Trigonal Prismatic or Octahedral Surrounding in Sheet Oxides?

Claude Delmas*, Jean-Jacques Braconnier, Claude Fouassier, and Paul Hagenmuller
Laboratoire de Chimie du Solide de CNRS, Université de Bordeaux I, 351, cours de la Libération, 33405 Talence Cedex, France

Dedicated to Prof. Dr. k. c. Oskar Glemser on the occasion of his 70th birthday
Z. Naturforsch. 36b, 1368–1374 (1981); received May 20, 1981

Layer Oxides, Intercalate, Trigonal Prismatic of Octahedral Surrounding

According to the oxygen packing two types of alkali ion surroundings (octahedral or trigonal prismatic) are possible in the $A_2MO_3$ sheet oxides or the related $A_2MO_4$ compounds. The stability of both environments is discussed from the geometrical and electrostatic view points. Structural transitions to metastable forms can be induced by high pressure, intercalation, desintercalation or exchange reactions. The possibility of room temperature transformations can be anticipated from the relationships between the various oxygen packings.

Introduction

While during the last decade the layer chalcogenides $A_2MX_2 (X = S, Se, Te) (x < 1)$, in which $A$ is an alkali ion and $M$ a transition element, have been intensively studied [1–5], only a small number of publications has been devoted to the homologous oxides [6–9]. All the structures can be schematically described from sheets containing a layer of metal atoms $M$ sandwiched between two layers either of chalcogen or of oxygen. The alkali ions are inserted (or intercalated) between two neighbouring slabs. Within the sheets the bonds are strongly covalent; on the contrary the alkali ion-divalent anion bonds are comparatively weak and allow ionic transport or easy slab gliding.

Due to sheet shifting the alkali ion surrounding may change. The purpose of this paper is to discuss the various types of environment from the crystal chemistry point of view.

While in chalcogenides the relatively small repulsion between two adjacent chalcogenide layers allow a binary $MX_2$ composition, in oxides the higher ionic character of the $M$-$O$ bonds requires $x > 0.5$. This remark implies that only stage I compounds may be obtained in oxides, in other words materials containing alkali ions in each sheet gap.

Crystal Chemistry

In the reviewed materials $M$ stands for a transition metal with two different oxidation states or for a mixture of tetravalent and trivalent (or divalent) elements. Fig. 1 summarizes the composition of some of them obtained in this laboratory by high temperature solid state reactions [6, 7, 10].

As shown in Fig. 2 the various structural types differ by the oxygen packing and by the alkali ion surrounding: trigonal prismatic (P) or octahedral (O). In the last case the structure anisotropy leads actually to a trigonal antiprismatic environment. To describe the various structural type the following notation is used. The letter P or O indicating the alkali ion surrounding is followed by a number indicating how many $(MO_2)_n$ sheets are in the unit cell. The ideal symmetry of these structures is...
always hexagonal or trigonal. When a crystallographic distortion occurs the symbol prime is added.

The ABCABC (O3) oxygen packing

This structural α-NaFeO₂ type can be considered as an ordered NaCl structure due to size and charge difference between A⁺ and M³⁺ ions. It is generally found for x ≈ 1. When the size difference between the cations is too large, the layer structure is no more stable and a 3D-structure related to high temperature cristobalite is obtained. It is the case for instance for KFeO₂ [11], β-KCoO₂ [12] . . .

For alkali ion deficient phases (x = 0.75) a strong monoclinic distortion may be observed:
N₈₀₋₇₅M₅₀₂₀/₃[13],
K₂CrO₂(O’3) (0.70 < x < 0.77) [14].
These last phases are isostructural with the Jahn-Teller distorted α-NaMnO₂ [13] and NaNiO₂ [15].

This structural type (O3) is very common in chalcogenides, particularly for large alkali ions [16].

The ABBCCA (P3) oxygen packing

In this structure alkali ions are inserted in trigonal prisms, which share one face with one MO₆ octahedron and three edges with three other MO₆ octahedra belonging to the other sheet (Fig. 2). The number of prisms is twice that of the formula units. All prisms are energetically equivalent, as a result the alkali ions are statistically distributed in them. As in chalcogenides this structural type is always obtained for phases with high vacancy content, so that the repulsion between opposite anions of the prisms is limited by larger distance of the adjacent sheets [6, 16].

The ABBA (P2) oxygen packing

As in the previous layer structure type, alkali ions occupy trigonal prismatic sites. There are two different types of prisms available which are sche-

Fig. 2. Various types of packings in layer oxides.

Fig. 3. a- and b-type trigonal prisms in a P2 type phase.
bouring a- and b-sites cannot be occupied simultaneously.

These remarks explain why in the stoichiometric layer phases \( \beta \text{-RbScO}_2 \) [17], \( \text{CsLnO}_2 \) [18], \( \text{TlInS}_2 \) [19] the monovalent ions lie only in the b-sites. In non-stoichiometric phases (oxides or chalcogenides) both sites can be occupied. The distribution has been studied by X-ray profile analysis of \( \text{K}_{0.72} \text{(In}_{0.72} \text{Sn}_{0.28}) \text{O}_2 \) [20] and by a NMR study of \( ^{23} \text{Na} \) in \( \text{Na}_x \text{(In}_{x} \text{Sn}_{1-x}) \text{S}_2 \) [21]. It should be noted that the NMR study on P2-type oxides has been so far impossible due to their high ionic character: because of the very strong quadrupole splitting the NMR absorption line disappears.

The P2-type is frequently observed in substituted intercalated dichalcogenides \( \text{A}_x \text{M}_{a;III} \text{M}_{x;IV} \text{X}_2 \) studied by J. Rouxel's group [21-23]. It is not observed in true intercalation compounds \( \text{A}_x \text{M}_{x;IV} \text{X}_2 \), if we except the high temperature forms of \( \text{NaTiS}_2 \) and \( \text{NaTiSe}_2 \) [24]. This difference in behaviour will be discussed in a following section of this paper.

**Remark**

The AB (O1) type of oxygen packing, which is very common for the lithium chalcogenides \( \text{Li}_x \text{MX}_2 \) does not appear in homologous lithium oxides. In such lattices related to NiAs-type, \( \text{Li}_x \text{Li}_x \) and \( \text{MX}_x \) octahedra share faces along the c axis. Consequently it is observed only when the host lattice is predominantly covalent, which reduces the interface cation-cation repulsion. Furthermore ternary lithium oxides are generally observed for \( x = 1 \). Would the O1-type exist for \( \text{LiMO}_2 \) oxides, the number of \( \text{Li}^+ - \text{M}^{3+} \) interactions through common faces would be very high.

Nevertheless for the P3- and P2-type oxides a large deviation from the third Pauling’s rule occurs. It should be noticed that in this case, phases are always non-stoichiometric and cannot be obtained for small alkali ions such as lithium.

**Classification**

Because of the electrostatic repulsion between adjacent oxygen layers trigonal prismatic surrounding is generally observed for large size alkali ions, small fractional occupancy and prevailing covalent host lattices.

From these criteria it is possible to classify the layer oxides in an ionicity-structure diagram analogous to Rouxel's diagram [25]. The radius of the alkali ion \( (R_{A^+}) \) is plotted vs the \( f_{A-O} \cdot f_{M-O} \) product, in which \( x \) is the alkali content, \( f_{A-O} \) the ionicity of the A-O bond and \( f_{O-M} \) that of the M-O bond. Such a product characterizes the charge distribution.

![Fig. 4. Classification of the \( \text{A}_x \text{MO}_2 \) in a \( R_{A^+} \) vs \( x f_{A-O} f_{M-O} \).](image)
carried by the anionic layers. As shown in Fig. 4, both types of surroundings are well separated [6].

Every phase represented in this diagram is a stable variety obtained by high temperature solid state reactions. It is worthwhile to study what happens under certain metastable preparation conditions. Transitions between trigonal prismatic and octahedral surroundings can be observed either by a horizontal displacement in the diagram (i.e. intercalation or desintercalation) or by a vertical displacement (i.e. exchange reactions). Another way to modify the distance between oxygen layers of adjacent sheets is indeed to apply pressure on a layer oxide containing a large size alkali ion.

**Influence of Pressure**

This study has not been undertaken on A$_2$MO$_2$ phases, but on A$_2$MO$_3$ phases whose structure is related to those of layer compounds.

Most of the A$_2$MO$_3$ phases show a layer type structure (O3) with the formulation A(A$_{1/3}$M$_{2/3}$)O$_2$. For a large cation size difference A$_2$MO$_3$ compounds crystallize under normal pressure with the K$_2$ZrO$_3$-type structure (1D) [26]. When M = Zr, Hf, Sn, Pb layer structures can be obtained under high pressure. Table I summarizes the various structural types obtained vs temperature and pressure. At 70 kb pressure the P2-type structure is obtained. An increase in pressure or temperature does not modify the packing of the most covalent phases (M = Sn, Pb). On the contrary layer phases with octahedral environment of the alkali ions are observed for the more electropositive tetravalent ions, which is the consequence of the increased repulsions between oxygen layers [27].

**Intercalation or Desintercalation**

The intercalation or desintercalation properties of layer dichalcogenides have been intensively investigated during the last five years. The possibility of application of the chalcogenides as cathodes in room temperature secondary batteries has stimulated the research effort in this field [1–5]. The homologous oxides do not seem to be so attractive from the point of view of the application.

As the MO$_2$ layer oxides do not exist as starting materials only two ways can be explored: desintercalation from AMO$_2$ and intercalation or desintercalation form A$_2$MO$_3$. The A$^+$ ions can be partially removed from the host lattice chemically or electrochemically. However the high oxidation power of the layer oxides and their relative instability restrict the use of chemical desintercalation.

From LiCoO$_2$ (O3) Goodenough et al. have removed nearly all the lithium present down to Li$_{0.7}$Co$_{0.3}$O$_2$, but this cathode shows a good reversibility only for 0.5 < x < 1. In this composition range the O3 structural type is preserved [8].

The behaviour of the Na$_2$CoO$_2$ phases is much more complicated, as four structural types exist in this system (Fig. 1).

When one of the phases P$'$3, O$'$3 or O3 is used as cathode two others appear during charge or discharge [28]. As Na$_2$CoO$_2$ can be slightly oxygen deficient the composition of the pure P$'$3, O$'$3 and O3 phases are correlated with the number of oxygen vacancies. Fig. 5 shows the e.m.f. vs composition curve obtained from Na$_{0.7}$CoO$_{1.72}$. As shown in Fig. 2 the structural difference between O3 and P$'$3 consists of a slippage of the second and third (CoO$_2$)$_n$ sheets within the unit cell. To illustrate this

---

**Tab. I. Various structural types of K$_2$MO$_3$ compounds vs temperature and pressure.**

<table>
<thead>
<tr>
<th>K$_2$MO$_3$</th>
<th>K$_4$TiO$_3$</th>
<th>K$_2$ZrO$_3$</th>
<th>K$_2$HfO$_3$</th>
<th>K$_2$SnO$_3$</th>
<th>K$_2$PbO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 °C, 1 bar</td>
<td>Normal pressure variety</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 °C, 70 kb</td>
<td>K$^\text{Pr.}$ (K$<em>{1/3}$M$</em>{2/3}$)$_2$ O$_2$ (P2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 °C, 110 kb</td>
<td>K$^\text{Oct.}$ (K$<em>{1/3}$M$</em>{2/3}$)$_2$ O$_2$ (O3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800 °C, 70 kb</td>
<td>(K$_{2/3}$M$^{4+}$)$_2$ O$_2$ (NaCl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

($R_K + R_M 4+$) (Å) | 0.78 | 0.66 | 0.67 | 0.69 | 0.61 |

f$_{1M-O}$ | 0.63 | 0.67 | 0.70 | 0.51 | 0.51 |
behaviour the spectra of all phases can be indexed in the monoclinic system. The monoclinic $a$ axis is parallel to the (1120) plane of the hexagonal unit cell, which is the direction of shear (Fig. 6). The O'3 phase can be considered as intermediate between the two others during gliding.

When the Na$_{0.7}$CoO$_{1.9e}$(P2) phase is used as cathode material the P2 structural type is preserved over the whole composition range 0.46 < $x$ < 0.83. The P2 structure differs from that of the P3 or O3 phases not only by sheet shifts, but also by a $\pi/3$ rotation of all CoO$_6$ octahedra of the second sheet within the unit cell. This means that a structural transition between P2 and P3 or O3 would require a Co–O bond breaking. As a result the P2 structural type is maintained during the whole electrochemical process.

Concerning chromium and nickel oxides only NaM0$_2$ can be obtained by high temperature solid state synthesis. The sodium desintercalation of both materials has been recently studied either electrochemically or chemically and for the first time Na$_x$CrO$_2$ and Na$_x$NiO$_2$ phases have been obtained [29]. A P3-type phase has been prepared from NaCrO$_2$ (O3), while in the nickel system a P'3-type phase in obtained from NaNiO$_2$ (O'3).
The behaviour of these new intercalation oxides must be compared to that of the chalcogenides. For the latter during the intercalation or the desintercalation the reversible transitions \( \text{O1} \rightarrow \text{P3} \rightarrow \text{O3} \) are observed with increasing \( x \) [30, 32]. It should be noticed that the intermediate phase \( \text{O3} \) has never been obtained for chalcogenides. As previously discussed the \( \text{O1} \)-type is not observed in oxides even under metastable form.

While chalcogenides are true intercalation compounds, oxides can be considered as insertion-intercalation compounds because a small alkali ion content is always necessary between the sheets to stabilize the layer structure.

From the previously related results it is worthwhile to discuss the existence of the \( \text{P2} \) structural type in chalcogenides. The intercalated chalcogenides are generally prepared by low temperature intercalation from \( \text{MX}_2(\text{O1}) \) or desintercalation from \( \text{AMX}_2(\text{O1} \text{ or } \text{O3}) \). \( \text{P2} \)-type has never been obtained by such elaboration methods. It is observed for oxides \( \text{A}_z\text{M}_x\text{O}_y \) (\( \text{A} = \text{Na}, \text{K} \)), \( \text{NaTiS}_2 \) [24] and substituted intercalated compounds \( \text{Na}_z\text{M}_{1-x}\text{M}_x^\text{III} \text{S}_{2x} \text{S}_2 \) studied by Rouxel \textit{et al.} [21, 22], but they are all prepared by high temperature solid state reactions. For the \( \text{Na}_z\text{M}_{1-x}\text{M}_x^\text{III} \text{S}_{2x} \text{S}_2 \) phases during the synthesis the starting sheets \( \text{M}^\text{IV}_2 \text{S}_2 \) and \( (\text{M}^\text{III} \text{S}_2)^{-} \) are destroyed and the most stable phase is obtained. It is possible that for intercalation compounds \( \text{A}_x\text{MX}_2 \) the investigated phases are metastable, so that \( \text{P2} \)-type cannot be obtained at low temperature, as it supposes an atomic rearrangement.

**Exchange Reactions**

Generally exchange reactions are used as a synthesis way of isostructural materials. Keeping in mind that trigonal prismatic environment cannot exist for lithium (Fig. 4) and that a structural transition between \( \text{P2} \) on one hand and \( \text{O1} \), \( \text{P3} \) or \( \text{O3} \) on the other hand is impossible at room temperature, the exchange reaction Li\(^+\)/Na\(^+\) from a Na\(_2\)M\(_2\)O\(_2\) (\( \text{P2} \)) phase can lead to a new layer structural type.

Such a reaction has been realized from Na\(_{0.7}\)CoO\(_2\) (\( \text{P2} \)) and has led to a new variety of LiCoO\(_2\) [33]. Because of the very strong oxidizing power of Co\(^{IV}\) in lithium layer oxides a redox reaction with the exchange solution occurs and LiCoO\(_2\) is obtained instead of Li\(_{0.7}\)CoO\(_2\). In this new structure LiO\(_2\) octahedra share a face with one CoO\(_2\) octahedron and three edges with three other octahedra belonging to the next sheet. Accordingly this phase is metastable and gives the usual LiCoO\(_2\) variety (\( \text{O3} \)) by heating at 250 °C.

---

[29] J. J. Braconnier, C. Delmas, and P. Hagenmuller, id., to be published.
[33] C. Delmas, J. J. Braconnier, and P. Hagenmuller, id., to be published.