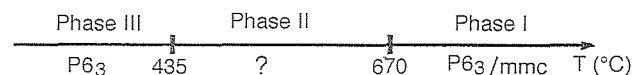


**PS11.05.47 FLUCTUATIONS IN THE STRUCTURE OF CALCITE.** IP Swainson (Atomic Energy Of Canada Limited, Chalk River, ON, K0J 1P0, CANADA), MT Dove (Dept of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK), MJ Harris and ME Hagen (ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK).

Calcite,  $\text{CaCO}_3(\text{I})$ , 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  $\text{CO}_3$  ions in the (0001) plane. Once the in-plane librational amplitude reaches a root mean of  $30^\circ$ , the crystal transforms into the disordered phase, with symmetry change  $R3c \Rightarrow R\bar{3}m$ . 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  $\nu = \nu_{TA}$  to  $\nu = 0$ . The TA mode is of symmetry  $F_2$ . This is also the symmetry of the soft mode for the high-pressure  $\text{CaCO}_3(\text{I})$ - $\text{CaCO}_3(\text{II})$  transition. The TA mode softens continuously, and the column grows in intensity as the  $T_c$  of the Z-point order-disorder transition is approached. This demonstrates that the Z-point disordering and F-point fluctuations are strongly coupled. Such a column of inelastic scattering has been seen in very few other systems. In all cases it appears to be associated with competing ordering schemes. It appears, therefore, that the diffuse scattering seen at ambient pressures at the F-point of  $\text{CaCO}_3(\text{I})$  is an incipient ordering associated with  $\text{CaCO}_3(\text{II})$ .

**PS11.05.48 X-RAY STUDY OF THE INCOMMENSURATE PHASE OF  $\text{LiKSO}_4$  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 ( $\text{LiKSO}_4$ ) crystals display a very interesting sequence of structural phase transitions at high temperature as schematized in the diagram below.



The symmetries of phases I and III are well established in the literature. In this work we present a X-ray study of the intermediate phase II. Our results show that this phase is, in fact, incommensurate, contrarily to a previous work which supported an orthorhombic normal  $Pm\bar{c}n$  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  $120^\circ$  to one another; the modulation is described by a single wave vector (1-q model) in each domain, with  $q = \chi a^*$ . 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.

**PS11.05.49 INFLUENCE OF THE DEFECTIVENESS OF THE CRYSTAL LATTICE ON THE METAMAGNETIC PHASE TRANSITIONS IN  $\text{Cd}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  (WHERE  $x \leq 0.2$ ) AND  $\text{ZnCr}_{2-x}\text{In}_x\text{Se}_4$  (WHERE  $x \leq 0.14$ ).** J. Warczewski, J. Krok-Kowalski, T. Grón, 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 spinels under investigation is confirmed by the x-ray studies [3] and the vacancy model [2]. Mixed valence of chromium ions ( $\text{Cr}^{2+}$ - $\text{Cr}^{3+}$ ) resulting from the defectiveness mentioned above is the main cause of the metamagnetic phase transition in  $\text{Cd}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ , where as in the case of  $\text{ZnCr}_{2-x}\text{In}_x\text{Se}_4$  it contributes to this effect by the increase of the values of the critical magnetic fields.

References:

- [1] H. Von Philipsborn, Z. Kristallogr., 133 (1971), 464.
- [2] T. Gron, Phil. Mag. B, 70 (1994), 121.
- [3] H. Rej, J. Warczewski and I. Okonska-Kozłowska, Materials Science Forum, Vol. 133-136 (1993), 733.

**PS11.05.50 PHASE TRANSITIONS IN  $[\text{Me}_{4-n}\text{Et}_n]_2\text{MX}_4$  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  $\text{A}_2\text{MX}_4$  system based on  $\text{A} = \text{Me}_n\text{Et}_{3-n}\text{N}^+$  cations. Previously we have shown that the structures of the  $(\text{Me}_4\text{Pc})_2\text{MX}_4$  series ( $\text{Pc} =$  group 6A element) assume the incommensurate phase bearing  $\text{K}_2\text{SO}_4$  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  $\text{K}_2\text{SO}_4$  structure type. Among the significant results to date are:

1. The  $(\text{Me}_2\text{Et}_2\text{N})_2\text{CuX}_4$  salts ( $\text{X} = \text{Cl}^-, \text{Br}^-$ ) undergo second order phase transitions at  $T_c \sim 35^\circ\text{C}$  (from  $P112_1/n$  to  $Pm\bar{c}n$ ). 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  $(\text{Me}_3\text{EtN})_2\text{CuX}_4$  salts have an acentric version of the parent structure with distortion at the zone center  $P2_1cn$  structure at room temperature. Both salts undergo two phase transitions below room temperature, with  $\sim -45^\circ\text{C}$  and  $\sim 15^\circ\text{C}$ . The shape of the DSC curves strongly suggests that the intermediate phase is incommensurate.
3. The  $(\text{Me}_3\text{EtN})_2\text{MnCl}_4$  salt crystallizes in the space group  $P12_1/n1$ , with a commensurate  $a^*/2$  modulation of the parent  $\text{K}_2\text{SO}_4$  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  $Y_2$  distortion of the parent structure.