

Studies on the Compounds in Ba-Fe-S System. I. Linear Chain Antiferromagnetism of Ba₂FeS₃ and Related Compounds Ba₂CoS₃ and Ba₂MnS₃. N. NAKAYAMA, K. KOSUGE, S. KACHI, T. SHINJO, AND T. TAKADA, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan. Magnetic susceptibilities of Ba₂FeS₃, Ba₂CoS₃, and Ba₂MnS₃ show rounded maxima at 130, 125, and 100°K, respectively, which are due to quasi-one-dimensional antiferromagnetic short-range ordering. Intrachain interactions, J/k , are estimated to be -20, -15, and -12°K, respectively. ⁵⁷Fe Mössbauer spectra of Ba₂FeS₃ and ⁵⁷Fe-doped Ba₂CoS₃ and Ba₂MnS₃ at 4.2 K show long-range antiferromagnetic ordering, due to the interchain interaction. The profile of Mössbauer spectra at 4.2°K is analyzed based on the coexistence of magnetic hyperfine and quadrupole interactions, and magnetic hyperfine fields at 4.2°K are estimated to be 36, 29, and 59 kOe, respectively.

Synthesis of Ba(V_{1-x}Ti_x)S₃ (0 ≤ x ≤ 1.0) Compounds and Their Structural Transitions. T. WADA, M. SHIMADA, AND M. KOIZUMI, The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan. The two-layer hexagonal perovskites Ba(V_{1-x}Ti_x)S₃ (0 ≤ x ≤ 1.0) are prepared in a H₂S stream. A structural phase transition from a hexagonal to an orthorhombic form takes place for the powder samples with 0 ≤ x ≤ 0.4 and their transition temperatures are determined to be 250°K for x = 0, 240°K for x = 0.1, 222°K for x = 0.2, 195°K for x = 0.3, and 160°K for x = 0.4, respectively. The phase transformation does not occur down to 90°K for the materials above x = 0.5.

Lattice Dynamics and Hyperfine Interactions of the Intercalation Compounds Fe_xTiS₂ (x = $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$) and Fe_{1/3}NbS₂ from ⁵⁷Fe Mössbauer Spectroscopy. MOTOMI KATADA AND R. H. HERBER, Department of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903. The intercalates Fe_xTiS₂ (x = $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$) and Fe_{1/3}NbS₂ have been prepared and characterized by ⁵⁷Fe Mössbauer effect spectroscopy. From isomer shift systematics it is inferred that the electron configuration of the iron atom in these compounds is formally +2, high spin. Fe_{1/2}TiS₂ shows magnetic ordering at temperatures below about 140°K, and the internal field at 4.2°K is approximately 30 kOe. Temperature-dependent Mössbauer measurements permit a calculation of the effective vibrating mass of the resonant moiety and a lattice temperature as probed by the Mössbauer atom. The former is nearly constant and that expected for a "bare" iron atom, while the latter varies over a significant range for the four title compounds, despite the similarity in the nearest-neighbor environment around the metal atom in all cases. This variation can be accounted for by the differences in the sulfur bonding modes in these compounds.

Synthesis and Structural Study of the New Rare Earth Magnesium Borates LnMgB₅O₁₀ (Ln = La...Er). BERNADETTE SAUBAT, MARCUS VLASSE, AND CLAUDE FOUASSIER, Laboratoire de Chimie du Solide CNRS, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence, Cedex, France. To obtain rare earth luminescent materials with weak concentration quenching, the B₂O₃-rich portion of the ternary diagram Ln₂O₃-MgO-B₂O₃ (Ln = rare earth) has been investigated. A ternary phase of composition LnMgB₅O₁₀ has been found for Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er. These compounds crystallize all in the monoclinic space group P2₁/c. The structure has been determined on a LaMgB₅O₁₀ crystal. A full-matrix least-squares refinement leads to R = 0.039. The structure can be described as being made of (B₅O₁₀⁵⁻)_n two-dimensional layers linked together by the lanthanum and magnesium ions. The rare earth atom coordination polyhedra form isolated chains. These borates are isostructural with some rare earth cobalt borates.

The Ionic Model Applied to Vacancy Ordering in NaCl-Type Materials. HUGO F. FRANZEN AND JEAN A. MERRICK, Ames Laboratory-DOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011. An order-disorder transition in Sc_{0.8}S (NaCl structure type) was studied by high-temperature X-ray diffraction and 700 ± 20°C was found to be the ordering temperature. A group of ordered sublattices on the rock salt lattice was generated and a Madelung energy and a configurational entropy were calculated for each assuming the lattice was made up of point charges. Mean field and pair interaction approximations were used to model long-range and short-range orderings, respectively. Results indicate that the ionic model is seriously in error in predicting short-range orderings of the type observed.

Comparison Des Champs De Force Des Niobates, Tantalates, Et Antimoniates De Structure Columbite Et Trirutile. E. HUSSON, Y. REPELIN, AND H. BRUSSET, Laboratoire de Chimie et Physico-Chimie Minérales, Institut de Chimie, Ecole Centrale des Arts et Manufactures, 92290 Chatenay-Malabry, France. A comparison is made between the force fields calculated for the M^{II}Nb₂^VO₆ and M^{II}Ta₂^VO₆

columbite and the $M^{II}Ta_2^YO_6$ and $M^{II}Sb_2^YO_6$ trirutile series. It is shown that the trirutile structure is remarkably more rigid than the columbite structure, which explains that it exists only for divalent cations of small size. Then the vibrational spectra of the rutile $FeSbO_4$ are compared with those of the trirutile MSb_2O_6 compounds.

The Crystal Structure of AgTlX Phases (X = S, Se, Te). J. C. TEDENAC, B. GARDES, G. BRUN, E. PHILIPPOT, AND M. MAURIN, Laboratoire de Chimie Minerale C, Universite des Sciences et Techniques du Languedoc Place E, Bataillon-34060 Montpellier Cedex, France. The isomorphism of ternary compounds $AgTlX$ ($X = S, Se, Te$) is pointed out. The compounds have an orthorhombic unit cell with four formulas and the space group is $Pnam$. The crystal structure of $AgTlTe$ has been solved with a final R value: 0.098. Silver and tellurium atoms are covalently bonded in chains of $AgTe_4$ tetrahedra-delimiting channels where thallium atoms are located.

High-Pressure Synthesis of Rock Salt-Type CdS Using Metal Sulfide Additives. KENZO SUSA, TOSHIO KOBAYASHI, AND SATOSHI TANIGUCHI, Central Research Laboratory, Hitachi Ltd., Tokyo 185, Japan. The retention of the high-pressure phase for CdS with the rock salt structure is investigated in the presence of metal sulfide additives. The most effective metal sulfides for the retention are CaS, SrS, PbS, SnS, GeS, and rare earth sulfides. X-Ray measurements of lattice parameters indicate that the retained CdS phases are metal-substituted solid solutions. The retention properties are discussed from the crystal chemistry point of view.

A Study of Magnetic Interactions in M_2EuRuO_6 ($M = Ca, Sr, Ba$) by ^{151}Eu Mössbauer Spectroscopy. T. C. GIBB AND R. GREATREX, Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds LS2 9JT, England. The series of compounds M_2EuRuO_6 ($M = Ca, Sr, Ba$) has been studied by ^{151}Eu Mössbauer spectroscopy. X-Ray data show them to be structurally derived from the ABO_3 perovskite lattice, but only the Ba compound gives positive evidence to suggest ordering of the Eu^{3+}/Ru^{5+} cations. The ^{151}Eu resonance shows magnetic hyperfine splitting at 4.2 K. The $Ru^{5+}-O-Eu^{3+}-O-Ru^{5+}$ exchange takes place by admixture of low-lying excited states into the diamagnetic $J = 0$ ground-state of the Eu^{3+} . The Curie temperatures are approximately 18, 31, and 42°K for the Ca, Sr, and Ba compounds. Detailed analysis shows that substantial disorder of cations occurs, being quite large for Ca, <8% for Sr, and <5% for Ba. However, it appears that considerable canting of the Ru^{5+} spins takes place in the Ba compound immediately below the Curie temperature as a result of the disorder and low anisotropy at the Ru sites. This effect is much reduced in the more distorted Sr compound.

Ionic Conductivity in Sodium, Potassium, and Silver β'' -Alumina. JACQUELINE L. BRIANT AND GREGORY C. FARRINGTON, General Electric Corporate Research and Development, P.O. Box 8, Schenectady, New York 12301. This paper presents measurements of the ionic conductivity in single crystals of β'' -alumina ($0.84M_2O \cdot 0.67MgO \cdot 5.2Al_2O_3$, $M = Na, K, Ag$). Single crystals of sodium β'' -alumina were grown from a melt of Na_2O , MgO , and Al_2O_3 at 1660 to 1730°C. Selected crystals were converted to the other isomorphs by ion exchange. The conductivity of sodium β'' -alumina varies from 0.18 to 0.010 (ohm cm) $^{-1}$ at 25°C according to crystal growth conditions. Potassium β'' -alumina has the unusually high room temperature conductivity of 0.13 (ohm cm) $^{-1}$. Silver β'' -alumina has a slightly lower conductivity, $4 \cdot 10^{-3}$ (ohm cm) $^{-1}$ at 25°C. The activation energies of sodium and potassium β'' -alumina decrease with increasing temperature while that of silver β'' -alumina is constant from -80 to 450°C.

Electrical, Magnetic, and EPR Studies of the Quaternary Chalcogenides $Cu_2A^{II}B^{IV}X_4$ Prepared by Iodine Transport. L. GUEN AND W. S. GLAUNSINGER, Laboratoire de Chimie des Solides, Faculte des Sciences, Universite de Nantes 44072 Nantes Cedex, France. Electrical, magnetic, and electron paramagnetic resonance (EPR) measurements have been made on crystals and powders of several quaternary chalcogenides of the type $Cu_2A^{II}B^{IV}X_4$, where $A^{II} = Zn, Mn, Fe, \text{ or } Co$; $B^{IV} = Si, Ge, \text{ or } Sn$; and $X = S \text{ or } Se$. The electrical properties of these compounds are extrinsic, but their magnetic properties do not appear to be affected by impurities. The magnetic moments of the Cu_2MnBX_4 compounds decrease with increasing covalency of the Mn-X bond, and those of Cu_2FeGeS_4 and Cu_2CoGeS_4 reflect an orbital contribution to the moment. Both the Weiss constants and the magnetic ordering temperatures in these compounds show an evolution from antiferromagnetism to ferromagnetism with increasing separation between the moments. Magnetic measurements on single crystals of Cu_2MnGeS_4 , Cu_2CoGeS_4 , and Cu_2FeGeS_4 indicate that only the latter is anisotropic. EPR measurements on crystals and powders of Cu_2ZnGeS_4 doped nominally with 0.1% Mn reveal that Mn^{2+} experiences an axial distortion and that the bond ionicity is the same as in ZnS.