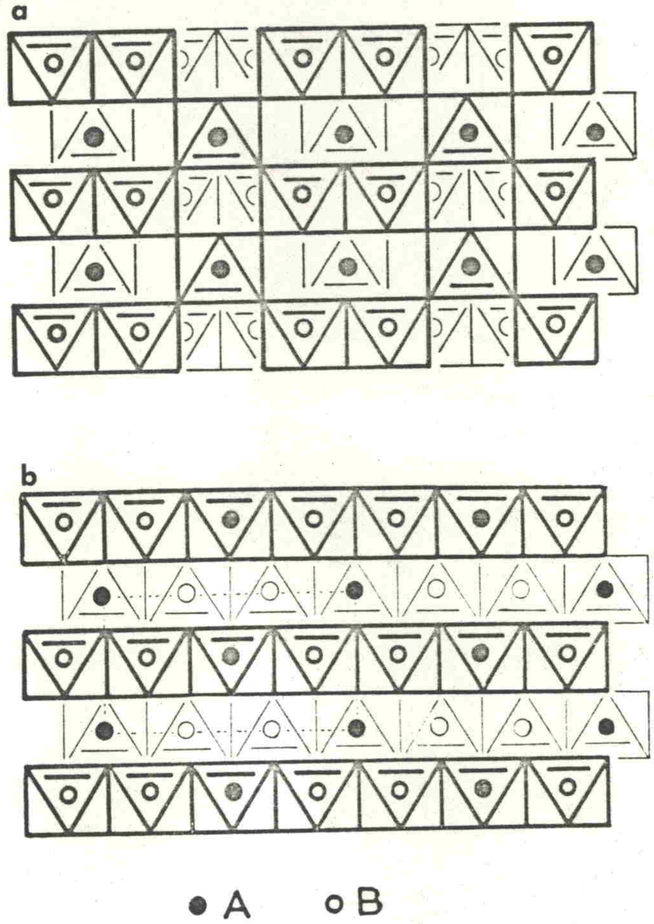

FIG. 2. In (*a*) the Li_2ZrF_6 structure type (Li_2NbOF_5) is given. In (*b*) the trirutile structure of the composition AB_2X_6. In both the structures, A corresponds to filled circles, and open circles are the B-atoms.

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, α-Li_2SnF_6 of the Li_2ZrF_6 type has been found to transform to a structure of the trirutile type, designated β-Li_2SnF_6 at 510°C (*4*).

Another interesting transformation was reported recently (*5*, *6*). At about 400°C, α-Li_2GeF_6, of the trirutile type, transforms to β-Li_2GeF_6 which has the Na_2SiF_6 type structure (*7*). Figure 4 shows the Na_2SiF_6 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_2SiF_6 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_2SiF_6 structure type may, in the reverse way, be geometrically derived directly from the ordered trirutile type. That β-Li_2SnF_6 and β-Li_2GeF_6 are formed as ordered compounds, with, respectively, the trirutile and Na_2SiF_6 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 α-PbO_2