

that the large structural changes are accompanied with the successive phase transitions.

Keywords: inorganic organic compounds, neutron X-ray scattering, structural phase transitions

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Powder neutron diffraction studies of inorganic ferroelectric phase transitions

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We shall present some of our recent results on the nature of the ferroelectric-paraelectric and other phase transitions in a variety of inorganic systems, as studied by variable temperature powder neutron diffraction. Examples will include the contrasting behaviours of the Aurivillius family of layered perovskites including $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and Bi_2WO_6 ; the former involves simply 'octahedral tilt' type transitions, whereas the latter involves a reconstructive transition from corner-shared to edge-shared octahedra. Other examples will include the unusual layered oxyfluoride $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$, which exhibits a remarkably high TC for a fluoride ($\sim 800\text{K}$), and which shows 3 ferroelectric phases below TC. Finally, the important multiferroic BiFeO_3 has been studied, and we will comment on its structural behaviour versus temperature, especially around TC, and including the possibility of a cubic paraelectric phase.

Keywords: ferroelectric, powder neutron diffraction, phase transitions

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Structural phase transitions in *trans*-1,2-diaminocyclohexane derivative

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trans-1,2-Diaminocyclohexane, a rigid molecule of C_2 symmetry and two equatorial C-N bonds, was used as a chiral element of hydrogen-bonded networks and also as a bidentate ligand for chiral catalysts. We reported the synthesis and room temperature crystal structure of *trans*-(1*R*,2*R*)-*N*-acetyl-*N,N'*-di-(4-bromophenyl)-1,2-diamino cyclohexane [1]. Quite unexpectedly we have found out two reversible phase transitions in the temperature range 100-295K. The previously published room-temperature crystal structure is monoclinic $P2_1$, with $Z'=1$. The structure is disordered: one of the bromine atoms occupies two alternative positions with equal probability (s.o.f.'s are 0.5). The anisotropic refinement of bromine atoms in both positions was very stable and led to perfectly reasonable geometries and U_{ij} values. On cooling down, below ca. 250K, the crystal undergoes the continuous phase transition to another monoclinic $P2_1$ phase, with a doubled value of the c unit-cell parameter, and two symmetry-independent molecules ($Z'=2$). The attempts were made to refine either the room temperature structure in the low temperature unit cell or vice versa, but none of these refinements led to reasonable results. Of course room temperature structure could be refined in a bigger unit cell, but the final effect was inferior to the original one. Above all, the new refinement did

not lead to the ordering of bromine atoms, and some displacement parameters became non-positive determined. Below 160K another phase transition takes place, this time to the triclinic $P1$ space group with two molecules in the unit cell (i.e., $Z'=2$). Both phase transitions are reversible; we were able to use the same crystal many times and observe the same diffraction patterns.

[1] M.Kwit et al., *Pol.J.Chem.* 77 (2003) 1669.

Keywords: phase transitions, intermolecular interactions, disorder

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Order parameters for phase transitions to structures with incommensurate modulations

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Given the k vector for a distortion in a parent crystalline structure, what resulting space-group symmetries are possible? We have answered this question (Stokes, Campbell & Hatch, 2007, *Acta Cryst.* A63, 365) for the case of one-dimensional incommensurate modulations where the resulting symmetries are described by (3+1)-dimensional superspace groups. Most recently, we have extended our group theoretical methods to the general case of any arbitrary set of N modulations where the symmetries are described by (3+N)-dimensional superspace groups.

Keywords: phase transitions in solids, incommensurate modulated structures, group theory

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Spontaneous strain in superconductors

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Recently, the change in the orthorhombicity of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ at the superconducting transition temperature T_c could be clearly detected by accurate lattice parameter measurement [1]. The introduction of a new critical exponent was considered necessary for explaining the result. The very small anomaly of the lattice parameters of intermetallic superconductor MgB_2 was also clearly observed near T_c [2]. This anomaly was considered to be independent of the superconductivity onset. We could also clearly detect the change in the lattice parameter of the high-temperature superconductor $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ at T_c [3]. For the first time, we showed that the change can be attributed to a spontaneous strain in the superconducting phase caused by the coupling between a superconducting order parameter and the strain. We indicated that the anomaly in MgB_2 can also be understood on the basis of the same coupling. Similar experiments on conventional superconductors are necessary to clarify whether such a phenomenon is common to all superconductors. We carried out powder X-ray diffraction experiments on $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$, which is a well-studied conventional superconductor with a simple cubic perovskite structure. The diffraction patterns were analyzed by the Rietveld

method to obtain accurate lattice parameters. The Meissner effect was also measured to determine the T_c . The change in the lattice parameter of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ could be detected at T_c , which can be attributed to the spontaneous strain in the superconducting phase. We can conclude that this phenomenon is common to all superconductors.

[1] Fujii Y. *et al.*, *Physica C*, 2002, **377**, 49. [2] Jorgensen J.D. *et al.*, *cond-mat/0205486*. [3] Fujishita H. *et al.*, *Solid State Commun.*, 2008, **145**, 246.

Keywords: spontaneous strain, superconductors, phenomenological theory

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Charge ordering, isosymmetrical phase transitions and magnetic properties of mixed valence vanadates

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The mixed valence vanadates $\text{MV}^{3+}\text{V}_3^{4+}\text{O}_8$ (M=Yb, Y, Lu) are structurally related to CaFe_2O_4 and are build of a framework of VO_6 -octahedra [1,2]. Two different phases (α and β), which differ only in the arrangement of the trivalent M-cations, are known. Their similarity favours the occurrence of polytypism. The magnetic susceptibility shows anomalies for the β -phases at ≈ 185 K (YbV_4O_8 , [3]) and 190 K (YV_4O_8 , [2]), respectively. For the α -phases, the anomalies occur below 100 K. Powder and single crystal diffraction as well as specific heat studies confirm the existence of first order isosymmetrical structural phase transitions. While above the phase transition the bond valence sums indicate no clear charge separation of the tri- and tetravalent V-ions, below the transition temperature a complete charge ordering is observed. The magnetic transitions can be understood assuming that the Curie-Weiss type d-electrons of the vanadium cations in the high temperature phases separate at the phase transition into d-electrons, which maintain their Curie-Weiss character and others, which lose their spin moment. The unusual complete charge ordering can thus be attributed not only to Coulomb repulsion between the cations, but also to possible spin gap formation [3]. Lattice parameter of the α -phase show a clear domain size effect: for samples with large domain sizes (≥ 100 Å) they show a smooth behaviour down to the phase transition temperature (65 K), while for samples with small domain sizes (≤ 40 Å) they are influenced by the phase transition in the β -phase (180 K).

[1] Y. Kanke, K. Kato, *Chem. Mater.* **9**, 141, 1997.

[2] M. Onoda, A.-C. Dhaussy, Y. Kanke, *Acta Crystallogr.* **B59**, 429, 2003.

[3] K. Friese, Y. Kanke, A. N. Fitch, A. Grzechnik, *Chem. Mater.* **19**, 4882, 2007.

Keywords: isosymmetrical phase transition, charge order, composit crystal

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Neutron diffraction study of quantum effects on structural phase transition in quartz

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A phenomenological theory describes the temperature dependences of the order parameter Q , which is atomic shifts in displacive structural phase transition, and of strain e , which is coupled to Q , near a phase transition. We can describe their temperature dependences at low temperature if we use the quantum expansion of a potential [1]. We carried out the X-ray structure analysis of quartz, which shows a structural phase transition at approximately 850K, at various temperatures between 298 and 1126K using a single crystal [2]. The atomic shift of Si and the change in the strain were shown to obey the classical phenomenological theory. Recently, Romero and Salje have carried out a precise X-ray lattice parameter measurement of quartz in the temperature range of 30-300K [3]. They showed that the strain obeys the quantum phenomenological theory with a characteristic temperature of 187K. Direct evaluation of the quantum phenomenological theory by measuring the order parameter in the entire temperature range is required to verify the effectiveness of the theory. We carried out the structure analysis of quartz by powder neutron diffraction at several temperatures in the temperature range of 10-250K. Powder neutron diffraction patterns were obtained using a high-resolution powder diffractometer with 64 detectors. The diffraction patterns were analyzed by the Rietveld method. Squares of the shift of the Si atom along the a-direction and the strain were found to show the proportional dependence of each other in the entire temperature region. The effectiveness of the theory was directly verified by the atomic shift.

[1] Salje E.F.K., *Acta Cryst.*, 1991, **A47**, 453. [2] Kihara K., *Eur. J. Mineral.*, 1990, **2**, 63. [3] Romero F. J., Salje E.K.H., *J. Phys.: Condens. Matter*, 2003, **15**, 315.

Keywords: quartz, structure analysis, quantum expansion of Landau potential

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Effect of temperature and pressure on the crystal structure of $\text{NaV}_6\text{O}_{11}$

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Since the discovery of its anomalous resistivity and ferrimagnetism, $\text{NaV}_6\text{O}_{11}$ received wide interest. Its structure ($P6_3/mmc$, $Z = 2$) consists of hcp layers of O and Na atoms. V(1) O_6 octahedra form a Kagome; lattice, while V(2) O_6 octahedra form a face-sharing dimer. V(3) cations are five-fold coordinated to oxygen. The compound shows two structural phase transitions at 243K ($P6_3/mmc$ ---