Preparation and Structure of Alkali Metal Intercalation Compounds

JEAN ROUXEL, L. TRICHET, P. CHEVALIER, P. COLOMBET, AND
O. ABOU GHALOUN

*Laboratoire de Chimie du Solide (L.A. au CNRS n° 279), Faculté des Sciences,
2 rue de la Houssinière, 44072 Nantes Cédex, France*

The preparation methods of intercalation compounds fall into four main groups: use of alkali metal solutions in liquid ammonia, organometallic reagents, electrochemical methods, and solid state processes. Each of these will be briefly described and a general comparison of the advantages and disadvantages will be made. Structural problems concern the positions occupied by the guest ions and their mobility from one site to one another in the host structure. The resulting ionic conductivity of the intercalation compounds depends on factors such as the ratio between available and occupied sites in the van der Waals gap, the ionicity of the bonds in the host structure, the site geometry, and the nature of the alkali metal.

The concept of the intercalation compound is not easy to define. Ions or molecules are accepted by a host lattice and generally result in geometric modifications manifested by a noticeable lattice expansion. This would be a classical process of insertion if it were not reversible. For intercalation compounds it must be possible to return reversibly to the initial state through appropriate electrical, thermal, or chemical actions. The definition of an intercalation compound assumes the idea of reversibility.

Some of the best host structures are to be found among solids with low dimensionality. Apart from the specific physical properties that these solids can show (Kohn anomalies, charge density waves, low-dimensional magnetism), they are basically chemical compounds with a high anisotropy in the chemical bonding. It is possible to find in the structure such units as $|MXn|$ arranged in slabs or fibers, in which there are strong iono-covalent bonds. The $|MXn|$ groups are linked in the structure by weak bonds, most of the time of the van der Waals type. The process of intercalation results in the pulling apart of those groups.

The intercalation species will be either very electropositive elements (alkali metal, for example) that will determine such ionization as $A^+ |MXn|^-$ and show a high mobility in the structure, or organic and inorganic molecules able to set weak bonds with the $|MXn|$ groups.

Preparation Methods of Alkali Metal Intercalation Compounds

(i) Use of Alkali Metal Solutions in Liquid Ammonia

Generally the use of alkali metal solutions in liquid ammonia leads to fast reactions and proves to be very interesting as it can be used for all alkali metals. On the other hand, it often leads to the fixing of ammonia which

one has to eliminate, and the working conditions are tricky. A good procedure consists of using, at room temperature, thick-walled sealed Pyrex tubes (1) with several branches allowing one, through chosen temperature gradients, to separate ammonia from the intercalated product and to prepare in situ the samples for X-ray analysis.

(ii) The Butyllithium Technique

In the case of lithium derivatives a solution of butyllithium in hexane serves as an excellent reagent to perform the intercalation. The use of butyllithium was first pointed out in the case of graphite intercalation compounds (2). It has recently proved to be also a mild and efficient reagent for intercalation in the case of transition metal chalcogenides (3, 4). The host structure is allowed to react with a diluted solution of butyllithium in hexane (0.2 M or less) and, if the reactor is cooled, there is no side reaction other than:

$$x\mathrm{C_4H_9Li} + \mathrm{host} \rightarrow \mathrm{Li}_x\mathrm{host} + \frac{x}{2}\mathrm{C_8H_{18}}.$$
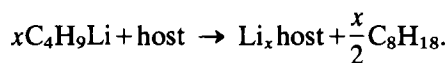
Other organometallic derivatives can be used, particularly in the case of sodium.

(iii) Solid State Reactions

In some cases such as A_xTX_2 derivatives of vanadium, niobium, and tantalum it is possible to heat weighed mixtures of the alkali metal with the metal dichalcogenides in evacuated quartz tubes for some days at 800°C (5). Mixtures of sulfides pressed in pellets can also be used. Ternary oxides can be allowed to react with H_2S or $H_2 + H_2S$.

(iv) Electrolysis

An electrolytic method, in which the host structure is used as the cathode, is a convenient way to intercalate hydrogen or alkali metals (6-8). The method has been intensively used in the case of sodium and lithium derivatives. The counter electrode was either a sodium one, which exhibits negligible polarization at the current densities employed in the investigation, or pure lithium metal (8). Alkali metal bronzes can also be used (8). The liquid electrolyte phase generally consists of a saturated solution of either sodium iodide or lithium perchlorate in propylene carbonate. Figure 1 shows a cell described by Steele (8).
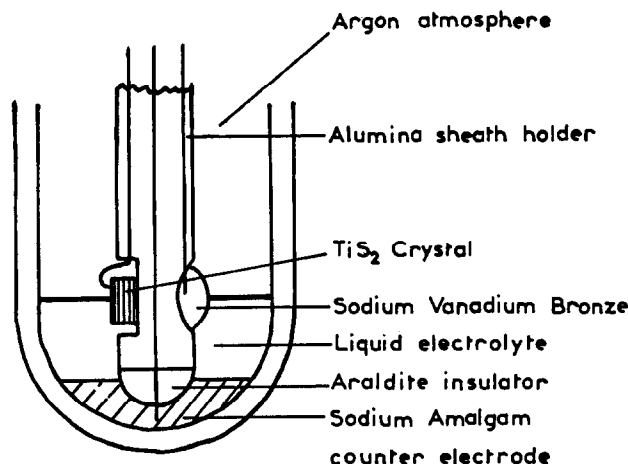

Argon atmosphere

Alumina sheath holder

TiS_2 Crystal

Sodium Vanadium Bronze

Liquid electrolyte

Araldite insulator

Sodium Amalgam counter electrode

FIG. 1. Electrolytic cell according to Steele (8).

(v) Redox Reactions in Alkali Halide Melts

Intercalation compounds such as $A_{0.5}TiS_2$ and $A_{0.5}NbS_2$ can be obtained by the reaction of TiS_2 and NbS_2 in alkali halide melts with H_2S in a flow reactor system at 800–1000°C as shown by Schöllhorn (9). The dichalcogenides are allowed to react with a 10-fold molar excess of alkali halide in an alumina crucible (Fig. 2).

(vi) Growth of Single Crystals

This problem has not yet been solved in a completely satisfying way. Single crystals of TiS_2, ZrS_2, or NbS_2 react with alkali metal solutions in liquid ammonia (10). Intercalation of the alkali metal occurs, but the crystallographic qualities of the crystals obtained in that way are very poor, particularly in the case of sodium (problems of two-phase domains) and also for the biggest alkali metals. Electrolytic methods lead to similar results. There is also a problem concerning the homogeneity of the intercalated crystals. The alkali metal diffuses from the edges of the crystals and it is always difficult to make sure that a complete homogeneous distribution in the bulk has been reached.

Reactions of layered transition metal disulfides with H_2S in alkali metal melts produce crystals, in thin platelets, of up to several millimeters in diameter (9). The problem in that case is to separate the crystals from the alkali halide matrix in which they are included. Washing with distilled water leads to hydrated phases.

(vii) In Situ Decomposition of Alkali Metal Derivatives

Lithium hydride reacts with a lamellar chalcogenide when a pellet of both compounds is heated at 900°C (10). NaN_3 can also be used for preparing sodium intercalation compounds (11). Hydrogen or nitrogen evolution is followed during the process.

(viii) Discussion

It appears that no method is utterly satisfactory. Each has its advantages and its limits. The use of alkali metal solutions in liquid ammonia allows one to cover the whole field of intercalation from lithium to cesium. It can readily be used to prepare nonstoichiometric phases, but the method presents experimental difficulties. For the smaller alkali metals, ammonia is often cointercalated with the metal, and the compounds require a thermal treatment in order to be ammonia free. Alkali metal solutions in liquid ammonia are powerful reducing solutions, and in the case of tellurides, polychalcogenides, and even some diselenides and disulfides (SnS_2, for example) a reduction of the host structure can occur.

The use of organometallic compounds is a convenient way to intercalate, but until now it has been proved to be really efficient only in the case of lithium. On the other hand this
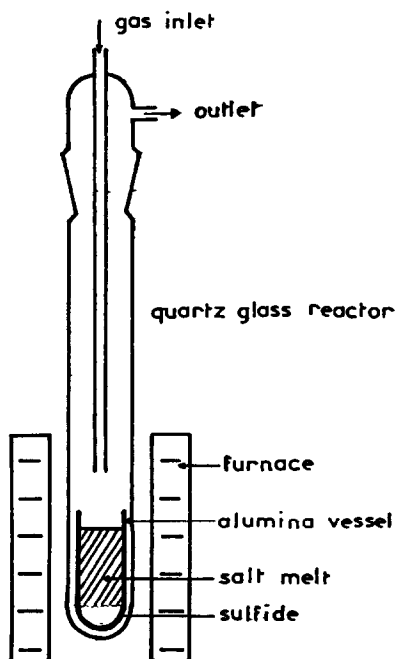

FIG. 2. The alkali halide process according to Schöllhorn (9).

method leads preferentially to the stoichiometric species.

Solid state reactions often undergo a reduction of the host structure. Homogeneous products are difficult to ascertain; however, the method has proved to be a convenient way to prepare $Na_x VS_2$ phases (*12*) since VS_2 did not then exist.

Electrointercalation involves electrolytic reduction in a suitable electrolysis cell using the dichalcogenide as cathode. The method is able to prove rapidly that intercalation really takes place. It allows one to prepare phases with a definite stoichiometry, but in the case of two-phase systems it can be difficult to recognize the phase limits. The method is also very sensitive to the stoichiometry of the host structure and this is probably related to kinetic aspects.

Redox reactions make it difficult to isolate anhydrous products. On removal of the alkali halide matrix by washing with distilled water, the ternary phases take up H_2O, and hydrated compounds are obtained.

The use of lithium hydride and of NaN_3 generally leads to inhomogeneous products.

The hydrogen or nitrogen pressure resulting from the decomposition creates experimental difficulties. Butyllithium has to be preferred to lithium hydride; however, NaN_3 can be a convenient way to prepare low-concentration sodium intercalation compounds (it is difficult, and it may be dangerous, to prepare the sodium-rich derivatives through this method).

Structural Problems: The A^+ Ions in the Host Structure

A great number of alkali metal intercalation compounds are now well characterized, especially in the case of transition metal dichalcogenides. It enables one to recognize the factors affecting the structure and chemical bonding in these compounds.

The alkali metal can occupy all the van der Waals gaps in the host structure (stage I compounds), only one out of two (stage II compounds), or one out of four (stage IV compounds). Its sulfur coordination can be either octahedral or trigonal prismatic (Fig. 3). It stems from three factors (*13*): the size
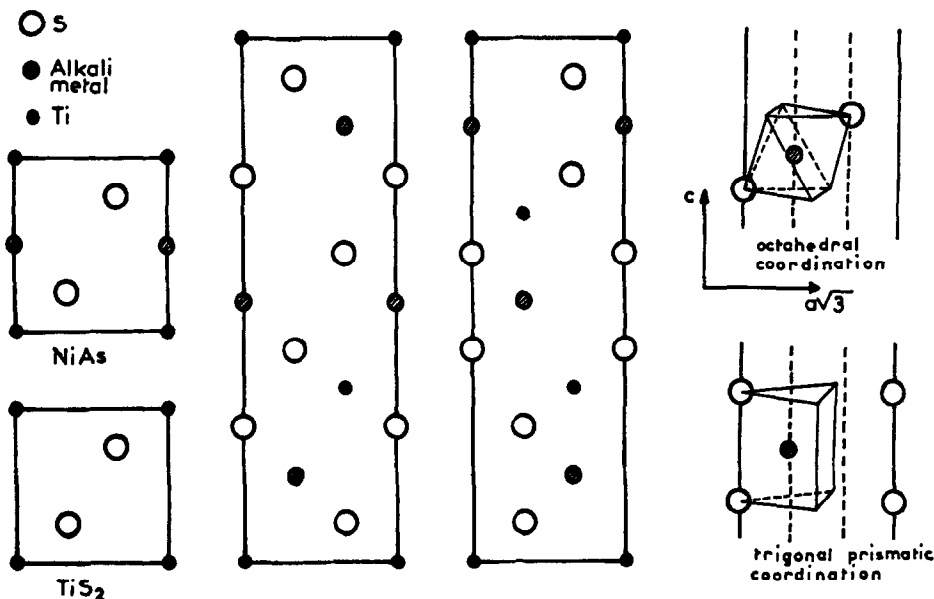

FIG. 3. Structural type for the intercalation compounds in a CdI_2-like host structure.

of the alkali metal, the amount of it, and the nature of the MX_2 slab of the host structure.

The influence and mutual relationship of these factors can be discussed according to the fact that an octahedron accommodates higher charges on the anions than a trigonal prism does (14). With a bigger alkali metal atom the sulfur layers are more distant and the trigonal prismatic structure is favored. The general ionization scheme $xA^+ \cdot MS_2^{x-}$ explains why for a given alkali metal the octahedral forms may appear for the higher values of x whereas the trigonal prismatic forms are obtained for the lower values of x. The last factor involves the covalency of the slabs of the host structure: ZrS_2, more ionic, favors the formation of the octahedral species, as compared to TiS_2. A general diagram concerning ionicity-structure in the intercalation compounds has been proposed (15). It takes into account the preceding factors and can be used in order to predict the structural types to be expected in a given series.

The repulsion between successive A^+ positive layers may be taken into account in order to explain the existence of stage II phases. Possibly the A^+ ions occupy at first more distant van der Waals layers thus lowering the repulsion. Toward these repulsions, the MS_2 slab of the host structure behaves as a screen. From this point of view

the $A_xTa_2S_2C$ phases are of some importance (16). The fact that no second-stage phases were observed in that case is probably related to the bigger screen effect due to a five-layer slab (S–Ta–C–Ta–S). It can be noticed that graphite with a very thin carbon slab is the most favorable case in which to observe multistage phases. Other factors such as the energy needed to pull apart the slabs have to be taken into account but we have experimental evidence that the screen effect of the slab plays an important role.

The band structure of the host chalcogenide seems also to play an important role in the kinetics of intercalation and in the stability of the products. Intercalation has been often found to be easier in chalcogenides with broad conduction bands (TiS_2, ZrS_2, $TiSe_2$) than in chalcogenides with narrow bands ($NbSe_2$, for example). This is probably due to a strong electron-electron repulsion in the half-filled dz^2 narrow band. Intercalation compounds formed with molybdenum dichalcogenides appear to be the most unstable: This can be related to the fact that the dz^2 band of the host structure is filled up (Fig. 4) and the electron lost by the alkali metal has to be accommodated in a higher level.

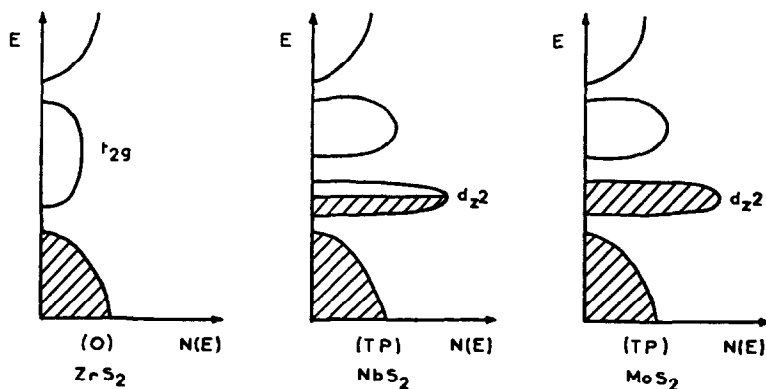In the lithium intercalates of transition metal lamellar oxyhalides, MOX, lithium is

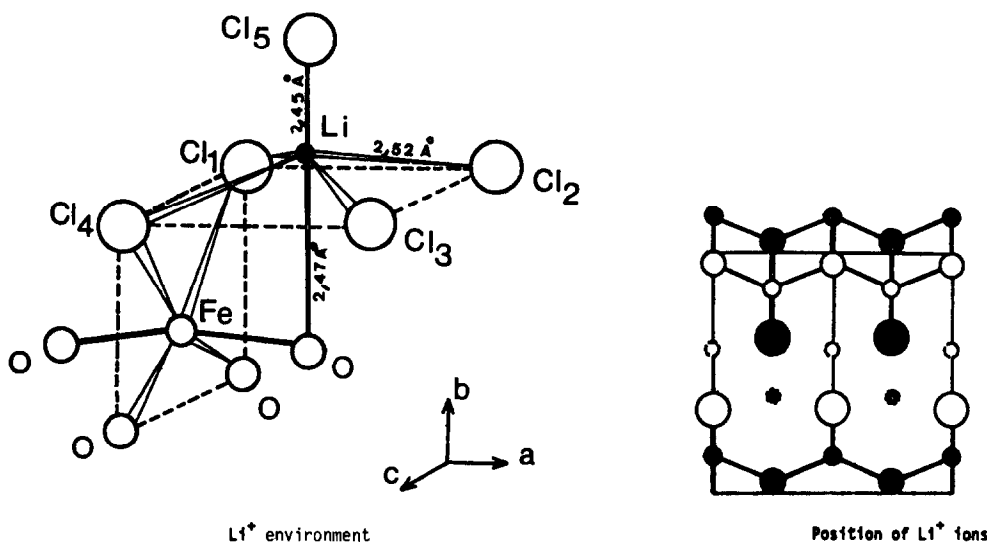FIG. 4. Band structure schemes for lamellar chalcogenides.

Li$^+$ environment   Position of Li$^+$ ions

FIG. 5. Position of Li$^+$ ions, Li$^+$ environment. Proposed structural model for Li–FeOCl intercalates.

probably located in octahedral positions according to site potential calculations (*17*, *18*). Figure 5 shows these positions in the FeOCl structure and it can be seen that the lithium–oxygen and lithium–chlorine distances would be in good agreement with the usual corresponding values (2.56 Å in LiCl and 2.30 Å in Li$_2$O). One lithium per unit cell is available under these conditions, as is also suggested by electrochemical studies. However, due to the poor quality of the X-ray spectra and the absence of parameter expansion, the chemical preparations through the butyllithium technique were not able to indicate the upper limit of intercalation and whether it takes place through a continuous mechanism or by steps.

The NiPS$_3$ structure is built up with slabs which are similar to the TiS$_2$ ones except that titanium has been replaced in the octahedral voids by nickel and P–P pairs with a ratio of $\frac{2}{3}$ and $\frac{1}{3}$ (Fig. 6). The formula may be expressed as Ni$_{2/3}$(P$_2$)$_{1/3}$S$_2$. At room temperature lithium is inserted in the octahedral sites up to the limit of Li$_{1.5}$NiPS$_3$ (*19*).

It should be noticed that according to the way they have been prepared the inter-

calation compounds can show significant structural differences, concerning mainly the stacking of the slabs. For example a 2H NaTiS$_2$ polytype is obtained by solid state techniques instead of the 3R compound provided by the liquid ammonia method.

In the case of lithium many structural results are not yet well understood. Despite the comparable size of the available octahedral sites one observes a parameter expansion in the direction perpendicular to the layer in some compounds (TiS$_2$), and no parameter evolution at all in other cases (NiPS$_3$).
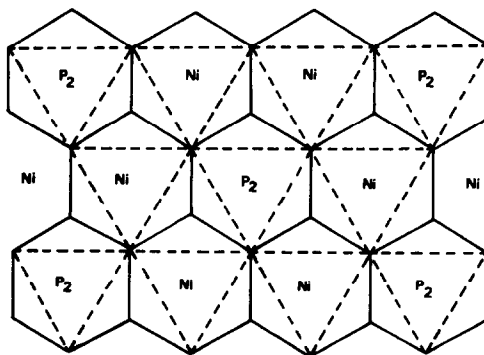

FIG. 6. The NiPS$_3$ slab (Ni $\frac{2}{3}$ (P$_2$) $\frac{1}{3}$ S$_2$).

A parameter evolution depends at least on two factors: a geometrical effect due to the size of the intercalated species, and an electrical effect due to the attraction between A^+ positive layers and MX_2^- negative slabs. The former would favor a parameter expansion that the latter would tend to compensate more or less. The geometrical effects being probably similar in each case the observed differences should be due to the second factor. Therefore it appears that the $|MXn|^-$ A^+ ionization scheme is a rough model. The nature of the band where the electrons lost by the alkali metal atoms are accommodated seems to play an important role, and one will have to consider at least a delocalization in a band resulting from the overlapping of metallic orbitals (in the heart of the slab) and a delocalization in a band involving partly anionic wave functions.

Recent results based on electrochemical experiments at low potentials have shown a lithium uptake exceeding the upper limits normally expected in relation to the occupancy of the octahedral holes in the host structure. This is the case of Li_2VSe_2 (20): An occupancy of at least part of the tetrahedral sites has to be considered. A similar behavior is not to be excluded in $NiPS_3$.

Structural Problems: The Mobility of the Intercalated Ions

Apart from the possibility of intercalating water or ammonia molecules in relation with the polarization power of the A^+ cation, the most important property of the intercalated ions is their mobility between the slabs of the host structure.

Some series of intercalated and substituted disulfides have been prepared with the general formula $A_xM'^{3+}_xM^{4+}_{1-x}S_2$ ($M' = $ In, Y, . . . ; $M = $ Zr, Sn, . . .). A substitution in the slabs has been performed at the same time as intercalation was made between the slabs according to the reaction:

$$xAM'S_2 + (1-x)MS_2 \rightarrow A_xM'_xM_{1-x}S_2.$$

This suppresses the electronic conductivity induced by intercalation and allows the study of ionic conductivity by means of complex impedance measurements and not only by the NMR technique. The $A_xM'_xM_{1-x}S_2$ has shown three structural models (Fig. 7): a $3R$ octahedral phase for the higher values of x, starting with $x = 1$ ($AM'S_2$), then a 2H phase with a trigonal prismatic coordination (a mixed trigonal prismatic–octahedral coordination could be possible in certain cases),
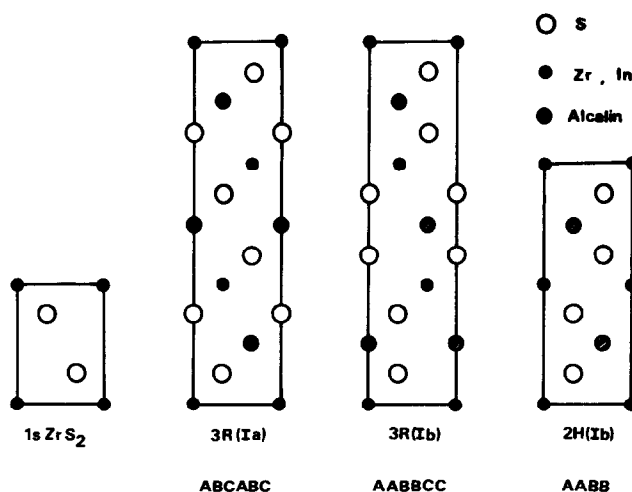

FIG. 7. Structural models for the $A_xM'_xM_{1-x}S_2$ compounds.

then a $3R$ trigonal prismatic phase. For a given series of compounds the nature of the M'^{3+} cation which has been introduced in the slabs of the host structure determines the relative width of these phases. According to the ionicity structure diagram of intercalates (15) the greater the fractional ionicity of the M'–S bond, the more the $3R$ octahedral species are stabilized.

Complex impedance measurements have been performed on different series of compounds. They have shown a strong dependence of the activation energy versus the structural type, the amount of intercalation, the nature of the alkali metal, and the covalency of the host structure.

In a given series of compounds the activation energy can change considerably with x, that is to say, with the ratio of occupied and available sites in the van der Waals gap. The best example is given by the $Na_xY_xZr_{1-x}S_2$ system, where the strong electropositive character of yttrium stabilizes a $3R$ octahedral phase over a wide range of compositions $(0.30 < x \leqslant 1)$. Figure 8 shows the evolution of the activation energy as a function of x.

The effect of the covalency of the host structure can be seen by comparing different compounds presenting the same structure, the same alkali metal, and the same value of x, but different slab components: The greater
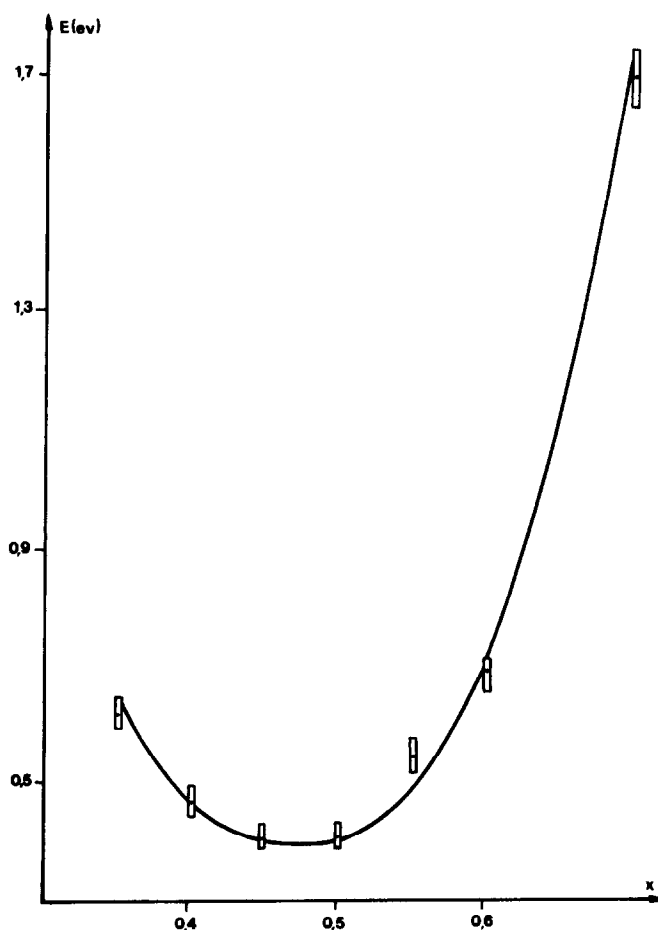

FIG. 8. Activation energy versus x in $Na_xY_xZr_{1-x}S_2$ octahedral phase.

the fractional ionicity of the M'–S or M–S bonds, the higher the activation energy. Similar conclusions have been drawn by Hagenmuller and co-workers in the case of the isostructural lamellar oxides (21).

The activation energy is generally found to be lower in trigonal prismatic sites than in octahedral sites: 0.28 eV in $Na_{0.80}In_{0.80}Zr_{0.20}S_2$ with the $3R$ octahedral form but 0.23 and 0.22 eV, respectively, in $Na_{0.50}In_{0.50}Zr_{0.50}S_2$ and $Na_{0.35}In_{0.35}Zr_{0.65}S_2$, both compounds presenting trigonal prismatic sites for the alkali metal.

All these factors are strongly correlated and the contribution of each of them cannot be clearly known at every moment: For example, the site geometry acts upon the activation energy but we shall notice that at the same time the ionicity of the structure is lower in trigonal prismatic structures than in octahedral forms. Furthermore, concerning this example, the symmetry of the electrical field gradient evolues with x; Fig. 9 shows the evolution of the quadrupolar broadening as a function of x in the $3R$ octahedral phase $Na_xIn_xSn_{1-x}S_2$ ($0.68 < x \leqslant 1$). This can be

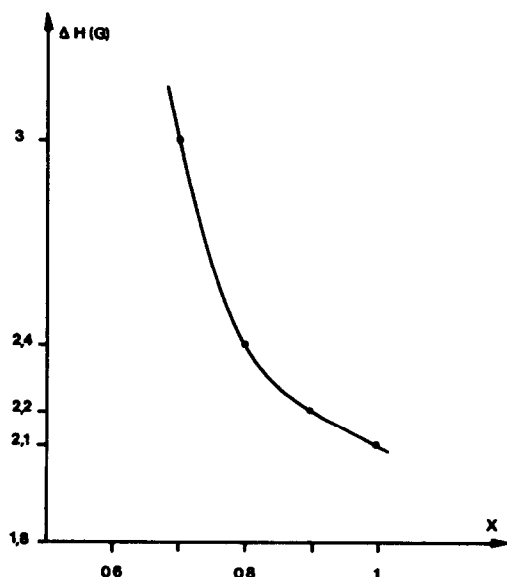related to a distortion of the site or to a nonisotropic effect due to a disorder between In and Sn, second neighbors in the slabs. In any case it will probably act upon the ionic mobility. The expected evolution according to one factor can be overwhelmed by the effect of another one.

The nature of the alkali metal has also to be considered. Whereas lithium is often the most favorable case in sulfides, sodium can present lower activation energies in selenides. It seems that the polarization power of the alkali metal plays an important role. The activation energy may take into account an increasing part of the energy of the A–S bond. Small dipolar complexes $A^{\delta+} - X^{\delta-}$ are probably formed, that have to be broken. This could also explain why, for the same alkali metal, the activation energies may be higher in selenides than in sulfides or oxides whereas the site potentials decrease at the same time.

NMR measurements lead to much lower values of activation energy. The results obtained for the $Na_xY_xZr_{1-x}S_2$ ($3R$ phase) are given in Table I and can be compared with the complex impedance measurements shown in Fig. 8. The values are substantially lower than those measured by the complex impedance technique except for $x = 0.50$. The most favorable case for a long-range diffusion. The NMR activation energies, derived from the T_1 dependence versus temperature, correspond to a self-diffusion activation energy from site to site. They

FIG. 9. Evolution of quadrupolar broadening with x in $Na_xIn_xSn_{1-x}S_2$.

TABLE I

NMR ACTIVATION ENERGIES
IN $Na_xY_xZr_{1-x}S_2$

x	E (eV)
0.35	0.47
0.40	0.44
0.45	0.42
0.50	0.44
0.70	0.46

strongly depend on the ionicity of the bonds in the layers, for the ionicity fixes the effective charge on the anions and the height of the potential barrier: 0.23 eV for $Na_{0.70}In_{0.70}Zr_{0.30}S_2$ but 0.46 eV for $Na_{0.70}Y_{0.70}Zr_{0.30}S_2$. If we consider the results obtained for the $Na_xY_xZr_{1-x}S_2$ series (Table I) we observe no significant variation, which is probably the result of a slight difference of ionicity between the Y–S and Zr–S bonds and also of an increase of the unit-cell volume (251 $Å^3$ for $x = 0.30$ and 271 $Å^3$ for $x = 1$) which compensates the preceding effect.

Other factors have also to be considered, particularly the disorder effect due to the random distribution of the M'^{3+} cations among the metallic sites of the slabs. This disorder should increase the ionic mobility (22).

A better diffusion is observed in chalcogenides with a broad conduction band. The lower values obtained in NbS_2 as compared to TiS_2 may be related to a poorer electronic conductivity. The electronic delocalization, as in many other series, seems once more to favor the ionic diffusion.

Conclusion

Most of the alkali metal intercalation compounds have been shown to be both good ionic and good electronic conductors. These remarks along with a charge–discharge mechanism involving intercalation and desintercalation of the A^+ ions enable one to use lamellar chalcogenides as cathodes in batteries. The structural aspects are now well known in most of the cases and some factors favoring ionic mobility have been recognized as shown in this paper.

The problems concerning the electron lost by the alkali metal are not so clear. It has been supposed that this electron is delocalized in the conduction band of the host structure. However, it has recently been shown that a partial localization on certain

sites is possible: This is, for example, the case of $NiPS_3$ intercalates, where electrons are partly trapped on P–P pairs (23). The question arises also whether the band structure of the host is modified or not during intercalation. The ability to intercalate seems also to be strongly related to the position of the conduction band (MoS_2), its width, its population (compare TiS_2 and NbS_2), and the initial gap between valence band and conduction band (24).

References

1. J. Cousseau, L. Trichet, and J. Rouxel, Bull. Soc. Chim. Fr. 3, 872 (1973).
2. M. Armand, in "Fast Ion Transport in Solids" (W. Van Gool, Ed.), North-Holland, Amsterdam (1973).
3. M. B. Dines, Mater. Res. Bull. 10, 287 (1975).
4. D. Murphy, F. Di Salvo, G. Hull, and J. Waszczak, Inorg. Chem. 15, 17 (1976).
5. W. P. F. A. M. Omloo and F. Jellinek, J. Less Common Metals 20, 121 (1970).
6. D. W. Murphy, F. Di Salvo et al., J. Chem. Phys. 62, 967 (1975).
7. S. Whittingham, J. Chem. Soc. Chem. Commun. 328 (1974); J. Electrochem. Soc. 123–3, 315 (1976).
8. D. A. Winn, J. M. Shemilt, and B. C. H. Steele, Mater. Res. Bull. 11, 559 (1976).
9. R. Schöllhorn and A. Lerf, J. Less. Common Metals 42, 89 (1975).
10. L. Trichet, M. Danot, and J. Rouxel, unpublished work.
11. M. Armand and R. Brec, unpublished work.
12. G. A. Wiegers, R. A. van der Meer, H. Van Heinigen, H. J. Kloosterboer, and A. J. A. Alberink, Mater. Res. Bull. 9, 1261 (1974).
13. A. Le Blanc, M. Danot, L. Trichet, and J. Rouxel, Mater. Res. Bull. 12, 345 (1977).
14. R. Huisman, R. de Jonge, C. Haas, and F. Jellinek, J. Solid State Chem. 3, 56 (1971).
15. J. Rouxel, J. Solid State Chem. 9, 358 (1974).
16. R. Brec, J. Ritsma, G. Ouvrard, and J. Rouxel, Inorg. Chem. 16, 660 (1977).
17. P. Palvadeau, L. Coïc, and J. Rouxel, Mater. Res. Bull. 13, 221–227 (1978).
18. P. Palvadeau, M. Armand, L. Coïc, and J. Rouxel, J. Power sources, in press.
19. R. Brec, A. le Mehaute, G. Ouvrard, and J. Rouxel, Mater. Res. Bull. 12, 1191 (1977); A. H. Thompson and M. S. Whittingham, Mater. Res. Bull. 12, 741 (1977).

20. M. S. WHITTINGHAM, *Mater. Res. Bull.* **13**, 959 (1978); D. W. MURPHY AND J. N. CARIDES, to be published.

21. C. DELMAS, C. FOUASSIER, J. M. REAU, AND P. HAGENMULLER, *Mater. Res. Bull.* **11**, 1081 (1976).

22. P. HAGENMULLER, personal communication.

23. C. BERTHIER, R. BREC, G. OUVRARD, AND J. ROUXEL, to be published.

24. D. SCHLEICH, R. BREC, G. OUVRARD, AND A. LOUISY, *Ann. Chim.* in press.