JOURNAL OF SOLID STATE CHEMISTRY **15**, 209–212 (1975)

Abstracts of Forthcoming Articles

Chalkogenides of the Transition Elements. X. X Ray, Neutron, Mössbauer and Magnetic Studies of Pentlandite and the π Phases π(Fe, Co, Ni, S), Co_8MS_8 and $Fe_4Ni_4MS_8$ (M = Ru, Rh, Pd). O. Knop, C. H. Huang, K. I. G. Reid, and J. S. Carlow. Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada. And F. W. D. Woodhams. Department of Natural Philosophy, University of Aberdeen, Aberdeen AB9 2UE, Scotland. The metal atoms in the cubic π phases $(Fe, Co, Ni, M)_9S_8$ occupy four-coordinated majority and six-coordinated minority sites in the ratio 8:1. X ray and neutron powder diffraction of Co_8MS_8 and $Fe_4Ni_4MS_8$ (M = Fe, Co, Ni, Ru, Pd) has shown that the structures are ordered, i.e., with M segregated in the minority sites, when M is a 4*d* element, and at best partially ordered when M is a 3*d* element. Magnetic susceptibility measurements and Mössbauer ^{57}Fe spectra show that Co_9S_8 and the natural π(Fe, Ni, S) phase, pentlandite, remain Pauli-paramagnetic down to 4.2°K, with no resultant magnetic moments on the metal atoms, and hence are broad-band metals. Linear dependence of the isomer shifts at the two types of sites in a variety of $(Fe, Co, Ni)_9S_8$ compositions indicates the existence of a composite *s–d* conduction band. Analysis of the variation of the quadrupole splitting at the majority site with composition leads to the conclusion that only a few levels at the bottom of the conduction band are occupied. The number of electrons in the band is approximately proportional to the total *d*-electron content of the unit cell. A tentative band scheme based on these results and on other available evidence is proposed. The effect of composition on the interactomic distances in the π phases is discussed.

Transition Metal Iodates. VII. Crystallographic and Nonlinear Optic Survey of the 4f-Iodates. S. C. Abrahams, J. L. Bernstein, and K. Nassau. Bell Laboratories, Murray Hill, New Jersey 07974. Thirteen crystallographically distinct families of 4*f*-iodates, including hydrates, have been investigated. The anhydrous Type *I* family, extending from Ce to Lu, crystallizes in the monoclinic system, space group $P2_1/a$; the lattice constants of $Gd(IO_3)_3$, for example, are $a = 13.389 \pm 0.006$, $b = 8.500 \pm 0.002$, $c = 7.106 \pm 0.002$ Å, $\beta = 99.73 \pm 0.03°$, with four formulas per unit cell. $Yb(IO_3)_3$ and $Lu(IO_3)_3$ also crystallize in Type *II* with monoclinic space group $P2_1/c$ and lattice constants for $Yb(IO_3)_3$ of $a = 8.685 \pm 0.005$, $b = 6.066 \pm 0.002$, $c = 16.687 \pm 0.009$ Å, $\beta = 115.01 \pm 0.18°$, and four formulas per unit cell. Polycrystalline samples only of the anhydrous Types *III*, *IV*, *V*, and *VI* have been prepared and typical powder patterns are given. All anhydrous 4*f*-iodates form in centrosymmetric space groups. La and Ce grow as hemihydrates in the orthorhombic space group $C222_1$, with $a = 19.26 \pm 0.01$, $b = 7.40 \pm 0.01$, $c = 6.76 \pm 0.01$ Å for $La(IO_3)_3 \cdot \frac{1}{2}H_2O$, and both generate second harmonics more efficiently than quartz. Ce, Pr, Nd, Pm, and Sm form monohydrates, space group $P2_1$, with lattice constants for $Sm(IO_3)_3 \cdot H_2O$ of $a = 10.080 \pm 0.007$, $b = 6.642 \pm 0.006$, $c = 7.250 \pm 0.008$ Å, $\beta = 112.9 \pm 0.1°$, and two formulas per unit cell. The monohydrates are also more efficient than quartz at generating second harmonics. Two dihydrated families grow: Type *I* from Tm to Lu and Type *II* from Nd to Er, both triclinic. ($Lu(IO_3)_3 \cdot 2H_2O$ has $a = 8.018 \pm 0.012$, $b = 9.956 \pm 0.021$, $c = 6.969 \pm 0.016$ Å, $\alpha = 99.8 \pm 0.2°$, $\beta = 93.8 \pm 0.2°$, $\gamma = 68.2 \pm 0.2°$ with two formulas in the unit cell, space group $P\bar{1}$. $Nd(IO_3)_3 \cdot 2H_2O$ has $a = 7.56 \pm 0.04$, $b = 10.77 \pm 0.05$, $c = 7.34 \pm 0.02$ Å, $\alpha = 105.3 \pm 0.4$, $\beta = 110.8 \pm 0.7°$, $\gamma = 97.9 \pm 0.6°$, with two formulas per cell and space group $P\bar{1}$. Polycrystalline Gd to $Lu(IO_3)_3 \cdot 4H_2O$, and Ce to $Sm(IO_3)_3 \cdot 5H_2O$ Type *I* form in centrosymmetric space groups; powder patterns for two tetrahydrates and the four pentahydrates are given. $La(IO_3)_3 \cdot 5H_2O$ and $Pr(IO_3)_3 \cdot 5H_2O$, Type *II*, are monoclinic, space group $P2_1/m$, with lattice constants for $Pr(IO_3)_3 \cdot 5H_2O$ of $a = 6.768 \pm 0.008$, $b = 23.120 \pm 0.039$, $c = 7.107 \pm 0.007$ Å, $\beta = 112.7 \pm 0.1$, and four formulas per unit cell.

Thermodynamic Characterization of Ternary Compounds. I. The Case of Negligible Defect Association. D. M. Smyth. Materials Research Center, Lehigh University, Bethlehem, Pennsylvania 18015. The complete thermodynamic specification of the state of a ternary compound requires control of one more experimental parameter than for the case of a binary compound. Two experimental approaches have been used: (a) equilibration with a fixed activity of one of the binary constituents of the ternary compound, and (b) the assumption of a fixed ratio of the two cationic species. It is shown that these two approaches are not equivalent, and that for the latter case, the activities of the binary constitutents can vary widely with changes in the equilibrium nonmetal activity. For example, a ternary oxide with a fixed ratio of the two cationic components may be driven out of the single phase region by changes in ambient oxygen pressure, in effect transforming an initial case (b) to case (a), as defined above. $BaTiO_3$ is used as a specific example, and is discussed for the limiting case of negligible coulombic interaction between point defects.

Study by Electron Microscopy and Electron Diffraction of Formation of Nickel Epitaxially Grown Catalysts. G. DALMAI-IMELIK, C. LECLERCQ, AND A. MAUBERT-MUGUET. C. N. R. S., Institut de Recherches sur la Catalyse, 69626-Villeurbanne, France. In order to study the influence of the crystallographic arrangement at the surface of a metal supported catalyst on its catalytic properties, catalysts have been prepared with well-faceted nickel crystallites presenting particular faces at their surface. Catalysts were obtained by reduction by hydrogen of nickel antigorite evacuated at different temperatures. The morphology and structure of nickel antigorite, the parent of catalyst, has been determined by electron microscopy and electron diffraction at different temperatures. Rolled or flat sheets were observed. The texture of the catalysts obtained after reduction was determined. The crystallites of nickel are hexagonal platelets with either their [111] or their [110] plane parallel to the sheet support, depending on the conditions of preparation and reduction. Study of the orientations of [111] type or [110] type was done.

Étude Structurale de Cs_2SnF_6. J. DURAND, J. L. GALIGNE, AND A. LARI-LAVASSANI. Laboratoire de Chimie Minerale C and Laboratoire de Mineralogie et Cristallographie, Universite des Sciences et Techniques du Languedoc, 34060 Montpellier, France. The Cs_2SnF_6 structure is of the K_2GeF_6 type (trigonal $P\bar{3}m1$). The unit cell dimensions are $a = 6.322(6)$ Å, $c = 5.032(5)$ Å; $Z = 1$. Each tin atom is linked to six fluorine atoms at the corners of a nearly regular octahedron with Sn–F = 1.952(7) Å. The SnF_6^{2-} anions are isolated. Each cesium atom is surrounded by 12 fluorine atoms. The final R index is $R = 0.045$ from 453 X ray reflections.

Magnetic Susceptibility of the One-Dimensional Conductor $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$. D. HEITKAMP AND H. S. RADE. Institut fur Chemie, Kernforschungsanlage Julich. AND H. J. KELLER AND H. H. RUPP. Institut fur Anorganische Chemie der Universitat Heidelberg, Germany. The magnetic susceptibility of the dioxalatoplatinate acid $(H_3O)_{1.6}[Pt(C_2O_4)_2]nH_2O$, a mixed valence planar (*MVP*) compound with columnar structure and one-dimensional metallic conduction properties, has been measured in the temperature range 1.5–300°K. The observed paramagnetism, like in other *MVP*-compounds, may be described by a linear $1/T$ dependence with a break in the slope at a characteristic temperature. The Curie constants as well as the point of discontinuity have been found to depend on the crystal water content. The results are discussed in terms of different theoretical concepts.

Formation Energies of Schottky Defects in Alkaline Earth Oxides. G. RAMANI AND K. J. RAO. Materials Science Division, National Aeronautical Laboratory, Bangalore-560017, India. Schottky defect formation energies of alkaline earth oxides have been calculated by the procedure of Mott and Littleton, employing two parameter repulsive potentials. It is found that the polarizability of oxygen ion must be substantially lower in the case of MgO to obtain meaningful defect formation energy. Use of both displacement and anion polarizabilities, obtained from respective dielectric data, for each oxide, yields defect formation energies that are in fair agreement with more recent experimental values, for all the alkaline earth oxides.

The Electrical Conductivity of Ammonium Perchlorate Single Crystals. A. G. KEENAN AND M. G. OHANIAN. Department of Chemistry, University of Miami, Coral Gables, Florida 33124. The electrical conductivity of single crystals of ammonium perchlorate has been studied from 25–180°C. Plots of log σT versus $1/T$ show two linear regions, one from 25–100°C and another from 100–180°C. Activation energies for the conduction processes in the low and high temperature regions are 0.12 and 1.04 eV, respectively. The conduction is a bulk process and not a surface mechanism. Conduction in the low temperature region is predominantly due to the migration of protons and is sensitive to the concen-