GALY AND ANDERSSON





FIG. 2. In (a) the  $Li_2ZrF_6$  structure type ( $Li_2NbOF_5$ ) is given. In (b) the trirutile structure of the composition AB<sub>2</sub>X<sub>6</sub>. In both the structures, A corresponds to filled circles, and open circles are the B-atoms.

indicated by the curved arrows, and without disorder. To our knowledge, no such transformation has been reported for the compounds  $Li_2NbOF_5$ and  $Li_2ZrF_6$ . However,  $\alpha$ -Li\_2SnF<sub>6</sub> of the  $Li_2ZrF_6$ type has been found to transform to a structure of the trirutile type, designated  $\beta$ -Li\_2SnF<sub>6</sub> at 510°C (4).

Another interesting transformation was reported recently (5, 6). At about 400°C,  $\alpha$ -Li<sub>2</sub>GeF<sub>6</sub>, of the trirutile type, transforms to  $\beta$ -Li<sub>2</sub>GeF<sub>6</sub> which has the Na<sub>2</sub>SiF<sub>6</sub> type structure (7). Figure 4 shows the Na<sub>2</sub>SiF<sub>6</sub> structure projected along the *c*-axis, and Fig. 5 the trirutile structure in an analogous projection. The geometrical relation between these structures can be shown by considering the Na<sub>2</sub>SiF<sub>6</sub> type. The cations in the octahedra drawn with heavy lines are at  $z = \frac{1}{2}$ , those in the lighter octahedra at z = 0. If the metal atoms at z = 0 in *m*-planes move to  $z = \frac{1}{2}$ , and those at  $z = \frac{1}{2}$  in *n*-planes to z = 0, the trirutile structure is obtained. This involves half the cations passing through octahedral faces along half the *c*-axis; the anion lattice remains intact. If the A and B atoms keep their relative order during the transformation, the ordered Na<sub>2</sub>SiF, structure type may, in the reverse way, be geometrically derived directly from the ordered trirutile type. That  $\beta$ -Li<sub>2</sub>SnF<sub>6</sub> and  $\beta$ -Li<sub>2</sub>GeF<sub>6</sub> are formed as ordered compounds, with, respectively, the trirutile and Na<sub>2</sub>SiF<sub>6</sub> structures, indicates that the geometrical proposals described here may very well be correct mechanisms.

All these compounds have approximately the same (hexagonally close packed) anion arrangement. At very high pressures the preferred cation arrangement seems to be like that in the  $\alpha$ -PbO<sub>2</sub>

FIG. type.

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