PSI1.05.47 FLUCTUATIONS IN THE STRUCTURE OF CALCITE. IP Swainson (Atomic Energy Of Canada Limited, Chalk River, ON, K0J 1PO, CANADA), MT Dove (Dept of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK), MJ Harris and ME Hagen (ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK).

Calcite, CaCO$_3$(I), undergoes a tricritical, order-disorder transition at approximately 1260 K. We present evidence from neutron powder diffraction measurements that this transition occurs by a continuous growth of librational amplitude of the CO$_3$ ions in the (0001) plane. Once the in-plane librational amplitude reaches a root mean of 30°, the crystal transforms into the disordered phase, with symmetry change R3c $\rightarrow$ R3m. This transition is associated with an instability at the Z-point of the Brillouin zone. However, considerable diffuse scattering is seen in X-ray and neutron scattering studies at the F-point of the Brillouin zone. Inelastic neutron scattering measurements have shown that a pronounced dip in the transverse acoustic (TA) branch exists at this point and that an anomalous continuous column of scattering exists down from $\omega_{\alpha}T_\alpha$ to $\omega_0$. The TA mode is of symmetry $F_2$. This is also the symmetry of the soft mode for the high-pressure CaCO$_3$(I)-CaCO$_3$(II) transition. The TA mode softens continuously, and the column grows in intensity as the $T_c$ of the Z-point order-disorder transition is confirmed by the x-ray studies [3] and the vacancy model [2]. Mixed valence of chromium ions (Cr$^{3+}$-Cr$^{4+}$) resulting from the defectiveness mentioned above is the main cause of the metamagnetic phase transition in Cd$_{0.9}$Cu$_{0.1}$Cr$_2$S$_4$, where as in the case of ZnCr$_2$In$_{0.5}$Se$_2$ it contributes to this effect by the increase of the values of the critical magnetic fields.

References:

PSI1.05.48 X-RAY STUDY OF THE INCOMMENSURATE PHASE OF LIKSO$_4$ UNDER UNIAXIAL PRESSURE. D. R. Ventura, N. L. Speziali and M. A. Pimenta. Departamento de Física, ICEX- UFMG, Belo Horizonte 30161-970 Brazil.

Lithium potassium sulfate (LIKSO$_4$) crystals display a very interesting sequence of structural phase transitions at high temperature as schematized in the diagram below.

<table>
<thead>
<tr>
<th>Phase III</th>
<th>Phase II</th>
<th>Phase I</th>
</tr>
</thead>
<tbody>
<tr>
<td>P6$_3$</td>
<td>435</td>
<td>670</td>
</tr>
</tbody>
</table>

$T_c$ ($^\circ$C)

The symmetries of phases I and III are well established in the literature. In this work we present X-ray studies of the intermediate phase II. Our results show that this phase is, in fact, incommensurate, contrary to a previous work which supported an orthorhombic normal Pmcn structure. The modulation wave vector was observed to be approximately constant with temperature. Experiments with applied uniaxial pressure showed that this phase corresponds to a superposition of three kinds of ferroelastic incommensurate domains oriented at 120° to one another; the modulation is described by a single wave vector (l-q model) in each domain, with $q = \frac{\pi a}{b}$. The application of uniaxial pressure inhibits one or two kinds of domains depending on the direction of applied pressure. The inhibition occurs for the domains that have a component of the wave vector $q$ in the direction of the applied pressure. Structural studies of the intermediate phase II are in progress.

PSI1.05.49 INFLUENCE OF THE DEFECTIVENESS OF THE CRYSTAL LATTICE ON THE METAMAGNETIC PHASE TRANSITIONS IN Cd$_{1-x}$Cu$_x$Cr$_2$S$_4$ (WHERE $x \leq 0.2$) AND ZnCr$_2$In$_{0.5}$Se$_2$ (WHERE $x \leq 0.14$). J. Warczewski, J. Krok-Kowalski, T. Grön, University of Silesia, Institute of Physics, ul. Uniwersytecka 4, PL-40-007 Katowice, Poland.

The stability of spinel crystal structures decreases with the increase of the anion radius. It is connected with the increase of the anion covalency [1] and the vacancy concentration [2] in the sequence: O,S,Se and Te.

High structure defectiveness of the spinel under investigation is confirmed by the x-ray studies [2] and the vacancy model [2]. Mixed valence of chromium ions (Cr$^{3+}$-Cr$^{4+}$) resulting from the defectiveness mentioned above is the main cause of the metamagnetic phase transition in Cd$_{0.9}$Cu$_{0.1}$Cr$_2$S$_4$, where as in the case of ZnCr$_2$In$_{0.5}$Se$_2$ it contributes to this effect by the increase of the values of the critical magnetic fields.

References:

PSI1.05.50 PHASE TRANSITIONS IN [Me$_{2}$Et$_{6}$]$_{n}$MX$_{4}$ SALTS. R. D. Willett, Y. Fujii, R. Nicholson, and M. Wei, Department of Chemistry, Washington State University, Pullman, WA 99164 USA.

We have initiated a study of the crystal chemistry of a new variation of the A$_2$MX$_4$ system based on A = Me$_{2}$Et$_{6}$N$^+$ cations. Previously we have shown that the structures of the (Me$_2$Pc)$_3$MX$_4$ series (Pc = group 6A element) assume the incommensurate phase bearing K$_3$SO$_4$ structure for small cation-anion radius ratios, while phases with a cubic aristotype are formed for large radius ratios. The same rule holds for this new series, with the n = 1 and n = 2 salts generally forming the K$_3$SO$_4$ structure type. Among the significant results to date are:
1. The (Me$_2$Et$_{2}$N)$_2$CuX$_4$ salts (X = Cl, Br) undergo second order phase transitions at $T_c \approx 35$C from P112/$n$ to Pmcn. We have measured the lattice constants of the bromide salt as a function of temperature through $T_c$, verifying the apparent second order nature of the transition. The volume is continuous. However, broadening of the diffraction peaks occurs near $T_c$. A major feature of the phase transition is a reorientation of the ethyl groups of the ammonium cations.
2. The (Me$_2$Et$_{2}$N)$_2$CuX$_4$ salts have an acentric version of the parent structure with distortion at the zone center P2$_1$/cn structure at room temperature. Both salts undergo two phase transitions below room temperature, with $\approx 45$C and $\approx 15$C. The shape of the DSC curves strongly suggests that the intermediate phase is incommensurate.
3. The (Me$_2$Et$_{2}$N)$_2$MnCl$_4$ salt crystallizes in the space group P12$_1$/a, with a commensurate a$^*$/2 modulation of the parent K$_3$SO$_4$ structure in the $a$ direction. This is the first example of a modulation in this direction of the lattice and corresponds to a previously unknown P2$_1$ distortion of the parent structure.