

*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  $\text{Ln}_2\text{M}_2\text{O}_7$  compounds ( $\text{Ln}^{3+} = \text{Europium}$ ,  $\text{M}^{4+} = \text{Tin}$ , Titanium and Zirconium) are investigated by X-ray diffraction, and by optical methods making use of the local structural probe character of  $\text{Eu}^{3+}$  ( $4f^6$ ). It is shown that  $\text{Eu}_2\text{Sn}_2\text{O}_7$  and  $\text{Eu}_2\text{Ti}_2\text{O}_7$  are mainly constituted of an ordered pyrochlore phase where the europium ion is effectively in a  $\text{D}_{3d}$  site with a center of inversion (no dipolar electric optical transitions). On the other hand  $\text{Eu}_2\text{Zr}_2\text{O}_7$  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  $\text{C}_{3v}$ , 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<sub>2</sub>.* A. NAVROTSKY. Department of Chemistry, Arizona State University, Tempe, Arizona 85281. Phase relations in the system  $\text{ZnO-MgO-GeO}_2$  were determined at  $1200^\circ\text{C}$ , in air. Subsolidus phase relations along the pseudobinary join  $\text{Zn}_2\text{GeO}_4\text{-Mg}_2\text{GeO}_4$  were determined between  $700$  and  $1200^\circ\text{C}$ ; the portion below  $900^\circ\text{C}$  was obtained hydrothermally. Only one spinel phase is formed at low temperatures; this phase extends from  $\text{Mg}_2\text{GeO}_4$  to  $(\text{Mg}_{0.73}\text{Zn}_{0.27})_2\text{GeO}_4$  at  $820^\circ\text{C}$ . Its highest temperature of stability is  $880^\circ\text{C}$ , with a composition of  $(\text{Mg}_{0.75}\text{Zn}_{0.25})_2\text{GeO}_4$ . The free energies of transformation from the olivine to the phenacite structures at  $1200^\circ\text{C}$  are estimated to be  $+6 \pm 1.0$  kcal/mole and  $-10 \pm 1.5$  kcal/mole for  $\text{Mg}_2\text{GeO}_4$  and  $\text{Zn}_2\text{GeO}_4$ , 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  $\text{M}_x\text{X}_b\text{O}_c$  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  $\text{Te}^{6+}$ ,  $\text{V}^{5+}$ ,  $\text{As}^{5+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{B}^{3+}$ ,  $\text{Be}^{2+}$  and  $\text{Zn}^{2+}$  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  $\text{K}_2\text{SO}_4$ . When applied to high-pressure transitions, these rules allow one to predict that small  $\gamma$ -values and strong M-O bonds will lower the pressure at which an increase in the coordination of X should occur.

*Propriétés Structurales, Magnétiques et Électriques de l'Oxyfluorure Cr<sub>x</sub>V<sub>1-x</sub>O<sub>2-x</sub>F<sub>x</sub>.* M. BAYARD, M. POUCHARD, ET P. HAGENMULLER. Service de Chimie Minérale 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  $\text{Cr}_x\text{V}_{1-x}\text{O}_{2-x}\text{F}_x$  ( $0 < x \leq 0.20$ ) by magnetic susceptibility and X-ray diffraction measurements. At small chromium concentrations the intermediate phases  $M_2$  and  $T$  of the system  $\text{Cr}_x\text{V}_{1-x}\text{O}_2$  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 Magnétiques et Électroniques de l'Oxyfluorure de Formule VO<sub>2-x</sub>F<sub>x</sub>.* 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.  $\text{VO}_{2-x}\text{F}_x$  samples ( $0 < x \leq 0.55$ ) have been prepared by solid state reaction in sealed platinum tubes. The crystallographic monoclinic  $\rightleftharpoons$  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  $\sim 22^\circ\text{C}$ , 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