[1] Seidel A., et al., *Phy. Rev.* B, 2003, **67**, 020405(R). [2] Sasaki T., et al., *Cond-Mat*, 0501691.
Keywords: spin-peierls, superlattice reflection, phase transition

P.08.06.33
Acta Cryst. (2005). A**61**, C326
Phase Transition in Li-Mn Spinels; *in situ* XRD and Impedance Spectroscopy Analysis
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Lithium-manganese stoichiometric spinel $LiMn_2O_4$ undergoes upon cooling phase transformation. In the present work stoichiometric and δ-spinels synthesized by sol-gel technique [1] and commercially available ones were studied at -25 to $+100^0$ C by in-situ XRD and impedance spectroscopy (in freq. Range 0.1Hz to 10 MHz). Rietveld as well as separate peaks (400) analysis were performed for phase and structure identification The correlation of the XRD profile parameters and conductivity was demonstrated. Additional phases in commercial objects seemingly containing only one phase were found and described. The lattice parameters of the regular and orthorhombic phases were determined. Accurate values of the phase transition temperatures for stoichiometric and δ-spinels were found. The change in the elementary cell volume was found to be less than 0.5%, distortion which should not influence the working parameters of battery electrodes. Appearance of electric polarization and decrease of the dc conductivity was explained by ordering of electronic charges between Mn^{3+} and Mn^{4+} in distorted spinel.

[1] Lisovytskiy D., Kaszkur Z., Baumer N.V., Pielaszek J., Molenda M., Dziembaj R., Marzec J., Molenda J., Dygas J.R., Krok F., Kopec M., *Molecular Physics Reports*, 2002, **35**, 26-30.
Keywords: spinel, phase transitions, refinement

P.08.06.34
Acta Cryst. (2005). A**61**, C326
Isosymmetric Phase Transitions in the Solid State
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The discontinuous transformations in crystalline solids without change of space symmetry, at high temperature and high pressure, attract special interest. It is convenient to attribute them to isostructural (isomorphous) phase transitions. However, the coincidence of the space groups on the both sides of the transition point is a necessary but not sufficient condition for such an attribution. The analysis of specific anomalies in the pressure/temperature-induced evolution of the certain parameters and their functional form should complement the identification procedure.

Different types of isosymmetric phase transitions, such as isostructural, anti-isostructural etc., will be defined and assigned to different non-symmetry breaking and symmetry breaking mechanisms. The role of the anharmonism of these mechanisms, and the coupling between them will be investigated.

The characteristic phase diagrams corresponding to every type of isosymmetric transformations will be presented. I will show specific details of the crossover between different transformation regimes and identify the corresponding critical points; these are the critical end point of the liquid-gas type and the Landau point.

Examples of isosymmetric transformations in rare-earth and transition metals, intermatallic compounds and oxides will be analyzed in the framework of a rigorous classification scheme.
Keywords: phase transition, phase diagram, critical point

P.08.06.35
Acta Cryst. (2005). A**61**, C326
Synchrotron Powder Diffraction Study of Phase Transitions in Rutile Type Halides
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The structures of $CaBr_2$, $CaCl_2$ and $CrCl_2$ have been investigated, using high-resolution synchrotron X-ray powder diffraction methods, at temperature of up to 800 °C. At room temperature all have an orthorhombic $CaCl_2$-type structure (*Pnnm* Z= 2). Heating $CaBr_2$ through 560 °C results in a continuous transition to a tetragonal rutile type structure ($P4_2/mnm$ Z = 2). Investigation, via either spontaneous strain or octahedral tilt angle, suggests that the transition is close to second order in nature, although the contribution from the sixth order term in the Landau potential cannot be neglected [1]. $CaCl_2$ shows a very similar transition, albeit at the lower temperature of 240 °C. By contrast the structure of $CrCl_2$ remains orthorhombic to 800 °C, and even at this temperature shows no signs of reversion toward the higher symmetry rutile structure. We observe strongly anisotropic thermal expansion in this material and, surprisingly, an increasing distortion of the $CrCl_6$ octahedron with increase in temperature.

[1] Kennedy B.J., Howard C.J., *Phys. Rev.* B, 2004, **70**, 144102.
Keywords: synchrotron X-ray diffraction, structural phase transitions, rutile-type halides

P.08.06.36
Acta Cryst. (2005). A**61**, C326
Displacive Transition Revisited by Coherent X-ray Diffraction
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The perovskite oxide $SrTiO_3$ undergoes a prototypical example of structural phase transition, which stabilizes below T_c=110 K a antiferrodistorsive modulation at the (1/2,1/2,1/2) reduced wave vector. However, this transition has been the first example where, in addition to the usual Lorentzian component in the critical x-ray scattering profiles, a sharp Lorentzian-squared component has been observed close to T_c. This sharp component was later found to be quite general in the class of structural phase transitions[1], and believed to correspond to a surface phase transition (10 to 100 μm depth), exhibiting a different critical behavior from the bulk (a second length scale) but the same transition temperature.

We show that the use of Coherent X-ray Diffraction (CXD) allows one I) to separate the different critical behaviors ii) to give evidence of the static character of the second length scale fluctuations and iii) to confirm it takes place in the near surface close to defects.

Beyond this experiment, we show that CXD is a valuable new tool to study phase transitions and defects in the low temperature ordering[2].

[1] Cowley R.A., *Physica Scripta*, 1996, T**66**, 24. [2] Le Bolloc'h D., et al., *in preparation*.
Keywords: phase transition, critical phenomena, perovskite oxide

P.08.06.37
Acta Cryst. (2005). A**61**, C326 -C327
Bifurcation and Metastable States in Phase Transitions of Nucleotide Hydrates
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The understanding of phase transitions of molecular crystals is