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 Températures, 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 $V_O^{2\cdot}$ 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.

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:$H_{1.71}MoO_3$ and $H_{0.36}MoO_3$. 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 $H_{1.71}MoO_3$ (red monoclinic) and $H_{0.36}MoO_3$ (blue orthorhombic) in the temperature range $77\,K < T < 450°K$. Rigid lattice dipolar spectra show that both compounds contain proton pairs, as OH_2 groups coordinated to Mo atoms in $H_{1.71}MoO_3$ and as pairs of OH groups in $H_{0.36}MoO_3$. The room temperature lineshape for $H_{1.71}MoO_3$ 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 $E_A = 22$ kJ $mole^{-1}$ and $\tau_c^0 \simeq 10^{-13}$ sec for $H_{1.71}MoO_3$ and $E_A = 11$ kJ $mole^{-1}$ and $\tau_c^0 \simeq 3 \times 10^{-8}$ sec for $H_{0.36}MoO_3$.

Crystal Structures of Some Niobium and Tantalum Oxides. VIII. The $5Rb_2O:14.6Ta_2O_5$ Phase—A Tunnel Structure. G. D. FALLON AND B. M. GATEHOUSE. Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia.

$Rb_{10}Ta_{29.20}O_{78}$ crystallizes in the hexagonal system with unit-cell dimensions (from single-crystal data) $a = 7.503(4)$ Å, $c = 36.348(4)$ Å 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 $I \ge 3\ \sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.057 ($wR = 0.039$). The structure of $Rb_{10}Ta_{29.20}O_{78}$ 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 Appliquee dé 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 $T = 140$ K are found to be: $g_x = 2.362$, $g_y = 2.340$, $g_z = 1.990$; $|A_x| = 85 \times 10^{-4}$ cm^{-1}, $|A_y| = 71 \times 10^{-4}$ cm^{-1}, $|A_z| = 203 \times 10^{-4}$ 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, $RTiO_3$; $R = Gd$, 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.