

Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan. Isothermal electrical conductivity measurements on niobium oxides were carried out over the temperature range from 1010 to 1300°C as a function of oxygen partial pressure in order to clarify the phase relations. Existence regions of the intermediate oxide phases between NbO₂ and Nb₂O₅ were found from the discontinuities in electrical conductivity curves. These oxide phases were also analyzed by a gravimetric method and by X-ray diffractometry. From these results the phase diagram for this system is proposed. The defect structures of these phases are also discussed.

Magnetochemical Properties of Tetranuclear Rhodoso and Pfeiffer Chromium(III) Complexes in a Series of Compounds. HANS U. GÜDEL AND URS HAUSER, Institut für anorganische und physikalische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland. Seven salts of the structurally related tetranuclear rhodoso and Pfeiffer chromium(III) complexes were prepared. Magnetic susceptibilities were measured and the energy splittings of the electronic ground state caused by exchange interactions were determined. There are marked differences in the low-temperature magnetic properties. Crystal packing and hydrogen bonding effects are the most likely causes for the differences in the exchange-splitting pattern.

Polymorphic Transformations of Bi₂MoO₆. A. WATANABE AND H. KODAMA, National Institute for Researches in Inorganic Materials, 1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki, 305 Japan. The polymorphism of Bi₂MoO₆ has been studied by differential thermal analysis, differential dilatometry, and differential scanning calorimetry with γ -form specimens having the kochlinite structure prepared by sintering the oxides Bi₂O₃ and MoO₃. Two stable γ and γ' forms and one metastable γ'' form were observed. The relative thermal stability of the γ form compared with the γ' form has been examined by isothermal heating of a mixture of the two forms under hydrothermal conditions. Thus the low-temperature stable γ form transformed reversibly to the γ'' form at 604 \pm 3°C, and on subsequent heating, the γ'' form transformed irreversibly to the high-temperature stable γ' form in the range 640 to 670°C, depending on heating rates; however, an isothermal treatment at a temperature above 604 \pm 3°C brought the gradual transition of the γ'' form into the γ' form.

The Isotropic Temperature Factors of Sr(Co_{1-x}Mn_x)O₃ (x = 0, 0.1, 0.5, 0.8 and 1.0). H TAGUCHI, M. SHIMADA, M. KOZUMI, AND F. KANAMARU, The Institute of Scientific and Industrial Research, Osaka University, Osaka 565, Japan. The cubic perovskite Sr(Co_{1-x}Mn_x)O₃ has a maximum value of a -axis at $x = 0.3$ and a change of spin state of Co⁴⁺ ion from low to high. To elucidate these properties, the isotropic temperature factor (B) of strontium, cobalt, manganese, and oxygen atoms for $x = 0, 0.1, 0.5, 0.8,$ and 1.0 have been derived from powder X-ray diffraction measurements. The isotropic temperature factor of oxygen for $x = 0, 0.1,$ and 1.0 is small and that for $x = 0.5$ and 0.8 is large. This fact suggests that the oxygen ion deviates from the centre of the Co-O-Mn bond in the solid solutions with $x \geq 0.3$. Larger CoO₆ octahedra and smaller MnO₆ octahedra, which are connected by corner sharing of oxygens of the octahedron, are distributed statistically.

Self-Diffusion of Yttrium in Monocrystalline Yttrium Oxide: Y₂O₃. R. J. GABORIAUD, Laboratoire du Métallurgie Physique, 40, Avenue du Recteur Pineau, 86022 Poitiers, France. Yttrium self-diffusion in monocrystalline yttrium oxide (Y₂O₃) is studied by means of the classical radiotracer technique. The few reliable diffusion data obtained in the temperature range 1600–1700°C lead to the diffusion coefficient $D = 3.5 \times 10^9 \exp(-72/RT)(\text{kcal/mole}) \text{m}^2 \text{sec}^{-1}$. Experimental errors on the above numerical values are large and give, for the preexponential and energy terms, respectively, $2 \times 10^{-7} < D_0 < 3 \times 10^{-10} \text{m}^2 \text{sec}^{-1}$ and $62 < Q < 82 \text{kcal/mole}$. Nevertheless these results seem in good agreement with those deduced from high-temperature and low-stress creep experiments. The theoretical aspect of self-diffusion of yttrium in Y₂O₃ is studied in terms of point defects and lattice disorder due to the equilibrium between the oxide and its environment. This last part is confined to the restricted range of high oxygen partial pressure in which oxygen interstitials are supposed to be majority defects. Intrinsic and extrinsic diffusion behaviors are both considered on the basis of a vacancy diffusion mechanism.

Study of Pr_{1-x}Mn_{1+x}O₃ Perovskites. EMIL POLLERT AND ZDENĚK JIRÁK, Institute of Physics, Czechoslovak Academy of Science, Na Slovance 2, 180 40 Praha 8, Czechoslovakia. The structural and magnetic properties of the Pr_{1-x}Mn_{1+x}O₃ perovskites were studied. The increase of x (i.e., Pr/Mn < 1)

leads to the decrease of the orthorhombic deformation and of the Néel temperature and, simultaneously, to an increase of the ferromagnetic contribution. The latter effect is explained from the suggested distribution of the cations $(\text{Pr}_{1-x}^{3+}\text{Mn}_x^{2+})_A(\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+})\text{O}_3^{2-}$ by the double exchange of $\text{Mn}^{3+} - \text{Mn}^{4+}$ pairs at the *B*-sublattice.

Ordering in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ Solid Solutions. A. AMIN, R. E. NEWNHAM, L. E. CROSS, S. NOMURA, AND D. E. COX, Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania. Compositional ordering was found to occur in the ferroelectric $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -antiferroelectric $x\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ solid solution system. X-Ray diffraction and neutron profile fitting structure refinement were used to refine one such composition with $x = 0.9$. The paraelectric structure of compositions with $x < 0.2$ is that of the disordered perovskite (space group *Pm3m*), whereas for $2.0 \leq x < 1.0$ the structure is that of ordered perovskite (space group *Fm3m*). The oxygen octahedra in the ordered state are regular but no longer equivalent.

Studies of Spinels. VII. Order-Disorder Transition in the Inverse Germanate Spinels $\text{Zn}_{2-x}(\text{Co}, \text{Ni})_x\text{GeO}_4$ ($x \approx 1$). J. PREUDHOMME AND P. TARTE, University of Liege, Institute of Chemistry, B-4000 Sart-Tilman par Liege 1, Belgium. A series of germanate spinels $\text{Zn}_{2-x}(\text{Ni}, \text{Co})_x\text{GeO}_4$ has been synthesized and investigated by X-ray diffractometry and infrared spectroscopy. Synthesis at 1200°C leads to cubic phases characterized by an inverse, disordered distribution of Ge and bivalent cations (essentially Ni or Co) over the octahedral sites; however, the presence of some short-range order is suggested by the infrared spectrum. Tempering at an appropriate temperature (between 800 and 900°C, depending on the Co/Ni ratio) leads to tetragonal spinel phases, corresponding to the 1 : 1 order between Ge and bivalent cation on octahedral sites. The transformation is sluggish and proceeds at a significant rate only in a narrow temperature range, just below the transition temperature. A comparison with the behavior of known inverse, ordered titanate spinels shows that, within the family of inverse II-IV spinels $\text{M}_2^{\text{II}}\text{M}^{\text{IV}}\text{O}_4$, the ratio of the octahedral cationic radii $r_{\text{M}^{\text{II}}}/r_{\text{M}^{\text{IV}}}$ is one of the factors determining the order-disorder transition temperature, and the importance of the tetragonal distortion.

Lanthanoid-Nickel Phosphides with ThCr_2Si_2 -Type Structure. WOLFGANG JEITSCHKO AND BEATE JABERG, Anorganische Chemie III, Universität Dortmund, Postfach 500500, D-4600 Dortmund 50, West Germany. The new compounds YNi_2P_2 and LnNi_2P_2 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$) were prepared by sintering the elemental components in silica tubes. Well-developed crystals were obtained using tin as a flux. They crystallize with the ThCr_2Si_2 (CeGa_2Al_2)-type structure which was refined from single-crystal X-ray data for EuNi_2P_2 to a conventional *R* value of 0.049 for 118 unique structure factors. While the P atoms in formally isotypic EuCo_2P_2 are isolated from each other, they form pairs in EuNi_2P_2 . This results in a different *c/a* ratio and an entirely different bonding situation. A comparison of cell volumes shows that Eu in EuNi_2P_2 has an intermediate valence.

Structure and Magnetic Properties of Sulfides of the Type CdRe_2S_4 and $\text{Mg}(\text{Gd}_x\text{Yb}_{1-x})_2\text{S}_4$. L. BEN-DOR AND I. SHILO, Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel. CdRE_2S_4 ($\text{RE} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Yb}$) and $\text{Mg}(\text{Gd}_x\text{Yb}_{1-x})_2\text{S}_4$ were prepared by solid-state reactions. All the cadmium-containing compounds are cubic, i.e., the Th_3P_4 structure for Gd, Tb, and Dy and the spinel type for all the others. The first three compounds were deficient in CdS. In the case of the Mg system, for $x = 1$ the system is cubic Th_3P_4 , for $x = 0$ cubic spinel, and for $0 < x < 1$ orthorhombic MnY_2S_4 (*Cmc2₁*). All the materials studied are paramagnetic above 77°K. Below 77°K in the magnesium family both cubic materials are paramagnetic down to 4.2°K and the orthorhombic materials show magnetic ordering. In the cadmium family all but CdTm_2S_4 show exchange coupling.