been proposed which are consistent with the observed twinning behavior and cell symmetry. The same ordered structures are suggested for HUP from our observations of the twinning behavior.

Studies of Layered Uranium (VI) Compounds. IV. Proton Conductivity in Single-Crystal Hydrogen Uranyl Phosphate Tetrahydrate (HUP) and in Polycrystalline Hydrogen Uranyl Arsenate Tetrahydrate (HUAs). ARTHUR T. HOWE AND MARK G. SHILTON. Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, England.

Single-crystal measurements on hydrogen uranyl phosphate tetrahydrate, $HUO_2PO_4 \cdot 4H_2O$ (HUP), have confirmed that the high proton conductivity is a bulk characteristic. The conductivity values were in substantial agreement with those previously reported for polycrystalline disks. A conductivity of $0.6\ \mathrm{ohm}^{-1}\ \mathrm{m}^{-1}$ at 290°K and an activation energy of 30 ± 1 kJ mole^{-1} were measured parallel to the structural layers of the crystal. The conductivity was at least 100 times lower when measured in the perpendicular direction. A reasonable attempt frequency ω_0 of approximately 10^{15} Hz could be derived from the parallel conductivity on the assumption that the charge carrier concentration was equal to that of the H_3O^+ ions. This implies a low proton mobility, of the order of $10^{-9}\ \mathrm{m}^2\ \mathrm{V}^{-1}\ \mathrm{sec}^{-1}$ at 290°K, in support of previous estimates. We have also shown that polycrystalline hydrogen uranyl tetrahydrate, $HUO_2AsO_4 \cdot 4H_2O$ (HUAs), has a high conductivity of $0.6\ \mathrm{ohm}^{-1}\ \mathrm{m}^{-1}$ at 310°K, with an activation energy of 31 ± 2 kJ mole^{-1}. Below the respective dielectric ordering transition temperatures of HUP and HUAs of 274 and 301°K, the lower conductivity values show a marked frequency dependence, which may be due to dispersion effects caused by water reorientations.

Topotaxial Decomposition of Calcite-Type KNO_3 Crystals. S. W. KENNEDY AND W. M. KRIVEN. Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, S.A. 5001, Australia.

The calcite-like form of potassium nitrate, KNO_3, decomposed under the transmission electron microscope to form KNO_2 which subsequently decomposed giving the high-temperature β form of K_2O. Two closely related orientation relations were observed for KNO_2. Referred to the four molecule cell of KNO_3, they were $[111]_{KNO_3} \| [111]_{KNO_2}$, $(0\bar{1}1)_{KNO_3} \| (0\bar{1}1)_{KNO_2}$; and $[100]_{KNO_3} \| [100]_{KNO_2}$, $(001)_{KNO_3} \| (001)_{KNO_2}$. These and a different published orientation relation for the decomposition of cadmium carbonate conform, respectively, to orientations resulting from a corresponding structural phase transformation in rubidium nitrate. β-K_2O formed with its cube axes parallel to those of KNO_2. Both nitrate and carbonate reactions can be regarded as topotaxial. Application of the crystallographic approach to orientations and accomodation of misregistry is discussed.

Structure Cristalline de la Phase β-KEr_2F_7 Composés Isotypes. S. ALEONARD, Y. LE FUR, M. F. GORIUS ET M. TH. ROUX. Laboratoire de Cristallographie, CNRS 166X-38042 Grenoble Cedex, France.

Potassium erbium fluoride β-KEr_2F_7 crystallizes in the orthorhombic system, space group $Pna2_1$, with the unit-cell dimensions $a = 11.820$ Å, $b = 13.333$ Å, $c = 7.816$ Å ($Z = 8$). The crystal structure has been solved from single-crystal diffractometer measurements (Ag$K\alpha$) by Patterson and Fourier synthesis and refined by a least-squares method. The final R value is 0.042 for 2374 independent observed reflections ($R_W = 0.051$). The four species of erbium atoms are surrounded by eight fluorine atoms. These fluorine atoms form, respectively, three quadratic antiprisms and one dodecahedron, derived from a distorted cube. Two antiprisms and the dodecahedron share two of their faces to form $(Er_3F_{17})^{8-}$ groups. These groups are bidimensionally linked and the planes they form are joined together by the third antiprism. A three-dimensional network is then produced, in the tunnels of which potassium atoms are located. Lattice parameters of compounds which are isotypes to the new structure type of β-KEr_2F_7 are given.

Thermodynamische Untersuchungen am System CoO/MgO. K. TORKER UND W. INSELSBACHER. Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, A-8010, Austria.

A series of solid solutions, $Co_xMg_{1-x}O$, was studied thermodynamically in the range 1100–1300 K by means of solid state galvanic cells using oxygen-ion conductors. The activities of CoO in the solid solutions show positive deviations from Raoult's law. The solid solutions are interpreted to be regular within the limits of error. The values of the free enthalpy of mixing are about 20% more positive than in the case of ideality; data of the excess enthalpies therefore are slightly positive.

Endothermic Decompositions of Inorganic Monocrystalline Thin Plates. II. Displacement Rate Modulation of the Reaction Front. G. BERTRAND, M. COMPERAT, AND M. LALLEMANT. Laboratoire de Recherches sur la Réactivité des Solides, Faculté des Sciences Mirande, B.P. 138, 21004 Dijon Cedex, France.
Copper sulfate pentahydrate dehydration into trihydrate was investigated using monocrystalline platelets with (110) crystallographic orientation. Temperature and pressure conditions were selected so as to obtain elliptical trihydrate domains. The study deals with the evolution, vs time, of elliptical domain dimensions and the evolution, vs water vapor pressure, of the D/d ratio of ellipse axes and on the other hand of the interface displacement rate along a given direction. The phenomena observed are not basically different from those yielded by the overall kinetic study of the solid sample. Their magnitude, however, is modulated depending on displacement direction. The results are analyzed within the scope of our study of endothermic decomposition of solids.

An Unusual Technique for the Study of Nonstoichiometry: The Thermal Emission of Electrons. Results for Y_2O_3 and TiO_2. PHILLIPPE ODIER AND JEAN-PIERRE LOUP. Centre de Recherche sur la Physique des Hautes Temperatures, 1D, avenue de la recherche scientifique, 45045 Orleans Cedex, France.
The thermal emission of electrons is presented as a useful technique for the study of nonstoichiometric oxides at high temperature. Results are reported for yttria and titanium dioxide, very different in their respective properties. For these compounds the density of emitted current follows a simple law, $J \propto P_{O_2}^x$, where P_{O_2} is the oxygen partial pressure and x is a constant that is not dependent on temperature. The electrical conductivity, when measured under the same conditions, follows a similar law. Therefore there is some evidence that at high temperature the chemisorption is not an important process, and the emission characteristics are then discussed in terms of a bulk nonstoichiometry. Data are obtained for yttrium oxide, as the width of the band gap $E_g = 5.5$ eV, the electron affinity $\chi = 2$ eV. A reasonable defect for this oxide consists of oxygen vacancies $V_O^{2'}$ and oxygen interstitials $O_i^{2'}$. The situation in the case of rutile is much more complicated as this oxide has a wide nonstoichiometric field with several suboxides and a nonisotropic structure. When the deviation to the stoichiometry is low the oxygen sublattice is stable and the main defects are titanium interstitial $Ti_i^{4\cdot}$. When the compound is more reduced a surface reorganization then occurs which seems related to a crystallographic transformation leading to the Ti_nO_{2n-1} suboxides. This technique gives a lot of data on the properties of nonstoichiometric compounds in the vicinity of the surface at high temperature.

^{99}Ru Mössbauer Spectra of Quaternary Ruthenium (V) Oxides with the Hexagonal Barium Titanate Structure. IMMACULADA FERNANDEZ, ROBERT GREATREX, AND NORMAN N. GREENWOOD. The University of Leeds, Department of Inorganic & Structural Chemistry, Leeds LS2 9JT, England.
^{99}Ru Mössbauer spectra have been recorded at 4.2°K for the quaternary oxides $Ba_3Ru_2MO_9$ (M = Mg, Ca, Sr; Co, Ni, Cu, Zn; and Cd), all of which crystallize with the hexagonal barium titanate structure. The Ca, Sr, and Cd compounds give sharp symmetrical singlets with chemical isomer shifts typical of ruthenium in the +5 oxidation state. The absence of magnetic hyperfine splitting is consistent with the published interpretation of magnetic susceptibility data in terms of binuclear intracluster spin pairing which leads to an $S = 0$ ground state. In contrast, magnetic hyperfine splitting *is* seen for the Mg, Zn, Co, Ni, and Cu compounds; this can be interpreted only in terms of long-range magnetic order and the absence of such an $S = 0$ ground state at 4.2°K. This differs from the published interpretation of the magnetic susceptibility data for $Ba_3Ru_2MgO_9$ in the low-temperature region. The magnetic flux densities at the ruthenium nuclei in the magnetically ordered compounds (32.5–51.6 T) are lower than those normally associated with ruthenium(V), and the spectra cannot be curve-fitted satisfactorily with single hyperfine patterns having the natural linewidth. Possible reasons for these observations are discussed.

The Reaction of Cubic Sodium Tungsten Bronzes, Na_xWO_3, with Metallic Iron. I. J. MCCOLM AND S. J. WILSON. School of Industrial Technology, University of Bradford, Bradford 7, England.