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Preparation and Properties of the Solid Solution Series $Zn_{1-x}Fe_xPS_3$ $(0 \leq x \leq 1)$[1]

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Members of the transition metal phosphorus trisulfide series $Zn_{1-x}Fe_xPS_3$ $(0 \leq x \leq 1)$ have been prepared by chemical vapor transport of the elements. All of the compositions prepared crystallized with the monoclinic space group *C2/m*. Electron microprobe results showed that the samples were homogeneous to within 2.0% in both zinc and iron. Chemical compositions were determined from the spectrophotometric analysis of iron present in the samples and agreed well with those assigned from microprobe results. Magnetic susceptibility data showed an increase of the Néel temperature as a function of increasing iron concentration. Magnetic susceptibility data, collected at temperatures well above the measured Néel point, gave paramagnetic moments consistent with iron having a high spin $3d^6$ electronic configuration in these compounds.

Introduction

A series of transition metal phosphorus trisulfide compounds with the general formula MPS_3 was prepared in 1969 by Klingen et al.[2,3] Klingen and his coworkers reported crystallographic data for samples prepared by direct combination of the elements at elevated temperatures. Klingen showed that $FePS_3$ crystallizes with the monoclinic space group *C2/m*. The exact determination of the crystal structure from intensity data was performed by Klingen[3] for $FePS_3$. However, three possible space groups for the compound $ZnPS_3$ and members of the series $Zn_{1-x}Fe_xPS_3$ $(x \neq 1)$ exist, namely, *C2/m*, *C2*, and *Cm*. The differences in the positions of the metal ions in these three possible space group assignments would not be large enough to affect the antiferromagnetic ordering of the substituted ions in the solution series. The structure of these materials (Figure 1) is closely related to the layer-type compound $CdCl_2$, with iron or zinc cations and phosphorus–phosphorus pairs occupying the cadmium positions and sulfur anions occupying the chloride positions. The structural arrangement results in a distorted face-centered cubic array of sulfur anions and a distorted octahedral coordination of the cations and phosphorus–phosphorus anion pairs.

Recently Taylor et al.,[4] using chemical vapor transport techniques, prepared single crystals of several MPS_3-type compounds and reported their physical properties. Using magnetic susceptibility and Mössbauer results, Taylor[5] showed that $FePS_3$ orders antiferromagnetically (Néel point T_N = 126°K), and that iron is present in a high spin $3d^6$ configuration. He also indicated that the diamagnetic susceptibility of $ZnPS_3$ is consistent with zinc having a $3d^{10}$ electronic configuration.

A problem which has attracted attention is the variation in properties as the concentration of a paramagnetic ion is increased within a diamagnetic host. The variation of the magnetic susceptibility as a function of temperature as well as the onset of magnetic order versus concentration of magnetically active atoms are of particular interest. Crystallographic similarity, near equal ionic radii (Zn^{2+} = 0.74 Å, Fe^{2+} = 0.76 Å), and the difference in magnetic properties of $ZnPS_3$ (diamagnetic) and $FePS_3$ (antiferromagnetic) make the cation substitution series $Zn_{1-x}Fe_xPS_3$ a good system for studying both the nature of a magnetic ion in a diamagnetic host (low concentration) and the onset of magnetic interactions as the paramagnetic (Fe $3d^6$) concentration is increased in this anion rich transition metal compound.

Experimental Section

Preparation. Single crystal samples of the solid solution series $Zn_{1-x}Fe_xPS_3$ were grown by chemical vapor transport.[6] Pretreatment of the reactant materials was as follows. High purity iron (99.999%) was reduced in a 15% H_2/85% Ar atmosphere for 20 hr at 980°. Zinc metal of high purity (99.999%) was treated with 3 *N* hydrochloric acid to eliminate any trace of surface zinc oxide and then washed with distilled water and dried with acetone. Electronic grade elemental phosphorus (99.999%) and sulfur (99.999%) were used as supplied.

Table I

Nominal compositions	Electron probe formula	Chemical analysis formula
$Zn_{0.30}Fe_{0.70}PS_3$	$Zn_{0.55}Fe_{0.45}PS_3$	$Zn_{0.52}Fe_{0.48}PS_3$
$Zn_{0.10}Fe_{0.90}PS_3$	$Zn_{0.27}Fe_{0.73}PS_3$	$Zn_{0.30}Fe_{0.70}PS_3$
$Zn_{0.03}Fe_{0.97}PS_3$	$Zn_{0.13}Fe_{0.87}PS_3$	$Zn_{0.15}Fe_{0.85}PS_3$

In order to prepare single crystals, stoichiometric quantities of the pretreated reactants were placed into silica tubes (26 cm × 12 mm) and evacuated to a pressure below 2 Torr. The silica transport tubes were then backfilled with Cl_2 to a pressure of 100 Torr and sealed. The chemical vapor transport reactions were carried out in a variable zone furnace capable of operating in the three modes shown in Figure 2.

Mode a. Reverse transport allows material which might have adhered to the growth region of the silica tube, during previous manipulations, to be transported to the charge zone. This procedure reduces the number of nucleation sites in the growth zone yielding fewer but larger well-formed crystals (duration: 1 day).

Mode b. External establishes near thermal equilibrium between the growth and charge zones, maintaining a slight reverse temperature gradient to prevent crystallization (duration: 2 hr).

Mode c. Profile establishes at a programmable rate the desired temperature gradient for exothermic crystallization in the growth zone. The final crystallization conditions were for $ZnPS_3$: T = 500° charge zone; T = 480° growth zone. For other compositions $Zn_{1-x}Fe_xPS_3$ $(0 < x \leq 1)$: T = 700° charge zone; T = 680° growth zone.

Typical crystals obtained by this procedure were flat platelets, weighing 80–200 mg and measuring up to 1 cm on an edge. $ZnPS_3$ crystallized as a transparent yellow material whereas other members of the solid solution series were black.

Analysis. (a) Electron Probe Analysis. An Applied Research Laboratories Electron-Microprobe apparatus was used to determine the homogeneity and chemical composition ($ZnPS_3$ and $FePS_3$ were used as standards).[7] These results showed that the crystals were homogeneous to within 2.0% in both zinc and iron. In addition, measurements on cleaved crystals showed the same degree of homogeneity and the same chemical composition as found on the surface. The formulas determined from the microprobe analysis are included in Table I.

(b) Chemical Analysis. A spectrophotometric determination of iron with potassium thiocyanate was carried out on a Spectronic 20 colorimeter.[8,9] Solutions of the unknown were prepared by dissolving a known quantity of each crystal in 50 ml of 1:3 nitric acid. This resulted in the formation of Fe(III) solutions. Oxides of nitrogen were expelled from these solutions by boiling and then the solutions were filtered to remove the precipitated sulfur. The filtrate was transferred to a 500 ml volumetric flask and diluted to 0.5 l. with iron-free distilled water. Standard solutions were made up by dissolving known amounts of purified metal iron by following the same process described above. A 0.6 *M* KSCN solution was prepared using iron-free distilled water. The absorbance of the red-colored iron(III) thiocyanate complex $[Fe(H_2O)_5(SCN)]^{2+}$ was measured at once at λ 480 mμ. The intensity of the color produced by the reaction of Fe(III) with thiocyanate depends upon many factors. A too long exposure to light

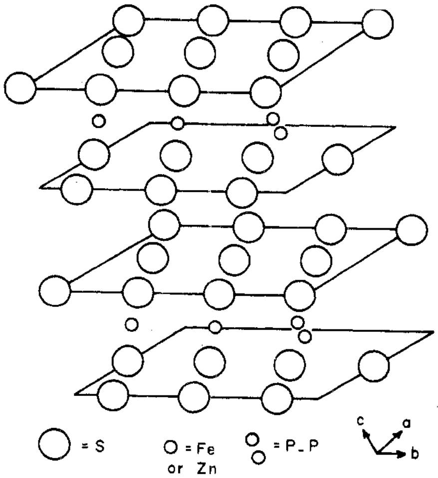

Figure 1. Structure of $ZnPS_3$ and $FePS_3$ showing the near octahedral coordination about the iron ions and the phosphurus-phosphorus pairs.

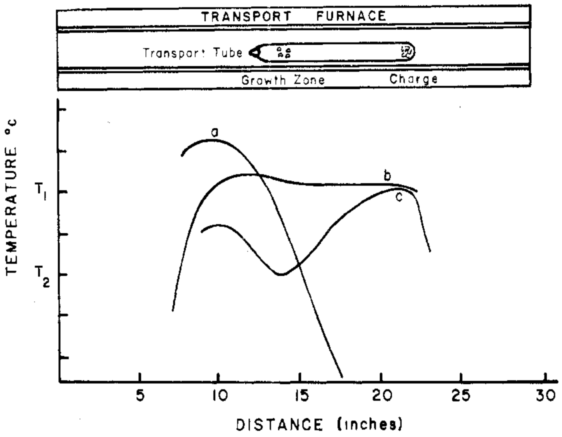

Figure 2. Schematic diagram of a transport furnace showing the temperature profile for the three modes of operation: a, reverse transport; b, external; and c, profile.

would lessen its intensity. Hence, the reading is done quickly after mixing and shaking the solution. With an excess of thiocyanate, the reaction undergoes further substitution and complexes such as $[Fe(H_2O)_4(SCN)_2]^+$ and $[Fe(H_2O)_5(SCN)]^{2+}$ are formed. To avoid this, the final SCN^- concentration is kept at 0.3 *M*. The acidity of the final solution is approximately 0.2 *N*. The compositions for several members of the series are given in Table I.

X-Ray Measurements

X-Ray diffraction data were collected on polycrystalline samples with a Norelco diffractometer using monochromatic radiation (AMR 202 Focusing Monochromator) and a high intensity copper source (λ Cu Kα_1 = 1.5405 Å). The results of a least-squares analysis of these measurements confirm the values of the lattice parameters reported by Klingen and Taylor.[2-4]

For $ZnPS_3$ a_0 = 5.96 (1), b_0 = 10.28 (1), c_0 = 6.73 (1), and β = 107.10 (9). For $FePS_3$ a_0 = 5.934 (6), b_0 = 10.28 (1), c_0 = 6.722 (7), β = 107.16 (9).

The similarity in the cell parameters for the two end members precludes the possibility of assigning meaningful stoichiometry for intermediate members of the solid solution series ($Zn_{1-x}Fe_xPS_3$) by X-ray diffraction analysis. However, X-ray diffraction patterns of intermediate preparations showed these materials to be single phase.

Magnetic Measurements

Magnetic measurements were made using a Faraday balance as described by Morris and Wold.[10] For each sample, the bulk magnetic susceptibility was measured as a function of field strength (Honda–Owens method).[11,12] These measurements showed an absence of ferromagnetic and ferrimagnetic impurities in all the materials studied. In addition, the magnetic susceptibility was measured as a function of temperature from 77 to 500°K. The upper temperature limit (500°K) was chosen to be well below the thermal decomposition point (720°K) as determined by thermal gravimetric analysis. Figure 3 shows the plots of inverse magnetic susceptibility vs. temperature for the different compositions. As shown, the compositions $Zn_{0.30}Fe_{0.70}PS_3$ and $Zn_{0.15}Fe_{0.85}PS_3$ exhibit antiferromagnetic behavior with Néel temperatures of 94 (4)°K and 111 (4)°K, respectively. For the composition $Zn_{0.52}Fe_{0.48}PS_3$, only paramagnetic behavior was observed above 77°K. The effective magnetic moments, Curie constants, and Curie–Weiss constants were determined from a least-squares fit of the data in the paramagnetic region. Table II summarizes the magnetic data for the different compositions.

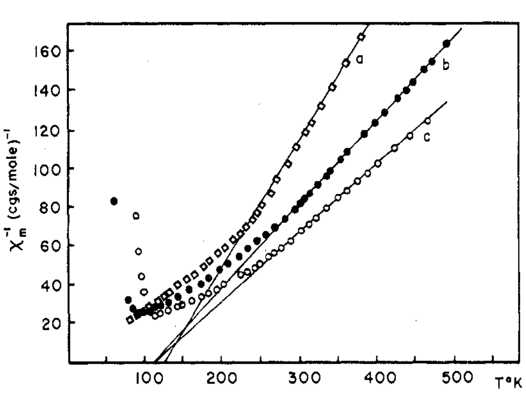

Figure 3. Reciprocal molar susceptibility vs. temperature for the composition: a, $Zn_{0.52}Fe_{0.48}PS_3$; b, $Zn_{0.30}Fe_{0.70}PS_3$, and c, $Zn_{0.15}Fe_{0.85}PS_3$.

Table II

Composition	C_m[a]	P_{eff}/Fe	Θ, °K	T_N, °K
$Zn_{0.52}Fe_{0.48}PS_3$	3.13 (1)	5.00 (1)	127 (1)	
$Zn_{0.30}Fe_{0.70}PS_3$	3.34 (2)	5.17 (1)	110 (1)	94 (4)
$Zn_{0.15}Fe_{0.85}PS_3$	3.28 (4)	5.13 (3)	112 (3)	114 (4)
$FePS_3$	3.13 (2)	5.00 (2)	109 (2)	127 (4)

[a] Curie constant per mole of iron.

Conclusion

This work has shown that the substitution of iron for zinc in the series $Zn_{1-x}Fe_xPS_3$ can be accomplished by chemical transport reactions. The crystallographic data obtained on powdered samples of each composition show that each compound probably belongs to the monoclinic space group *C2/m*. This is consistent with the single crystal data reported by Klingen[3] for $FePS_3$. Magnetic susceptibility measurements (see Figure 3) indicate that compositions $Zn_{1-x}Fe_xPS_3$ for $x > 0.7$ are antiferromagnetic with Néel temperatures for specific compositions given in Table II. The analyzed samples given in Tables I and II report a concentration of zinc higher than that weighed out for the nominal compositions of the charges. This indicates the necessity of performing chemical analysis in the single crystals obtained from chemical transport. Undoubtedly, zinc tends to form far more volatile intermediates than iron at the transport temperatures used for single crystal growth. The effective magnetic moments per mole of Fe determined in the paramagnetic region indicate the presence of high-spin divalent iron ions in a nearly octahedral environment. Magnetic susceptibility measurements also show an increase in the Néel temperature as a function of increasing iron composition. This behavior is indicative of increased magnetic interactions as iron is substituted for zinc.

Registry No. $ZnPS_3$, 56172-70-4; $FePS_3$, 12140-43-1.

References and Notes

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Synthesis of Tetramethylaurate(III). Studies on the Structures of Li[$(CH_3)_2$Au] and Li[$(CH_3)_4$Au] in Solution

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Reaction of CH_3Li with $(CH_3)_3AuP(C_6H_5)_3$ in diethyl ether solution gives essentially a quantitative conversion to Li[$(CH_3)_4$Au]. Both the Raman and proton magnetic resonance spectra are consistent with a structure in solution involving solvated Li^+ ions and essentially square planar $(CH_3)_4Au^-$ anions, i.e., solvent-separated ion pairs. The d^8 anion is coordinatively saturated, for $P(C_6H_5)_3$ does not interact with it. This system provides a good example of the declining significance of dπ–dπ back bonding as an explanation of the stabilization of electron rich systems. The analogous gold(I) species, Li[$(CH_3)_2$Au], produced by the known reaction between CH_3Li and $CH_3AuP(C_6H_5)_3$ also occurs as a solvent-separated ion pair with a coordinatively saturated d^{10} anion. This has a linear skeletal structure, and the Raman active vibrations correlate smoothly with those of $(CH_3)_2Hg$, $(CH_3)_2Tl^+$, and $(CH_3)_2Pb^{2+}$. The strengths of the metal–carbon bonds decrease from Au to Pb in a reversal of the usual variation with nuclear charge. Ether solutions of CH_3Li give weak Raman scattering, and the spectrum is compared with that of *t*-C_4H_9Li and discussed in terms of the nature of the lithium alkyls in solution.

Introduction

Although the existence of simple dialkylaurate(I) species was suggested by Coates and Parkin[1] in 1962 and a compound characterized as $[Et_4N^+][((C_6H_5)_3Ge)_2Au^-]$ was isolated by Glockling and Wooten[2] in the same year, only recently have studies on the simple dimethylaurate(I) and its higher homologs been reported.[3,4] This is in marked contrast to the analogous copper compounds, the "homocuprates", which have been considered since 1952.[5] Their chemistry and applications in organic synthesis have been reviewed recently.[6]

Lithium dimethylaurate(I) has been reported by Tamaki and Kochi to be formed as a clear, colorless solution in diethyl ether or dimethoxyethane according to reaction 1. Proton

$$CH_3AuPR_3 + CH_3Li \rightarrow (CH_3)_2AuPR_3Li \qquad (1)$$

NMR showed the methyl groups in the product to be equivalent, yielding a single resonance unsplit at −70°. It was concluded[4] that the phosphine was not coordinated to gold based on (i) the absence of ^{31}P coupling to the methyl–gold protons, (ii) the chemical shift of the ^{31}P resonance of the phosphine, (iii) the separation, on cooling, of the triphenylphosphine from a sample prepared from CH_3AuPPh_3, and (iv) Raman spectra obtained by us on a sample of $(CH_3)_2AuPPh_3Li$ provided by Professor Kochi.

In this paper we report the synthesis of the first peralkylgold(III) complex, lithium tetramethylaurate(III). In spite of the fact that alkyl derivatives of gold(III) along with platinum(IV) were the first stable metal alkyls isolated,[7] the aurate(III) species have not been observed previously. As discussed by Wilkinson,[8] one way in which an alkyl can be stabilized against decomposition is by coordinative saturation of the metal. This appears to be the case for both the aurate(I) and aurate(III) species. Extensive studies using laser Raman and ^1H NMR spectroscopy have been carried out on both the dimethylaurate(I) and tetramethylaurate(III) species in solution, and conclusions concerning their structures have been drawn.

Experimental Section

Synthesis. Diethyl ether used for solutions was distilled from $LiAlH_4$ under dry nitrogen immediately before use. Sample preparation was carried out under an atmosphere of prepurified nitrogen or argon which had been passed through a drying column. A solution of halide-free methyllithium in diethyl ether was prepared from $(CH_3)_2Hg$ and lithium sand; excess lithium and lithium amalgam were removed by filtration. Methyllithium-d_3 was prepared by reaction of methyl iodide-d_3 with lithium wire. Elemental analyses were carried out in the Departmental Microanalytical Laboratory.

$CH_3AuP(C_6H_5)_3$ and $CD_3AuP(C_6H_5)_3$. These were prepared by the method of Coates and Parkin.[1] Anal. Calcd for $C_{19}H_{18}PAu$: C, 48.1; H, 3.82. Found: C, 48.0; H, 4.08. Calcd for $C_{19}H_{15}D_3PAu$: C, 47.8; H, 4.43. Found: C, 47.2; H, 4.53.

$(CH_3)_3AuP(C_6H_5)_3$ and $(CD_3)_3AuP(C_6H_5)_3$. These were synthesized by the procedure of Coates and Parkin[9] using $Cl_3Au(py)$ as the starting material. Anal. Calcd for $C_{21}H_{24}PAu$: C, 50.0; H, 4.80. Found: C, 49.9; H, 4.58. Calcd for $C_{21}H_{15}D_9PAu$: C, 49.1; H, 6.47. Found: C, 49.4; H, 6.61.

Li[$(CH_3)_2$Au] and Li[$(CD_3)_2$Au]. The aurate(I)'s were prepared from the corresponding alkyl(triphenylphosphine)gold(I) complex after the method of Tamaki and Kochi.[3] In a typical experiment, 0.1446 g (0.305 mmol) of $CH_3AuP(C_6H_5)_3$ was placed in a thin-walled NMR tube capped with a serum stopple, an argon atmosphere was provided, and 1.0 ml of 0.5 *M* CH_3Li in ether was syringed into the tube. The ether-insoluble $CH_3AuP(C_6H_5)_3$ readily dissolved with shaking.

Li[$(CH_3)_4$Au] and Li[$(CD_3)_4$Au]. These were prepared by a procedure analogous to that used for the aurate(I)'s employing $(CH_3)_3AuP(C_6H_5)_3$ and $(CD_3)_3AuP(C_6H_5)_3$, respectively, as starting