

14.877(4) Å, $z = 2$, and space group $Pnmm$. $K_3TiTa_7O_{21}$ crystallizes in the hexagonal system with unit-cell dimensions $a = 9.095(3)$, $c = 12.063(4)$ Å, $z = 2$ and space group $P6_3/mcm$. The structures were solved by conventional Patterson and Fourier techniques, the former using 283 unique reflections ($I \geq 3\sigma(I)$) was refined by full-matrix least-squares techniques to an R of 0.0551 ($R_w = 0.0496$), the latter using 343 unique reflections ($I \geq 3\sigma(I)$) was refined using the same technique to an R of 0.0354 ($R_w = 0.0279$). Intensity data were measured using counter methods and the " ω " scan technique. KTi_3TaO_9 is isostructural with KTi_3NbO_9 , whose structure was previously derived from powder data, and $K_3TiTa_7O_{21}$ adopts the same structure as found for the nonstoichiometric phase $K_{5.5}Ta_{15.7}O_{42}$ in this laboratory. Both materials were obtained as single crystals by the use of a flux in their preparation. The distribution of titanium and tantalum over the octahedral sites is discussed relative to previously determined structures.

Kinetics and Mechanistic Aspects of the Reduction of Chromium Dioxide. R. SAEZ-PUCHE AND M. A. ALARIO-FRANCO,* Laboratoire de Cristallographie, CNRS 166 X, 38042 Grenoble Cédex, France. Thermogravimetric experiments on very small, single-crystalline, acicular particles of CrO_2 , of homogeneous size and shape, indicate that the reduction of CrO_2 by hydrogen, to produce $CrOOH$, can be explained by means of a unidimensional diffusion mechanism. Hydrogen diffuses along the empty tunnels that exist parallel to the c -axis in the rutile-like unit cell. The corresponding diffusion equation is: $D = 10^{-6}(-19.3 \pm 2.3/RT)$ cm²/sec, and is valid for 490 K < T < 519 K and 30 < P_{H_2} < 110 Torr.

Rare Earth Transition Metal Sulfides, $LnMS_3$ ($Ln = \text{Rare Earth}$; $M = \text{Transition Metal}$). T. MURUGESAN, S. RAMESH, J. GOPALAKRISHNAN, AND C. N. R. RAO,* Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, 560012, India. Ternary rare earth-transition metal sulfides $LnMS_3$ with $Ln = La, Nd, Gd$, and $M = V, Cr$ as well as $Ln = La$ and $M = Mn, Fe, Co, Ni$ have been prepared and characterized. The vanadium and chromium sulfides crystallize in a monoclinic layer structure isotypic with $LaCrS_3$ while the other $LnMS_3$ sulfides crystallize in a hexagonal structure. Chemical shifts of the metal K -absorption edge and XPS binding energies of core levels indicate that the transition metal is trivalent in the V and Cr sulfides, while it is divalent in the Mn, Fe, Co, and Ni sulfides. Electrical and magnetic properties of the sulfides are discussed in terms of their structure and electronic configurations of the transition metal ions.

Kationenverteilungen in einigen Zinnspinel-Mischkristallen. G. VON BECKH, P. ZEGREANU, AND M. TROMEL,* Institut für Anorganische Chemie der Johann Wolfgang Goethe Universität, Niederurseler Hang, D-6000 Frankfurt a.M. 50, Bundesrepublik Deutschland. In inverse tin spinels $(Mg, M)_2SnO_4$ (with $M = Zn, Co, \text{ or } Ni$), the distribution of bivalent metal atoms was determined from samples which had been quenched from 1473 to 1073 K or cooled slowly. In Mg_2SnO_4 , zinc preferentially occupies tetrahedral sites with ΔG° values of about 18 kJ/g-atom. Cobalt and magnesium are equally distributed over octahedral and tetrahedral sites, whereas nickel occupies octahedral sites only. Lattice constants of $(Mg, Zn)_2SnO_4$ solid solutions deviate largely from Vegard's law, but depend linearly on the zinc concentrations in tetrahedral and octahedral sites according to $a = c_0 + c_1 [Zn(\text{tetr.})] + c_2 [Zn(\text{oct.})]$. Zinc in tetrahedral sites causes a lattice contraction; in octahedral sites, however, a lattice expansion.

Deuteron Magnetic Resonance and Hydrogen Bond Network of Ammonium Trihydrogen Selenite. I. S. VINOGRADOVA, L. V. Kirensky Institute of Physics, Academy of Sciences USSR, Siberian Branch, Krasnoyarsk, 660036, USSR. The DMR spectra of single-crystal $ND_4D_3(SeO_3)_2$ have been studied. The principal values and the direction cosines of field-gradient tensor of deuterons located on three nonequivalent O . . O hydrogen bonds have been determined. The lengths of hydrogen bonds have been calculated from eQq/h values; the deuterons have been located on hydrogen bonds. The comparison with the DMR data of isomorphous compound $RbD_3(SeO_3)_2$ is made, and influence of N-H . . O hydrogen bonds on the structural parameters of O . . O hydrogen bonds is discussed.

Les Différentes Formes Cristallines de Y_3ReO_8 : Relations avec la Structure Fluorine. G. BAUD, J. - P. BESSE, R. CHEVALIER,* AND M. GASPÉRIN, Equipe de Cristallographie et Physico-Chimie des Matériaux, associée au CNRS (ERA 897), Université de Clermont II, B.P. 45, 63170 Aubiere, France. The monoclinic $Y_3ReO_8\beta$ phase is synthesized at 40 kbar and 900°C. The crystal structure is solved to

an R value of 0.058 for 1341 observed reflections, by conventional methods using automated four-circle diffractometer data. This structure can be visualized as a fluorite-related superstructure, the large difference between the ionic radii of Re^{7+} and Y^{3+} being favorable to cation ordering. The heating to 500°C of this phase under atmospheric pressure leads to a disordered fluorite structure of the form $\text{Y}_3\text{ReO}_8\alpha$. An intermediary metastable phase $\text{Y}_3\text{ReO}_8\alpha'$ is obtained by heating a $\text{Y}_3\text{ReO}_8\beta$ single crystal to 350°C . The structural relations among these three crystalline forms of Y_3ReO_8 and the fluorite structure are discussed.

Relation between the Crystal Structures of Some Salts of the Type $\text{Me}(\text{OCOCH}_3)_2 \cdot n\text{H}_2\text{O}$ and Their Ability to Form Mixed Crystals or Double Salts ($\text{Me}^{2+} = \text{Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd}$). CHR. BALAREW AND D. STOILOVA,* Chemical Reagents and Preparations Laboratory, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria. An attempt is made to find the relation between the crystal structures of some salts of the type $\text{Me}(\text{OCOCH}_3)_2 \cdot n\text{H}_2\text{O}$ ($\text{Me}^{2+} = \text{Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd}$) and their ability to form mixed crystals or double salts, by taking into account the difference in the ground-state configurations of the metal (II) ions. Such a treatment is based on the theoretical argument that the formation of isomorphous and isodimorphous mixed crystals occurs when the admixed ion may assume the coordination environment of the substituted ion in the crystal structure of the host salt. Double salts are formed mainly between the acetates of the d^5 -, d^{10} -, and p^6 -metal ions, i.e., for ions that allow strong angular deformations of the coordination polyhedra or when at least one of the metal ions meets this condition so that acetate bridge bonding may occur.

Neutron Powder Diffraction on RbCrI_3 and Magnetic Measurements on RbCrI_3 and CsCrI_3 . H. W. ZANDBERGEN* AND D. J. W. IJDO, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands. β - RbCrI_3 ($a = 13.772(3)$, $b = 8.000(2)$, $c = 7.069(2)$ Å, $\beta = 95.85(1)^\circ$, $z = 4$, $C2m$ at 293 K) and γ - RbCrI_3 ($a = 13.586(2)$, $b = 7.923(2)$, $c = 14.094(3)$ Å, $\beta = 96.88(1)^\circ$, $z = 8$, $C2$ at 1.2 K) are isostructural to β - RbCrCl_3 and γ - RbCrCl_3 and are both Jahn Teller distorted BaNiO_3 structures. In both compounds elongated octahedra occur. γ - RbCrI_3 has most probably a magnetic spiral structure at 4.2 and 1.2 K. Theoretically a spiral propagating along the b -axis is expected. A model with $\mathbf{k} = 9/19\mathbf{b}^*$ yielded the best result. However, no good fit was obtained possibly because of a misfit in \mathbf{k} and canting of the magnetic moments due to anisotropy. χ vs T single-crystal measurements on β - CsCrI_3 are in accordance with its magnetic structure. The 3-d magnetic ordering temperature T_c is estimated as 27(1) K. From the χ vs T curves of γ - RbCrI_3 T_c could not be determined. From fits to χ vs T powder data J/k of CsCrI_3 and RbCrI_3 are estimated to be $-14(2)$ and $-11(1)$ K, respectively.

Solid State Reaction between p -Benzoquinone and Dihydroxybenzene. N. B. SINGH* AND H. C. SINGH, Department of Chemistry, Gorakhpur University, Gorakhpur (U.P.), India. Reaction kinetics of p -benzoquinone- p -dihydroxybenzene; p -benzoquinone- m -dihydroxybenzene, and p -benzoquinone- o -dihydroxybenzene systems have been studied in the solid state using capillary, gravimetric, and dilatometric techniques. It is found that p -benzoquinone is the diffusing species. The diffusion occurs through surface migration and depends very much on the symmetry of the dihydroxybenzene molecules. Gravimetric studies indicate that cracks are formed in the product during reaction and that the reaction reaches completion. Dilatometric studies indicate that the reaction products are more compact and contraction in volume takes place during the course of reaction.