city ratio N:N (N=1,3,4,6,8,12,16, 24,32,48) or M:3M (M=1,2). Structures in which the occupied RSPs have one, two or three free go Ts by type (2). The number of free parame-ters will be reduced by one or by two for the transformed RSP. Transformations by type (1+2) are possible in structural types where simul-taneously two or more RSPs of the same symmetry and with the different absolute values of free or/and fixed parameters are occupied. The above of structure elements in the unit cell is consof an RSP are due to the expansion coefficients of pair bonds with respect to any scalar exter-nal parameter (temperature, hydrostatic pres-sure, dimension of structure elements) are different even in macroscopically isotropic struc-tures, for example between similar, but unequ-ally spaced structure elements, or between different, but equally spaced elements, or between di-ferent, but equally spaced elements. Crystallo-chemical approach to the analysis of continuous transformations should also take into account the real dimensions of the structure elements and the values of tolerance factors for diffe-rent coordinational polyhedrons. The obtained system of transformations comprises all the second order transitions considered by the theo retical-group methods and some others, for exretical-group methods and some others, for ex-ample Pm3m ~ P23, Im3m ~ I23, Fm3m ~ F23 e t c. The thermodynamical analysis was not performed but the coordinates of moving points may be used as a parameter of the free energy expansion.

05.1-31 THE STUDIES ON THE PHASE TRANSITION OF LiIO3. By Liang Jing-kui, Zhang Yu-ming, Institute of physics, Academia Sinica, BEIJING, China.

The phase transition mechanism of LiIO3 at normal pressure has been studied by DTA, DSC, isothermal heat-treatment, and X-ray powder diffraction at high and room temperature.

When over-heated melt is cooled and solidified, we have discovered four new phases of LiIO3 ---a group phases δ , η , δ and θ (θ_i and θ_1), which are formed by cooling from two main kinds of $\overline{\delta}$ phase. The phase transition processes of LiIO3 as shown in the following diagram:



---- the process of fluctuations of temperature

- δ,-LiIO₃; cubic, a=6.968Å
- η; tetragonal, a=11.563Å, c=9.342Å
- g; orthorhombic,a=5.722Å, b=9.505Å,c=10.589Å
- θ; cithorhombic,a=7.870Å, b=7.970Å,c=7.356Å
- ; orthorhombic,a=6.498Å, b=7.118Å,c=12.265Å

There are three phases of LiIO₃, β , $\tilde{\gamma}$ and $\tilde{\sigma}$, existing relatively stably in high temperature and they can directly melt respectively. Their melting point correspondingly are:

- phase $\beta = --432$ °C;
- phase $\eta = --421$ °C;
- phase 5 --- 416°C;

Their melting point, thermal process and the existing temperature range all show, that the order of their thermodynamical stability is:

 $\beta > \gamma > \delta$ In dry air and at room temperature, the 3-LiIO₃ stands long periods of time without any change as well as phase α and β . At the existing tem-perature range of α -LiIO₃, phase 3 does not transform into phase α , although it is heattreated for a long time. The temperature of phase transition of s to β is higher than that of α to β . The existence of phase β in the phase $\mathcal F$ has a promotive effect on the phase transition of $\mathcal F$ to β just as a to β . The existence of phase 3 in the phase α has also a promotive effect on α to β , the phase θ , as the phase γ , is also an intermediate metastable phase in the phase transition processes of LiIO3.

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In perovskite (ABX₃) compounds such as $CaTiO_3$ and $NaNbO_3$ phase transitions due to the condensation of soft modes occur and can be interpreted in terms of the tilting of the BX6 octahedra around one or some of their tetrahedral axes in the low temperature phases. Glazer (Acta Cryst. (1972) <u>B28</u>, 3384), classified the structure of these phases in terms of the correlation of tilting along these axes.

In the ABX_4 compounds these octahedra are not, unlike the perovskite case, vertex-shared in the third dimension. Still all of these materials undergo transitions which may be interpreted in terms of condensation of soft modes, yielding low temperature phases with tilted octahedra (M.Hidaka et al., J.Phys.C.Sol.St.Phys. (1979).12, 2737; J.Phys.C.Sol.St.Phys.(1979).12, 1799; Phys.stat. sol.(a)(1982).72, 809).

Electron diffraction experiments are reported which confirm some of these transitions. In RbFeF_4 however it is found that, although the reflections are quite weak, the c-axis is doubled at room temperature (RT) whereas this doubling disappears when cooling down to liquid nitrogen temperature (LNT) as can be seen in fig.1. This would invalidate the RT structure proposed by M. Hidaka et al. (J.Phys.C.Sol.St.Phys.(1979). 12, 1799).

In $RbVF_4$ there are indications that, in contradiction with the description by M. Hidaka et al. (Phys.stat.sol. (a) (1982). $\underline{72}$, 809), the doubling of the c-axis does not vanish at 413K. All of the investigated compounds seem to be very sensitive to decomposition under electron irradiation, probably through evaporation of fluorine. This evaporation forces the BX6 .oxtahedra to become locally edge-shared thus deforming the lattice, which