

upon convolution with the undistorted lattice could give rise to Moiré fringes as were observed in the images. High resolution EM substantiated by image computation confirms the existence of these defects on an atomic scale.

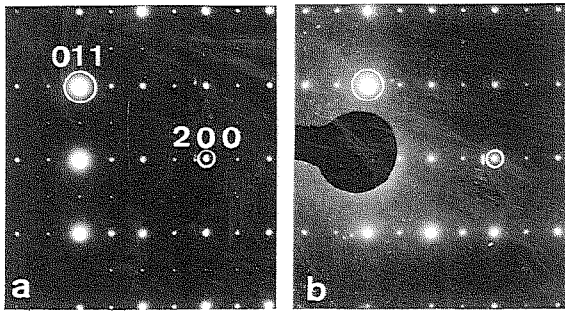


Fig. 1 : Phase transition in RbFeF_4 as observed with electron diffraction in a $[011]$ zone pattern. (a) RT (b) LNT

05.1-33 AN X-RAY DIFFRACTION STUDY OF THE PHASE TRANSITION IN PbHPO_4 . By A. Katrusiak* and R.J. Nelmes, Department of Physics, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, U.K.

PbHPO_4 (hereafter LHP) has a second-order phase transition at $T_C = 310$ K. Phenomenologically this transition is very similar to that in KH_2PO_4 (hereafter KDP). LHP has a particularly simple crystal structure in which the PO_4 groups are linked into one-dimensional chains by hydrogen bonds. Above T_C the protons are disordered over two sites in these bonds, and below T_C become fully ordered onto one of the sites — as in KDP. It is generally assumed that such transitions, of the KDP type, are "driven" by this proton ordering. One respect in which LHP differs from KDP is that its spontaneous polarisation, P^S , rises only slowly with falling temperature below T_C , and does not reach saturation until approximately $T_C - 100$ K. A neutron-diffraction study (Nelmes, Ferroelectrics (1980) 24, 237) has shown that the degree of proton ordering (from 50/50 above T_C , through 75/25, to 100/0 at $-T_C - 100$ K) has the same temperature dependence as P^S . But, by contrast, the heavy-atom displacements (e.g. the distortion of the PO_4 groups) were found to reach their saturated values only ~ 10 K below T_C . This difference is an unexpected and puzzling result that challenges the generally accepted understanding of transitions of this kind as being "driven" by the proton ordering, with strong coupling between the proton and heavy-atom fluctuations. To check the neutron-diffraction result for the (rather small) heavy-atom displacements, and obtain information about these displacements closer to T_C , we have now carried out a careful, high-resolution X-ray diffraction study of LHP. Data have been collected at $T_C + 10$ K, in the range $T_C - 2$ K to $T_C - 20$ K, and at $\sim T_C - 100$ K. The combined results of the neutron-diffraction and X-ray diffraction studies will be presented. *On leave from A. Mickiewicz Univ., Poland.

05.1-34 THE INCOMMENSURATE-COMMENSURATE PHASE TRANSITION IN Rb_2ZnCl_4 . By K. H. Ehses, U. Schürmann, Fachrichtung Kristallographie, Universität des Saarlandes, D-6600 Saarbrücken Federal Republic of Germany.

For the investigation of the modulation vector in incommensurate (IC) phases, a high resolution in reciprocal space is necessary. Such a resolution can be obtained by means of our double-axis-diffractometer 'AMADEUS' in the dispersion free arrangement, where the resolution is only determined by the sample quality.

In the space group Pcmn for Rb_2ZnCl_4 the incommensurate wave number is $q_z = (1/3 - \delta)c^*$. The half width of the IC-reflections is clearly greater than that of the main reflections. The temperature dependence of the parameter δ coincides over a large temperature range with that of previous measurements (H. Mashiyama, J. Phys. Soc. Jap. (1982) 51, 2538). But at T_C the transition temperature to the ferroelectric phase, we find a discontinuous behaviour of δ . There is a region of about two degrees, where the IC- and the commensurate (C) peaks coexist. In this range the half width of the IC-reflection increases to T_C , the commensurate one remains constant. The integrated intensity of the IC-satellite decreases to T_C , whereas that of the corresponding C-reflection increases, the sum remaining nearly constant.

The influence of an electric field on the behaviour of δ has been investigated.

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05.1-35 LOW TEMPERATURE PHASE TRANSITIONS IN LiKSO_4 : A NEUTRON DIFFRACTION STUDY. By Sandhya Bhakay-Tamhane, A. Sequeira and R. Chidambaram, Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

A single crystal neutron diffraction study of the low-temperature structural phase transitions in LiKSO_4 has been carried out using the closed-cycle cryo-tip on the 4-circle diffractometer at the CIRUS reactor, Trombay. Various other techniques (laser Raman, EPR, NMR, IR, etc.) employed earlier for studying these phase transitions have given somewhat different descriptions of the phases and the transition temperatures in this system.

The room temperature neutron diffraction structure of LiKSO_4 (Bhakay-Tamhane, Sequeira & Chidambaram, Acta Cryst. C, (1984)) has the space group P6_3 with $a = 5.140(1)$, $c = 8.636(2)$ Å and $Z = 2$ (though the alternate space group P2_1 could not be ruled out) and all the samples studied show merohedral twinning about the $[110]$ axis. The intensities and profiles (in θ - 2θ scan) of a group of 20 Bragg reflections were studied from room temperature down to 150K. Cooling the sample down to about 200K resulted in a small general increase in the intensities of the reflections which could be accounted for by the Debye-Waller factor. Below 200K however, the Bragg intensities undergo pronounced changes. This transition to a new phase takes over a day to equilibrate at 190K. From about 189K, many of the Bragg reflection profiles are characterised by split peaks (which start as shoulders to the main profile) and this continues to the lowest temperatures reached in this study. The relative strengths and positions of the various peaks within a profile, however, change with temperature and time. These changes are very sluggish and the system takes several days to

equilibrate. There are indications for the existence of a mixed phase in this temperature range between 190K and 150K. All the phase changes in this system have been found to have hysteresis.

Single crystal neutron diffraction data have been collected at 190K, 178.5K, 168K and 150K (upto $\sin\theta/\lambda = 0.50\text{\AA}^{-1}$, $\lambda = 1.036\text{\AA}$). The kinetics of the phase transitions and the structural details of various phases will be presented.

05.1-36 POLYTYPISM AND PHASE TRANSITION OF $\text{Sb}_5\text{O}_7\text{I}$.
2. THE ORDER PARAMETER. By W. Altenburger, G. Bosch, I.R. Jahn, W. Prandl and M. Verhein, Institut für Kristallographie der Universität Tübingen; and V. Krämer, Kristallographisches Institut der Universität Freiburg, Germany.

In this paper we report on birefringence measurements performed at the antiferrodistortive phase transitions of all polytypes of $\text{Sb}_5\text{O}_7\text{I}$ (SOI) identified up to now. Details of the structure, polytypism and notation are given in the accompanying contribution (I.R. Jahn, W. Altenburger and V. Krämer, this conference). The phase transitions ranging between 438 K and 481 K can be described by a zone boundary soft mode. Consequently, the birefringence follows the square of the order parameter.

The most common centrosymmetric basic type 2MC has been studied as a function of temperature and hydrostatic pressure (up to 0.5 GPa). Furthermore, in the mixed system $[\text{Sb}_{1-x}\text{As}_x]_5\text{O}_7\text{I}$ the antimony ions have been replaced by arsenic ions up to $x = 0.13$.

We find the following results: In 2MC the ferroelastic phase transition is weakly of first-order, the order parameter can be well described by the classical Landau formalism with a negative 4th order term. Hydrostatic pressure increases the transition temperature of pure 2MC by 10 K / 0.1 GPa, whereas the discontinuity is practically not affected by pressure. In the mixed system, however, the As content leads to a drastic lowering of T_C and a remarkable increase of the discontinuity.

The 2MA and the higher polytypes all of which contain the acentric 2MA behave completely different from the 2MC compound: the birefringence cannot be interpreted in terms of a free-energy expansion with even powers of the order parameter only. This deviation from the "normal"

Landau theory and the symmetry of the 2MA lattice, both point to a Potts-type interaction as in the case of $\text{Pb}_3(\text{PO}_4)_2$ (E. Salje, B. Wruck, Phys. Rev. (1983) B28, 6510). We, therefore, have to consider a term of third order in the Landau theory.

During these experiments, the results were often affected by multiple light beam reflection within the sample. In SOI the phenomenon occurs in a pronounced manner because of the ideal cleavage and the very high refractive indices, and it shows up as a wavyness of the monotonic birefringence curves. To get a feeling for the multiple reflection effects in birefringent plates, we performed calculations for the given experimental conditions and were able to reproduce the observations.

05.1-37 STRUCTURAL PHASE TRANSITION IN $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$.
By A. Hoser and J. Ihringer, Institut für Kristallographie der Universität Tübingen, West-Germany.

Hexammine nickel chloride $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ was studied with a focusing x-ray powder diffractometer between 297 and 35 K. The room temperature phase has Fm3m space group (CaF₂-type). The low temperature phase, which exists below 78 K has a monoclinic symmetry with $a = 9.2982(7)$, $b = 6.8819(5)$, $c = 7.6985(5)$ Å, $\beta = 92.36(1)^\circ$, $Z = 2$, (35 K). The phase transition deforms the cubic unit cell strongly. The change of the cell constants a - a_{cub} and c - $a_{\text{cub}}\sqrt{2}$ at T_C amount to -6 % and + 9 % respectively. We found the contraction of the unit cell volume at 78 ± 1 K to be 0.5 %. We cannot confirm the suggestion (e.g. Jenkins & Bates, J. Phys. C: Sol. State Phys. (1981), 14, 817) that the primitive volume of the unit cell doubles at the transition. In $\text{Fe}(\text{NH}_3)_6\text{Cl}_2$ this doubling does not occur either: it can easily be demonstrated that the powder pattern reported by Aseh (Aseh et al., J. Chem. Phys. (1975), 62, 6, 2335) may be referred to a cell which is similar to the cell we find for the Ni-compound. Nevertheless, if hydrogen ordering should play a role, the definitive unit cell parameters can be determined from a neutron experiment only.

The profile refinement (Rietveld, J. Appl. Cryst. (1969), 2, 65) was made in the space group I2/m ($R_{\text{nuc}} = 0.096$) rather than C2/m because of the close relation to the cubic cell. The hexammine nickel octahedron remains essentially undistorted, and the bond distances Ni - N stay within their expected values. The octahedra are rotated by 11° around the monoclinic b-axis ($\hat{a}[110]$ direction is the cubic phase). - A neutron diffraction investigation is in progress.