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Abstracts of Forthcoming Articles

On the Existence of Bivalent Ions in the Apatite Channels: A New Example, Phosphocalcium Cyanamido-Apatite. J. C. Trombe* and G. Montel, Laboratoire de Physico-Chimie des Solides et des Hautes Temperatures, ERA No. 263, 38, rue des 36 Ponts, 31400, Toulouse, France. A new apatite, phosphocalcium cyanamido-apatite $Ca_{10}(PO_4)_6\,CN_2\square$, is obtained by treatment under low pressure at high temperature (900–1000°C) of a mixture of the corresponding hydroxyapatite and calcium cyanamide. In this apatite, one CN_2^{2-} ion associated with a vacancy replaces two hydroxyl ions in the channels. The formation of a cyanamide-containing apatite also occurs by treatment of an *A*-type carbonated apatite by ammonia at 600–900°C: in the latter case, the reaction seems more difficult and more limited than in the former. The cyanamido apatite is decomposed by heating in air, and it gives rise first to an *A*-type carbonated apatite, with release of both ammonia and nitrogen oxide, and second to hydroxyapatite by hydrolysis of the *A*-type carbonated apatite.

Etude spectroscopique des ions cuivre (II) en coordinence tetraedrique dans les silicates synthetiques de type milarite. J. Choisnet*, D. Cornet, J.-F. Hemidy, N. Nguyen, and Y. Dat, Laboratoire de Cristallographie et Chimie du Solide, ISMRA—Université de Caen, 14032 Caen Cedex, France. ESR spectra of copper containing silicates $Na_2Mg_{5-x}Cu_xSi_{12}O_{30}$ with a milarite structure have been recorded at two frequencies (X band and Q band) and at several temperatures in the range 298–77 K. For x lower than 0.5 the well-resolved powder spectrum is characteristic of tetrahedral copper ions in orthorhombic symmetry with $g_{zz} = 2.517$; $g_{xx} = 2.135$; $g_{yy} = 2.091$. The hyperfine structure is completely resolved at 77 K ($A_{zz} = 45.9 \times 10^{-4}\,cm^{-1}$; $A_{yy} = 23.0 \times 10^{-4}\,cm^{-1}$; $A_{xx} = 41.0 \times 10^{-4}\,cm^{-1}$). The ESR parameters may be interpreted in terms of an admixture of $4p_z$ wave function into the $3d_{xy}$ ground state. The results are in good agreement with diffuse reflectance spectra and crystal field calculations.

Single Crystal Growth and Crystal Structure Refinement of $CuAlO_2$. T. Ishiguro,* A. Kitazawa, N. Mizutani, and M. Kato, Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan. Single crystals of the delafossite-type compound $CuAlO_2$ were grown from Al_2O_3–Cu_2O melt by a slow-cooling method from 1200°C. Three types were found in as-grown crystals (single crystals, short-columnar twin crystals with concave angles, and laminar twin crystals). The twinning form is similar to the spinel-type twin. $CuAlO_2$ is rhombohedral, $R\bar{3}m$, $a = 2.8604(7)$, $c = 16.953(5)$ Å, $Z = 3$, $Dx = 5.12$ g/cm^3, and $Dm = 5.06$ g/cm^3. The crystal structure of $CuAlO_2$ was analyzed by means of single crystal X-ray diffraction with a conventional R value $= 0.038$. The value of the U_{11} component of the thermal parameter of Cu^+ was twice as large as U_{33}.

Electrical Conduction of Bis(1,2-diondioximato) Metal(II) and Their Partially Oxidized Complexes at High Pressures. I. Shirotani,* A. Onodera, and Y. Hara, The Institute for Solid State Physics, The University of Tokyo, Minato-ku, Tokyo 106, Japan. The resistivity of one-dimensional d^8-metal complexes with various kinds of 1,2-diondioxime (dimethylglyoxime, nioxime, and diphenylglyoxime) ligands has been measured at high pressures. The resistivity of $M(dmg)_2$ and $M(niox)_2$ decreased with increasing pressure. The resistivity of $M(dmg)_2$ is much lower than that of $M(niox)_2$ at high pressure though M–M distances and optical energy gaps in both salts are almost the same at atmospheric pressure. An anomalous low resistivity has been observed in $Pt(dmg)_2$ at about 40 kbar. The electrical resistivity of $M(niox)_2$ and $M(dmg)_2$ oxidized by oxidizing agents decreased with increasing pressure. The resistivity of partially oxidized Pt complexes is significantly higher than that of the parent compounds at high pressure. On the contrary, partially oxidized Ni and Pd complexes are more conductive than unoxidized compounds at high pressures. The electrical resistivity of unoxidized and partially oxidized Pt complexes increased with increasing pressure at higher pressures. The resistivity minimum at high pressure has been observed only in Pt complexes. The infrared spectra of the d^8-

Note. Asterisks denote author to be addressed.

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metal complexes and their partially oxidized complexes have been investigated. The frequency of the C=N stretching vibration in $M(\mathrm{dmg})_2$ and $M(\mathrm{niox})_2$ salts increases in the order Ni > Pd > Pt; on the other hand, the frequency of $M(\mathrm{niox})_2X_n$ increases in the order Ni < Pd < Pt. The frequency of the C=N stretching vibration is closely related to the effect of metal–ligand π^* back bonding in d^8-metal complexes. Some anomalies in the resistance–pressure curve have been found in $\mathrm{Ni(dpg)_2}$, $\mathrm{Ni(dpg)_2I}$, $\mathrm{Ni(dpg)_2I_{0.5}}$, and $\mathrm{Ni(dpg)_2I_{0.14}}$. The anomalies are explained by new pressure-induced phase transitions.

The Kinetics of Oxidation of Phi Phase Terbium Oxide: $\frac{7}{2}Tb_2O_{3+\delta} + (\frac{3}{4} - \frac{7}{4}\delta)\mathrm{O_2} \rightarrow Tb_7O_{12}$. T. Sugihara, S. H. Lin, and L. Eyring,* Department of Chemistry and Center for Solid State Science, Arizona State University, Tempe, Arizona 85281. Kinetic and thermodynamic studies of the terbium oxides between the $\mathrm{Tb_2O_{3+\delta}}$ ($n = 4$) and $\mathrm{Tb_7O_{12}}$ ($n = 7$) phases of the homologous series, $\mathrm{Tb}_n\mathrm{O}_{2n-2}$, have been carried out as a function of oxygen pressure at 708, 740, 772, and 806°C. The thermodynamic study shows a reproducible hysteresis loop which depends on the temperature and pressure. The kinetic study was carried out by measuring the weight gain of an oxide sample in an oxygen atmosphere as a function of time. The results are interpreted by a mixed-model mechanism of diffusion and phase boundary reaction control. The relative fit of the data with other models, including the phenomenological model previously found satisfactory for a related reaction, is shown. The kinetics in the final stage are strongly affected by the existence of pseudophase behavior near $\mathrm{Tb_7O_{12}}$. From measurement of the oxygen pressure and temperature dependence of the observed rate constants, the activation energies for the diffusion process and phase boundary reaction process were determined to be −14 and 10 kcal/mole, respectively.

Mössbauer Studies of Thiospinels: V. The Systems $Cu_{1-x}Fe_xMe_2S_4$. *Me = Cr, Rh and* $Cu_{1-2}Fe_xCr_2(S_{0.7}Se_{0.3})_4$. E. Riedel,* R. Karl, and R. Rackwitz, Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-1000 Berlin 12, Germany. With the exception of $\mathrm{FeRh_2S_4}$, powder samples of all systems studied have been obtained as spinel phase without essential impurities. The lattice constants follow Vegard's law. From the Seebeck coefficients and the Mössbauer spectra the valence distribution $\mathrm{Cu}^{+1}_{1-x}\mathrm{Fe}^{+2}_{2x-1}\mathrm{Fe}^{+3}_{1-x}[Me_2^{+3}]\mathrm{X}_4^{-2}$ is derived for $0.5 \leq x \leq 1$, while there is only Fe present for $0 < x \leq 0.5$. Samples with the overall composition $\mathrm{FeRh_2S_4}$ contain mostly $\mathrm{Rh_2S_3}$ and iron sulfide phases, but less than 20% of a spinel phase.

Thermodynamic Study of Nonstoichiometric Tungsten Trioxide WO_{3-x} *by EMF Measurements at High Temperature.* J.-F. Marucco* and A. Htiwech, Laboratoire des Composés non-stoechiométriques, Université de Paris-Sud, Centre d'Orsay, 91405 Orsay Cédex, France. The values of $\Delta G(\mathrm{O_2})$, $\Delta H(\mathrm{O_2})$, and $\Delta S(\mathrm{O_2})$ have been determined from electrochemical cell measurements, within the whole homogeneity range of WO_{3-x}, between 700 and 900°C. The samples have been previously prepared by equilibration of $\mathrm{WO_3}$ pellets with CO–$\mathrm{CO_2}$ mixtures and their composition has been determined by thermogravimetry. A single phase has been found between $\mathrm{WO_3}$ and $\mathrm{WO_{2.9760}}$. The results may be understood by considering a structure involving point defects, singly ionized oxygen vacancies $V_0^{\cdot}$ between $\mathrm{WO_3}$ and $\mathrm{WO_{2.9880}}$. For larger departures from stoichiometry, the variations of $\Delta H(\mathrm{O_2})$ and $\Delta S(\mathrm{O_2})$ suggest the formation of more complex defects. The enthalpy of formation of $V_0^{\cdot}$ has been calculated: 78 $\mathrm{kcal \cdot mole^{-1}}$.

NQR Study of Ternary Chalcogenides A_3BX_3, ABX_2, *and ABX Where A = Cu, Ag, or Tl, B = As or Sb, and X = S or Se.* T. J. Bastow and H. J. Whitfield,* CSIRO Division of Chemical Physics, P.O. Box 160, Clayton, Victoria, Australia 3168. $^{121}\mathrm{Sb}$, $^{123}\mathrm{Sb}$, $^{75}\mathrm{As}$, $^{63}\mathrm{Cu}$, and $^{65}\mathrm{Cu}$ NQR resonances are reported for $\mathrm{CuSbSe_2}$, $\mathrm{Tl_3SbSe_3}$, $\mathrm{Tl_3SbS_3}$, $\mathrm{Tl_3AsS_3}$, $\mathrm{Tl_3AsSe_3}$, $\mathrm{Ag_3AsSe_3}$, $\mathrm{TlSbS_2}$, CuAsS, AgAsS, and $\mathrm{Cu_5SbS_3I_2}$. $\mathrm{Tl_3SbSe_3}$ is an incongruently melting compound not observed in an earlier phase-diagram study of the pseudobinary system $\mathrm{Tl_2Se{-}Sb_2Se_3}$. For isostructural arsenic and antimony chalcogenides the ratio of $^{75}\mathrm{As}$ to $^{121}\mathrm{Sb}$ quadrupole coupling constants is 0.42, and for the BX_3 group in binary or ternary corresponding pairs of sulfides and selenides the ratio of quadrupole coupling constants for $^{75}\mathrm{As}$ or $^{121}\mathrm{Sb}$ is 0.83. A reversible phase transition was observed at 130 K for $\mathrm{Ag_3AsSe_3}$. Unit cell parameters are reported for crystals of $\mathrm{TlSbS_2}$ and $\mathrm{Cu_5SbS_3I_2}$.

Optical Spectra and Magnetic Susceptibility of Two Different Salts of Sèveral Phenothiazine Derivatives. A. Ortiz,* A. Gonzalez, and J. I. Fernandez-Alonso, Departamento De Quimica-

Fisica y Quimica Cuantica, Centro Coordinado CSIC–UAM, Facultad de Ciencias C-XIV, Cantoblanco, Madrid 34, Spain. Two different salts, perchlorates and bromides, of six phenothiazine derivatives substituted in R_2 and R_{10} were prepared. Magnetic susceptibility and diffuse reflectance have been used to study the contribution of the different substituents R_2 and R_{10} and the counteranions to the electronic properties of these compounds in the solid state. Within a type of salt, the R_2 substituents are capable of producing a variation of χ_m depending on their electron donating or electron withdrawing power upon the π electronic structure of the phenothiazine nucleus. Between the two types of salts it can be seen that the χ_m varies as the counteranion size varies. The effect produced by the R_{10} depends on the counter anion size. These characteristics are also shown in the charge-transfer band in the solid state.

Two Polymorphous Lithium Stannoferrites $LiFeSnO_4$: A Ramsdellite Type and a Hexagonal Close-Packed Structure. J. Choisnet, M. Hervieu, B. Raveau,* and P. Tarte, Laboratoire de Cristallographie et Chimie du Solide, LA 251, ISMRA—Universite de Caen, 14032 Caen Cedex, France. The stannoferrite $LiFeSnO_4$ has been synthesized and investigated by X-ray diffraction and electron microscopy. Two forms have been characterized. High-temperature $LiFeSnO_4$ is orthorhombic, isotypic with MnO_2 ramsdellite: $a = 3.066$ Å, $b = 5.066$ Å, $c = 9.874$ Å; low-temperature $LiFeSnO_4$ is hexagonal with $a = 6.012$ Å, $c = 9.776$ Å and isotypic with $Li_{1.6}Zn_{1.6}Sn_{2.8}O_4$. Both structures have been refined. This polymorphous transition and relationships between the two forms and spinel structure are discussed.

The Structure and Oscillational Motion of ^{57}Fe Atoms in Interstitial Sites in Al as Determined from Interference of Mössbauer γ Radiation. L. Pauling. Linus Pauling Institute of Science and Medicine, 440 Page Mill Road, Palo Alto, California 94306. The first excited state of the ^{57}Fe atom entrapped in an interstitial site in aluminum, as reported by Petry *et al.* from a Mössbauer spectroscopic study of a single crystal, is analyzed by consideration of the value of the Hooke's law constant of the Fe–Al bonds obtained from the values for elemental Fe and Al. The eight wave functions for the eightfold nearly degenerate excited state are described as $2s1p1d1f$ hybrids of three-dimensional harmonic oscillator wave functions relative to the center of the undistorted Al_6 octahedron or as localized $1s$ functions relative to the center of the distorted octahedron. These considerations provide a qualitative understanding of the observations on this system.

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