Ordre et Desordre dans Certains Composés du type Pyrochlore. M. Faucher and P. Caro. Laboratoire des Terres Rares du C.N.R.S., 92 Meudon-Bellevue, France. Three $Ln_2M_2O_7$ compounds (Ln^{3+} = Europium, M^{4+} = Tin, Titanium and Zirconium) are investigated by X-ray diffraction, and by optical methods making use of the local structural probe character of Eu^{3+} ($4f^6$). It is shown that $Eu_2Sn_2O_7$ and $Eu_2Ti_2O_7$ are mainly constituted of an ordered pyrochlore phase where the europium ion is effectively in a D_{3d} site with a center of inversion (no dipolar electric optical transitions). On the other hand $Eu_2Zr_2O_7$ appears to be, both from X-ray diffraction and optical spectra, a mixture of a disordered phase where the europium is at a site without inversion center, very likely C_{3v}, because of the existence of dipolar electric transitions, and of a phase, more abundant at high temperature, which could be an ordered pyrochlore.

Thermodynamic Relations among Olivine, Spinel, and Phenacite Structures in Silicates and Germanates. IV. The System ZnO–MgO–GeO$_2$. A. Navrotsky. Department of Chemistry, Arizona State University, Tempe, Arizona 85281. Phase relations in the system ZnO–MgO–GeO_2 were determined at 1200°C, in air. Subsolidus phase relations along the pseudobinary join Zn_2GeO_4–Mg_2GeO_4 were determined between 700 and 1200°C; the portion below 900°C was obtained hydrothermally. Only one spinel phase is formed at low temperatures; this phase extends from Mg_2GeO_4 to $(Mg_{0.73}Zn_{0.27})_2GeO_4$ at 820°C. Its highest temperature of stability is 880°C, with a composition of $(Mg_{0.75}Zn_{0.25})_2GeO_4$. The free energies of transformation from the olivine to the phenacite structures at 1200°C are estimated to be $+6 \pm 1.0$ kcal/mole and -10 ± 1.5 kcal/mole for Mg_2GeO_4 and Zn_2GeO_4, respectively.

Bond Strength Considerations Applied to Cation Coordination in Normal- and High-Pressure Oxides. R. D. Shannon, J. Chenavas, and J. C. Joubert. Laboratoire des Rayons X, C.N.R.S., 38 Grenoble, France. For cations with radius ratios close to the critical value of 0.414, 2 rules are developed to predict a preference for tetrahedral or octahedral coordination: (1) If for $M_aX_bO_c$ the ratio $\gamma = a/b$ is greater than a certain critical value (generally $\gamma_c \simeq 1.0$), X prefers tetrahedral coordination; (2) the greater the M–O bond strength, the greater the tendency for octahedral coordination of X. These rules follow from a consideration of Pauling's electrostatic valence rule and reflect the probability of having strong M–O bonds to compete with X–O bonds. The coordination of Te^{6+}, V^{5+}, As^{5+}, Ge^{4+}, Ti^{4+}, Fe^{3+}, Ga^{3+}, Al^{3+}, B^{3+}, Be^{2+} and Zn^{2+} in many oxides are consistent with these rules. Exceptions occur when the cations are found in highly stable structures such as perovskite, spinel, quartz, garnet, scheelite, and K_2SO_4. When applied to high-pressure transitions, these rules allow one to predict that small γ-values and strong M–O bonds will lower the pressure at which an increase in the coordination of X should occur.

Propriétés Structurales, Magnetiques et Electriques de l'Oxyfluorure $Cr_xV_{1-x}O_{2-x}F_x$. M. Bayard, M. Pouchard, et P. Hagenmuller. Service de Chimie Minerale Structurale de l'Université de Bordeaux I, C.N.R.S., 351 cours de la Libération, 33405 Talence, France. The authors have determined the phase diagram of the system $Cr_xV_{1-x}O_{2-x}F_x$ ($0 < x \leqslant 0.20$) by magnetic susceptibility and X-ray diffraction measurements. At small chromium concentrations the intermediate phases M_2 and T of the system $Cr_xV_{1-x}O_2$ have been observed. At higher concentration ($x > 0.09$) only the rutile phase R is present. The magnetic and transport properties have been determined and discussed.

Propriétés Magnetiques et Electroniques de l'Oxyfluorure de Formule $VO_{2-x}F_x$. M. Bayard, M. Pouchard, P. Hagenmuller, and A. Wold. Service de Chimie Minérale Structurale de l'Université de Bordeaux I, C.N.R.S., 351 cours de la Libération, 33405 Talence, France. $VO_{2-x}F_x$ samples ($0 < x \leqslant 0.55$) have been prepared by solid state reaction in sealed platinum tubes. The crystalographic monoclinic $\rightleftarrows$ rutile transition occurs at a quickly decreasing temperature as fluorine replaces oxygen. The crystallographic, magnetic, and transport properties have been determined and discussed.

Solid State Chemistry of Organic Polyvalent Iodine Compounds. IV. Topotactic Transformations of 2-Iodo-3′-Chlorodibenzoyl Peroxide and the Crystal Structure of m-*Chlorobenzoic Acid.* J. Zanos Gougoutas and L. Lessinger. Department of Chemistry, University of Minnesota, Minneapolis, Minnesota. Single crystals of 2-iodo-3′-chlorodibenzoyl peroxide (P) undergo several competitive and consecutive topotactic transformations: upon standing in the laboratory atmosphere or during X-ray photography at ~22°C, crystalline P is transformed to pseudomorphs containing preferentially oriented single crystal phases of *o*-iodosobenzoic acid (E), *m*-chlorobenzoic acid (D), and an as yet unidentified novel phase, "X." (Topotactic rearrangement of P to the known acicular polymorph of its benzoxiodole isomer,3-oxo-3H,2,1-benzoxiodol-1-yl *m*-chlorobenzoate, occurs only at elevated temperatures, ~55°C). In a much slower, consecutive transformation, during further continuous exposure to X-rays, "X" is photochemically reduced to *o*-iodobenzoic acid (C), which also is formed as a single crystal phase. The resulting single crystal domains of D and E in decomposed pseudomorphs of P are mutually oriented in a manner which reflects their strikingly similar crystal structures. The structure of D has been determined by single crystal X-ray analysis in order to compare the aligned molecular packing arrangements of D and C, and P and D. The mutual alignment of P and E is also presented in this report. All of these topotactic products are aligned so as to conserve the point group symmetry of the parent crystal, P (conservative twinning).

Characterization of CoO–ZnO Solid Solutions. F. Pepe, M. Schiavello, and G. Ferraris. Istituto di Chimica Generale ed Inorganica, Universita di Roma, Rome, Italy. Lattice parameters, magnetic susceptibilities (over the temperature range 98–298°K) and reflectance spectra (uv and visible) of solid solutions of CoO–ZnO up to 10% molar CoO have been studied. It is shown that true solid solution is achieved and that Co^{2+} ions substitute for the Zn^{2+} ions in tetrahedral positions. The effect of the addition of Co^{2+} is to increase the *a* lattice parameter and to decrease the *c*/*a* ratio. The magnetic moment of Co^{2+} has been found to be $4.54 \times 0.05\ \mu_B$ by extrapolation. A discussion of the structural and magnetic data in terms of the presence of a C_{3v} effective symmetry is given.