

05.1-27 THE EFFECT OF COOLING RATE ON  $\alpha$ -PHASE ORDERING IN Cu-25at.%Al ALLOY. By Z.Bojarski, J.Lelątko, J.Kwarciak and H.Morawiec, Institute of Physics and Chemistry of Metals, Silesian University, Katowice, Poland

The presence of  $\alpha_2$  or  $\alpha_3$ -superstructure was studied by electron microscopy on samples consisting of  $\alpha+Y_2$  eutectoid cooled from 500°C to 25°C at a rate from 25°C/min. to 0.2°C/min.

The D-parameter which determinates the position of the superstructure spots in the reciprocal lattice was used to describe the kind of superstructure. With decrease in cooling rate the D-parameter increases. The value of  $D=0.357=5/14$  was obtained for  $\alpha_3$ -phase at a higher cooling rate and  $D=0.375=3/8$  corresponds to the  $\alpha_2$ -phase at the lowest cooling rate. With decrease of cooling rate an increase of ordered  $\alpha_2$ -regions was observed in the dark field image.

The ordering of  $\alpha$ -phase was also studied for isothermal annealing at 240°C and 300°C for 300 hours. The lower annealing temperature formed the  $\alpha_3$ -superstructure whereas annealing at 300°C - the  $\alpha_2$ -superstructure.

The studies of the ordering process was carried out by measuring the heat of the thermal effect by DTA and DSC methods. The magnitude of the thermal effect during heating of the ordered samples was dependent on the degree of  $\alpha$ -phase order. A correlation was stated between the D-parameter and the heat absorbed due to disappearance of order in the  $\alpha_2$ -superstructure while heating.

05.1-28 INVESTIGATION OF THE X-RAY WAVE-LENGTH DEPENDENCE OF A CRITICAL DIFFRACTION EFFECT AT THE PHASE TRANSITION OF  $V_2O_5$ . By S. Åsbrink, Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden, L. Gerward, Laboratory of Applied Physics III, Technical University of Denmark, DK-2800 Lyngby, Denmark and J. Staun Olsen, Physics Laboratory II, H.C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark.

In a previous X-ray single crystal diffraction investigation of the phase transition in  $V_2O_5$ , an instantaneous strong increase in peak intensity together with a peak broadening was observed for the strong reflexions at the phase transition temperature 155°C, MoK $\alpha$ -radiation being used (Åsbrink and Hong, Nature (1979) 279, 624). In subsequent measurements using a diffractometer of Bond type (Łukaszewicz, Kucharczyk, Malinowski and Pietraszko, Krist. und Techn. (1978) 13, 561), the observations were repeated with MoK $\alpha$ -radiation; however, no such effects could be seen using CuK $\alpha$ -radiation (Åsbrink, Wołczyr and Hong, Phys. Stat. Sol., to be published). The present investigation was undertaken in order to study the wave-length dependence in greater detail, using a spectrometer for energy dispersive diffraction (Staun Olsen, Buras, Gerward and Steenstrup, J. Phys. E: Scient. Instrum. (1981) 14, 1154). The paper discusses the experimental results in relation to several possible interpretations of the effect.

05.1-29 STRESS-INDUCED ELECTROGYRATION AND GYROTROPIC PHASE TRANSITIONS IN ALUMS. By H.-J. Weber, Institut für Physik der Universität Dortmund, D-4600 Dortmund, FRG

We have performed the first measurements of stress-induced electrogyration in crystals. In methylammonium aluminium alum (MASD) most of the impact of externally applied pressure  $p$  on electrogyration ( $\delta\rho/\delta E$ ) can be traced back to an interference of induced birefringence with induced optical rotation. Nevertheless it is possible to work out another intrinsic effect which is described by  $\delta^2\rho/\delta E\delta p$ . It has a value of  $10^{-17}$  deg.m<sup>3</sup>/V.N, changes its sign at about 210 K and increases drastically near the phase transition at 177 K.

Furthermore we have measured the effect in chromium-doped MASD-crystals and in hydrazine- and ammonium- aluminium alums. The results show that the phase transitions in different alums are similar in respect to their gyrotropic character although they differ in their ferroelectric behaviour.

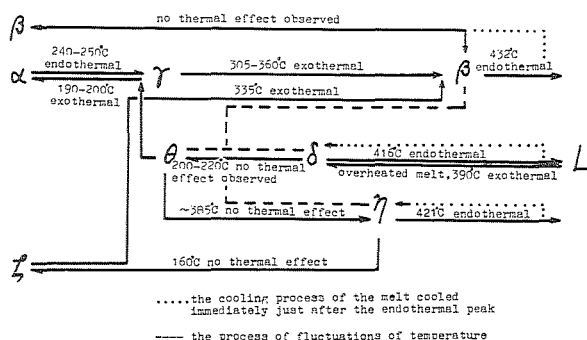
05.1-30 ON THE SYSTEMATIZATION OF CONTINUOUS TRANSFORMATIONS FOR STRUCTURAL TYPES. D.M.Mazo, Institute of Solid State Physics, Academy of Science of the USSR, Chernogolovka. Among different structural types that falls into the given space group part is not capable to continuous transformations (T) due to the change of the scalar external parameter, the others can undergo these T by one or several ways. Within the limits of a given space group structural types differ from one another by the number and (or) kinds of regular systems of points (RSP) occupied by elements of structure. For cubic structures number of different RSPs comes to 154, among which the 55 are met in different space groups and rest are unique. Six space groups (P2<sub>1</sub>3, I2<sub>1</sub>3, P4<sub>3</sub>32, P4<sub>1</sub>32, I4<sub>1</sub>32, I43d) contain exceptionally unique RSPs. The number of dissimilar regular systems of points related to one site of Bravais lattice (RSPB) reduces to 127 among which the 69 are unique. Only the space group I43d is described by exceptionally unique RSPBs. Crystall-geometrical analysis of topological relations between RSPs (RSPBs) make it possible to reveal all the Ts for all structural types and find the symmetry of external parameter assisting the given transformation of the RSP (within a given crystal symmetry class or between classes) and illustrate possible mechanisms of transformations. The present paper describes the Ts that are within the limits of cubic structures due to the change of a scalar external parameter and correspond to the following topological relations: (1) an RSP comprises several RSPs, (2) two RSPs coincide at certain values of free parameters in the points coordinates, and (1+2). It is found that the Ts by type (1) can occur in structures in which, in particular, the occupied RSPs have the multipli-

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  $Pm\bar{3}m \rightleftharpoons P23$ ,  $Im\bar{3}m \rightleftharpoons I23$ ,  $Fm\bar{3}m \rightleftharpoons F23$  etc. The thermodynamical analysis was not performed but the coordinates of moving points may be used as a parameter of the free energy expansion.

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  $\delta$ ,  $\eta$ ,  $\zeta$  and  $\theta$  ( $\theta_1$  and  $\theta_2$ ), which are formed by cooling from two main kinds of  $\delta$  phase. The phase transition processes of  $LiIO_3$  as shown in the following diagram:



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

- $\delta$  -  $LiIO_3$ ; cubic,  $a=6.968\text{\AA}$
- $\eta$ ; tetragonal,  $a=11.563\text{\AA}$ ,  $c=9.342\text{\AA}$
- $\theta$ ; orthorhombic,  $a=5.722\text{\AA}$ ,  $b=9.505\text{\AA}$ ,  $c=10.589\text{\AA}$
- $\theta_2$ ; orthorhombic,  $a=7.870\text{\AA}$ ,  $b=7.970\text{\AA}$ ,  $c=7.356\text{\AA}$
- $\zeta$ ; orthorhombic,  $a=6.498\text{\AA}$ ,  $b=7.118\text{\AA}$ ,  $c=12.265\text{\AA}$

There are three phases of  $LiIO_3$ ,  $\beta$ ,  $\eta$  and  $\delta$ , existing relatively stably in high temperature and they can directly melt respectively. Their melting point correspondingly are:

- phase  $\beta$  --- 432°C;
- phase  $\eta$  --- 421°C;
- phase  $\delta$  --- 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  $\delta$ - $LiIO_3$  stands long periods of time without any change as well as phase  $\alpha$  and  $\beta$ . At the existing temperature range of  $\alpha$ - $LiIO_3$ , phase  $\delta$  does not transform into phase  $\alpha$ , although it is heat-treated for a long time. The temperature of phase transition of  $\delta$  to  $\beta$  is higher than that of  $\alpha$  to  $\beta$ . The existence of phase  $\beta$  in the phase  $\delta$  has a promotive effect on the phase transition of  $\delta$  to  $\beta$  just as  $\alpha$  to  $\beta$ . The existence of phase  $\delta$  in the phase  $\alpha$  has also a promotive effect on  $\alpha$  to  $\beta$ , the phase  $\theta$ , as the phase  $\gamma$ , is also an intermediate metastable phase in the phase transition processes of  $LiIO_3$ .

05.1-32 PHASE TRANSITIONS AND DECOMPOSITION IN  $KFeF_4$ ,  $RbFeF_4$ ,  $RbVF_4$ . By R. Deblieck<sup>1</sup>, J. Van Landuyt<sup>1</sup>, B.J. Garrard<sup>2</sup>, B.M.R. Wanklyn<sup>2</sup> and S. Amelinckx<sup>1</sup>. /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  $BX_6$  octahedra to become locally edge-shared thus deforming the lattice, which