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 com-

Printed in Great Britain