

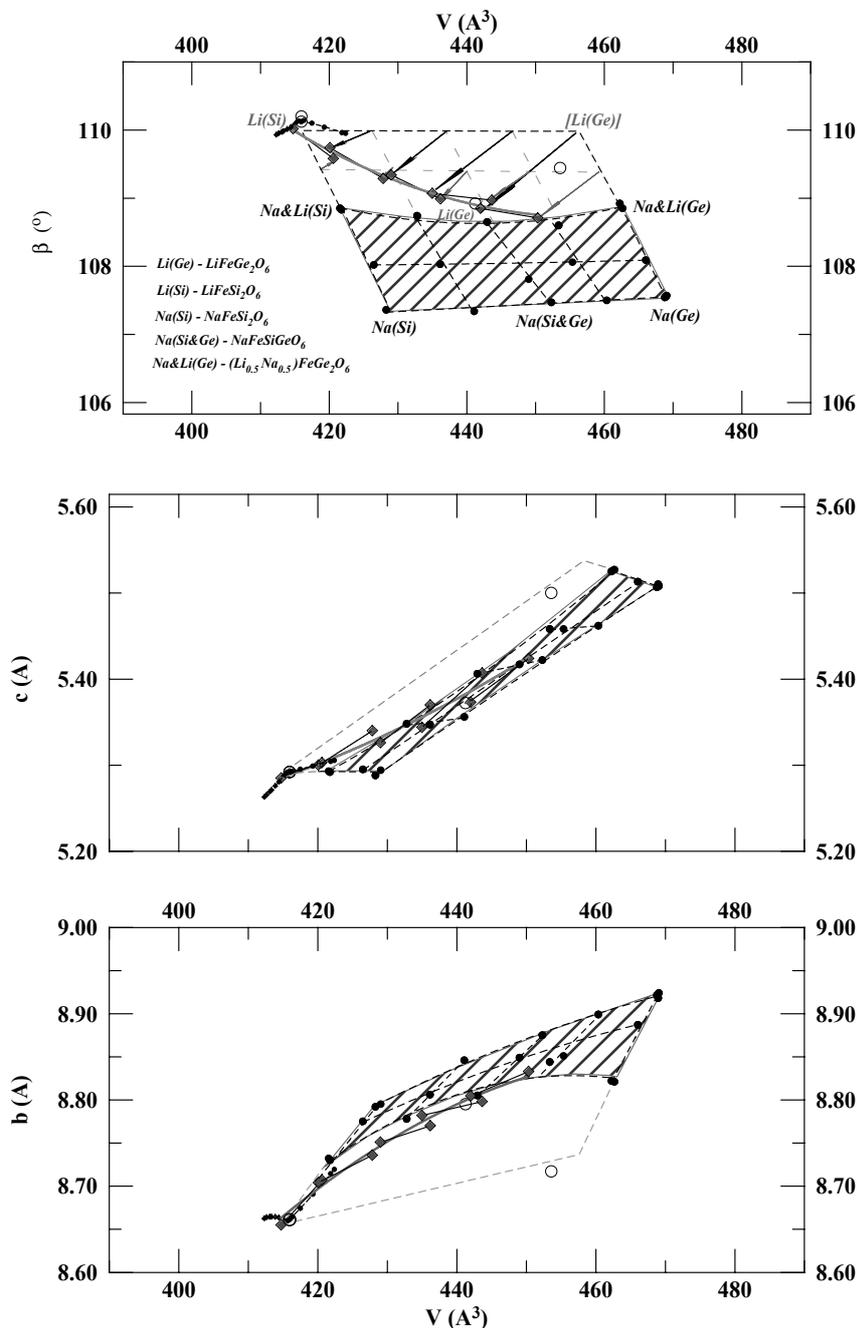
## STRUCTURAL TRANSFORMATION C2/c - P2<sub>1</sub>/c IN THE LI-NA-SI-GE PYROXENE SOLID SOLUTION

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The solid solution  $\text{Na}_x\text{Li}_{1-x}\text{FeSi}_y\text{Ge}_{1-y}\text{O}_6$  with pyroxene structure is in details studied by the X-ray powder diffraction and nuclear gamma resonance methods. For the first time the substitution of ions in both M2 position and in tetrahedra is carried out in all area of existence of a solid solution. This system

gives the opportunity to study the elastic response of a solid solution structure to substitution of ions in each of these two crystallographic positions.



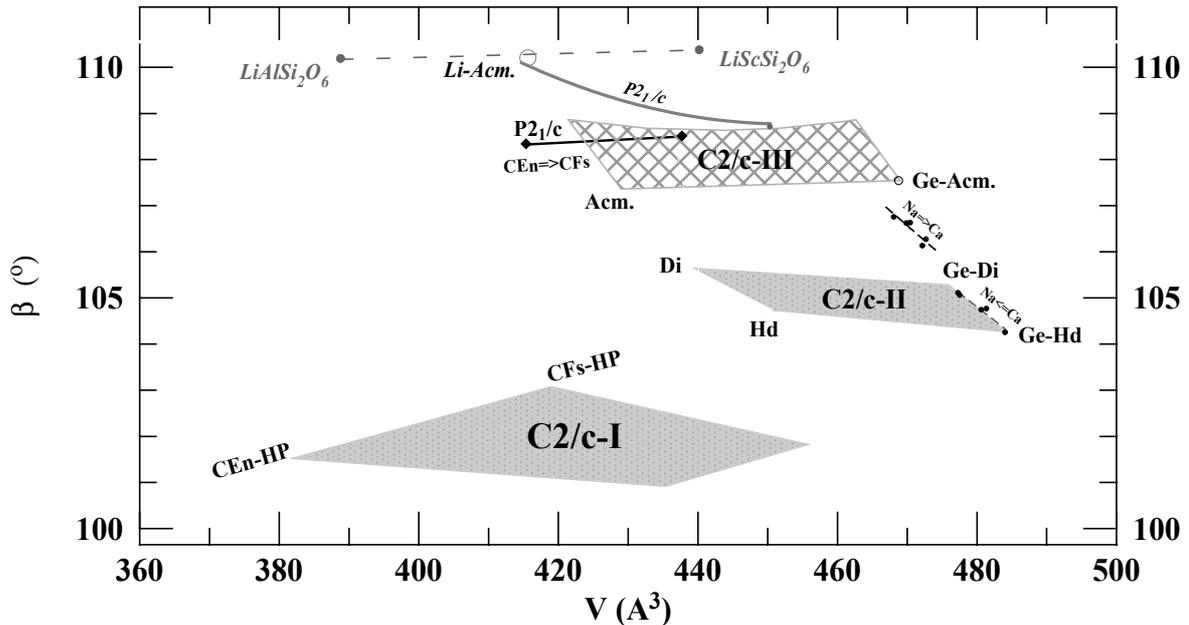
Received in coordinates "unit cell Parameter"- "Volume"[1] the experimental X- and Y-trends ( $\text{Na} \rightarrow \text{Li}$  and  $\text{Si} \rightarrow \text{Ge}$ ) permit one to determine for the solid solution of any composition the strain tensor parameters at selective substitution in each of two crystallographic positions.

As it is clear from data, presented on fig. 1, the Na rich ( $x=0.5-1$ ,  $y=0-1$ ) solid solution occupies the topological niche, which shape resembles the parallelogram. Using the data on the end members for hypothetical Si-Ge-Mg-Fe and Si-Ge-Mg-Fe-Ca solid solutions with pyroxene structure the similar shape of a niches has been received for two distinct modifications of monoclinic (C2/c) pyroxene structures [1].

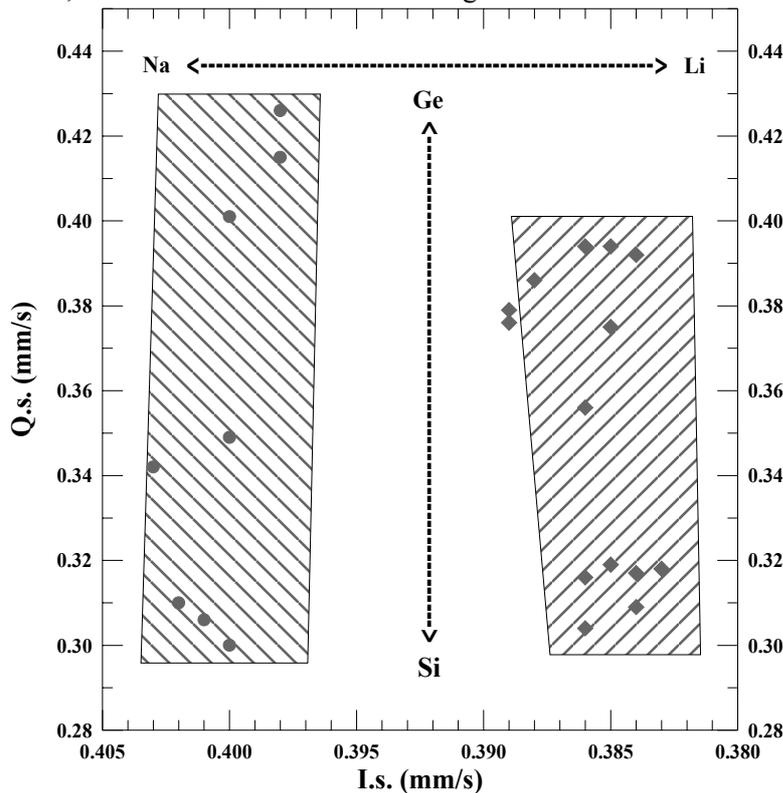
In contrast, the part of solid solution  $\text{Na}_x\text{Li}_{1-x}\text{FeSi}_y\text{Ge}_{1-y}\text{O}_6$ , rich with lithium ( $x=0-0.25$ ,  $y=0-1$ ), gives

the X-trends  $\text{Na} \rightarrow \text{Li}$  and  $\text{Si} \rightarrow \text{Ge}$ , forming in aggregate an unusual topological cord-like niche. Found out in diffractograms of samples of this solid solution reflexes with the odd sum  $h+k$  allow to attribute them to the structure with sp. gr. P2<sub>1</sub>/c, what is supported by the literature data on  $\text{LiFeGe}_2\text{O}_6$ . Coordinates of a niche define areas of stability of each of two monoclinic structural modifications of solid solution  $\text{Na}_x\text{Li}_{1-x}\text{FeSi}_y\text{Ge}_{1-y}\text{O}_6$  with sp. gr. C2/c and P2<sub>1</sub>/c, which elastic properties, as it is found out, are specifically distinct. In work it is determined, that elastic properties of the Li rich solid solution, appreciably vary at change of relative content of Si, while elastic properties of the Na rich solid solu-

tion, which structure is characterized by space group C2/c, practically do not depend on the composition of solid solution. The "□- niches " for some of monoclinic pyroxene structures with sp. gr. C2/c and P2<sub>1</sub>/c and their known Geanalogues are presented on the fig. 2, as well as the consisting of two



branches the X-trend  $\text{Ca} \rightarrow \text{Na}$  for the solid solution "Ge-Hd - Ge-Acm" –  $\text{Na}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ . It is obvious, that the end member – Ge-analogue of acmite "Ge-Acm" – does not belong to two distinguished



branches of the trend. Apparently, Ge-Acm, which has been received by a method of solid state chemical reaction in open ampoules, as against other members of the join synthesized in pumped out and then sealed-in ampoules, could have some specific different structural features, indeed. The study is in progress.

The parameters of a local fields in position M1 in both structural modifications of the solid solution are investigated by method nuclear gamma-resonance. It is shown, that rich- and poor- sodium samples demonstrate some small, but definite difference of  $\text{Fe}^{3+}(\text{M1})\text{-O}$  bonding. Small, but statistically significant distinction of isomer shift for these two structures (fig. 3), could be referred to the different Debye temperature

for rich- and poor- sodium samples. The gradient of an electric field on nucleus  $^{57}\text{Fe}$  which in case of ions  $\text{Fe}^{3+}$  directly reflects a degree of distortion of octahedrons M1, specifies that the greatest distortions of octahedron M1 take place at Li/Na and Si/Ge ratio, close to 1. Splittings of components was not fixed.

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## References:

1. *Novikov G.V., Sipavina L.V., Sokolov Yu.A. (1999) Comparative crystal chemistry of mantle silicate and their structural analogs. Experiment in Geosciences. 8, 88-90.*

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