Wideline ^1H NMR Study on Hydrated Layered Sulfides $K_{0.5}(H_2O)_y[NbS_2]$ and $Na_{0.5}(H_2O)_y[NbS_2]$

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H NMR spectra of different hydration stages show that the water molecules in hydrated layered niobium sulfides $A_{0.5}(H_2O)_y[NbS_2]$ are rather mobile at room temperature. A structural scheme of water arrangement in the interlayer space is proposed with the C_2-axis of the H_2O molecules parallel to the basal planes of the NbS_2 layer units.

Introduction

Layered ternary chalcogenides A_xMX_2 (A = alkali metal, M = transition metal, X = S, Se) of group IV b to VI b elements may be prepared either by reactions at high temperatures (600–1000 °C) from the elements[1] and *via* alkali halide melts[2] or at low temperatures from the corresponding binary phases MX_2 by intercalation of alkali metals from liquid ammonia[3]. Both series of compounds were found to be able to undergo topotactic solvation reactions with polar solvents[4]. Structurally the resulting phases $(A^+)_x(solv)_y[MX_2]^{x-}$ have to be described in terms of negatively charged $[MX_2]^{x-}$ layer units with solvated cations A^+ between the chalcogenide sheets. The chemical behaviour of these compounds is characterized by their polyelectrolyte nature, *i.e.* easy exchange of solvent molecules and cations in contact with electrolyte solutions.

The solvated niobium and tantalum phases are of particular interest with respect to their physical properties, as they are the first known group of superconducting polyelectrolytes[5]. Variation of cations and solvent molecules allows a systematic study on the influence of the interlayer composition on the physical properties of the electronically conducting MX_2 layer units. Recent studies[6] have shown that *e.g.* in the hydrated alkali series $(A^+)_{0.3}(H_2O)_y[TaS_2]^{0.3-}$ the superconducting transition temperature T_c is strongly dependent upon the alkali metal and the solvation state. In order to understand these relationships, it is necessary to know more about the structure of the interlayer matter. Single crystal X-ray investigations on $K_{0.5}(H_2O)_yNbS_2$ and $K_{0.3}(H_2O)_yTaS_2$ revealed, however, that the localization of cation and water molecules at room temperature is not possible presumably because of the high mobility of these species[7].

We therefore decided to undertake a ^1H NMR study on $K_{0.5}(H_2O)_yNbS_2$ and $Na_{0.5}(H_2O)_yNbS_2$ in order to determine orientation and mobility of the water molecules in the hydrated phases. Both compounds differ characteristically in their hydration behaviour: two basic hydration stages are known for the Na phase corresponding to monomolecular and bimolecular layers of water between the chalcogenide sheets with interlayer distances of *ca.* 9 Å and *ca.* 12 Å, whereas in the case of the K phase only the hydrate type with monomolecular water layers can be observed. In this communication we report on results of ^1H NMR measurements at

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300 K of the compounds under consideration. A comparison is made with ^{1}H NMR data published on hydrated layer silicates and on the intercalation compound $TaS_2 \cdot NH_3$. From the data obtained a simple structural model is derived for the arrangement of the interlayer water.

Experimental

The compounds K_xNbS_2 and Na_xNbS_2 were prepared by reaction of 2H–NbS_2 in KCl respectively NaCl melts at 900 °C in an H_2S-atmosphere as reported previously[2]. The solids were freed from the salt matrix by washing with destilled water. In the course of this process the sulfides take up H_2O forming the hydrates $K_{0.5}(H_2O)_yNbS_2$ and $Na_{0.5}(H_2O)_yNbS_2$. The water uptake is accompanied by an increase of the interlayer distance to 8.91 Å (K phase) and 11.7 Å (Na phase) in the fully hydrated state.

For complete dehydration the preparations were kept in a vacuum system (10^{-3} Torr) at different temperatures and sealed in glass ampoules. At temperatures above 90 °C H_2S formation indicated a slow hydrolysis of the sulfide layers. Complete rehydration was performed by keeping the substances in a closed vessel with an inert gas atmosphere saturated with water vapor at 25 °C. Intermediate hydration steps of the Na compound were achieved by storing the solid in an atmosphere of defined water vapor pressure (H_2SO_4 solutions of different concentrations) for several days. All operations described were performed under exclusion of dioxygen in inert gas atmosphere.

X-ray powder diffraction methods (Cu_{K_α} radiation) were used for structural investigations. ^{1}H NMR measurements were made on a Varian VF 16 wide line NMR spectrometer at room temperature. The stabilized RF frequency was 60 MHz at a magnetic field of 14092 G.

Results and Discussion

Typical examples of NMR spectra at 25 °C obtained from the hydrated layered chalcogenides $Na_{0.5}(H_2O)_yNbS_2$ and $K_{0.5}(H_2O)_yNbS_2$ treated under different conditions are given in Fig. 1.

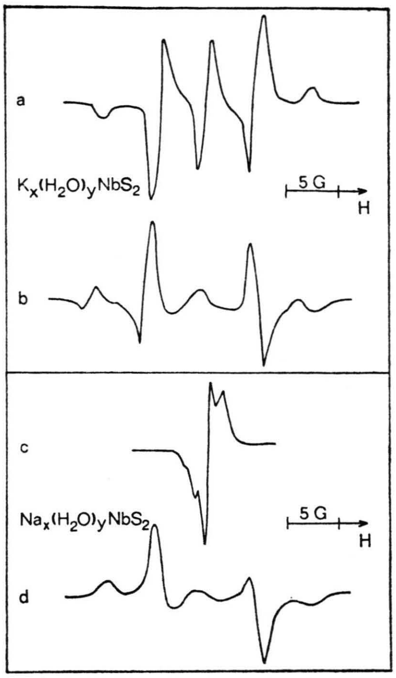

Fig. 1. ^{1}H NMR spectra of hydrated niobium sulfides under different conditions.

After equilibrating at 25 °C the fully hydrated K phase with N_2 saturated with water vapor for 24 h, a spectrum is found which shows three signals (Fig. 1a): two doublets indicating two different types of oriented water molecules and one central line. On partial dehydration at 60 °C/10^{-1} Torr the spectrum shown in Fig. 1b is observed, in which the two doublets appear at almost the same distance and intensity as in spectrum 1a. X-ray powder diagrams showed no change in the interlayer spacing between both phases; this is in agreement with our investigations which established that the interlayer spacing of hydrated layered phases with large cations does remain constant over a wide range of water vapor partial pressure. We can assume thus that the water molecules responsible for the two doublets reside in the interlayer space. In contrast the intensity of the central line – which has the same shift as the proton spectrum of water – decreases rapidly after partial dehydration and must result from water in capillary spaces between the crystal faces which can easily leave the sample. This is supported by the observation that on rapid hydration of single crystals of the ternary starting phases A_xNbS_2 the prism faces show numerous microscopic cracks along the basal planes originating from mechanical tension during the intercalation step. Macroscopially this process is associated with a considerable increase in crystal volume.

After heating the hydrated K phase to 100 °C at 10^{-3} Torr the proton signals disappear entirely. If this completely dehydrated sample is treated at 25 °C with N_2 saturated with H_2O vapor, the spectrum indicated in Fig. 1b is obtained again after a few days.

The first hydration stage of the Na compound (interlayer distance = 9 Å) was prepared by storing the fully hydrated phase under a water vapor pressure of 5 Torr for one week. The NMR spectrum obtained is shown in Fig. 1d and is completely identical with the spectrum of the K phase given in Fig. 1b. In the second hydration stage *i.e.* in the fully hydrated state (12 Å phase) a different NMR spectrum is found with an intense central line and a doublet which is only partially resolved (Fig. 1c); it is similar to that observed by Wiegers[8] for a hydrated Na phase $Na_{0.6}(H_2O)_{3.6}VS_2$ which is supposedly equivalent to a 2nd stage hydrate.

The line widths in the spectra of the K compound and of the first stage Na compound amount to 0.7–1.25 G and are to some extent dependent upon the pretreatment of the samples (repeated hydration and dehydration cycles). As the central line and the doublet overlap, the line width of the doublet cannot be determined exactly in the case of the 2nd stage sodium compound.

The magnitude of the doublet splitting in the K phase and the Na phase (first hydration stage) corresponds to 9 G for the inner doublet and to 19.4 G for the outer doublet. Under the assumption of completely isolated water molecules in a rigid lattice[9] an intramolecular proton-proton distance of 1.66 Å can be calculated from the splitting value of the inner doublets. This distance leads to a tetrahedral angle for the water molecules of 117° which differs considerably from the normal value of 109°. Similar high values of tetrahedral angles in H_2O can be found only in solid hydrates of transition metal salts, if the water molecules are coordinated to the transition metal cation[10]. In the compounds under discussion the H_2O molecules can, however, only be coordinated to the s-shell alkali cations and no strong interaction comparable to that of transition metal cation/water can be expected.

The concept of totally rigid H_2O molecule is a strongly idealized model hardly found in real crystals. Water molecules in a rigid lattice with protons in their normal distance 1.58 Å lead to a doublet splitting of 10.8 G[9], yet in most cases the water molecules rotate around their twofold symmetry axes and a decrease of the doublet splitting down to 2.7 G is observed[11]. We therefore assume that the doublet splitting of 9 G in the hydrated alkali phases results from a strongly hindered rotation of the water molecules, although – considering the unusual environment of H_2O in contact with four coplanar positive charges – an explanation of the experimental value in terms of a strong deformation of the tetrahedral angle H–O–H cannot be excluded. If we interprete the ^{1}H NMR spectrum of the second stage Na hydrate in similar terms, we find a doublet splitting of *ca.* 2.5 G which is close to the value expected for isolated water molecules with free rotation.

A group of compounds with structures that are basically similar to the structures of the hydrated chalcogenides are the mica type hydrated layer silicates[12]. The latter are built up by negatively charged Si/Al/O sheets held together by exchangeable cations that are able to undergo hydration. According to earlier models, the water molecules in layered silicates were expected to form a network determined by (i) hydrogen bonding between neighbouring water molecules, (ii) hydrogen bonding between H_2O and O^{2-} ions of the layer surface and (iii) by the interaction cation-water. In contrast, the ^{1}H NMR data at room temperature are consistent only with water molecules in rapid motion with little intermolecular interaction. In terms of the NMR results the interlayer water is to be considered as a dynamic phase with permanent destruction and rebuilding of water/water and cation/water clusters[13]. Wide line NMR spectra of layer silicates in lower hydration stages show a pattern essentially similar to that of the hydrated niobium sulfides[14]. It consists of a central line and a doublet signal, the line width of the silicate doublet and that of the inner doublet of the hydrated sulfides being almost equal. As the line width gives information on molecular motions and intermolecular interactions, we conclude that these phenomena are basically similar in both systems. In contrast to the layered silicates the doublet splitting is considerably larger in the hydrated niobium sulfides which is to be explained in terms of a stronger rotation of the water molecules in the silicates. This conclusion is rather surprising, since one should assume that the rotation of H_2O is hindered in silicates to a greater extent as compared to the sulfides as a consequence of the possibility of hydrogen bond formation between H_2O and the oxide layers. Because of the low energy of O–H ··· S bonds the interaction between H_2O and the sulfide layers should be negligible. Although at the moment we cannot give a conclusive explanation, the reason for this contradictary result may be correlated with the fact that the interlayer cation density of the sulfides investigated is notably higher than the cation density of layered silicates and that – in contrast with the silicates – the negative charges of the electronically conducting sulfide layers are delocalized. The question of the outer doublet splitting in the sulfide spectra remains open; an analoguous signal was not observed for layer silicates and the calculation of the H–H distance from the splitting constant leads to an unreasonably short value.

^{1}H NMR data on the intercalation compound of ammonia with the layered sulfide TaS_2 were recently reported in a series of papers by **Gamble** and **Silbernagel**[15]. The spectrum of $TaS_2 \cdot (NH_3)_{1.0}$ showed no doublet splitting down to temperatures of liquid helium. The authors interprete their low temperature data with a preservation of the free rotation of NH_3 around the C_3-axis, while diffusional motions and reorientation of the C_3-axis are assumed to be frozen in. In spite of this rotational freedom some doublet splitting should be expected in the spectrum. The complete absence of splitting even at low temperatures may be explained by a structural model put forward recently by **Schöllhorn** and **Zagefka**[16], who found that the intercalation proceeds *via* a redox reaction leading to the ionic compound $(NH_4^+)_{0.1}(NH_3)_{0.9}[TaS_2]^{0.1-}$ which is closely related to the structure of the hydrated sulfides $A_x^+(H_2O)_y[MS_2]^{x-}$. Since, however, NH_4^+ ions and NH_3 molecules both are present in the interlayer space, a rapid proton transfer should be expected. This exchange reaction may result in the absence of an expected doublet, if the rate of proton exchange is equal to or greater than the expected doublet splitting constant as discussed by **Woesner** and **Snowden** for layered silicates[11].

For the first stage hydrated sulfides a simple model of the water arrangement consistent with the ^{1}H NMR data can be derived from our present knowledge on these systems. The transition element in the negatively charged S–Nb–S layers resides in a trigonal prismatic environment *i.e.* the S atom of the two close packed sulfur sheets which comprise one single NbS_2 layer are stacked atop each other in direction of the hexagonal *c*-axis. Since the sulfur atoms of different sheets also lie directly above each other[7], trigonal prismatic holes are generated in the interlayer space. Although two holes exist between the layers (related to one half unit cell), only one can be occupied by either water or alkali ions for geometrical reasons. The analytical composition of $K_{0.5}(H_2O)_{0.5}NbS_2$ corresponds well with the maximal possible occupancy. The average distance between the interlayer species within the basal plane amounts thus to 3.3 Å. Since 50% of the trigonal prismatic holes are occupied by water and alkali cations A^+ in a ratio of 1:1, each water molecule is surrounded in an idealized scheme by six next nearest neighbours within the layer: four A^+ ions and two water molecules (Fig. 2). The water dipoles must be oriented with their negative charge center towards the A^+ ions. The hydrogen atoms which bear a partial positive charge should be in contact with the negatively charged sulfide layers, so that the C_2-axes of the H_2O molecules lie parallel to the sulfide sheets (Fig. 3). It is reasonable to assume that there are potential barriers for reorientation of the C_2-axis for the H_2O molecules between the neighbouring A^+ ions and for rotation around the C_2-axis. In turn, defects in the water/cation phase are likely to allow translational motion of both species in two dimensions parallel to the basal planes of the MX_2 sheets. The model discussed is in agreement with our X-ray structure data which show that at room temperature it is not possible to localize the interlayer species.

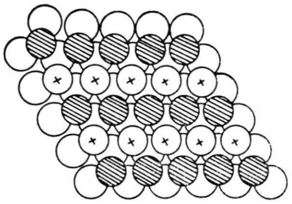

Fig. 2. Structural model for the arrangement of water and alkali ions in the interlayer space of $A^+_{0.5}(H_2O)_{0.5}[NbS_2]^{0,5-}$; ⊕ = alkali cation, ⊘ = water molecule, ○ = sulfur atom.

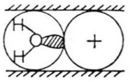

Fig. 3. Scheme of proposed arrangement for water molecules between the sulfide layers (cross section; negative layer charges ommitted).

Conclusion

The investigations presented show that the water molecules in the hydrated sulfides $A_x(H_2O)_yNbS_2$ are mobile at room temperature. The structural model proposed must, however, be refined – especially with respect to twodimensional molecular diffusion – by ^{1}H NMR measurements at lower temperatures and by neutron diffraction studies which are in progress. Angular dependence of the proton spin-lattice relaxation should give information on the expected anisotropic reorientation of the C_2-axis of H_2O.

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