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Abstracts of Forthcoming Articles

The System TiO_2–MnO_x: A Structural, Thermogravimetric and Magnetic Study. M. VALIGI AND A. CIMINO. Centro di Studio (C.N.R.) su "Struttura ed Attivita Catalitica di Sistemi di Ossidi," Istituto Chimico, Universita di Roma, Roma, Italy. The unit cell parameter variations of TiO_2 on addition of up to 8% atomic ratio of manganese oxide have been investigated. Magnetic susceptibilities in the range 98–600°K have been measured, and weight loss in hydrogen atmosphere has been recorded up to 1173°K. The results show that, at 1273°K in air, manganese is incorporated as Mn^{4+} in the TiO_2 structure up to 1.24% atomic wt. Manganese in excess (with respect to the solubility value) reacts with TiO_2 to form $MnTiO_3$. The Mn^{4+} ions in solid solution are reduced by hydrogen in the temperature range 723–923°K to Mn^{2+}, which precipitate as $MnTiO_3$.

Magnetic Behavior and Infrared Spectra of Jarosite, Basic Iron Sulfate and Their Chromate Analogs. D. A. POWERS, G. R. ROSSMAN, H. J. SCHUGAR, H. B. GRAY. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91109. The magnetic behavior and infrared spectroscopic features of $KFe_3(SO_4)_2(OH)_6$ (jarosite), $(H_3O)Fe_3(SO_4)_2(OH)_6$ (hydronium jarosite), $KFe_3(CrO_4)_2(OH)_6$, $Fe(OH)SO_4$ (basic iron sulfate), and $Fe(OH)CrO_4$ (basic iron chromate) are reported. Spectroscopic data are in accord with X-ray data which show that $KFe_3(SO_4)_2(OH)_6$, $(H_3O)Fe_3(SO_4)_2(OH)_6$, and $KFe_3(CrO_4)_2(OH)_6$ are isostructural with $KAl_3(SO_4)_2(OH)_6$ (akunite). All the species exhibit negative deviations from Curie–Weiss behavior over the temperature range 300–76°K. The compounds $KFe_3(CrO_4)_2(OH)_6$ and $Fe(OH)CrO_4$ undergo ferrimagnetic transitions at 73 and 71°K, respectively. Maxima occur in the susceptibilities of $KFe_3(SO_4)_2(OH)_6$ and $(H_3O)Fe_3(SO_4)_2(OH)_6$ at 45 and 50°K, respectively.

Effet Jahn–Teller Cooperatif et Affinité Tetraedrique des Ions Mn^{2+} et Zn^{2+} dans le Système Mn_3O_4–Zn_2SnO_4. M. NOGUES AND P. POIX. E. R. 83 du C.N.R.S. Université de Paris XI, Laboratoire de Chimie Minérale, Bâtiment 420-91405 Orsay, France. Comparison between synthesis in air and in vacuum of the solid solution $tMn_3O_4 + (1\text{-}t)Zn_2SnO_4$, and cristallographic study of the nonoxidized compounds allowed us to establish the distribution and the electronic configuration of cations in tetrahedral (A) and octahedral (B) sites. The competitive aspect of Zn^{2+} and Mn^{2+} ions to occupy tetrahedral sites is discussed. In air, the nonoxidizable character of Mn^{2+} on an A-site is clearly borne out, whereas the B-site displaced manganese oxidizes to Mn^{3+}. In vacuum, the critical concentration of Mn^{3+} ion at the octahedral site, involving a cooperative Jahn–Teller effect, is about 50%. An important fact has also been put forward: the microscopic distortion of the oxygen octahedra, which the ratio of long and short anion–cation distances expresses, is equal to the unit-cell macroscopic deformation that the ratio $c/a\sqrt{2}$ represents.

Magnetic Susceptibility of the Uranium Nitrides. R. TROC. Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland. The magnetic susceptibility of UN, and of the higher uranium nitrides has been measured over a wide temperature range, i.e., 4.2–950°K. A large temperature-independent term χ_0 equal to $310 \pm 10 \times 10^{-6}$ emu/mole has been derived from the total susceptibility data of UN. The obtained χ_M values of UN are also related to the Knight shift data from literature. For the higher nitrides U_2N_{3+x} the magnetic susceptibility has been measured for N:U ratios between 1.55 and 1.80. Antiferromagnetic phase transitions have been found for all the examined compositions. The transition temperature T_N gradually decreases as the nitrogen content increases, varying from 94°K for $UN_{1.55}$ to about 8°K for the maximum composition of $UN_{1.80\pm0.02}$. The magnetic properties of the higher nitrides are discussed in terms of mixed valency states, either U^{4+} and U^{6+} or U^{4+} and U^{5+} for the stoichiometric U_2N_3.

Oxydes de Plomb. 1. Structure Cristalline du Minium, Pb_3O_4, à Temperature Ambiante (293°K). J. R. GAVARRI AND D. WEIGEL. Laboratoire de Chimie, Physique du Solide, E.R.A. au C.N.R.S.