

SrCoO_{3-x} , $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ ($0.5 \leq x \leq 1.0$) and $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ ($0 \leq x \leq 1.0$). From the result, it is found that Sr^{2+} and La^{3+} ions strongly affect the spin state of the Co^{3+} ion and that the Mn^{4+} ion located at the octahedral site affects the spin state of Co^{4+} ion. The magnetic properties (T_c , T_θ , and σ) are explained by the magnetic interaction $\text{Co}^{3+}-\text{O}-\text{Co}^{3+}$, $\text{Co}^{3+}-\text{O}-\text{Co}^{4+}$, $\text{Co}^{4+}-\text{O}-\text{Co}^{4+}$, $\text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$, and $\text{Mn}^{4+}-\text{O}-\text{Co}^{4+}$ in these systems.

A New Monoclinic Phase in the $\text{Fe}_2\text{O}_3-\text{TiO}_2$ System. I. Structure Determination and Mössbauer Spectroscopy. M. DROFENIK,* L. GOLIC, D. HANZEL, V. KRASEVEC, A. PRODAN, M. BAKKER, AND D. KOLAR. Jozef Stefan Institute, E. Kardelj University, Jamova 39, 61000 Ljubljana, Yugoslavia. Single crystals with compositions within the $\text{Fe}_2\text{O}_3-\text{TiO}_2$ system were grown from a flux containing various amounts of the basic oxides. Apart from the known pseudo-brookite (Fe_2TiO_5) and rutile (TiO_2) structures, a new monoclinic polytype of Fe_2TiO_5 was found, which was isostructural with V_3O_5 . The structure was determined by X-ray analysis and Mössbauer spectroscopy contributed data on hyperfine parameters and the magnetic ordering temperature.

A New Monoclinic Phase in the $\text{Fe}_2\text{O}_3-\text{TiO}_2$ System. II. The Defect Structure. V. KRASEVEC,* A. PRODAN, M. BAKKER, M. DROFENIK, L. GOLIC, D. HANZEL, AND D. KOLAR, Jozef Stefan Institute, E. Kardelj University, Jamova 39, 61000 Ljubljana, Yugoslavia. Defects in monoclinic Fe_2TiO_5 were studied by electron microscopy and diffraction. The monoclinic structure found, which is isostructural with V_3O_5 , can be derived in a simple way from a hexagonal close packed structure and can be considered as a member of the family of crystallographic shear structures, derived from rutile. Two different slips corresponding to two hexagonal basal ones, were found to cause stacking faults, antiphase boundaries, and two different crystallographic shear planes.

La solution solide $\text{Cr}_{1-x}\text{Ir}_x\text{O}_2$. P. MAESTRO, G. DEMAZEAU, ET M. POUCHARD,* Laboratoire de Chimie du Solide, Université de Bordeaux I, 351, cours de la Libération, 33405 Talence Cedex, France. A new solid solution $\text{Cr}_{1-x}\text{Ir}_x\text{O}_2$ ($0 \leq x \leq 1$) has been prepared using oxidizing agents under pressure. The magnetic study shows the importance of the spin-orbit coupling and the weakening of the ferromagnetic interactions with increasing iridium content.

$\text{Ln}(\text{Fe}^{3+}, \text{M}^{2+})\text{O}_4$ Compounds with Layer Structure [$\text{Ln} = \text{Y}, \text{Er}, \text{Tm}, \text{Yb}, \text{and Lu}; \text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Cu}, \text{and Zn}$]. N. KIMIZUKA* AND E. TAKAYAMA, National Institute for Research in Inorganic Materials, 1-1, Namiki, Sakuramura, Niiharigun, Ibaraki-ken, Japan 305. A series of new compounds $\text{Ln}(\text{Fe}^{3+}, \text{M}^{2+})\text{O}_4$ [$\text{Ln} = \text{Y}, \text{Er}, \text{Tm}, \text{Yb}, \text{and Lu}; \text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Cu}, \text{and Zn}$] were successfully synthesized and their lattice constants were determined. These compounds have the same crystal structure as YbFe_2O_4 and Fe^{3+} and M^{2+} are both surrounded by five oxygen ions forming a trigonal bipyramid. The synthetic conditions are presented. They are strongly dependent upon the constituent cations of the compound.

Electrical and Thermoelectric Properties of Undoped MnO Single Crystals. M. PAI AND J. M. HONIG,* Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. The electrical resistivity and Seebeck coefficients of pure MnO single crystals have been measured above the Néel temperature. The material is p type in this temperature range. The results are interpreted on the basis of small-polaron hopping involving charge carriers in one or more sets of transport levels.

Crystal Chemistry of M_{12}P_7 Phases in Relation with the M_2P Phosphides. S. MAAREF, R. MADAR, P. CHAUDOUET, J. P. SENATEUR,* AND R. FRUCHART, E.R. 155, Section de Genie Physique ENSIEG, Domaine Universitaire, B.P. 46, 38402 St. Martin d'Heres, France. A structural model for the description of transition metal phosphides has been applied to the determination of the structural relation between M_{12}P_7 and M_2P hexagonal phases. The correctness of this approach has been tested by the prediction of the substitutional ordering in M_{12}P_7 phases.

Lattice Vibration Spectra. XXVI. Far-Infrared Spectra of the Ternary Skutterudites $\text{CoP}_{3-x}\text{As}_x$, $\text{CoAs}_{3-x}\text{Sb}_x$, and $\text{MGe}_{1.5}\text{Y}_{1.5}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}; \text{Y} = \text{S}, \text{Se}$). H. D. LUTZ* AND G. KLICHE. Laboratorium für Anorganische Chemie der Universität Siegen, Adolf-Reichwein-Strasse, D-5900 Siegen 21, West Germany. The infrared spectra of the skutterudite solid solutions $\text{CoP}_{3-x}\text{As}_x$ and $\text{CoAs}_{3-x}\text{Sb}_x$ and the ordered ternary skutterudites $\text{MGe}_{1.5}\text{Y}_{1.5}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}; \text{Y} = \text{S}, \text{Se}$) have been studied. In the system $\text{CoP}_{3-x}\text{As}_x$ a complete mixed crystal series has been obtained. In the system $\text{CoAs}_{3-x}\text{Sb}_x$ a miscibility gap has been found. The infrared spectra of the mixed crystals are influenced

by large plasmon-phonon interactions with anomalous temperature shifts of the resonance frequencies. Substitution of arsenic in CoAs_3 by small amounts of phosphorus or antimony results in an additional short-waved mode at 362 and 342 cm^{-1} , respectively, which can be assigned to an internal vibration of the four-membered anionic rings not allowed in the binary skutterudites. The infrared spectra of the ordered ternary skutterudites $M\text{Ge}_{1.5}\text{Y}_{1.5}$ ($M = \text{Co}, \text{Ir}$) show a large number of the total of 64 ir-allowed lattice modes, whereas the spectra of the rhodium compounds are mainly of the free carrier type. $\text{RhGe}_{1.5}\text{S}_{1.5}$ and the firstly obtained $\text{RhGe}_{1.5}\text{Se}_{1.5}$ exhibit small deviations from the formerly claimed pseudocubic cell. The lattice constants (space group $R\bar{3}$) are $a = 828.2(1)$ pm, $\alpha = 89.85(1)^\circ$ and $a = 854.6(1)$ pm, $\alpha = 89.86(1)^\circ$, respectively.

Monoclinic-Trigonal Transition in Some $M_3M'XO_4$ Compounds: The High-Temperature Form of $(\text{NH}_4)_3\text{In}(\text{SO}_4)_3$. B. JOLIBOIS, G. LAPLACE, F. ABRAHAM,* AND G. NOWOGROCKI. Universite des Sciences et Techniques de Lille, B.P. 36, 59655 Villeneuve d'Ascq Cedex, France. The high-temperature form of $(\text{NH}_4)_3\text{In}(\text{SO}_4)_3$ is rhombohedral, $R\bar{3}c$, with $a = 15.531(12)$, $c = 9.163(8)$ Å, $Z = 6$. The structure was solved to $R = 0.023$ for 570 independent reflections measured at about 140°C. The structure is built up of $[\text{In}(\text{SO}_4)_3]_\infty$ columns extending along the c axis and composed of InO_6 octahedra and SO_4 tetrahedra linked together; this arrangement is very similar to that found in the low-temperature form. To explain the transition mechanism, existence of an intermediate phase of point symmetry $\bar{3}m$ is postulated. This phase would be the prototypic structure of the possibly ferroelastic low-temperature modification which can apparently exist only with non-spherical monovalent cations.

Lithium Substituted Cobalt Oxide Spinel $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M = \text{Co}^{2+}, \text{Zn}^{2+}; 0 \leq x \leq 0.4$). N. K. APPANDAIRAJAN, B. VISWANATHAN,* AND J. GOPALAKRISHNAN, Department of Chemistry, Indian Institute of Technology, Madras 600 036, India. Substitution of Li^+ into Co_3O_4 and ZnCo_2O_4 gives rise to the solid solution series $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M = \text{Co}^{2+}$ or Zn^{2+}) having the spinel structure up to $x = 0.4$. X-Ray diffraction intensities show that the spinel solid solutions are likely to have the following cation distribution: $(\text{Co}^{2+})_1[\text{Li}_x^{2+}\text{Co}_{2-3x}^{2+}\text{Co}_{2x}^{2+}]_0\text{O}_4$ and $(\text{Zn}^{2+})_1[\text{Li}_x^{2+}\text{Co}_{2-3x}^{2+}\text{Co}_{2x}^{2+}]_0\text{O}_4$. Electrical resistivity and Seebeck coefficient data indicate that the electron transport in these systems occurs by a small polaron hopping mechanism.

X-Ray Study of $\text{Hg}_2\text{Cl}_2\text{-Br}_2$ and $\text{HgCl}_2\text{-HgBr}_2$ Reactions in Solid State. S. MEHDI* AND S. M. ANSARI. X-Ray Division, Regional Research Laboratory, Hyderabad 500 009, Andhra Pradesh, India. The reactions (i) $\text{Hg}_2\text{Cl}_2(\text{s}) + \text{Br}_2(\text{g})$ and (ii) $\text{HgCl}_2(\text{s}) + \text{HgBr}_2(\text{s})$ have been investigated by an X-ray method. Both the reactions yield two forms of the mixed halide HgClBr designated as $\alpha\text{-HgClBr}$ and $\beta\text{-HgClBr}$. The cell parameters of the two are as follows: $\alpha\text{-HgClBr}$: $a = 6.196$ Å, $b = 13.12$ Å, $c = 4.37$ Å, $Z = 4$, $\rho = 5.91$ g/cm^3 . The powder pattern and cell parameters are similar to that of HgCl_2 . Therefore it is probable that the chlorine atoms, in the linear halogen-Hg-halogen molecules of HgCl_2 structure have been replaced by bromines, and since the radius of bromine atom is larger than that of chlorine, the lattice is larger in this case. $\beta\text{-HgClBr}$: $a = 6.78$, $b = 13.175$ Å, $c = 4.17$ Å, $Z = 4$, $\rho = 5.40$ g/cm^3 . These parameters are the same as those reported in the literature for $\beta\text{-Hg}(\text{ClBr})_2$, and its X-ray powder pattern is similar to HgCl_2 . Therefore this phase also has linear halogen-Hg-halogen molecules but the distribution of Cl and Br atoms is perhaps random. Heating the products (i) and (ii) up to the melting point increases the amount of α -phase and decreases the β -phase, whereas crystallisation increases the β -phase. DTA study has supported the X-ray findings.

Reduction of the Titanium Niobium Oxides. I. TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. S. K. E. FORGHANY AND J. S. ANDERSON,* Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia. Reduction of the titanium-niobium oxides follows a common pattern. TiO_2 is eliminated, to form a new phase richer in titanium than the original compound, and Nb(IV) replaces Ti(IV) in the original block structure, which is thereby enriched in niobium. With TiNb_2O_7 , the second phase is a $\text{TiO}_2\text{-NbO}_2$ solid solution, with the rutile structure, initially with a high titanium content, in equilibrium with a solid solution of composition Me_3O_7 , isostructural with TiNb_2O_7 . At $\log P_{\text{O}_2}$ (atm) about -9.0 this reaches the limiting composition $\text{Ti}_{0.72}\text{Nb}_{2.28}\text{O}_7$, in equilibrium with $\text{Ti}_{0.56}\text{Nb}_{0.44}\text{O}_2$. The Me_3O_7 block structure then transforms into the $\text{Me}_{12}\text{O}_{29}$ block structure ($\text{Ti}_2\text{Nb}_{10}\text{O}_{29}\text{-Nb}_{12}\text{O}_{29}$ solid solution), which rapidly increases in niobium content as reduction continues. Reduction of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ at oxygen fugacities above $\log P_{\text{O}_2}$ (atm) = -9.0 forms the Me_3O_7 phase as the titanium-rich phase. At $\log P_{\text{O}_2} = -9.0$, and a composition about $\text{Ti}_{1.6}\text{Nb}_{10.4}\text{O}_{29}$, the rutile