The Incoherent Inelastic Neutron Spectra of $\text{TaS}_2 \cdot \text{NH}_3$
and $\text{TaS}_2(\text{NH}_3)^{1/3}(\text{H}_2\text{O})^{2/3}$

C. Riekel *
I. L. L., F-38042 Grenoble, France
R. Schöllhorn
Institut für anorganische Chemie der Universität Münster **
and J. Tomkinson
Rutherford Laboratory, Chilton, Didcot, Oxon, OX11 0Ox, U. K.

Z. Naturforsch. 35 a, 590–594 (1980); received March 20, 1980

Incoherent, inelastic neutron spectra of $\text{TaS}_2(\text{NH}_3)$, $\text{TaS}_2(\text{NH}_3)^{1-2}$ and $\text{TaS}_2(\text{NH}_3)^{2/3}(\text{H}_2\text{O})^{2/3}$ were measured in the range 250 cm$^{-1}$ → 1600 cm$^{-1}$. The data suggest the presence of $\text{NH}_4^+$ cations and are in agreement with an ionic structure model proposed for these compounds.

I. Introduction

The intercalation compounds of layered dichalcogenides $\text{MX}_2$ ($\text{M} =$ transition metal, $\text{X} =$ S, Se) with Lewis base guest molecules have received considerable attention due to their interesting physical properties and structural anisotropy [1]. The most simple molecule that is known to intercalate is the thermodynamically stable compound $\text{NH}_3$; extensive work has been devoted to the characterization of the intercalation reactions and the products $\text{MS}_2(\text{NH}_3)$. The theoretical treatment of the interaction host lattice/guest molecules in terms of whole-complex molecular orbitals [2] or the Mulliken charge-transfer formalism [3] suggests a transfer of electron density towards the dichalcogenide layers. Recent investigations were able to demonstrate, however, that the intercalation process is correlated with redox reactions, and an ionic structure model [4] was presented that involves the presence of $\text{NH}_4^+$ ions: $(\text{NH}_4^+)^x(\text{NH}_3)^{1-x}[\text{MS}_2]^x$. An alternative model, suggested recently, implies hydride formation [5] with hydrogen atoms in the intralayer position as observed for $\text{H}_2\text{TaS}_2$ [6]. The basic structure schemes for the different models are given in Figure 1.

Evidence for the presence of cations in the van der Waals gap was derived from ion exchange reactions [4] and time differential perturbed angular correlation studies of the $^{185}\text{Ta}$ nuclear quadrupole frequency [7]. Structural studies which have been performed by X-ray diffraction [8,9] suffer from inherent disorder in the intercalated compounds and the lack of accuracy for detection of hydrogen. IR and Raman spectroscopy have been unsuccessful, which may be due to the metallic conductivity of the intercalated phases. In this communication we report on inelastic incoherent neutron scattering (INS) studies on $\text{TaS}_2 \cdot \text{NH}_3$.

As the spectra are dominated by hydrogen scattering due to the high incoherent scattering cross section of hydrogen [10], they can be expected to reflect principally the intercalated molecules. Both model II and model III assume that the majority of intercalated molecules are ammonia molecules. To increase the scattering contrast of the bands, corresponding to either $\text{NH}_4$ or hydride vibrations,
several spectra on partly desorbed TaS$_2$(NH$_3$)$_{1-x}$ were measured. A further comparison is made with TaS$_2$(NH$_3$)$_{1/3}$(H$_2$O)$_{2/3}$ [11] which has been formulated as (NH$_4^+$)$_{1/3}$(H$_2$O)$_{2/3}$[TaS$_2$]$_{1/3}$ [12].

II. Materials and Methods

The different phases were prepared from 10 gr. 2H-TaS$_2$ each. Ammonia was intercalated at $-10^\circ$C in an aluminium can, connected to a high vacuum line [13]. The spectrum of sample and container was measured on the beryllium filter spectrometer -IN1B at the I. L. L. Grenoble at liquid N$_2$ temperature. Ammonia was desorbed subsequently at $10^\circ$C, $25^\circ$C and $45^\circ$C. After each desorption, a spectrum was measured. The stoichiometry of TaS$_2$(NH$_3$)$_{1-x}$ was determined from the change in the background at $1300$ cm$^{-1}$, assuming that the change is proportional to the hydrogen content ($X = 0.0, 0.3, 0.5, 0.7$ for the four measurements). TaS$_2$(NH$_3$)$_{1/3}$(H$_2$O)$_{2/3}$ was prepared from 21% aqueous ammonia solution and measured under the same conditions. A further 10 gr. 2H-TaS$_2$ were measured as background. No prominent lattice modes were found in this spectrum for the frequency range explored $(250$ cm$^{-1} \rightarrow 1600$ cm$^{-1}$). All spectra were corrected by subtracting the scattering due to the 2H-TaS$_2$ host lattice.

III. Results and Discussion

The corrected spectra are shown in Figures 2 a, b. For comparison, the spectrum of solid NH$_3$ measured at $8.5$ K is given in Figs. 2 c and d. The $v_2$ band of solid NH$_3$ at $1066(10)$ cm$^{-1}$ (IR: $1060(12)$ cm$^{-1}$) [14] is also found in the TaS$_2$·NH$_3$ spectrum ($1066$ cm$^{-1}$) but not in the TaS$_2$(NH$_3$)$_{1/3}$(H$_2$O)$_{2/3}$ spectrum. This suggests that no NH$_3$ molecules are present in the latter phase (see below). Upon desorption from TaS$_2$·NH$_3$, the $v_2$ band disappears as expected.

The vibrational spectrum of solid NH$_3$ has been interpreted in terms of monomeric molecules, coupled weakly in the crystal lattice [14]. A similar conclusion applies obviously to TaS$_2$·NH$_3$. Thermodynamic data suggest that weak hydrogen bonding, found in solid ammonia [15], is also present in TaS$_2$·NH$_3$ [16]. The pyridine molecules in TaS$_2$(C$_5$H$_5$N)$_{0.5}$ appear likewise not to be coupled strongly in the crystal lattice as the bands were only found to be slightly perturbed as compared to solid C$_5$H$_5$N by IINS spectroscopy [17].

Lattice vibrations, including librational modes, were assigned to the frequency range <500 cm$^{-1}$ in crystalline NH$_3$ [14]. The TaS$_2$·NH$_3$ spectrum is less structured in this range than the NH$_3$ spectrum (Figures 2 a, c). A dramatic change occurs however upon desorption, resulting in the formation of TaS$_2$(NH$_3$)$_{1-x}$, as two new bands, centered at $390(10)$ cm$^{-1}$ and $590(10)$ cm$^{-1}$, appear. It is suggested that these two bands are due to a second molecular fraction, already present in the TaS$_2$·NH$_3$ phase. We exclude the possibility of an increasing population of isolated NH$_3$ molecules as the desorption at $T > 0^\circ$C leads to higher stage layer packets, i.e. a more or less ordered sequence of completely empty and filled van der Waals gaps [18]. We note furthermore that two bands at $415(10)$ cm$^{-1}$ and $\approx 590$ cm$^{-1}$ are also found for TaS$_2$(NH$_3$)$_{1/3}$(H$_2$O)$_{2/3}$

$$\approx (\text{NH}_4^+)^{1/3}(\text{H}_2\text{O})_{2/3}[\text{TaS}_2]^{1/3}.$$ The band at $\approx 590$ cm$^{-1}$ is in fact a double band with a rather sharp band at $566(10)$ cm$^{-1}$ and a shoulder, due to a broader band at $\approx 625(15)$ cm$^{-1}$.

The $390$ cm$^{-1}$ band in TaS$_2$(NH$_3$)$_{1-x}$ must be due to a librational mode of intercalated molecules as the lowest band in H$_0$1TaS$_2$ was found at $712$ cm$^{-1}$ [19]. A librational mode of NH$_3$ is improbable, as the $v_2$ band is absent in TaS$_2$(NH$_3$)$_{1/3}$(H$_2$O)$_{2/3}$.

Assume now the presence of NH$_4^+$ cations (model II). The IINS spectra of ammonium halides in the range of the librational modes are well documented [20, 21]. For NH$_4$Cl three bands at $389$ cm$^{-1}$ (librational), $574$ cm$^{-1}$ and $760$ cm$^{-1}$ (combination modes: librational + internal) were found at $100$ K [20]. The frequencies of these bands depend on the anion chosen.

The assignment of IINS bands, based on a simplified expression of the scattering law, may be fallacious [6, 19]. We have used instead an empirical relationship to correlate the vibrations of the NH$_4^+$ cations in TaS$_2$·NH$_3$ and the ammonium halides. The frequency of a librational mode is assumed to depend on the cation-anion interaction which is related to the cation-anion distance. Using
Goldschmidt ionic radii, corrected for the different site symmetries of the cations [22], a linear relationship between the librational and combination bands of the ammonium halides (100 K) and the ionic radii becomes evident (Figure 3). The effective radius of sulphur in 2H-TaS\textsubscript{2} is 1.66 Å (\(\equiv a/2\)) and Fig. 3 shows that the bands observed for \(\text{TaS}_2(\text{NH}_3)_{1-x}\) and \(\text{TaS}_2(\text{NH}_3)_{1/3}(\text{H}_2\text{O})_{2/3}\) fit the empirical scheme reasonably well. A further weak band at 810(10) cm\(^{-1}\) for \(\text{TaS}_2(\text{NH}_3)_{1/3}(\text{H}_2\text{O})_{2/3}\) is now identified as a combination mode. In analogy to \(\text{TaS}_2(\text{NH}_3)_{1-x}\) we assign the broader band at 625(15) cm\(^{-1}\) to a combination mode of an \(\text{NH}_4^+\) ion. The sharper band at 566 cm\(^{-1}\) may be due to wagging vibrations of H\(_2\)O molecules, which are in the range 480 — 550 cm\(^{-1}\) for hydrates [23]. Rocking vibrations are found in the range 760 — 850 cm\(^{-1}\). A shoulder, found in the \(\text{TaS}_2(\text{NH}_3)_{1/3}(\text{H}_2\text{O})_{2/3}\) spectrum at \(\approx 900\) cm\(^{-1}\) could be either such a rocking mode or a further combination mode of an \(\text{NH}_4^+\) cation. The difference in the band positions of \(\text{TaS}_2(\text{NH}_3)_{1-x}\) and \(\text{TaS}_2(\text{NH}_3)_{1/3}(\text{H}_2\text{O})_{2/3}\) ap-
pears to be significant and may be due to the difference in hydrogen bonding N-H...N and N-H...O.

The different site symmetries obviously play a minor role (NH₄Cl, NH₄Br, NH₄I cubic; NH₄F tetrahedral; TaS₂·NH₃ trigonal prismatic). The distance of the center of the trigonal prismatic site to the sulphur atoms in TaS₂·NH₃ (≈3.5 Å) is likewise not too different from the N...Cl distance in NH₄Cl (≈3.3 Å). The success of the empirical relationship may be due to a reduced ionic charge on the sulphur anions. Such a reduction is already derived from the simple model of a fractional charge in the Ta-S bond (=0.22), based on the difference in electronegativities of Ta and S [24].

A further band with a double peak at ≈300 cm⁻¹ and ≈350 cm⁻¹ has been found by IINS spectroscopy for TaS₂·NH₃ [25]. The assignment of this band to NH₃ vibrations must however await further measurements in this frequency range.

The conclusions may be summarized as follows:
1. The data are best represented by model II, i.e. NH₃ molecules and NH₄⁺ cations are present. The amount of NH₄⁺ cations and the conditions under which they are formed have not been the subject of this study.
2. The model of an \((\text{NH}_3)_{1-x}^+\) intercalate layer may be an idealization as further decomposition products cannot be excluded. Thus the hydride band in H₂TaS₂ might overlap with the librational band centered at 590 cm⁻¹. A further band at ≈1400 cm⁻¹ present in TaS₂(NH₃)½(H₂O)½ and TaS₂(NH₃)₁-x would be in the range of the first harmonics of H₂TaS₂ [19]. A shoulder to the \(v_2\) band is however also evident for NH₃. Further experiments to elucidate this point are planned by replacing NH₄⁺ by K⁺ before desorption [4].
3. The NH₄⁺ cation is not rotating freely at liq. N₂ temperature. Quasielastic neutron scattering experiments on NH₄Cl single crystals have been used to derive a model for the rotational jumps near the order-disorder transition [26]. It would be of interest to study the dynamic behaviour of an intercalated NH₄⁺ ion to obtain information on the host lattice-intercalate interaction.