07.3–4 THE ATOMIC STRUCTURE OF IONIC CONDUCTORS $Li_3Sc_2(PO_4)_3$ AND $Li_3Fe_2(PO_4)_3$ AT 293 AND 593 K. By B.A.Maksimov, E.A.Genkina, L.A.Muradyan and V.I.Simonov, Institute of Crystallography, USSR Acad.Sci., Moscow, USSR.

At 600 K the conductivity of $Li_3Sc_2(PO_4)_3$ and $Li_3Fe_2(PO_4)_3$ crystals, obtained by solid-phase synthesis reaches $(2-5)\cdot10^{-2}\Omega^{-1}cm^{-1}$ (M.Pintard-Screpel, F.d'Yvoire, E.Bretley, Solid State Chem.Proceed.(1982), 215-218)(E.A.Genkina, L. N.Demyanets et al., JETP letters(1983),v.38, N°5, p.257-259).According to electro-chemical measurements these compounds become fast ionic conductors at T~540 K. The X-ray intensity data were collected using MoK_α radiation on a CAD-4F diffractometer equipped with a graphite monochromator(step scanning method, W-technique, $\sin\theta/\lambda = 1.0$ Å^{-1}).

At room temperature $Li_3Sc_2(PO_4)_3$ crystals are monoclinic, Fedorov group $P2_1/n$, a=8.851(1), b=12.271(2), c=8.800(1)Å, γ=90.02°,V=953Å^3, z = 4. In the fast-ionic state, at T=593 K, the symmetry is changed to orthorhombic (Fedorov group Pcan D^{14}_{2h}, a=8.801(1), b=12.393(2), c=8.822(2) Å, V = 962 Å^3,z=4.The $Li_3Fe_2(PO_4)_3$ unit cell have the following dimensions: a = 8.545(2), b = 12.003(3), c = 8.604(2) Å at T= =293 K; and a = 8.592(1), b = 12.129(2), c = = 8.637(2) Å at T = 593 K.

The basis of the structure of lithium-scandium phosphate and lithium-iron phosphate at room temperature (293 K) and at temperature 593 K, exceeding the phase transition point ~~is three~~-dimensional framework , formed by M^{2+}-octahedra (M^{2+}- Sc, Fe) and P-tetrahedra, connected by common vertices. The cavities in the framework are occupied by single-charged lithium atoms.

The analysis of the change in the structure parameters accompanying the considered phase transition to the fast-ionic state showed that $\{[M_2(PO_4)_3]^{3-}\}$ frameworks are virtually identical both below and above the phase transition point. After the phase transition the displacement of M^{2+}, P and O atoms does not exceed 0.2 Å. There are significant differences only in the location of Li atoms at 293 and 593 K. At T = 293 K the 12 lithium atoms of a unit cell fully occupy three four-fold complexes. At T = 593 K in $Li_3M_2(PO_4)_3$ structures Li atoms occupy also three, although 8-fold complexes: only one 8-fold site is fully occupied, the other two are occupied by Li with the probability of 1/4. The Li_1 atom is positioned inside a distorted tetrahedra, Li-O distance being 1.91(2)-2.08(2) Å. Coordinational polyhedra of Li_2 and Li_3 atoms have five vertices, the distances being: Li_2-O = 2.15(2) - 2.43(2) Å, Li_3-O = 1.99(2)- -2.60(2) Å. The Li polyhedra are connected by common edges and vertices.

The mutual arrangement of Li atoms at 593 K indicates a highly probable and essential anisotropy of the conductivity.

07.3–5 PHASE TRANSITIONS IN SUPERIONIC CONDUCTOR $CsHSO_4$ STUDY BY NEUTRON DIFFRACTION AND INELASTIC SCATTERING. By A.V. Belushkin, I. Natkaniec, N.M. Plakida, L.A. Shuvalov*, J. Wasicki, 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 (IINS) on a powder sample of $CsHSO_4$ in the temperature range of 5÷423 K have been performed at the IBR-2 pulsed reactor. Three phase transitions have been detected by ND when a sample was heated from the room temperature up to 423 K. As it is seen from the IINS spectra the dynamics of protons significantly changes at the first transition near 325 K and at the superionic transition at 414 K as well. The phase upper 325 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 8% resolution at the 4,9 meV elastic line. Using vibrational frequency obtained from IINS we estimate the diffusion coefficient for protons:

$$D = 2{,}7\cdot10^{-6}\,cm^2/sec.$$

Necessary resolution to observe such a diffusion is of the order of 0,02 meV.

07.4–1 THE ORGANIC CONDUCTORS $(TMTSF)_2TaF_6$ AND $(TMTTF)_2TaF_6$. 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 $(TMTSF)_2X$ and $(TMTTF)_2X$ (for recent results, see J. Physique (1983), Colloque C3, pp. 767-1136). TMTSF is tetramethyltetraselenafulvalene, TMTTF is its sulfur analogue tetramethyltetrathiafulvalene, and X^- is an anion, e.g. BF_4^-, ClO_4^-, ReO_4^-, PF_6^- or TaF_6^-. These materials exhibit unusual physical features such as low-dimensional metallic transport properties, and superconductivity has been demonstrated in several cases including $(TMTSF)_2TaF_6$ at temperatures below 1 K and pressures above 10 kbar.

The crystals are all isostructural at room temperature and they consist of TMTSF cation-radicals stacked along the *a* 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, 1236).

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	α	β	γ
TMTSF salt	7.291	7.728	13.936	82.86	85.33	71.66
TMTTF salt	7.182	7.646	13.555	81.44	83.47	73.86