Magnetic Properties of Ammonia Intercalates of Some IV B and V B Transition Metal Disulfides*

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Intercalates 3R-VS$_2$NH$_3$ and 3R-TaS$_2$NH$_3$, isostructural with 3R-TiS$_2$NH$_3$, are described for the first time. Magnetic properties of 3R-TiS$_2$NH$_3$, 3R-VS$_2$NH$_3$, and 2H-TaS$_2$NH$_3$ respectively are interpreted in terms of a charge transfer (in agreement with an ionic model) from the intercalant to the lowest conduction band which consists mainly of e_g, a_{1g} and a_1' transition metal d states. © 1987 Academic Press, Inc.
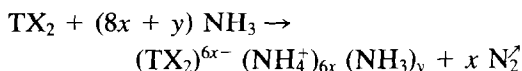
Introduction

Lewis base molecules, such as NH$_3$, pyridine, and long chain amines are easily intercalated in the van der Waals gap of layered transition metal dichalcogenides, TX$_2$ (*1–3*).

Based on the work of Schöllhorn and Zagefka (*4*) it is now believed that the intercalation of ammonia is accompanied with a redox reaction,

$$2\,NH_3 \rightarrow N_2 + 6\,H^+ + 6\,e^-$$
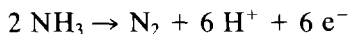
the overall intercalation reaction being

$$TX_2 + (8x + y)\,NH_3 \rightarrow$$
$$(TX_2)^{6x-}\,(NH_4^+)_{6x}\,(NH_3)_y + x\,N_2^{\nearrow}$$

In the resulting ionic structure part of the ammonia is present as NH$_4^+$ ions solvated

by neutral molecules NH$_3$; $6x = 0.1–0.3$, $6x + y = 1$. A similar reaction scheme has been proposed for pyridine-intercalated phases because of the formation of dipyridine (*5*).

Bernard *et al.* (*6*) came to the same conclusion from an analysis of the products released during deintercalation of 3R-TiS$_2$NH$_3$ (in the following we will use this formula, disregarding the presence of NH$_4^+$); the amount of NH$_4^+$ per unit TiS$_2$ was estimated to be 0.2.

The magnetic susceptibilities of NH$_3$-intercalated transition metal dichalcogenides are also in favor of a charge transfer to the TX$_2$ sandwiches (to be discussed below).

The structure of the ammonia intercalates of the transition metal disulfides is such (Fig. 1) that ammonia is present in sites with trigonal prismatic coordination by sulfur atoms of neighboring sandwiches TS$_2$; the coordination of the transition metal atoms by sulfur atoms is the same as in the host for intercalation, viz., a trigo-

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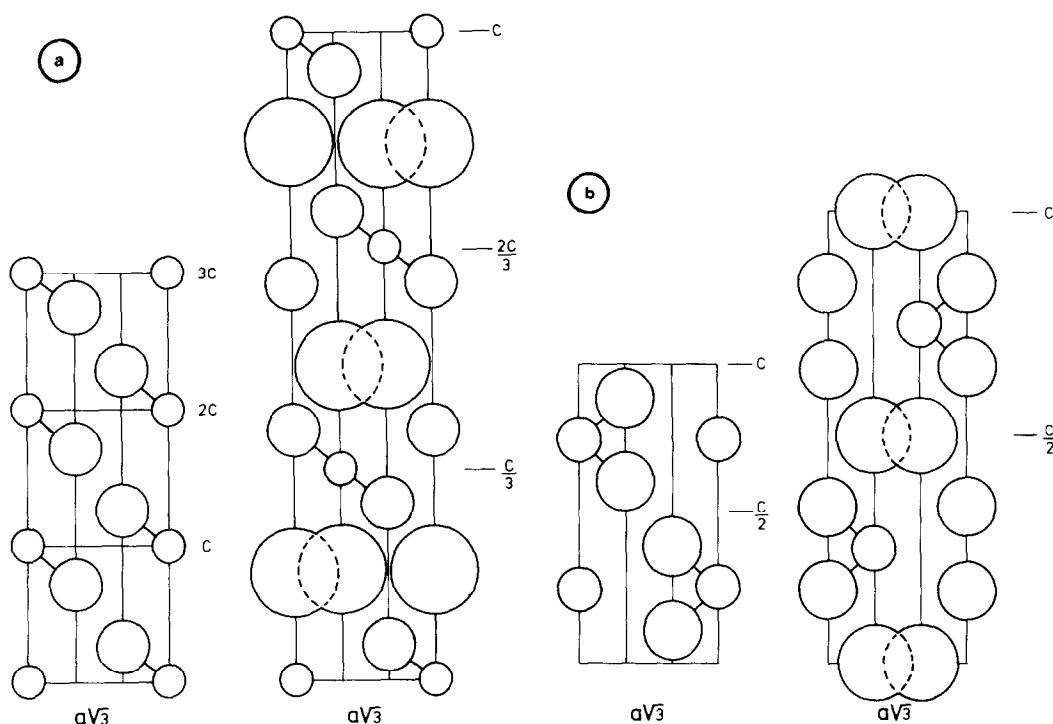‡ To whom correspondence should be addressed.

FIG. 1. (11$\bar{2}$0) section of the structures of the hosts for intercalation and the NH$_3$ intercalates. (a) Transition metal dichalcogenide with 1T structure (left) and their NH$_3$ intercalates (right); (b) 2H-TaS$_2$ (left) and 2H-TaS$_2$NH$_3$ (right). Both trigonal-prismatic sites are (statistically) occupied by NH$_3$ (large circles). Small circles represent transition metal atoms.

nally distorted octahedron for intercalates based on transition metal disulfides with 1T-TS$_2$ structures (TiS$_2$, ZrS$_2$) and a trigonal prism for intercalates based on 2H-NbS$_2$ and 2H-TaS$_2$ (1–3).

From X-ray and neutron powder diffraction of 2H-TaS$_2$ND$_3$ (7–9) and 3R-TiS$_2$ND$_3$ (10) it was found that ND$_3$ (and ND$_4^+$) occupies statistically the trigonal prismatic sites in the van der Waals gap. It was not possible to discriminate between ND$_3$ and ND$_4^+$. A model with a spherically symmetric distribution of deuterium around nitrogen with the N–D distance equal 1.0 Å explained the intensities of the powder lines reasonably well but it is quite well possible that the true distribution of deuterium differs in some detail from a spherically symmetric distribution. Dynamically this model corresponds to isotropically rotating ND$_3$ and ND$_4^+$.

NMR studies of ammonia-intercalated 2H-TaS$_2$ and 1T-TiS$_2$ are in favor of a model with the C$_3$ axis of NH$_3$ molecules in the midplane between sulfur layers; the molecules are spinning rapidly around the trigonal axis and the C$_3$ axis also performs reorientations mainly in the basal plane (11–14). Rapid spinning and/or reorientation of the C$_3$ axis and rapid diffusion of the molecules was found by Riekel et al. (15) using quasi-elastic neutron scattering of 2H-TaS$_2$NH$_3$.

The now commonly accepted ionic model explains the observed midway position of nitrogen between sulfur layers in terms of an ion–dipole interaction of a central NH$_4^+$ group with neighboring NH$_3$

molecules. From this model one expects fast proton exchange; this was, however, not found from NMR (*11–14*). Bernard *et al.* (*6*) suppose that the protons are in fixed positions due to the interaction with the negatively charged sulfur layers. It is, however, also possible that the proton is not bound to the ammonia molecule but present as H^+ or as neutral H inside the TS_2 sandwich. This possibility is supported by the observation that D in D_xNbS_2 and H in H_xTaS_2 are in the plane of the transition metal atoms (*16*). Our neutron diffraction results of TiS_2ND_3 are, however, not in favor for this view (*10*).

In this paper we report on the structures of the NH_3 intercalates of $1T$-VS_2 and $1T$-TaS_2 prepared for the first time. The magnetic properties of the intercalates are discussed in relation with those of the hosts.

Experimental

The transition metal dichalcogenides were prepared from the elements. $1T$-VS_2 was obtained by oxidation of $LiVS_2$ with I_2 in acetonitrile solution (*17*). $1T$-VSe_2 was prepared at rather low temperature (450°C) in order to prevent the growth of a self-intercalated sample $V_{1+x}Se_2$. Since the ammonia intercalates are hygroscopic and exhibit a considerable NH_3 pressure at room temperature, all sample handling had to be carried out in an atmosphere of dry NH_3 gas. This was done by conventional gas handling methods; NH_3 gas of 1 atm was dried using a column filled with powdered KOH.

The intercalation of powdered TX_2 with NH_3 was performed by condensing an excess of dry NH_3 gas into a 120-ml autoclave containing about 4 g of the dichalcogenide. The autoclave was then sealed and left at room temperature for 2–4 days. The NH_3 pressure raised to 10 atm. Afterward the excess NH_3 was removed under a pressure of 1 atm using a gas handling system. The

product was transferred into a sampling tube from which samples for X-ray diffraction and magnetic measurements could easily be obtained. To avoid contact with air the coupling was performed as fast as possible and under a continuous outlet of NH_3 gas.

The samples were analyzed by X-ray diffraction using a Debye-Scherrer camera ($CuK\alpha$ radiation) with the samples enclosed in sealed capillaries; intensities were estimated.

Attempts to prepare NH_3 intercalates of $1T$-$TiSe_2$ and $1T$-VSe_2 were not successful. Since the dichalcogenides showed rather broad diffraction lines after the experiments we feel that intercalation might have taken place at 10 atm, followed by deintercalation at 1 atm.

X-Ray Diffraction

The cell constants of the intercalates of this study are summarized in Table I. X-ray powder data of $3R$-VS_2NH_3 and $3R$-TaS_2NH_3 are given in Tables II and III. The cell constants of $2H$-TaS_2NH_3 are in good agreement with those of Chianelli *et al.* (*7*); less agreement is present for $3R$-TiS_2NH_3, also reported by Chianelli *et al.* (*7*). This is probably due to a different composition; those of Chianelli *et al.* refer to a somewhat smaller NH_3 content.

Intercalates of $1T$-VS_2 and $1T$-TaS_2 were not described before; the NH_3 intercalate of

TABLE I

CRYSTAL DATA OF THE HOSTS FOR INTERCALATION (FROM LITERATURE AND THE NH_3 INTERCALATES OF THIS STUDY)

	a(Å)	c(Å)		a(Å)	c(Å)
$1T$-TaS_2	3.365	5.896	$3R$-TaS_2NH_3	3.380(1)	27.67(2)
$1T$-VS_2	3.221	5.755	$3R$-VS_2NH_3	3.250(1)	27.37(2)
$1T$-TiS_2	3.407	5.695	$3R$-TiS_2NH_3	3.428(1)	27.05(3)
$2H$-TaS_2	3.316	12.070	$2H$-TaS_2NH_3	3.311(1)	18.28(2)

Note. Standard deviations in parentheses.

TABLE II

Observed and Calculated X-Ray Powder Data of 3R-VS$_2$NH$_3$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}	hkl
9.214	9.124	100	100	003
4.586	4.562	5	3	006
3.042	3.042	1	1	009
2.762	2.757	20	7	012
2.591	2.063	1	1	104
2.507	2.503	50	22	015
2.280	2.281	1	<1	0012
2.175	2.174	20	11	018
1.964	1.962	10	5	1010
1.865	1.864	1	2	0111
1.687	1.686	10	6	1013
1.625	1.625	10	5	110
1.599	1.599	10	4	113
1.519	1.521	1	1	0018
1.462	1.462	1	1	1016
1.399	1.400	1	<1	202
1.364	1.363	1	2	205
1.301	1.302	1	2	208
1.110	1.110	1	1	1118

Note. Debye-Scherrer camera, Cu$K\alpha$ radiation. Atoms: V at (0, 0, 0); S at ±(0, 0, 0.385); NH$_3$ at ±(0, 0, 0.1667) occupied for one-half; space group $R\bar{3}m$. $a = 3.250(1)$ Å, $c = 27.37(2)$ Å.

1T-TaS$_2$ was always found to be contaminated by the host. The cell constants of the intercalates point to the same structure as other 1T-TX$_2$ intercalates, viz., 3R-TiS$_2$NH$_3$ (7) and 3R-ZrS$_2$NH$_3$ (18). The structures of 3R-TiS$_2$NH$_3$ and isotypes and 2H-TaS$_2$NH$_3$ together with the host lattices of 1T-TiS$_2$ and 2H-TaS$_2$ are shown in Fig. 1. The coordination of the transition metal in the intercalates is the same as in the host. It is seen that the sandwiches are displaced so that NH$_3$ resides in the trigonal-prismatic holes between sulfur layers of neighboring sandwiches. The resulting structures are rhombohedral, space group $R\bar{3}m$ or $R3m$, in the case of the 1T-TX$_2$ intercalates and hexagonal, space group $P6_3/mmc$ or $P6_3mc$ in the case of 2H-TaS$_2$NH$_3$. The choice between the possible space groups depends upon the occupation of the two trigonal-

prismatic sites in the gap. When only one of these sites is occupied, then the structures have the noncentrosymmetric space groups. In the case that both sites are occupied statistically (for one-half) the centrosymmetric space groups must be adopted. Since the van der Waals diameter of a NH$_3$ molecule is 3.35 Å (the N–N distance in solid ND$_3$ (19)), the distance between the centers of the two trigonal-prismatic sites being $\frac{1}{3} a\sqrt{3} = 2.0$ Å, it may safely be assumed that neighboring sites generally are not occupied simultaneously. Because of the equivalence of the two sites it is expected that domains corresponding to the two possible occupancies are present in a crystallite. X-ray powder diffraction

TABLE III

Observed and Calculated X-Ray Powder Data of 3R-TaS$_2$NH$_3$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}	hkl
9.117	9.224	100	100	003
4.662	4.612	20	11	006
3.068	3.075	1	2	009
2.907	2.911	10	8	101
2.861	2.864	20	15	012
2.694	2.696	5	5	104
2.588	2.588	20	19	015
2.352	2.353	10	7	107
2.309	2.306	5	2	0012
2.237	2.235	10	10	018
2.013	2.011	10	7	1010
1.904	1.908	5	4	0111
1.845	1.845	5	1	0015
1.721	1.722	10	5	1013
1.689	1.690	10	5	110
1.660	1.662	10	6	113
1.586	1.587	5	3	116
1.537	1.537	5	1	0018
1.488	1.489	5	2	1016
1.457	1.456	5	2	202
1.417	1.415	5	2	205
1.347	1.348	1	1	208
1.248	1.246	1	2	1115

Note. Debye-Scherrer camera, Cu$K\alpha$ radiation. Atoms: Ta at (0, 0, 0); S at ±(0, 0, 0.389); NH$_3$ at ±(0, 0, 0.167) occupied for one-half. Space group $R\bar{3}m$. $a = 3.380(1)$ Å, $c = 27.67(2)$ Å.

cannot give conclusive information regarding these possibilities because of the rather small difference in the powder intensities for the centrosymmetric and noncentrosymmetric space groups. From neutron powder diffraction of $2H\text{-}TaS_2ND_3$ (8, 9) and $3R\text{-}TiS_2ND_3$ (10) it was found that both sites are occupied statistically.

Magnetic Measurements

Magnetic measurements of NH_3 intercalates were obtained in the temperature range 4.2 to 300 K, using techniques described before (20). The results are shown in Figs. 2–4. All phases show a Pauli paramagnetism of the conduction electrons plus possible contributions due to van Vleck type band paramagnetism. While these are almost temperature independent in the case of $1\text{-}TiS_2$, $2H\text{-}TaS_2$, and the corresponding intercalates with NH_3 (Figs. 3 and 4), a significant paramagnetic upturn at decreasing temperature is observed in the molar magnetic susceptibility (χ_m) versus temperature curves of $1T\text{-}VS_2$ and $3R\text{-}VS_2NH_3$ (Fig. 2). From the measured curves, it may be concluded that the same kind of contributions are acting in $1T\text{-}VS_2$ and $3R\text{-}VS_2NH_3$. If a paramagnetic contribution

FIG. 3. Molar magnetic susceptibility (χ_m) versus temperature of $1T\text{-}TiS_2$ powder (○, lower curve) and $3R\text{-}TiS_2NH_3$ powder (⊡, upper curve) for an applied field of 8.75 kOe.

from interlayer $V^{2+}(3d^3)$ is assumed, the measured χ_m can be written as a sum of an intrinsic part χ_i and a paramagnetic Curie term $\chi_p = C/T$; $C = 1.875$ for spin-only V^{2+} $(S = \frac{3}{2})$. Nearly temperature independent susceptibilities are obtained after correcting the total susceptibility of each of the samples for paramagnetic contributions of 0.23 at.% of interlayer V^{2+}.

Similar considerations, i.e., assuming interlayer Ti^{2+} (discussed in our paper on $1T\text{-}TiS_2$ and $2H\text{-}TiS_2$ (21)), account for the relatively small paramagnetic upturn ob-

FIG. 2. Molar magnetic susceptibility (χ_m) versus temperature of $1T\text{-}VS_2$ powder (○, lower curve) and $3R\text{-}VS_2NH_3$ powder (⊡, upper curve) for an applied field of 8.75 kOe.
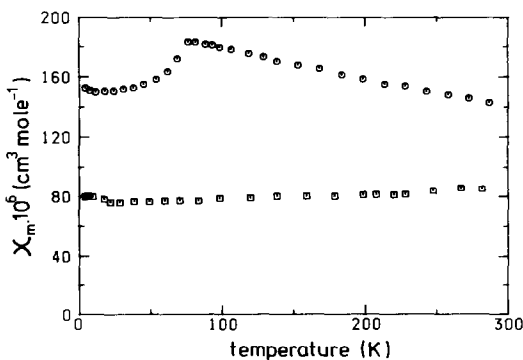
FIG. 4. Molar magnetic susceptibility (χ_m) versus temperature of $2H\text{-}TaS_2$ powder (○, upper curve) and $2H\text{-}TaS_2NH_3$ powder (⊡, lower curve) for an applied field of 8.75 kOe.

served below 50 K in χ_m of $1T\text{-}TiS_2$ and $3R\text{-}TiS_2NH_3$ (Fig. 3).

Our χ_m versus temperature curves of $1T\text{-}VS_2$ and $3R\text{-}VS_2NH_3$ do not show CDW/PLD type transitions; the transition found by Murphy et al. (17) of $1T\text{-}VS_2$ at 305 K is just outside the temperature range of our measurements. Intercalates Li_xVS_2 show an increase in χ for small amounts of lithium but a complicated behavior of χ with temperature for larger Li content (17). Intercalation of $1T\text{-}TiS_2$ with alkali metal also leads to an increase in χ.

The magnetic susceptibility versus temperature curve of $2H\text{-}TaS_2$ shows an anomaly at 78 K due to a CDW/PLD transition (22). The disappearance of the anomaly and the simultaneous decrease in χ_m on intercalation with NH_3 (Fig. 4) was also observed by Schöllhorn and Zagefka (4). The χ_m versus temperature curve of $2H\text{-}TaS_2$ obtained by deintercalation of $2H\text{-}TaS_2NH_3$ during 2 hr at 450 K in vacuo (data points not shown) follows that of $2H\text{-}TaS_2$ quite closely; the anomaly at 78 K is smeared out, but the onset temperature is not reduced. X-ray powder diffraction of $2H\text{-}TaS_2$ obtained by deintercalation showed broad diffraction lines due to small particle size and/or disorder introduced during intercalation and deintercalation. Our magnetic measurements exclude the possibility of formation of a hydrogen intercalate H_xTaS_2 on heating the NH_3 intercalate in vacuo; such a hydrogen intercalate can be prepared by cathodic reduction of $2H\text{-}TaS_2$ (23).

No measurements were made of the NH_3 intercalate of $1T\text{-}TaS_2$, because the sample obtained on intercalation consisted of a two-phase mixture of the intercalate and $1T\text{-}TaS_2$.

The changes in χ_m of different host dichalcogenides on intercalation with NH_3 can be understood qualitatively from the band structure of the hosts, considering that the Pauli χ_m is proportional to the total

density of states at the Fermi surface ($N(E_F)$) and assuming a rigid band formalism. In the rigid band formalism one assumes that the band structure of the host is not changed on intercalation and that the only change is the filling of the lowest lying unoccupied or partly filled band by electrons from the intercalant.

From band structure calculations of $1T\text{-}TiS_2$ (24), $1T\text{-}VS_2$ (25), and $2H\text{-}TaS_2$ (26), one finds that on electron donation the total density of states at E_F will increase for $1T\text{-}TiS_2$ and $1T\text{-}VS_2$ and decrease for $2H\text{-}TaS_2$. Schematic density of states versus energy plots are shown in Fig. 5; the symmetry characters are those at Γ in the Brillouin zone. In these schematic density of states plots the e_g conduction band of $1T\text{-}TiS_2$ is empty while the conduction band of $1T\text{-}VS_2$ and $2H\text{-}TaS_2$, respectively, a_{1g} (mainly $3d_{z^2}$) and a'_1 (mainly $5d_{z^2}$) are half-filled. From these simple schemes one expects on electron donation a decrease of $N(E_F)$ in the case of $2H\text{-}TaS_2$ and $1T\text{-}VS_2$ and an increase in $N(E_F)$ for $1T\text{-}TiS_2$. A comparison with the total density of states versus energy plot given by Myron (25) shows, however, that on intercalation of $1T\text{-}VS_2$ with electron donating species, $N(E_F)$ will increase.

The observed trends in χ_m of the NH_3 intercalates, corresponding to a lowering of $N(E_F)$ in the case of $2H\text{-}TaS_2$ and to an increase in $N(E_F)$ for $1T\text{-}TiS_2$ and $1T\text{-}VS_2$, are therefore in agreement with electron donation of intercalated NH_3.

Johnston (27) analyzed the magnetic susceptibility data of a number of intercalates of $2H\text{-}TaS_2$ quantitatively on the basis of the rigid band model. He deduced for the NH_3 intercalate an electron transfer of 0.28 electron per Ta which agrees with the value of 0.25 electron per Ta found by Butz and Lerf (28) from the shift in the ^{181}Ta nuclear quadrupole frequency of $2H\text{-}TaS_2NH_3$ with respect to that of $2H\text{-}TaS_2$. About the same fraction of charge per intercalated NH_3 fol-
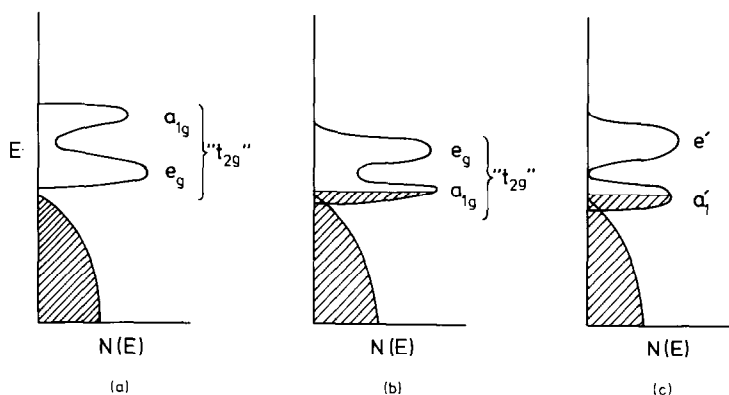
FIG. 5. Schematic band models with density of state versus energy diagrams of (a) 1T-TiS$_2$, lowest d band (e_g) unoccupied; (b) 1T-VS$_2$, one electron in the lowest d band (a_{1g}); and (c) 2H-TaS$_2$, lowest d band (a_1') half-filled.

lowed from the experiments performed by Bernard (6) on 3R-TiS$_2$NH$_3$ discussed in the Introduction.

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