

localized versus itinerant electrons or to extended electrons within Fe- X - M interactions (M = transition metal and X = anion). The existence of a quadrupole splitting for iron atoms in intrinsically cubic fields is only possible where the β -spin electron outside a closed α -spin half-shell is localized and Jahn-Teller coupled to lattice vibrations to form vibronic states. This situation is distinguished from quadrupolar fields associated with local-site symmetries formed from cubic symmetry as well as from the case where the formation of itinerant β -spin electrons inhibits the formation of vibronic states.

Etude de la Conductivite Ionique des Hydrurofluorures CaF_{2-x}H_x. REMI LEVEQUE, MICHEL ZANNE, DENISE VERGNAT-GRANDJEAN, AND JEAN-FRANCOIS BRICE, Laboratoire de Chimie du Solide Minéral, Université de Nancy I, 54037 Nancy Cedex, France. The present work is concerned with the electrical conductivity of the calcium hydride fluorides CaF_{2-x}H_x between 20 and 200°C. The study was made using the complementary methods of complex admittance conductivity measurements and dielectric loss measurements. The influence of quenching and doping by Na⁺ has permitted us to identify the two conductivity domains observed. The low-temperature domain, which is characterized by a slight thermal increase in conductivity, corresponds to the reorientation of [V_{(F,H)}^{*}-Na'_{Ca}]^{*} dipoles due to impurities. The second domain corresponds to the first stage of ionic conduction which results from the migration of V_{(F,H)}^{*} vacancies formed by the thermal dissociation of [V_{(F,H)}^{*}-Na'_{Ca}]^{*} complexes. The H⁻/F⁻ substitution increases the mobility of charge carriers and the conductivity increases by the factor 10³ between the compositions CaF₂ and CaFH. Thus calcium hydride fluorides can be considered to be electrolytic solids with medium conductivity (CaF_{1.06}H_{0.94}: $\sigma = 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at 130°C).}}}

A Kinetic Study of Oxidation of Praseodymium Oxides: PrO_{1.714} + 0.032 O₂ → PrO_{1.778}. H. INABA, S. P. PACK, S. H. LIN, AND L. EYRING, Department of Chemistry, Arizona State University, Tempe, Arizona 85281. Kinetic and thermodynamic studies between the iota ($n = 7$) and the zeta ($n = 9$) phases of the homologous series of the praseodymium oxides (Pr_nO_{2n-2}) have been carried out as a function of oxygen pressure at 535, 540, 550, and 570°C. The thermodynamic study was carried out by measuring the weight of the oxide sample at equilibrium at these temperatures as a function of pressure. The existence of a reproducible hysteresis loop which depends on the temperature and pressure is shown. The kinetic study was carried out by measuring the weight change of the sample as a function of time after a sudden increase of oxygen pressure initiated the reaction. In order to interpret the kinetic data, various theoretical models assumed, for example, to depend upon diffusion, a moving-boundary, a phase-boundary reaction-control, or nucleation and growth have been examined. None of these models, however, is capable of correlating the experimental data. It was found that for the powder sample diffusion of oxygen is much faster than the rate of reaction and the reaction kinetics is first order with respect to both the concentration of reactant and the ambient oxygen pressure. A linear plot of the reaction rate versus the ambient pressure extrapolates to a finite pressure at zero rate, suggesting that the reaction does not begin until this pressure is attained. It has been shown that this pressure corresponds to the minimum required to produce zeta phase as shown by the isothermal hysteresis loop along the oxidation path. From the measurements of the oxygen pressure and the temperature dependence of the observed rate constants, the activation energy of the reaction was determined to be 45.3 kcal/mole.

Tetragonal-to-Cubic Transformation of Hausmannite. EMIL POLLERT, Institute of Physics, Czechoslovak Academy of Science, Na Slovance 2, 180 40 Praha 8, Czechoslovakia. The tetragonal-to-cubic transformation of hausmannite, Mn₃O₄, was studied by X-ray, high-temperature analysis. The transformation exhibits properties characteristic for diffusionless processes, i.e., the coexistence of regions of the tetragonal and cubic phases, and hysteresis. The position of the coexistence region with regard to the temperature depends on the oxygen stoichiometry and/or concentration of Mn³⁺ ions.

Magnetism and Phase Relations of the PrAl₂-CaAl₂, GdAl₂-CaAl₂ Systems. TOMAS RIVILLO AND W. E. WALLACE, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania. The magnetic properties and phase relations of the ternary systems Pr_{1-x}Ca_xAl₂ and Gd_{1-x}Ca_xAl₂ are reported. The first system exhibits complete miscibility whereas the second shows a miscibility gap extending from $x = 0.5$ to 0.8. The ternaries were examined magnetically to ascertain whether anti-ferromagnetism could be produced by replacing the trivalent rare earth ion with divalent Ca. Results for the (Pr, Ca)Al₂ system give some indication that the exchange changes sign when 80% or more of the Pr is replaced by Ca. The α phase (Gd-rich) alloys in the (Gd, Ca)Al₂ system are ferromagnetic with Curie temperatures only modestly reduced from that of GdAl₂. The β phase (Ca-rich) alloys in this system are

paramagnetic to 4.2°K. The evidence suggests that PrAl₂ and CaAl₂ are electronically similar with regard to band structure and both differ in band structure from that in GdAl₂.

Crystal Structure and Magnetic Properties of Ba₂Ni₃F₁₀. M. LEBLANC, G. FERREY, AND R. DE PAPE, Laboratoire des Fluorures et Oxyfluorures Ioniques, Route de Laval, 72017 Le Mans Cedex, France. Ba₂Ni₃F₁₀ is monoclinic (space group *c2/m*) $a = 18.542(7) \text{ \AA}$, $b = 5.958(2) \text{ \AA}$, $c = 7.821(3) \text{ \AA}$, $\beta = 111^\circ 92(10)$. Ba₂Co₃F₁₀ and Ba₂Zn₃F₁₀ are isostructural. The structure has been refined from 995 reflections by full-matrix least-squares refinement to a weighted *R* value of 0.048 (unweighted *R*: 0.047). The three-dimensional network can be described either by complex chains connected to each other by octahedra sharing corners or with a 18L dense packing sequence. The basic unit (Ni₃F₁₀)⁴⁻ is discussed and compared to a different one existing in Cs₄Mg₃F₁₀. Antiferromagnetic properties of Ba₂Ni₃F₁₀ ($T_N = 50 \text{ K}$) are described.

Infrared Spectrum of Several Double Oxides with Corundum Structure Resulting from the Transformation of Lacunar γ Phases with a Spinel Structure. B. GILLOT, F. BOUTON, F. CHASSAGNEUX, AND A. ROUSSET, Laboratoire de Recherches sur la Réactivité des Solides, BP 138, 21004 Dijon, Cedex, France. When aluminum or chromium is substituted by Fe³⁺ ions in α -Fe₂O₃, all the ir bands gradually shift toward high frequencies. Alternatively, for the α phases of type (Fe₂Cr_{4-y}Al_y)O₉ the transition occurs sharply for a composition *y* close to 2. For α phases substituted by (Fe_{6-y}Cr_y)O₉-type chromium a linear variation of frequency with chromium content is observed. From ir data it has been shown that, under given temperature and time conditions, an α phase less rich in chromium than the initial product could be obtained by oxidizing iron chromite. The ir spectrum of the oxidation of pure magnetites whose size is between 1400 and 15 000 Å evolves versus the latter to yield either the γ -Fe₂O₃ or the α -Fe₂O₃ phase which can be formed from γ -Fe₂O₃ or by direct oxidation of Fe₃O₄.

Preparation and Mössbauer Effect of Cr_{1-x}Fe_xOOH (0 ≤ x ≤ 1.0) with the InOOH-Type Structure. K. YABUTA, N. KINOMURA, M. SHIMADA, F. KANAMARU, AND M. KOIZUMI, The Institute of Scientific & Industrial Research, Osaka University, Osaka 565, Japan. The complete solid solutions of Cr_{1-x}Fe_xOOH with the InOOH-type structure were synthesized under high pressures. They were antiferromagnetic with Néel temperatures 570 K for FeOOH, 454 K for Cr_{0.2}Fe_{0.8}OOH, 332 K for Cr_{0.4}Fe_{0.6}OOH, and 160 K for Cr_{0.6}Fe_{0.4}OOH determined by the Mössbauer effect measurements.

Synthese et Caracterisation Cristallographique et Physique d'une Serie de Composes ACu₃Ru₄O₁₂ de Type Perovskite. M. LABEAU, B. BOCHU, J. C. JOUBERT, AND J. CHENAVAS, Laboratoire de Génie Physique, ENSIEG, BP 46, 38402, Saint-Martin-D'Herès, France. A series of ruthenates with the perovskite-like arrangement has been synthesized. The general formula is (ACu₃)(Ru₄)O₁₂ where (ACu₃) and (Ru₄) occupy the *A* and *B* sites of the ideal ABO₃ perovskite structure, respectively; *A* = Na⁺, Ca²⁺, Sr²⁺, Cd²⁺, La³⁺, Pr³⁺, and Nd³⁺. The change of the *A* site charge is balanced by a change of the ruthenium valence (+3, +4, or +5). The stability of the structure is strongly related to the relative size of the cations on the dodecahedral and octahedral sites. The magnetic susceptibility of the compounds with *A* = Na, Ca, and La is temperature independent above 70°K (for Ca), 120°K (for La) or 220°K (for Na) (Pauli paramagnetism). Resistivity measurements made on sintered samples between 77 and 300°K confirm the metallic nature of these compounds.

Crystal Structure of Na₃PCr₃O₁₃ · 3H₂O, A New Type of Chromophosphoric Anion. M. T. AVERBUCH-POUCHOT, A. DURIF, AND J. C. GUITEL, Laboratoire de Cristallographie, CNRS 166X, 38042 Grenoble Cedex, France. We describe chemical preparation and crystal structure of a new sodium phosphochromate: Na₃PCr₃O₁₃ · 3H₂O. This salt is orthorhombic with $a = 11.72(3)$, $b = 14.89(3)$, $c = 16.59(3) \text{ \AA}$, and $Z = 8$, Space group: *Pbc2₁*. The final *R* value is 0.063 for 2133 independent reflexions. The main feature of this atomic arrangement is the existence of a new type of chromophosphoric anion: PCr₃O₁₃. Infinite chains of NaO₆ run along the *a* direction. A survey of some phosphochromates previously described by the authors is given.

Semiconductivity, Optical Properties, and EPR Spectra of Phenothiazine Derivatives in the Solid State. A. ORTIZ, J. I. FERNÁNDEZ-ALONSO, A. PARDO, AND J. LLABRES, Departamento de Química-Física y Química Cuántica, Universidad Autónoma de Madrid, Cantoblanco, Madrid, 34, Spain. The optical, EPR, and electrical properties of phenothiazine derivatives have been investigated as a function of R₂ substituents. Diffuse reflectance spectra show a charge transfer complex transition between 600 and