

Abstracts of Forthcoming Articles

Mise en évidence d'une solution solide de type spinelle dans le diagramme de phase du système In-S. A. LIKFORMAN, M. GUITTARD, A. TOMAS, AND J. FLAHAUT, Laboratoire de Chimie Minérale Structurale, Faculté de Pharmacie 4, avenue de l'Observatoire 75270, Paris Cedex 06, France. Evidence is presented for normal-spinel domain of homogeneity between the compositions $\text{InS}_{1.50-\epsilon}$ and $\text{InS}_{1.35}$. Structural study of a single crystal of composition $\text{InS}_{1.44}$ indicates indium vacancies on the tetrahedral sites. The compound In_2S_3 , regardless of conditions of formation, is a tetragonal superstructure of the spinel lattice (a_0) with $a = a_0 2^{1/2}$ and $c = 3a_0$. The spinel-type domain shows peritectic decomposition at 850°C for the composition $\text{InS}_{1.40}$.

Existence of a Magnetic Susceptibility Anomaly in the Ternary Systems $M'_{1-x}M_x\text{C}_8$. G. FURDIN, D. BILLAUD, A. HEROLD, C. ZELLER, AND A. MARCHAND, Laboratoire de Chimie du Solide, Service de Chimie Minérale Appliquée, 54037 Nancy Cedex, France. Like the binaries, MC_8 , the ternaries $M'_{1-x}M_x\text{C}_8$ (M and $M' = \text{K}, \text{Rb}, \text{Cs}$) have a positive magnetic susceptibility which is isotropic and temperature independent. It undergoes a very drastic variation as a function of composition, for which a qualitative explanation is proposed.

Crystal and Molecular Structure of Tris(hexaamminerhodium(III))trikakis(trichlorostannato(II)) (tetrachlorostannato(II))rhodate(I)hexachlorostannate(II)tetrahydrate. TAKASHI KIMURA AND TOSIO SAKURAI, The Institute of Physical and Chemical Research, Wako-Shi, Saitama, 351, Japan. The crystal and molecular structure of the title compound, $[\text{Rh}(\text{NH}_3)_6]_3[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)](\text{SnCl}_6) \cdot 4\text{H}_2\text{O}$, has been determined by the single-crystal X-ray diffraction method. The compound crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 16.581(2)$, $b = 11.010(4)$, $c = 16.024(2)$ Å, $\beta = 90.76(1)$, and two molecules per unit cell. The structure was solved by Patterson's method and refined by the least-squares technique to give a final R factor of 0.031. The three cations, $[\text{Rh}(\text{NH}_3)_6]^{3+}$, are a regular octahedron with an average Rh-N bond length of 2.07 Å. The rhodium anion, $[\text{Rh}(\text{SnCl}_3)_4(\text{SnCl}_4)]^{5-}$, is a trigonal bipyramid with the two axial Rh-Sn bonds 2.493 Å in length, and the three equatorial ones 2.546, 2.540, and 2.540 Å. One of the three tin atoms in the equatorial trigonal plane forms a distorted trigonal bipyramid with two short Sn-Cl bonds 2.384 Å in length and two long ones 2.733 Å. The other four tin atoms have a distorted tetrahedral arrangement with an average Sn-Cl bond length of 2.42 Å. The tin anion, $[\text{SnCl}_6]^{4-}$, which is not coordinated to rhodium, forms extremely long Sn-Cl bonds of 2.763, 2.800, and 2.893 Å in a distorted octahedral arrangement.

Influence des variétés allotropiques de Bi_2O_3 sur les caractéristiques électriques des varistances à base d'oxyde de zinc. ROGER SALMON, MICHEL GRACIET, GILLES LE FLEM, AND PAUL HAGENMULLER, Laboratoire de Chimie du Solide, Université de Bordeaux I, 33405 Talence Cedex, France. The I-V characteristics of zinc oxide-based varistors have been studied as a function of the variety of bismuth oxide stabilized during the cooling process. An improvement of the nonlinear exponent at low current densities and a minor change in the characteristics after a pulse of current are observed for slowly cooled samples.

$(2H)_2-2C$ -Type Superstructure of $\text{TiS}_{1.62}$, Determined by High-Resolution Electron Microscopy. Y. BANDO, M. SAEKI, M. ONODA, I. KAWADA, AND M. NAKAHIRA, National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan. A superstructure of $\text{TiS}_{1.62}$ is determined by 100-kV high-resolution electron microscopy, in which the arrangement of metal vacancies is obtained from structure images. The crystal has monoclinic symmetry (pseudo-hexagonal) with lattice parameters $a = 11.9$, $b = 6.85$, $c = 11.5$ Å, and $\beta = 90^\circ$. The space group is considered as $F2/m$. Metal vacancies are confined to every second metal layer and ordered within the partly filled metal layer, resulting in formation of a $(2H)_2-2C$ type of superstructure. The ordered metal vacancy layers are arranged in $2C$ -type stacking sequence along the c axis, while sulfur atoms are arranged in $2H$ -type stacking sequence along the c axis, while sulfur atoms are arranged in $2H$ -type stacking sequence along the c axis.

The Raman Spectrum of Monetite, CaHPO₄. F. CASCIANI AND R. A. CONDRADE, Sr., NYS College of Ceramics at Alfred University, Alfred, New York 14802. The Raman spectrum was measured for monetite, CaHPO₄. A consistent set of band assignments were made for both the Raman and infrared spectra. The effects of factor group and two-site effect are discussed.

A Mössbauer and X-Ray Study of Fe₂P_{1-x}B_x Compounds (x < 0.15). R. CHANDRA, S. BJARMAN, T. ERICSSON, L. HAGGSTROM, C. WILKINSON, R. WAPPLING, Y. ANDERSSON, AND S. RUNDQVIST, Institute of Chemistry, University of Uppsala Box 531, S-751 21 Uppsala, Sweden. Boron/phosphorus substitution in Fe₂P has been studied by ⁵⁷Fe Mössbauer spectroscopy. The magnetic ordering temperature increases rapidly with increasing boron content. Replacement of a phosphorus atom by boron in the immediate environment of an iron atom results in a substantial increase of the magnetic hyperfine field, while the centroid shift and the quadrupole splitting are almost unchanged. The hyperfine parameters for iron atoms at larger distances from the boron atom remain unaffected. Boron substitutes preferentially for phosphorus at the singlefold P(2) position in the Fe₂P structure.

Mössbauer Studies of Thiospinels: I. The System FeCr₂S₄-FeRh₂S₄. E. RIEDEL AND R. KARL, Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D 1000 Berlin 12, West Germany. Spinel compounds FeCr_{2-x}Rh_xS₄ have been obtained as single-phase products for 0 ≤ x ≤ 1.2. The ionic distribution is Fe⁺²[Cr_{2-x}Rh_x⁺³]₂S₄⁻². Room-temperature Mössbauer spectra of ⁵⁷Fe consist of several overlapping doublets of almost identical isomer shifts but different quadrupole splittings which are attributed to tetrahedral Fe⁺² with different numbers of Rh atoms as nearest octahedral site neighbors. The spectra have been compared with the unresolved doublet of Fe⁺³ in Cu_{0.5}⁺¹Fe_{0.5}⁺³[Cr⁺³Rh⁺³]₂S₄⁻².

Les orthoarseniates de sodium et de terre rare. CLAUDE PARENT, ROGER SALMON, GERARD DEMAZEAU, AND GILLES LE FLEM, Laboratoire de Chimie du Solide, Université de Bordeaux I, 33405 Talence Cedex, France. Sodium rare-earth arsenates Na₃Ln(AsO₄)₂ may occur in five allotropic varieties. Their structural evolution has been studied as a function of rare-earth size, temperature, and pressure. The structures are isotypic with those of homologous phosphates and vanadates previously described.

Structural Intergrowth Phenomena in the Sb_xWO₃ System. T. EKSTRÖM, M. PARMENTIER, AND R. J. D. TILLEY, School of Materials Sciences, University of Bradford, Bradford BD7 1DP, West Yorkshire, England. The Sb_xWO₃ system has been examined by powder X-ray diffraction and high-resolution electron microscopy. In the composition range Sb_{0.01}WO₃ to Sb_{0.07}WO₃ a series of perovskite-related tungsten bronzes form. In the composition range approximately Sb_{0.12}WO₃ to Sb_{0.20}WO₃, a series of structures were found which can be regarded as more or less ordered intergrowths of lamellae of the WO₃ and hexagonal tungsten bronze structures. The WO₃ slabs are n octahedra thick and a knowledge of the value of n allows the chemical composition of the phases, x = 1/2n + 1, to be calculated. No n values below 2 were observed and for x > 0.15, fairly large regions with the ordered n = 2 structure were found.