

9- or 8-fold coordination (trigonal prism with capped rectangular faces or cube). Ba-S distances are about 3.4 Å, Fe-S distances are 2.26 Å. In  $\text{Ba}_3\text{FeS}_5$ , single, isolated tetrahedra are present. In  $\text{Ba}_{15}\text{Fe}_7\text{S}_{25}$  there are eight isolated trinuclear units, formed by a central tetrahedron sharing one edge and one corner, respectively, with two terminal tetrahedra, and four isolated single tetrahedra in the unit cell. The  $\text{BaS}_6$  trigonal prisms form infinite columns by sharing the triangular faces. The columns share edges to form distorted hexagonal rings. Within the rings are additional S and Ba ions, and Fe in tetrahedral sites. The main difference between the two structures is the filling of the tetrahedral sites inside the hexagonal rings. The effective paramagnetic moment in  $\text{Ba}_{15}\text{Fe}_7\text{S}_{25}$  is  $5.5 \mu_B$  in good agreement with a value expected from 6  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  from the stoichiometry. The room temperature Mössbauer spectrum shows isomer shifts of 0.2 mm/sec. The data indicate that electron delocalization occurs across the edge-shared tetrahedra so that an effective charge distribution  $5\text{Fe}^{3+}$  and  $2\text{Fe}^{2.5}$  is present. The material has a room temperature electrical resistivity of  $10^5$  ohm/cm. The effective magnetic moment for  $\text{Ba}_3\text{FeS}_5$  is  $5.1 \mu_B$  as might be expected for  $\text{Fe}^{2+}$  or  $\text{Fe}^{4+}$ . One quadrupole-split Mössbauer spectrum is observed with an isomer shift of 0.2 mm/sec, a value usually observed for  $\text{Fe}^{3+}$ . The observations are reconciled by postulating the delocalization of an electron within the tetrahedral configuration. The room temperature electrical resistivity is  $10^5$  ohm/cm.

*Observation Directe par Microscopie Electronique a Haute Resolution de la Transformation des Hydroxycarbonates de Terres Rares (Type B) en Oxycarbonates (Type II).* H. DEXPERT, G. SCHIFFMACHER, AND P. CARO. Laboratoire des Terres Rares, 1, Place Aristide Briand, 92190 Meudon-Bellevue, France. Type B rare earth hydroxycarbonate  $(\text{LnOH})\text{CO}_3$  is a lamellar hexagonal structure isomorphous to bastnaesite ( $\text{LnFCO}_3$ ). Type II oxycarbonate  $(\text{LnO})_2\text{CO}_3$  is another hexagonal lamellar structure built on an  $(\text{LnO})_n^{n+}$  complex cation of ternary symmetry. Lattice images were obtained for both compounds directly exhibiting the lamellar character. The thermal decomposition of the hydroxycarbonate into the oxycarbonate was followed in the electron microscope. The transition is topotactic and the crystallographic orientations were determined. The two compounds may have their triad axes and the [110] (hydroxycarbonate) and [010] (oxycarbonate) axes in common, or the two triad axes may be parallel and the lamellar structures merge together. The oxycarbonate appears then in the form of bubbles in the hydroxycarbonate matrix, because of a slight deficiency (12 to 14) in the number of rare earth atom planes for the same distance along the triad axes for the oxycarbonate versus the hydroxycarbonate.

*Identification of Binary Compounds in the System  $\text{Ce}_2\text{O}_3$ - $\text{WO}_3$ .* M. YOSHIMURA, F. SIBIEUDE, A. ROUANET, AND M. FOEX. Laboratoire des Ultra-Refractaires, Odeillo, 66120 Font-Romeu, France. The system  $\text{CeO}_2$ - $\text{Ce}_2\text{O}_3$ - $\text{WO}_3$  and  $\text{Ce}_2\text{O}_3$ - $\text{WO}_3$ -W are studied at high temperature. Six compounds were found as stable phases in the system  $\text{Ce}_2\text{O}_3$ - $\text{WO}_3$ . The compound  $3\text{Ce}_2\text{O}_3 \cdot \text{WO}_3$  has a fluorite-like cubic structure of  $a_0 = 11.040$  Å and forms solid solutions with constituent oxides or  $\text{CeO}_2$ . The compound  $3\text{Ce}_2\text{O}_3 \cdot 2\text{WO}_3$ , which seems to be isostructural with  $3\text{La}_2\text{O}_3 \cdot 2\text{WO}_3$ , is stable only in the temperature range of  $1545 \sim 1730^\circ\text{C}$ . The compound  $\text{Ce}_2\text{O}_3 \cdot \text{WO}_3$ , which has a monoclinic structure, transforms reversibly at  $1360^\circ\text{C}$  to a tetragonal structure with the cell parameters  $a_0 = 5.469$  Å,  $c_0 = 8.790$  Å. The compound  $\text{Ce}_2\text{O}_3 \cdot 2\text{WO}_3$ , identified as monoclinic, also has a reversible transformation at  $1105^\circ\text{C}$ . Its high-temperature phase has a cubic cell with the cell parameter  $a = 7.046$  Å. As is well known,  $\text{Ce}_2\text{O}_3 \cdot 3\text{WO}_3$  appeared to have a high-temperature behavior similar to that of  $\text{La}_2\text{O}_3 \cdot 3\text{WO}_3$ . The compound  $2\text{Ce}_2\text{O}_3 \cdot 9\text{WO}_3$ , whose structure could not be analyzed, melts congruently at  $1026^\circ\text{C}$ .

*On the Formation of  $\text{FeSe}_2$  Single Crystals by Chemical Transport Reactions.* J. PICKARDT, B. REUTER, E. RIEDEL, AND J. SÖCHTIG. Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, 1 Berlin 12, Germany. The formation of synthetic ferroselite single crystals,  $\text{FeSe}_2$ , during chemical transport experiments in the system Fe-Cr-Se was observed. The crystals are orthorhombic,  $a = 4.804(2)$ ,  $b = 5.784(3)$ , and  $c = 3.586(2)$  Å. They were characterized by X-ray structure analysis and refined atom parameters are reported.

*Evidence for the Existence of Iron Tungsten Bronzes.* I. J. MCCOLM AND R. J. D. TILLEY. School of Materials Science, University of Bradford, Bradford BD7 1DP, Yorkshire, England. C. P. M. BARTON AND N. N. GREENWOOD. Department of Inorganic and Structural Chemistry, University of Leeds,

Leeds LS2 9JT, England. X-ray diffraction, high-resolution electron microscopy and Fe-57 Mössbauer spectroscopy have been used to study the  $\text{WO}_3$ -Fe system. The results from the diffraction methods can be interpreted either on a scheme involving bronze formation leading to a phase  $\text{Fe}_x\text{WO}_3$ , or on a scheme whereby a reduced tungsten oxide is in equilibrium with  $\text{FeWO}_4$ . The Mössbauer results show, however, that up to  $x = 0.0193$  in  $\text{Fe}_x\text{WO}_3$  a bronze is formed with either an orthorhombic or a tetragonal structure, while above  $x = 0.0193$  the phases are  $\text{FeWO}_4$  and reduced tungsten oxides. The  $\text{Fe}_x\text{WO}_3$  bronze contains a few isolated [102] crystallographic shear planes, which implies a very slight deviation from the ratio  $\text{WO}_3$ . Reaction of Fe with  $\text{WO}_3$  and W at  $950^\circ\text{C}$  under vacuum leads to the bronze phase.

*Les Hypovanadates Alcalinoterreux. Evolution Structurale de la Serie  $\text{CaV}_n\text{O}_{2n+1}$  ( $n = 1, 2, 3, 4$ ).* J. C. BOULOUX AND J. GALY. Laboratoire de Chimie du Solide, Université de Bordeaux I, 351 cours de la Liberation, 33405 Talence, France. Six vanadates (+IV) have been synthesized by solid state reactions and characterized in the  $\text{MO}-\text{VO}_2$  systems ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ):  $\text{CaVO}_3$ ,  $\text{CaV}_2\text{O}_5$ ,  $\text{CaV}_3\text{O}_7$ ,  $\text{SrV}_3\text{O}_7$ ,  $\text{CaV}_4\text{O}_9$ , and  $\text{SrV}_5\text{O}_{11}$ . Structural data are given. The structural evolution of the series  $\text{CaV}_n\text{O}_{2n+1}$  is described as  $n$  increases from  $n = 1$  to  $n = 4$ ; the vanadium +IV has a fivefold square pyramid coordination.

*An Electron Microscope Study of Tungsten Oxides in the Composition Range  $\text{WO}_{2.90}$ - $\text{WO}_{2.72}$ .* R. PICKERING AND R. J. D. TILLEY. School of Materials Science, University of Bradford, Bradford BD7 1DP, Yorkshire, England. The structure of tungsten oxides occurring in the composition range  $\text{WO}_{2.90}$ - $\text{WO}_{2.72}$  has been studied by transmission electron microscopy. In the oxygen-rich part of the phase range,  $\text{W}_n\text{O}_{3n-2}\text{CS}$  phases exist. The lowest value of  $n$  found for extensive areas of ordered material was 16. At the oxygen-poor end of the phase range,  $\text{W}_{18}\text{O}_{49}$  exists. No evidence was found to indicate that this phase has an appreciable composition range. Between the  $\text{W}_n\text{O}_{3n-2}$  oxides and  $\text{W}_{18}\text{O}_{49}$  a previously unreported oxide was found. Its structure has been partly elucidated by high-resolution electron microscopy and it has been shown to bear more resemblance to a tunnel structure than to a CS phase.

*On the Cobalt Induced Moments in Ternary Gadolinium-Yttrium Compounds.* E. BURZO AND D. P. LAZAR. Institute for Atomic Physics, P.O. Box 5206, Bucharest, Romania. The results of magnetic measurements on  $(\text{Gd}_x\text{Y}_{1-x})\text{Co}_2$  compounds between 4.2 and  $1300^\circ\text{K}$  are presented. The experimental data are analyzed assuming that the cobalt atoms present a paramagnetic moment or an exchange-enhanced paramagnetism. Both models showed that the cobalt ordered moments are linearly dependent on the exchange field acting on these atoms ( $H_{ex}/M_{\text{Co}}^0 \approx 3 \times 10^6 \text{Gs}/\mu_B$ ), being essentially induced by the magnetic interactions. The experimental data seem to be in agreement with the presence of the cobalt paramagnetic contribution. No first-order transition in these systems is observed.

*Transition de Phase Ferroelectrique-Antiferroelectrique par Inversion de l'Energie d'Echange.* P. GONNARD, L. EYRAUD, Y. FETIVEAU, AND M. TROCCAZ. Laboratoire de Genie Electrique et Ferroelectricite, Institut National des Sciences Appliquees de Lyon, Batiment 504, 69621 Villeurbanne, France. Some solid solutions are investigated with the help of two-sublattice model proposed by Néel in ferromagnetism. We suppose, like Kittel, that the F-AF transition occurs when the interlattice coefficient of molecular field  $W_{ab}$  changes sign. The high-temperature transition is F/P or AF/P according to the sign of  $v = dW_{ab}/dT$ . Under hydrostatic compression the transition is F  $\rightarrow$  AF in agreement with the negative sign of  $\eta = dW_{ab}/dp$ . In each case, the molecular field coefficient of each sublattice  $W_{aa}$  is much more important than  $W_{ab}$ .

*Les Hypovanadates de Magnesium  $\text{MgVO}_3$  et  $\text{MgV}_2\text{O}_5$ . Structure Cristalline de  $\text{MgVO}_3$ .* J. C. BOULOUX, I. MILOSEVIC, AND J. GALY. Laboratoire de Chimie du Solide du C.N.R.S., Université de Bordeaux I, 351 cours de la Liberation, 33405 Talence, France. Two phases have been investigated in the  $\text{MgO}-\text{VO}_2$  system at  $900^\circ\text{C}$ .  $\text{MgVO}_3$  crystallizes in the orthorhombic system, space group  $\text{Cmc}2_1$ , with  $a = 5.243$ ,  $b = 10.028$ , and  $c = 5.290$ . The structure is built up from square pyramids  $\text{VO}_5$  and  $\text{MgO}_5$  sharing edges and forming sheets connected through oxygen atoms. Its structure is related to the  $\text{ReO}_3$  and  $\text{Mg}_2\text{NF}$  structures.  $\text{MgV}_2\text{O}_5$  is orthorhombic with  $a = 3.696$ ,  $b = 9.965$ , and  $c = 11.019$ ; the space group is  $\text{Cmc}2_1$ ,  $\text{Cmcm}$ , or  $\text{C}2\text{cm}$ .