Storylines in intercalation chemistry

Journal:	*Dalton Transactions*
Manuscript ID:	DT-ART-01-2014-000203.R2
Article Type:	Perspective
Date Submitted by the Author:	07-May-2014
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Storylines in intercalation chemistry

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Abstract

Intercalation chemistry is soon hundred years old. The period of the greatest activity in this field of solid state chemistry and physics was from about 1970 to 1990. The intercalation reactions are defined as topotactic solid state reactions and the products – the intercalation compounds – clearly distinguished from inclusion and interstitial compounds. After a short historical introduction emphasizing the pioneering work of Ulrich Hofmann the central topics and concepts will be reviewed and commented. The most important ones in my view are: dichalcogenide intercalation compounds, the electrochemical intercalation and search for new battery electrodes, the physics of graphite intercalation compounds, the staging and interstratification phenomena. The relation to other fields of actual research and demands for forthcoming research will be also addressed.

Introduction

As far as I found the verb „to intercalate“ and the term „intercalation“ has been used for the first time by McDonnell et al. in 1951 without any explanation for using it.[1] In 1959 Rüdorff used the phrase „intercalation compounds“ in the title of a review about all chemical derivatives of graphite.[2] In these compounds atoms or ions have been inserted (alternatively, intercalated, or in German „eingelagert") under expansion of the lattice perpendicular to the nearly unchanged graphite layers. It is worth noting that Henning used the term "interstitial compounds", to name the same compounds at the same time.[3] This term was applied also to assign compounds like the hydrides, the carbides or the nitrides of the early transition metals in which there are also close topological relationships between the structure of the starting metals and the products obtained, and in which the ratio of the inserted atoms with respect to the host lattice is nonstoichiometric.[4] Some years later Barrer merged the graphite compounds, the zeolites, the clay minerals, the gas hydrates and other solids under the new headline „inclusion complexes“.[5]

These three terms („inclusion complexes, „interstitial compounds“, and „intercalation compounds“) should not be intermixed because they allow to assign definite groups of complex solids. The term „inclusion complexes“ should be used exclusively for those solids, in which the guest component is occluded in the host during preparation (see the chapters of H.M. Powell, J. Lipkowski, J. Hannotier, P. de Radzitzky and G. A. Jeffrey in vol. 1 and vol. 2 of ref. [7]). The guest species can only be removed from the intracrystalline cavities by destruction of the complex. A further characteristic feature of these systems is that the crystal structure of the host only is very often different from the structure of the host adopted in the presence of the guest species (compare Fig. **1**).

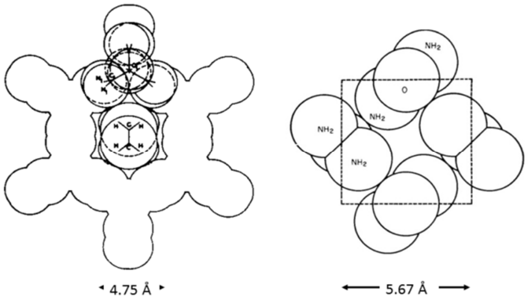

Figure 1
Structure of an urea/alkane (left) inclusion complex and the structure of the pure urea (right). Figures taken from K. Takemoto and N. Sonoda in ref. [7], vol. 2, chapt. 2, p. 47. Reproduced with permission of N. Sonoda and Elsevier (successor of Academic Press). Both figures are based on A.E. Smith, *Acta Crystallogr.* 1952, **5**, 224 (permission of the IUCr).

The term „interstitial compounds“ should be restricted to those inorganic solids, in which the additional atoms occupy empty lattice sites of the host structure with small crystal expansions. These compounds are prepared at high temperatures, and the atoms taken up in the solid are immobile at room temperature. In order to keep electrical neutrality the host lattice must have the tendency to change the oxidation state. These compounds have strong relationships to nonstoichiometric compounds (examples are the above mentioned hydrides, carbides or nitrides of the early transition metals).

In contrast to the solids forming interstitial compounds the hosts forming intercalation compounds consist of structural elements like chains and layers held together by weak van der Waals forces (i.e. graphite or the layered dichalcogenides) or they are framework structures containing channels and cavities with diameters of 3 – 11 Å (like the zeolites, the Aluminium phosphates or the mesoporous systems with larger pores[5, 8, 9]). In these compounds there are much more unoccupied lattice sites than in normal densely packed solids. Therefore the mobility of the inserted species can be very high allowing intercalation reactions at room temperature making new compounds accessible which are not stable at high temperatures. Intercalation is considered as the reversible uptake of atoms, ions, molecular cations or molecules at low temperature while the structure of the host lattices is conserved.

Whereas in the framework structures only those compounds can be taken up, which fit into the sizes of the channels or cavities, the layered or chain host lattices can expand in one or two dimensions without serious restriction. This allows the accommodation of species like large metal complexes or organic cations. Layer expansions up to 50 Å has been observed. However, in the chain structures the insertion of additional species, even if they are bulky, weakens the interaction between the chains, thus leading to an easy disintegration of the solid. In the layer compounds the two-dimensional structural elements give enough stability to prevent this disintegration, at least for moderate layer separations. This ideal combination of easy access to the interlayer galleries and the stability of the final products is the reason why layer compounds are the preferred objects for intercalation reactions and why most of the intercalation compounds are layered structures.[10-22] If the lattice expansion is not too large, the topological relationships between the host and the final products are almost retained, meaning that the stacking variant of the starting material is not changed by the intercalation process. These strong crystallographic relations led Schöllhorn to the statement, that intercalation reactions are topotactic solid state reactions.[23]

This paper is a very personal view on intercalation chemistry in layered host lattices strongly coloured by the experience collected during education and own scientific work mostly in collaboration with physicists. After a sketchy description of the historical development of the field some special topics will be discussed in greater details. Some of the topics chosen were in the limelight and earned a lot of attention in special time windows. This is the case for the interplay of charge density waves/superconductivity of layered dichalcogenides or the electrochemical intercalation and its importance for the construction of reloadable batteries, others had value in the development of the field of intercalation compounds or would have deserved more attention by the community. Today intercalation is just a preparative tool to construct new artificial nanocomposites.

Historical remarks

Already in 1841 Schafhäutl[24] observed the swelling of graphite in concentrated sulfuric acid and slightly later Way[25] and Thomson[26] the ion exchange properties of clays. In 1855 Brodie[27] described the preparation of graphite oxide (GO) and 1896 Hofmann[28] the layered nickel cyanides. Now we can sum up these events under the headline of intercalation chemistry, but at the time of the authors the nature and structure of these observations and the new compounds could not be clarified. Already within 20 years after the development of technical equipment for X-Ray Diffraction (XRD) the structure of the H_2SO_4/graphite compound[29] and the alkali metal/graphite compound[30] and the clay mineral concept[20] were clearly established.

At this place the essential contributions of U. Hofmann in the development of intercalation chemistry have to be honoured (photo of him, Fig. 2). He did not only determine the structure of the graphite sulphuric acid intercalation compound (together with his Ph.D. student W. Rüdorff), but gave also essential contributions to the understanding of graphite oxide properties.[31] He and his co-workers described the phenomenon of osmotic swelling in graphite oxide and in montmorillonite, the staging in the graphite sulphuric acid compounds, the phenomenon of interstratification in the hydration of clay minerals, the Hofmann-Klemen effect (the transition of lithium ions in the empty lattice sites of the octahedral layer in dioctahedral 1:2 clay minerals; structures of both types of clay minerals are sketched in Fig. **3**) to mention just a few of his contributions. He also made essential discoveries of value for the industrial application of clay minerals (i.e. an explanation for the plasticity of clay minerals and the structural model of the house of card structures in clay gels). More information about the scientific work of U. Hofmann is given by Beneke and Lagaly.[32]

Figure 2

Ulrich Hofmann (1903 – 1986).[32] Foto reproduced with pemission of K. Beneke.[32]

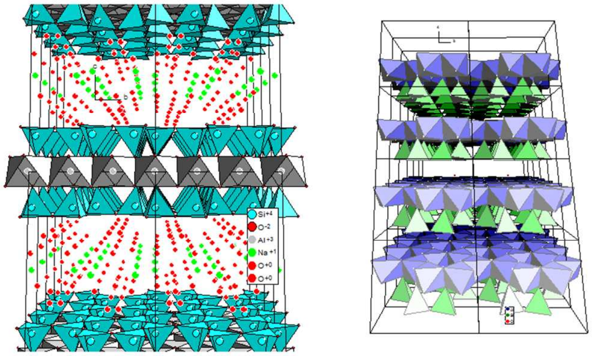

Figure 3

Perspective view of the structure of a 2:1 clay mineral (left) and a 1:1 clay mineral. View done with DIAMOND - Visual Information system for crystal structures. Prof. Dr. G. Bergerhoff, Gerhard-Domagk-Str. 1, 53121 Bonn. First published in ref. [38]. Reproduced with kind permission of Elsevier.

Hofmann was one of the few scientists who worked in both fields: clay chemistry and graphite intercalation. Both fields developed strongly after the 2nd world war. The overwhelming amount of information on clay chemistry has been reviewed thoroughly by Grim.[20] Starting from the early work on graphite intercalation chemistry in the 1930ties Rüdorff, Herold, Croft, Henning and Ubbelohde extended the number of species to be intercalated into graphite. The most important ones are: bromine, interhalogene compounds, fluorine and main group metal and transition metal halides.[2, 3, 33, 34] Due to the strong development in both fields after the 2nd world war no scientist was able to cope with the flood of publications in both fields. Therefore, two communities evolve which have almost no overlap in interests. This may be at least in part due to the fact that both classes of materials have very different chemical properties (see Table 1) at least in the first glance.

Table 1
Comparison of the properties of clay minerals and graphite intercalation compounds

Clay chemistry	Graphite intercalation chemistry
➢ Heterogeneity of the cation distribution in the clay sheets	➢ Homogeneity of the C-layers
➢ Electronic insulators	➢ Electronic conductors
➢ Ion exchange dominant reaction	➢ Redox reactions
➢ Swelling with water	➢ Positively and negatively charged carbon layers
➢ Uptake of other solvents	➢ Highly sensitive to oxygen and water (deintercalation)
➢ Influence of the layer charge	➢ staging
➢ interstratification	

Since the clay minerals are natural compounds which are ubiquitous in many environmental compartments they are of importance in geological processes and in the structure and properties of soils and they are easily accessible and cheap resources which found a lot of low tech applications in the everyday life.[20, 35] Therefore, mainly mineralogists, geologists, soil scientists and industrial chemists are working in this field. To the contrary graphite intercalation compounds (GICs) are laboratory products with unusual physical properties due to the anisotropic structure. Many other intercalation compounds are also laboratory products and found therefore more interest among chemists and physicists. The division can be seen in the organization of meetings: one has the big clay minerals conferences and the much smaller ones for the other intercalation compounds. Very rarely you find clay scientists in the intercalation conferences and vice versa.

Soon after the 2nd world war new host lattices and new types of intercalation compounds have been discovered. This development started very slowly with the observation of Mac Ewan[36] that water in halloysite can be replaced by other solvents, has been reviewed selectively by Barrer[5] in 1964 and reached its peak around 1975. An overview of essential discoveries is given in Table **2** (The structure of the some of the host lattices mentioned in the table are shown in Fig. **4**).The greatest push obtained the field of intercalation chemistry by the interest of solid state physicists on the physical properties (conductivity, superconductivity, magnetism) of the highly anisotropic compounds which can be easily modified by the type of intercalated species. This interest was triggered by the outstanding review of Wilson and Yoffe on the layered transition metal dichalcogenides.[37]

Table **2**
The early invention of new intercalation processes and the discovery of new host lattices for intercalation. A more detailed time table of highlights in intercalation chemistry is given in ref.[38]

1957	Weiss et al.[39]	Amines in uranium micas
1959	Rüdorff and Sick[40]	Alkali metals in MoS_2 and WS_2 (from liquid NH_3), later on in TiS_2, ZrS_2, TaS_2 and NbS_2 (Rouxel, Jellinek, Wiegers, after
1959	Wada[41]	1967)[18]
1960	Weiss and Weiss[42]	alkali acetates in halloysite
1961	Weiss[43]; Wada[44]	alkylammonium ions in $Na_2Ti_2O_5$
1962	Hagenmuller et al.[45]	uptake of urea in kaolinite; K-acetate in kaolinite
1965/67	Michel and Weiss[46]	intercalation of ammonia in FeOCl, later on Herber and others[10]
		amines in Zr-Phosphate, later on Lagaly, Yamanaka, Alberti and
1968	Weiss and Ruthardt[47]	Costantino[10]
1976	Yamanaka et al.[48]	N_2H_4, NH_3, organic molecules in TiS_2
		Amines in MPS_3 (M = Mg, Mn, Zn)[10]

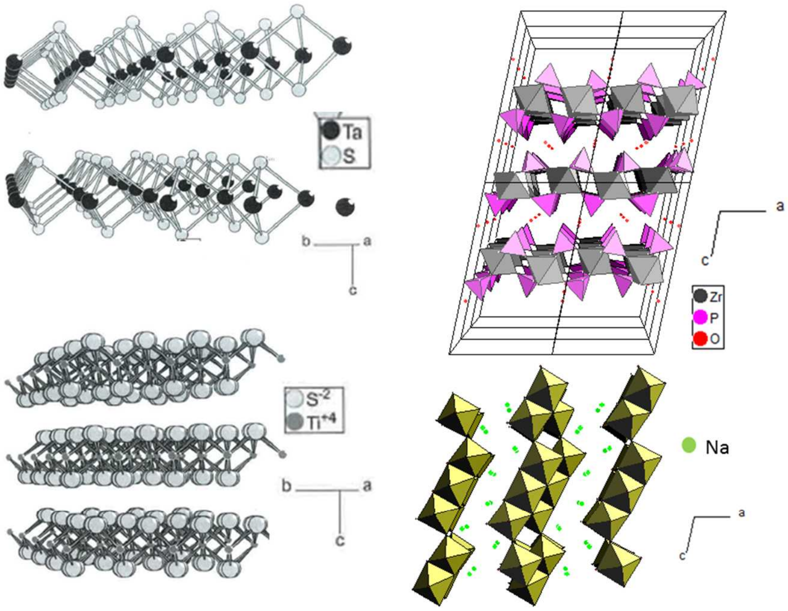

Figure 4

Perspective view of the structure of 2H-TaS_2 (left, top), TiS_2 (left, bottom, α-Zirconiumphosphate (right, top) and a layered titanate (right, bottom). View done with DIAMOND - Visual Information system for crystal structures. Prof. Dr. G. Bergerhoff, Gerhard-Domagk-Str. 1, 53121 Bonn.. First published in ref. [38]. Reproduced with kind permission of Elsevier.

Topics in intercalation chemistry

The main topics in intercalation chemistry after 1970 which shall be discussed here are the superconducting properties and the interplay with charge density formation in 2H-TaS_2 and its intercalation compounds, the anisotropic physical properties of the graphite intercalation compounds, and the electrochemical intercalation with the aim of searching for new battery electrodes.

Intercalation compounds of dichalcogenides and their superconducting properties

The starting point of this field was the discovery of Gamble et al. [49, 50] that intercalation of molecules like ammonia or pyridine leads to an increase of the transition temperature to the superconducting state (T_c) from 0.8 K for the pure 2H-TaS_2 to about 4 K for the intercalation compounds. This discovery has an interesting prehistory: Gamble and his coworkers triggered by the hypothesis of the excitonic superconductivity searched for T_c enhancement in metals by adsorption of aromatic molecules. [51] The result of these investigations was disappointing and the authors considered as a limiting factor the experimentally achievable surface area of the metals. At this point Weiss and Ruthardt‘s compounds gave the opportunity to use the huge intracrystalline surfaces of a solid. The enormous T_c enhancement seems to confirm the conclusion, but it was clear very soon that this effect is a consequence of the charge density wave suppression by the electron transfer accompanied with intercalation, and that the dichalcogenide intercalation compounds are normal BCS-superconductors (BCS stands for Bardeen, Cooper and Shriver, who gave an explanation of the superconducting state by formation of so-called Cooper pairs occupying as bosons one quantum state), but with a strong anisotropy.

The invention of the molecule intercalation into the layered dichalcogenides and the struggle about the chemical nature of these compounds is an interesting story shading some light on the question how science proceeds. The intercalation of the same molecules in TiS_2 which have been intercalated before in kaolinite brought Weiss to the conclusion that the breakup of weak interactions between the host layers (O-H-O hydrogen bonds in kaolinite, van der Waals bonds between the MS_2 layers) is the essential cause of intercalation. Gamble et al. extended the number of species intercalated in layered MS_2 compounds. Since most of these molecules were amines or N-heterocycles these authors assumed that Lewis acid base interaction between the lone electron pairs of the N-containing molecules and the metal atoms as electron pair acceptors is the driving force for the formation of the intercalation compounds. In that case one would expect that the lone pairs of the nitrogen atoms are oriented perpendicular to the dichalcogenide layers to minimize the distance between the N atoms and the metal sites within the dichalcogenide layers. However, the C_3 axis of the ammonia molecules [52] and the C_2 axis of pyridine (through the line N-C4; molecular plane perpendicular to the MX_2 layers) [53] are oriented parallel to the dichalcogenide layers showing maximum distance between the N atoms and the metal atoms! The solution of the puzzle is that these two compounds are in reality ternary systems of the composition $(NH_4^+)_{0.33}(NH_3)_{0.66}MS_2$ [54] and $(pyH^+)_x(py)_{0.5-x}MS_2$ [55], in which ammonium and pyridinium ions compensating the negatively charged dichalcogenide layers are solvated by free ammonia and pyridine. Thus, the intercalation must be driven by redox reactions as in the alkali metal intercalation of the dichalcogenides. Although confirmed by publications of other authors [56, 57] this result was not generally accepted in the community.[58] The problem is the following: if one offends a generally accepted explanation, he has to demonstrate the new mechanism for any type of known compounds; in case of the molecule intercalation compounds this would afford a lot of effort. Nobody will do that, because it is a tedious and time consuming business resulting in small scientific merits. Summing up this story leads on to the following lesson: wrong ideas may lead to an expected result and can therefore survive very long.

The discovery of superconductivity in the molecular ion intercalation compounds triggered the search for superconductivity in the alkali metal intercalation compounds of other dichalcogenides. This search was successful first in case of the alkali metal intercalation of MoS_2 [59], later on in the alkali compounds of other dichalcogenides (Zr, Hf, Nb, Ta).[58,60] Careful hydrolysis of the compounds A_xMS_2 (M = Ti, Zr, Ta, Nb, Mo, W, A = alkali metals) leads to the hydrated compounds $A_x(H_2O)_yMS_2$ showing different degrees of hydration depending on the water vapor pressure in the surrounding, ion exchange reactions and exchange of water by other solvents [61, 62]; that means they show similar properties as the 2:1 clay minerals with low to medium layer charges (e.g. the vermiculites). It is not surprising that these reactions have been discovered in the laboratory of Armin Weiss, where there was experience with the ion exchange and hydration behavior of clay minerals.

The hydrated alkali metal intercalation compounds are also superconducting, and especially metal compounds $A_{0.33/v}(H_2O)_y[TaS_2]^{0.33-}$ (2H stacking as in the starting material; v = valence of the cation) with a charge transfer n = 0.33, A = Na, K, La in the fully hydrated state show the highest T_c values found for the 2H-TaS_2 intercalation compounds (see Fig. **5**).[65] Deviation of the charge transfer from the ideal value n = 0.33, reduction of water content and other cations than those mentioned in the figure lead to a decrease in T_c. Neither the influence of the charge and the size of the cations nor the influence of water have found an explanation up to now. Here, a surprising curiosity has to be mentioned: in 2003 Takada et al. published an almost similar variation of T_c with charge transfer for the layer compound $Na_x(H_2O)_yCoO_2$ with a maximum in T_c (4.3 K) for x ~ 0.3 [66], where Co occupies octahedral holes between densely packed oxygen layers (brucite like arrangement)

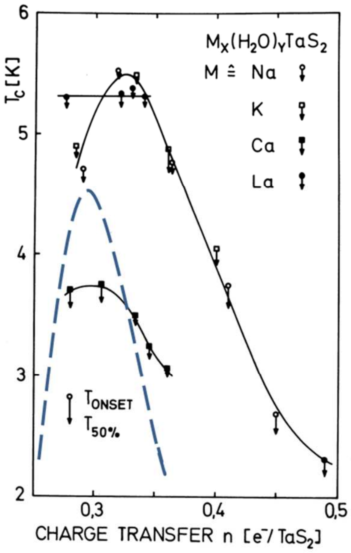

Figure 5

Transition temperatures to the superconducting state as function of charge transfer n (intercalate concentration x) for $A_x(H_2O)_yTaS_2$ containing different caions (taken from ref. [63]). The dashed parabola shows the T_c vs. x for $Na_x(H_2O)_yCoO_2$ (data taken from ref. [64]).The original figure is reproduced with kind permission of Springer.

To get more insight in the factors determining the T_c-values of the TaS_2 intercalation compounds we have measured the specific heat of some samples with different intercalated species as function of temperature down to 2 K.[65] From these data one can deduce the γ-term which is proportional to the density of states in the conduction band and the β-term which allows to determine the Debye-temperature Θ_D giving information about the phonon spectrum of the compounds (Table 3). The γ-values vary only in a small range without any correlation with the charge transfer to the TaS_2 conduction band. The Debye temperatures correlate roughly with the layer distance of the intercalation compounds: it is highest for the empty host; it drops down to 180 K for samples with a layer distance of ~9 Å and shows the lowest value for the highest layer distance of 12 Å for the pyridine intercalation compound.

Table 3

Specific heat data for various 2H-TaS_2 intercalation compounds taken from ref. [65] (dmpy = 2,6-dimethylpyridine, py = pyridine, MB = methylene blue)

Compounds	d [Å]	T_c [K]	γ [mJ/molK^2]	β [mJ/molK^4]	Θ_D[K]
2H-TaS_2	7.05	0.8	8.9	0.37	236
$(dmpy)_{0.2}TaS_2$	9.6	2.8	9.5	1.65	152
$(collidine)_{0.17}TaS_2$	9.7	3.2	9.5	1.65	152
$(py)_{0.5}TaS_2$	11.8	3.3	9.1	2.32	136
		3.7	8.9	2.07	141
$K_{0.33}TaS_2$	8.2	3.9	8.7	0.99	180
$MB_{0.07}$ TaS_2	9.1	5.2	8.9	0.95	184

Schlicht et al. could show that there is a linear relationship between T_c and a corrected Debye temperature Θ_D^{corr} (Fig. 6);[65] the correction parameter is $\sqrt{M_{ic}d_{ic}/M_0d_0}$ with M_{ic} the formula mass and d_{ic} the layer distance of the intercalation compound, M_0 the formula mass and d_0 the layer distance of the pure host 2H-TaS_2. This can be considered as an indication that the phonon spectrum is essential for the differences in the T_c values. In case of the hydrated sodium Co-oxide the superconducting properties are explained by means of electronic states only.[64, 66] In the light of our specific heat data for the TaS_2 compounds, the authors may miss an important point. In conclusion we are left behind with interesting results and open questions, but with only a small chance to catch the interest of theoreticians, because they are now more interested in high T_c superconductors like the layered iron arsenides[67] with very similar structures as our compounds.

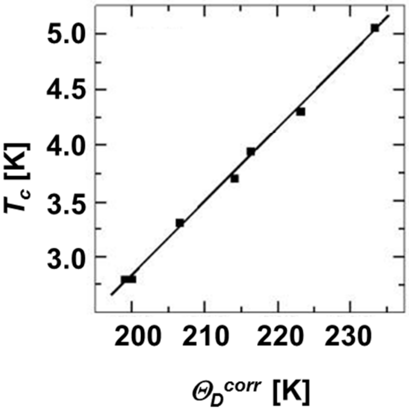

Figure 6

Superconducting transition temperature T_c as function of the corrected Debye temperature Θ_D^{corr}; modified from ref. [65]. The original figure is reproduced with permission of the American Chemical Society.

The graphite intercalation compounds

The second boom in the research of graphite intercalation compounds started with the discovery of extremely high metallic conductivity in C_xAsF_6 by Vogel in 1976[68] (later uncovered as an experimental fault) and lasts till the invention of fullerenes and carbon nanotubes at the end of the 80ties. The topics treated in this period of time are excellently reviewed by Zabel and Solin. [69] Here only the most important ones shall be listed:

- Structural properties and phase transitions (stage disorder, intercalate correlations in the liquid state, 2d melting processes of the intercalate, modulated 2d liquids, phase transitions and ordered state, intercalate diffusion)
- Transport properties and magnetic ordering phenomena in metal halide intercalation compounds (2d magnets)
- Lattice dynamics
- Staging transitions and their kinetics
- New ternary intercalation compounds [70, 71]: among these are solvated alkali metal GICs which have taken up ammonia (these compounds have been described already in

the 1950ies [2]) or other polar solvents (stable against reduction) like for the layered dichalcogenides. Unique are the ternary compounds which contain aromatic hydrocarbons beside the alkali metals; these compounds can be understood if one takes into account that the electrons of the alkali metals in the graphite interlayers are kept near by the metals and are only partially transferred to the graphite conduction band; thus they behave more like free alkali metals and not as cations as in case of the dichalcogenide intercalation compounds. In addition the alkali metal GIC can take up additionally other main group elements like Bi or Hg, Tl. Apart from these metals also hydrogen can be inserted in the alkali metal GICs.

- These ternary GICs of the type $C_{4n}AM_x$ (n = here stage number; A = K, Rb, Cs; M = Hg, Bi, Tl) show superconducting properties [72]: the T_c values are higher than in the alkali metal GICs (<200 mK) but do not exceed 4 K; the superconducting properties are mainly determined by the electronic properties of intermetallic phases in the interlayer space.

Here, it is interesting to compare the T_c values of the K-GIC and K-carbon compounds K_3C_{60} and K-picene ($K_xC_{22}H_{14}$) prepared recently by the same method as K-GIC. Whereas the first becomes superconducting below 100 mK [72, 73] the other are superconductors with T_c-values of 16 K [74] and 18 K [75], respectively. The picene potassium compound is the first example of a polyaromatic hydrocarbon (PAH)/donor complex showing metallic/superconducting properties.[74] Its T_c-value is the highest for an organic superconductor. Within a period of two years other PAH/K compounds with superconducting properties have been described.[75] The potassium PAH salts as well as the potassium fulleride are BCS superconductors showing a strong electron phonon coupling, and this could be the most important difference to the potassium GIC.[74, 76]

It is worth mentioning also, that in 2005 the long known intercalation compounds C_6Yb and C_6Ca have been found to be superconducting with T_c values of 6.5 and 11.5 K, respectively.[77, 78] These T_c-values are the highest observed for GICs up to now.

Graphite oxide (GO) and graphite fluoride are peculiar GICs, because the oxidant oxygen and fluorine are covalently attached to the carbon grid.[2, 3] GO has been known for more than 150 years and its unusual chemical properties are known since the work of U. Hofmann and his students.[31] It was always a curiosity in solid state chemistry[79] till the discovery of Geim and Novoselov[80] that isolated single layers of graphene show metallic conductivity. This suddenly awoken attention is mainly due to the fact that GO can be reduced easily to graphite, and thus this property seems to pave the way for a cheap access to large quantities of single graphene layers. The covalently attached oxygen is changes the surface properties from hydrophobic to hydrophilic determining the chemical properties of GO, c.f. the tendency for osmotic swelling till a colloidal suspension is formed. The number of publications on GO increases so dramatically, that it is impossible to cope with them (good impression of the state of the discussion is given in Dreyer et al.[81]) However, despite a lot of effort the structure of GO is still not fully resolved. The mostly accepted model is a modification of Hofmann's first structural model containing alcohol functions beside epoxide functions and islands of unreacted graphite.[82] GO is not a stoichiometric compound. Though, the ratio of the different functional groups may vary with the method of preparation, the exact conditions of preparation and the workup of the samples. Up to now the mechanism of oxidation is not clear: are the epoxides formed first and then hydrolysed by water during workup or are vicinal OH functions formed first and then transferred to epoxides by the highly concentrated sulphuric acid? What is clear is that the first step of GO formation is the formation of the sulphuric acid/nitric acid intercalation compound. However, it seems to be an idealisation that always a pure 1st GIC is reached. Hence, not all interlayer spaces are accessible for the oxidant, thus preventing the formation of pure single layer colloidal dispersions.

Since the evidence is growing that graphite oxide is a highly dynamic system which changes continuously (see for example the paper of Dimiev et al. [83] and the references cited therein) one should not discard one of the different structural models of GO proposed through the last 100 years. One cannot rule out that they could be of importance for intermediate states under the crude preparation and work up conditions or of subsequent alteration processes (Fig. **7**): for example the transition the transition from the Lerf-Klinowski GO towards a GO with structural elements of the Boehm model is easily reached by vacuum dehydration at 70 °C or by treatment with iodide.[82]

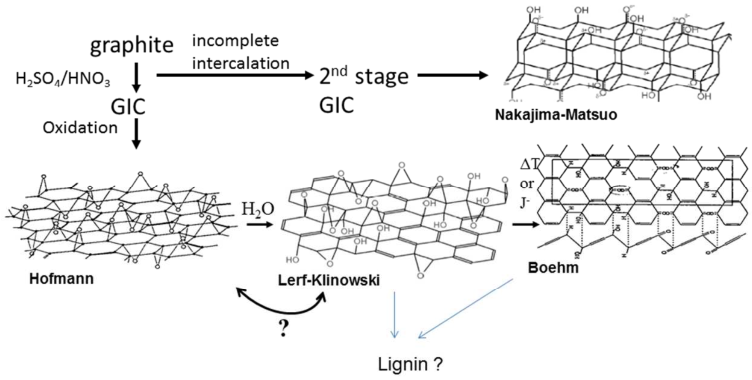

Figure 7
Tentative relations between the different structural models of GO. T. Szabo provided the schematic drawing of the structural models.

Electrointercalation

In 1974 Whittingham [84], Schöllhorn and Meyer [85] and Subba Rao and Tsang [86] found – almost simultaneously – the electrochemical intercalation of hydrated, solvated and unsolvated alkali metal ions in the layered dichalcogenides. Almost at the time Besenhard et al. described the electrochemical intercalation of solvated alkali metals in graphite (solvents were DMSO, DME (1,2-Dimenthoxyethane) and PC (propylene carbonate).[87] (an excellent review of the electrochemical properties of carbon is given in ref. [88]) It is worth noting that Rüdorff and Hoffman[30] already used electrointercalation for the preparation of the sulfuric acid intercalation of graphite, Thiele [89] used electrochemical oxidation for the formation of GO and Rüdorff [2] and Henning [3] and their coworkers for the electrochemical intercalation of alkylammonium ions from liquid ammonia and amines.

This boom in electrochemistry started soon after the 1st oil crisis in 1973 with the search for new energy sources for electrotraction, electrochemical energy storage systems and for hydrogen production via photoelectrolysis of water.[90-92] Electrochemical methods can be used for the preparation of new solid compounds and simultaneously allow insight in solid state processes. A prerequisite of these investigations is that the samples under investigation are electronic conductors. Interesting examples of the preparation of new compounds are the just mentioned electrointercalation processes [84-89] or the synthesis of organic metals (e.g. the PAH salts, the Tetramethyltetraselenafulvalene salts (the so-called Bechgaard salts), the Bis-ethylenedithia-tetrathiafulvalene (ET) salts [93]) or the synthesis of conducting polymers (i. e. polyaniline, polypyrrol or polythiophene derivatives [94]). If one monitors the potential change during electrointercalation one gets insight in the progress of the reaction. This shall be demonstrated in an idealized sketch for the uptake of lithium into graphite (Fig. **8**). [95] Under galvanostatic conditions (that is under constant current; usually a few μA) one observes a sequence of constant potential plateaus and jump like transitions between them. In solid state reactions a constant potential means two-phase regions. In case of the lithium intercalation these plateaus correspond with the staging transitions: ≥4th/3rd, 3rd/2nd, 2nd/1st (there is a complication due to the appearance of two 2nd stage phases with different intercalate concentration). Under conditions of a potential sweep the intercalation current is highest in the two-phase regions.

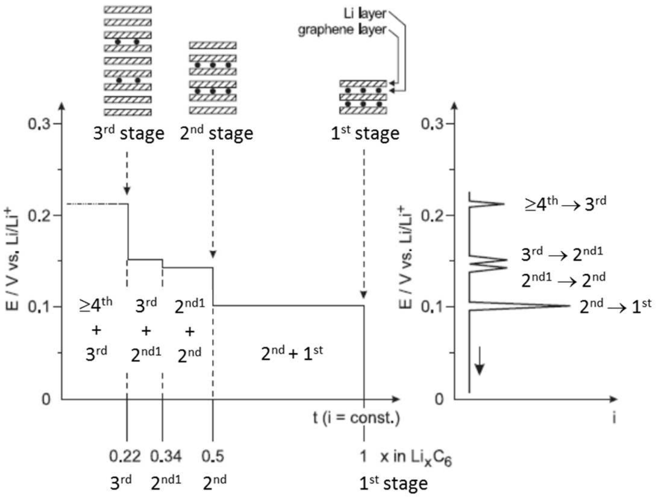

Figure 8

Stage formation during electrochemical intercalation of lithium into graphite. Left: schematic galvanostatic curve. Right: schematic voltammetric curve. Modified from ref. [95]. The original figure is reproduced with permission of Wiley-VCH.

After the discovery of electrochemical intercalation it was immediately clear that solids taking up ions could be used as battery electrodes. Forthcoming investigations uncover classical battery electrodes as intercalation electrodes (mostly of protons) and within a few years many electronic conductors with empty sites have been found to take up ions easily.[90] These investigations were mainly restricted to the uptake of Li^+. It is the smallest and lightest metal ion and should therefore be the most mobile ion. One important byproduct of these studies was the observation that in high power density systems H^+ or Li^+ are inserted/depleted in both electrodes. Although the first prototypes of rechargeable batteries with layered dichalcogenides (TiS_2 and MoS_2 because of power density) looked promising, modern high density batteries use Li-graphite (instead of Li metal) as cathode and Li_xCoO_2 (structure visualized in Fig. **9**) as the counter electrode.[95-97] This combination of electrodes gives the highest electrochemical potential difference (~3.8 V) of such a battery and marks at present the limit for electrochemical energy sources.

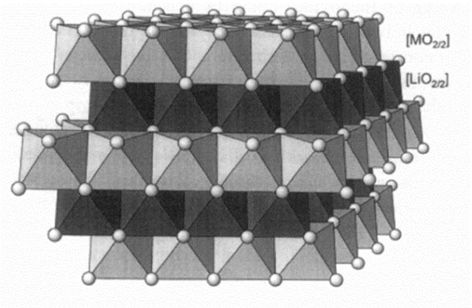

Figure 9

A perspective view of the crystal structure of $LiMO_2$ (M = Ni, Co, V, etc.; $NaFeO_2$-type).

The CoO_2^- layers have the same structure as TiS_2. Image taken from ref. [95]. Reproduced with permission of Wiley-VCH

Concepts in intercalation chemistry

Staging versus random interstratification

Both phenomena are known for a long time. Staging (regular alternation) has been described first by Rüdorff and Hoffmann[30] for the intercalation and deintercalation of sulphuric acid into graphite. Random interstratification has been observed in clay chemistry.[20, 98]

The term "staging" is used to assign the fully regular mixing of intercalated and empty interlayer spaces. 1st, 2nd and 3rd stage means intercalation in any interlayer gap, in any second and in any third gap. This phenomenon occurs commonly in GICs. In such regular mixing there is only one series of integral *00l* reflections. For a metal intercalation compound shown schematically in Fig. **10** (left) one finds *00l* reflections leading to layer distances of 5.4 Å, 5.4+3.5=8.9 Å and 5.4+3.35+3.35=12.1 Å for the 1st, the 2nd and the 3rd stage, respectively. A regular alternation of two types of layers is also found in chlorite (brucite-type and 1:2 clay layers) and other mixed-layer clay minerals.[20, 98] Daumas and Hérold [99] introduced a more realistic model for staging (Fig. **10**, right), which allows to explain the transition in a sequence of stages from 3rd → 2nd → 1st occurring in the course of an intercalation process with increasing intercalate content (c.f. lithium intercalation in Fig. **8**). The Daumas-Hérold type staging, staging transitions and the relation to the intercalation process has been investigated thoroughly in the 80ties mainly by Kirczenow and his coworkers.[100]

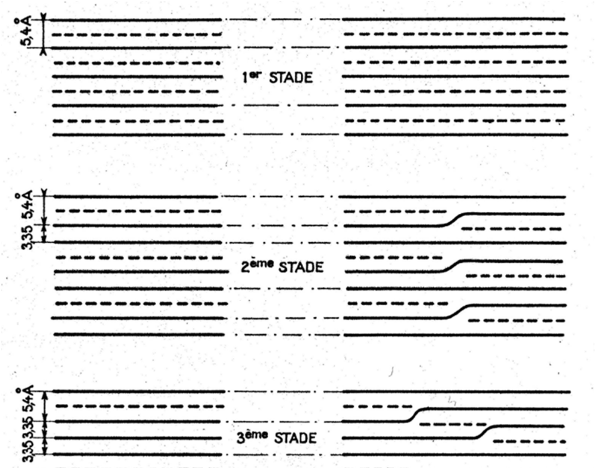

Figure 10

Comparison of the idealized view (modèle classique, left) of various stage phases for a metal GIC with the sketch of the realistic model (showing the Daumas-Hérold-type defects (modèle propose, right). Figure taken from ref. [99] with kind permission of the French academy of Sciences

The other extreme case is a fully random sequence of intercalated and non-intercalated interlayer spaces or two different states of intercalation (c.f. hydrate phases with one or two densely packed water layers). In that case there is a series of *00l* peaks which are not normal Bragg reflections and the higher order reflections are non-integral (called also irrational). The peak position shifts continuously between the two values of layer distances depending on the fractions of both types of layers. These peaks can be rather sharp, but normally they are broader and have lost some intensity. In addition the stacking order is almost lost, thus there are no *hkl* reflections. If one of both layer types is dominating it is hard to decide when the minority component (i.e. empty interlayer gaps) is gone completely. Therefore, it can be rather difficult to determine the point of full intercalation in any interlayer space. The phenomenon has been discovered in clay minerals in the 1930ties. [20, 98] The first theoretical analysis of the consequences of interstratification for XRD has been carried out by Hendricks and Teller. [101] In the meantime various routines have been developed to analyse XRD patterns of interstratified samples. [98] The most recent one by Lanson. [102] If there is some sort of an ordering the interstratification is not random and two *00l* series will appear changing their intensity depending on the ratio of both types of layer spacing. That interstratification phenomena play a role in intercalation processeshave been discovered for the first time at about 1940 by Hendricks and Jefferson [103] and Hofmann and Hausdorf [104] in the hydration behaviour of montmorillonites.Interstratification can nicely be visualized in high-resolution electron microscopic images, if the samples have been expanded with octadecylammonium ions (Fig. **11**).[105] The expanded samples are embedded in a resin and cut perpendicular the clay platelets. Thus, the view shown is parallel to the layers. This is the best real space representation of inhomogeneous intercalate distribution.

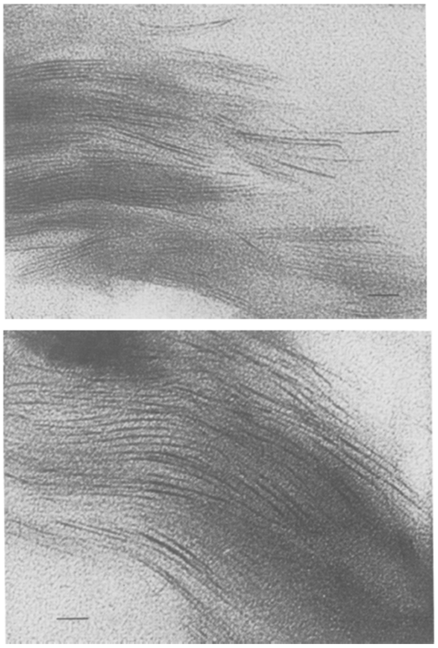

Figure 11
High reslotion electron microscopic images of solvent and octadecylammonium ions into a montmorillonite. Images taken from Vali and Köster [105] . Reproduced with the kind permission of the Mineralogical Society of Great Britain & Ireland.

Interstratification and intercalation mechanism

Compared with the number of publications on intercalation compounds the number of papers devoted to intercalation mechanisms is rather limited. These papers are concerned with many different intercalation/host systems and the investigations have been carried out with a lot of different methods. However, it is very difficult to figure out how these results are related.

Since the monitoring of the potential of the electrode during electrointercalation allows some insight in the reaction progress one example shall be discussed here in detail: the intercalation of hydrated potassium in 2H-TaS_2 which can be carried out in large single crystals. Simultaneous monitoring of crystal expansion during the electrointercalation enhances the amount of information on the reaction process gained in a single experiment. The potential change and the simultaneous crystal expansion in the course of the reaction are shown in fig. **12**, left.[63, 106]

As in the case of the lithium intercalation into graphite (see Fig. **8**) the reaction starts with a two-phase region followed by a single phase region (not observed in case of Li/graphite) in which the potential changes continuously. This single phase region starts at n = 0.27 and is limited at about n ~ 0.45 since the potential for water decomposition is reached. Below n = 0.27 there are two two-phase regions. The transition between both regions is at n = 0.27/2. Shortly before this charge transfer is reached the potential starts to deviate from its constant value . In contrast to a single phase region the potential drifts to less negative values immediately when the current is switched off, indicating deviation from equilibrium. Changing from reduction to oxidation the hydrated potassium is deintercalated near to the empty 2H-TaS_2.

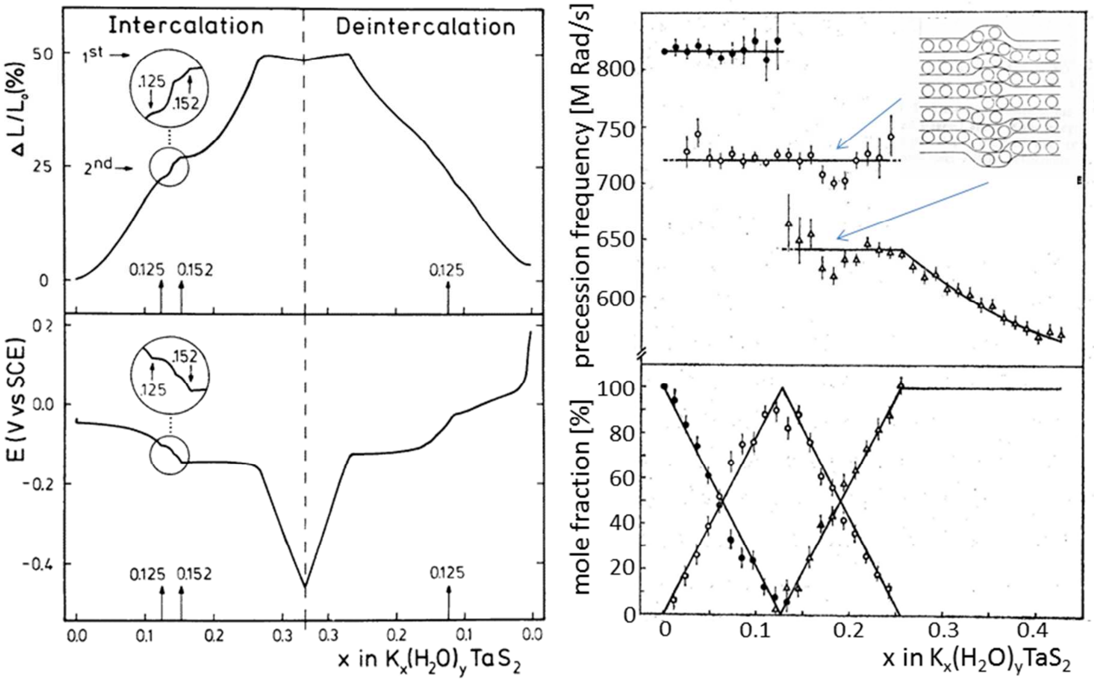

Figure 12

Electrochemical intercalation of hydrated potassium ions in 2H-TaS_2. Left: part of the figure shows the electrochemical potential E and crystal expansion $\Delta L/L_0$ vs. intercalate content x (taken from ref. [636] ; reproduced with permission of Springer). Right: quadrupole precession frequency <ω> at ^{181}Ta and mole fraction as function of x (modified from ref. [107]). (SCE standard calomel electrode). The original verson this figure is used with kind permission of Elsevier

According to the in-situ dilatometry the onset of the single phase region coincides exactly with the point where the maximum crystal expansion is reached. Hence, one can safely conclude that the crystal has a uniform thickness at this point. To zeroth order, the crystal expands linearly up to their maximum value at the onset of the single phase 1st-stage compound. [63, 106] Hence, the crystal has a uniform thickness throughout the entire intercalation process. This means that no coherent intercalation front builds up. Otherwise one would expect a biconcave or "ashtray" thickness profile and, consequently, an over-proportional response of the dilatometer. Such a situation occurs if the in-plane growth of a nucleus is fast compared to that perpendicular to the layers and also fast compared to the formation of new nuclei.

In the potential as well as in the dilatometer record three sharp kinks occur at x = 0.125, 0.141, and 0.152 in the vicinity of half of the maximum crystal expansion. The average of these values is roughly x = 0.27/2. Hence, all three kinks occur during the formation of the 2nd stage phase as confirmed by XRD data. The potassium concentration of the intercalated layers is identical with that of the lower limit of the 1st-stage phase. Thus, there is a fixed packing density x = n = 0.27 throughout the whole two-phase region. Consequently, domains with fixed packing density must have been formed at the prism surface of the crystals from the beginning of the reaction.

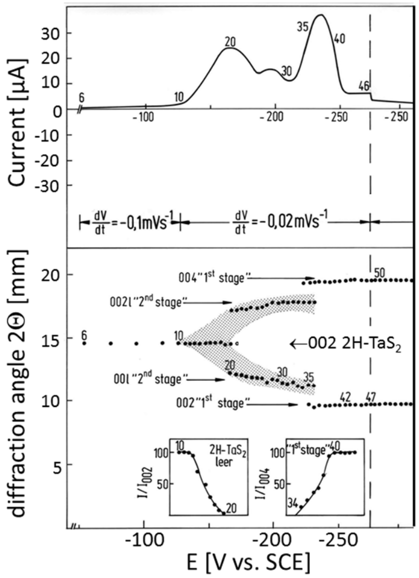

Figure 13

XRD data collected in-situ during electrochemical intercalation (under voltametric conditions) of hydrated potassium ions into 2H-TaS$_2$. Top: current vs. potential E; bottom: diffraction angles vs. E; black dots: position of the maximum of the XRD peaks; grey: area of severe line broadening; numbers: spectra run; inserts: intensity variation of the peaks of 2H-TaS2 and the final product $K_x(H_2O)_yTaS_2$. (A. Lerf, habilitation thesis 1991, unpublished).

Since the kinks mentioned before vary in different runs with different crystals from different batches and because of the potential drift in switch off state in that range of x, these features can be assigned to kinetic hindrances at the transition from the 2nd to the 1st stage compound due to the Daumas-Hérold type defects. The small size and the stacking disorder of the Daumas-Hérold regions clearly show up in the very broad XRD peaks (Fig. **13**) and in unusually large widths for the superconducting transition temperature ($\Delta T_c \sim$ 1-2 K for the two-phase regions compared to $\Delta T_c = 0.1$ K for the single phase region [63]) The *00l* reflections assigned to the 2nd-stage phase has no fixed value but shifts continuously towards its final value in the whole range of its appearance (Fig. **13**) indicating random interstratification phenomena in the beginning of the intercalation reaction.

In the existence range of the 2nd-stage phase there is a plateau in the dilatometer record followed by an over-proportional expansion. This means very likely that intercalate packing density increases. Such temporary intercalate concentration pile-ups are likely to occur as a consequence of surmounting the Daumas Herold type defects. By means of time differential perturbed γ-γ-angular correlation (TDPAC) we could show this concentration pile-up in the following way: the nuclear quadrupole precession frequency $<\omega>$ at the probe atom ^{181}Ta decreases continuously with increasing charge transfer from ~820 MRad/s for the empty host lattice 2H-TaS_2 to ~360 MRad/s for $LiTaS_2$; thus, the minimum of $<\omega>$ in both phases at the transition from the 2nd- to the 1st-stage phase indicates a momentary increase of the intercalate concentration in both phases (Fig. **12**, right).[107]

The constancy of $<\omega>$ for the 2nd- and the 1st-stage phase is an additional proof for the statement, that the packing density in the two-phase regions remains constant. It should be mentioned also, that the mole fraction of the empty host lattice becomes exactly zero when the 2nd phase reaches its maximum content; and as expected its amount is zero when the pure 1st-stage (x = 0.27) is obtained. To the contrary the *002* peak of the empty host lattice (see insert in Fig. 13) disappeared when its amount in the TDPAC experiment has been decreased to about 50%. Thus, the intensity of XRD peaks cannot be used to determine the mole fraction of educts or products when the reaction is dominated by the appearance of interstratification.

An in-situ dilatometer record during electrochemical intercalation of sulfuric acid into graphite shows similar results as observed for the $K_x(H_2O)_yTaS_2$:[106] there is again a fixed packing density x = 0.042 for the clearly resolved 3rd-, the 2nd and the 1st-stage phases; again the crystals have a uniform thickness throughout the entire intercalation process and, consequently, the in-plane growth of a nucleus is fast compared to that perpendicular to the layers and also fast compared to the formation of new nuclei. The difference to the $K_x(H_2O)_yTaS_2$ is the better pronounced staging behaviour and the lower density of stacking defects as confirmed by a XRD investigation.[88] Again for the 3rd stage and higher stages there is a shift of the XRD peak indicating interstratification for low uptake of sulphuric acid.[88] Thus, a constant packing density, a fast in-plane growth of a nucleus compared to the formation of new nuclei, and the tendency for random interstratification seem to be closely related.

A sequence of two-phase regions associated with the transition from 3rd → 2nd → 1st (also constant packing densities) is also observed for the lithium intercalation into graphite (Fig. **8**).[95] The Li-graphite intercalation has been analysed theoretically by Kirczenow[100] and the model proposed can be transferred very probably to the other cases described before.

A fixed packing density, intermediate phases and interstratification seem to be realized also in case of the reductive intercalation of hydrated sodium ions into $VOPO_4$ [108] and for the intercalation of some carboxylic acids in LDHs[109].

In other cases a direct transformation of the host to the intercalation compound without intermediate states seems to occur. This is the case for the uptake of ethanol in $VOPO_4$ [108] and some ion exchange processes in LDHs [109] containing other anions (c.f. NO_3^- instead of Br-) before reaction. Such a scenario can occur if there is a relative smooth intercalation front and if the nucleation process of intercalation and the nuclei growth perpendicular to the host layers is faster than the movement of the intercalation front. In such a case the progress of the reaction should be phase boundary controlled and, indeed, this has been found by Beneš et al. [108]. In contrast to the expectation the reactions discussed by Williams et al. are diffusion controlled.[109] Should this be a hint that these reactions are not true topotactic reactions, but instead dissolution/precipitation processes?

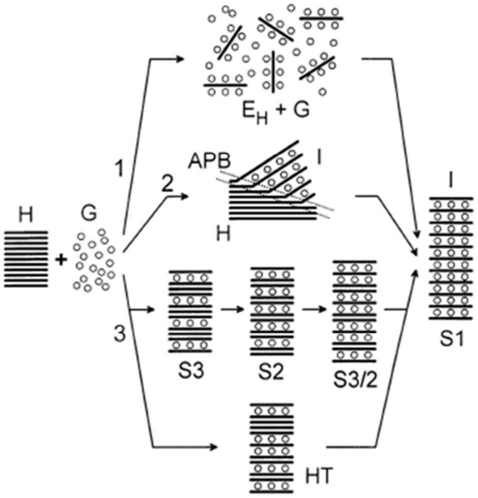

Figure 14

Schematic representations of intercalation mechanisms. Figure taken from ref.[108]. H = host, G = guest, I = intercalated phase, EH = exfoliated host layers, APB = advanced phase boundary, Sn = staging phases, HT = Hendricks-Teller disordered intercalation compound.

Beneš et al.[108] have made a classification of different intercalation mechanisms as shown in Fig. **14**. Scenario “1” shows not a true intercalation process, it is a dispersion/flocculation process typical for colloid chemical processes. The other three scenarios are in my opinion not exclusive mechanisms, but different shaping due to different host guest interactions, tendency for ordering in the intercalate, intercalate packing density and host properties. I would not be surprised if for one and the same host/guest combination a change between the three scenarios “1”, “2” and “3” would occur depending on the reaction conditions, i.e. on the supply of the intercalate and the reaction conditions (temperature, pressure). Fig. **15** shows schematic views of different possible variations of intercalation processes. These are not considered as an alternative interpretation but as a supplement to the sketch of Beneš. At the end of this chapter it should be mentioned that a conclusive interpretation of the intercalation processes cannot be obtained using just one method of investigation.

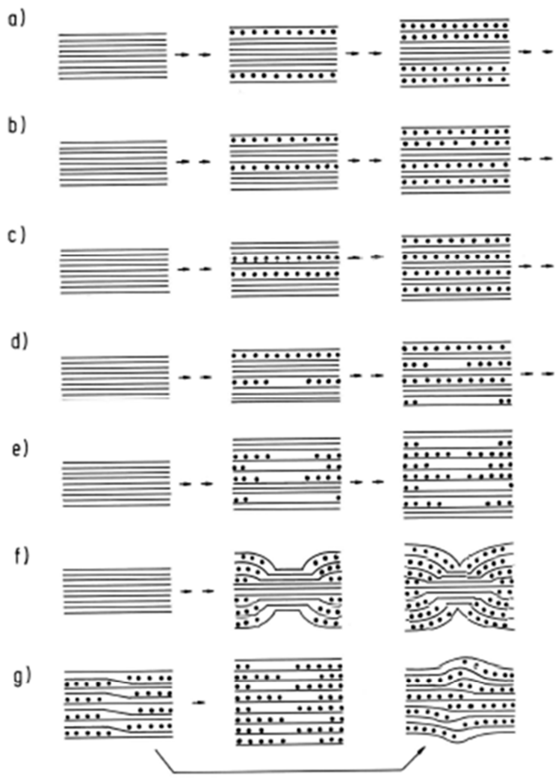

Figure 15

Schematic views of different intercalation scenarios: a-c: fast movement of the intercalate in opened interlayer galleries; intercalation layer by layer, random interstratification, staging; d, e: slowing down of intercalate movement and simultaneous opening of interlayer galleries; creation of a rough interface between intercalated and empty galleries; f: movement of the intercalate very slow; formation of a clear phase boundary and an “ashtray profile”; g: overcoming Daumas-Hérold type defects (see also the insert in Fig. **12, right)**. (A. Lerf, habilitation thesis 1991, unpublished).

Intercalate packing density, unit layer charge area and intercalate ordering

The size, the shape and the degree of free rotational motion of the intercalated species plays some role for the intercalate packing density. However, the most dominant factor is the charge distribution on the host lattice layers. It determines the number of counter-ions in the interlayer space to guarantee overall charge neutrality. In case of charged and electronically insulating host lattices – and this is the largest number of known layered host lattices – the charge distribution is fixed in the as-prepared state. There is more freedom in case of electronically conducting host lattices: first the position of the counter-ions is not directly fixed by the position of the charge on the host layers; their distribution is much more homogeneous and controlled by the symmetry of the host lattice and the electrostatic repulsion between the intercalated ions, which is to some extent reduced by the shielding due to the conduction electrons in the host layers; ion distributions which are commensurate with the host lattice structure will lead to energy minima and in principle it is possible that there are more than one arrangement with different ion densities. Such a situation is found regularly for the metal intercalation compounds of the layered dichalcogenides, where one can find superstructures with $x = 1/3, 1/2, 2/3$. [110]

The density of charges on the layers or vice versa the unit layer charge area A_{ch} determines the extent of intercalation. The determination of A_{ch} is straightforward if the chemical formula and the structure of the host lattice are known. This is the case for example for the GICs and for the intercalation compounds of the layered dichalcogenides (both cases are metallic conductors). The calculation of A_{ch} is also straightforward for electronic insulators containing two metals in different oxidation states if the metals are randomly distributed throughout the structure determining element (i.e. the LDHs). In case of the 2:1 clay minerals, in which the chemical formula cannot always be unambiguously deduced from the chemical composition, the cation exchange capacity is necessary to calculate A_{ch}. Again it is taken for granted that the metal cations in the octahedral layers and the Si and Al ions in the tetrahedral layers are distributed homogenously. Various methods have been developed to determine the unit layer charge area. [111] One of them is the intercalation of all-trans N-alkylammonium ions with varying chain length from 1 – 18 C-atoms. These molecules have a defined cross section of ~25 Å^2. If the chain length is large enough the molecules are oriented with their long axes more or less perpendicular to the clay sheets. From the total layer distances and the increase of the expansion per C-atom one can get an idea about the arrangement of the alkylammonium ions in the interlayer galleries and from that one can deduce the area available for the ammonium ions.[112] Apart from questions whether the ideal all-trans configuration is always realized, whether full intercalation is reached or domains of clustered alkylammonium ions and free space alternate, it became clear very soon that the ideal arrangement is not realized in many systems investigated and that this is related with inhomogeneous metal distributions in different layers and within the layers.[111]

Weiss has found a correlation for charged electronic insulating layered compounds between their A_{ch} and their feasibility to take up water: [113, 5] compounds with $A_{ch} < 25$ Å^2 (micas) do not swell, whereas compounds with $A_{ch} > 45$ Å can swell with sodium ions in the interlayer space to infinity forming colloidal dispersions. Apart from the classification of the hydration behaviour the A_{ch}-values give in general a hint for the ability to undergo intercalation reactions: hosts with a charge density like the micas or the LDHs show limited tendency for intercalation, whereas hosts with a high area per charge allow to uptake many different species. In case of the LDHs this statement seems to be in conflict with the overwhelming number of intercalation compounds of this class of host lattices (see the other papers in ref. [114]) unless it is taken as a hint that these compounds are probably not formed by true topotactic solid state reactions.

Intercalate packing, 3d-ordered structures in intercalation compounds, order-disorder phenomena

A_{ch} determines together with the expansion of the interlayer space L_e ($L_e = d_{ic} - d_0$; d_{ic} means the layer distance of the intercalation compound and d_0 the layer distance of the empty host lattice) the volume available for intercalated species. This volume in combination with the known dimensions of the unit cell in the host layer planes and the known (or estimated) dimensions of the intercalated species allows to get an idea about the arrangement of the intercalated species in the interlayer space. Of course, this is just an educated guess about interlayer arrangement of the intercalated species, but more cannot be done, since single crystal determinations have been possible for less than 10% of the known/possible intercalation compounds (there are 500 - 1000 species intercalated in ~30 layered host lattices resulting in a few thousand guest/host combinations). Here it should be mentioned that the most used organic molecules intercalated are the *n*-alkylammonium ions with various length of the alkylchains: They have been intercalated for the time in clay minerals in 1949; [115] later these species were the first organic intercalates applied to new host lattices.

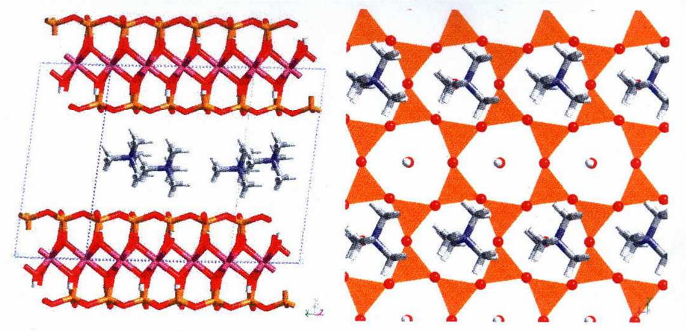

Figure 16

Simulated arrangement of tetramethylammonium ions in vermiculite. Figure used with permission of Pavla Čapkova .

Since about 20 years methods of molecular simulations allow substantial improvement of the modelling of the arrangement of intercalated species. Here, I will mention just two examples: tetramethylammonium (TMA) vermiculite [116] and of $Ru(bipy)_3^{2+}$-fluorohectorite[117]. The simulated structure of the TMA-vermiculite compound is shown in Fig. **16**. The paper of Čapkova et al. [116] led to a reinterpretation of a single crystal structure determination of Guggenheim et al..

Many intercalation compounds show in powder XRD only up to three broad peaks of *00l* and *hk0* reflections, indicating severe disorder. There are many reasons why an ordering of intercalate is not observed: high mobility of intercalated species and statistical distribution over possible atom positions, disorder due to incomplete intercalation, randomly oriented domains of ordered intercalate, inhomogeneous layer charge distribution, stacking order defects in the starting materials and so on. These phenomena are only rarely mentioned or investigated. Exceptions are some investigation on graphite intercalation compounds [69], or the kink formation and reorganisation of alkylammonium ions in clay minerals [112]. Severe disorder, lattice defects and inhomogeneous charge distribution is unambiguous for natural clay minerals leading to increased disorder in the derived intercalation compound. These problems can be overcome by synthetic clay minerals. [118] For example a synthetic Cs-tainiolite orders properly and also the intercalation compound shows three-dimensional ordering (Fig. 1**7**). This marks a revolution in clay chemistry and can be of utmost importance for high tech applications of clay minerals.

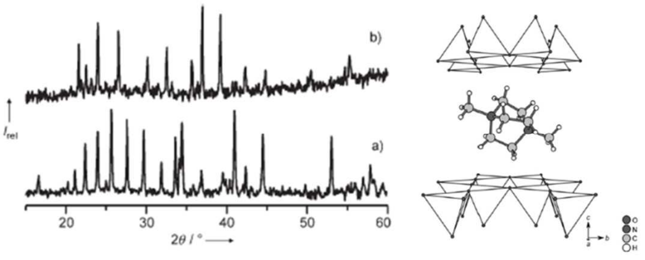

Figure 17

DABCO intercalation compound. Left: Powder XRD of synthetic Cs-tainiolite (a) and the Me_2DABCO intercalation compound (b). Right: viewgraph of the structure. Figures taken from ref.[118]. Me_2DABCO = N,N-Dimethyl-1,4-diazabicyclo[2.2.2]octane dication. Reproduced with permission of Wiley-VCH.

Outlook

If one considers the development of intercalation chemistry one can get the impression that the field is at the moment in a phase of saturation. Its phase of highest growth was in the 70ies. After a slow beginning and a phase of strong growth a slowing down of the activities followed. Such a sigmoidal curve is found normally for all open systems with clear-cut boundaries, for example innovation cycles, industrial production, economy or for the exploitation of materials resources as well (an informative discussion with respect to the resources is given by Bardi[119]). In science the situation is as follows: the pioneers (in the field of intercalation chemistry: U. Hofmann, W. Rüdorff, J. Rouxel, F. Jellinek, A. Hérold to mention just a few) follow their intuition and have to struggle for attention and to convince their surrounding; if their students keep on working in the same field, more people are working on the same field, more publications appear and the field is more visible, if spectacular results are obtained other scientist join the field, new methods are applied and give the field a strong push. After a while all obvious experiments are done and the number of new objects fitting in the field is decreasing. This leads to a slowing down of the progress. At the end people leave the field continuously especially if other topics appear in the scene, which looks more promising. Though, scientists behave as all "normal" human beings in everyday live. There is nothing special for science as has been shown by a look at the scientific process.[120] The saturation does not exclude new activities in the field when new unexpected observations like the discovery of new superconductors among the GICs or new stimuli from outside like the discovery of graphene to the GO business give the topic of intercalation a new push.

Intercalation chemistry is recently not in the limelight of solid state chemistry and physics. This is especially true for the physical properties of the intercalation compounds, perhaps due to the moderate quality of the samples (defects and disorder increases normally by solid state reactions at room temperature or a few hundred °C). What is left after roughly 100 years of effort in intercalation chemistry?

- Clay minerals found a lot of application in technical processes (c.f. drilling fluids, adsorption materials in waste disposal sites);[121]
- Clay minerals have been used as adsorption media in the food chemistry and for cat litter (a trivial but important example for pat holders), fillers and pigments in paper, paints and lacqueur, but also and, therefore, you can find them in a lot of products of everyday life.[121]
- Intercalation chemistry elucidated the electrode reactions in high power density batteries, and triggered the search for new electrode materials.
- In the 90ies it was proposed to form new mesoporous systems by inserting thermally stable pillars in the interlayer space. Because of the tendency of these pillars to adsorb also on the external surfaces of the host lattices (mainly clays) and the inhomogeneous distribution of the pillars in the interlayer space (charge inhomogeneities) the materials showed a bimodal pore size distribution, and thus, the expectation could not be realized. The most recent investigations of Breu et al. [118, 122] may change the situation.

> Due to the perfect ordering of the divalent organic cations there are defined pores in the interlayer space. (See also the promising remarks to this paper [123]).

A recently flourishing field of activities is based on the tendency of intercalation compounds to form colloidal solutions by swelling to infinity (formation of isolated monolayers) under suitable conditions (to exfoliate). This phenomenon is long known for low charged clay minerals. [124] Many of the applications mentioned above are based on clay colloids (a most recent overview of this field is given in ref. [125]). Now many other intercalation compounds are known to undergo exfoliation: dichalcogenides[126], layered oxides (ref.[127] and literature cited therein) and others. Exfoliated inorganic layer compounds can be used for the fabrication of polymer/inorganic nanocomposites. [128] They show increased flame retardance compared with the pure polymers, reduced gas permeability. Transparent and textured films of them are useable as transparent windows in electronic equipment. [129] A prerequisite for optimized properties is the formation of isolated monolayers of the inorganic components.

Exfoliated monolayers can be further modified by covalent attachment of organic species. This has been demonstrated recently for layered silicates by Takahashi und Kuroda [130] (it should be mentioned that the covalent attachment to layers has been called earlier “grafting”; this phenomenon has been shown for the first time for $FeOCH_3$ [131], and for clay minerals [132])). The exfoliated systems can also be used for the fabrication of complex artificial layer structures (partially by layer by layer deposition) with new functionalities (i.e. artificial photoelectrochemical devices, or for optical applications, the beginning of these developments have been reviewed [38,133, 134]). The number of publications in the fields of nanocomposites mentioned is countless.

A very interesting prospect for new functional intercalation compounds has been demonstrated by Pinnavaia et al. [135]: they could show for the first time that it is possible to get a regular alternation of interlayer spaces filled with different types of intercalated species. In this context $K_4Nb_6O_{17}$ should be mentioned. It consists of oxide layers which create two alternating structurally different interlayer spaces favouring different intercalation behaviour. [136]

Crucial for all these applications is that in the exfoliated systems real monolayers prevail. Although intercalation compounds are only the precursors of the exfoliated state, the homogeneous intercalation of the starting materials is a decisive prerequisite. To fulfil this goal the extension of our knowledge of the above discussed interstratification and staging phenomena, the intercalation mechanisms and the reduction of disorder and defect formation is highly desirable.

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