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**Keywords:** spin-peierls, superlattice reflection, phase transition

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#### Phase Transition in Li-Mn Spinel; *in situ* XRD and Impedance Spectroscopy Analysis

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Lithium-manganese stoichiometric spinel  $\text{LiMn}_2\text{O}_4$  undergoes upon cooling phase transformation. In the present work stoichiometric and  $\delta$ -spinel synthesized by sol-gel technique [1] and commercially available ones were studied at -25 to +100<sup>0</sup> 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  $\delta$ -spinel 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  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  in distorted spinel.

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**Keywords:** spinel, phase transitions, refinement

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#### 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, intermetallic compounds and oxides will be analyzed in the framework of a rigorous classification scheme.

**Keywords:** phase transition, phase diagram, critical point

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#### Synchrotron Powder Diffraction Study of Phase Transitions in Rutile Type Halides

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The structures of  $\text{CaBr}_2$ ,  $\text{CaCl}_2$  and  $\text{CrCl}_2$  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  $\text{CaCl}_2$ -type structure ( $Pnmm$   $Z=2$ ). Heating  $\text{CaBr}_2$  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].  $\text{CaCl}_2$  shows a very similar transition, albeit at the lower temperature of 240 °C. By contrast the structure of  $\text{CrCl}_2$  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  $\text{CrCl}_6$  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

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#### Displacive Transition Revisited by Coherent X-ray Diffraction

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The perovskite oxide  $\text{SrTiO}_3$  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<sup>1</sup>, and believed to correspond to a surface phase transition (10 to 100  $\mu\text{m}$  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<sup>2</sup>.

[1] Cowley R.A., *Physica Scripta*, 1996, T66, 24. [2] Le Bolloc'h D., et al., *in preparation*.

**Keywords:** phase transition, critical phenomena, perovskite oxide

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#### Bifurcation and Metastable States in Phase Transitions of Nucleotide Hydrates

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The understanding of phase transitions of molecular crystals is

important from the view points of solid-state chemistry and material sciences. We have been investigating the first-order phase transitions of nucleoside and nucleotide hydrates [1]. Conformational changes and shifts of molecular layers were observed coupled with increase or decrease of crystal water molecules. In addition, the transitions are characterized by hysteresis and emergence of metastable states.

One typical example is the transition of disodium 2'-deoxyguanosine 5'-phosphate (Na<sub>2</sub>dGMP) between the tetrahydrate and the anhydrous forms. Besides hysteresis, bifurcation of phase transition was observed. The tetrahydrate transforms to two different anhydrous forms, A and B. The ratio depends on the transition temperature which is correlated to vapor pressure of water. In the reverse process, anhydrous form A transforms to the tetrahydrate directly. On the other hand, an intermediate state appears in the adsorption process of anhydrous form B as is the case of guanosine [2]. By comparison of the crystal structure of the tetrahydrate with those of anhydrous forms A and B, it is concluded that interfacial and strain energy contributions in the nucleation process at the transition point are dominant factors in bifurcation, hysteresis, and emergence of the metastable states observed in the phase transitions.

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**Keywords:** phase transitions, nucleotides, hydrates

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#### Spin-Peierls Transition in Halogen-Bridged Mixed-Valence MMX Chain Compounds

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One-dimensional halogen-bridged mixed-valence dinuclear metal complexes, MMX chain compounds, have attracted much attention because of their characteristic physical properties originating from strong electron-lattice interactions and electron correlation [1].

The SQUID measurements of the novel 1-D iodo-bridged mixed-valence dinickel(II,III) complexes, Ni<sub>2</sub>(RCS<sub>2</sub>)<sub>4</sub>I (R=Et, n-Pr), revealed that the magnetic susceptibilities abruptly drop to singlet states accompanying by the spin-Peierls transition around 45 K. The X-ray diffraction images measured using the LTV X-ray camera at the SPring-8 BL02B1 showed superlattice reflections corresponding to 2-fold repetition length of the MMX units below 40 K. Single crystal structure analysis of Ni<sub>2</sub>(EtCS<sub>2</sub>)<sub>4</sub>I at 26 K including the superlattice reflections revealed the distorted structure like the ACP states observed for the LT phase of Pt<sub>2</sub>(RCS<sub>2</sub>)<sub>4</sub>I (R=Et, n-Bu) [1].

[1] Mitsumi M., Kitamura K., Morinaga A., Ozawa Y., Kobayashi M., Toriumi K., Iso Y., Kitagawa H., Mitani T., *Angew. Chem. Int. Ed.*, 2002, **41**, 2767.

**Keywords:** spin-peierls transition, 1-D mixed valence compound, synchrotron radiation crystallography

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#### Fe(II), Fe(III) and Co(II)-Complexes with Aromatic Nitrogen-Containing Ligands

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Spin crossover compounds change electronic state in response to external perturbations such as change in temperature, pressure or irradiation. Complexes of Fe(II), Fe(III) and Co(II) can exhibit spin crossover behavior combined with suitable ligands. In this work 2,6-bis(2-pyridyl)-4(1H)-pyridone (OHterpy) 4'-Chloro-2,2':6',2"-terpyridine (Clterpy), 2,3,7,8-Tetrakis(2-pyridyl)pyrazino[2,3-g]quinoxaline (BL2), and 2,3,2',3'-tetrakis(2-pyridyl)-6,6'-biquinoxalyl (BL3) are used as ligands to obtain new spin crossover compounds. The spin crossover and possible hysteresis effects are highly dependent on intermolecular interactions within the crystals; changing the counter ion or solvent can affect both the crossover

temperature and the evolution of it, as well as the hysteresis properties. [Co(II)(OHterpy)<sub>2</sub>]X<sub>2</sub>·nH<sub>2</sub>O exhibits spin crossover with X = ClO<sub>4</sub><sup>-</sup> [1]. [Co(II)(OHterpy)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O was synthesized and crystals were obtained by slow diffusion of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and OHterpy in methanol. The compound crystallizes in the triclinic space group P  $\bar{1}$  with unit cell dimensions:  $a = 8.831 \text{ \AA}$ ,  $b = 8.875 \text{ \AA}$ ,  $c = 18.588 \text{ \AA}$ ,  $\alpha = 86.13^\circ$ ,  $\beta = 84.01^\circ$ ,  $\gamma = 89.00^\circ$ . Co-N distances in this hexacoordinated complex are 1.893 Å for both Co-N<sub>central</sub> and vary from 2.069 to 2.086 Å for the four Co-N<sub>distal</sub>. The data were collected at 153 K, and judging from the Co-N distances only, the compound is predominantly low spin at this temperature.

[1] Gaspar A.B., Munoz M.C., Niel V., Real J.A., *Inorg. Chem.*, 2001, **40**, 9.

**Keywords:** transition metal complexes, aromatic nitrogen-containing ligands, spin crossover

#### P.08.06.40

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#### Spin Crossover in Solvates of an Iron(II) Complex with Solvent Mixtures

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Recently it has been shown that the family of crystalline alcohol solvates of [Fe<sup>II</sup>(2-pic)<sub>3</sub>]Cl<sub>2</sub> display a range of spin transition scenarios: two-step transitions with and without hysteresis (2-propanol and ethanol), continuous transitions (methanol, 2-butanol) as well as the absence of any spin crossover (1-propanol, *tert*-butanol) [1]. These findings raise the question about the properties of solvates crystallized from mixtures of two alcohols. We present the structures and magnetic properties of three such mixed solvates of [Fe<sup>II</sup>(2-pic)<sub>3</sub>]Cl<sub>2</sub> as obtained from diffraction and SQUID measurements. The mixed 1-propanol:2-propanol and ethanol:2-propanol solvates show continuous spin transitions, while the methanol:ethanol mixture shows a two-step transition.

The thermal and positional disorder of the solvent molecules is found to be coupled with the spin conversion of the bi-stable [Fe<sup>II</sup>(2-pic)<sub>3</sub>] complex, an observation which will also be discussed theoretically.

[1] Hostettler M., et al., *Angew. Chem. Int. Ed.*, 2004, **43**, n.35, 4589.

**Keywords:** spin crossover, phase transition, order-disorder

#### P.08.06.41

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#### Dopant Atom Influence on the $\alpha \rightarrow \beta$ Phase Transition in Thermoelectric Zn<sub>4</sub>Sb<sub>3</sub>

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Zn<sub>4</sub>Sb<sub>3</sub> is a high performance thermoelectric material with an extremely high thermoelectric Figure of Merit at relatively low temperatures. Furthermore, previous studies by Jet Propulsion Laboratory have shown that the thermoelectric Figure of Merit can be improved by doping Zn<sub>4</sub>Sb<sub>3</sub> with Cd.

Zn<sub>4</sub>Sb<sub>3</sub> exists in three crystalline forms; the  $\alpha$ ,  $\beta$ , and  $\gamma$  phase before melting at 841 K. Only the  $\beta$ -phase (stable between 263 and 765K) has good thermoelectric properties. It is therefore of interest to examine what effect the dopant atom substitutions has on the  $\alpha \rightarrow \beta$  phase transition.

Multi temperature data was measured on a series of M<sub>x</sub>Zn<sub>4-x</sub>Sb<sub>3</sub> (M = Hg, Sn, Pb, Mg, Cd) using the large Debye Scherrer camera at beamline BL02B2 at Spring 8 in Japan. The data have been Rietveld refined in order to follow the phase transition.

The physical properties of the samples were measured on a Quantum Design Physical Property Measurement System, to