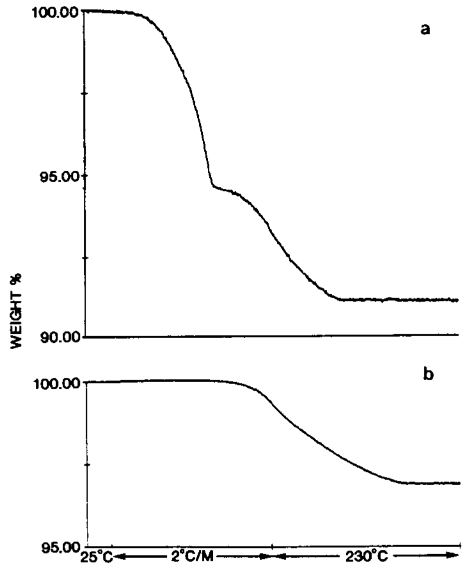

FIG. 2. TGA curves for the thermal deintercalation of $(NH_4^+)_{0.23}(NH_3)_{0.39}TiS_2^{0.23-}$ (a) and $(NH_4^+)_{0.20}TiS_2^{0.20-}$ (b). The low- and high-temperature steps originate from NH_3 and NH_4^+ deintercalation, respectively.

Results and Discussion

(1) TGA and Compound Stability

Typical TGA curves for the thermal deintercalation of $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$ and $(NH_4^+)_{y'}TiS_2^{y'-}$ are shown in Fig. 2. The low- and high-temperature steps in the deintercalation curve for $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$ are due to NH_3 (<150°C) and NH_4^+ (>150°C) deintercalation, respectively. Comparison of this curve to that for $(NH_4^+)_{y'}TiS_2^{y'-}$ in Fig. 2 reveals that the NH_3-deintercalation step is totally absent. Hence, it is possible to isolate the pure ammonium intercalate without any detectable concentration of NH_3 by vacuum deintercalation slightly below 150°C. Great care must be taken in the handling and storage of $(NH_4^+)_{y'}TiS_2^{y'-}$, since it is extremely air sensitive and is also a powerful absorber of NH_3 as well as other small polar molecules.

(2) DSC

In agreement with the TGA studies, DSC indicates that two distinct thermal events occur during the deintercalation of $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$, as shown in Fig. 3. Also shown in Fig. 3 is the same DSC curve after correcting for the exponential background. Since essentially the same exponential

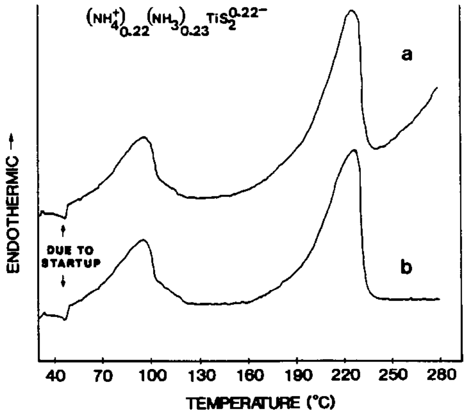

FIG. 3. DSC curves for $(NH_4^+)_{0.22}(NH_3)_{0.23}TiS_2^{0.22-}$ before (a) and after (b) background correction.

background occurs for completely deintercalated TiS_2, it is characteristic of the calorimeter and not the sample.

The onset temperatures for the low- and high-temperature endothermic peaks are the same within experimental error to those determined in the TGA experiments. Therefore, the low-temperature peak is due to the deintercalation of NH_3, whereas the high-temperature peak reflects the deintercalation of NH_4^+. The enthalpies estimated from the peak areas for NH_3 and NH_4^+ deintercalation are approximately 10.5 kcal/mole NH_3 and 22 kcal/mole NH_4^+, respectively. These enthalpies are estimated to be accurate to about ±20% due to the experimental errors inherent in this type of analysis, especially when the thermal events occur over such broad temperature ranges with concurrent evolution of different gases (see Eqs. (4) and (5)). The larger enthalpy for NH_4^+ deintercalation suggests that it is bound more strongly between the host TiS_2 layers, which is plausible because of the more favorable ionic, as opposed to dipole, interactions of NH_4^+ with the negatively charged TiS_2 layers. However, according to Eq. (5), a chemical reaction occurs upon NH_4^+ deintercalation, but the enthalpy change for this reaction is estimated to be rather small in view of the relatively low NH_4^+ and NH_3 deintercalation enthalpies. Our reasoning is as follows. The deintercalation reaction can be written $NH_4^+ + e^- \rightarrow NH_3 + \frac{1}{2}H_2$. The enthalpy change for this reaction is $\Delta H_D = \Delta H_C + \Delta H'_D$, where ΔH_C and $\Delta H'_D$ are the redox and nonredox contributions to the measured deintercalation enthalpy, respectively. If the redox reaction occurs in the interior of the TiS_2 particles, then NH_3 and H_2 must deintercalate, and, neglecting $\Delta H'_D$ for H_2, we estimate that $\Delta H_C \simeq \Delta H_D - \Delta H'_D\,(NH_3) \simeq 12$ kcal/mole. However, if the redox reaction occurs at the edges of the TiS_2 particles, then NH_4^+ must diffuse from the interior of the particles to the edges. In this case we estimate that $\Delta H_C = \Delta H_D - \Delta H'_D\,(NH_4^+) \lesssim \Delta H_D - \Delta H'_D\,(NH_3) \lesssim 12$ kcal mole, because of the enhanced electrostatic interactions of NH_4^+ with the negatively charged TiS_2 layers. In either case, ΔH_C is relatively small and of the order of 10 kcal/mole.

It is instructive to compare these results to those of Dines and Levy (*7*) for nominally $(NH_3)_{0.93}TaS_2$, taking into account that similarly prepared intercalates have been shown to have the formula $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$, where $y' \approx 0.1$ (*11*). Assuming the weight loss after the TGA inflection at approximately 94.5 wt% appearing in Fig. 3b of their paper (*7*) is due to NH_4^+, then we estimate the formula for this intercalate to be $(NH_4^+)_{0.08}(NH_3)_{0.84}TaS_2^{0.08-}$. Furthermore, assuming the main enthalpy peak shown in Fig. 3a of their paper (*7*) is symmetrical, we find that the enthalpies of NH_3 and NH_4^+ deintercalation for $(NH_4^+)_{0.08}(NH_3)_{0.84}TaS_2^{0.08-}$ are roughly 8 and 19 kcal/mole, respectively. Although this is a rather crude estimation, it does suggest that the deintecalation energetics in ammoniated TiS_2 and TaS_2 are comparable, even though the electronic properties of these hosts are quite different, with TiS_2 being an extrinsic semiconductor (*16, 21, 22*) and TaS_2 exhibiting metallic behavior (*23*). Furthermore, this result is consistent with the idea that the intercalation process involves rather weak host–intercalant and intercalant–intercalant interactions, which underlies the reversibility characteristic of intercalation reactions.

(*3*) *Vapor-Pressure Measurements*

The volumetric deintercalation and reintercalation of NH_3 can be described by the reaction

$$(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-} \leftrightarrow (NH_4^+)_{y'}TiS_2^{y'-} + y''NH_3. \quad (6)$$

The temperature dependence of the NH_3 vapor pressure for the forward and reverse

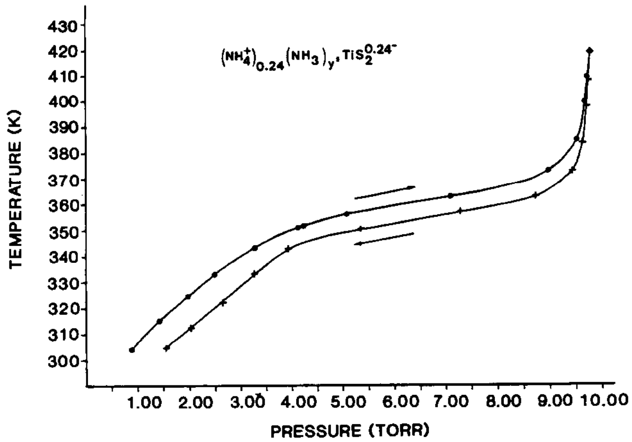

FIG. 4. Hysteresis in the NH_3 vapor pressure vs temperature curves for $(NH_4^+)_{0.24}(NH_3)_{y''}TiS_2^{0.24-}$. The top and bottom curves represent the deintercalation and reintercalation processes, respectively.

reactions is given in Fig. 4. It is clear in Fig. 4 that the same NH_3 pressure and sample composition (y'') achieved during deintercalation requires a lower temperature to attain during reintercalation. The observation of hysteresis shows that the intercalation process is not always truly reversible, experimentally, as is often assumed. Although it is conceivable that the observed hysteresis is due to slow kinetics, we believe that this is not the case because the data in Fig. 4 were taken only after equilibrium had been attained and also because of the linearity of the Clausius-Clapeyron plots discussed below. Due to this hysteresis, the absolute value of the NH_3 deintercalation enthalpy is expected to be greater than the absolute value of the NH_3 reintercalation enthalpy, i.e., $|\Delta H_D| > |\Delta H_R|$.

By making the approximation that separate equilibria exist for the NH_3 deintercalation and reintercalation curves and plotting $\ln P$ vs $1/T$ for different compositions, a direct comparison of the deintercalation and reintercalation enthalpies can be made. Such Clausius-Clapeyron plots for NH_3 deintercalation and reintercalation are shown in Figs. 5 and 6, respectively. By integrating the enthalpy as a function of composition for $(NH_4^+)_{0.24}(NH_3)_{y''}TiS_2^{0.24-}$ for $0.00 \leq y'' \leq 0.23$, we find $|\Delta H_D| = 15.5$ kcal/mole NH_3 and $|\Delta H_R| = 13$ kcal/mole NH_3.

A summary of the deintercalation and reintercalation enthalpies for ammoniated TiS_2 and TaS_2 is given in Table I. The agreement between the enthalpies determined by DSC and vapor pressure measurements is considered reasonable in view of the limitations on the accuracy of these methods.

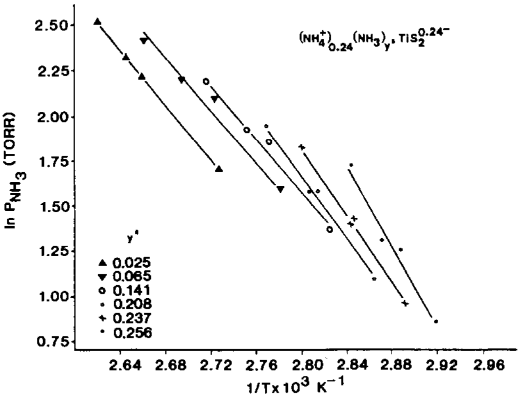

FIG. 5. Clausius-Clapeyron plots for the deintercalation of NH_3 from $(NH_4^+)_{0.24}(NH_3)_{y'}TiS_2^{0.24-}$ for different NH_3 stoichiometries.

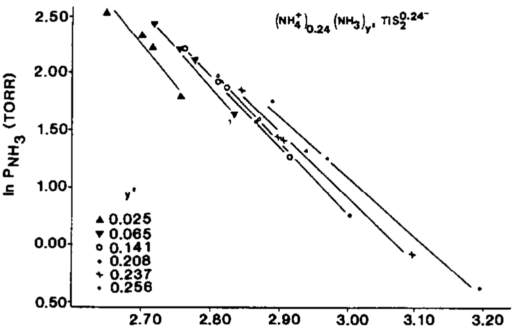

FIG. 6. Clausius-Clapeyron plots for the reintercalation of NH_3 into $(NH_4^+)_{0.24}(NH_3)_{y''}TiS_2^{0.24-}$ for different NH_3 stoichiometries.

The average value of ΔH_D is 13 kcal/mole NH_3 for $y'' = 0.23$. The somewhat higher ΔH_D determined from vapor pressure studies, apart from experimental error, may be due in part to the slightly higher NH_4^+ content in the vapor pressure samples ($y' = 0.24$) compared to DSC samples ($y' = 0.22$), since the enhanced ion–dipole interactions in the former compounds should increase ΔH_D. In addition, both $|\Delta H_D|$ and $|\Delta H_R|$ decrease progressively during NH_3 deintercalation and reintercalation, with nearly equal values when y'' is near 0.00 for $(NH_4^+)_{0.24}(NH_3)_{y''}TiS_2^{0.24-}$. Although it is tempting to speculate about the origin of the relative magnitudes of $|\Delta H_R|$ and $|\Delta H_D|$ and their variation with NH_3 composition, we prefer to refrain from this exercise because there are too many unknown factors that can influence these enthalpies, including host–intercalant and intercalant–intercalant interactions; areal and mechanical effects associated with the contraction and expansion of the TiS_2-layer spacing upon deintercalation and reintercalation, respectively; and possible composition-dependent structural changes, such as staging of NH_4^+, which are discussed below.

(4) X-ray Diffraction

Both the initial intercalation compound $(NH_4^+)_{0.24}(NH_3)_{0.32}TiS_2^{0.24-}$ as well as the same material after complete NH_3 deintercalation and reintercalation were single-phase, stage- I, 3*R* structures having identical cell parameters within experimental error of (**c** = 26.1 Å and **a** = 3.42 Å). The finding of a simple stage I structure in which every van der Waals gap is occupied does not necessarily mean that NH_4^+ and NH_3 are not staged in some fashion in this compound, since such ordering would be nearly impossible to detect with powder X-ray diffraction due to the very similar X-ray scattering factors for NH_4^+ and NH_3. However, as discussed below, the structural situation is more complex for lower NH_3 contents.

If all the NH_3 in $(NH_4^+)_{0.24}(NH_3)_{0.32}TiS_2^{0.24-}$ is deintercalated to form the ionic compound $(NH_4^+)_{0.24}TiS_2^{0.24-}$, then the stage I phase is absent and the largest *d* spacing in the new diffraction pattern is 7.21 Å. If this *d* spacing is attributed to a stage II phase, then the interlayer distance **c**/**n**, where *n* is the number of layers per unit cell, should be 14.42 Å. This repeat distance is in good agreement with the value of 14.4 Å calculated from the sum of the interlayer spacing for the stage I phase (8.7 Å) and that of the TiS_2 host having an empty van der Waals gap (5.7 Å). However, the remainder of the diffraction pattern could

TABLE I

DEINTERCALATION AND REINTERCALATION ENTHALPIES FOR AMMONIATED TiS_2 AND TaS_2

Compound	Process[a]	Method[b]	Enthalpy (kcal/mole)
$(NH_4^+)_{0.22}(NH_3)_{0.23}TiS_2^{0.22-}$	$(NH_3)_D$	DSC	10.5
	$(NH_4^+)_D$	DSC	22
$(NH_4^+)_{0.24}(NH_3)_{0.23}TiS_2^{0.24-}$	$(NH_3)_D$	VP	15.5
	$(NH_3)_R$	VP	−13
$(NH_4^+)_{0.08}(NH_3)_{0.84}TaS_2^{0.08-c}$	$(NH_3)_D$	DSC	≃8[c]
	$(NH_4^+)_D$	DSC	≃19[c]

[a] D and R denote deintercalation and reintercalation, respectively.

[b] DSC and VP denote differential scanning calorimetry and vapor pressure, respectively.

[c] Composition and enthalpies estimated from data given in Ref. (7).

not be indexed completely to a simple stage II compound having c/n = 14.4 Å. Since this pattern cannot be indexed on the basis of any simple structural model, the possible presence of more than one phase for $(NH_4^+)_{0.24}TiS_2^{0.24-}$ cannot be ruled out.

After complete NH_3 deintercalation and reintercalation of 85% of the NH_3 for $(NH_4^+)_{0.24}(NH_3)_{0.32}TiS_2^{0.24-}$, at least two phases were present. The stage I structure was dominant and had a 1% decrease in its interlayer spacing compared to the same sample prior to the deintercalation–reintercalation procedure. The largest d spacing not belonging to the stage I phase was 7.57 Å. If this d spacing corresponds to a stage II intercalation compound, then c/n = 15.14 Å and the expansion of every other layer for the stage II intercalate would be 3.75 Å. This is much larger than the 2.9- or 3.2-Å expansion expected from the van der Waals diameters of NH_4^+ (*24*), NH_3,[1] respectively. Consequently, it seems unlikely that the 7.57-Å d spacing corresponds to a simple stage II structure, especially since the rest of the diffraction pattern could not be indexed on this basis. This d spacing may be related to the 7.21 Å spacing observed for $(NH_4^+)_{0.24}TiS_2^{0.24-}$, which is consistent with $(NH_4^+)_{0.24}TiS_2^{0.24-}$ not being a simple stage II compound. However, if both the 7.57- and 7.21-Å d spacings do not belong to the same phase, then at least three phases exist over the range of NH_3 compositions investigated in Figs. 4, 5, and 6. Hence, the structural variations accompanying NH_3 deintercalation and reintercalation appear to be relatively complex, with at least two phases being present.

Conclusions

The deintercalation and reintercalation enthalpies in ammoniated TiS_2 and TaS_2 are approximately 10–20 kcal/mole, which are probably typical of TS_2 compounds. The interpretation of such enthalpies, even for the simple NH_3 molecule, is complicated by the many factors that can influence the intercalation process. Since intercalation energetics involves a delicate balance of several contributing processes, it can best be elucidated by precise, systematic studies of a broad spectrum of TS_2 hosts. On the basis of this study, it is clear that detailed structural determinations of intercalation compounds will be necessary to help evaluate some of the key contributions to the enthalpy, such as NH_4^+–NH_3 ion–dipole interactions, as well as changes in these contributions due to structural changes accompanying intercalation. As a first step in this direction, we are currently undertaking a structural investigation of $(ND_4^+)_{0.24}TiS_2^{0.24-}$ by powder neutron diffraction.

Acknowledgments

We acknowledge the X-ray Diffraction Facility at Arizona State University for use of the powder diffraction equipment.

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[1] This value is estimated from the van der Waals radii of N and H.

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