

Structural Relationships in Close-Packed AB_2O_4 Oxides Involving Spinel, Olivine, and Hexagonal $LiFeSnO_4$ Structures

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Close-packed structures with formula AB_2O_4 were studied in terms of polyhedra arrangement. The junction between octahedral layers (kagome) and mixed (octahedral and tetrahedral) layers were analyzed; this association allows one to determine two types of double layers whose packing leads to three closely related structural types: spinel, double-hexagonal $LiFeSnO_4$, and a hypothetical hexagonal structure. Olivine structure shows a polyhedral arrangement closely related to those of these three structures and can be described alike in terms of mixed layers and double layers. AB_2O_4 close-packed oxides can exhibit polymorphism; from this analysis a mechanism, involving geometrical operations applied to the double layers, is proposed for the different transitions, really observed as (DH) $LiFeSnO_4$ spinel and olivine—spinel or theoretical as (DH) $LiFeSnO_4$ —hypothetical hexagonal and olivine—hypothetical hexagonal.

Introduction

Close-packed oxides corresponding to the AB_2O_4 formulation can exhibit a polymorphism according to the experimental conditions. This is the case of several silicates A_2SiO_4 for which an olivine—spinel transition has been observed (1). Recently, a new structural type, characterized by a double-hexagonal close-packing of the oxygen atoms (ABAC), has been isolated for $Sn_{2.8}Li_{1.6}M_{1.6}O_8$ ($M = Zn, Mg$) (2) and for the low-temperature form of $LiFeSnO_4$ (3). Moreover, our study of the antimonates $Li_2Cr_{3-x}M_xSbO_8$ (4) has shown a double hexagonal—spinel transition. In order to explain the mechanism of these transitions, it was thus necessary to compare the three structural types olivine, spinel, and double

hexagonal. Thus the present work deals with the comparative analysis of these structures, but unlike the descriptions generally made for close-packed structures, we have taken into consideration the polyhedra arrangements.

Spinel and Double Hexagonal: Analysis and Structural Principles

The spinel and the double-hexagonal (DH) $LiFeSnO_4$ structures are both characterized by a close-packing of the oxygen atoms, the sequence of the stacking being (ABCABC) along $\langle 111 \rangle_S$ in the former and double hexagonal, i.e., (ABAC) along $\langle 001 \rangle_{(DH)}$ in the latter. In both structures, the cationic lattices are closely related: the occupancy factors of the different sites are the



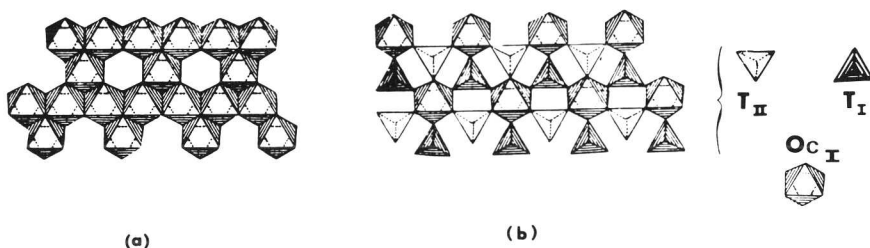


FIG. 1. (a) $[Oc_3]$, kagome octahedral layer. (b) $[Te_2Oc]$, mixed layer.

same for the two structures— $\frac{1}{2}$ for the octahedral sites and $\frac{1}{8}$ for the tetrahedral sites—and their arrangements both correspond to those observed for Laves phases—i.e., C_{14} -type $MgZn_2$ for (DH) $LiFeSnO_4$ and C_{15} -type $MgCu_2$ for spinel (3).

Octahedral and mixed layers. Although these oxides cannot be considered as forming layer structures, they can be described as the stacking of two sorts of layers of polyhedra: cation-deficient octahedral layers (Fig. 1a), whose cationic lattice is called kagome (5), and which will be denoted $[Oc_3]$, and mixed layers built up from corner-sharing octahedra and tetrahedra (Fig. 1b), denoted $[Te_2Oc]$.

Layers junction. Both structures, being built up from the alternate stacking of identical $[Oc_3]$ and $[Te_2Oc]$ layers, will differ from the other only by the junction of these layers. This junction, which results from the sharing of the corners of the polyhedra belonging to two successive layers, i.e.,

one $[Oc_3]$ and one $[Te_2Oc]$ layer, can be characterized by taking the kagome window (Fig. 1a) of the $[Oc_3]$ layer into consideration.

An (ABC) stacking of three oxygen layers will be obtained by blocking a kagome window with a tetrahedron (Fig. 2); this junction, in which one tetrahedron T shares three corners with the octahedra of the kagome window, will be denoted $J_{K/T}$. An (ABA) stacking of three oxygen layers will be realized by blocking the kagome window with an octahedron (Fig. 3); this junction, which corresponds to an octahedron sharing its corners with those of the kagome window, will be denoted $J_{K/O}$.

Using these two types of junctions, it can easily be seen that the spinel structure which involves an (ABC ABC) stacking of the oxygen atoms will only be characterized by $J_{K/T}$ -type junctions, while the (DH) $LiFeSnO_4$ structure, which corresponds to an (ABAC) stacking of the oxygen atoms,

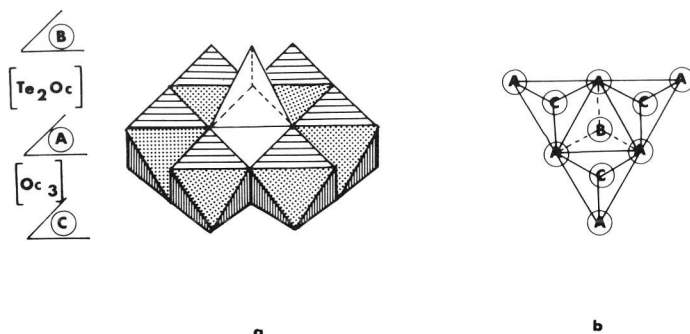


FIG. 2. (a) Kagome window blocked with a tetrahedron in a $J_{K/T}$ junction. (b) Projection of the corresponding close-packed oxygen layers (ABC).

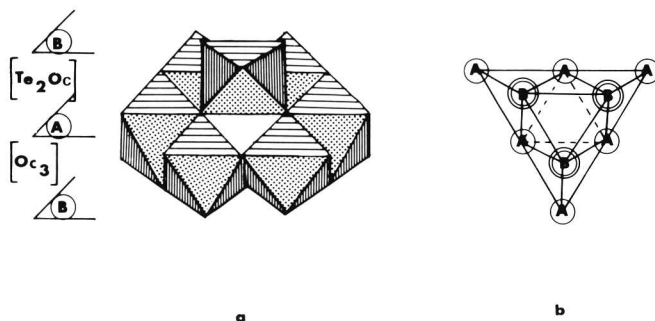


FIG. 3. (a) Kagome window blocked with an octahedron in a $J_{K/O}$ junction. (b) Projection of the corresponding close-packed oxygen layers (BAB).

will exhibit alternately a $J_{K/T}$ and a $J_{K/O}$ junction.

Double layers: D.L. Since in both structures, two successive layers are always, respectively, an $[Oc_3]$ and a $[Te_2Oc]$ layer, it seems useful to describe these structures from double layers $[Oc_3Te_2Oc]$. Due to the two types of junctions between two successive layers, two types of double layers are obtained: the double-layer "S," characterized by the $J_{K/T}$ junction (Fig. 4), the only one observed in spinels, and the double-layer "H," characterized by the $J_{K/O}$ junction (Fig. 5), observed only in the hexagonal structure.

Double-layers junction. The double-layers junction is ensured, like for the single layers, by $J_{K/T}$ or $J_{K/O}$ junctions.

Considering only the association of identical double layers, "H" or "S," through identical junctions $J_{K/T}$ or $J_{K/O}$, four combinations are obtained, leading to three structural types as shown in Table I.

It can thus be stated that these structural types can be characterized in the following way:

—The spinel structure, which corresponds to the anionic (ABC ABC) stacking, results from the association of three "S" double layers through $J_{K/T}$ junctions (Fig. 6).

—The hypothetical hexagonal close-packed structure, which corresponds to the

anionic (ABAB) stacking, results from the association of only "H" double layers through $J_{K/O}$ junctions. It has never been observed.

—The double-hexagonal $LiFeSnO_4$ type (Fig. 7), which corresponds to the anionic (ABAC) stacking, can be described as the association either of two "S" double layers through $J_{K/O}$ junctions or two "H" double layers through $J_{K/T}$ junctions, as shown in Table II.

It must be outlined that numerous hypothetical structures can be obtained when the association of the double layers is ensured by more complicated sequences of

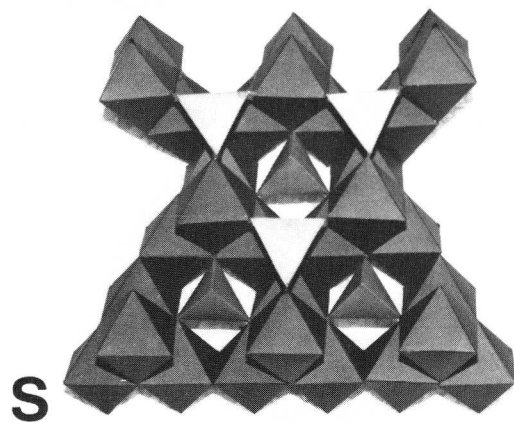


FIG. 4. Double-layer "S" characterized by the $J_{K/T}$ junction.

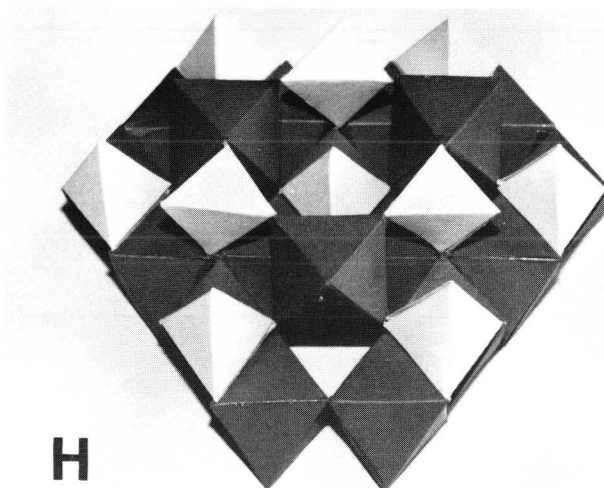


FIG. 5. Double-layer "H" characterized by the $J_{K/O}$ junction.

$J_{K/T}$ or $J_{K/O}$ junctions. This is not considered here.

(DH) $LiFeSnO_4$ —Spinel Transformation

In order to explain the (DH) $LiFeSnO_4$ —spinel transition observed for $Li_2Cr_{3-x}M_xSbO_8$ antimonates (4), we can determine the sequence of the geometrical operations which must be applied to the double layers previously described. Taking into account the periodicity along c of (DH) $LiFeSnO_4$,

which corresponds to the stacking of two double layers, and that of the spinel along $\langle 111 \rangle_S$, which is characterized by the stacking of three double layers, it results that six double layers must be considered to explain the (DH) $LiFeSnO_4$ —spinel transition.

Definition of the geometrical operations. The geometrical operations involved in this transformation will be successively applied to six double-layers "S" of the (DH) $LiFeSnO_4$ structure.

We can take the first double layer as be-

TABLE I
STRUCTURAL TYPES OBTAINED BY THE COMBINATION OF IDENTICAL DOUBLE LAYERS

| | | | | | |
|----------------------------|-------------|------------------|-----------|---|-----------|
| Layer junction | $J_{K/T}$ | $J_{K/O}$ | $J_{K/O}$ | $J_{K/T}$ | $J_{K/O}$ |
| Double-layer type | "S" | | "H" | | |
| Double-layer junction type | $J_{K/T}$ | $J_{K/O}$ | $J_{K/T}$ | $J_{K/O}$ | $J_{K/O}$ |
| Sequence | ... ccc ... | ... hch ... | ... | ... hh ... | ... |
| Structural type | spinel | (DH) $LiFeSnO_4$ | | Hypothetical hexagonal close-packed structure | |

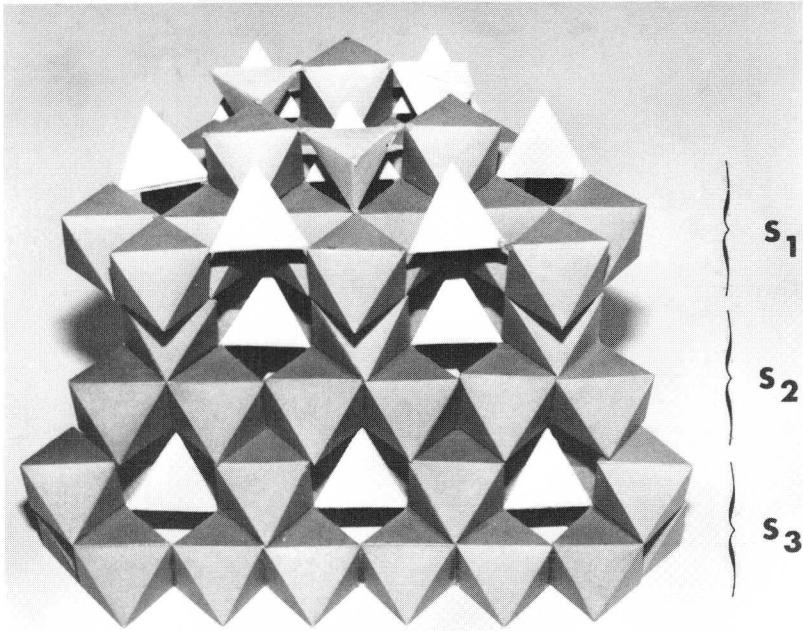


FIG. 6. Spinel structure built up from three "S" double layers.

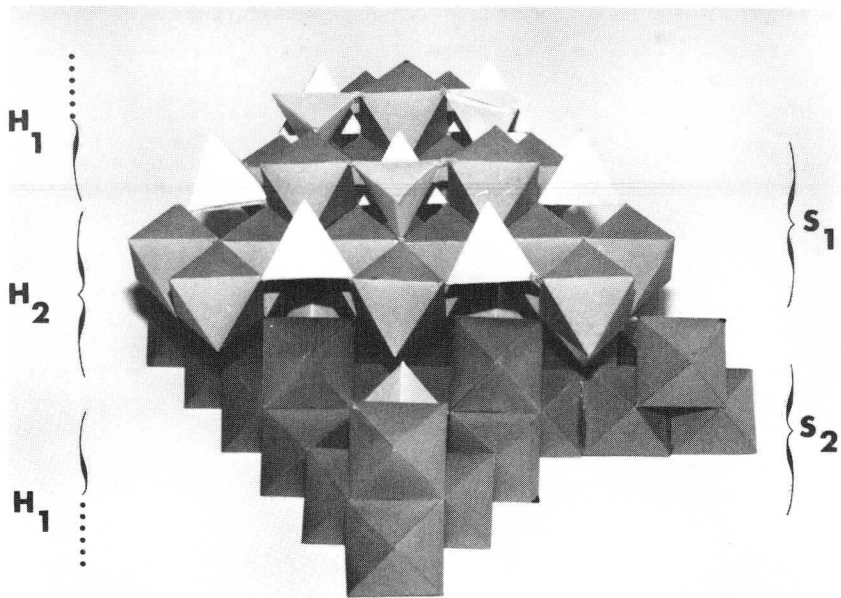


FIG. 7. (DH) LiFeSnO_4 structure built up from two "S" double layers.

TABLE II
ASSOCIATION OF TWO "S" DOUBLE LAYERS OR TWO "H" DOUBLE LAYERS IN (DH) $LiFeSnO_4$ STRUCTURE

| | Oxygen layer | Polyhedral layer | Junction | Double layer |
|---|--------------|------------------|------------------|-------------------|
| c | c | A | J _{K/O} | "S ₁ " |
| | h | B | J _{K/T} | |
| | c | A | J _{K/O} | "S ₂ " |
| | h | C | J _{K/T} | |
| | c | A | J _{K/O} | "H ₂ " |
| | c | A | J _{K/O} | |

TABLE III
SEQUENCE OF THE OPERATIONS INVOLVED IN (DH) $LiFeSnO_4$ -SPINEL TRANSFORMATION

| (DH) $LiFeSnO_4$ structure | | | | Operation | Spinel structure | | | |
|----------------------------|------------------|----------------------|--------------|------------------|------------------|----------------------|------------------|-------------------|
| Double layer | Junction | Polyhedral layer | Oxygen layer | | Oxygen layer | Polyhedral layer | Junction | Double layer |
| "S ₁ " | J _{K/O} | [Te ₂ Oc] | B | I | B | [Te ₂ Oc] | J _{K/T} | "S ₁ " |
| | J _{K/T} | [Oc ₃] | A | | A | [Oc ₃] | J _{K/T} | |
| | J _{K/O} | [Te ₂ Oc] | C | | C | [Te ₂ Oc] | J _{K/T} | |
| "S ₂ " | J _{K/T} | [Te ₂ Oc] | A | RT ₁ | B | [Te ₂ Oc] | J _{K/T} | "S ₂ " |
| | J _{K/O} | [Oc ₃] | B | | A | [Oc ₃] | J _{K/T} | |
| | J _{K/O} | [Te ₂ Oc] | B | | A | [Te ₂ Oc] | J _{K/T} | |
| "S ₁ " | J _{K/T} | [Te ₂ Oc] | A | T | C | [Te ₂ Oc] | J _{K/T} | "S ₃ " |
| | J _{K/O} | [Oc ₃] | C | | B | [Oc ₃] | J _{K/T} | |
| | J _{K/O} | [Te ₂ Oc] | C | | B | [Te ₂ Oc] | J _{K/T} | |
| "S ₂ " | J _{K/T} | [Te ₂ Oc] | A | ROc ₁ | A | [Te ₂ Oc] | J _{K/T} | "S ₁ " |
| | J _{K/O} | [Oc ₃] | B | | C | [Oc ₃] | J _{K/T} | |
| | J _{K/O} | [Te ₂ Oc] | B | | C | [Te ₂ Oc] | J _{K/T} | |
| "S ₁ " | J _{K/T} | [Te ₂ Oc] | A | T | B | [Te ₂ Oc] | J _{K/T} | "S ₂ " |
| | J _{K/O} | [Oc ₃] | C | | A | [Oc ₃] | J _{K/T} | |
| | J _{K/O} | [Te ₂ Oc] | C | | A | [Te ₂ Oc] | J _{K/T} | |
| "S ₂ " | J _{K/T} | [Te ₂ Oc] | A | RT ₁ | C | [Te ₂ Oc] | J _{K/T} | "S ₃ " |
| | J _{K/O} | [Oc ₃] | B | | B | [Oc ₃] | J _{K/T} | |
| | J _{K/O} | [Te ₂ Oc] | B | | B | [Te ₂ Oc] | J _{K/T} | |

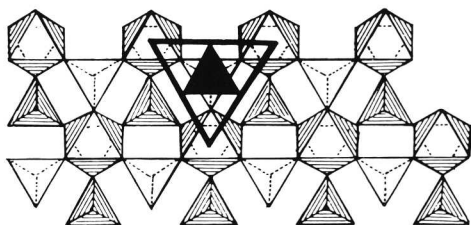


FIG. 8. Idealized scheme of the $J_{K/T}$ junction of "S" double layers required in the spinel structure.

ing the same in both structures as a reference, involving for the first operation the identity I . Two other kinds of operations are then used: rotation and translation. They are denoted, respectively, by the following symbols:

$R_{T_1} = \pm \pi/3$ rotation about the 3-fold axis of a T_1 tetrahedron;

$R_{Oc_1} = \pm \pi/3$ rotation about the $\bar{3}$ -fold axis of a Oc_1 octahedron;

$T =$ translation of $\frac{a_H}{3} \sqrt{3}$ along a direction $|110|$ of the hexagonal lattice.

Proposition of a formal mechanism. Due to the six double layers which need to be considered for the periodicity, five operations are necessary to explain the transformation (DH) $LiFeSnO_4$ -spinel, taking one double layer identical as a reference. Each operation deals with two double layers and their junction.

The sequence of the operations is sum-

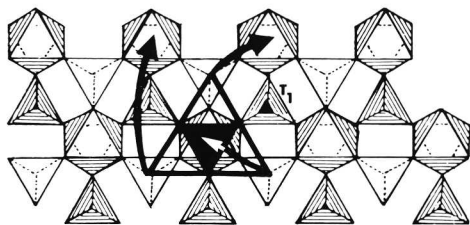


FIG. 9. 2nd operation: $\pi/3$ rotation of the second double layer about the 3-fold axis of the T_1 tetrahedron of the first double layer.

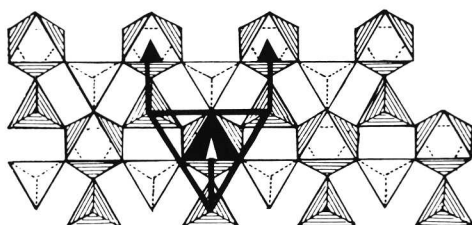


FIG. 10. 3rd operation: translation of $\frac{a_H}{3} \sqrt{3}$ of the third double layer with regard to the second one.

marized in Table III. The corresponding transformations are given in Figs. 8 to 11. In these schemes only the mixed layers (Te_2Oc) are drawn; moreover, the second mixed layer, which moves, is schematically represented by two triangles, in heavy lines, as the kagome window and the corresponding tetrahedron, respectively. It must be emphasized that after any operation, the junction between the two double layers will be always a $J_{K/T}$ junction. Thus every operation must lead to the idealized scheme of Fig. 8, with two tetrahedra facing each other through the kagome window as required in the spinel structure.

In the three next operations (Figs. 9–11) the two double layers are shown in their primitive configuration, black arrows representing the nature of the operation. All these operations led to a $J_{K/T}$ junction (Fig. 8) characteristic of the spinel structure.

Relationships with the Olivine and the Hexagonal Hypothetical Structures

The olivine–spinel transition observed in

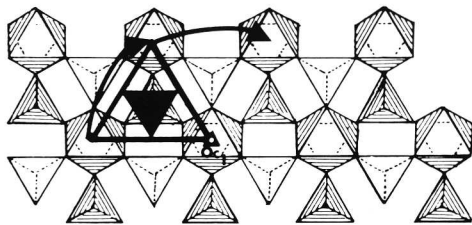


FIG. 11. 4th operation: $\pi/3$ rotation of the fourth double layer about the $\bar{3}$ -fold axis of an Oc_1 octahedron of the third one.

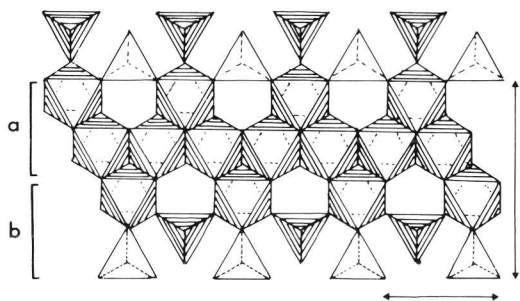


FIG. 12. $[\text{TeOc}_2]$ mixed layer formed of double ribbons of edge-sharing octahedra (a) and of double ribbons of corner-sharing of octahedra and tetrahedra (b).

silicates such as $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ (1) has been studied from the theoretical point of view. Hornstra (6) has shown the relationships between the olivine lattice and a stacking fault often observed in the spinel structure. Looking at the olivine structure in terms of polyhedra allows one to show close relationships between this structure and those of spinel and (DH) LiFeSnO_4 . Only one type of layer with composition (TeOc_2) built up from octahedra and tetrahedra is necessary for describing the olivine structure as shown in Fig. 12. The analysis of this type

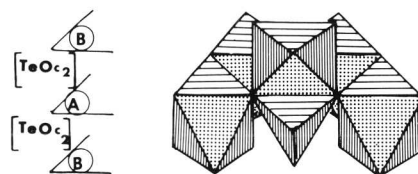


FIG. 13. Window bounded by four octahedra and one tetrahedron observed in the $[\text{TeOc}_2]$ olivine layers.

of layer shows that it is formed of double ribbons of edge-sharing octahedra similar to those observed in the octahedral layers $[\text{Oc}_3]$ (Fig. 12) and of double ribbons of corner-sharing octahedra and tetrahedra similar to those observed in the mixed layers $[\text{Te}_2\text{Oc}]$ (Fig. 1) previously described for (DH) LiFeSnO_4 . The olivine layers $[\text{TeOc}_2]$ can thus be described as the intergrowth of the $[\text{Oc}_3]$ and $[\text{Te}_2\text{Oc}]$ layers, involving for the olivine a structure which can be considered as related to the three structures spinel, (DH) LiFeSnO_4 , and hypothetical hexagonal.

Owing to the (ABAB) hexagonal close-packing of the oxygen atoms, the olivine is more closely related to the hypothetical hexagonal structure. The relationships be-

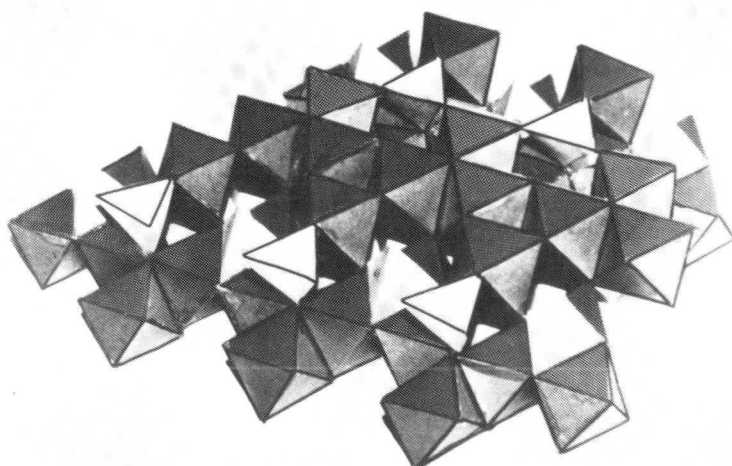


FIG. 14. Stacking of the $[\text{TeOc}_2]$ layers through $J_{K'10}$ junction in the olivine structure.

tween these two structures can be shown by considering the new type of window of the $[\text{TeOc}_2]$ olivine layers. This window, which is bounded by four octahedra and one tetrahedron (Fig. 13), has one of its sides similar to that of the kagome window and is thus bounded by six oxygen atoms; its other side, limited by five oxygen atoms, is, however, different. It will thus be denoted K' . In both structures, hypothetical hexagonal and olivine, the K and K' windows are blocked on both sides by an octahedron. It results that the hexagonal hypothetical structure can be described as a stacking of $[\text{Oc}_3]$ and $[\text{Te}_2\text{Oc}]$ layers alternately through $J_{K/O}$ junctions, while the olivine structure can be considered as a stacking of the $[\text{TeOc}_2]$ layers through $J_{K'O}$ junctions (Fig. 14). The similarity between these structures can also be shown by the stacking of their double layers $[\text{Oc}_3\text{-Te}_2\text{Oc}]$ and $[\text{TeOc}_2\text{-TeOc}_2]$, which exhibit similar junctions, $J_{K/O}$ and $J_{K'O}$, respectively.

In the same way, a close relation between (DH) LiFeSnO_4 and the hexagonal hypothetical structure can be described. Considering the double-layers "H" of (DH) LiFeSnO_4 with a $J_{K/T}$ junction, a simple R_{T_2}

rotation ($\pm \pi/3$ rotation about the three-fold axis of the T_2 tetrahedron) of one double layer out of two allows one to obtain the hexagonal hypothetical structure as shown in Table IV.

Conclusion

The comparison of the three close-packed structures (DH) LiFeSnO_4 , spinel, and olivine shows an important geometrical difference which results from the different types of junctions of the layers in these structures. The spinel structure is built up from tetrahedra and blocks of four edge-sharing octahedra: $[\text{Oc}_4]$ blocks. In the double-hexagonal structure two types of blocks are observed: the $[\text{Oc}_4]$ blocks are similar to those observed in the spinel, whereas the $[\text{TeOc}_3]$ blocks are built up from one tetrahedron and three octahedra sharing their edges (Fig. 5); the olivine structure, which is more distorted, exhibits only $[\text{TeOc}_3]$ blocks. These blocks characterize the shortest metal-metal distances in these phases and will certainly be of importance for considering the stabilization of these different structures. However, at the present stage of the investigations, the pa-

TABLE IV
SEQUENCE OF THE OPERATIONS INVOLVED IN THE (DH) LiFeSnO_4 -HYPOTHETICAL HEXAGONAL TRANSFORMATION

| (DH) LiFeSnO_4 structure | | | | Hypothetical hexagonal structure | | | |
|-----------------------------------|-----------|--------------------------|--------------|----------------------------------|------------------|-----------|-------------------|
| Double layer | Junction | Polyhedral layer | Oxygen layer | Operation | | | |
| | | | | Oxygen layer | Polyhedral layer | Junction | Double layer |
| "H ₁ " | $J_{K/T}$ | $[\text{Te}_2\text{Oc}]$ | C | $\xrightarrow{R_{T_2}}$ | C | $J_{K/O}$ | "H ₁ " |
| | $J_{K/O}$ | $[\text{Oc}_3]$ | A | | A | $J_{K/O}$ | |
| | $J_{K/T}$ | $[\text{Te}_2\text{Oc}]$ | B | | C | $J_{K/O}$ | |
| "H ₂ " | $J_{K/O}$ | $[\text{Te}_2\text{Oc}]$ | A | \xrightarrow{I} | A | $J_{K/O}$ | "H ₁ " |
| | $J_{K/T}$ | $[\text{Oc}_3]$ | C | | C | $J_{K/O}$ | |

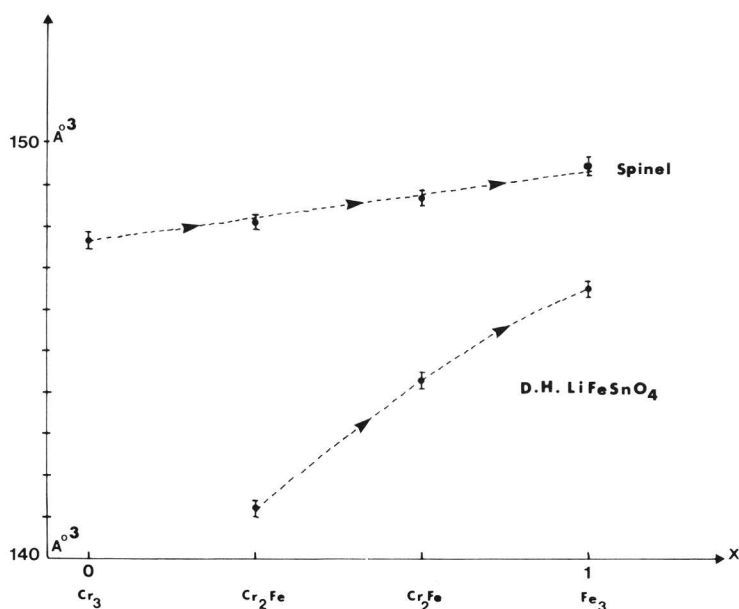


FIG. 15. $Li_2Cr_{3-x}Fe_xSbO_8$ antimonates molar volumes of spinel type and DH $LiFeSnO_4$ -type phases.

rameters which govern the stability of these blocks—size, electronic structure, polarizability of the ions, and also electrostatic repulsion between two neighboring cations—cannot be defined. Nevertheless, it is worthy to note that in the $[TeO_3]$ blocks of the (DH) $LiFeSnO_4$ structure, the less charged cation—lithium—is located in the tetrahedron and the more charged cations in the octahedra, involving a smaller electrostatic repulsion than in the spinel form which would have the same composition; this is also in agreement with the fact that for the same compound, namely, $Li_2Cr_2FeSbO_8$, $Li_2CrFe_2SbO_8$, or $Li_2Fe_3SbO_8$, the compacity of the spinel form is smaller than that for the double-hexagonal one, as evidenced by the comparison of the corresponding molar volumes (Fig. 15). In a similar manner, the occupancy of the tetrahedron of the $[TeO_3]$ blocks by elements such as Si, P, or Ge, characterized by

strongly covalent $M-O$ bonds, induces a distortion of the polyhedra resulting in a less compact structure than that of spinel as shown from the olivine–spinel transitions previously studied (7–9).

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