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Abstracts of Forthcoming Articles

Neutron Diffraction Study of β-Uranium Pentafluoride between 77 and 403°K. J. C. Taylor and A. B. Waugh, Chemical Technology Division, AAEC Research Establishment, Lucas Heights, Private Mail Bag, Sutherland, New South Wales, 2232, Australia. The structure of β-UF_5 has been refined by neutron powder profile analyses at 77, 293, 348, and 403°K. The structure is relatively temperature insensitive within this range and at 403°K there is a slow conversion to α-UF_5. The coordination polyhedron may be described either as a square antiprism or a dodecahedron, the former polyhedron giving the better fit with the observed atomic positions.

Structure cristalline de la phase β-KYb_2F_7. Y. Le Fur, S. Aléonard, M. F. Gorius, and M. Th. Roux, Laboratoire de Cristallographie (CNRS), 166X-38042 Grenoble Cedex, France. β-KYb_2F_7 crystallizes in the monoclinic system with parameters $a = 6.528(1)$ Å, $b = 4.217(1)$ Å, $c = 6.435(1)$ Å, $\beta = 115.94°$, $Z = 1$, and space group $P2$. The structure has been solved from single-crystal automatic four-circle diffractometer data by three dimensional Patterson and Fourier syntheses and refined by least-squares method. The final R value is 0.040. Structural relations with KLu_2F_7 are shown. The structures are characterized by chains of edge-sharing semi regular pentagonal bipyramids fused together by corner sharing in two directions perpendicular to the chains. Large tunnels, in which potassium atoms are located, are formed by the stacking of these planes.

Silver Ionic and Electronic Conductivity in Ag_9GaS_6, Ag_9AlS_6, $AgGaS_2$, $AgAlS_2$ and $AgAl_5S_8$. E. E. Hellstrom and R. A. Huggins, Department of Materials Science and Engineering, Stanford University, Stanford, California 94305. Silver ionic and electronic conductivity in phases in the Ag_2S–M_2S_3, M = Al, Ga, systems have been investigated using dc methods with ionically reversible electrodes and ac methods. Measurements on the mixed conductors Ag_9GaS_6 and the new phase Ag_9AlS_6, both with high silver ionic conductivity, the chalcopyrites $AgGaS_2$ and $AgAlS_2$, both with predominant silver ionic conductivity, and the mixed conducting spinel, $AgAl_5S_8$, are reported. In addition, a schematic version of the Ag_2S–Al_2S_3 phase diagram is presented.

Thermodynamics of the Lanthanum–Hydrogen System at 917°K. P. Dantzer and O. J. Kleppa, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. The binary system lanthanum-hydrogen has been studied at pressures up to 1 atm at 917°K by a calorimetric-equilibrium method. From the calorimetric measurements we found the enthalpy of formation of LaH_2 at 917°K to be -45.7 kcal $mole^{-1}$ with an estimated uncertainty of ± 0.3 kcal $mole^{-1}$. This result is about 4 kcal $mole^{-1}$ less negative than the values derived indirectly from plateau pressure equilibrium measurements by Mulford and Halley, and by Korst and Warf. A comparison between the calorimetric and equilibrium measurements at 917°K provides information on the partial entropy of hydrogen in lanthanum and in the dihydride $LaH_{2\pm\delta}$. The excess entropy of hydrogen in lanthanum is about 6 cal K^{-1} $mole^{-1}$ at 917°K; this value is essentially fully accounted for by the estimated vibrational entropy contribution of the hydrogen atoms. In $LaH_{2\pm\delta}$ the partial entropy of hydrogen changes from small negative values at $X \approx 1.95$ to positive values for $X > 2$. This entropy change is explained by an assumed intrinsic disorder of hydrogen in LaH_2 of about 0.02.

Empirische Beziehungen zur Sauerstoffkoordination um Antimon(III) und Tellur(IV) in Antimoniten und Telluriten. M. Tromel, Institut für Anorganische Chemie der Johann Wolfgang Goethe-Universität, Niederurseler Hang, D-6000 Frankfurt a.M. 50, Bundesrepublik Deutschland. The strong variability of bond length between Sb(III) or Te(IV) and oxygen is correlated with distances to more distant oxygen atoms in the *trans* position. Closer approach of the *trans*-oxygen atom leads to lengthening of the bond in question. Hyperbolic functions represent suitable approximations for the correlations and give the bond lengths on the average within 0.04 Å. The distance relations are discussed for various limiting coordinations corresponding to 3, 4, and 5.

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The Crystal Structure of Topotactically Dehydrated Copper(II) Formate Tetrahydrate. John R. Günter, Institute for Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland. Thermal dehydration of copper(II) formate tetrahydrate leads to a different modification of the anhydrous salt than the direct preparation of the latter. As the dehydration is a topotactic process, the known crystal structure of the tetrahydrate and the topotactic orientation relations can be used to deduce the crystal structure of the product. Single-crystal X-ray diffraction patterns of decomposed pseudomorphs yield the following unit-cell parameters for the dehydrated formate: monoclinic, $a = 8.195 \pm 0.006$ Å, $b = 7.925 \pm 0.006$ Å, $c = 3.620 \pm 0.005$ Å, $\beta = 122.21 \pm 0.09°$, probable space group $P2_1/a\text{-}C^5_{2h}$. The structure contains copper formate layers very similar to those in the tetrahydrate, stacked in such a way that columns of distorted coordination polyhedra, linked by formate bridges, are formed. The topotactic dehydration occurs in such a way that two-dimensional elements of the structure are unaltered but the mode of stacking is changed.

Magnetic Behaviour in Solid Solution Systems: I. $(MnMg)Tb_2S_4$. L. Ben-Dor and I. Shilo, Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel. The solid solutions in the sytem $Mn_xMg_{1-x}Tb_2S_4$ for $0 \leq x \leq 1$ all have the orthorhombic MnY_2S_4 structure, space group $Cmc2_1$. In the temperature range 77–300°K the materials are paramagnetic and the Curie–Weiss law is obeyed. At low temperatures, ca. 20°K, there is a deviation from linearity of the curve of χ^{-1} vs T. The curves of magnetization as a function of the magnetic field at 4.2°K are reminiscent of saturation curves, especially for low values of x. The magnetic interactions between the metal ions are discussed.

Magnetic Behaviour in Solid Solution Systems: II. $(MnMg)Gd_2S_4$ and $(MnMg)Yb_2S_4$. L. Ben-Dor and I. Shilo, Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel. The solid solutions in the systems $(MnMg)Gd_2S_4$ and $(MnMg)Yb_2S_4$ have the cubic Th_3P_4 (space group $I\bar{4}3d$) and the cubic spinel (space group $Fd3m$) structure, respectively. All materials are paramagnetic above 77°K. The spinel (higher symmetry) family shows a downward curvature to the origin below 60°K. The Th_3P_4 family exhibits two differing behaviors: for $x = 0.1$ the Curie–Weiss law is obeyed down to 4.2°K; for $0 < x < 1$ some magnetic ordering is observed.

Crystallographic and Magnetic Studies of Cation-Deficient Spinels $M_{2/3+x}Cr_{2-x}S_4$ ($M = Al, Ga, In$). I. Nakatani, National Research Institute for Metals, Nakameguro, Meguro-ku, Tokyo 153, Japan. Crystallographic studies are carried out on the cation-deficient spinel compounds $Ga_{2/3}Cr_2S_4$ and $Al_{2/3+x}Cr_{2-x}S_4$ ($1/3 \leq x \leq 5/3$). X-Ray analysis on both compounds indicates that there exist 1/3 vacancies per formula unit in $8a$ positions and chromium atoms in $16d$ positions, and that the rest of the metal positions are occupied by gallium or aluminum atoms. Aluminum atoms give a wide range of substitution for chromium atoms, but gallium atoms do not. It is found by electron diffraction that vacancy ordering occurs in $Ga_{2/3}Cr_2S_4$ below about 1100°C, as well as in $InCr_{5/3}S_4$. Magnetic properties are investigated on these compounds. Both $InCr_{5/3}S_4$ and the disordered form of $Ga_{2/3}Cr_2S_4$ exhibit weak ferromagnetism at low temperatures. The facts are explained in terms of the vacancy distribution in the $8a$ positions.

Spectroscopie Photoelectronique ESCA (XPS) de Chalcogenures de Thallium. L. Porte and A. Tranquard, Université Claude Bernard, Lyon I, Laboratoire de Physico-Chimie Minérale III, 43 boulevard du 11 novembre 1918, 69621 Villeurbanne Cedex, France. The thallium chalcogenides Tl_2S, TlS, Tl_2Se, TlSe, Tl_5Te_3, TlTe, and Tl_2Te_3 have been investigated by using the X-ray photoelectron spectroscopy approach. Measurements from both the core and the valence levels are reported. In the thallium telluride series the relative variations of the core level binding energies and the evolution in the valence band structure are consistent with an increase of ionic contribution from Tl^{III} to Tl^{I} compounds. Valence band structures of thallium sulfides and thallium selenides are analyzed with regard to the crystallographic structures and particular attention is devoted to the structure derived in major part from the Tl6s level. An explanation of the variations observed for this structure in various compounds is advanced, taking account of the peculiarity of Tl6s level participation in the chemical bonds.

Lead Alkali Apatites without Hexad Anion: The Crystal Structure of $Pb_8K_2(PO_4)_6$. M. Mathew, W. E. Brown, M. Austin, and T. Negas, Center for Material Science, National Bureau of Standards, Washington, D.C. 20234. The crystal structure of $Pb_8K_2(PO_4)_6$ has been determined by single-crystal

X-ray diffraction. The crystals are hexagonal, space group $P6_3/m$ with $a = 9.827(1)$ and $c = 7.304(1)$ Å. The structure was refined to a final $R = 0.034$ for 551 observed reflections. The structure is that of apatite, $A_6B_4(XO_4)_6Y_2$ with the hexad anion site Y completely vacant. The 6*h* sites are occupied by Pb alone whereas the 4*f* sites contain equal amounts of Pb and K. A short Pb–O distance of 2.24 Å indicates a covalent bond which may account for the incorporation of lead into bone mineral. The presence of lone pairs of electrons from the lead atoms in the vicinity of the hexad site may explain why this site remains empty.

Temperature Dependence of Anderson–Grüneisen Parameter of Ionic Solids. S. P. SRIVASTAVA, Analytical Physics Laboratory, Indian Institute of Petroleum, Dehradun, India. A new relation, including the volume-dependent and the cubic-and quartic-term anharmonic contributions, is derived for the Anderson–Grüneisen parameter δ for ionic solids. This equation is applied to the KCl crystal to study the temperature dependence of δ, and the role of the volume-dependent and anharmonic contributions is explained. The wider applicability of the present equation is discussed.

Mise en évidence de $CaFe_4O_6$ et détermination des structures cristallines des ferrites de calcium $CaFe_{2+n}O_{4+n}$ ($n = 1,2,3$): nouvel exemple d'intercroissance. O. EVRARD, B. MALAMAN, F. JEANNOT, A. COURTOIS, H. ALEBOUYEH, AND R. GERARDIN, Laboratoires de Chimie du Solide Minéral. Université de Nancy I, C.O. 140-54037 Nancy Cedex, France. The synthesis of a new calcium ferrite $CaFe_4O_6$ has been carried out at 1125°C under a controlled atmosphere of H_2–H_2O. The existence of this compound modifies a part of the diagram Fe–Ca–O. The crystal structures of the ferrites $CaFe_{2+n}O_{4+n}$ ($n = 1,2,3$) have been resolved on a series of single crystals; these ferrites crystallize in the orthorhombic system, space group *Cmcm* with the average parameters $a = 3.04$ Å, $b = 10$ Å, $c = 10+2.65n$ Å. The three structures derive from each other through an intergrowth process, in the direction of the c axis, with $CaFe_2O_4$ blocks between the FeO blocks. The coordination of the iron atoms is slightly changed by the nature of the neighbouring blocks during stacking.

Etude de la Magnetoresistance de Composes Ferromagnetiques $Cr_3Se_{4-x}Te_x$ ($x = 2.5$ et $x = 3$). D. BABOT AND M. CHEVRETON, Laboratoire d'Etude des Matériaux, Batiment 303, 20 avenue Albert-Einstein, 69621 Villeurbanne Cedex, France. Longitudinal and transverse magnetoresistances are studied on two ferromagnetic compounds in the $Cr_3Se_{4-x}Te_x$ series. Measurements are carried out on a polycrystalline sample ($x = 3$) and on a small monocrystalline plate ($x \approx 2.5$), with the four-point probe method, at temperatures between 5 and 300°K in a variable 0- to 50-kOe magnetic field. For each temperature, in the whole magnetic field range, both magnetoresistances are negative. All curves $-(\Delta\rho_\perp/\rho_0) = f(T)$ and $-(\Delta\rho_\parallel/\rho_0) = f(T)$ have a pronounced peak in the vicinity of the Curie temperature. This maximum approaches 10^{-1} for $H = 49$ kOe. The results are discussed in terms of the magnetic component variation of the resistivity. The electrical resistivity reduction is closely related to decrease of the thermal spin disorder.

Structure and "Oxidation Behavior" of $W_{24}O_{70}$, a New Member of the {103} CS-Series of Tungsten Oxides. MARGARETA SUNDBERG, Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden. Reduced tungsten trioxide crystals WO_{3-x}, formed by vapor transport from a preparation with bulk composition $WO_{\approx 2.90}$, have been studied by X-ray diffraction and electron microscopy. A single-crystal X-ray investigation showed the existence of the ordered {103} CS-structure $W_{24}O_{70}$, a new member of the homologous series W_nO_{3n-2}. Electron diffraction patterns of crystal fragments, with a few exceptions, showed the presence of the $W_{24}O_{70}$ phase (composition $WO_{2.917}$). Lattice images, however, indicated a fairly ordered {103} CS-phase, $W_{24}O_{70}$, intergrown with slabs of WO_3 giving gross compositions of the examined crystals in the range $WO_{2.93}$–$WO_{2.96}$. The wide WO_3 slabs were probably formed by an oxidation process during the preparation.

Un Nouveau Conducteur Ionique (LaO)AgS. MARCEL PALAZZI, CLAUDE CARCALY, AND JEAN FLAHAUT, Laboratoire de Chimie Minerale, Universite Rene Descartes, 4, avenue de l'Observatoire, 75270 Paris Cedex 06, France. The compound (LaO)AgS is prepared by reaction of Ag_2S and La_2O_2S, in presence of a small proportion of iodine, between 580 and 640°C. The cell is tetragonal, space group $P4/n$ or $P4/nmm$. The structure is not known, but is probably formed by alternating (LaO) and (AgS) sheets. The electric conductivity is determined by complex impedance method, with blocking electrode, and by emf measurements; it is mainly ionic, with $\sigma = 10^{-3}$ to $10^{-1}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ between 25 and 250°C. The activation energy is 0.195 ± 0.005 eV.

Uber Sauerstoffperowskite mit fünf- und vierwertigem Iridium Verbindungen vom Type $Ba_2B^{3+}Ir^{5+}O_6$ *und* $Ba_3B^{3+}Ir_2^{4.5+}O_9$. I. THUMM, U. TREIBER, AND S. KEMMLER-SACK, Institut für Anorganische Chemie der Universität Tübingen Auf der Morgenstelle 18, D-7400 Tübingen, Germany. Perovskites with pentavalent iridium of type $Ba_2B^{3+}Ir^{5+}O_6$ are for B^{3+} = La, Nd, Sm, Gd, Dy, Y cubic and with B^{3+} = In hexagonal [$6L$ structure of $BaTiO_3$ type; sequence $(hcc)_2$]. According to the intensity calculations on powder patterns for $Ba_3SmIr_2O_9$ and $Ba_3YIr_2O_9$ the new series $Ba_3B^{3+}Ir_2O_9$ (B^{3+} = Sm, Eu, Gd, Dy, Ho, Yb, Sc, Y, In; mean oxidation state of iridium +4.5) crystallize in a hexagonal $6L$ structure of $BaTiO_3$ type [space group $P6_3/mmc$; sequence $(hcc)_2$]. The intensity related R' value is 8.6% for B^{3+} = Sm and 10.0% for B^{3+} = Y. In the octahedral net the double groups of face-connected octahedra are occupied by the iridium atoms, which are dislocated from their ideal positions such that the Ir–Ir distance has increased (2.72_0 Å(Sm) or 2.63_2 Å (Y)). The infrared spectra are reported and discussed in connection with the corresponding factor group analysis.

Neutron Powder Diffraction Study of the Structures of $CeTaO_4$, $CeNbO_4$, *and* $NdTaO_4$. A. SANTORO, M. MAREZIO, R. S. ROTH, AND D. MINOR, National Measurement Laboratory, National Bureau of Standards, Washington, D.C. 20234. The crystal structures of $CeTaO_4$, $CeNbO_4$, and $NdTaO_4$ have been refined with the Rietveld method using neutron powder diffraction data collected at room temperature. The results of these refinements show that the coordination of the Ce and Nd cations is 8 with an average Ce–O distance of 2.520 Å in $CeTaO_4$ and 2.480 Å in $CeNbO_4$, and an average Nd–O distance of 2.451 Å in $NdTaO_4$. The Nb and Ta cations in $CeNbO_4$ and $NdTaO_4$ are surrounded by six oxygen ions with Nb–O distances varying between 1.851 and 2.482 Å and Ta–O distances varying between 1.861 and 2.353 Å. The structural arrangement of $CeTaO_4$ can be regarded as that of an oxidized ABO_3 perovskite. The difference in structure of $CeTaO_4$ and $NdTaO_4$ is most likely due to the difference in size of the rare-earth cations.

Low-Temperature Heat Capacity of Some Alkali Metal Tungstates. P. H. PAN, H. R. SHANKS, A. J. BEVOLO, AND G. C. DANIELSON, Ames Laboratory, USDOE, and Department of Physics, Iowa State University, Ames, Iowa 50010. Heat capacity measurements have been made on the two triclinic tungstates, $Li_{0.2}WO_3$ and $Na_{0.33}WO_3$, from 1 to 60°K. In addition to the normal Debye term the data show a large contribution which can be fit to a single Einstein mode associated with the oscillation of the alkali ions in the holes formed by the corner bonding of six WO_6 octahedra. The Einstein characteristic temperatures obtained are 71 ± 2°K and 78 ± 2°K for $Li_{0.2}WO_3$ and $Na_{0.33}WO_3$, respectively. The results are compared with those reported earlier for the hexagonal tungsten bronzes.

The Crystal Structure and Stability of $Ba_5Fe_4S_{11}$. S. COHEN, N. KIMIZUKA, AND H. STEINFINK, Department of Chemical Engineering, The University of Texas, Austin, Texas 78712. The crystal structure of $Ba_5Fe_4S_{11}$ is orthorhombic, $a = 16.060(1)$ Å, $b = 7.260(1)$ Å, $c = 8.863(1)$ Å, $Z = 2$, $Pmn2_1$. The structure was solved from a three-dimensional analysis using 1452 reflections with intensities $I \geq 2\sigma(I)$. The refinement converged to $R = 0.0204$, $wR = 0.0216$. The structure consists of BaS_6 distorted trigonal prisms and an irregular BaS_7 pentagonal bipyramid which articulate into a three-dimensional framework enclosing a cavity which contains the tetranuclear unit Fe_4S_{11}. The four FeS_4 tetrahedra form an isolated cluster in which a central tetrahedron shares one edge with another tetrahedron and the two remaining corners with two additional tetrahedra. The phase is stable below 750°C although the kinetics for formation are slow.

Magnetic Properties of the Mixed-Valence Compounds $CaMn_3O_6$ *and* $CaMn_4O_8$. W. S. GLAUNSINGER, H. S. HOROWITZ, J. M. LONGO, AND A. CHANG, Department of Chemistry, Arizona State University, Tempe, Arizona 85281. The preparation of two new mixed-valence compounds, $CaMn_3O_6$ and $CaMn_4O_8$, is described and their magnetic and EPR behavior investigated. The Mn moments in both compounds have nearly spin-only values. $CaMn_3O_6$ and $CaMn_4O_8$ order ferrimagnetically near 3 and 89°K, respectively. The broad, Lorentzian EPR lines indicate a significant exchange interaction between Mn^{3+} and Mn^{4+} ions. The magnetic and EPR results suggest a strong ferromagnetic interaction between Mn^{3+} and Mn^{4+} ions and a comparable antiferromagnetic Mn^{3+}–Mn^{3+} and/or Mn^{4+}–Mn^{4+} interaction.