Phase Transitions II

MS11.05b.01 RECONSTRUCTIVE TRANSFORMATIONS IN CRYSTAL STRUCTURES. V.P. Dmitriev, Institute of Physics, Rostov State University, Rostov on Don 344090, Russia

Most of the phase transformations occuring in crystalline objects possess a reconstructive character, with an absence of group-subgroup relarionship between the symmetries of the structures of the phases surrounding the transition. There exists however a close relationship between the preceding structures. A modern view will be presented on the theory of reconstructive phase transitions [1] which makes use of a density-wave description of the structures instead of the traditional approach based on purely symmetry considerations. The basic ideas of this modified theory of reconstructive phase transitions will be presented through the examples of compounds displaying a complex polymorphism, such as carbon, ice, silicium dioxide and cryogenic crystals.

[1]. P. Toledano and V. Dmitriev, "Reconstructive Phase Transitions" (World Scientific, Singapore, 1996).

MS11.05b.02 X-RAY STUDY OF ORDER - DISORDER PHASE TRANSITIONS. A. Pietraszko, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland

The microscopic mechanism of the order-disorder phase transitions is a topic of considerable interest. Disorder occurs in the crystalline phases of many kinds of organic and inorganic compounds and may be the result of dynamic processes in the crystal structure (dynamic disorder). Static disorder is a result of two or more different orientations of molecule in a crystal with similar energies, or random distribution of atoms among equivalent positions with the occupancy <1. X-ray diffraction effects will be discussed for two cases: (*i*) when the positions of atoms are well resolved (*e.g.* in crystals $RbLiSO_4$ and $CsLiSO_4$ of $AA'BX_4$ type), (*ii*) when and due to small displacements of atoms their positions overlap and cannot be resolved (*e.g.* $Cd_2NB_2O_7$ crystals). We define a model for $AA'BX_4$ crystal structures with non-dynamic disorder of the orientational subsystems and examine the coupling the disordered tetrahedra BX_4 with the distortion of the lattice parameters.

Dynamic disorder of one or more sublattices in the crystal is the distinguishing feature of the ionically conducting solids. The disorder can be a result of either a temperature increase or of an order-disorder structure phase transition. The X-ray study of proton superionic conductors of $Me_4LiH_3(XO_4)_4$ and $(NH_4)_3H(SeO_4)_2$ will be presented.

Recently many works have been devoted to X-ray investigations of the pretransitional phenomena with order-disorder phase transitions, because they can help to explain the nature of these transformations. The existence of such phenomena in the $RbLiSO_4$ and $CsLiSO_4$ crystals will be presented.

MS11.05b.03 STRUCTURAL CHANGES IN SINGLE CRYSTALS BY TIME-OF-FLIGHT NEUTRON LAUE DIFFRACTION. C C Wilson, ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 OQX, UK.

The study of phase transitions can be carried out in two ways using neutron time-of-flight Laue diffraction. The first is the conventional manner in which full data sets are collected under each set of physical conditions, from which full refinements can yield the significant structural changes. The second exploits the ability of the time-of-flight Laue method to access a large volume of reciprocal space in a single measurement. The method assumes the transition can be characterised by the changes in a small subset of reflections, the aim being to reduce the amount of data collected to a single frame [1].

The possibilities for monitoring phase transitions in single crystals using both methods are considered. The possibilities for rapid collection of full data sets will be discussed, emphasising the flexibility of the time-of-flight Laue technique. For the single frame case, methods for choosing the optimal single frame to best reflect the structural change of interest will be examined, along with techniques for refinement in this case.

Examples discussed will include the temperature dependence of proton transfer in benzoic acid [2] and the hydrogen atom ordering in the mineral $PbHAsO_4$ [3].

These measurements have shown that the time-of-flight Laue method yields real potential for 'dynamic' measurements of single crystal materials using neutrons.

[1] C C Wilson (1995). *J. Appl. Cryst.*, **28**, 7-13.

[2] C C Wilson, N Shankland & A J Florence (1996). *Chem. Phys. Letts.*, submitted.

[3] C C Wilson (1996). *J Synchrotron Rad*, **3**, 20-23.

MS11.05b.04 NMR OF PHASE TRANSITIONS IN SEMIDISORDERED CRYSTALS. R. Blinc, J. Stefan, Institute, University of Ljubljana, Ljubljana, Slovenia

The usefullness of NMR for the study of the local structure and phase transitions in partially disordered systems is illustrated on the example of: i) proton glasses and quadrupolar glasses, ii) triple q modulated incommensurate crystals and iii) ferroelectric and antiferroelectric smectic liquid crystals. Specifically we show how NMR is used to determine the local polarization distribution function and the Edwards-Anderson order parameter in the deuteron glass $Rb_{1-x}(ND_4)_xD_2PO_4$ and the quadrupolar glass $K_{1-x}Na_xCN$, the soliton density in incommensurate Ag_3AsS_3 and the polar and bipolar orientational order parameters in the ferroelectric liquid crystal CE-8 and the antiferroelectric liquid crystal MHPOBC. In all the above cases we deal with small deviations from the average structure which are hard to detect by scattering techniques but which can be easily seen by quadrupole perturbed NMR. The results of 87Rb and 2H NMR in $Rb_{1-x}(ND_4))_xD_2PO_4$ and of 14N NMR in $K_{1-x}Na$ CN show that the T-dependence of the Edwards-Anderson order parameter can be described by the random bond- random field model but not by random fields only. 75As NMR and NQR results show that the soliton density is the order parameter of the I-C transition in proustite. In the ferroelectric liquid crystal CE-8 the bipolar order parameter is larger than the polar one over the whole ferroelectric SmC* phase except close to the SmA-SmC* transition.

MS11.05b.05 PHASE TRANSITIONS IN PROTON CONDUCTING $Me_3H(AO_4)_2$. R. Melzer, Institut für Mineralogie, TU Berlin, D-10587 Berlin

The different types of temperature-dependent phase transitions, which can be observed in the proton conductor family $Me_3H(AO_4)_2$ with Me = NH_4, K, Rb, Cs and A= S, Se, will be discussed with special emphasis on their behaviour, origin and symmetry reduction.

Two-dimensional rhombohedral proton conducting phases of this family are stable at moderate temperatures above room temperature (see e.g. Pawlowski et al., 1990). They are characterised by disordered hydrogen bridges accompanied by strong librations of the AO_4 tetrahedra (see e.g. Bohn et al., 1995). On lowering the temperature all family members show one or more (up to 6) phase transitions into lower-symmetry phases. Different ordering mechanisms are responsible for the, generally ferroic, transitions, which can be classified as follows: