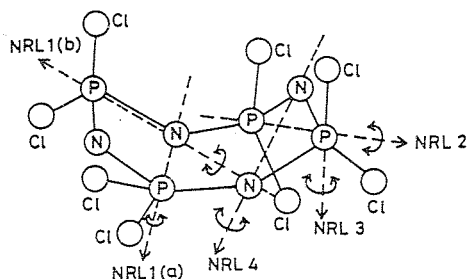


for the K-form in terms of T and L tensors for the rigid-body motions of the molecule as a whole as well as for the internal motions. The nonrigid-body librations analysed are NRL1, NRL2, NRL3 and NRL4 (Fig.). Incorporation of NRL2 and NRL4 produce good agreement between the observed and calculated U_{11} 's reducing the R-value to 3.5% from 23.0% for the 25°C data and 2.3% from 21.9% for the 40°C data. The librational amplitudes NRL2 and NRL4 which correspond to the motions of N and PCl_2 groups respectively increase with temperature. The relevance of these observations to the conformational isomerization in the molecule is discussed.



04.4-5 PHASES AND THERMAL DECOMPOSITION CHARACTERISTICS OF HYDRO-SODALITES $Na_{6+x}[AlSiO_4]_6(OH)_x \cdot nH_2O$. By Ch. Buhl, J. Felsche and S. Luger, Department of Chemistry, University of Konstanz, West Germany.

Reinvestigation of the hydro-sodalite system does not verify the solid solution character of the series in respect to a steady variation in properties of the samples. Thermoanalyses of carefully prepared pure phases reveal an antagonistic volume/concentration effect of hydrate water in the two end-member series $Na_6[AlSiO_4]_6(OH)_2 \cdot nH_2O$, $0 \leq n \leq 4$ ('basic series') and $Na_6[AlSiO_4]_6 \cdot nH_2O$, $0 \leq n \leq 8$ ('non-basic series'), however. Thermogravimetry and X-ray diffraction heating experiments confirm partial collapse of the sodalite framework upon dehydration of phases of the basic hydro-sodalites which is the common behaviour of framework compounds in decomposition or ion exchange experiments. Contrary, phases of the non-basic sodalite hydrate series $Na_6[AlSiO_4]_6 \cdot nH_2O$ show significant expansion of the alumino-silicate framework when $0 \leq n \leq 8$ are released at temperatures of 350-450 K under open system conditions. This antagonistic effect on the sodalite type host lattice is discussed in terms of hydrogen bonding, which has been verified by supplementary neutron diffraction analyses for the non-basic hydro-sodalites, distinctively.

From IR- and X-ray diffraction heating experiments strong evidence is given for the dynamical nature of interactions between all the non-framework constituents with increasing activation barriers for the hydrogen, oxygen and sodium atoms, respectively. The cubo-octahedral geometry of the sodalite cage in the given 1:1 alumino-silicate matrix controls the corresponding interactions, which result in some new stereochemical features of the aqueous hydroxyl-groupings $[O_nH_{2-n}]^{1-}$ in the basic hydro-sodalite phases with different hydrate water contents ($1 < n \leq 3$).

04.4-6 Al VACANCIES IN $\alpha-Al_2O_3$ FORMED BY DEHYDRATION OF $\alpha-AlOOH$. By K. Hagiya and M. Ohmasa, Institute of Materials Science, University of Tsukuba, Japan.

Many people have so far investigated the dehydration of goethite ($\alpha-FeOOH$) and diaspora ($\alpha-AlOOH$) and established that hematite ($\alpha-Fe_2O_3$) and corundum ($\alpha-Al_2O_3$) are derived from precursor in an orientated manner (topotaxy) with twinning developing during the transformation. Lima-de-Faria (J. Lima-de-Faria, Z. Kristallogr., 1963, 119, 176-203) showed that the products revealed distinct satellite reflections on oscillation photographs in the early stage of the reaction. He thought that the satellite could be derived from the structure with alternation of zones having complete cation distribution and those having incomplete ones. Recently Watari and his coworkers (F. Watari, P. Delavignette and S. Amelinckx, Solid State Chem., 1979, 29, 417-442) have carried out electron microscopic studies on dehydration of goethite and thought that the satellite reflections were not caused by the modulation of cation distribution but by the periodic arrangement of voids in the structure of $\alpha-Fe_2O_3$. The present studies have, therefore, been carried out to elucidate the origin of satellite reflections of the dehydration products.

Single crystals of diaspora from Shokoizan, Hiroshima, Japan were selected for experiments. The specimen was heated to 500°C quickly, kept at 500°C for 30 minutes and then quenched in air. Two kinds of diffraction patterns were observed on X-ray photographs. One of them corresponds to the precursor and the other to the product. The latter indicates satellite reflections. Since the validity of the above models can be checked by determination of the ratio of Al to O, averaged structure was determined. Intensities of main reflections correspond to the averaged structure were measured on an automated four-circle diffractometer (Rigaku AFC-5) equipped with RU-200 X-ray generator (operation condition: 50 kV, 120mA), using $MoK\alpha$ radiation monochromatized by graphite. The cell parameters determined are $a=4.752(3)$ and $c=12.989(11)$ Å and the same space group $R\bar{3}c$ as normal $\alpha-Al_2O_3$ was adopted from the extinction rule. In order to avoid the effects of precursor, ω -scanning was employed for intensity measurements. 369 reflections were used for refinement. Least-squares refinement of the site occupancy of Al, atomic positions and anisotropic temperature factors using RFINE2 (L. W. Finger, 1969), yielded $R=0.138$ and $R_w=0.115$. According to the model proposed by Watari et al., the occupancy of the cation must be 1.0, because they interpreted the satellite as diffraction by periodic arrangement of voids and perfect $\alpha-Fe_2O_3$ crystallites from their high resolution electron micrographs. The occupancy of Al was determined to be 0.751(5) from the present determination of the averaged structure. The result suggests that the origin of the satellites is the modulation of the Al occupancy. It must be reasonable to consider that the same phenomena occur in the dehydration product of $\alpha-FeOOH$. We have also determined the amplitude of the modulation and suggested from the result that the feature of the satellites ascribe the modulation to a periodic distribution of Al-deficient layers (M. Ohmasa et al., Acta Cryst., 1984, A40, C-256). In the Al-deficient layers, the electric charge is not neutral and protons could migrate in those layers to compensate the unbalance. Such structure could easily evaporate in the high flux of charged particles (electrons) and in the high vacuum, and would form a periodic arrangement of voids. Two thirds of octahedral sites are occupied in normal $\alpha-Al_2O_3$, and 75% of Al sites are occupied in the modulated $\alpha-Al_2O_3$. The ratio of Al to O in the latter is 1:2. Since this value is same as the ratio of Al to O in $\alpha-AlOOH$, the modulated $\alpha-Al_2O_3$ must be the nucleus of the dehydration product, and behavior of the satellites must be very important to analyze the process of formation of the new phase.