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Solvation Reactions of Layered Ternary Sulfides A_xTiS_2, A_xNbS_2, and A_xTaS_2

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Layered ternary phases A_xMS_2 (A = alkali metal; M = Ti, Nb, Ta) undergo topotactic solvation reactions at ambient temperature in inorganic and organic solvents of adequate polarity. The reaction products are characterized by their polyelectrolyte behavior; they are built up by negatively charged two-dimensional $[MX_2]^{x-}$ lattice units with mobile and exchangeable solvated cations in the interlayer space. Two well-defined hydration stages are found in the case of water as the solvent for alkali and alkaline earth cations. They are described in terms of a model which is based on the hydration properties of the cations. A series of known intercalation compounds of the binary transition metal dichalcogenides is shown to be closely related to the solvated ternary phases with respect to basic structure and chemical reactivity. The compounds investigated represent a novel class of electronically conducting crystalline polyelectrolytes, whose physical properties can be varied by topotactic exchange reactions at room temperature.

Introduction

Ternary chalcogenides of transition metals with strongly electropositive elements, i.e., alkali and alkaline earth metals, are often characterized by highly anisotropic structures, the transition metal and the chalcogen forming frequently distinct one- or two-dimensional lattice elements. This has to be explained in terms of the fact that the bonding between the transition element and the chalcogen atoms tends to exhibit considerable covalency in character, whereas the electropositive group 1A and 2A elements prefer ionic bonding. The resulting "structural segregation" leads in many cases to chain and layer type compounds, e.g., $KFeS_2$[1] or A_xTiS_2.[2] The anisotropy with respect to bonding and structure affects not only the physical properties but also the chemical reactivity of these solids. We were able to show in previous studies that many of the layered ternary compounds $A_xM_nX_m$ (A = group 1A or 2A metal, M = transition metal, X = chalcogen) may easily undergo solvation reactions with polar inorganic and organic liquids[3,4] according to eq 1. All these reactions proceed in a topotactic

$$A_xM_nX_m + y(\text{solv}) \rightarrow A^+_x(\text{solv})_y[M_nX_m]^{x-} \qquad (\text{solv} = \text{solvent}) \qquad (1)$$

way: the polar molecules are taken up into the interlayer space solvating the electropositive ions; the transition metal chalcogenide layers remain unchanged as negatively charged matrix elements. As a consequence of the high mobility of the solvated cations in the interlayer space ion-exchange reactions can be performed with ambient electrolyte solutions. The solvated phases are thus a novel class of inorganic polyelectrolytes which exhibit semiconductor or metallic properties.[7]

The ternary compounds of group 4B and 5B metals are of special interest with respect to their high reactivity and relative stability; the phases known so far are nonstoichiometric compounds with large phase range.[2,5] Recently we reported on a method to prepare ternary chalcogenides of these elements with defined stoichiometry from alkali halide melts.[6] We found that the corresponding hydrated forms of Nb and Ta phases are superconducting, the transition temperature T_c being dependent on the nature of the exchangeable cations and on the solvate phase.[7] A reliable interpretation of the physical properties of these compounds requires a thorough understanding of the chemical properties and stability as well as the knowledge of the detailed structures of these phases. In this communication we present our results on a study of the solvation properties of the compounds $A_{0.5}TiS_2$, $A_{0.5}NbS_2$, and $A_{0.3}TaS_2$.

Methods

The ternary phases A_xMX_2 were prepared from alkali halide melts according to the procedure described previously.[6] On removal of the solid salt matrix with water the corresponding hydrated phases were obtained. Analysis was performed by flame spectrophotometry (alkali and alkaline earth cations) and wet methods (transition metal and sulfur). All reactions with these compounds were carried out at room temperature under an inert atmosphere. Crystallographic data were obtained from polycrystalline samples and single crystals by powder and Weissenberg methods using Cu Kα radiation. For the investigation of fully hydrated phases the preparations were kept—if not otherwise stated—in contact with 1 M electrolyte equilibrium solution. Aqueous sulfuric acid solutions of defined concentrations served for maintaining defined water vapor pressure over polycrystalline samples in closed vessels. In order to reach the true equilibrium states it was necessary to store the compounds for several days or weeks under these conditions. Cation exchange was performed by treating the samples repeatedly with 1 M solutions of halides or sulfates of the cations to be introduced until quantitative reaction was achieved. For the preparation of organic solvated phases the hydrates or unhydrated ternary phases were treated with an excess of the purified and dried organic reagent. Colloid solutions were formed by high-speed stirring of suspensions of the solvated compounds in the corresponding liquid phase. Preparations of solvated phases by cathodic reduction of the binary chalcogenides and by reaction of alkali metal intercalation compounds with solvents were described in earlier reports.[3,4,8,13,19]

Results and Discussion

Hydrated Phases. On contact with water vapor or with liquid water, the ternary alkali phases $A_{0.5}TiS_2$, $A_{0.5}NbS_2$, and $A_{0.3}TaS_2$ undergo spontaneous hydration according to eq 1. The water molecules are taken up into the lattice and crystalline hydrates $A^+_x(H_2O)_y[MX_2]^{x-}$ are obtained. The reaction is a topotactic process which can easily be demonstrated by investigating single crystals of the ternary phases which turn over to single crystals of the hydrated compounds. All phases can be indexed on a hexagonal base; the lattice parameters of the alkali series are given in Table I. As a result of the hydration process, the interlayer spacing *d* between successive MX_2 sheets increases, whereas the *a*-axis values remain almost constant. A comparison with the *a*-axis parameters of the corresponding binary phases TiS_2 (a = 3.40 Å), 2H-NbS_2 (a = 3.31 Å), and 2H-TaS_2 (a = 3.32 Å) indicates that the deformation of the layers is very small. The metallic appearance of the ternary phases is retained in the hydrated forms, the colors observed were golden yellow for Ti compounds and blue to gray for Nb and Ta compounds. Water content found analytically for K^+ and Na^+ phases corresponded to $y \simeq 0.7$ (K), $y \simeq 1.8$ (Na) for Ta hydrates and $y \simeq 0.5$ (K), $y \simeq 1.6$ (Na) for Nb and Ti hydrates.

From the data given in Table I it is seen that two sets of interlayer spacings are found corresponding to ca. 9 Å and ca. 12 Å. In order to be able to compare the values from the Ti, Nb, and Ta series it is necessary to account for the small differences in the thickness of the chalcogenide layers: the use of the interlayer distance d_0 of the binary phases TiS_2 (5.71 Å), NbS_2 (5.95 Å), and TaS_2 (6.05 Å) as the van der Waals

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Table I. Hexagonal Lattice Constants, Interlayer Spacings *d* (Å), and Interlayer Heights Δ*d* (Å) of Hydrated Alkali Phases $A^+_x(H_2O)_y[MS_2]^{x-}$

	$A^+_{0.5}(H_2O)_y[TiS_2]^{0.5-}$				$A^+_{0.5}(H_2O)_y[NbS_2]^{0.5-}$				$A^+_{0.3}(H_2O)_y[TaS_2]^{0.3-}$			
A^+	*a*	*c*	*d*	Δ*d*	*a*	*c*	*d*	Δ*d*	*a*	*c*	*d*	Δ*d*
Li^+	3.38	11.40	11.40	5.69	3.35	22.82	11.41	5.46	3.33	23.29	11.65	5.60
Na^+	3.43	11.43	11.43	5.72	3.34	23.37	11.69	5.74	3.33	23.63	11.82	5.77
K^+	3.45	8.86	8.86	3.15	3.35	17.81	8.91	2.96	3.35	18.18	9.09	3.04
NH_4^+ [a]	3.45	8.83	8.83	3.12	3.34	17.95	8.98	3.03	3.34	17.94	8.97	2.92
Rb^+	3.46	8.91	8.91	3.20	3.33	17.96	8.98	3.03	3.33	18.18	9.09	3.04
Cs^+	3.46	9.19	9.19	3.48	3.34	18.36	9.18	3.23	3.32	18.53	9.27	3.22

[a] Obtained by cation exchange.

Table II. Interlayer Spacings *d* (Å) and Interlayer Heights Δ*d* (Å) of Hydrated Alkaline Earth Phases $A^{2+}_{x/2}(H_2O)_y[MS_2]^{x-}$ Obtained by Cation Exchange from the Corresponding Sodium Compounds

	M = Ti		M = Nb		M = Ta	
A^{2+}	*d*	Δ*d*	*d*	Δ*d*	*d*	Δ*d*
Mg^{2+}	11.94	6.23	11.74	5.79	11.98	5.93
Ca^{2+}	11.68	5.97	11.77	5.82	11.88	5.83
Sr^{2+}	11.73	6.02	11.84	5.89	11.95	5.90
Ba^{2+}	11.81	6.10	11.90	5.95	11.99	5.94

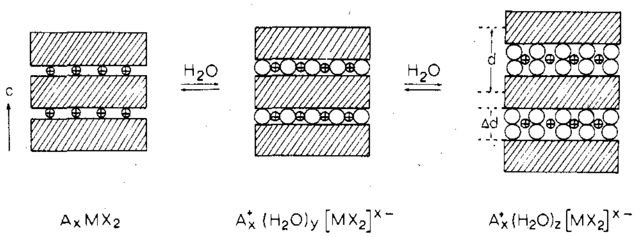

Figure 1. Scheme of hydration reaction of ternary layered chalcogenides A_xMS_2 (delocalized negative charges on the MX_2 layers are omitted).

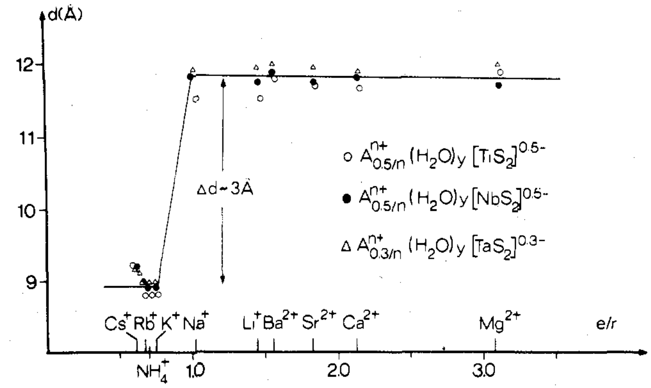

Figure 2. Dependence of the interlayer spacing *d* of hydrated sulfides $A^{n+}_{x/n}(H_2O)_y[MS_2]^{x-}$ on the charge:radius ratio of the exchangeable cations A^{n+}.

height of the layers is a reasonable assumption as was proved in earlier investigations. If we now calculate the difference $\Delta d = d - d_0$ for the compounds listed in Table I, we arrive at values for the height of the space between the dichalcogenide layers. With the exception of Cs^+, whose diameter is significantly larger than that of water, these distances range between 2.9 and 3.2 Å and between 5.6 and 5.8 Å; they obviously compare rather well to once and twice the van der Waals diameter of a water molecule (ca. 2.8 Å). We found similar values before on related layered hydrates; they have been interpreted by us[3,4,8] in terms of a structural model which assigns monolayers of water to hydrates with Δ*d* of ca. 3 Å and bilayers for hydrates with Δ*d* of ca. 5.5–6 Å; i.e., the size of the water molecules is obviously responsible in both cases for the interlayer distance observed (Figure 1). In the case of bilayers of water we were able to show earlier by one-dimensional Fourier synthesis that the cations are located in the central plane between the two H_2O sheets.[3] Hydrates with bilayers of water are also formed by the alkaline earth derivatives $A^{2+}_{x/2}(H_2O)_y[MS_2]^{x-}$ (A = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}; M = Ti, Nb, Ta) which we obtained from the alkali forms by cation exchange. Interlayer distances are presented in Table II. In order to explain the two distinct sets of interlayer distances observed for the hydrates it is necessary to elucidate the role of the exchangeable cation. In the alkali series a simple relationship is apparent: all hydrates of cations with ionic radii >1 Å show interlayer distances corresponding to monolayers of water, whereas bilayers are found for cation radii <1 Å. To include the alkaline earth derivatives with their bivalent cations in this discussion it is reasonable to base a comparison of the hydrates on the charge:radius ratio e_0/r. The correlation between this ratio and the interlayer distance *d* is shown graphically in Figure 2: a clear step again separates cations with $e_0/r < 1$ and $e_0/r > 1$. Considering the fact that the charge:radius ratio itself is correlated with the hydration energies of the cations it is presumed that the latter must be the decisive factor determining the hydrate structure. Thus, the small monovalent cations Li^+ and Na^+ as well as all of the bivalent alkaline earth ions from Mg^{2+} to Ba^{2+} may stabilize bilayers of water. Large cations of low charge, e.g., K^+, NH_4^+, Rb^+, and Cs^+, with lower hydration energies may only form monolayers of water between the chalcogenide sheets. In fact, the *d* values of the monolayer forms are slightly higher for the large size ions Rb and Cs: both cations have a diameter larger than that of water molecules and thus *d* is actually governed here directly by the cation diameter (Table I, Figure 2).

What is certainly surprising—when we compare the hydrates under discussion with the well-known hydrates of charged layer silicates—is that the relationship between interlayer distances and hydration energies is remarkably simple for the chalcogenide hydrates, as opposed to the behavior of the layer silicates. The latter have been studied for a long time with respect to their hydration properties.[9] Typical representatives are montmorillonite and vermiculite which are essentially built up by layers consisting of oxygen anions with Si and Al in tetrahedral and octahedral holes, respectively, the layer units being held together by alkali or alkaline earth ions. Hydration phenomena of these silicates are rather complex. It is known that the interlayer spacings—which may reach values up to more than 50 Å in H_2O for montmorillonite—depend strongly on a number of parameters such as cation type, electrolyte concentration, density of the localized negative layer charges, etc. Although the problem of the degree of organization of H_2O molecules in layer silicates under different conditions is not yet entirely solved, it is clear that the basic reason for the complex behavior found comes from the influence of two competitive factors which are (i) hydration of the cations and (ii) hydration of the negatively charged oxide layers via O–H···O bonding. From a recent neutron scattering study on the Li^+ and Na^+ forms of

Table III. Influence of Electrolyte Concentration on the Interlayer Spacing *d* for $Na^+_{0.3}(H_2O)_y[TaS_2]^{0.3-}$

c_{Na^+}, M	*d*, Å	Δ*d*, Å	c_{Na^+}, M	*d*, Å	Δ*d*, Å
10^{-5}	11.96	5.91	2	11.86	5.81
10^{-1}	11.86	5.81	4	11.79	5.74
1	11.86	5.81			

montmorillonite and vermiculite it is concluded that at increasing water content, i.e., increasing interlayer distance, the influence of the dynamic ordering of H_2O by the silicate surface rapidly decays;[10] the type of cation seems to be of minor importance under these conditions. For lower *d* values (lower H_2O content) it is found that in the case of the small divalent cations the influence of cation hydration is dominating, whereas for the larger divalent ions as well as for monovalent ions the influence of the layer is dominant.[11]

The situation is quite different for the hydrated layer chalcogenides. In these compounds the solvated cations must be homogeneously distributed in the space between the layers, since these are electronically conducting and the negative charges are thus delocalized. Hydrogen bonds O–H···S are known to have very small bonding energies[12] so that the solvation of the $[MX_2]^{x-}$ layers by the hard ampholyte H_2O is expected to be negligible. This is supported by the investigation of the oxidation reactions of the hydrated chalcogenides:[4,13] on oxidation the negative layer charge density becomes zero; i.e., no positive ions are left between the MX_2 units. The water molecules are found to leave the interlayer space and the layers collapse to yield the binary chalcogenides MX_2; potential metastable hydrates $MX_2 \cdot yH_2O$ have not been observed. It is thus evident that the solvation properties of the cations must govern the hydrate structure in these phases. Multilayers of water were not found for alkali and alkaline earth ions in the chalcogenide case. Although as a consequence of the spatial restrictions in the two-dimensional electrolyte the hydration energies of the cations in the interlayer space are certainly lower than those for ions in homogeneous aqueous solutions, it can be assumed that the relative energies of hydration do follow a sequence similar to that known for homogeneous electrolytes. An additional significant point contributing to the striking difference in hydration behavior of layer silicates and layer chalcogenides is certainly the fact that the chalcogenide layer surfaces can be considered as quasi-planar interfaces, whereas in the silicate case the layer surface contains a regular pattern of large holes (oxygen anion defects) which are large enough to accommodate water molecules or cations of appropriate size.

The interlayer spacings of layer silicates in aqueous suspension are known to be strongly dependent on electrolyte concentration:[9] here again a quite different behavior shows up for the layer chalcogenides. In Table III interlayer spacings are given for $Na^+_{0.3}(H_2O)_y[TaS_2]^{0.3-}$ suspended in aqueous NaCl solution for different Na^+ concentrations. It can be seen that a variation of the concentration from 10^{-5} to 4 N results in a minute change only for *d* of 0.17 Å. The interlayer cation–water structure is thus rather stable under these conditions which is partially to be attributed to the higher density of exchangeable cations in hydrated chalcogenides as compared to montmorillonite.

Water may, however, reversibly be removed from the chalcogenide hydrates by lowering the water vapor pressure above powdered samples or single crystals. This effect is most readily demonstrated for compounds with bilayers of H_2O. Wet samples, e.g., of the Li^+ and Na^+ compounds under dry inert gas at 25 °C collapse after a period of a few hours to give monolayer forms according to eq 2. On treatment with

$$A^+_x(H_2O)_y[MS_2]^{x-} \rightleftarrows A^+_x(H_2O)_{y-n}[MS_2]^{x-} + nH_2O \qquad (2)$$

H_2O the bilayer form is rapidly obtained again. This process may be easily studied on a powder diffractometer flushed alternately with dry and wet inert gas by the change in the relative intensities of the 001 diffraction lines of mono- and bilayer forms. In order to investigate the equilibrium states powdered fully hydrated samples were stored under an atmosphere of defined water vapor pressure for extended periods of time. In Figure 3 the interlayer spacings of the Na^+ forms of hydrated Ti, Nb, and Ta chalcogenides are shown as a function of the ambient water vapor pressure after equilibration at 25 °C. With decreasing p_{H_2O} the *d* values remain essentially constant up to a certain threshold pressure of ca. 10 Torr; below this value a sudden decrease in *d* is observed down to a value of ca. 9 Å which corresponds to monolayers of water. A further decrease of p_{H_2O} until 10^{-2} Torr does not result in significant changes of the interlayer spacing. No intermediate *d* values were observed: only two hydrate structures are stable in the pressure range investigated. For the bilayer region it was found by gravimetric studies that small amounts of water can reversibly leave the lattice with decreasing p_{H_2O} at constant *d* value. This zeolite type hydration may be explained in terms of cation–water clusters of definite height which stabilize the bilayer structure even though a certain amount of H_2O has left the crystal lattice leaving water defects. At a critical defect concentration the bilayer structure becomes unstable and breaks down which results in a stepwise transition to the monolayer phase. The fact that the negative charge density and cation density are different for $A_{0.3}(H_2O)_y[TaS_2]$ phases and $A_{0.5}(H_2O)_y[NbS_2]$ or $A_{0.5}(H_2O)_y[TiS_2]$ phases does not influence the transition; all three compounds show the same critical threshold pressure. At higher temperatures (50–100 °C) and a low pressure of 10^{-2}–10^{-5} Torr further dehydration of the monolayer phases proceeds. In the case of $Na_{0.3}(H_2O)_y[TaS_2]$ a *d* value is finally reached of 7.47 Å which is close to the value for the ternary phase $Na_{0.3}TaS_2$ (7.27 Å). The lines of powder diagrams of these samples are, however, broadened in these phases which must be due to slight distortions of the layers by small amounts of residual H_2O molecules, since the line broadening disappears on rehydration.

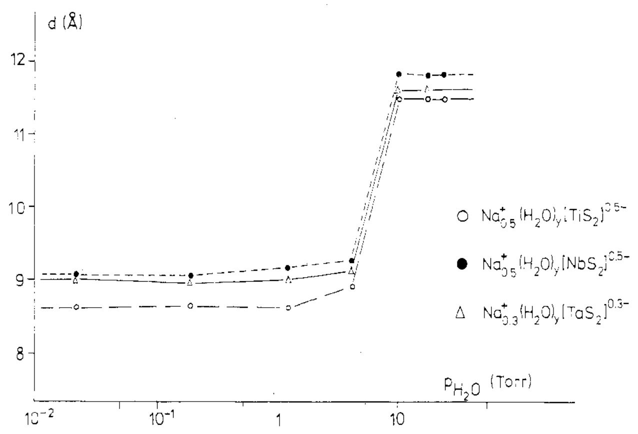

Figure 3. Dependence of interlayer spacing *d* of hydrated layered sulfides on water vapor pressure.

Line broadening is also observed for alkaline earth derivatives $A^{2+}_{x/2}(H_2O)_y[MX_2]^{x-}$ on lowering the p_{H_2O} pressure, although a defect water bilayer structure is retained down to $p_{H_2O} = 10^{-2}$ Torr. This is to be considered as a consequence of the higher hydration energies of the divalent cations and the greater stability of their hydrate complexes. The interlayer cation density is only 50% for alkaline earth phases as compared to that of alkali derivatives. It is conceivable that after partial loss of water the sulfide layers in the resulting "island structure" become slightly distorted because of the increased distance between the cation–water clusters which, however, still stabilize the bilayer form as deduced from the

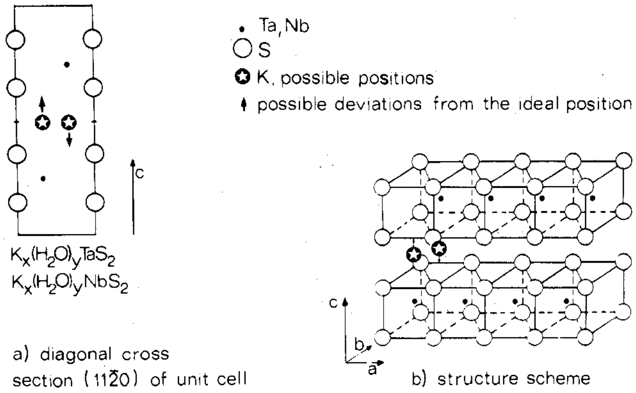

Figure 4. Structure of the hydrates $K_{0.5}(H_2O)_y[NbS_2]$ and $K_{0.3}(H_2O)_y[TaS_2]$.

d values. At 10^{-2} Torr the lines of the 001 series become nonintegral and *hkl* reflections are absent, but hydration restores the original lattice.

Controlled partial oxidation of the hydrated chalcogenides by dioxygen leads to intermediary "second-stage" phases $A^+_n(H_2O)_y[M_2S_4]^{n-}$ (eq 3) which contain hydrated alkali

$$2[MX_2]^{x-} \rightarrow [M_2X_4]^{n-} + (x-n)e^- \qquad (3)$$

atoms between negatively charged double-layer units $[MX_2]_2$.[4] Since these are easier to obtain from the alkaline earth hydrates, we studied the stability of the second-stage compounds of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} forms (M = Ta). Down to water vapor pressures of 10^{-2} Torr we observed constant interlayer distances of 17.6 and 18.1 Å for the smaller ions Mg^{2+} and Ca^{2+} which correspond to the values calculated for bilayers of H_2O. For compounds with the larger ions Sr^{2+} and Ba^{2+} a critical threshold pressure was found again which increases from Sr^{2+} (0.5×10^{-2} Torr) to Ba^{2+} (10^{-1} Torr). The discrepancy between normal and second-stage alkaline earth derivatives is presumably due to the distribution of the negative charge over the volume of two adjacent layers which may result in differences in the Coulomb interaction of the localized positive charges with the layers.

For a detailed picture of the structure of the chalcogenide hydrates it is necessary to find out the exact location of the atoms in the space between the MX_2 layers by three-dimensional structure analysis. We found that on careful preparation all of the fully hydrated chalcogenide phases exhibit a regularly ordered crystal lattice. Single crystals of adequate quality can readily be obtained by preparation of the ternary starting phases via the alkali halide method. There are, however, three basic problems interfering: (i) the location of light atoms such as H and O and cations with low atomic number in the presence of heavy transition metal atoms, (ii) the high mobility of H_2O and solvated cations between the layers at room temperature, and (iii) the occurrence of stacking faults typical for layered structures. Recent single-crystal studies at ambient temperature allowed us, however, to establish the basic structure of $K_{0.3}(H_2O)_y[TaS_2]$ and $K_{0.5}(H_2O)_y[NbS_2]$.[14] Both compounds are isotypic; the space group is $P\bar{6}2c$-$D_{3h}{}^4$. The structure scheme is given in Figure 4. The transition metal atoms are located in trigonal prisms of sulfur atoms as they are in the layers of the binary chalcogenides 2H-TaS_2 and 2H-NbS_2. This agrees with the observation that on complete oxidation of the hydrated forms the 2H-MX_2 modifications can be isolated.[4] A trigonal-prismatic coordination for the K atoms between the layers is very likely, since the sulfur atoms of different layers are stacked directly above each other. We expect that neutron diffraction and low-temperature studies which are in progress will allow a determination of H_2O and alkali atom positions in these phases.

Table IV. Interlayer Spacings *d* (Å) of Solvated Phases $Na^+_x(solv)_y[MS_2]^{x-}$

Solvent	M = Ti	M = Nb	M = Ta
Formamide	16.03	16.37	16.35
N-Methylformamide	∞	19.27	18.91
N,N-Dimethylformamide	17.02	17.21	17.10
N-Methylacetamide			16.69
Ethanol	9.80		10.04
Glycol	13.97		14.42
Butanediol-2,3			18.33
Glycerine	13.90		14.42
Diglyme	14.39	14.69	14.53
Poly(ethylene glycol)	14.26	14.45	14.65
Phosphoric acid trimethyl ester	13.36	13.61	13.65
Hexamethylphosphoric acid triamide	18.82	9.94	14.97
Tri-*n*-butylphosphine oxide	15.18		15.44
Dimethyl sulfoxide	16.83	16.82	18.63

Nonaqueous Solvate Phases. Water is certainly an outstanding case among the solvents with respect to its donor and acceptor properties and self-aggregation ability. We found, however, that the reactivity of the ternary chalcogenides is not confined to this solvent only; a large number of other polar solvents may indeed be accepted by the lattice of these phases. Organic solvent molecules are of special interest, since they provide a large variety of compounds with functional groups of varying polarity and with different molecular size and geometry. There is also the possibility of substitution at different positions of a given carbon framework which is useful for systematic studies on the solvation properties. Although it is possible in many cases to obtain these compounds by direct reaction between the ternary chalcogenide and the organic solvent, it is more convenient to prepare them by reaction of the hydrated forms with the desired solvent as indicated in eq 4. The exchange reaction of water–organic solvent proceeds

$$A^+_x[MS_2]^{x-} \xrightarrow{+\text{solv}} A^+_x(\text{solv})_z[MS_2]^{x-} \xleftarrow[-H_2O]{+\text{solv}} A^+_x(H_2O)_y[MS_2]^{x-} \qquad (4)$$

readily within minutes or hours for powdered material, whereas complete reaction may require days or weeks for single crystals. Direct solvation is slow as well and for larger molecules or compounds with extended hydrophobic substituents kinetic reasons seem to prevent a reaction under these conditions. Small amounts of water were found to destabilize the solvate structures and to lead to strongly reduced interlayer distances. Among the compounds which easily react with the hydrated forms are, e.g., alcohols, ethers, aliphatic, cyclic, and aromatic amines, heterocyclic compounds, phosphines, phosphine oxides, thioethers, etc. Replacing water by organic solvents results in most cases in products with interlayer spacings exceeding those of bilayer hydrates. In Table IV *d* values are given for a series of solvated chalcogenides $Na^+_x(solv)_z[MS_2]^{x-}$ with aliphatic alcohols, with carbonic acid amides, and with molecules containing phosphorus and sulfur as components of the functional group.

In the amide series interlayer spacings are rather high, ranging between 16.03 and 19.27 Å. Flat-lying molecules of these compounds with the N–C–O plane parallel to the chalcogenide layer surface have a van der Waals height of ca. 4–5 Å. As the size of the formamide molecule is small compared to that of the alkyl-substituted members, a bilayer arrangement is conceivable in this case. Intercalation compounds of acid amides with the binary sulfides TiS_2, NbS_2, and TaS_2 show considerably lower *d* values of only 9.6–11.5 Å;[15,16] this difference must be due to the presence and solvation properties of alkali ions in the ternary phases. Formamide intercalation complexes of metal disulfides $MX_2 \cdot xHCONH_2$ are exceptional and show higher *d* spacings of 16.07 (Ti),[16] 13.16 (Nb), and 13.15 Å (Ta)[15] which is presumably a result of the strong intermolecular hydrogen-bonding ability of the

Table V. Interlayer Spacings *d* (Å) of Solvated Phases $A^{n+}_{x/n}(DMF)_y[MS_2]^{x-}$

A^{n+}	M = Ti	M = Nb	M = Ta
Li^+	16.58	17.09	17.10
Na^+	17.02	17.21	17.10
K^+	11.48	11.81	11.89
Rb^+	11.87	11.69	11.97
Cs^+			10.92
Mg^{2+}	19.27	19.44	16.93
Ca^{2+}	16.73	17.39	17.38
Sr^{2+}	16.97	17.22	17.37
Ba^{2+}	16.85	15.11	16.85

unsubstituted parent compound.[12]

The structure of the solvate in the interlayer space should be influenced essentially by (i) molecular size and geometry of the solvent molecule which are responsible for steric restrictions and (ii) the cation–solvent and layer–solvent interactions. The solvation energy of small spherical cations in homogeneous solution is known to be considerably smaller in organic solvents than in water, and it can be assumed that this observation also pertains qualitatively to solvated alkali chalcogenides. If the cation–solvate interaction is of significance in the present case, one should expect a dependence of solvate structure on cation charge and radius. We therefore undertook a study on this correlation in the *N*,*N*-dimethylformamide series $A_x(DMF)_y[MS_2]$. Interlayer spacings of these compounds with alkali and alkaline earth ions are given in Table V. It is obvious for the alkali compounds that similar to the behavior of the hydrates two series of *d* spacings are found: 16.6–17.2 Å for the cations with a radius of <1.3 Å and 11.5–11.9 Å for the large cations with $r > 1.3$ Å. No solvate derivatives with DMF are obtained for the Cs^+ compounds of the Ti and Nb phases; besides the low solvation energy of Cs^+ ion, the higher cation density of the Ti and Nb forms as compared to the Ta compounds and the resulting steric restrictions are probably responsible for the lack of reactivity with large solvent molecules. The average interlayer height Δd is calculated to be ca. 6 Å for K^+ and Rb^+ and ca. 11 Å for Li^+ and Na^+. Thus the *d* values could be interpreted in a first approximation on grounds of a simple monolayer/bilayer model of solvate molecules. In view of our lack of knowledge on the positions of the cations and the potential variety of ordering of the anisometric organic molecules this assumption appears yet to be questionable. The remarkable variation of the interlayer distance between 15 and 19 Å for the divalent alkaline earth cations (Table V) shows that the structural situation is fairly complex as compared to the hydrate case. Anyhow the results are convincing evidence for a strong influence of cation size and charge on the structure of the interlayer matter. In addition it is to be expected that in the case of organic solvent molecules an interaction with the sulfide ions at the layer surface—which can be considered as "soft bases"—is of some importance. Moreover, hydrogen bonds N–H···S have been reported recently to have relative short bond lengths and bonding energies higher than those of O–H–S bonds;[12] they may play a role in the case of monosubstituted and unsubstituted acid amides.

A comparison between *N*-methylformamide (NMF), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) with different alkali cations suggests that the dielectric constant of the solvent and the variation of the interlayer distance with the cation are interrelated. For NMF which has a rather high DC value ($\epsilon = 170$) only a relative small decrease occurs for *d* with increasing ionic radius of A^+ (Table VI). The interaction with the cation is obviously strong even for large ionic radii and intermolecular H bonds as well as H bonds between MX_2 layer and NMF may contribute to stabilize extended solvate structures. The dielectric constants for DMF ($\epsilon = 36$) and DMSO ($\epsilon = 45$) are considerably smaller and H bonding is not possible. In both cases the corresponding compounds $A_x(DMF)_y[MS_2]$ and $A_x(DMSO)_y[MS_2]$ show a pronounced transition to lower *d* values with increasing cation radius (Tables V and VI).

Table VI. Dependence of Interlayer Spacings *d* (Å) on the Exchangeable Cation A^+ for alkali phases $A^+_{0.3}(NMF)_y[TaS_2]^{0.3-}$ and $A^+_{0.3}(DMSO)_y[TaS_2]^{0.3-}$

A^+	NMF	DMSO	A^+	NMF	DMSO
Na^+	18.9	18.6	Rb^+	17.4	13.8
K^+	17.3	17.1	Cs^+	17.5	13.6

For derivatives of aliphatic alcohols and ethers (Table IV) interlayer spacings were found to be notably lower than those of the amides which must be attributed to the higher polarity and solvation power of the latter solvents. Since the van der Waals height of the aliphatic chain amounts to ca. 4 Å, the *d* values of ethanol and glycol/glycerine phases could well be interpreted in terms of mono- and bilayers of solvent molecules lying with their C–C planes parallel to the layer surface; similar arguments apply to the ether derivatives. The Nb phases are exceptional for intercalating only ethers but not alcohols. The former are known to be stronger electron pair donors than aliphatic alcohols and the Nb compounds might be critical in terms of their cation density which is the highest among the three chalcogenide types considered.

Many other polar molecules may react to give solvate phases with strongly varying interlayer spacing, e.g., the organic phosphorus compounds listed in Table IV. In view of the manifold of possibilities for cations and solvent molecules to arrange themselves in the space between the chalcogenide layers, it is necessary to await more detailed structural data for further discussion.

Colloid Phenomena. In solvents with high dielectric constant, e.g., formamide or *N*-methylformamide, deep coloration of the liquid phase was observed frequently in suspensions of the corresponding solvates $A^+_x(solv)_y[MS_2]^{x-}$. A preliminary investigation of this effect revealed a marked dependence on particle size. Under the influence of weak shear forces, e.g., rapid stirring of suspensions, the solid phase completely disappeared and homogeneous colloid solutions of intense blue color were obtained rapidly with finally divided starting material. The reactions were primarily carried out with $Na^+_x(NMF)_y[TiS_2]^{x-}$ which is most easily turned over into the colloid state. Dilute dark blue solutions of this compound in high purity NMF at room temperature were stable for periods of several months, provided oxygen and water traces are rigorously excluded. Solutions of a few weight percent were found to obey Beer's law; i.e., no particle association effects occur in this concentration range. The absorption maximum in the optical range appears at 580 nm. An investigation of the electrophoretic behavior was carried out in solutions of the colloid with 10^{-1} M NaCl in *N*-methylformamide as electrolyte under inert-gas atmosphere. The movement of the blue colloid phase toward the positive electrode was clearly visible in these experiments. It is to be concluded that the colloid is of electrocratic nature and consists of negatively charged dichalcogenide layers surrounded by a diffuse layer of solvated alkali cations. The anisotropic character of the colloid particle units is also confirmed by the streaming birefringence phenomena which we observed in dilute solutions. The stability of anionic electrocratic colloids is known to be strongly influenced by electrolyte concentration and by the charge of the electrolyte cation. It turned out that in NMF solutions only addition of trivalent cations, e.g., La^{3+}, resulted in flocculation, whereas monovalent and divalent electrolyte cations, e.g., Na^+ and Ca^{2+}, up to the concentration limit of these ions in NMF did not affect the stability of the colloid. Powder diagrams of the coagulated solid showed severe line broadening due to strong lattice disorder.

Table VII. Interlayer Spacings *d* (Å) and Interlayer Heights Δ*d* (Å) for Na^+ and K^+ Forms of Hydrated Chalcogenides $A^+_x(H_2O)_y[MX_2]$

M	X	$d(Na^+)$	$\Delta d(Na^+)$	$d(K^+)$	$\Delta d(K^+)$	$\Delta d(Na^+)/\Delta d(K^+)$
Ti	$S^{a,b}$	11.56	5.85	8.72	3.01	1.94
	Se^a	12.06	6.05	9.31	3.30	1.83
Nb	S^a	11.63	5.68	8.94	2.99	1.90
	Se^a	12.08	5.81	9.40	3.13	1.86
Ta	S^a	11.74	5.69	9.04	2.99	1.90
	Se^a	12.88	6.54	9.71	3.37	1.94
Cr	S^c	11.33	5.32	8.59	2.58	2.06
Mo	S^b	11.97	5.83	9.09	2.95	1.98
W	S^b	12.12	5.94	9.41	3.23	1.84
Re	S^b	12.29	6.19	9.50	3.40	1.82
Sn	$S^{a,b}$	12.64	6.74	9.29	3.39	1.99

[a] Prepared by cathodic reduction of MX_2 in aqueous electrolytes. [b] Prepared by hydration of the alkali metal intercalation compound.[3,25] [c] Prepared by hydration of $NaCrS_2$.[25]

The fact that the layered chalcogenides do not form colloids spontaneously, as, e.g., the hydrated layer silicates, but need shear forces to induce this process must be attributed to their particle size which even after extended grinding time is still considerably larger than that of the silicates which amounts to 100–500 Å. Whether the DLVO theory on colloid stability which is well established for electrocratic aqueous colloid solutions will be applicable to describe the stability of dichalcogenide colloids in organic solvents will depend on a systematic collection of data for critical flocculation concentration and influence of solvent DC.

We found that solvated phases with formamide and NMF prepared from the Rüdorff alkali metal intercalation compounds[2] or by cathodic reduction of binary chalcogenides[13] yield blue colloids whose behavior is in agreement with that of the compounds described above. Hydrated phases $A_x(H_2O)_y[TaS_2]$ prepared by reduction of 1T-TaS_2 may form colloids even in aqueous medium when A = Li^+ or Na^+, but these solutions are extremely susceptible to pH variations and are poorly stable because of slow hydrolysis of the MX_2 layers. It remains to be clarified which kind of relationship is existing between the colloids under consideration and those formed on direct reaction of acid amides with TiS_2[17] or by electrolytic reduction of TaS_2 in H_2SO_4 and subsequent treatment with surface-active reagents.[18]

Related Solvated Phases. The solvation phenomena discussed above for ternary chalcogenides from alkali halide melts are basically very similar to those which we observed for ternary phases obtained (i) by reduction of layered chalcogenides in aqueous or nonaqueous electrolytes and (ii) by intercalation of MX_2 with alkali metals at higher temperatures or dissolved in liquid ammonia.[3,4,13,19] This is easily seen from a comparison of the ratio $\Delta d(Na)/\Delta d(K)$ of hydrated Na^+ and K^+ derivatives prepared by these methods (Table VII); the values vary between 1.8 and 2.0 and correspond well to the monolayer/bilayer hydration model. The hydrated alkali derivatives of the sulfide carbide Ta_2CS_2 which, like the layered chalcogenides of group 4B–6B metals, is characterized by close-packed sulfur planes at the "surfaces" of the S–Ta–C–Ta–S sandwich units lead to similar values.[8]

Wiegers recently reported on the structure of the hydrated vanadium sulfide $Na_{0.6}(H_2O)_y[VS_2]$ which also shows the occurrence of mono- and bilayer hydrates. A neutron diffraction study of this author[20] confirmed that Na is positioned between the two H_2O sheets in the bilayer hydrate as it is in $Na^+_{0.5}(H_2O)_y[TiS_2]^{0.5-}$.[3] Whittingham proposed structures for the arrangement of water in octahedral and trigonal-prismatic sites in hydrated ternary sulfides of Ti and Ta.[21] Wiegers suggested on grounds of 3D-Fourier data a model in which the oxygen atoms are in a close packing with the sulfur lattice; hydrogen bonding of water molecules within the H_2O sheets as well as to the sulfide layers is assumed. For reasons given above the latter possibility, however, seems rather unlikely. Moreover, our data show (Table VII) that selenides—in which a close packing of H_2O and Se anions would certainly exclude hydrogen-bonded networks because of the large Se–Se distance—give similar mono- and bimolecular water layers as the sulfides. We conclude from our arguments and from the relatively low stoichiometric ratio H_2O/A^+ that the cation–solvent interaction is the factor which essentially governs the hydrate structure in these compounds.

Gamble[5] and Subba Rao[24] reported on the reaction of alkali hydroxides AOH with layered chalcogenides MX_2 to give intercalated phases $MX_2 \cdot AOH$. Whittingham[21] determined the composition of some of these phases and proposed structures on grounds of x-ray powder data. He also investigated the reaction product of aqueous NH_3 with TaS_2 for which he found a composition of $(NH_3)_{1/3}(H_2O)_{2/3}TaS_2$. We were able to show earlier that the formation of these hydrated phases is correlated with hydrolysis and redox reactions leading again to negatively charged layers and solvated cations in the interlayer space.[4] The composition of these compounds is consequently $A^+_x(H_2O)_y[MX_{2-n}O_n]^{x-}$ and $(NH_4^+)_x(H_2O)_y[MX_{2-n}O_n]^{x-}$; they undergo cation-exchange reactions, the interlayer distances being closely similar to those of the corresponding phases prepared from ternary compounds A_xMX_2 or by reduction of MX_2. The powder lines are, however, broadened because of the attack of the chalcogenide layers by hydrolysis. The compounds $(KOH)_{0.88}(H_2O)_{0.54}TiS_2$ and $(KOH)SnS_2$ were reported by Rouxel to form on reaction of K_xTiS_2 and Na_xSnS_2 with water vapor at low pressure.[22,23] Our investigations showed that these phases also undergo cation exchange and belong to the ionic hydrates $A^+_x(H_2O)_y[MS_2]^{x-}$, the interlayer spacing depending on the ratio e_0/r of A^+. On treating the hydrogen intercalation compound H_xTaS_2—which forms on cathodic reduction of TaS_2 in mineral acids[28]—with alkali hydroxides, we found that this compound behaves as a solid Bronsted acid and yields hydrated phases $A^+_x(H_2O)_y[TaS_2]^{x-}$ on acid–base titration. Intercalation compounds of Lewis base molecules with dichalcogenides have recently been shown to be ionic compounds with exchangeable solvated cations in the interlayer region.[29]

All of the layered chalcogenide hydrates which exhibit the typical monolayer/bilayer hydrate structures are characterized by layers whose intracrystalline "surfaces" consist of sheets of close-packed chalcogen atoms and thus are to be considered as quasi-planar. The simple charge–radius correlation between hydrate type and exchangeable cation is, however, no longer valid in cases where the sulfur planes are not in a close-packed arrangement. We observed, e.g., that the ternary sulfide $K_2Pt_4S_6$, which is built up by S–Pt–S sandwich layers, after partial oxidation yields the hydrate $K_{2-x}(H_2O)_y[Pt_4S_6]^{(2-x)-}$ which readily undergoes cation-exchange reactions.[25] No clear step was found for the transition monolayer/bilayer hydrate in the alkali and alkaline earth ion series. We attribute this fact to a perturbation of the cation/water system by the large sulfur "holes" characteristic for the Pt_4S_6 layer units.[26] Hydrated layered transition metal oxide bronzes as well cannot be interpreted in terms of the simple hydration model as was shown by us for the layered Mo bronzes $A^+_x(H_2O)_y[MoO_3]^{x-}$.[27] Here it is obvious that hydrogen bonding between the negatively charged oxide layers and interlayer water becomes a dominant element in determining the hydrate structure.

Conclusion

The solvated layer chalcogenides present rather unique chemical systems at the borderline between solid-state chemistry, molecular chemistry, and interface chemistry. Their reactivity is characterized by a typical polyelectrolyte behavior on grounds of reversible topotactic exchange reactions. As opposed to the case of layered oxides, a fairly simple concept based on the ion–dipole interaction of the exchangeable cations with the solvent molecules is able to explain the experimental phenomena observed for water as solvent. The basic chemical reactivity of these phases is relatively independent of layer composition (M, X) and relative ordering and of the layer charge density in the range of $0.2 \le x \le 0.5$. They represent thus interesting models for the investigation of quasi-two-dimensional electrolyte films on intracrystalline semiconducting and metallic surfaces with low defect concentrations as compared to those of outer surfaces. As pointed out above, the chemical properties of many intercalation compounds of the binary chalcogenides MX_2 can be easily understood in terms of the polyelectrolyte concept.

The physical properties of the solvated compounds are, however, strongly dependent on layer composition as well as on the nature of solvent, exchangeable cation, and layer charge density.[7] Exchange and redox properties allow an extraordinary variety of ways for modifying ("tailoring") at ambient temperature the chemical composition of the interlayer space, while retaining the $[MX_2]^{x-}$ units. On grounds of these topotactic reactions the solvated chalcogenides also provide most versatile model compounds for the investigation of the physical properties of electronically conducting two-dimensional lattice units.

Registry No. $Li^+_{0.5}(H_2O)_y[TiS_2]^{0.5-}$, 57126-92-8; $Na^+_{0.5}(H_2O)_y[TiS_2]^{0.5-}$, 57126-88-2; $K^+_{0.5}(H_2O)_y[TiS_2]^{0.5-}$, 57126-95-1; $NH_4{}^+_{0.5}(H_2O)_y[TiS_2]^{0.5-}$, 63988-71-6; $Rb^+_{0.5}(H_2O)_y[TiS_2]^{0.5-}$, 57126-84-8; $Cs^+_{0.5}(H_2O)_y[TiS_2]^{0.5-}$, 57088-27-4; $Li^+_{0.5}(H_2O)_y[NbS_2]^{0.5-}$, 63988-61-4; $Na^+_{0.5}(H_2O)_y[NbS_2]^{0.5-}$, 57126-89-3; $K^+_{0.5}(H_2O)_y[NbS_2]^{0.5-}$, 57126-96-2; $NH_4{}^+_{0.5}(H_2O)_y[NbS_2]^{0.5-}$, 63988-60-3; $Rb^+_{0.5}(H_2O)_y[NbS_2]^{0.5-}$, 63988-63-6; $Cs^+_{0.5}(H_2O)_y[NbS_2]^{0.5-}$, 63988-59-0; $Li^+_{0.3}(H_2O)_y[TaS_2]^{0.3-}$, 63988-79-4; $Na^+_{0.3}(H_2O)_y[TaS_2]^{0.3-}$, 63988-81-8; $K^+_{0.3}(H_2O)_y[TaS_2]^{0.3-}$, 63988-78-3; $NH_4{}^+_{0.3}(H_2O)_y[TaS_2]^{0.3-}$, 63988-77-2; $Rb^+_{0.3}(H_2O)_y[TaS_2]^{0.3-}$, 63988-82-9; $Cs^+_{0.3}(H_2O)_y[TaS_2]^{0.3-}$, 55763-49-0; $Mg^{2+}_{0.5/2}(H_2O)_y[TiS_2]^{0.5-}$, 63988-70-5; $Ca^{2+}_{0.5/2}(H_2O)_y[TiS_2]^{0.5-}$, 63988-68-1; $Sr^{2+}_{0.5/2}(H_2O)_y[TiS_2]^{0.5-}$, 63988-72-7; $Ba^{2+}_{0.5/2}(H_2O)_y[TiS_2]^{0.5-}$, 63988-67-0; $Mg^{2+}_{0.5/2}(H_2O)_y[NbS_2]^{0.5-}$, 63988-62-5; $Ca^{2+}_{0.5/2}(H_2O)_y[NbS_2]^{0.5-}$, 63988-58-9; $Sr^{2+}_{0.5/2}(H_2O)_y[NbS_2]^{0.5-}$, 63988-64-7; $Ba^{2+}_{0.5/2}(H_2O)_y[NbS_2]^{0.5-}$, 63988-57-8; $Mg^{2+}_{0.3/2}(H_2O)_y[TaS_2]^{0.3-}$, 63988-80-7; $Ca^{2+}_{0.3/2}(H_2O)_y[TaS_2]^{0.3-}$, 55763-46-7; $Sr^{2+}_{0.3/2}(H_2O)_y[TaS_2]^{0.3-}$, 63988-83-0; $Ba^{2+}_{0.3/2}(H_2O)_y[TaS_2]^{0.3-}$, 63988-76-1; $Na^+_{0.5}$(formamide)$_y[TiS_2]^{0.5-}$, 64045-24-5; $Na^+_{0.5}$(DMF)$_y[TiS_2]^{0.5-}$, 64082-20-8; $Na^+_{0.5}$(ethanol)$_y[TiS_2]^{0.5-}$, 64045-38-1; $Na^+_{0.5}$(glycol)$_y[TiS_2]^{0.5-}$, 64045-39-2; $Na^+_{0.5}$(glycerine)$_y[TiS_2]^{0.5-}$, 64045-42-7; $Na^+_{0.5}$(diglyme)$_y[TiS_2]^{0.5-}$, 64045-40-5; $Na^+_{0.5}$(poly(ethylene glycol))$_y[TiS_2]^{0.5-}$, 64070-35-5; $Na^+_{0.5}$(phosphoric acid trimethyl ester)$_y[TiS_2]^{0.5-}$, 64045-25-6; $Na^+_{0.5}$(hexamethylphosphoric acid triamide)$_y[TiS_2]^{0.5-}$, 64045-26-7; $Na^+_{0.5}$(tri-*n*-butylphosphine oxide)$_y[TiS_2]^{0.5-}$, 64045-27-8; $Na^+_{0.5}$(DMSO)$_y[TiS_2]^{0.5-}$, 64045-29-0; $Na^+_{0.5}$(formamide)$_y[NbS_2]^{0.5-}$, 64045-13-2; $Na^+_{0.5}$(NMF)$_y[NbS_2]^{0.5-}$, 64070-36-6; $Na^+_{0.5}$(DMF)$_y[NbS_2]^{0.5-}$, 64045-14-3; $Na^+_{0.5}$(diglyme)$_y[NbS_2]^{0.5-}$, 64045-15-4; $Na^+_{0.5}$(poly(ethylene glycol))$_y[NbS_2]^{0.5-}$, 64045-16-5; $Na^+_{0.5}$(phosphoric acid trimethyl ester)$_y[NbS_2]^{0.5-}$, 64045-18-7; $Na^+_{0.5}$(hexamethylphosphoric acid triamide)$_y[NbS_2]^{0.5-}$, 64045-19-8; $Na^+_{0.5}$(DMSO)$_y[NbS_2]^{0.5-}$, 64045-21-2; $Na^+_{0.3}$(formamide)$_y[TaS_2]^{0.3-}$, 64045-54-1; $Na^+_{0.3}$(NMF)$_y[TaS_2]^{0.3-}$, 64045-55-2; $Na^+_{0.3}$(DMF)$_y[TaS_2]^{0.3-}$, 64045-56-3; $Na^+_{0.3}$(*N*-methylacetamide)$_y[TaS_2]^{0.3-}$, 64045-58-5; $Na^+_{0.3}$(ethanol)$_y[TaS_2]^{0.3-}$, 64045-60-9; $Na^+_{0.3}$(glycol)$_y[TaS_2]^{0.3-}$, 64045-61-0; $Na^+_{0.3}$(butanediol-2,3)$_y[TaS_2]^{0.3-}$, 64045-63-2; $Na^+_{0.3}$(glycerine)$_y[TaS_2]^{0.3-}$, 64045-64-3; $Na^+_{0.3}$(diglyne)$_y[TaS_2]^{0.3-}$, 64045-66-5; $Na^+_{0.3}$(poly(ethylene glycol))$_y[TaS_2]^{0.3-}$, 64045-67-6; $Na^+_{0.3}$(phosphoric acid trimethyl ester)$_y[TaS_2]^{0.3-}$, 64045-68-7; $Na^+_{0.3}$(hexamethylphosphoric acid triamide)$_y[TaS_2]^{0.3-}$, 64070-33-3; $Na^+_{0.3}$(tri-*n*-butylphosphine oxide)$_y[TaS_2]^{0.3-}$, 64045-50-7; $Na^+_{0.3}$(DMSO)$_y[TaS_2]^{0.3-}$, 64045-51-8; $Li^+_{0.5}$(DMF)$_y[TiS_2]^{0.5-}$, 64045-30-3; $K^+_{0.5}$(DMF)$_y[TiS_2]^{0.5-}$, 64045-31-4; $Rb^+_{0.5}$(DMF)$_y[TiS_2]^{0.5-}$, 64045-52-9; $Mg^{2+}_{0.5/2}$(DMF)$_y[TiS_2]^{0.5-}$, 64045-32-5; $Ca^{2+}_{0.5/2}$(DMF)$_y[TiS_2]^{0.5-}$, 64045-33-6; $Sr^{2+}_{0.5/2}$(DMF)$_y[TiS_2]^{0.5-}$, 64045-34-7; $Ba^{2+}_{0.5/2}$(DMF)$_y[TiS_2]^{0.5-}$, 64045-35-8; $Li^+_{0.5}$(DMF)$_y[NbS_2]^{0.5-}$, 64045-17-6; $K^+_{0.5}$(DMF)$_y[NbS_2]^{0.5-}$, 64045-20-1; $Rb^+_{0.5}$(DMF)$_y[NbS_2]^{0.5-}$, 64045-53-0; $Mg^{2+}_{0.5/2}$(DMF)$_y[NbS_2]^{0.5-}$, 64045-22-3; $Ca^{2+}_{0.5/2}$(DMF)$_y[NbS_2]^{0.5-}$, 64045-36-9; $Sr^{2+}_{0.5/2}$(DMF)$_y[NbS_2]^{0.5-}$, 64045-57-4; $Ba^{2+}_{0.5/2}$(DMF)$_y[NbS_2]^{0.5-}$, 64045-59-6; $Li^+_{0.3}$(DMF)$_y[TaS_2]^{0.3-}$, 64045-37-0; $K^+_{0.3}$(DMF)$_y[TaS_2]^{0.3-}$, 64045-62-1; $Rb^+_{0.3}$(DMF)$_y[TaS_2]^{0.3-}$, 64045-65-4; $Cs^+_{0.3}$(DMF)$_y[TaS_2]^{0.3-}$, 64045-41-6; $Mg^{2+}_{0.3/2}$(DMF)$_y[TaS_2]^{0.3-}$, 64045-43-8; $Ca^{2+}_{0.3/2}$(DMF)$_y[TaS_2]^{0.3-}$, 64045-44-9; $Sr^{2+}_{0.3/2}$(DMF)$_y[TaS_2]^{0.3-}$, 64045-23-4; $Ba^{2+}_{0.3/2}$(DMF)$_y[TaS_2]^{0.3-}$, 64070-37-7; $K^+_{0.3}$(NMF)$_y[TaS_2]^{0.3-}$, 64045-45-0; $Rb^+_{0.3}$(NMF)$_y[TaS_2]^{0.3-}$, 64045-46-1; $Cs^+_{0.3}$(NMF)$_y[TaS_2]^{0.3-}$, 64045-47-2; $K^+_{0.3}$(DMSO)$_y[TaS_2]^{0.3-}$, 64045-48-3; $Rb^+_{0.3}$(DMSO)$_y[TaS_2]^{0.3-}$, 64045-49-4; $Cs^+_{0.3}$(DMSO)$_y[TaS_2]^{0.3-}$, 64045-28-9; $Na^+_{0.5}(H_2O)_y[TiSe_2]^{0.5-}$, 63988-73-8; $Na^+_{0.5}(H_2O)_y[NbSe_2]^{0.5-}$, 63988-66-9; $Na^+_{0.3}(H_2O)_y[TaSe_2]^{0.3-}$, 63988-75-0; $K^+_{0.5}(H_2O)_y[TiSe_2]^{0.5-}$, 63988-69-2; $K^+_{0.5}(H_2O)_y[NbSe_2]^{0.5-}$, 63988-65-8; $K^+_{0.3}(H_2O)_y[TaSe_2]^{0.3-}$, 63988-74-9.

References and Notes

(1) W. Bronger, *Z. Anorg. Allg. Chem.*, **359**, 225 (1968).

(2) W. Rüdorff, *Chimia*, **19**, 489 (1965); A. Le Blanc-Soreau, M. Danot, L. Trichet, and J. Rouxel, *Mater. Res. Bull.*, **9**, 191 (1974).

(3) R. Schöllhorn and A. Weiss, *Z. Naturforsch., B*, **28**, 711 (1973); *J. Less Common Met.*, **36**, 229 (1974).

(4) R. Schöllhorn, E. Sick, and A. Lerf, *Mater. Res. Bull.*, **10**, 1005 (1975); R. Schöllhorn and A. Lerf, *Z. Naturforsch., B*, **29**, 804 (1974); R. Schöllhorn, Abstracts of the 8th International Symposium on the Reactivity of Solids, Göteborg, 1976, No. 524.

(5) F. R. Gamble and T. H. Geballe, *Treatise Solid State Chem.*, **3** (1976).

(6) R. Schöllhorn and A. Lerf, *J. Less Common Met.*, **42**, 89 (1975); Abstracts, Fourth International Conference on Non-aqueous Solutions, Vienna, 1974.

(7) R. Schöllhorn, A. Lerf, and F. Sernetz, *Z. Naturforsch., B*, **29**, 810 (1974); F. Sernetz, A. Lerf, and R. Schöllhorn, *Mater. Res. Bull.*, **9**, 1597 (1974); A. Lerf, Dissertation, München, 1976; A. Lerf, F. Sernetz, and R. Schöllhorn, to be submitted for publication.

(8) R. Schöllhorn and W. Schmucker, *Z. Naturforsch., B*, **30**, 975 (1975).

(9) R. E. Grim, "Clay Mineralogy", 2nd ed, McGraw-Hill, New York, N.Y., 1968.

(10) S. Olejnic and J. W. White, *Nature (London), Phys. Sci.*, **236**, 15 (1972).

(11) R. C. Mackenzie, *Ber. Dtsch. Keram. Ges.*, **41**, 696 (1964).

(12) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968; J. Donohue, *J. Mol. Biol.*, **45**, 231 (1969).

(13) R. Schöllhorn and H. Meyer, *Mater. Res. Bull.*, **9**, 1237 (1974).

(14) H. A. Graf, A. Lerf, and R. Schöllhorn, *J. Less Common Met.*, **55**, 213 (1977).

(15) R. Schöllhorn and A. Weiss, *Z. Naturforsch., B*, **28**, 172 (1973).

(16) A. Weiss and R. Ruthardt, *Z. Naturforsch., B*, **24**, 355, 1066 (1969).

(17) A. Weiss and R. Ruthardt, Offenlegungsschrift 1767190 (1971); R. Ruthardt, Dissertation, München, 1969.

(18) D. W. Murphy and G. W. Hull, *J. Chem. Phys.*, **62**, 973 (1975).

(19) J. O. Besenhard, H. Meyer, and R. Schöllhorn, *Z. Naturforsch., B*, **31**, 907 (1976); J. O. Besenhard and R. Schöllhorn, *J. Power Sources*, **1**, 267 (1977).

(20) G. A. Wiegers, R. van der Meer, H. van Heinigen, H. J. Kloosterboer, and A. J. A. Alberink, *Mater. Res. Bull.*, **9**, 1261 (1974); A. J. A. Boos-Alberink, R. J. Haange, G. Stüler, and G. A. Wiegers, Abstracts of the Fifth International Conference on Solid Compounds of Transition Elements, Uppsala, 1976, No. 60.

(21) S. Whittingham, *Mater. Res. Bull.*, **9**, 1681 (1974).

(22) M. Danot, A. Le Blanc, and J. Rouxel, *Bull. Soc. Chim. Fr.*, 2670 (1969).

(23) A. Le Blanc, M. Danot, and J. Rouxel, *Bull. Soc. Chim. Fr.*, 87 (1969).

(24) G. V. Subba Rao and J. C. Tsang, *Mater. Res. Bull.*, **9**, 921 (1974).

(25) R. Schöllhorn and A. Lerf, in preparation.

(26) W. Rüdorff, A. Stössel, and V. Schmidt, *Z. Anorg. Allg. Chem.*, **357**, 264 (1968).

(27) R. Schöllhorn, R. Kuhlmann, and J. O. Besenhard, *Mater. Res. Bull.*, **11**, 83 (1976).

(28) D. W. Murphy, F. J. Di Salvo, G. W. Hull, J. V. Waszczak, S. F. Mayer, G. R. Stewart, S. Early, J. V. Acrivos, and T. H. Geballe, *J. Chem. Phys.*, **62**, 967 (1975); M. S. Whittingham, *J. Chem. Soc., Chem. Commun.*, 328 (1974).

(29) R. Schöllhorn and H. D. Zagefka, *Angew. Chem.*, **89**, 193 (1977); *Angew. Chem. Int. Ed. Engl.*, **16**, 199 (1977).