

## 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 occurring in crystalline objects possess a reconstructive character, with an absence of group-subgroup relationship 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, silicon 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  $\text{RbLiSO}_4$  and  $\text{CsLiSO}_4$  of  $\text{AA}'\text{BX}_4$  type), (ii) when and due to small displacements of atoms their positions overlap and cannot be resolved (e.g.  $\text{Cd}_2\text{NB}_2\text{O}_7$  crystals). We define a model for  $\text{AA}'\text{BX}_4$  crystal structures with non-dynamic disorder of the orientational subsystems and examine the coupling the disordered tetrahedra  $\text{BX}_4$  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  $\text{Me}_4\text{LiH}_3(\text{XO}_4)_4$  and  $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$  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  $\text{RbLiSO}_4$  and  $\text{CsLiSO}_4$  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 0QX, 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  $\text{PbHAsO}_4$  [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 usefulness 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 deuterium glass  $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{PO}_4$  and the quadrupolar glass  $\text{K}_{1-x}\text{Na}_x\text{CN}$ , the soliton density in incommensurate  $\text{Ag}_3\text{AsS}_3$  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  $^{87}\text{Rb}$  and  $^2\text{H}$  NMR in  $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{PO}_4$  and of  $^{14}\text{N}$  NMR in  $\text{K}_{1-x}\text{Na}_x\text{CN}$  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.  $^{75}\text{As}$  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  $\text{SmC}^*$  phase except close to the  $\text{SmA-SmC}^*$  transition.

**MS11.05b.05 PHASE TRANSITIONS IN PROTON CONDUCTING  $\text{Me}_3\text{H}(\text{AO}_4)_2$ .** 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  $\text{Me}_3\text{H}(\text{AO}_4)_2$  with  $\text{Me} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$  and  $\text{A} = \text{S}, \text{Se}$ , 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  $\text{AO}_4$  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:

1. freezing of one type of  $\text{AO}_4$  libration
2. ordering of the two-dimensional hydrogen bridge system
3.  $\text{AO}_4$  dimer switching
4. proton ordering within a hydrogen bridge

A complete survey of all known transitions will be presented and examples of the different ordering mechanisms will be analysed in view of experiment and theory.

#### References:

- Pawlowski, A., Pawlaczyk, Cz., Hilczer, B.: *Solid State Ionics* 44 (1990) 17-19.  
 Bohn, A., Melzer, R., Sonntag, R., Lechner, R.E., Schuck, G., Langer, K. (1995).  
*Solid State Ionics* 77, 111 - 117.

**MS11.05b.06 STRUCTURE DETERMINATION AT HIGH PRESSURES FROM MOLECULAR DYNAMICS SIMULATIONS.** S. K. Sikka, Surinder M. Sharma, R. Chidambaram, High Pressure Physics Division, Bhabha Atomic Research Center Bombay - 400 085

We describe the use of molecular dynamics (MD) simulations to determine the structures of some high pressure phases which give only a few Bragg peaks in their diffraction patterns. In  $\alpha$ -quartz, Kingma et al<sup>1</sup> had reported the diffraction pattern of a new phase before amorphization at 21 GPa. Using the coordinates derived from MD simulations, employing the pair potentials of Tsuneyuki et al<sup>2</sup>, we got x-ray patterns in excellent agreement with experimental results - indicative of a tripling of the  $\alpha$ -quartz unit cell in its basal plane. A monoclinic cell could then be derived.<sup>3</sup>

In  $\text{LiCsSO}_4$ , there has been a controversy about the number and nature of pressure induced phases. We have carried out x-ray diffraction studies on this and have detected two c-c transitions at 4 and 7 GPa and amorphization at  $\sim 19$  GPa<sup>4</sup>. Our data rule out the earlier conjecture that the 4 GPa transition is the orthorhombic to monoclinic (a low temperature phase) one. Instead the x-ray pattern here strongly resembles the one calculated from the coordinates of 9.8 GPa phase of  $\text{LiKSO}_4$  as computed by an earlier MD simulation<sup>5</sup>. This new structure is related to the ambient one through the softening of the (1/3, 1/2, 0) mode and has higher oxygen coordination for Li atoms.

Another application to solve the intermediate structure between fcc and hcp structures of Xe in the pressure range 12-75 GPa will also be described.

1. K. J. Kingma, R. J. Hemlely, H. K. Mao and D. R. Velten, *Phys.Rev.Lett* **70**, 3927 (1993).
2. S. Tsuneyuki, Y. Tsukada and H. Aoki, *Phys Rev.Lett.* **61**, 869 (1988).
3. M. S. Somayazulu, S. M. Sharma and S. K. Sikka, *Phys.Rev.Lett.* **73**, 98 (1994).
4. S. M. Sharma, N. Garg, V. Chitra and S. K. Sikka -to be published.
5. S. L. Chaplot and S. K. Sikka, *Phys Rev. B* **47**, 5710 (1993).

## Analysis of Atomic Displacement Parameters

### MS11.06.01 NORMAL MODE ANALYSIS FROM ELASTIC DIFFRACTION DATA IS POSSIBLE! WHY AND HOW?

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It is generally believed that atomic mean square displacement parameters (ADP) obtained from an elastic diffraction experiment provide information on the motion of individual atoms, but cannot say anything on the cooperative displacements of groups of atoms unless assumptions of questionable validity are made. This opinion is correct with respect to ADP's pertaining to a single temperature; it is untenable, however, when ADP's at several temperatures are available. Why is this so?

ADP's can be considered as a superposition of the contributions from many normal modes. The absolute atomic displacements of a mode depend on its energy ( $\nu$ ), its effective or reduced mass ( $\mu$ ), on temperature ( $T$ ) and on relative displacement ( $A$ ) according to  $A \cdot h / (8 \cdot \pi^2 \cdot \mu \cdot \nu) \cdot \coth [h \cdot \nu / (2 \cdot k \cdot T)]$ . At sufficiently low temperatures this expression can be approximated by  $A \cdot h / (8 \cdot \pi^2 \cdot \mu \cdot \nu)$ . At sufficiently high temperatures the corresponding approximation is  $A \cdot k \cdot T / (4 \cdot \pi^2 \cdot \mu \cdot \nu^2)$ .

Now, suppose that a mean squared displacement  $U$  is the result of a superposition of two normal modes only and that it has been measured at a low and at a high temperature; then  $U(\text{low } T) = A1 \cdot h / (8 \cdot \pi^2 \cdot \mu 1 \cdot \nu 1) + A2 \cdot h / (8 \cdot \pi^2 \cdot \mu 2 \cdot \nu 2)$   
 $U(\text{high } T) = A1 \cdot k \cdot T / (4 \cdot \pi^2 \cdot \mu 1 \cdot \nu 1^2) + A2 \cdot k \cdot T / (4 \cdot \pi^2 \cdot \mu 2 \cdot \nu 2^2)$ .

From the two independent observations the two normal frequencies can be determined, provided  $A1$  and  $A2$  are known. This simple argument can be generalized to more than two frequencies and to the corresponding relative displacements if the coth-dependence and the three-dimensional information contained in the ADP's are taken into account. In practice, ADP's need to be measured at a sufficient number of appropriate temperatures.

### MS11.06.02 MODELLING THE THERMAL MOTION OF FREELY ROTATING MOLECULES.

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All molecular gas-phases become crystalline when subjected to sufficient pressure. Spectroscopic studies show that the molecules are freely rotating while near the freezing point for many of these phases. As pressure increases the motion is constrained and a lowering of symmetry occurs. In order to model the freely rotating molecule we calculated molecular electron-density wave functions using the *Gaussian92* program for energy-optimized model molecules. The electron-density was then spherically averaged in order to mimic the rotations. The Fourier transform of this spherically averaged electron density provides the scattering factor for the rotating molecule. The displacement parameters obtained from the structure refinement then provide estimates of translational motion.

### MS11.06.03 LATTICE-DYNAMICAL CALCULATION OF ATOMIC DISPLACEMENT PARAMETERS (ADPs).

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ADPs comparable with the corresponding values obtained from crystal structure refinement can be derived from Born-von Karman lattice dynamics. A rigid ion model has been assumed, where atomic charges and VFF parameters have been deduced from best fit to the vibrational frequencies of a series of similar compounds, either molecular crystals or even ionic, non-molecular