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A Neutron Powder Diffraction Study of ND_3 Intercalated Titanium Disulfide, 3*R*-TiS_2ND_3

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Neutron powder diffraction of rhombohedral 3*R*-TiS_2ND_3 (a = 3.419 Å, c = 27.03 Å at 300 K, space group $R\bar{3}m$) has shown that ND_3 molecules and ND_4^+ ions, present in a ratio of about 5 to 1 from chemical and physical evidence, occupy statistically the trigonal-prismatic holes between TiS_2 sandwiches. One cannot distinguish between ND_3 and ND_4^+. Powder intensities calculated for a model with spherically symmetric ND_3 molecules (corresponding to isotropically rotating ND_3 and ND_4^+) in the trigonal-prismatic holes were in reasonable agreement with the observed intensities. Attempts to obtain information on the precise orientation of ND_3 and ND_4^+ in the TiS_2 lattice using refinements with structure factors were not successful; the reliability R factor was 0.093 for spherical symmetric ND_3 molecules with nitrogen in the center of the trigonal-prismatic holes.

Introduction

Like the alkali metals, 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 (*1–3*). The lone pair orbital of nitrogen appears to play an important factor in the stability. In fact intercalation of substituted pyridines into 2H-TaS_2 will not take place when the substituent greatly decreases the basicity of the molecule (*4*). The alkyl backbone of long chain amines and amides (*n*-octylamide. stearamide) is perpendicular to the sandwiches TX_2 with the NH_2 group oriented toward the layers (*5*). This orientation suggests that the stability is due to the energy gain from the overlap of the lone pair electrons of the NH_2 group with d orbitals of the transition metal.

The structures of the ammonia intercalates of transition metal sulfides, e.g., 3*R*-TiS_2NH_3 and 2H-TaS_2NH_3, are such that NH_3 resides in trigonal-prismatic holes between sulfur layers of neighboring sandwiches TS_2 (T = Ti, Ta). The coordination of the transition metal atoms is the same as in the host used for intercalation, a trigonally distorted octahedron for titanium and a trigonal prism for tantalum. The sandwiches are displaced with respect to the stacking in the host, sulfur atoms of neighboring sandwiches being on top of each other as shown in Fig. 1 for 3*R*-TiS_2NH_3. The resulting structure of the intercalate is

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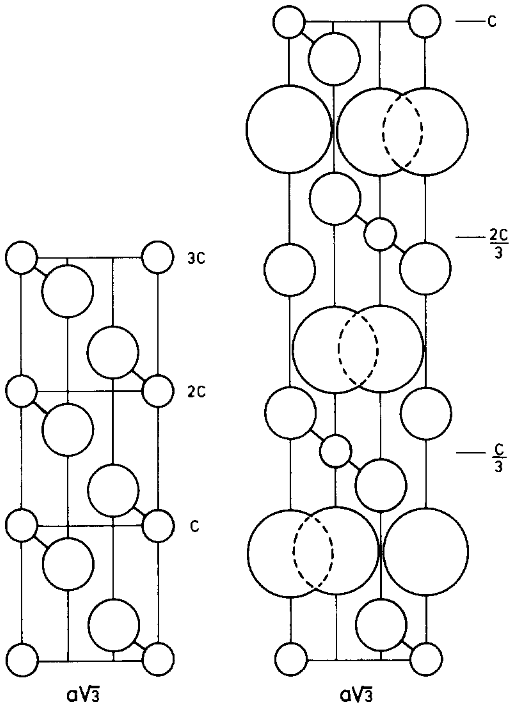

FIG. 1. (11$\bar{2}$0) section of the structure of 1*T*-TiS_2 (left) and 3*R*-TS_2NH_3(right). Both trigonal prismatic sites are (statistically) occupied by NH_3 (large circles); small circles represent titanium atoms.

rhombohedral, space group $R3m$ in the case that only one of the trigonal-prismatic holes (two per unit TiS_2) is occupied by NH_3. When both sites are occupied statistically then the average structure has the centrosymmetric space group $R\bar{3}m$.

Based on the work of Schöllhorn and Zagefka (*6*) it is now believed that the intercalation of ammonia is accompanied by a redox reaction,

$$2NH_3 \rightarrow N_2 + 6H^+ + 6e^-,$$

the overall intercalation reaction being:

$$TX_2 + (8x + y)\,NH_3 \rightarrow (TX_2)^{6x-}(NH_4)^+_{6x}(NH_3)_y + xN_2\nearrow.$$

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 (*7*).

Bernard *et al.* (*8*) came from an analysis of the products released during deintercalation of TiS_2NH_3 (in the following we will use this formula to indicate a fully intercalated compound disregarding the presence of NH_3) to the same conclusion: the amount of NH_4^+ per unit TiS_2 was estimated to be 0.2.

Several models were proposed for the orientation of NH_3 (and NH_4^+) inside the trigonal prism of sulfur atoms. The model proposed in the early stage of the study of NH_3 intercalates was that by Cousseau *et al.* (*9*); they assumed that the lone pair orbital of nitrogen (along the C_3 axis) is perpendicular to the sandwiches (plugged in model, Fig. 2a). X-ray powder diffraction of NH_3 intercalated TiS_2 showed that nitrogen is in the midplane between sulfur layers (*10*). Neutron powder diffraction of 2H-TaS_2ND_3 by Riekel *et al.* (*11, 12*) was also in favor of a midplane position of nitrogen. On the basis of the intensities of the 00*l* reflections these authors could not distinguish between a model with isotropically rotating ND_3, nitrogen being in the center of the trigonal prism of sulfur, and a model with the C_3 axis of ND_3 in the midplane of sulfur, the molecules spinning around the trigonal axis.

NMR studies of ammonia intercalated 2H-TaS_2 and 1*T*-TiS_2 are in favor of a parallel orientation of the lone pair orbital of nitrogen (Fig. 2b). The molecules spin rapidly around the trigonal (C_3) axis and the C_3 axis also performs reorientations mainly in the basal plane (*13–16*). Rapid spinning and/or reorientation of the C_3 axis was also found by Riekel *et al.* (*17*) using quasi-elastic neutron scattering of 2H-TaS_2NH_3.

The now commonly accepted ionic model explains the observed midway position of nitrogen in the lattice of the interca-

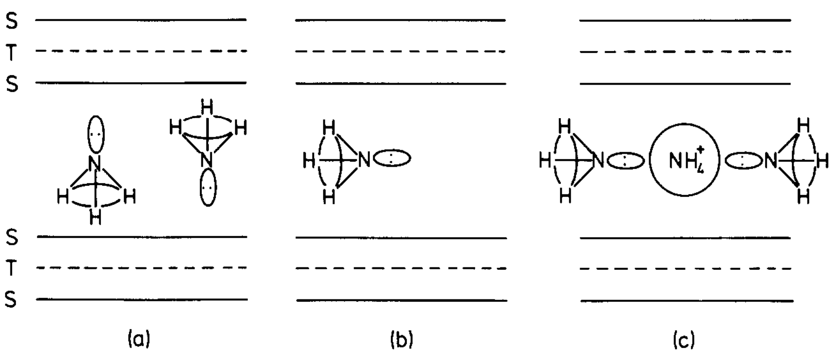

FIG. 2. The orientation of the ammonia molecule in the van der Waals gap. (a) Plugged in model; the C_3 axes point toward the sulfur layers of sandwiches *T*S_2. (b) C_3 axes parallel to the sandwiches; nitrogen in the midplane. (c) NH_4^+ surrounded by NH_3 molecules.

late in terms of an ion–dipole interaction of a central NH_4^+ group with neighboring NH_3 molecules (Fig. 2c). From this model one expects fast proton exchange; this was however not found from NMR (*13–16*). Bernard *et al.* (*8*) supposed that the protons are in fixed positions due to the interaction with the negatively charged sulfur layers.

In this study we report the results of a structure analysis by neutron powder diffraction of TiS_2ND_3 at 300 and 4.2 K. We choose this compound because it is well characterized by chemical methods, X-ray diffraction, and NMR.

Experimental

TiS_2 was prepared from the elements at 600°C. The presence of interlayer titanium was checked by the measurement of the magnetic susceptibility. It was found from the very small paramagnetic upturn at very low temperature (*18, 19*) that the amount of interlayer titanium is negligibly small.

Since the ammonia intercalates are hygroscopic and exhibit considerable ammonia pressure at room temperature, all sample handling had to be carried out in an atmosphere of dry ND_3 gas. This was done by conventional gas handling methods; ND_3 gas, obtained from Matheson Laboratories, was dried using a column filled with powdered KOH. The intercalation of TiS_2 was performed by condensing an excess of dry ND_3 gas into a 120-ml autoclave containing about 20 g powdered TiS_2. The autoclave was then sealed and left at room temperature for 4 days. The ND_3 pressure raised to 10 atm. Afterward the excess ND_3 was removed under a pressure of 1 atm. The transfer into the sample tube for neutron powder diffraction was proceeded as fast as possible and under a continuous outlet of dry ND_3 gas.

Neutron Powder Diffraction of 3*R*-TiS_2ND_3

Collection of powder data was performed at the high-flux reactor of the ECN at Petten, The Netherlands. Neutrons of wavelength 2.59 Å were obtained from the (111) plane of a copper crystal. The λ/n components were reduced to less than 0.1% using a filter of pyrolytic graphite. Soller slits with a horizontal divergence of 30′ were placed between the reactor and monochromator and in front of the four ^3He counters. The diagrams were taken with the sample at 300 and 4.2 K; the diagram taken at 300 K is shown in Fig. 3. The diagram is split up in parts because of the over-

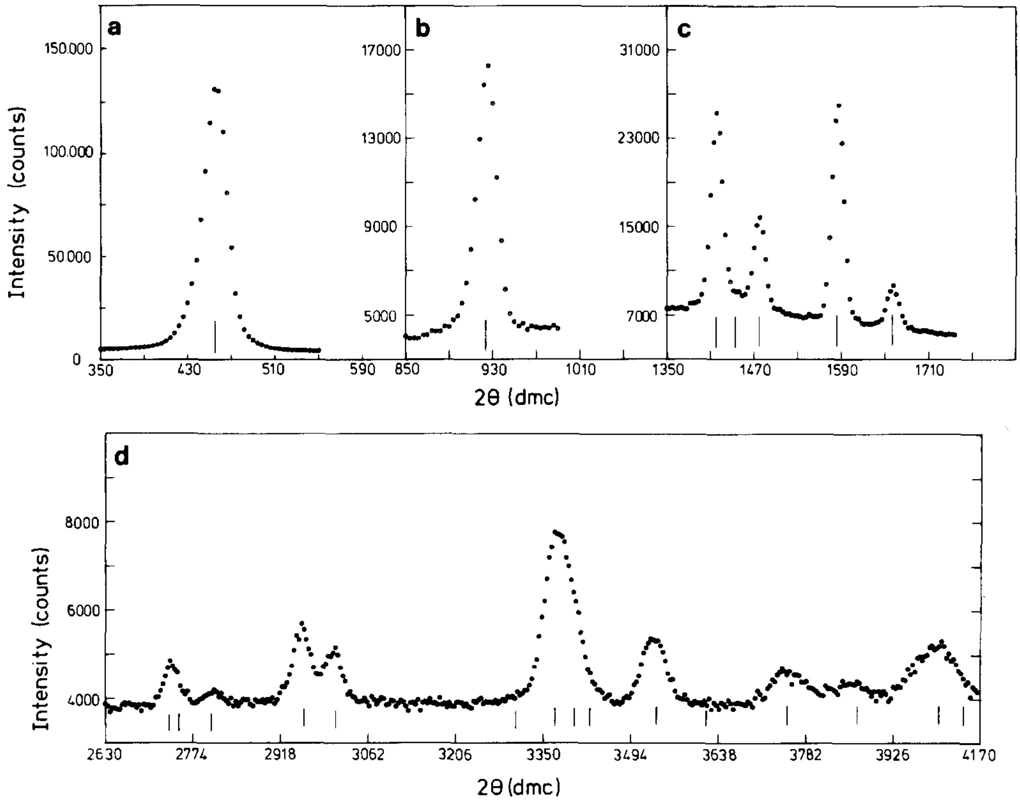

FIG. 3. Neutron diffraction diagram of TiS_2ND_3 taken at 300 K; the diagram is split in several parts. (a) 350–590 dmc (003); (b) 850–1010 dmc (006); (c) 1350–1740 dmc; (d) 2630–4170 dmc. The calculated positions (Table I) are indicated at the bottom.

whelming intensity of 003. No drastic changes are noticed in the relative intensities of the diffraction lines recorded at both temperatures. The reflections correspond to the rhombohedral unit cell discussed above, with a = 3.419(1) Å, c = 27.030(14) Å at 300 K and a = 3.405(2) Å, c = 26.689(22) Å at 4.2 K (hexagonal setting; standard deviations are in parentheses). The cell constants at 300 K differ from those reported by Chianelli *et al.* (*10*) for $3R$-TiS_2NH_3, a = 3.427(2) Å, c = 26.55 Å. This is probably due to a different ammonia content since the main difference is in the length of the c axis. Integrated intensities obtained from the number of counts after correcting for the background scattering are given in Table I. The intensity of 003 was given the relative value 1000. Some of the observed peaks consist of overlapping reflections.

Intensities were calculated on the basis of the rhombohedral structure from X-ray diffraction (*10*). Model calculations were performed similar to those used in our neutron powder diffraction study of the intercalate $Na_{0.6}(D_2O)_2VS_2$ and $Na_{0.6}(D_2O)_2VSe_2$ (*20*). In this intercalate the Na^+ ion is surrounded by "rotating" D_2O molecules. The same type of calculations were later used by Riekel *et al.* (*11, 12*) in a neutron diffraction study of $2H$-TaS_2ND_3.

It was assumed that the N–D bond length is 1.0 Å (equal to the N–D distance in solid

TABLE I

Observed and Calculated Neutron Powder Diffraction Intensities of $3R$-TiS_2ND_3 at 300 K

hkl	$2\theta^d$(dmc)	$I(o)^a$	$I(c)^b$
003	457.4	1000	1322
006	926.2	75	98
009	1416.9	104	94
101	1450.0	<2	1
012	1477.5	50	41
104	1584.2	100	97
015	1661.3	20	20
107	1857.4	<2	0
0012	1947.1	<2	0
018	1974.7	<2	1
1010	2245.8	<2	1
0111	2400.0	*c*	—
0015	2549.3	*c*	—
110	2737.7	7	5
1013	2751.6		3
113	2804.4	3	3
0114	2953.7	15	16
116	3008.2	10	5
0018	3306.1	<2	1
119	3371.1	59	41
021	3401.7		9
202	3427.8		1
1016	3449.3	<2	0
024	3535.3	17	17
205	3619.6	<2	1
0117	3752.0	10	13
027	3866.8	<2	4
1112	4001.5	24	16
208	4046.7	<2	0

[a] I(o): the observed intensities from the number of counts: I(o) of 003 was given the relative value 1000.

[b] I(c): intensities calculated for isotropically rotating ND_3 with parameters given in Table II. Scaling with I(o) using 006, 009, 012, 104, and 015.

[c] Reflections omitted because of interference with peaks from the sample holder.

[d] 2θ in dmc; 360° = 10^4 dmc.

ND_3 (*21*)). The scattering lengths of atoms (b(N) = 0.93, b(D) = 0.667, b(Ti) = −0.35, b(S) = 0.285: all in units of 10^{-12} cm) are from a compilation by Koester and Yelon (*22*).

The model for which the intensity of the powder lines can easily be calculated and for which a refinement procedure can be performed using the X-ray system (*23*) is the model with nitrogen at the center of the trigonal prism of sulfur atoms and deuterium at the surface of a sphere around nitrogen with a radius of 1.0 Å. The scattering length of this isotropically rotating ND_3 molecule is given by (*24*)

$$b = \frac{b(\mathrm{N}) + 3b(\mathrm{D}) \sin(kR)}{kR},$$

in which b(N) and b(D) are the scattering lengths of nitrogen and deuterium, respectively; R, the N–D distance, is 1.0 Å, and $k = 4\pi \sin \theta/\lambda$. The powder intensities of the Bragg reflections were calculated using

$$I = m^*|F|^2/(\sin \theta \sin 2\theta),$$

where F is the structure factor, m the multiplicity, and ($\sin \theta \sin 2\theta$) the geometrical factor (*25*).

The intensities calculated in space group $R\bar{3}m$ (both trigonal-prismatic sites occupied statistically for one-half) with an overall isotropic temperature factor of the atoms were in reasonable agreement with the observed intensities of Table I. The same calculation in space group $R3m$ (ND_3 present in only one of the two sites) was considerably worse. The intensities of some reflections calculated in $R\bar{3}m$ differ considerably from the observed intensities: this may be due to the fact that (a) the model is in principle correct but the temperature motion is more complicated than assumed, (b) the model of an isotropically rotating ND_3 molecule is not correct and other models for intercalated ND_3 must be considered, e.g., models with the C_3 axis of the ND_3 molecules parallel to the TiS_2 sandwiches. There were no indications of strong preferent orientation of the powder particles in the sample holder; one expects in that case 00*l* reflections and 10*l* reflections with *l* large to be systematically weaker than expected.

A further analysis was made using the X-ray system (*23*) on the basis of the structure factors calculated from the observed

TABLE II

COORDINATES AND THERMAL PARAMETERS OF $3R$-TiS_2ND_3 FROM A REFINEMENT USING THE X-RAY SYSTEM

Atom	Site	Coord.	n	z	U (Å^2)
Ti	3a	(000)	1	0	0.031(19)
S	6c	±(00z)	1	0.386(1)	0.022(14)
ND_3	6c	±(00z)	0.5	0.167(1)	0.167(35)

Note. The atoms are on special positions 3a and 6c of space group $R\bar{3}m$; n is the occupancy. Standard deviations are in parentheses.

intensities. For isotropically rotating ND_3 molecules, the scattering factor can be introduced quite simply. A refinement with individual isotropic temperature factors of titanium, sulfur, and the ND_3 molecule revealed a R_f of 0.093. The final parameters are given in Table II. A refinement of the occupancy of the ND_3 site did not lead to significant changes. The isotropically rotating ND_3 molecules show a very large temperature factor; $U = 0.167$ Å^2, which corresponds to a root-mean-square amplitude of vibration of 0.41 Å. A refinement with an anisotropic temperature factor for ND_3 did not improve the agreement; there is only a slight difference between U_{11} (in the ab plane) and U_{33} (along c). A difference Fourier synthesis did not show deviations at the ND_3 site from which a significant change in the model could be deduced; the main difference densities are in the planes of sulfur and titanium. The difference density is negative at the titanium site and positive at the sulfur site. There is also some density at the unoccupied sites at the trigonal axes in the planes of titanium and sulfur, negative for sites in the titanium plane and positive for sulfur. There are no indications that deuterium is in the plane of titanium as has been found for deuterium atoms in D_xTaS_2 and hydrogen atoms in the case of H_xNbS_2 (*26*).

One may compare these results with those of Riekel *et al.* (*11, 12*) from a neutron powder diffraction study of $2H$-TaS_2ND_3. On the basis of the intensities of the $00l$ reflections only, they could not distinguish between a model of isotropically rotating molecules and a model with the molecules having their C_3 axes lying in the midplane between sulfur layers. It may be noted that from the $00l$ reflections only, no information can be obtained from a possible preferred orientation of the C_3 axis in the midplane of sulfur. Structure factors for a model with ND_3 molecules spinning around the trigonal axis, which adopts three by symmetry related orientations in the midplane of sulfur, can be calculated with the scattering amplitude for deuterium atoms equal to $b = 3b(\mathrm{D})J^0(x)$ with $J^0(x)$ the zero-order Bessel function with argument x, $x = kR \sin \alpha$, $k = 4\pi \sin \theta/\lambda$, $R = 0.95$ Å, and α is the angle between the plane of the rotating deuterium atoms and the reflecting plane (*24*). For this and more complicated models with a midplane C_3 axis, e.g., those with a spread in orientations of the C_3 axis, refinement programs are not available.

For a definite conclusion about the orientation of ammonia and also information about the presence of ND_4^+ one needs a much larger data set, preferably from a single crystal, from which deviations of the spherical symmetric distribution of deuterium around nitrogen can be traced. So far we feel from the information of the difference Fourier synthesis that the model of a spherically symmetric ND_3 molecule must be quite good.

The model of a spherically symmetric ND_3 molecule in our calculations corresponds physically either to a statistical distribution of ND_3 (and ND_4^+) in all possible orientations or, dynamically, to rotating ND_3 as well as ND_4^+.

The observation that the intensities change only slightly in going from 300 to 4.2 K indicates a distribution of orientations even at 4.2 K; at 300 K the molecules must also perform rapid reorientations and diffusion as was found from NMR (*13–17*).

The neutron diffraction diagrams, taken at 300 K as well as 4.2 K, also show an increased background intensity with a maximum at $d = 3.0$ Å, a distance close to the intermolecular N–N distance of 3.35 Å in solid ND_3 (*21*). This diffuse scattering may be due to ND_3 not registered with the TiS_2ND_3 lattice.

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