

The reaction of the cubic sodium bronzes, Na_xWO_3 , with powdered iron metal has been studied by heating samples *in vacuo* and also at high pressure. Evidence for reaction is found at unexpectedly low temperatures. The reaction is an overall reduction which proceeds via an increase in the sodium content of the bronze phase up to some temperature-dependent limiting composition for which $x < 1$. The existence of this limit, its temperature dependence, and the identity of the other products of reduction have been explained in terms of the partial oxygen pressure of the system. The course of the reduction has been followed through the evolution of the bronze lattice parameter and a reaction mechanism is postulated. No evidence of significant incorporation of iron into a stable cubic sodium bronze phase has been found.

NMR Study of Hydrogen Molybdenum Bronzes: $\text{H}_{1.71}\text{MoO}_3$ and $\text{H}_{0.36}\text{MoO}_3$. R. C. T. SLADE, T. K. HALSTEAD, AND P. G. DICKENS. Department of Chemistry, University of York, Heslington, York YO1 5DD, England.

Proton NMR relaxation times (T_2 , T_1 , and $T_{1\rho}$) and absorption spectra are reported for the compounds $\text{H}_{1.71}\text{MoO}_3$ (red monoclinic) and $\text{H}_{0.36}\text{MoO}_3$ (blue orthorhombic) in the temperature range $77 \text{ K} < T < 450 \text{ K}$. Rigid lattice dipolar spectra show that both compounds contain proton pairs, as OH_2 groups coordinated to Mo atoms in $\text{H}_{1.71}\text{MoO}_3$ and as pairs of OH groups in $\text{H}_{0.36}\text{MoO}_3$. The room temperature lineshape for $\text{H}_{1.71}\text{MoO}_3$ shows that the average chemical shielding tensor has a total anisotropy of 20.1 ppm. The relaxation measurements confirm that hydrogen diffusion occurs and give $E_A = 22 \text{ kJ mole}^{-1}$ and $\tau_c^0 = 10^{-13} \text{ sec}$ for $\text{H}_{1.71}\text{MoO}_3$ and $E_A = 11 \text{ kJ mole}^{-1}$ and $\tau_c^0 = 3 \times 10^{-8} \text{ sec}$ for $\text{H}_{0.36}\text{MoO}_3$.

Crystal Structures of Some Niobium and Tantalum Oxides. VIII. The $5\text{Rb}_2\text{O}:14.6\text{Ta}_2\text{O}_5$ Phase—A Tunnel Structure. G. D. FALLON AND B. M. GATEHOUSE. Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia.

$\text{Rb}_{10}\text{Ta}_{29.20}\text{O}_{78}$ crystallizes in the hexagonal system with unit-cell dimensions (from single-crystal data) $a = 7.503(4) \text{ \AA}$, $c = 36.348(4) \text{ \AA}$ and space group $P6_3/mmc$, $z = 1$. The structure was solved using three-dimensional Patterson and Fourier techniques. Of the 666 unique reflections measured by counter techniques, 515 with $I \geq 3 \sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.057 ($wR = 0.039$). The structure of $\text{Rb}_{10}\text{Ta}_{29.20}\text{O}_{78}$ consists of layers of corner-sharing groups of six edge-shared octahedra separated by layers of single octahedra and double hexagonal tungsten bronze-like layers, these layers being perpendicular to the hexagonal c -axis. Nine-coordinate tricapped trigonal prismatic sites between the hexagonal tungsten bronze-like layers are partially occupied by Ta(V) ions.

Ion Exchange Properties of β -Eucryptite (LiAlSiO_4): EPR Investigation on Copper-Doped Single Crystals. JEAN-LOUIS BERCHOT, DANIEL VIVIEN, DIDIER GOURIER, JEANINE THERY, AND ROBERT COLLONGUES. Laboratoire de Chimie Appliquée de l'état Solide, 11, Rue P. et M. Curie 75231 Paris Cedex 05, France.

Investigation of the ion exchange properties of β -eucryptite (LiAlSiO_4) single crystals indicates that it is impossible to substitute Li^+ with other bigger univalent cations such as Na^+ , K^+ , or Ag^+ . On the contrary, Li^+ exchange with bivalent cations, Cu^{2+} or Mn^{2+} , is very easy. For a general orientation of the crystal with respect to the magnetic field, the EPR spectrum of Cu^{2+} ions in β -eucryptite consists of 12 sharp lines partially superimposed on a broad one. The sharp lines are attributed to isolated copper ions in the conducting channels. Cu^{2+} lies in sixfold, coordinated Li'' sites, but not in the fourfold coordinated Li' ones. The corresponding spin-Hamiltonian parameters at $T = 140 \text{ K}$ are found to be: $g_x = 2.362$, $g_y = 2.340$, $g_z = 1.990$; $|A_x| = 85 \times 10^{-4} \text{ cm}^{-1}$, $|A_y| = 71 \times 10^{-4} \text{ cm}^{-1}$, $|A_z| = 203 \times 10^{-4} \text{ cm}^{-1}$. The broad line is attributed to clusters of Cu^{2+} located in neighboring Li'' sites.

Ferrimagnetism in the Rare Earth Titanium (III) Oxides, RTiO_3 ; $R = \text{Gd, Tb, Dy, Ho, Er, Tm}$. CARL W. TURNER AND J. E. GREEDAN. Institute for Materials Research and Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada.

The series of compounds $RTiO_3$, $R = \text{Gd, Tb, Dy, Ho, Er, and Tm}$, were obtained as single-phase materials via solid state reaction between Ti_2O_3 and R_2O_3 at ca. 1500°C in welded molybdenum crucibles under argon. $YbTiO_3$ and $LuTiO_3$ could not be obtained as single-phase materials using this procedure. Lattice constants for all compounds were determined from powder X-ray data and are compared with previous results. All of these materials order magnetically between 30 and 70°K . From the appearance of the χ_m^{-1} vs T curve the type of order can be identified as ferrimagnetic. High-temperature susceptibility data have been fitted to a two-sublattice molecular field model and the intra- and intersublattice interaction constants have been extracted. It is found that the Ti-Ti interaction is ferromagnetic and relatively constant from $R = \text{Gd}$ to $R = \text{Lu}$. Low-temperature magnetization-field data suggest the existence of complex magnetic structures or large magnetocrystalline anisotropy or both. The magnetic properties of the $RTiO_3$ series are compared to those of the chemically similar and better-known RMO_3 phases where $M = \text{Al, V, Cr, Mn, and Fe}$. The observed differences are shown to follow from the sign of the M - M interaction, which is ferromagnetic for $M = \text{Ti}$ and antiferromagnetic for $M = \text{V, Cr, Mn, and Fe}$, together with the implications of the crystal symmetry for the R - M interaction.

Thermodynamics of Hydrogen Trapping in Intermetallic Compounds: Application to LaNi_5/H . TED B. FLANAGAN, C. A. WULFF, AND B. S. BOWERMAN. Department of Chemistry, University of Vermont, Burlington, Vermont 05405.

It has been observed for several intermetallic compound/H systems that deviations from Sieverts' law of ideal solubility occur which are in the opposite direction from the deviations from ideality which occur in pure metal/H systems. The principal source of nonideality in both types of interstitial solutions arises from the changes of the relative partial molar enthalpy of H_2 solution, ΔH_{H} , with H content. The variations of ΔH_{H} with H content are, however, in the opposite directions for intermetallic- and pure metal/H interstitial solutions. Relative partial molar entropies for solution of H_2 in the α -phase of the LaNi_5/H system are given at 298.2°K . These have been determined from calorimetric determinations of ΔH_{H} and measurements of ΔG_{H} ($= RT \ln p_{\text{H}_2}^{1/2}$). The partial entropies show unusual extrema as a function of H content. A model based on trapping of H atoms is proposed which explains the variations of ΔH_{H} and ΔS_{H} . Since the deviations from ideality arising from an increase of ΔH_{H} with H content seem to be limited to solids with at least two different ordered metal components, e.g., intermetallic compounds, it seems reasonable to assign the trapping sites to interstices which result from an interchange of metal atoms. This interchange may create interstices rich in those nearest-neighbor metal atoms which have the greatest affinity for H.

Lead Phosphate Apatites Substituted by Rare Earth, Sodium, and Potassium Ions. I. MAYER, A. SEMADJA, AND V. WEISS. Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel.

Rare-earth-substituted lead apatites of the $\text{Pb}_{10-2x}\text{Ln}_x\text{M}_x(\text{PO}_4)_6\text{Y}_2$ ($\text{Ln} = \text{La, Nd, Eu, Gd, Dy, and Y}$; $M = \text{Na and K}$; $Y = \text{F and Cl}$) systems were prepared and studied by X-ray diffraction and infrared methods. The powder patterns of all the compounds show the apatite-like hexagonal structure. Single-crystal precession data reveal that the space group of the $\text{Pb}_6\text{Ln}_2(\text{PO}_4)_6\text{F}_2$ compounds is probably $P\bar{6}$ while that of $\text{Pb}_6\text{Ln}_2\text{K}_2(\text{PO}_4)_6\text{F}_2$ is $P6_3/m$. Analysis of the spectra of substituted Ca, Ba, and Pb compounds shows the effect of substituted ions on the spectra and supports the assumption that substitution in the Ba and Pb systems is an ordered process. Ordering of the substituted ions in the systems studied is discussed in view of changes in lattice parameters, size conditions, and polarizing properties of the ions.

Neutron Diffraction Study on the Mechanism of the Topotactic Reduction of 2H-TaS_2 Electrodes. C. RIEKEL, H. G. REZNIK, AND R. SCHÖLLHORN. Anorganisch-chemisches Institut der Universität, Gievenbecker Weg 9, 4400 Münster, West Germany.

The dynamic investigation by neutron diffraction of the topotactic reduction of 2H-TaS_2 electrodes in $\text{K}^+/\text{D}_2\text{O}$ electrolyte to the ionic layered hydrate $\text{K}_{0.5}^+(\text{D}_2\text{O})_{0.5}[\text{TaS}_2]^{0.5-}$ is shown to proceed via third-stage $\text{K}_x^+(\text{D}_2\text{O})_y[\text{TaS}_2]_3^{x-}$, second-stage $\text{K}_x^+(\text{D}_2\text{O})_y[\text{TaS}_2]_2^{x-}$, and first-stage $\text{K}_x^+(\text{D}_2\text{O})_y[\text{TaS}_2]^{x-}$ intermediates. A comparative study by X-ray diffraction on the cathodic intercalation of 2H-TaS_2 and