

Formation and Reactions of Hydrated Layered Chromium Sulfides $A_x(H_2O)_y[CrS_2]$

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Partial oxidation of $NaCrS_2$ in neutral aqueous electrolyte solutions results in the topotactic formation of the hydrated phase $Na_x^+(H_2O)_y[CrS_2]^{x-}$ which consists of negatively charged $[CrS_2]^{x-}$ layers with solvated mobile alkali ions between the chromium sulfide sheets. Cation- and water-exchange reactions demonstrate the polyelectrolyte character of this compound. Electrochemical investigations by galvanostatic methods showed that on oxidation $0.6 e^-$ are transferred from the layers resulting in a value of $x = 0.4$ in the oxidized state; the process is reversible in the range of $0.7 \geq x \geq 0.4$. The product obtained on oxidation in acid electrolytes, described in earlier studies as "CrS₂," was found to be a hydrogen phase $H_{0.3}CrS_2$ which exhibits Brønsted acid character and forms Lewis base intercalation compounds. The chemical reactivity of $KCrS_2$ which is isotopic with $NaCrS_2$ is similar to that of the sodium form.

Introduction

In contrast to most transition elements of group IVB to VIB—which are known to form nonstoichiometric ternary sulfides A_xMS_2 (A = alkali metal, M = transition metal, X = chalcogen)—well characterized stoichiometric phases $ACrS_2$ have been reported in the case of chromium. The structures of the latter are, however, basically similar to those of the above mentioned compounds. Chromium and sulfur form S—Cr—S sandwich layers with chromium in octahedral position; the monovalent alkali cations are situated in octahedral holes between these layers (1-3). Schneider, who first isolated $NaCrS_2$ in 1897, reported on a

binary phase CrS_2 which he prepared from sodium thiochromate by treatment with mineral acids in the presence of oxygen (4); Rüdorff later confirmed the decomposition of $NaCrS_2$ in water (5) and Schwarz and Rüdorff determined lattice parameters for CrS_2 (hexagonal, $a = 3.30 \text{ \AA}$, $c = 5.65 \text{ \AA}$) and for a related phase $CrSe_2$ obtained by hydrolysis and oxidation of $KCrSe_2$ (6).

We described in earlier studies hydration, exchange, and redox reactions of nonstoichiometric layered ternary transition-metal chalcogenides A_xMX_2 (7) and were thus interested in a more detailed investigation on the reactivity of the structurally related chromium phases. Moreover, the question on the nature and stability of chromium disulfide CrS_2 is still open; no phase of this composition can be obtained from the elements in the binary system Cr/S (8) which extends from $Cr_{1.0}S$ to $Cr_{0.63}S$.

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Methods

Ternary phases NaCrS_2 and KCrS_2 were prepared from reagent grade starting materials according to the methods described in the literature (5). At increased reaction temperatures crystal plates up to 20 mm in diameter could be isolated from the polysulfide melts. Oxidation with O_2 was performed in stirred aqueous suspensions or buffer solutions of single crystals or polycrystalline material. Electrolyte solutions 1 M served for cation-exchange purposes; the treatment was repeated until analysis indicated quantitative exchange. Reaction kinetics depended strongly on cation type and varied between ca. 10 min to a few days. For solvent exchange the hydrates were immersed repeatedly in the liquid organic phases which had been purified by conventional methods. Quantitative analysis was performed by wet methods (Cr, S), flame spectrophotometry (alkali and alkaline earth ions), and microanalysis (C, H, N). X-Ray investigations were carried out by powder and Weissenberg methods with $\text{CuK}\alpha$ radiation; polycrystalline hydrated phases were measured under equilibrium solution in sealed glass capillaries.

For galvanostatic experiments potentials were measured versus a saturated aqueous calomel electrode (SCE) or a Ag/AgCl electrode, separated by two fritted tubes filled with working electrolyte and connected to the working electrode by a Luggin capillary. All measurements were carried out in cells of the double-H type (two Pt counter electrodes) fitted with an inlet for inert gas (9). Current was controlled by a potentiostat via a constant voltage decay at an external resistance. Polycrystalline samples were pressed into Pt gauze at 5000 kg cm^{-2} and sandwiched between porous glass electrodes to avoid loss caused by exfoliation. Current densities given correspond to the geometrical electrode surface and represent approximate values.

Results and Discussion

Oxidation in Neutral Solution

In stirred suspensions of NaCrS_2 crystals in distilled water under argon atmosphere no changes in composition or X-ray powder lines of the solid could be observed even after periods of a few days; pH values of these suspensions remain close to 7. After replacing argon by dioxygen, however, a rapid increase in pH was found. Within 1–3 min values were measured close to $\text{pH} = 12$ and sodium ions were released into the aqueous phase. Single crystals of NaCrS_2 , which are transparent red, change their color to dark black in the course of this reaction while retaining their morphology. After a few hours the original solid is quantitatively transformed to a crystalline phase which does contain Na^+ , H_2O , Cr, and S. The ratio S/Cr was found equal to 2, whereas the ratio Na/Cr had decreased to ca. 0.4. Reactions with single crystals of NaCrS_2 showed that the product remains a single crystal, although reflections were broadened. Powder diagrams of polycrystalline material, which also exhibited line broadening, could be indexed rhombohedrally with the lattice parameters in hexagonal description $a = 3.3_8 \text{ \AA}$ and $c = 34.4_1 \text{ \AA} = 3 \times 11.4_7 \text{ \AA}$. The distance d between neighboring layers (interlayer spacing), which for NaCrS_2 is equivalent to $c/3 = 6.4_5 \text{ \AA}$ (3), increases significantly after hydration and amounts to $d = c/3 = 11.4_7 \text{ \AA}$ for the reaction product $\text{Na}_x(\text{H}_2\text{O})_y[\text{CrS}_2]$. The a -axis value changes from $a = 3.55 \text{ \AA}$ for NaCrS_2 to $a = 3.3_8 \text{ \AA}$ for the oxidation product.

The hydrated sodium phase was found to undergo rapid ion exchange with electrolyte solutions containing mono- or bivalent cations. Interlayer spacings for alkali and alkaline earth derivatives obtained by cation exchange are given in Table I. The extent of hydration is reflected by the interlayer spacing; two sets of d values with 8.6–8.8 \AA and 11.4–11.5 \AA can easily be distinguished. The

TABLE I
INTERLAYER SPACING d OF HYDRATED
CHROMIUM SULFIDES $A_{x/n}^{n+}(\text{H}_2\text{O})_y[\text{CrS}_2]^{x-}$ AND
CALCULATED VALUES FOR THE INTERLAYER
SPACE HEIGHT Δd

A	d (Å)	Δd (Å)
Li ⁺	11.36	5.4
Na ⁺	11.47	5.5
K ⁺	8.56	2.6
NH ₄ ⁺	8.61	2.6
Rb ⁺	8.64	2.7
Cs ⁺	8.83	2.8
Mg ²⁺	11.39	5.4
Ca ²⁺	11.48	5.5
Sr ²⁺	11.49	5.5

interlayer space height Δd can be estimated by the difference $\Delta d = d - d_0$ with $d_0 = 6 \text{ \AA}$ being the approximate van der Waals thickness of the CrS_2 layer calculated from the structural data of NaCrS_2 by using ionic radii for the sulfur atoms. The Δd parameters obtained thus (Table I) show values of 2.6–2.8 Å and of 5.4–5.5 Å and correspond reasonably well to once and twice, respectively, the van der Waals radius of water molecules (ca. 2.8 Å), i.e., to mono- and

bimolecular water layers between the CrS_2 sheets (7). In the fully hydrated state the interlayer spacings are dependent on the hydration energy of the exchangeable cations which is demonstrated by the correlation charge/radius ratio of A^{n+} versus d given in Fig. 1. These observations are in perfect agreement with the behavior of hydrated layered chalcogenides of other transition elements which have been discussed in detail before (7, 10). Indexing of the phases $(\text{NH}_4)_{0.4}(\text{H}_2\text{O})_y[\text{CrS}_2]$ and $\text{Ca}_{0.2}(\text{H}_2\text{O})_y[\text{CrS}_2]$ showed that both types of hydrates are rhombohedral (lattice parameters in hexagonal setting: NH_4 form $a = 3.3_6 \text{ \AA}$, $c = 25.8_3 = 3 \times 8.6_1 \text{ \AA}$; Ca^{2+} form $a = 3.3_2 \text{ \AA}$, $c = 34.4_4 = 3 \times 11.4_8 \text{ \AA}$). Cation exchange with organic ions, e.g., n -alkylammonium ions $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)^+$, also proceeds rapidly. The latter adopt a paraffin-like order in the interlayer space with bilayers of cations leading to rather large interlayer distances as indicated in Fig. 2. Under the assumption of extended alkyl chains in all-*trans* conformation an inclination angle of the chain axes versus the CrS_2 layer planes may be calculated of ca. 63°

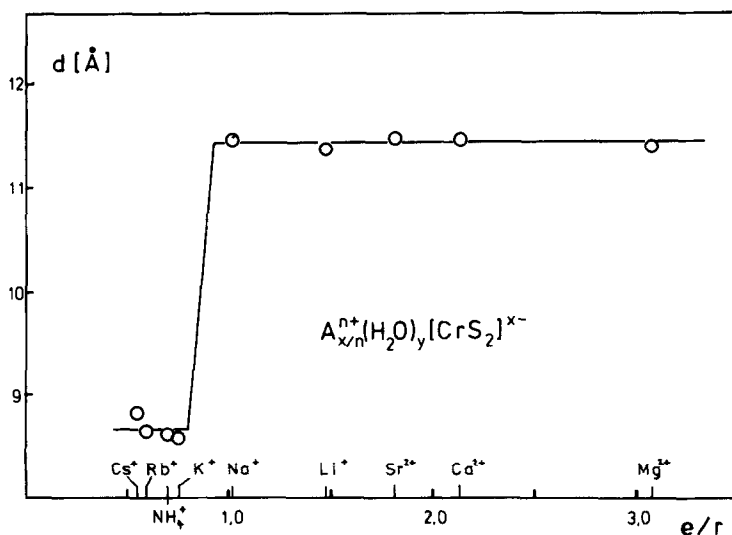


FIG. 1. Dependence of interlayer spacing d on the charge/radius ratio e/r of the exchangeable cations A for hydrated layered chromium sulfides $A_{x/n}^{n+}(\text{H}_2\text{O})_y[\text{CrS}_2]^{x-}$.

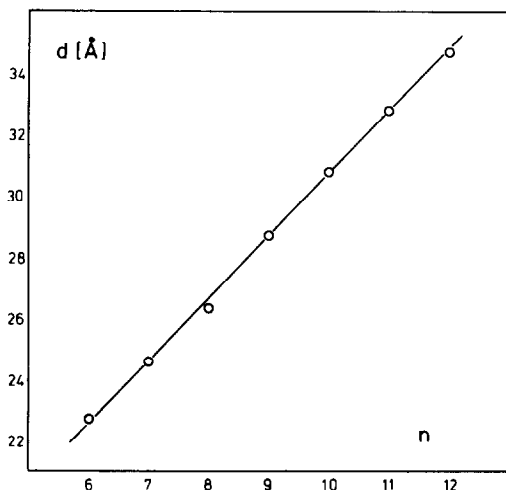


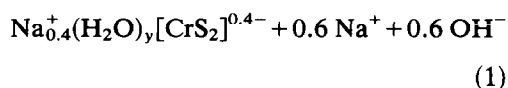
Fig. 2. Dependence of interlayer spacing d on the alkyl chain length for layered chromium sulfides exchanged with n -alkylammonium ions. (n) Number of carbon atoms per alkyl chain.

from chain dimensions and increase of d values per additional carbon atom. Closely related structures were found by us for several other layered chalcogenides (7, 10).

The water molecules present in the interlayer space may be exchanged for other solvent molecules like alcohols, amines, acid amides, ethers, etc. Quantitative exchange usually requires a few hours and results in an increase of the interlayer spacing depending on the size of the solvent molecules and the strength of the ion-dipole interaction. The spacings measured e.g., for the Ca^{2+} phase after reaction with acid amides are 15.94 Å (formamide), 14.52 Å (*N*-methylformamide), and 16.74 Å (*N,N*-dimethylformamide).

It is obvious from the chemical reactivity of the hydrated chromium sulfides that they are polyelectrolytes consisting of negatively charged $[\text{CrS}_2]^{x-}$ layers with solvated cations between the metal sulfide units. The fact that NaCrS_2 is not able to react directly with water under formation of hydrates is easy to understand, if one takes into consideration the high alkali ion density between the CrS_2 layers (all octahedral sites occupied) which

prevents the formation of an adequate hydration sphere of water molecules around the cations. Only after oxidation, which leads to a reduced negative-charge density of the layers and thus to a reduced cation density in the interlayer space, water molecules are able to diffuse into empty lattice positions. The final reaction product with O_2 as oxidant in neutral suspension is the non-stoichiometric phase $\text{Na}_x^+(\text{H}_2\text{O})_y[\text{CrS}_2]^{x-}$ with $x = 0.4$. Values obtained for the sodium content decrease somewhat on extended washing with water due to protolysis, i.e., exchange of Na^+ for H_3O^+ . The extent of the electron transfer from the CrS_2 layers to O_2 was calculated from the Na^+ content to be $0.6 e^-/\text{Cr}$ for $x = 0.4$ [Eq. (1)]. Volumetric determination of the O_2 quantity taken up by the suspension leads to a similar value: Rapid consumption of O_2 occurs until an amount had reacted which was equivalent to a transfer of $0.6 e^-/\text{Cr}$; after that the process continued at a slow rate with further oxidation to products which were not identified. The same result is obtained on anodic oxidation of NaCrS_2 pressed-powder electrodes in neutral aqueous Na_2SO_4 electrolyte. As indicated in Fig. 3 a sharp step in potential

$$\text{NaCrS}_2 + 0.15 \text{O}_2 + (y + 0.3)\text{H}_2\text{O} \rightarrow$$


is found after a transfer of $0.6 e^-/\text{Cr}$. X-Ray powder photographs of the product isolated from the working electrode are identical with those of the hydrated phase produced by oxidation of NaCrS_2 with O_2 in water and show an interlayer distance of 11.45 Å. A further potential step is found at a transfer of $5 e^-/\text{Cr}$ and corresponds formally to a quantitative oxidation of sulfide ions to sulfur and of Cr^{III} to Cr^{IV} ; the product obtained, however, turned out to be amorphous to X-rays. On oxidation to the first potential step in aqueous Na_2SO_4 and subsequent cathodic reduction up to the

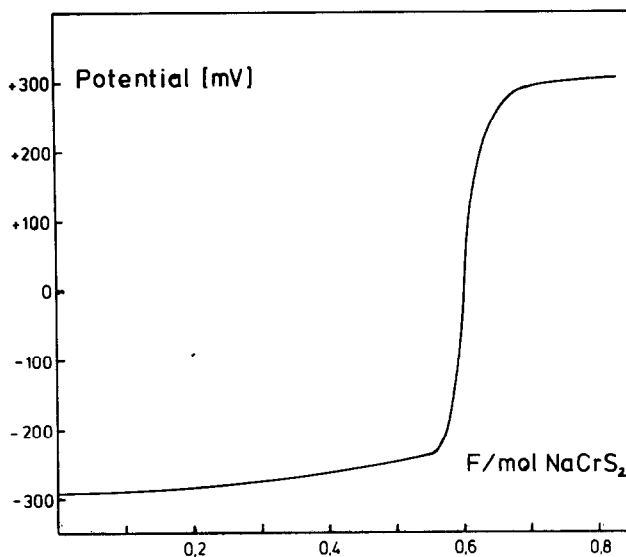
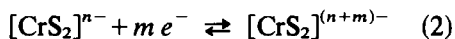


FIG. 3. Galvanostatic oxidation of NaCrS_2 . Potential of pressed-powder electrodes in 1 M aqueous Na_2SO_4 solution vs Ag/AgCl . (i) $300 \mu\text{A}/\text{cm}^2$.

potential of solvent decomposition a clear step showed up again, corresponding to an uptake of $0.3 e^-/\text{Cr}$; the interlayer spacing of the reduced phase is decreasing only slightly to 11.3_5 \AA . This demonstrates that in the range of $0.7 \geq x \geq 0.4$ the $[\text{CrS}_2]^{x-}$ layer units are able to undergo a reversible topo-tactic redox reaction according to Eq. (2).



Oxidation of potassium thiochromate KCrS_2 , which is isotypic with NaCrS_2 , was found to proceed considerably more rapid as compared to the latter compound. The hydrated phase $\text{K}_x^+(\text{H}_2\text{O})_y[\text{CrS}_2]^{x-}$ can be indexed on a rhombohedral base with the lattice parameters in hexagonal setting $a = 3.3_4 \text{ \AA}$, $c = 25.7_1 = 3 \times 8.5_7 \text{ \AA}$. As expected, derivatives prepared by ion exchange were found to be identical with those of the corresponding compounds obtained via the hydrated sodium phase.

Oxidation in Acid Electrolytes

The oxidation of NaCrS_2 suspensions with O_2 in dilute mineral acids resulted in a black

sodium-free product " CrS_2 " with a S/Cr ratio of 1.95; the same compound was obtained by oxidation of KCrS_2 under these conditions. X-Ray powder patterns showed relatively few lines which were broadened. Single crystals also yielded patterns with strongly broadened reflections. Reactions in 1 N H_2SO_4 turned out to give the best products by X-ray standard with nine powder diffraction lines; indexing led to the lattice parameters $a = 3.4_8 \text{ \AA}$ and $c = 18.0_3 = 3 \times 6.0_1 \text{ \AA}$ (hexagonal setting). Since the interlayer spacing of this compound, which amounts to 6.0_1 \AA , is rather close to the van der Waals thickness of one CrS_2 unit neither Na^+ ions nor H_2O molecules can be present between the chalcogenide layers. The preparations do not undergo hydration in the presence of water.

On combustion of " CrS_2 " after drying at 10^{-3} Torr/ 40°C we found that small amounts of H_2O were formed. This observation has been made before in earlier investigations which attribute this fact to residual water molecules between the layers ($\text{CrS}_2 \cdot x\text{H}_2\text{O}$) or to hydrolysis phenomena

(4-6). There is, however, still the possibility that hydrogen is a constitutional element of this compound, which because of its small size could occupy octahedral or tetrahedral interlayer positions without contributing to an increase in the interlayer spacing. Direct oxygen analysis seemed not to be useful, since the presence of small amounts of oxygen formed by hydrolysis on the layer edges of the crystallites certainly had to be expected and an interpretation of the hydrogen content would thus be doubtful on this base. We therefore decided to study the electron transfer during the oxidation of NaCrS_2 by galvanostatic methods. On anodic oxidation of NaCrS_2 working electrodes in 1 *N* H_2SO_4 a well reproducible potential step was found at a transfer of $0.7 e^-/\text{Cr}$; the powder pattern of the oxidized phase was identical with that of "CrS₂." No further potential steps (e.g., at a transfer of $1 e^-/\text{Cr}$) were observed and the oxidation continued at constant potential to give products which were amorphous to X-rays.

It can be concluded from the results above that the product of NaCrS_2 oxidation in acid solution represents a hydrogen phase with the composition $\text{H}_{0.3}\text{CrS}_2$ and is not to be considered as a binary sulfide "CrS₂." Although the broadening of diffraction lines observed for this compound could be interpreted in terms of lattice disorder originating e.g., from deformation of the CrS₂ layers by small amounts of isolated residual H₂O molecules, it is also possible that this effect results from an intrinsic deformation of the layers due to increased Cr-S covalent bonding (Cr^{IV}), since the fully hydrated phases show the same phenomenon.

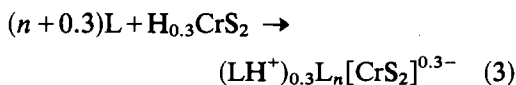
$\text{H}_{0.3}\text{CrS}_2$ is a thermally unstable phase which can, however, be stored at ambient temperature for years without noticeable change in composition or structure. Slight decomposition is visible by thermogravimetric analysis already at ca. 50°C; a strong weight loss appears between 350-450°C. Among the volatile products H₂S, H₂, and

sulfur were identified qualitatively. Between 700-800°C no significant decomposition occurs and the total weight loss at this stage amounts to 19.9%, equivalent to an approximate formula of the solid residue of Cr_{0.78}S. Thermodynamically stable sulfur compounds are known in this range, yet the solid isolated turned out to be amorphous.

Preliminary magnetic measurements indicated that $\text{H}_{0.3}\text{CrS}_2$ is paramagnetic in the temperature range of 90-295°K; in agreement with the thermogravimetric data a break occurs in the χ_M^{-1} versus *T* curve above ca. 300°K which is correlated with irreversible reactions.

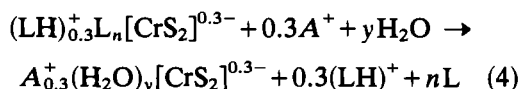
Cathodic galvanostatic reduction of $\text{H}_{0.3}\text{CrS}_2$ in neutral Na₂SO₄ solution resulted in a transfer of $0.4 e^-/\text{Cr}$. The powder pattern of the product—which was identical with that of $\text{Na}_{0.7}(\text{H}_2\text{O})_y[\text{CrS}_2]^{0.7-}$ —showed that the hydrogen phase can be reduced reversibly.

The formation of intercalation compounds of $\text{H}_{0.3}\text{CrS}_2$ with Lewis bases L according to the reaction scheme given in Eq. (3) reveals the



Brønsted acid character of this phase. Aqueous solutions of, e.g., NH₃, N₂H₄, and imidazole react with the hydrogen phase within a few minutes to hours. The interlayer spacing increases by the reaction and amounts to 8.6₁, 8.9₂, and 10.6₀ Å, respectively, for the NH₃, N₂H₄, and imidazole compound. Quantitative analysis showed that the guest molecules are taken up in a ratio higher than that required for "neutralization" of the interlayer protons. Varying amounts of water were found depending on the type of guest molecule and on its concentration in the aqueous solution. The ionic character of these intercalation compounds is demonstrated by their reaction with solutions of alkali and alkaline earth

salts which results in quantitative ion exchange according to Eq. (4). X-Ray powder line patterns and interlayer spacings



of the exchanged phases turned out to be identical within a range of 0.1–0.2 Å to those of the hydrates given in Table I. In agreement with the acid/base nature of the intercalation, Lewis bases with higher K_B values, e.g., pyridine, are not able to undergo reaction with $\text{H}_{0.3}\text{CrS}_2$.

Conclusions

With respect to hydration and exchange properties the hydrated phases of NaCrS_2 and KCrS_2 behave very similar to the nonstoichiometric layered chalcogenides A_xMX_2 of group IVB to VIB metals; as a consequence of the higher alkali ion density hydration sets in only after partial oxidation. Reversible reactions are, however, limited to the range of a formal oxidation state of Cr between +3.3 and +3.7; on further oxidation the sulfide layers decay. This is consistent with the observation that chromium is not able to accept an integral valency of +4 versus sulfur in Cr/S compound systems. Preliminary measurements of the electronic conductivity of pressed-powder samples of $\text{H}_{0.3}\text{CrS}_2$ indicate that the conductivity values are several orders higher than those of NaCrS_2 which indicates a strong decrease in ionic bonding. The Brønsted-acid character of $\text{H}_{0.3}\text{CrS}_2$ agrees well with that of the layered hydrogen bronzes H_xTaS_2 and H_xMoO_3 for which we recently found similar reactivity with respect to Lewis base intercalation and ion exchange (7, 11).

No information is available at present with respect to the problem of the hydrogen sites in $\text{H}_{0.3}\text{CrS}_2$; it cannot be excluded that hydrogen is located inside the chalcogenide layers as demonstrated recently by neutron diffraction investigations for the hydrogen bronzes D_xTaS_2 and H_xNbS_2 (12).

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