07. Materials Science

07.3-4 The Atomic Structure of Ionic Conductors Li$_3$Sc$_2$(PO$_4$)$_3$ and Li$_3$Fe$_2$(PO$_4$)$_3$ at 293 and 593 K. By B.A. Makinov, B.A. Genkina, L.A. Muradyan and V.I. Simonov, Institute of Crystallography, USSR Acad. Sci., Moscow, USSR.

At 600 K the conductivity of Li$_3$Sc$_2$(PO$_4$)$_3$ and Li$_3$Fe$_2$(PO$_4$)$_3$ crystals, obtained by solid-phase synthesis, reaches (2-5) x 10$^{-14}$ cm$^{-1}$V$^{-1}$cm$^{-1}$K$^{-1}$ (E.A. Genkina, L.A. Muradyan, L. N. Demyanets et al., Zh. Obshch. Khim. 52, 822-825 (1982)). According to electro-chemical measurements, these compounds become fast ionic conductors at T>540 K. The X-ray intensity data were collected using MoK$_x$ radiation on a CAD-4F diffractometer equipped with a graphite monochromator (step scanning method, w-technique, sin$\theta$/2$\theta$ = 1.0$^\circ$).

At room temperature Li$_3$Sc$_2$(PO$_4$)$_3$ crystals are monoclinic, Fedorov group P2$_1$/n, a=8.501(1), b=12.271(2), c=8.801(1), $\beta$=90.020, $\rho_{max}$=1.093 A. The fast-ionic state is reached at T=540 K. The X-ray intensity data were collected using MoK$_x$ radiation on a CAD-4F diffractometer equipped with a graphite monochromator (step scanning method, w-technique, sin$\theta$/2$\theta$ = 1.0$^\circ$).

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07.3-5 Phase Transitions in Superionic Conductors CaHSO$_4$ Study by Neutron Diffraction and Inelastic Scattering. By A.V. Belashkin, L. Katenko, A.A. Platonova, J. Nascimbé, Joint Institute for Nuclear Research, 141980 Dubna, USSR, * Institute of Crystallography, 117333 Moscow, USSR.

Simultaneous measurements of neutron diffraction (ND) and inelastic incoherent neutron scattering (INS) on a powder sample of CaHSO$_4$ in the temperature range of 5-423 K have been performed at the IBR-2 pulsed reactor. Three phase transitions have been observed in the temperature range of 5-423 K. As it is seen from the INS spectra the dynamics of protons significantly changes at the first transition near 325 K and at the superionic transition at 414 K. The conductivity of CaHSO$_4$ at 423 K has a metastable character and can be easily supercooled. Proton jumps in the superionic phase at 423 K should have a frequency lower than 10$^{-11}$ sec, because we have not observe quasi-elastic broadening within our 6% resolution at the 4.9 meV elastic line. Using vibrational frequency obtained from INS we estimate the diffusion coefficient for protons:

D = 2 x 10$^{-6}$ cm$^2$/sec.

Necessary resolution to observe such a diffusion is of the order of 0.02 meV.

07.4-1 The Organic Conductors (TMTSF)$_2$TaF$_6$ and (TMTTF)$_2$TaF$_6$. By N. Thorup and G. Rindorf, Chemistry Dept. B, Technical University of Denmark, DK-2800 Lyngby, Denmark.

During the past few years extensive studies have been made on two series of molecular metals, namely (TMTSF)$_2$X and (TMTTF)$_2$X (for recent results, see J. Physique (1983), Colloque C3, pp. 767-1136). (TMTSF)$_2$TaF$_6$ is tetramethyltetraselenafulvalene, (TMTTF)$_2$TaF$_6$ is tetramethyltetraselenafulvalene, and X is an anion, e.g. BF$_4$, CIO$_4$, ReO$_4$, PF$_6$ or TaF$_6$. These materials exhibit unusual physical properties below 1 K and superconductivity at temperatures below 1 K and pressures above 10 kbar.

The crystals are all isostructural and room temperature and they consist of TMTSF cation-radicals stacked along the c axis. The stacks are connected (via Se-Se or S-S contacts) to sheets separated by anion layers parallel to the ab plane (see e.g. Thorup et al. Acta Cryst. (1981) B37, 1256).

The present work focuses on the structural details of the title compounds and, in particular, the differences between them. In both cases, however, the octahedral anions seem to be disordered in a very similar fashion. Each octahedron can take one of two orientations, which are very close. The triclinic cell dimensions at 295 K are:

- a
- b
- c
- $\alpha$
- $\beta$
- $\gamma$

(TMTSF)$_2$TaF$_6$ salt 7.291 7.728 13.555 82.86 85.33 71.66
(TMTTF)$_2$TaF$_6$ salt 7.182 7.646 13.936 82.86 85.33 71.66

07.4-2 The Organic Conductors (TMTSF)$_2$TaF$_6$ and (TMTTF)$_2$TaF$_6$. By N. Thorup and G. Rindorf, Chemistry Dept. B, Technical University of Denmark, DK-2800 Lyngby, Denmark.