

ELECTRON/ION-TRANSFER REACTIONS OF SOLIDS WITH DIFFERENT LATTICE DIMENSIONALITY

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Abstract - The reversible insertion of mobile atomic or molecular ionic guest species into appropriate crystalline solid host lattices via electron/ion transfer represents a well defined type of solid state reaction that proceeds at low temperatures. Specific correlations are considered between reactivity and structure, physical properties, kinetics and host/guest interaction.

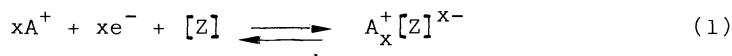
INTRODUCTION

The majority of solid state reactions proceed only at higher temperatures and involve as a rule the complete reorganization of the lattice structure of the starting material in the course of the reaction process (Ref. 1). For those reactions that take place at lower temperatures, however, partial or total retention of the original solid structure can frequently be observed. Of particular interest in this respect are the so-called intercalation reactions which occur at low temperatures (usually close to 300 K) via reversible topotactic insertion of mobile guest species into a solid host lattice that provides an interconnected system of vacant lattice sites of appropriate geometry and energy for the diffusion of guest species (Ref. 2-4). The term "topotactic" means that the atoms of the host lattice matrix do not undergo bulk translational motion in the course of the solid state reaction except for small local displacement. Under the aspects of reaction mechanism, intercalation processes can be classified into three basic categories:

- (i) intercalation of neutral species
- (ii) intercalation via ion exchange reactions
- (iii) intercalation via redox reactions (electron/ion transfer)

Host lattices with insulator properties, e.g. layered silicates, are restricted to (i) and (ii), while electron/ion transfer reactions require host lattices that exhibit electronic conductivity. The latter type of reaction has been studied extensively in the past decade and will be the major subject of this discussion. The main lines of present interest in this field are (i) the synthesis of new and metastable compounds not accessible by other methods of preparation, (ii) the investigation of reaction mechanisms, (iii) the changes in physical properties by intercalation of conductor host solids and (iv) the potentials of application of these systems, e.g. as reversible battery electrodes.

A simplified description of an electron/ion transfer process is given by eq. 1, which illustrates the insertion of a mobile guest cation (A) into a



solid matrix (Z) and the compensation of the guest ion charge by simultaneous uptake of an equivalent amount of electrons into the conduction band of the host via chemical or electrochemical reduction. Graphite is the only host lattice of importance for which the corresponding process of electron/anion transfer is observed (Ref. 5); we shall therefore be concerned essentially with topotactic redox reactions proceeding by electron/cation transfer.

From a structural point of view the large variety of host lattices can be classified formally as three-, two- and one-dimensional systems (Fig. 1).

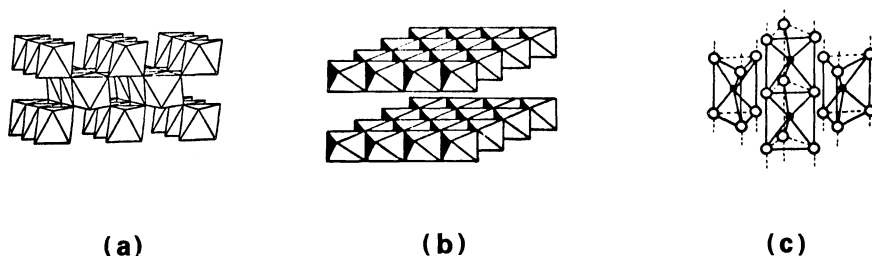
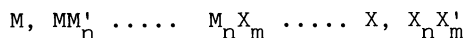


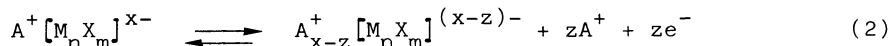
Fig. 1. Host lattices with different dimensionality. (a) framework structure of rutile (e.g. TiO_2 , MoO_2); (b) layered structure (CdI_2 type, e.g. TiS_2 , 1T-TaS_2); (c) chain structure (NbSe_3 type).

As will be discussed below the reactivity characteristics of a given host solid are strongly correlated with its structural dimensionality. Under the aspect of composition a wide variety of compounds is known to undergo the type of reaction under discussion:



By far the most important group are transition metal/nonmetal compounds $\text{M}_n \text{X}_m$; many transition elements M and their alloys are able moreover to intercalate hydrogen and at the other end we find among the nonmetal elements graphite as a most versatile host lattice (Ref. 5). Among nonmetal compounds $\text{X}_n \text{X}'_m$ the only reported case is polysulfur nitride $(\text{SN})_x$ which intercalates bromine (Ref. 6).

The investigation of topotactic redox reactions of ternary phases $\text{A}_x \text{M}_n \text{X}_m$ has received particular attention recently. These phases which are obtained by reaction of the elements at high temperatures do not represent intercalation compounds according to the definition given above. They are, however, characterized (i) by the presence of monovalent lattice cations A (A = alkali cation, Cu^+ , Ag^+ , Tl^+) that are mobile at room temperature (bulk diffusion) and (ii) by electronic conductivity. As a consequence, these phases are able to engage in topotactic redox reactions according to



For $z = x$ new "empty" host lattices can thus be prepared that are able in turn to intercalate other cationic guest species.

Although we have at present models that describe the basic mechanism of topotactic redox reactions, there seems to be still a long way towards an understanding the details of the reaction process which requires a complete description of the topological changes as well as the changes in chemical bonding and physical properties in the course of the intercalation reaction. We shall consider here some aspects of particular models for the reaction mechanisms of solids with different lattice dimensionality and discuss the importance of parameters such as lattice defects, hysteresis phenomena, electronic aspects, host/guest interaction and processes leading to partial irreversibility.

REACTION MECHANISM AND STRUCTURAL ASPECTS

The description of the topological changes of the host solid on the way to the final product via intermediate states is one basic aspect for the understanding of the reaction mechanism. As mentioned above, the changes of atom positions within the matrix elements correspond to small displacement motions only that can be considered in a first approximation to be correlated primarily with the charge transfer to the host matrix (Fig. 2). It is clear, however, that changes in the electronic properties of the host as well as

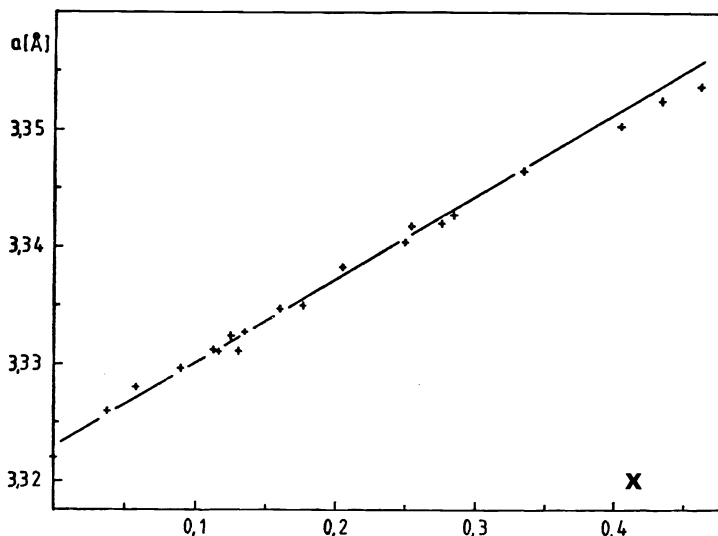


Fig. 2. Variation of the hexagonal a-axis with the charge transfer (x): formation of $K_x^+(H_2O)_y[NbS_2]^{x-}$ by intercalation of $2H-NbS_2$ with hydrated K^+ ions via cathodic reduction (Ref. 57).

type, location and charge of the guest species will also be of importance. Most of the reactions discussed proceed at or close to room temperature; at higher temperatures the matrix atoms will also become mobile with the consequence of irreversible nontopotactic reactions. Although it is to be expected that due to the strong decrease of the mobility of guest species inside the solid the reactivity below 300 K will inhibit the reaction, several systems have been found to operate reversibly even at temperatures of 370 K and below, e.g. the intercalation of alkali metal ions from solutions in liquid ammonia into layered dichalcogenides (Ref. 7 & 8) or Mo_6S_8 (Ref. 9) and the formation of some hydrogen bronzes (Ref. 3 & 4).

Isothermal cross sections of the phase diagram and thermodynamics can readily be obtained by coulometric electrochemical titration of host lattices with appropriate guest cations in galvanic cells. An attempt for a quantitative description of the changes of the potential with the charge transferred has been made using the Nernst equation with one term that accounts for the increasing occupation of a given set of vacant lattice sites and a second term related to the band occupancy (Ref. 10). However, for an adequate understanding of the appearance of intermediate phases and the maximum uptake of electrons and guest species in real systems more refined models that allow for additional interaction terms have to be developed. The influence of lattice strain mediated attractive guest-guest interaction on the appearance of hysteresis and two phase regions has been discussed recently (Ref. 11). At present even "simple" systems such as Na^+/TiS_2 (Ref. 12) still provide problems with respect to the experimental establishment of the true phase regions due to the influence of kinetics (nonequilibrium states, primary and secondary defects).

The reactivity and the observed structural changes upon intercalation are dependent upon the dimensionality of the host lattice. Most severe restrictions for the uptake of guest ions are found for host lattices with framework structures; the minimum diameter of the diffusion channels is responsible for the existence of upper critical radii for potential guest species (Ref. 4). However, if the channel size is appropriate, even large guest cations, e.g. Tl (Ref. 13 & 14), K (Ref. 15), Cs (Ref. 16) are found to be mobile at room temperature in the host lattice. In turn, it is surprising that even host phases with close packed oxygen lattice may react with small guest ions such as Li^+ which has been demonstrated by recent studies on

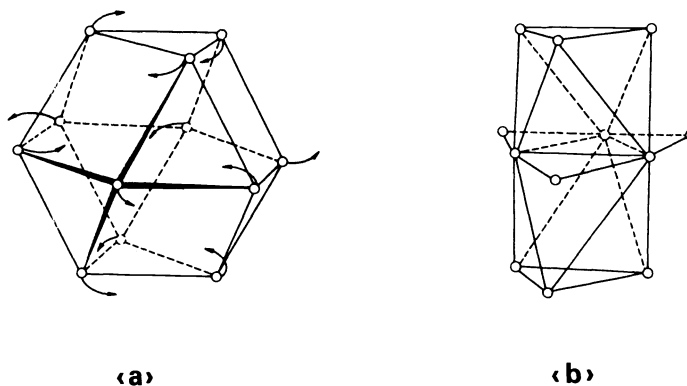


Fig. 3. Twist of the 12-coordinate cubooctahedral cavity of ReO_3 upon formation of LiReO_3 and Li_2ReO_3 via Li^+ intercalation (Ref. 23).

spinel type phases, e.g. Mn_3O_4 , $\text{Li}_x\text{Mn}_2\text{O}_4$ (Ref. 17 - 20) and $\text{Li}_x\text{Ti}_2\text{O}_4$ (Ref. 21).

Changes in the lattice parameters for three-dimensional host structures are usually small but sensibly related to the charge transfer for a given host as has been shown particularly for molybdenum cluster chalcogenides Mo_6X_8 ($\text{X} = \text{S}, \text{Se}$) (Ref. 4 & 22). Substantial local strain can, however, be observed in certain cases leading to significant distortion of the original host lattice. Examples are the insertion of Li in ReO_3 , where displacements of the host oxygen atoms up to 0.4 \AA have been measured (Ref. 23) (Fig. 3). The intercalation of rutile type MoO_2 yields LiMoO_2 with distorted NiAs type structure and Mo-Mo pairs (Ref. 25). Single crystals of MoO_2 of 5 mm in size show indeed breakdown upon Li intercalation to particles of ca. 0.5 mm in diameter (Ref. 26).

Significant and characteristic changes of the host overall structure are observed for layered systems, whose reactivity towards a broad variety of atomic and molecular guest species is due to the elastic adaptation of the sheet matrix system to the intercalate structures and dimensions. The reversible changes of atom positions within the layered matrix units remain small, however, in most cases. The major structural reorganization types are stacking changes of the layer units and the appearance at low guest concentrations of higher stages, i.e. systems with alternate sequences of filled and vacant van der Waals gaps between the layers (Fig. 4). Both effects are frequently correlated.

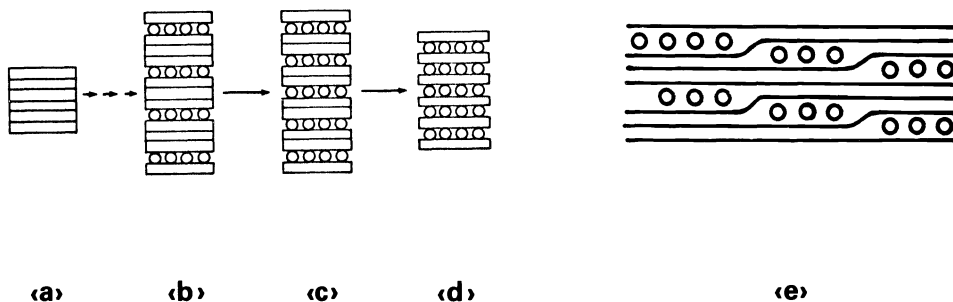


Fig. 4. Staging models for layered systems. (a) host lattice, (b) third stage phase, (c) second stage, (d) first stage, (e) domain model after Hérold for third stage phase (Ref. 5).

Most extensive studies have been performed on stacking changes observed in alkali metal intercalates of layered dichalcogenides A_xMX_2 (A = alkali metal, M = transition metal, X = S, Se). The coordination of the alkali metal, i.e. either trigonal prismatic or distorted octahedral was found to depend upon the following factors: (i) size of the guest cation, (ii) amount of the intercalated ion and (iii) nature of the host layers (i.e. composition M, X and ionicity of the $M-X$ bond)(Ref. 8 & 27). The structurally related oxide systems, e.g. A_xCoO_2 , A_xTiO_2 exhibit similar behaviour (Ref. 28 - 30). The origin of these stacking changes may be more complex in fact as discussed recently for the Na_xTiS_2 system, where ^{23}Na -NMR data suggest that the transition from trigonal prismatic to octahedral guest coordination is related to a change in the electronic band structure (Ref. 12). Stacking changes involving tetrahedral-tetrahedral transitions observed e.g. for Cu_xTiS_2 (Ref. 26 & 31), Ag_xTiS_2 and Ag_xTaS_2 (Ref. 32) are not yet well understood; they are most likely related to covalent interaction between the strongly polarizable monovalent guest cations and the host lattice.

Hydrated layered chalcogenides $A_x(H_2O)_y[MX_2]$ show stacking changes octahedral/trigonal prismatic depending upon the hydrate structure, which itself is related to the charge/radius ratio of the cation; similar stacking changes are observed on the intercalation of molecular ions; anisometric ions (e.g. pyridine H^+) may in addition give rise to different intercalation structures depending upon the charge transfer (Ref. 33).

Studies on single crystals suggest that the initial process of the intercalation in layered hosts can be described by the adsorption of the guest species on the outer basal planes of the crystallites and successive reaction of adjoining layers (Ref. 34 & 35). A clear proof of such a mechanism results from studies on the formation of the layered hydrogen bronze $H_{0.2}MoO_3$ from MoO_3 single crystals, which shows that the basal planes react first; subsequently the reaction proceeds from both basal planes towards the center of the crystal (Ref. 3). Since MoO_3 is an optically transparent semiconductor, while the hydrogen bronze is an opaque metallic conductor, the phase boundaries can be observed as sharp lines until the end of the process.

At low concentrations of intercalated guest ions staging phenomena are usually encountered. Graphite exhibits a variety of different stages (Ref. 5), while for layered dichalcogenides 4th stage, 3rd stage and 2nd stage phases have been reported (Ref. 8, 33, 36 & 37). A most simple explanation of the appearance of higher stage compounds at low guest concentration is based upon the conclusion that the lattice energy of a first stage system with a low concentration of guest cations homogeneously distributed in the interlayer region - i.e. large void regions - is likely to be higher as compared to a system with the same composition and cations concentrated in a fraction of the available interlayer gaps. There are, however, additional factors that have to be considered such as the electrostatic interaction of neighbouring cation layers and the energy needed for the separation of the layers upon intercalation. Also, the mechanism of transitions from stages with uneven numbers to stages with even numbers (e.g. third stage \rightarrow second stage) is rather puzzling and suggests the influence of kinetic factors. A model which is widely accepted by now has been proposed that explains the structure of staged intermediates on grounds of domain formation (Ref. 5) (Fig. 4). Models involving lattice strain mediated interactions and thermodynamic considerations to explain the formation of staging phenomena have recently been put forward (Ref. 11, 38 & 39)(Fig. 5). However, these models describe systems that are in thermodynamic equilibrium which is not necessarily true for intercalation compounds forming at ambient temperature. Also, the model described in Ref. 39 predicts generally the formation of first stage phases at high temperatures independent of the guest concentration. This is not in agreement e.g. with the recent observation, that $Cu_{1/3}NbS_2$ formed at high temperatures, is a second stage phase, i.e. $Cu_{2/3}(NbS_2)_2$ (Ref. 40).

The idea that a minimum energy is required to open the van der Waals gap of layered phases, particularly if stacking changes and staging are involved, has been discussed by several authors (Ref. 34, 41-43). This would consequently lead to initial two phase regions and for most intercalation systems this is in fact in agreement with the experimental observation. Apparent exceptions e.g. Li_xTiS_2 are most likely to be explained by technical problems in the detection of small two phase regions particularly with small guest ions of low atomic number.

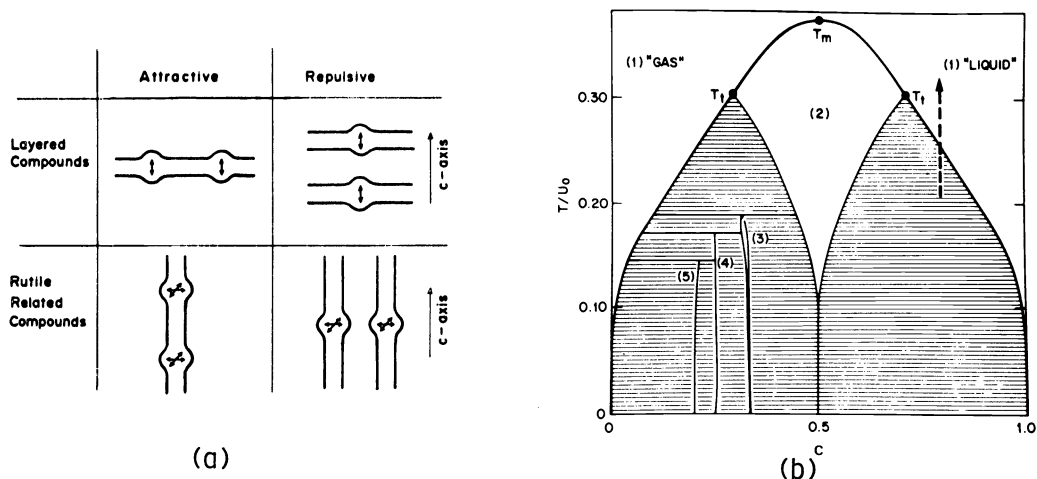


Fig. 5. (a) scheme of strain induced interaction between intercalated atoms in layered and framework (isolated parallel channels) systems (Ref. 11 & 45), (b) phase diagram for the formation of higher stage layered compounds; T/U_0 = normalized temperature, c = concentration (Ref. 39).

Structural, electrochemical and NMR studies have been devoted to the question of local and long range ordering states of the guest cations. For lithium ions in Li_xTiS_2 there is evidence for two-dimensional order depending upon the stoichiometry as well as for imperfect three-dimensional order (Ref. 44 & 45). Electron microscopy studies on Li_xTiS_2 and Na_xTiS_2 revealed the presence of high dislocation defect concentrations (Ref. 46). Temperature dependent ordering states have also been reported for copper and silver intercalated layered dichalcogenides, e.g. Ag_xNbS_2 , Cu_xVS_2 and for Li_xZrSe_2 (Ref. 47-49). The cointercalation of two mobile guest ions into a host lattice is an interesting way to new intercalation compounds, although this possibility has been exploited only in a few instances, e.g. $\text{H}_x\text{Na}_y(\text{H}_2\text{O})_n[\text{MoO}_3]$ (Ref. 4), Li_xKFeS_2 (Ref. 50), $\text{Li}_x\text{Na}_y\text{V}_2\text{O}_5$ (Ref. 51), $\text{Ni}_x\text{H}_y\text{Mo}_6\text{S}_8$ (Ref. 31). Structural data are not available presently for the positions of the two types of cations; for $\text{Ni}_2\text{H}_2\text{Mo}_6\text{S}_8$ a cluster type $(\text{Ni}_2\text{H}_2)^{2+}$ structure has been proposed. A mechanism for the cooperative intercalation of potassium and mercury into graphite under formation of KHgC_4 has been suggested recently (Ref. 52).

REACTIVITY, LATTICE DEFECTS AND KINETICS

It is obvious that topotactic solid state reactions at ambient temperature will be strongly affected by lattice defects originating from local defects (inherent or impurity type) or extended defects. These defects may either be present in the original host lattice or evolve as secondary defects in the course of the intercalation reaction. They may lead to partial or total irreversibility and are thus of importance with respect to the technical application of intercalation systems. The dimensionality of the host lattice is related to the appearance of characteristic defects. A typical original defect in layered dichalcogenides that strongly affects the intercalation kinetics is the presence of excess transition metal atoms in the van der Waals gap, e.g. $\text{Ti}_{1+x}\text{S}_2$ (Ref. 53). The existence of molybdenum point defects in the channels of the framework structure of Mo_6S_8 has recently been related to the maximum guest concentration (Ref. 54). A special case are framework systems with isolated parallel channels. Shear defects in these structures will exclude a partial volume of the crystallites from reaction (Ref. 55, Fig. 6). It is interesting to note that ternary phases prepared thermally, e.g. $\text{K}_x\text{Ti}_3\text{S}_4$, TlV_5S_8 , TlV_6S_8 (Ref. 13-15) will deintercalate readily, while the binary phases prepared at high temperatures, e.g. Nb_3S_4 show usually only partial reaction. This can be explained by the assumption that the extended defect concentration in lattices of ternary phases with the channels filled up with cations is significantly lower as compared to that of binary phases with empty channels (thermal preparation).

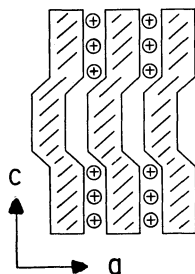


Fig. 6. Partially inaccessible channel volume originating from extended defects in framework structures with isolated parallel channels (Ref. 55).

Secondary defects are known to appear on intercalation/deintercalation cycles and may lead at higher cycle numbers to high defect concentrations and pseudo-amorphous behaviour (Ref. 56). Characteristic for layered structures is the appearance of total one-dimensional disorder, if weak shear forces are applied to phases with large interlayer spacings. A typical example is the formation of layered hydronium phases $(\text{H}_3\text{O}^+)_x(\text{H}_2\text{O})_y[\text{MX}_2]^{x-}$. With decreasing pH values of the electrolyte different phases are formed successively on electrochemical reduction of e.g. NbS_2 in aqueous mineral acids: monolayer and bilayer hydrates with well ordered structures, triple layer hydrates with one-dimensional disorder and colloidal states with total disorder and interlayer spacings of >5 nm (Ref. 3). The disorder evolving in the course of an intercalation reaction can, however, be quite reversible. The intercalation of hydrated K^+ ions in TaS_2 proceeds via intermediates of third, second and first stage phases. The halfwidth of the Bragg reflections changes characteristically in the course of the reaction: host lattice with sharp lines, third and second stages strong broadening of characteristic reflections and first stage phase again with small halfwidth of the reflections (Ref. 36 & 57). Quantitative reoxidation of intercalated phases frequently produces problems, although this is dependent upon the host lattice type. While the unchanged host lattice can usually be recovered readily from framework host lattices, layered systems show stronger defects and the lattice parameters of the deintercalated phases (first cycle) deviate somewhat from the original ones. "Residue compounds" with small amounts of guest species left after deintercalation in the interlayer region or close to defect centers have been observed early with graphite as the host (Ref. 58). Quasi one-dimensional host systems like transition metal trichalcogenides (Ref. 59) or PV_2S_{10} (Ref. 60) are - due to their structural characteristics - strongly susceptible to the introduction of secondary lattice defects (two-dimensional disorder) which may be one of the reasons that only few studies have been devoted to these materials.

Secondary defects may also be created by partial solvolysis of transition metal dichalcogenide layers, e.g. via S/O exchange in the course of the intercalation of hydrated cations; this process is naturally strongly dependent upon the electrolyte pH value (Ref. 33). Similar reactions are observed with FeOCl as the host lattice (Ref. 61). For some phases, e.g. Li_xCrO_y (Ref. 62), Li_xWO_3 (hexagonal) (Ref. 63 & 64) complete structural desintegration is found above critical concentration values of the intercalated ions. Examples have been reported for irreversible transformation of intercalated phases to ordered compounds with different structure, e.g. the rutile/spinel transformation $\text{Li}_x\text{MnO}_2 \rightarrow \text{Li}_x|\text{Mn}_2\text{O}_4|$, (Ref. 18), the transition $\text{KFeS}_2 \rightarrow \text{Li}_x\text{KFeS}_2$ (Ref. 50) and the deintercalation of $\text{Li}_7\text{Ge}_{12}$ to allo-germanium (Ref. 65).

An interesting recent approach pertains to the investigation of topotactic redox reactions of amorphous phases. Studies on the amorphous chalcogenides MoS_3 , WS_3 , V_2S_5 , MoS_2 , TiS_2 revealed marked differences between the intercalation behaviour of amorphous and crystalline phases (Ref. 66 & 67). Some of these compounds show surprisingly high discharge capacities, although the reaction mechanism is still uncertain. Amorphous tungsten oxide WO_3 can be

used for passive electrochromic displays via the reversible formation of colored hydrogen bronzes H_xWO_3 (Ref. 68). The reversible intercalation of Na^+ and Li^+ in semiconducting phosphovanadate glasses has been reported (Ref. 69).

Adequate ionic mobility is an obvious prerequisite for topotactic redox reactions at room temperature and will strongly influence reaction kinetics. Although ionic conductors have been studied widely in the past decade, our knowledge on transport phenomena in electronic/ionic conductors is still rather limited. In a first approximation one may assume that the reasons for electronic and ionic conductivity are independent, electronic conductivity being related essentially to the band structure, while ionic conductivity will be dependent mainly upon structural aspects (Ref. 70). In most systems liable to topotactic redox reactions the electrons are more mobile than the guest ions. However, the specific screening of the mobile ionic charges by the electrons in different structures and the fact that the screening charges are mobile (as opposed to insulator type ionic conductors with localized balancing charges) are most likely related to ionic mobility; this could be checked by the investigations of systems that involve stoichiometry dependent changes in the electronic structure, e.g. Li_xZrSe_2 (Ref. 71). Studies on substituted layered systems $Na_x[M_xM'_{1-x}S_2]$ (with $M = Zr, Sn$; $M' = Y, In$ etc.) have led to the conclusion that the cation mobility is dependent upon the stoichiometry x , the fractional ionicity of the $M-S/M'-S$ bonding and the site geometry of the guest cation (Ref. 72). The activation energy was found to be lower in trigonal prismatic coordination as compared to octahedral sites. Beside the size additional properties of the cations will also be related to ionic conductivity. For high mobilities of heavy metal ionic conductors it has been suggested that the cations should be stable in environments of low coordination number (transition states) and should be highly polarizable (Ref. 73). In fact $Cu(I)$ and $Ag(I)$ are found to exhibit high mobilities in host lattices with soft anions such as S^{2-} , Se^{2-} , Te^{2-} ; in oxide lattices with "hard" O^{2-} anions, however, copper ion mobility is significantly lower which demonstrates the influence of the host lattice anions.

Solvated metal cations in layered systems usually exhibit high mobilities as a consequence of the mobility of the surrounding neutral molecules (Ref. 33). The latter may exhibit strong anisotropic behaviour (Ref. 74 & 75). Anisotropic mobility of unsolvated guest cations has been reported e.g. for Li_xTiO_2 (Ref. 76) and hydrogen in H_xWO_3 and H_xMoO_3 (Ref. 77) at low x values.

Metallic conductivity of host lattices has frequently been considered as an advantage for solid electrode materials; it has been shown, however, that for practical purposes semiconductors will be the better choice. This is due to the fact that rapid equilibration of ionic concentration gradients is achieved more readily in the presence of high inner electric fields in semiconductor electrodes ("enhanced motion") (Ref. 78).

A highly unusual phenomenon is the observation of fast mobility of transition metal ions ($T = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}$) at ambient temperature in cluster chalcogenides $T_xMo_6X_8$ ($X = S, Se$) (Ref. 3, 4, 9 & 79) which is rather surprising, since bivalent ions should exhibit high activation energies for site changes. Several models are conceivable to explain this behaviour (Ref. 26 & 80):

(i) the transition metal ion is present as T^+ species with guest-guest metal bonding, (ii) the site change is correlated with the reaction $T^{2+} + e^- \rightleftharpoons T^+$, i.e. the bivalent ion accepts reversibly an electron from the conduction band during the transition state, (iii) a small equilibrium concentration of T^+ is present along with electron transfer reactions. The electron exchange $T_A^{2+} + T_B^+ \rightleftharpoons T_A^+ + T_B^{2+}$ may proceed either via direct contact of the ions or by mediation of the conduction band of the matrix. Similar mechanisms have been proposed for the observed mobility of Tl^{3+} in $Tl_xV_5S_8$ phases (Ref. 13). A different explanation could also be envisaged that involves T^{2+} ions and assumes that at a certain critical diffusion channel size and geometry (in relation to the ion size) the anisometric screening by the balancing charges is such that the activation energy for translation is strongly reduced leading to fast ionic transport at ambient temperature. We predict that the Mo_6X_8 system is not a singular case and that more transition metal ion conductors will be found in future studies (Ref. 26).

Qualitative studies on the question of reaction kinetics by cyclic voltammetry and electrochemical cycling at variable current densities have been reported for many topotactic redox systems. Studies on time laws, nucleation and

induction periods and differentiation between diffusion controlled and phase boundary processes, respectively, have remained scarce. Kinetic studies have been performed on the chemical reaction of layered dichalcogenides with NH_3 (Ref. 81-83), alkali hydroxides (Ref. 84) and hydrazine (Ref. 82); the intercalation mechanisms are, however, of a rather complex nature in these systems (cf. below). The reaction rate of butyllithium with TaS_2 was measured by hyperfine spectroscopy; no attempt has been made to interpret the results beyond a qualitative scheme (Ref. 43).

Hysteresis phenomena on intercalation and deintercalation due to nonequilibrium states are frequently observed for layered systems as well as for framework host lattices, e.g. H_xMoO_3 (Ref. 3, 4) and $\text{Cu}_x\text{Mo}_6\text{S}_8$ (Ref. 79). Partial irreversibility can be due to changes in the electronic transport properties of the host system upon intercalation or deintercalation which is clearly demonstrated by formation of e.g. H_xMoO_3 . The reduction of MoO_3 to $\text{H}_{0.2}\text{MoO}_3$ is correlated with an insulator/metal transition. Electrochemical reduction of MoO_3 single crystals shows that the reaction proceeds only at a triphase boundary MoO_3 /electrical lead (e.g. Pt)/electrolyte. On the reoxidation of the final product H_2MoO_3 via several metallic intermediate phases the reaction stops at the two phase region $\text{H}_{0.2}\text{MoO}_3$ / MoO_3 due to the formation of a thin layer of insulating MoO_3 which inhibits further electron transfer (Fig. 7).

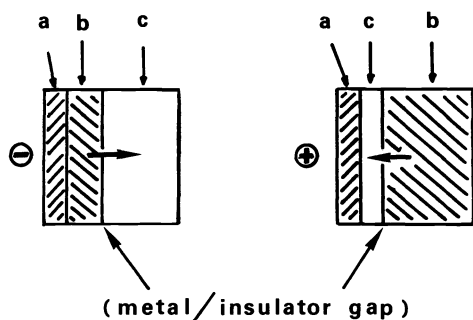


Fig. 7

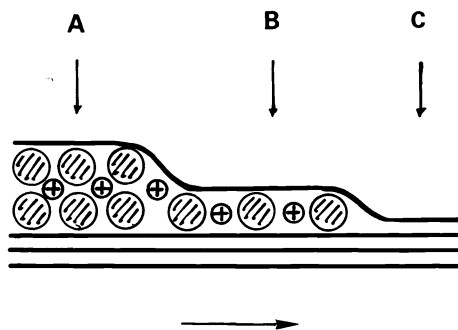


Fig. 8

Reduction

Oxidation

Fig. 7. Influence of the metal/insulator phase transition on the kinetics of the electrochemical reaction $\text{MoO}_3 + 0.2\text{H}^+ + 0.2\text{e}^- \rightleftharpoons \text{H}_{0.2}\text{MoO}_3$. (a) current lead, (b) $\text{H}_{0.2}\text{MoO}_3$, (c) MoO_3 . Reduction: progress of phase boundary due to the formation of metallic $\text{H}_{0.2}\text{MoO}_3$; Oxidation: inhibition of electron transport by the formation of an insulating MoO_3 layer between current lead and $\text{H}_{0.2}\text{MoO}_3$.

Fig. 8. Model of the phase boundary region for the formation of bilayer hydrate phases. (A) bilayer hydrate zone, (B) monolayer hydrate zone, (C) unreacted host lattice.

The appearance of higher stages in layered systems is again strongly dependent upon kinetics as is demonstrated by the intercalation of $\text{K}^+/\text{H}_2\text{O}$ into TiS_2 :

low current density:	3rd stage	→	2nd stage	→	1st stage
Intermediate current densities:			2nd stage	→	1st stage
high current densities:				→	1st stage

While under quasi-equilibrium conditions third and second stage phases are formed successively, higher stage formation is suppressed with increasing current density (Ref. 57). Similarly, higher stages are not observed, if the guest cation size (large molecular ions, e.g. $(\text{C}_5\text{H}_5)_2\text{Co}^+$, Ba^{2+} cryptate) leads to a significant increase in interlayer spacing (Ref. 36). This can be explained by the strong mechanical deformation of layers necessary to introduce large ions; obviously the direct formation of a first stage product with high guest concentration is energetically favoured as compared to the formation of higher stages that would require high activation energies for the deformation of double or triple sheet packet units. Although high interlayer spacings are observed on the formation of hydrated phases with bilayers and triple layers of water, higher stages are found as intermediates. There is evidence, however, that in this case the system can relax energetically by the formation of a reaction front with successive mono- and bilayer structure (Ref. 26, Fig. 8). The elastic properties of the sheet units in layered

systems also play a significant role. For "thick" layers like Ta_2S_2C and MoO_3 no higher stage formation has been observed even for small metal guest ions which is assumed to be due to the fact that the mechanical energy for the deformation of double or triple sheet units would become energetically highly unfavourable (Ref. 85). The formation of higher phases is thus dependent upon the reaction kinetics, the "stiffness" of the layers and the magnitude of interlayer spacing induced by the guest species.

The intercalation of strongly electropositive metal ions with high solvation energy (large charge/radius ratio) from aprotic organic electrolytes into layered dichalcogenides leads frequently to systems that are metastable with respect to solvent cointercalation. It has been found that on extended cycling (e.g. Li_xTiS_2 , Ref. 53) solvent molecules penetrate into the interlayer space with the consequence of a strong increase in interlayer spacing. This is a disadvantageous process in the application of these compounds as battery electrodes.

REACTION MECHANISM: BONDING AND CHARGE TRANSFER

The basic reaction given in equation 1 for electron/ion transfer processes obviously requires quantitative charge transfer to the conduction band of the host matrix under the assumption of a rigid band structure. If we neglect steric effects and Coulomb repulsion between guest ions, we should be able to predict the maximum uptake of guest ions and thus the maximum charge transfer directly from the band structure of the host lattice. Recent studies give, however, evidence that the simple model discussed has to be refined in several respects depending on the specific properties of the different systems (Ref. 80).

The combination of host lattices with high electron affinity E_A (e.g. transition metal oxides MO_n with M in a high valence state) and metal guest cations with low ionization energies, e.g. $Li_x^+[TiO_2]^{x-}$, $Li_x^+[MoO_3]^{x-}$ leads to systems which can be described in a good approximation by the idealized model. If we replace oxygen by the less electronegative and more polarizable sulfur or selenium ions, we find already discrepancies. Lithium ions in Li_xTiS_2 exhibit a variation of the Knight shift (7Li -NMR) with increasing Li concentration (Ref. 86); the same is true for Na_xTiS_2 (Ref. 12) which in addition is supposed to undergo an electronic phase transition. Significantly higher Knight shift values were observed for $Li_xMo_6S_8$ (Ref. 80) and LiC_6 (Ref. 87). Graphite is in this respect an outstanding host lattice because of its low electron affinity. It has been suggested early that first stage graphite compounds with electropositive metals should be described by a partial charge transfer, e.g. $Cs^{(1-x)+}[C_8]^{(1-x)-}$ with an estimated value for x of ca. 0.3 (Ref. 87). Similar partial charge transfer phenomena have been observed for the intercalation of transition metals in Mo_6S_8 (Ref. 31). The partial transfer can be explained basically in terms of two models (i) by the formation of covalent host/guest bonds, (ii) by a model proposed recently that involves the "storage" of electrons via metal-metal bonding in guest clusters, i.e. either two electron bonding or delocalized electron deficient multicenter bonding between guest cations (Ref. 80). In fact we have to assume that both models can be applied depending upon the system studied. The present results can be summarized for atomic guest species in the following scheme:

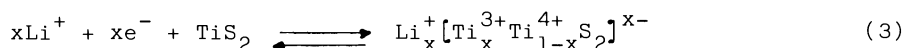
- (i) quantitative charge transfer to the host matrix, characterized by high electron affinity E_A of the host lattice, low ionization energy E_I of the guest species, low guest concentration and high free energy of formation of the intercalated phase.
- (ii) partial charge transfer, favoured by low E_A of the host lattice, high E_I of the guest species and high guest concentration x. Usually Δ_{RG} is found to be low in these systems. Two different bonding situations may appear:
 - (i) formation of guest-guest clusters with metal bonding
 - (ii) covalent bonding between host and guest (e.g. H^+ , Cu^+ , Ag^+)

A border case has been observed recently on the deintercalation of TlV_5S_8 : the host lattice matrix V_5S_8 is not involved in the electron transfer process and the redox reaction proceeds exclusively via stoichiometry dependent changes of the guest cation (Ref. 13).

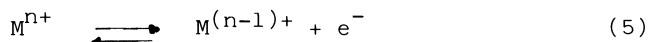
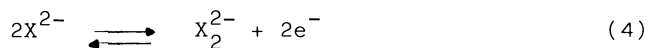
If electronic phase transitions occur in the course of intercalation processes the reactivity and the charge transfer scheme may of course vary strongly dependent upon the nature of the change in band structure.

Recently topotactic redox reactions have been reported for the layered vanadium phosphate $\text{VOPO}_4(\text{H}_2\text{O})_2$ (Ref. 88). The compound is a wide gap semiconductor and because of its very low electronic conductivity electrochemical intercalation has not been possible, while chemical reduction with e.g. I^- , SO_3^{2-} , Fe^{2+} was found to proceed readily. A similar case is presented by layered RuCl_3 which can be reduced to the stage of $[\text{RuCl}_3]^{1-}$ only by chemical reduction, e.g. $\text{S}_2\text{O}_4^{2-}$ (Ref. 89). An explanation for this phenomenon is the assumption that the electrons are not transported across the bulk of the solid but that the reducing species migrate into the interlayer space and effect a local reduction in close contact with the transition metal matrix ions. As a consequence of the Donnan equilibrium, anionic species may also be present (though in small concentration) in the interlayer space which explains the reactivity of anionic electron donors, e.g. $\text{S}_2\text{O}_4^{2-}$ in the absence of adequate bulk electronic conductivity of the host lattice (Ref. 80).

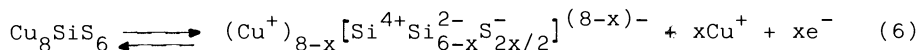
In host lattices representing transition metal/nonmetal compounds MX_n the simple chemical bonding model describes the redox process formally as the reduction of the transition metal atoms to a lower valent state, e.g. Li_xTiS_2 (eq. 3). One could imagine also, however, a process that takes place



via a host lattice anion redox mechanism. Suitable systems with redox activity could be the less electronegative nonmetal elements, e.g. S, Se, P. Chalcogenides are known to undergo reversible reactions in homogeneous solution according to eq. 4.



The question whether host anions or host cations are subject to redox reactions depends upon the internal redox balance (eqs. 4 & 5) of the subsystems. If this is clearly in favour of the anion, the system can react only via anion redox processes. An example for this kind of reaction is the argyrodite type copper silicon sulfide Cu_8SiS_6 (Ref. 26) which was found to react according to eq. 6, since Si^{4+} does not change its valency. It is most likely



that trichalcogenides of transition metals react at least to some extent in a similar way. It is possible of course that the chalcogen-chalcogen bond is delocalized (resonance model) above a critical temperature and localized below, so that electronic phase transitions are to be expected in these systems. A rather interesting case are the phosphorous sulfides MPS_3 with P-P units in octahedral sites; depending upon M (Fe, Co, Ni) either the metal or the P-P bonds are assumed to be primarily involved in the redox reaction (Ref. 90).

Complex reaction mechanism are found for the reaction of transition metal dichalcogenides with alkali hydroxides and neutral molecular guest species leading to partially irreversible changes. The intercalation of neutral guest molecules, e.g. NH_3 , pyridine is accompanied by a partial oxidation of the guest species and irreversible formation of the reaction products N_2 and dipyridine, respectively; the overall process is, however, clearly equivalent to an electron/ion transfer process (Ref. 3, 4 & 80). The formation of dipyridine on the reaction of layered ironoxychloride with pyridine has been reported and suggests a similar process (Ref. 3 & 91); this has been confirmed recently by Mössbauer spectroscopy studies (Ref. 92). The intercalation of alkali hydroxides into transition metal dichalcogenides MX_2 proceeds via two steps: partial hydrolysis of the layers via nucleophilic attack of the M-X bond by OH^- , the released S^{2-} acts as the redox species and is oxidized to S_n and polysulfide anions (Ref. 33 & 93).

Among the graphite intercalation compounds resulting from electron/anion transfer reactions the intercalation of bromine has long been debated with respect to the charge transfer problem. Recent structural studies support the model of a formation of anionic polymer chains Br_n^{x-} , i.e. partial charge transfer to the host lattice and formation of extended guest/guest bonds (Ref. 94). Similar chains are probably present in the intercalation compounds $(\text{SN})\text{Br}_y$ of the quasi one-dimensional host system polysulfurnitride with bromine (Ref. 6).

CONCLUSIONS

We have described above the influence of several factors on the reactivity of solids accessible to electron/ion transfer reactions. It is obvious that qualitative predictions on suitable host lattices are possible on the basis of the models presently available. There are, however, problems to correlate electronic and geometrical structures of host lattices in a more quantitative way with factors such as the upper phase limits, appearance and ranges of intermediate stages, stoichiometry dependent changes in structure and electronic properties, reaction kinetics and host/guest bonding. A tedious task remains also the structural determination of ordering states of the guest sublattice and of specific secondary lattice defects. For the investigation of phase ranges, hysteresis effects and rapid kinetics, in situ studies with fast X-ray methods (position sensitive detectors) are likely to become a convenient and economic technique.

An area that is gaining increasing attention is the formation of new metastable phases by deintercalation of thermal ternary and quaternary phases via topotactic redox reactions. Like for intercalation, lithium compounds are particularly versatile in this respect due to the high mobility of Li^+ even in close packed framework lattices and the large number of compounds available. More attention should be paid to the intercalation of hydrogen because of the practical importance of these systems (e.g. hydrogen storage, passive display devices, heterogeneous catalysis, corrosion)(Ref. 3 & 4). Attempts should be made also to find host systems that are able to undergo electron/anion transfer reactions; it is most unlikely that graphite should be unique in this respect.

A rather stimulating new field seems to be photochemical intercalation of semiconductor host lattices with appropriate band gap (Ref. 95). These systems have been proposed for use in solar energy conversion and storage as well as for optical information storage.

REFERENCES

1. P.P. Budnikov and A.M. Ginstling, Principles of Solid State Chemistry, K. Shaw, ed., Mac Laren, London (1968).
2. M.S. Whittingham and A.J. Jacobson, eds., Intercalation Chemistry, Academic Press, New York (1982).
3. R. Schöllhorn, Inclusion Compounds, J.L. Atwood, J.E.D. Davies and D.D. Mac Nicol, eds., Academic Press, New York (1984), p. 249.
4. R. Schöllhorn, Angew. Chem. **92**, 1015 (1980); Angew. Chem. Int. Ed. Engl. **19**, 983 (1980).
5. A. Hérold, Intercalated Layered Materials, F. Lévy, ed., p. 321, D. Reidel, Dordrecht (1979).
6. G.B. Street, R.H. Geiss, W.D. Gill, J. Kuyper and R.D. Smith, Synthesis and Properties of Low-Dimensional Materials, J.S. Miller and A.J. Epstein, eds., The New York Acad. Sciences, New York (1978).
7. W. Rüdorff, Chimia **19**, 489 (1965).
8. J. Rouxel, Intercalated Materials, F. Lévy, ed., p. 201, D. Reidel, Dordrecht (1979).
9. R. Schöllhorn, M. Kümpers and J.O. Besenhard, Mat. Res. Bull. **12**, 781 (1977).
10. M.B. Armand, Materials for Advanced Batteries, D.W. Murphy, J. Broadhead and B.C.H. Steele, eds., p. 145, Plenum Press, New York (1980).
11. W.R. Mc Kinnon and R.R. Haering, Solid State Ionics **1**, 111 (1980).
12. P. Molinié, L. Trichet, J. Rouxel, C. Berthier, Y. Chabre and P. Segransan, J. Phys. Chem. Solids **45**, 105 (1984).

13. W. Schramm, R. Schöllhorn, H. Eckert and W. Müller-Warmuth, Mat. Res. Bull. **18**, 1283 (1983).
14. H. Eckert, W. Müller-Warmuth, R. Schöllhorn, Solid State Ionics **13**,1(1984)
15. R. Schöllhorn, W. Schramm and D. Fenske, Angew. Chem. **92**, 477 (1980); Angew. Chem. Int. Ed. Engl. **19**, 492 (1980).
16. D.W. Murphy, J.L. Dye and S.M. Zahurak, Inorg. Chem. **22**, 3681 (1983).
17. M.M. Thackeray, W.I.F. David, P.G. Bruce and J.B. Goodenough, Mat. Res. Bull. **18**, 461 (1983).
18. W.I.F. David, M.M. Thackeray, P.G. Bruce and J.B. Goodenough, Mat. Res. Bull. **19**, 99 (1984).
19. M.M. Thackeray, P.J. Johnson, L.A. de Picciotto, P.G. Bruce and J.B. Goodenough, Mat. Res. Bull. **19**, 179 (1984).
20. A. Mosbah, A. Verbaere and M. Tournoux, Mat. Res. Bull. **18**, 1375 (1983).
21. D.W. Murphy, M. Greenblatt, S.M. Zahurak, R.J. Cava, J.V. Waszak, G.W. Hull and R.S. Hutton, Rev. Chim. Min. **19**, 441 (1982).
22. K. Yvon, Superconductivity in Ternary Compounds, Ø. Fischer and M.B. Maple, eds., p. 87, Springer Verlag, Berlin/New York (1982).
23. J. Cava, A. Santoro, D.W. Murphy, S.M. Zahurak and R.S. Roth, J. Solid State Chem. **50**, 121 (1983).
25. D.E. Cox, R.J. Cava, D.B. Mc Whan and D.W. Murphy, J. Phys. Chem. Solids **43**, 657 (1982).
26. P. Buller, M. Schulte, P. Dolscheid, M. Otto and R. Schöllhorn, in preparation.
27. J. Rouxel, J. Solid State Chem. **17**, 223 (1976).
28. K. Mizushima, P.C. Jones, P.J. Wisemann and J.B. Goodenough, Mat. Res. Bull. **15**, 783 (1980).
29. C. Delmas, J.J. Braconnier, C. Fouassier and P. Hagemuller, Solid State Ionics **3/4**, 165 (1981).
30. A. Mazaaz, C. Delmas, P. Hagemuller, J. Inclusion Phenomena **1**, 45 (1983).
31. R. Schöllhorn, Physics of Intercalation Compounds, L. Pietronero and E. Tosatti, eds., p. 33, Springer Verlag, Berlin/New York (1981).
32. G.A. Scholz and R.F. Frindt, Mat. Res. Bull. **15**, 1073 (1980).
33. R. Schöllhorn, Intercalation Chemistry, M.S. Whittingham and A.J. Jacobson, eds., p. 315, Academic Press, New York (1982).
34. J.G. Hooley, Chem. Phys. Carbon **5**, 321 (1969).
35. R.R. Chianelli, J.C. Scanlon and B.M.L. Rao, J. Solid State Chem. **29**, 323, (1979).
36. C. Riekel, H.G. Reznik and R. Schöllhorn, J. Solid State Chem. **34**, 253 (1980).
37. T. Hibma, J. Solid State Chem. **34**, 97 (1980); Physica B99, 136 (1980).
38. J.R. Dahn, D.C. Dahn and R.R. Haering, Solid State Comm. **42**, 179 (1982).
39. S.A. Safran, Phys. Rev. Letters **44**, 937 (1980); Synthetic Metals **2**, 1 (1980).
40. W. Thulke, Dissertation, Universität Kiel (1984).
41. J.G. Hooley, Preparation and Crystal Growth of Materials with Layered Structures, R.M.A. Lieth, ed., p. 1, D. Reidel, Dordrecht/Boston (1977).
42. J. Rouxel, Physica B99, 3 (1980).
43. T. Butz and A. Lerf, Rev. Chim. Min. **19**, 496 (1982).
44. A.H. Thompson, Phys. Rev. Letters **40**, 1511 (1978).
45. J.R. Dahn, W.R. Mc Kinnon and R. R. Haering, Can. J. Phys. **58**, 208 (1980); J.R. Dahn and R.R. Haering, Solid State Comm. **40**, 245 (1981).
46. D. Cherns and G.P. Ngo, J. Solid State Chem. **50**, 7 (1983).
47. F.W. Boswell, A. Prodan and J.M. Corbett, Mat. Res. Bull. **15**, 1567 (1980).
48. D. Colaitis, D. van Dyck, P. Delavignette and S. Ammellinckx, J. Solid State Chem. **49**, 269 (1983).
49. Y. Chabre, C. Berthier and P. Segransan, Solid State Ionics **9/10**, 467 (1983).
50. A.J. Jacobson, M.S. Whittingham and S.M. Rich, J. Electrochem. Soc. **126**, 887 (1979).
51. I.D. Raistrick and R.A. Huggins, Mat. Res. Bull. **18**, 337 (1983).
52. A. Hérold, D. Billaud, D. Guérard, P. Lagrange and M. El Makrini, Physica B105, 253, 1981).
53. M.S. Whittingham, Progr. Solid State Chem. **12**, 41 (1978).
54. J. Mizusaki, S.Y. Han, K. Fueki and K. Kitazawa, Solid State Ionics **11**, 293 (1984); Y. Yamamoto, K. Matsui, M. Wakahira and M. Taniguchi, Mat. Res. Bull. **18**, 1311 (1983).
55. R. Schöllhorn and W. Schramm, Z. Naturforsch. **34b**, 697 (1979).
56. M. Armand, Thesis, Université de Grenoble (1978).
57. P. Buller, Dissertation, Universität Münster (1984).
58. A.R. Ubbelohde, Intercalated Layered Materials, F. Lévy, ed., p. 1, D. Reidel, Dordrecht/Boston (1979).

59. D.W. Murphy and F.A. Trumbore, J. Electrochem. 123, 960 (1976).
60. R. Brec and G. Ouvrard, Solid State Ionics 9/10, 48 (1983).
61. P. Hagenmuller, J. Portier, B. Barbe and P. Bouclier, Z. anorg. allg. Chem. 355, 209 (1967); S. Kikkawa, F. Kanamaru and M. Koizumi, Inorg. Chem. 19, 259 (1980).
62. J.O. Besenhard, J. Heydecke, E. Wudy and H.P. Fritz, Solid State Ionics 8, 61 (1983).
63. R. Schöllhorn, Rev. Chim. Minérale 19, 534 (1982).
64. K.H. Cheng, A.J. Jacobson and M.S. Whittingham, Solid State Ionics 5, 355 (1981).
65. A. Grüttner, R. Nesper and H.G. von Schnering, Angew. Chem. 94, 933 (1982); Angew. Chem. Int. Ed. Engl. 21, 912 (1982).
66. M.S. Whittingham, R.R. Chianelli and A.J. Jacobson, Materials for Advanced Batteries, D.W. Murphy, J. Broadhead and B.C.H. Steele, eds., Plenum Press, New York (1980).
67. M.S. Whittingham, J. Electroanalytical Chem. 118, 229 (1981).
68. R.J. Colton, A.H. Guzman and J.W. Rabalais, Acc. Chem. Res. 11, 170 (1978); B.W. Faugham and R.S. Crandell, Display Devices, J. Pankove, ed., p. 181, Springer Verlag, Berlin/New York (1980).
69. T. Pagnier, M. Fouletier and J.L. Souquet, Mat. Res. Bull. 18, 609 (1983).
70. L. Heyne, Solid Electrolytes, S. Geller, ed., p. 169, Springer Verlag, Berlin/New York (1977).
71. C. Berthier, Y. Chabre, P. Segransan, P. Chevalier, L. Trichet and A. Le Mehauté, Solid State Ionics 5, 379 (1981).
72. J. Rouxel, Fast Ion Transport in Solids, P. Vashishta, J.N. Mundy and G.K. Shenoy, eds., p. 125, North Holland, Amsterdam (1979).
73. R.D. Armstrong, R.S. Bolmer and T. Dickinson, J. Solid State Chem. 8, 219 (1973).
74. U. Röder, W. Müller-Warmuth and R. Schöllhorn, J. Chem. Phys. 75, 412 (1981); 70, 2864 (1979).
75. F.R. Gamble, B.G. Silbernagel, J. Chem. Phys. 63, 2544 (1975); B.G. Silbernagel, M.B. Dines, F.R. Gamble, L.A. Gebhard and M.S. Whittingham, J. Chem. Phys. 65, 1906 (1976).
76. O.W. Johnson, Phys. Rev. 136, A284 (1964).
77. C. Ritter, W. Müller-Warmuth, H.W. Spiess and R. Schöllhorn, Ber. Bunsenges. Phys. Chem. 86, 1101 (1982).
78. W. Weppner, Materials for Advanced Batteries, D.W. Murphy, J. Broadhead and B.C.H. Steele, eds., p. 269, Plenum Press, New York (1980).
79. R. Schöllhorn and M. Kümpers, Mat. Res. Bull. 14, 1039 (1979).
80. R. Schöllhorn, Comments in Inorg. Chem. 2, 271 (1983).
81. M.B. Dines and R. Levy, J. Phys. Chem. 79, 1979 (1975).
82. J.V. Acrivos, C. Delios, N.Y. Topsoe and J.R. Salem, J. Phys. Chem. 79, 3003 (1975).
83. C. Riekel and R. Schöllhorn, Mat. Res. Bull. 11, 369 (1976).
84. G.V. Subba Rao and M.W. Shafer, J. Phys. Chem. 79, 557 (1975).
85. R. Schöllhorn and W. Schmucker, Z. Naturforsch. 30b, 975 (1975).
86. B.G. Silbernagel and M.S. Whittingham, J. Chem. Phys. 64, 3670 (1976).
87. G. Roth and K. Lüders, Physics of Intercalation Compounds, L. Pietronero and E. Tosatti, eds., p. 150, Springer Verlag, Berlin/New York (1981).
88. J.W. Johnson and A.J. Jacobson, Angew. Chem. 95, 422 (1983); Angew. Chem. Int. Ed. Engl. 22, 412 (1983).
89. R. Schöllhorn, R. Steffen and K. Wagner, Angew. Chem. 95, 559 (1983); Angew. Chem. Int. Ed. Engl. 22, 555 (1983).
90. C. Sourisseau, J.P. Forgerit and Y. Mathey, J. Solid State Chem. 49, 134 (1983).
91. D. Zagefka, Dissertation, Universität Münster (1980).
92. H. Eckert and R.H. Herber, J. Chem. Phys. 80, 4526 (1984).
93. R. Schöllhorn, E. Sick and A. Lerf, Mat. Res. Bull. 10, 1005 (1975).
94. D. Ghosh and D.D.L. Chung, Mat. Res. Bull. 18, 1179 (1983); 18, 727 (1983).
95. H. Tributsch, Solid State Ionics, 9/10, 41 (1983).