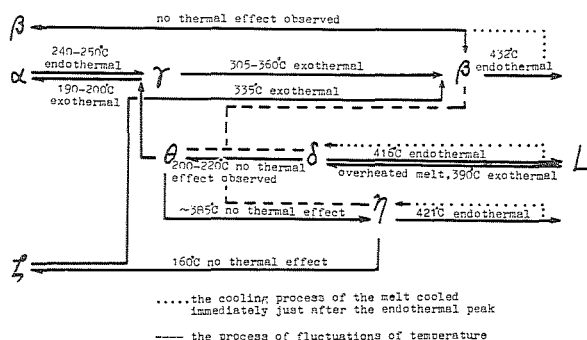city ratio N:N (N=1,3,4,6,8,12,16, 24,32,48) or M:3M (M=1,2). Structures in which the occupied RSPs have one, two or three free parameters in the points coordinates can undergo Ts by type (2). The number of free parameters will be reduced by one or by two for the transformed RSP. Transformations by type (1+2) are possible in structural types where simultaneously two or more RSPs of the same symmetry and with the different absolute values of free or/and fixed parameters are occupied. The above Ts are analyzed on conditions that the number of structure elements in the unit cell is constant or changed. The displacements of points of an RSP are due to the expansion coefficients of pair bonds with respect to any scalar external parameter (temperature, hydrostatic pressure, dimension of structure elements) are different even in macroscopically isotropic structures, for example between similar, but unequally spaced structure elements, or between different, but equally spaced elements. Crystallochemical approach to the analysis of continuous transformations should also take into account the real dimensions of the structure elements and the values of tolerance factors for different coordinational polyhedrons. The obtained system of transformations comprises all the second order transitions considered by the theoretical-group methods and some others, for example $Pm3m \rightleftharpoons P23$, $Im3m \rightleftharpoons I23$, $Fm3m \rightleftharpoons F23$ e t c. The thermodynamical analysis was not performed but the coordinates of moving points may be used as a parameter of the free energy expansion.

The crystal systems and lattice parameters of these new phases are follows:

δ_1 -$LiIO_3$; cubic, a=6.968Å

η ; tetragonal, a=11.563Å, c=9.342Å

θ_1 ; orthorhombic,a=5.722Å, b=9.505Å,c=10.589Å

θ_2 ; orthorhombic,a=7.870Å, b=7.970Å,c=7.356Å

ζ ; orthorhombic,a=6.498Å, b=7.118Å,c=12.265Å

There are three phases of $LiIO_3$, β , η and δ , existing relatively stably in high temperature and they can directly melt respectively. Their melting point correspodingly are:

  phase β ---432°C;

  phase η ---421°C;

  phase δ ---416°C;

Their melting point, thermal process and the existing temperature range all show, that the order of their thermodynamical stability is:

$$\beta > \eta > \delta$$

In dry air and at room temperature, the δ -$LiIO_3$ stands long periods of time without any change as well as phase α and β. At the existing temperature range of α-$LiIO_3$, phase δ does not transform into phase α,although it is heat-treated for a long time. The temperature of phase transition of δ to β is higher than that of α to β . The existence of phase β in the phase δ has a promotive effect on the phase transition of δ to β just as α to β. The existence of phase δ in the phase α has also a promotive effect on α to β , the phase θ ,as the phase γ , is also an intermediate metastable phase in the phase transition processes of $LiIO_3$.

05.1—31   THE STUDIES ON THE PHASE TRANSITION

OF $LiIO_3$. By Liang Jing-kui, Zhang Yu-ming,

Institute of physics, Academia Sinica, BEIJING,

China.

The phase transition mechanism of $LiIO_3$ at normal pressure has been studied by DTA, DSC, isothermal heat-treatment, and X-ray powder diffraction at high and room temperature.

When over-heated melt is cooled and solidified, we have discovered four new phases of $LiIO_3$---- a group phases δ , η , ζ and θ (θ_1 and θ_2), which are formed by cooling from two main kinds of δ phase. The phase transition processes of $LiIO_3$ as shown in the following diagram:

..... the cooling process of the melt cooled immediately just after the endothermal peak

---- the process of fluctuations of temperature

05.1—32   PHASE TRANSITIONS AND DECOMPOSITION IN $KFeF_4$, $RbFeF_4$, $RbVF_4$. By R. Deblieck[1], J. Van Landuyt[1], B.J. Garrard[2], B.M.R.Wanklyn[2] and S. Amelinckx[1]./1/ Universiteit Antwerpen, RUCA, Groenenborgerlaan 171, B-2020 Antwerp, Belgium. /2/ Clarendon Laboratory, Oxford University, Oxford OX1 3PU, United Kingdom.

In perovskite (ABX_3) compounds such as $CaTiO_3$ and $NaNbO_3$ phase transitions due to the condensation of soft modes occur and can be interpreted in terms of the tilting of the BX_6 octahedra around one or some of their tetrahedral axes in the low temperature phases. Glazer (Acta Cryst.(1972).B28, 3384), classified the structure of these phases in terms of the correlation of tilting along these axes.
In the ABX_4 compounds these octahedra are not, unlike the perovskite case, vertex-shared in the third dimension. Still all of these materials undergo transitions which may be interpreted in terms of condensation of soft modes, yielding low temperature phases with tilted octahedra (M.Hidaka et al.,J.Phys.C.Sol.St.Phys.(1979).12, 2737; J.Phys.C.Sol.St.Phys.(1979).12, 1799; Phys.stat. sol.(a)(1982).72, 809).
Electron diffraction experiments are reported which confirm some of these transitions. In $RbFeF_4$ however it is found that, although the reflections are quite weak, the c-axis is doubled at room temperature (RT) whereas this doubling disappears when cooling down to liquid nitrogen temperature (LNT) as can be seen in fig.1. This would invalidate the RT structure proposed by M. Hidaka et al. (J.Phys.C.Sol.St.Phys.(1979). 12, 1799).
In $RbVF_4$ there are indications that, in contradiction with the description by M. Hidaka et al.(Phys.stat.sol. (a)(1982).72, 809), the doubling of the c-axis does not vanish at 413K. All of the investigated compounds seem to be very sensitive to decomposition under electron irradiation, probably through evaporation of fluorine. This evaporation forces the BX_6 oxtahedra to become locally edge-shared thus deforming the lattice,which

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.
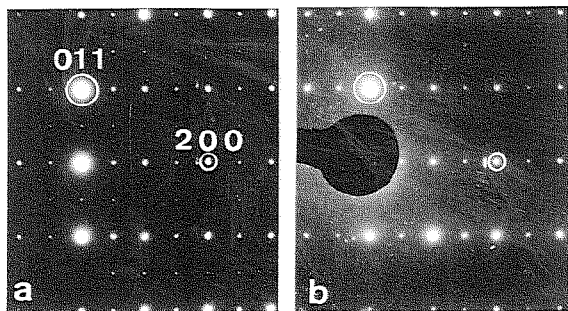

Fig. 1 : Phase transition in $RbFeF_4$ as observed with electron diffraction in a $[01\bar{1}]$ zone pattern.
        (a) RT   (b) LNT

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, too 100/0 at $\sim T_c - 100$ 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 incommensurable (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 incommensurable 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.

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) A 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