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 $[V^{\bullet}_{(F,H)}\text{–}Na'_{Ca}]^*$ dipoles due to impurities. The second domain corresponds to the first stage of ionic conduction which results from the migration of $V^{\bullet}_{(F,H)}$ vacancies formed by the thermal dissociation of $[V^{\bullet}_{(F,H)}\text{–}Na'_{Ca}]^*$ complexes, The H^-/F^- substitution increases the mobility of charge carriers and the conductivity increases by the factor 10^3 between the compositions CaF_2 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: $PrO_{1.714} + 0.032\ O_2 \rightarrow PrO_{1.778}$. 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, Mn_3O_4, 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 Mn^{3+} ions.

Magnetism and Phase Relations of the $PrAl_2$–$CaAl_2$, $GdAl_2$–$CaAl_2$ 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 $Pr_{1-x}Ca_xAl_2$ and $Gd_{1-x}Ca_xAl_2$ 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 antiferromagnetism could be produced by replacing the trivalent rare earth ion with divalent Ca. Results for the (Pr, Ca)Al_2 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)Al_2 system are ferromagnetic with Curie temperatures only modestly reduced from that of $GdAl_2$. The β phase (Ca-rich) alloys in this system are