The Incoherent Inelastic Neutron Spectra of $TaS_2 \cdot NH_3$ and $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$

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Incoherent, inelastic neutron spectra of $TaS_2(NH_3)$, $TaS_2(NH_3)_{1-x}$ and $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$ were measured in the range 250 cm^{-1} → 1600 cm^{-1}. The data suggest the presence of NH_4^+ cations and are in agreement with an ionic structure model proposed for these compounds.

I. Introduction

The intercalation compounds of layered dichalcogenides MX_2 (M = transition metal, 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 NH_3; extensive work has been devoted to the characterization of the intercalation reactions and the products $MS_2(NH_3)$. 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 NH_4^+ ions: $(NH_4^+)_x(NH_3)_{1-x}[MS_2]^{x-}$. An alternative model, suggested recently, implies hydride formation [5] with hydrogen atoms in the intralayer position as observed for H_xTaS_2 [6]. The basic structure schemes for the different models are given in Figure 1.

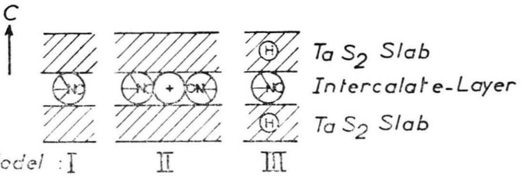

Fig. 1. Scheme of structure models proposed for the NH_3 intercalation of 2H-TaS_2. I. ammonia molecules present exclusively: $TaS_2 \cdot NH_3$ [2, 8, 9]. II. ammonia molecules and ammonium cations $(NH_4^+)_x(NH_3)_{1-x}[TaS_2]^{x-}$ [4]. III. ammonia molecules and hydrogen in intralayer position $(NH_3)[H_xTaS_2]$ [5].

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 ^{181}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 (IINS) studies on $TaS_2 \cdot NH_3$.

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 NH_4 or hydride vibrations,

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several spectra on partly desorbed $TaS_2(NH_3)_{1-x}$ were measured. A further comparison is made with $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$ [11] which has been formulated as $(NH_4^+)_{1/3}(H_2O)_{2/3}[TaS_2]^{1/3-}$ [12].

II. Materials and Methods

The different phases were prepared from 10 gr. 2H-TaS_2 each. Ammonia was intercalated at −10 °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 °C, 25 °C and 45 °C. After each desorption, a spectrum was measured. The stoichiometry – $TaS_2(NH_3)_{1-x}$ 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). $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$ 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 ν_2 band of solid NH_3 at 1066(10) cm^{-1} (IR: 1060(12) cm^{-1} [14] is also found in the $TaS_2 \cdot NH_3$ spectrum (1066 cm^{-1}) but not in the $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$ spectrum. This suggests that no NH_3 molecules are present in the latter phase (see below). Upon desorption from TaS_2. NH_3, the ν_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 $TaS_2 \cdot NH_3$. Thermodynamic data suggest that weak hydrogen bonding, found in solid ammonia [15], is also present in $TaS_2 \cdot NH_3$ [16]. The pyridine molecules in $TaS_2(C_5H_5N)_{0.5}$ 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_5H_5N by IINS spectroscopy [17].

Lattice vibrations, including librational modes, were assigned to the frequency range $< 500\ cm^{-1}$ in crystalline NH_3 [14]. The $TaS_2 \cdot NH_3$ 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 $TaS_2 \cdot NH_3$ phase. We exclude the possibility of an increasing population of isolated NH_3 molecules as the desorption at $T > 0$ °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

$$TaS_2(NH_3)_{1/3}(H_2O)_{2/3} \mathrel{\hat{=}} (NH_4^+)_{1/3}(H_2O)_{2/3}[TaS_2]^{1/3-}.$$

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 $H_{0.1}TaS_2$ was found at 712 cm^{-1} [19]. A librational mode of NH_3 is improbable, as the ν_2 band is absent in

$$TaS_2(NH_3)_{1/3}(H_2O)_{2/3}.$$

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_4Cl 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 $TaS_2 \cdot NH_3$ 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

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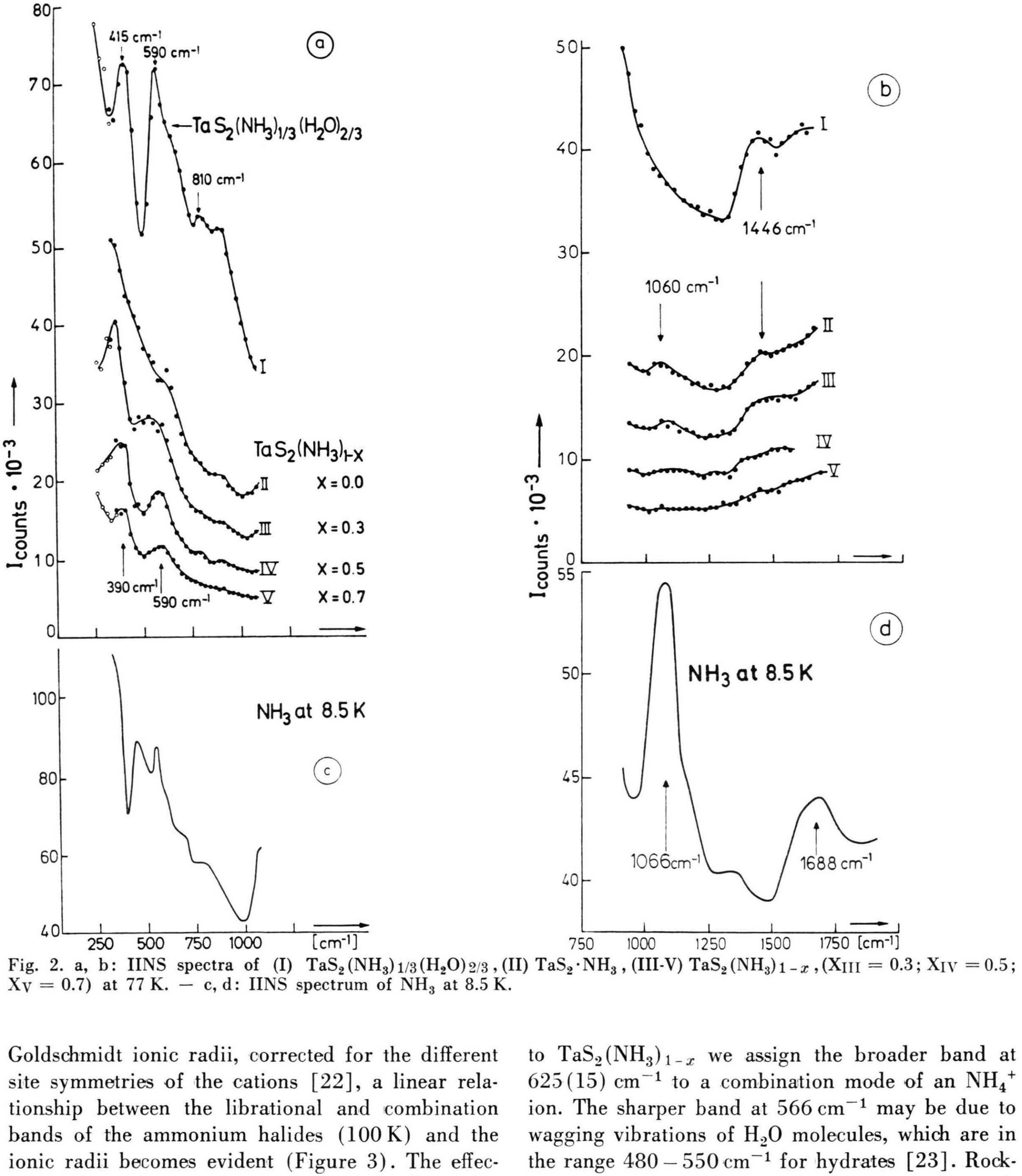

Fig. 2. a, b: IINS spectra of (I) $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$, (II) $TaS_2 \cdot NH_3$, (III-V) $TaS_2(NH_3)_{1-x}$, ($X_{III} = 0.3$; $X_{IV} = 0.5$; $X_V = 0.7$) at 77 K. — c, d: IINS spectrum of NH_3 at 8.5 K.

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_2 is 1.66 Å ($\equiv a/2$) and Fig. 3 shows that the bands observed for $TaS_2(NH_3)_{1-x}$ and $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$ fit the empirical scheme reasonably well. A further weak band at 810(10) cm^{-1} for $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$ is now identified as a combination mode. In analogy to $TaS_2(NH_3)_{1-x}$ we assign the broader band at 625(15) cm^{-1} to a combination mode of an NH_4^+ ion. The sharper band at 566 cm^{-1} may be due to wagging vibrations of H_2O 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 $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$ spectrum at $\approx$ 900 cm^{-1} could be either such a rocking mode or a further combination mode of an NH_4^+ cation. The difference in the band positions of $TaS_2(NH_3)_{1-x}$ and $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$ ap-

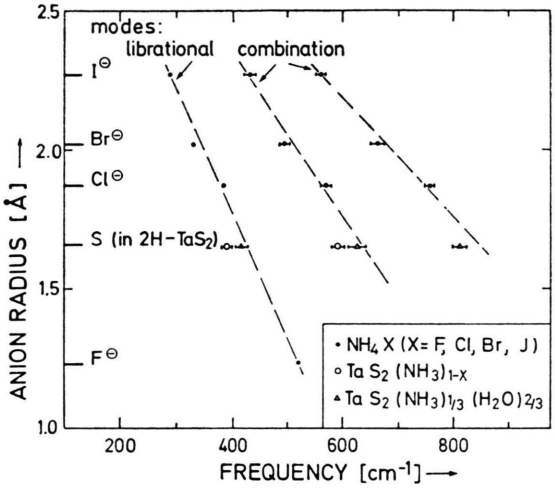

Fig. 3. Correlation of anion radius r_X librational and two combination modes for NH_4X lattices. Position of the frequencies observed for $TaS_2(NH_3)_{1-x}$(○) and $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$(△) are included.

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 (NH_4Cl, NH_4Br, NH_4I cubic; NH_4F tetrahedral; $TaS_2 \cdot NH_3$ trigonal prismatic). The distance of the center of the trigonal prismatic site to the sulphur atoms in $TaS_2 \cdot NH_3$ (≈ 3.5 Å) is likewise not too different from the N...Cl distance in NH_4Cl (≈ 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 $\approx 300\ cm^{-1}$ and $\approx 350\ cm^{-1}$ has been found by IINS spectroscopy for $TaS_2 \cdot NH_3$ [25]. The assignment of this band to NH_3 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. NH_3 molecules and NH_4^+ cations are present. The amount of NH_4^+ cations and the conditions under which they are formed have not been the subject of this study.
2. The model of an $\{(NH_3)_{1-x}(NH_4)_x^+\}$ intercalate layer may be an idealization as further decomposition products cannot be excluded. Thus the hydride band in H_xTaS_2 might overlap with the librational band centered at $590\ cm^{-1}$. A further band at $\approx 1400\ cm^{-1}$ present in $TaS_2(NH_3)_{1/3}(H_2O)_{2/3}$ and $TaS_2(NH_3)_{1-x}$ would be in the range of the first harmonics of H_xTaS_2 [19]. A shoulder to the ν_2 band is however also evident for NH_3. Further experiments to elucidate this point are planned by replacing NH_4^+ by K^+ before desorption [4].
3. The NH_4^+ cation is not rotating freely at liq. N_2 temperature. Quasielastic neutron scattering experiments on NH_4Cl 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 NH_4^+ ion to obtain information on the host lattice-intercalate interaction.

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