

12.2-14 ETUDE DES TRANSITIONS DE PHASE ORDRE-DESORDRE DU FERROCENE  $Fe(C_2H_5)_2$  ET DU NICKELOCENE  $Ni(C_2H_5)_2$ , PAR DIFFRACTION DES RAYONS X SUR POUFRE, G. Calvarin, J.F. Bézar et D. Weigel, Laboratoire de Chimie-Physique du Solide, Ecole Centrale de Paris et Université Paris-Nord, France.

Les structures du ferrocène et du nickelocène sont isomorphes et partiellement désordonnées à 295 K. Ils cristallisent dans le système monoclinique, groupe spatial  $P2_1/a$ . Alors qu'une transition ordre-désordre a été mise en évidence par différents auteurs pour le ferrocène, aucune étude dans ce sens n'a été signalée pour le nickelocène. Nous avons déterminé, de façon très précise, la variation des paramètres de la maille du ferrocène et du nickelocène entre 300 et 5 K par diffraction des rayons X sur poudre. L'évolution structurale de ces deux composés est très anisotrope et tout à fait différente. La variation des paramètres du ferrocène présente une discontinuité à 164 K, la maille est triclinique au dessous de cette température. Cette transition est du 1er ordre et est probablement du type ferroélastique, elle se superpose à la transition ordre-désordre qui est étalée de 130 à 220 K. La maille du nickelocène reste monoclinique, mais à partir de 240 K sa structure présente des domaines de déformation élastique se traduisant par un élargissement dissymétrique de certains pics de diffraction. Cet élargissement est maximum vers 120 K.

Nous avons déterminé la variation entre 300 et 5 K des directions et des coefficients principaux de dilatation thermique. Les graphes  $\alpha = f(T)$  présentent des pics de dilatation, positif ( $\alpha > 0$ ) ou négatif ( $\alpha < 0$ ), dans certaines directions à la fois pour le ferrocène et le nickelocène, mais ces directions ne se correspondent pas dans les deux composés. Une hypothèse relative au mécanisme de la transition et à la configuration de la molécule dans la phase ordonnée du ferrocène a été déduite de la connaissance des graphes  $\alpha = f(T)$ . Une telle étude est actuellement en cours pour le nickelocène.

12.2-15 TRIMETHYL-SILYL-, -GERMYL- AND -STANNYL-HYDRAZINES: A PLASTIC CRYSTAL CLASS, M. Veith, Institut für anorganische Chemie, Universität Karlsruhe, Englerstr. 11, BRD.

Hydrazines of the general formula  $(R_3E)_n(R_3E')_{4-n}N_2$  ( $E, E' = Si, Ge, Sn$ ;  $R = CH_3$ ;  $n = 0, 1, 2$ ) form plastic crystals at room temperature as found by X-ray diffraction and solid NMR-measurements. They all crystallize in a cubic face centered lattice with 4 molecules per unit cell. On cooling single crystals or powders down to 60 K two phase transitions are observed at about 170 K and 120 K: the first phase shows a cubic primitive lattice with 4 molecules per unit cell and the second is a lattice of lower than cubic symmetry. The temperatures of the first transition point of different derivatives are a linear function of their moments of inertia.

The phenomena can be explained by a simple model: the reorientation (rotational movement) of the molecules, which are all approximately tetrahedral in geometry, is stepwise restricted with decreasing temperature. At room temperature the point symmetry of the molecule in the crystal is at least 432, with a general reorientation taking place in the crystal. Below 170 K the symmetry of the fourfold axis is lost and reorientation takes place only about the remaining triad axis. Below 120 K the triad axis disappears and the molecules are at rest.

12.2-16 ARTIFICIAL RANDOM LAYER STRUCTURE OF METATORBERNITE CRYSTALS, William G.R. de Camargo & J.B. de Madureira Filho, Institute of Geosciences, University of S. Paulo, São Paulo, Brazil.

Some minerals, with pronounced preferential cleavage (chlorites, clay minerals, micas, etc.) may exhibit spontaneous structural changes, known as random layer structures and stacking faults. Artificial changes of similar kind may be obtained by a rather intensive grinding, as already demonstrated by H. Shirozu (Min. Journ. Jap., 2, 209, 1958) in chlorites and in some secondary uraniferous minerals, such as autunite and meta-autunite (W.G.R. de Camargo, Intern. Conf. on Electron Diffraction and Crystal Defects, Melbourne, Australia, 1965).

The same kind of artificial change has been reported in metatorbernite, also a secondary uranium mineral. Metatorbernite crystals may produce anomalous X-ray patterns when intensively ground for preparing samples for powder X-ray diffraction. The X-ray diagrams merely present the Bragg reflections  $00l$  (pinacoidal) and  $hk0$  (prismatic) as theoretically predicted by R.E. Warren (Phys. Rev. 59, 693, 1941), W.H. Zachariasen (Phys. Rev. 71, 715, 1947) and A.J.C. Wilson (Acta Cryst. 2, 245, 1949) for bidimensional lattices of carbon blacks. The  $hk0$  reflections are completely absent, for no regular  $hk0$  spacings may be observed, after the random shift of the crystal layers. The reported  $00l$  and  $hk0$  reflections are diffuse and have a very feeble intensity. This anomalous behaviour may be ascribed to haphazard shift of the structure layers parallel to  $(001)$ , which splits the crystals into a

numberless two-dimensional lattices.

The investigations have been carried out in a systematic way on metatorbernite samples from Cornwall, England, which have been ground from 30 seconds to 30 minutes. The resulting X-ray patterns were compared and discussed.

After being ground for only 30 seconds in an agate mortar the sample begins to present disorder signs. The X-ray powder photographs indicate mixtures of the two phases, the ordered and the disordered. Consequently, the crystalline lines may be seen in the powder photographs, superimposed by broad and diffuse reflections produced by two-dimensional lattices. The  $00l$  may show a symmetrical profile, but the  $hk0$  are asymmetrical tail reflections.

The random layer structure may be the result of various sorts of shift of the  $00l$  planes. The crystal sheets could be moved by translation, after a or b axis, or both at the same time, by rotation after an axis normal to the plane of shifting, or even by combination of both movements. The combined movement, which is the general kind, is obviously the more frequent one.

The random layer structure is favoured by the extremely weak bond between crystal layers, and it seems very common among hydrated minerals or substances with zeolitic water. This kind of water enters and goes out from the crystal structure, without substantial changes of the lattice. As a counterpart, the bonds linking atoms of the same layer have an extremely strong character.

12.3- 1 IN-SITU ELECTRON MICROSCOPIC OBSERVATION OF THE FERROELECTRIC AND FERROELASTIC PHASE TRANSITION OF GMO: G.Honjo, N.Yamamoto and K.Yagi, Dept. of Physics, Tokyo Institute of Technology, Oh-okayama, Tokyo, Japan

In a previous paper, present authors reported electron microscopic observation of the ferroelectric and antiphase domain structures of GMO ( $Gd_2(MoO_4)_3$ ) (N. Yamamoto, K.Yagi and G.Honjo; Phil.Mag. 30(1974)1161). This paper describes the formation process of these domains at the phase transition temperature.

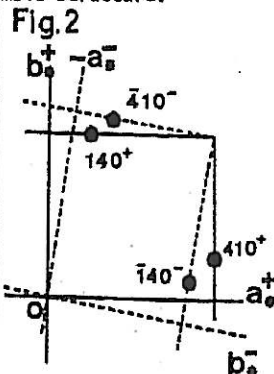
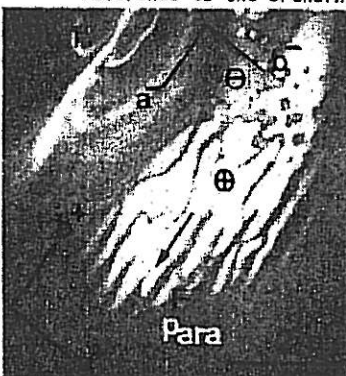
Fig.1 shows an electron micrograph of an (001)\* GMO crystal plate in the course of the transformation at 160°C from the tetragonal structure to the orthorhombic structure. The latter structure with a unit cell twice as large as that of the tetragonal one produces the superlattice reflections in the electron diffraction as shown in Fig.2. A pair of the superlattice reflections, 410 and  $\bar{1}40$  from the two ferroelectric domains with the antiparallel polarizations have different structure factors, but are located closely side by side. Fig.1 is a dark field electron micrograph at Bragg setting for this pair of superlattice reflections. The region marked "Para" of the high temperature phase are seen to be dark because of the absence of the superlattice reflections, but the regions of the low temperature phase are seen to be bright. Since the structure factor of the 410 reflection is larger than that of  $\bar{1}40$  reflection, the domain with + polarization is brighter than the domains with - polarization. The phase boundaries are parallel to the (100) plane along which the mismatch between lattices of the high and low temperature phases is smaller than along the (010) plane. These observations agree with the previous results by light microscopic study (T.Nakamura, T.Kondo and A.Kumada; Solid State Commun. 9(1971)2265).

When the specimen is cooled further, the phase boundaries move in the [010] direction (indicated by the arrow in Fig.1). As the bright region extends, sometimes the

formation of the antiphase boundaries is observed as seen in Fig.1. The formation of them is initiated by the formation of a bright region (marked F in Fig.1) in the dark region of high temperature phase. At first, the boundary between this bright region and the already formed bright region is seen to be a broad dark band, but later, it becomes to show the characteristic image contrast of the antiphase boundary in GMO, which is to be discussed in detail in a separate paper presented to this congress (K.Yagi, N.Yamamoto and G.Honjo; in this collected abstracts). Since the phase boundary moves along the [010] direction, the antiphase boundaries tend to lie along the direction of the arrow in Fig.1. The appearance of the bright regions such as region F in Fig.1 is considered to be due to the formation of low temperature phase with the condensing soft mode which is out of phase from that in the other bright regions.

A further extension of the study to an in-situ observation of the behaviours of the domains under electric fields is now in progress.

\*) Directions and lattice planes are denoted in reference to the orthorhombic structure.



12.3- 2 HIGH TEMPERATURE STRUCTURE INVESTIGATION OF ANORTHITE ( $CaAl_2Si_2O_8$ ) USING X-RAY AND ELECTRON MICROSCOP. M. Czank, F. Laves, H. Schulz, Institut für Kristallographie, ETH Zürich, Switzerland, and Max-Planck-Institut für Festkörperforschung, Stuttgart, BRD.

The structure of a plagioclase from Monte Somma, Vesuvius (Italy) with 98% An-content was re-fined at 20°C, 240°C, 650°C, 1000°C and 1430°C. At 240°C a primitive (PI) and a body-centered (II, using the same unit cell) model were calculated and it was shown that the body-centered is better. The PI - II transformation of the (Si-O-Al)-framework was fixed at 230°C. It is a displacive type of transformation. At high temperatures the Ca atoms must be considered as split atoms. The occupation probabilities of the split positions are different from 0.5 to 0.5 until 1400°C. For that reason a domain texture was supposed.

E.M.-investigations at high temperatures show results in accordance with the X-Ray results. Below 230°C large anti-phase domains exist, with a displacement vector:  $\frac{1}{2}[+a, +b, +c]$ , which are associated with the whole structure. Above the critical temperature  $T_C=230^\circ C$  the anti-phase domains disappear. Dark-field images with diffuse c-reflections ( $h+k+l = 2n+1$ ) show bright patches in a dark matrix. The bright patches are caused by only those Ca atoms which are in some unit cells of the body-centered framework in primitive ordered arrangement. They will be called "Ca-domains". In the dark parts the Ca atoms are either also in a body-centered or in a disordered arrangement.

12.3- 3 STUDY OF THE SPONTANEOUS DEFORMATION AT THE FERROELECTRIC PHASE TRANSITION OF  $KH_2PO_4$  BY  $\gamma$ -RAY DIFFRACTOMETRY, P. Bastie, J. Bornarel, J. Lajzerowicz, Laboratoire de Spectrométrie Physique, B.P. 53, 38041 Grenoble Cedex and J. R. Schneider, Institut Laue Langevin, B.P. 156, 38042 Grenoble Cedex, France.

$\gamma$ -ray diffractometry is a new method to study structural phase change. It has been applied to the ferroelectric phase transition of  $KH_2PO_4$ . This transition which occurs at 120°K is also of ferroelastic character: the spontaneous polarization is linearly coupled to the spontaneous deformation, and these two quantities change their sign while going from one domain to the other. The value of the spontaneous shear is of the order of 30'. Due to the existence of domains, Bragg peaks are splitted in two parts whose relative orientation is a function of the temperature. The angle between the parts can be measured at zero applied field, so this measurement of the order parameter is not being disturbed as in the most other techniques.

Due to the high penetration of the radiation used ( $\lambda = 0,03 \text{ \AA}$ ), we study a bulk property and are able to assure a very good temperature control ( $\Delta T/T \sim 3.10^{-5}$ ).

Due to the well collimated beam (30" of divergence) and the "perfect" monochromaticity ( $\Delta\lambda/\lambda = 10^{-6}$ ), the angle was measured within  $\pm 4$  seconds of arc.

We will report measurements of the spontaneous shear angle as a function of the temperature, compare the results to those obtained by other techniques and discuss the possibilities to study other phase transition by this method.