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Preparation and Properties of Some Transition Metal Phosphorus Trisulfide Compounds*

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Transition metal phosphorus trisulfide compounds with the general formula MPS_3, with M = Mn, Fe, Ni, have been prepared by chemical vapor transport, vapor sublimation, and direct combination of the elements. Chemical transport is accomplished by using 75 Torr of chlorine gas as a transport agent and a temperature gradient of 750° → 690°C or 700° → 640°C. The structure of these three compounds, which belongs to the monoclinic space group C2/m, is related to that of $CdCl_2$ with a distorted cubic close-packing of the sulfur atoms. Metal atoms and phosphorus–phosphorus pairs occupy the trigonally distorted octahedral holes in a ratio of 2:1 and are ordered throughout the structure. Magnetic susceptibility measurements indicate that all three compounds are antiferromagnetic. The paramagnetic moments indicate that the metal ions in each case exist in the divalent high-spin state.

Introduction

Transition metal phosphorus trisulfide compounds, which generally form as thin-platelet crystals, were first prepared and characterized by Klingen et al. (*1–4*). Their studies were primarily concerned with preparation and crystal structure determination. The preparative technique entailed reacting the elements for prolonged periods of time (2 to 3 months) in evacuated silica tubes. This technique produced powders, or at best small crystals suitable for X-ray studies. Nitsche and Wild (*5*) were able to produce larger crystals of $FePS_3$ and $MnPS_3$ (up to $0.1 \times 10 \times 10$ mm) by chemical vapor transport with iodine. Klingen (*6*) performed the crystal structure determination of $FePS_3$ and found it to have a monoclinic unit cell (space group C2/m) with the lattice parameters $a_0 = 5.934$ Å, $b_0 = 10.28$ Å, $c_0 = 6.722$ Å, and $\beta = 107.16°$. The structure is related to that of cadmium chloride, with iron ions and phosphorus–phosphorus pairs occupying the cadmium positions and sulfur ions occupying the chloride positions. In this way the iron ions and P–P pairs are approximately octahedrally coordinated in a distorted cubic close-packed lattice. The octahedral coordination about the iron ions and P–P pairs is shown in Fig. 1 by the shaded circles. The P–P bond lies along the octahedral threefold axis.

Studies of these mixed anion phases were

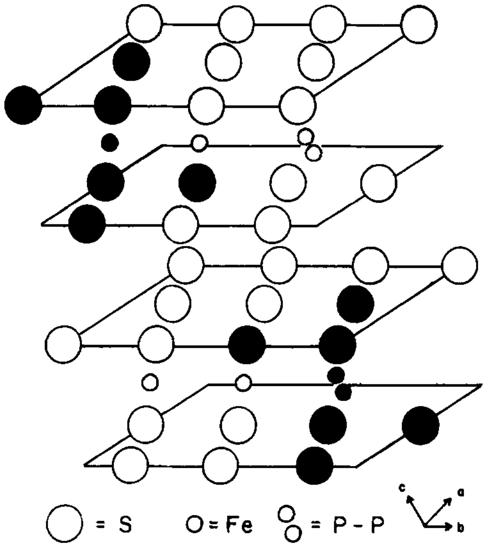

FIG. 1. Structures of $FePS_3$. The octahedral coordination about the Fe^{2+} ions and P–P pairs is shown by the darkened circles.

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initiated in order to investigate the magnetic properties of $FePS_3$, as well as those of the isostructural compounds $MnPS_3$ and $NiPS_3$.

Experimental

Sample Preparation

Single crystals of $MnPS_3$, $FePS_3$, and $NiPS_3$ have been prepared by reacting stoichiometric amounts of the high purity elements (99.99% or better) in sealed silica tubes evacuated to 2 μm Hg. These compounds can be formed at temperatures between 600° to 750°C. Direct combination (DC) samples have been prepared by heating the elements for 1 month at 650°C in a one-zone furnace, pulverizing the sample under dry nitrogen to insure homogeneity, and heating a second time at 650°C for 1 to 2 months.

Vapor sublimation (VS) and chemical transport (CT) techniques (*7*) have also been employed. These methods enable one to obtain larger crystals in a shorter length of time, primarily due to the higher temperatures used and the mineralizing effect of the chemical transport agent. Both vapor sublimation and chemical transport (using 75 Torr of chlorine gas) have been performed in a two-zone furnace, which could be programmed up and down in temperature (*8*). In the case of vapor sublimation (no transport agent) the material is sublimed from the hotter to the cooler zone. Temperature gradients of 750° → 640°C produce excellent crystal growth in 6 to 10 days. Conditions for preparation of each sample are shown in Table I.

X-Ray Analysis

The samples prepared by the above procedures have been analyzed by both fast- and slow-scan X-ray diffraction patterns to insure that the materials were single phase and to obtain precision lattice parameters. Fast scans have been obtained at a scan speed of 60°/hour in 2θ, whereas slow scans have employed a scan speed of 15°/hour. In the case of the slow scans, magnesium oxide was used as an internal standard. In both cases a Norelco diffractometer with monochromatic radiation and a high intensity copper source was used [$\lambda(CuK\alpha_1) = 1.5405$ Å]. The space group assignments were made from Weissenberg photographs, using molybdenum radiation [$\lambda(MoK\alpha_1) = 0.70926$ Å] and focal spot size of 1 × 1 mm.

TABLE I

METHOD OF PREPARATION

	Sample #	Method	Temp. grad. (°C)	Duration
$MnPS_3$				
	BET#1-480	VS[a]	750 → 690	7 Days
	BET#1-454	CT[b]-Cl_2	700 → 655	6 Days
	BET#1-478	CT-Cl_2	750 → 690	6 Days
	BET#1-308	DC[c]	650	3 Months
	BET#1-276	CT-Cl_2	670 → 610	6 Days
$FePS_3$				
	BET#1-258	CT-Cl_2	750 → 690	2 Weeks
	BET#1-298	DC	650	3 Months
	BET#1-284	CT-Cl_2	750 → 690	10 Days
	BET#1-328	CT-Cl_2	700 → 640	10 Days
	BET#1-386	VS	700 → 650	10 Days
$NiPS_3$				
	BET#1-388	VS	750 → 690	10 Days
	BET#1-262	CT-Cl_2	750 → 690	9 Days
	BET#1-300	DC	650	3 Months
	BET#1-446	CT-Cl_2	750 → 690	14 Days
	BET#1-448	VS	750 → 690	14 Days

[a] VS = vapor sublimation.
[b] CT = chemical transport.
[c] DC = direct combination.

TABLE II

CRYSTALLOGRAPHIC DATA

	Sample #	a_0	b_0	c_0	β^0	D_c gm/cm^3	D_m gm/cm^3
$MnPS_3$	BET#1-276(CT)	6.088	10.526	6.800	107.27	2.907	2.921(4)
	BET#1-308(DC)	6.078	10.530	6.799	107.38	2.913	2.918(11)
	BET#1-454(CT)	6.099	10.534	6.799	107.33	2.901	2.900(2)
	BET#1-478(CT)	6.081	10.532	6.800	107.32	2.909	2.921(16)
	BET#1-480(VS)	6.091	10.528	6.797	107.27	2.906	2.920(8)
	Average	6.087(2)	10.530(3)	6.800(2)	107.31(5)	2.907(4)	
$FePS_3$							
	BET#1-258(CT)	5.970	10.282	6.722	107.25	3.085	3.094(5)
	BET#1-298(DC)	5.942	10.289	6.719	107.15	3.097	3.078(5)
	BET#1-284(CT)	5.948	10.287	6.720	107.13	3.093	3.083(3)
	BET#1-328(CT)	5.938	10.291	6.720	107.17	3.098	3.093(6)
	BET#1-386(VS)	5.948	10.293	6.719	107.17	3.093	3.070(9)
	Average	5.949(12)	10.288(4)	6.720(1)	107.17(4)	3.093(5)	
$NiPS_3$							
	BET#1-388(VS) (crystals)	5.808	10.079	6.628	107.00	3.327	3.296(4)
	BET#1-388(VS) (charge)	5.810	10.076	6.628	106.98	—	—
	BET#1-262(CT)	5.806	10.081	6.627	106.97	3.328	3.300(5)
	BET#1-300(DC)	5.810	10.076	6.629	107.00	3.326	3.296(8)
	BET#1-446(CT)	5.826	10.072	6.627	106.93	3.319	3.388(9)
	BET#1-448(VS)	5.806	10.073	6.627	106.90	3.321	3.391(2)
	Average	5.811(7)	10.076(3)	6.628(1)	106.96(4)	3.326(2)	

TABLE III[a]

$MnPS_3$			$FePS_3$			$NiPS_3$		
hkl	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	*hkl*	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	*hkl*	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$
130	0.06568	0.06579	130	0.06879	0.06884	130	0.07182	0.07181
131	0.08923	0.08930	131	0.09274	0.09283	131	0.09642	0.09641
$13\bar{2}$	0.10343	0.10332	$13\bar{2}$	0.10740	0.10721	$13\bar{2}$	0.11121	0.11116
003	0.12674	0.12682	003	0.12983	0.12952	132	0.15054	0.15054
$13\bar{3}$	0.16440	0.16436	$13\bar{3}$	0.16980	0.16957	$13\bar{3}$	0.17521	0.17513
060	0.19265	0.19262	060	0.20175	0.20174	060	0.21036	0.21037
$06\bar{1}$	0.20660	0.20671	004	0.23025	0.23025	064	0.44652	0.44655
133	0.22084	0.22086	$26\bar{2}$	0.29448	0.29454	$20\bar{6}$	0.49005	0.49013
004	0.22549	0.22546	005	0.35992	0.35977	$13\bar{7}$	0.72622	0.72620
$26\bar{2}$	0.28191	0.28185	064	0.43206	0.43199			
005	0.35240	0.35229	$20\bar{6}$	0.47662	0.47655			
064	0.41808	0.41808	$13\bar{7}$	0.70663	0.70683			
$20\bar{6}$	0.46477	0.46482						
$13\bar{6}$	0.51666	0.51658						
$20\bar{7}$	0.62916	0.62917						
$13\bar{7}$	0.69029	0.69035						

[a] Only reflections used in precision lattice parameter calculations are shown.

TABLE IV

	Sample #	C_m	P_{eff}	θ°K	T_n°K	n_s
$MnPS_3$	BET#1-480(VS)	4.83	6.22	−262	111	5.30
	BET#1-454(CT)	4.90	6.26	−265	111	5.34
	BET#1-478(CT)	4.83	6.22	−276	111	5.30
	BET#1-308(DC)	4.73	6.15	−245	108	5.23
	BET#1-276(CT)	4.70	6.13	−278	110	5.21
	Average	4.80(8)	6.20(5)	−265(13)	110(1)	5.28(5)
$FePS_3$						
	BET#1-386(VS)	3.74	5.46	+21	127	4.56
	BET#1-298(DC)	3.70	5.45	+ 9	127	4.49
	BET#1-284(CT)	3.76	5.48	+18	125	4.57
	BET#1-258(CT)	3.59	5.34	+ 8	126	4.44
	Average	3.70(8)	5.43(6)	+14(6)	126(1)	4.52(6)
$NiPS_3$						
	BET#1-262(CT)	1.65	3.63	−514	260	2.77
	BET#1-446(CT)	1.55	3.54	−557	255	2.68
	BET#1-300(DC)	1.86	3.86	−506	240	2.99
	BET#1-448(VS)	1.68	3.68	−611	255	2.81
	Average	1.69(13)	3.68(13)	−558(69)	253(9)	2.81(12)

Density Measurements

Density measurements of both single crystal and powder samples were made by a hydrostatic technique (*9*) using perfluoro(1-methyldecalin) as the liquid. In all cases the liquid was first calibrated using a high purity crystal of silicon with its density taken as 2.328 gm/cm^3. All measurements were carried out at 25° ± 2°C.

Magnetic Measurements

Magnetic susceptibility measurements on ground polycrystalline samples were carried out using a Faraday balance (*10*) equipped with a Cahn RG Electrobalance over the temperature range 77°–298°K in the case of $MnPS_3$ and $FePS_3$ and 77°–600°K in the case of $NiPS_3$. Measurements were performed at field strengths between 6.25 and 10.30 *k*Oe.

Mössbauer Measurements

The iron-57 Mössbauer spectra of $FePS_3$ were measured with a Model NS-1 Mössbauer spectrometer (Nuclear Science and Engineering Corp.) operating in the constant acceleration mode. The 14.4 keV γ-radiation source (13 mCi ^{57}Co diffused into palladium) was detected with a gas proportional counter (Amperex Corp.) and collected with a 400-channel analyzer (Nuclear Chicago Corp.) operating in time-sequence scaling mode. The source and drive were calibrated against a single crystal of sodium iron(III) nitropentacyanide dihydrate (National Bureau of Standards, Standard Reference Material No. 725). The quadrupole splitting for the standard was taken as 1.7048 mm/sec (*11*). Isomer shift values are reported with respect to the zero position of the standard. The sample cross section was 57 mg/cm^2, corresponding to 17 mg/cm^2 total iron. The data were computer fit with a maximum likelihood regression analysis program to a product of Lorentzian profiles superposed on a parabolic base line, a result of the drive geometry. All parameters—peak positions, half-widths, and heights—were allowed to vary independently. Cryogenic measurements were made in a variable temperature Dewar (Andonian Associates, Inc.).

Results and Discussion

The crystallographic data obtained on powdered samples of each composition, prepared under various conditions, is presented in Table II. Single crystal Weissenberg data of each compound has shown them to belong to the mono-

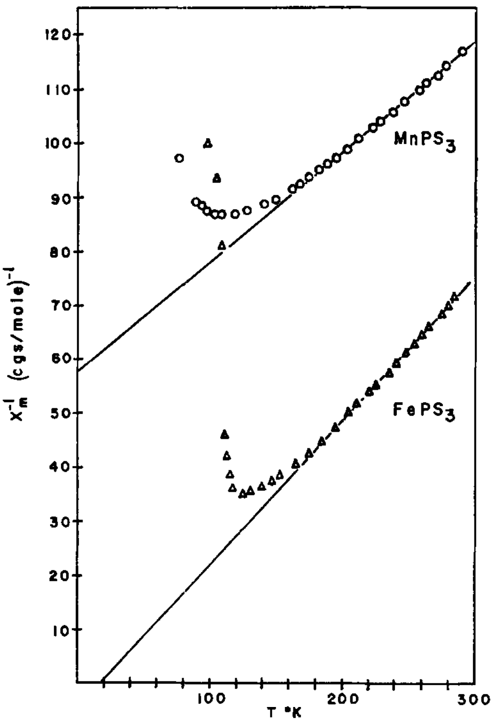

FIG. 2. Reciprocal molar susceptibility versus temperature (°K) for MnPS$_3$ and FePS$_3$.

clinic space group C2/m, as previously reported by Klingen et al. (*3*). A detailed single crystal structure analysis of FePS$_3$ carried out by Klingen (*6*) has shown that the structure is closely related to the cadmium chloride layer structure. The powder diffraction patterns and Weissenberg photographs of MnPS$_3$ and NiPS$_3$ show that they are isostructural with FePS$_3$. Table III gives the *hkl* values and observed and calculated $\sin^2\theta$ values for each compound.

TABLE V

MÖSSBAUER EFFECT DATA

T°K	Isomer shift[a] (mm/sec)	Quadrupole splitting (mm/sec)	Intensity ratio
296	1.13(2)	1.525(9)	0.56
195	1.18(2)	1.180(9)	0.58

[a] Isomer shift relative to sodium iron (III) nitropentacyanide dihydrate.

Magnetic susceptibility measurements indicate that MnPS$_3$, FePS$_3$, and NiPS$_3$ are antiferromagnetic with Neél temperatures of 110(1)°, 126(1)°, and 253(9)°K, respectively. The Weiss constants (θ) for each compound are −263(14)°, +14(6)°, and −558(69)°K, and the magnetic moments determined in the paramagnetic region are 6.20(5), 5.43(6), and 3.68(13)BM, respectively. These moments indicate the presence of significant spin-orbit coupling, but the values are within the range expected for the high-spin divalent metal ions in a nearly octahedral environment. Magnetic data for each sample are presented in Table IV. Plots of χ_m^{-1} versus T°K

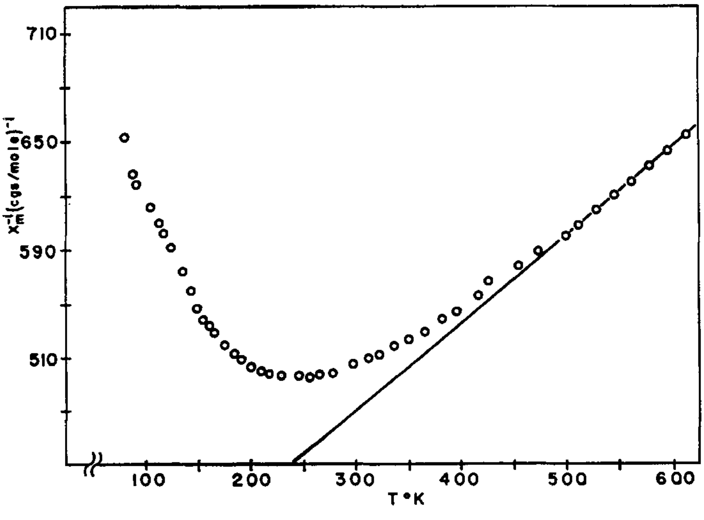

FIG. 3. Reciprocal molar susceptibility versus temperature (°K) for NiPS$_3$.

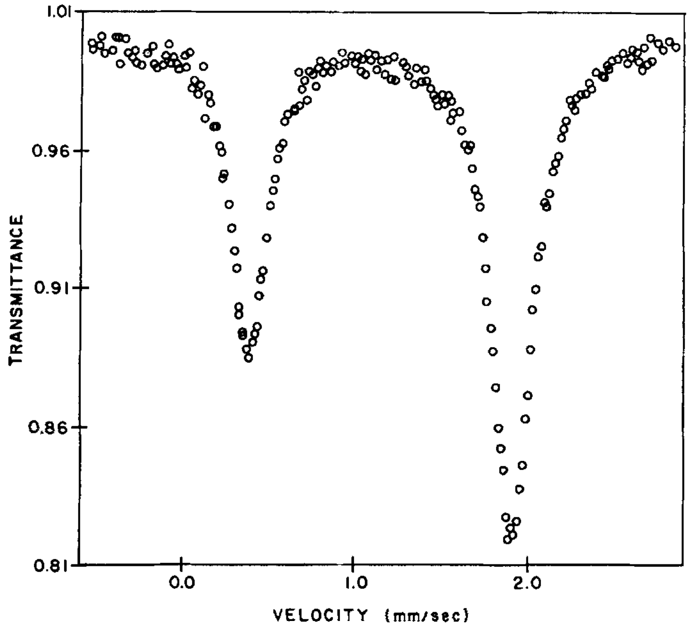

FIG. 4. Mössbauer spectrum of $FePS_3$ taken at 296°K.

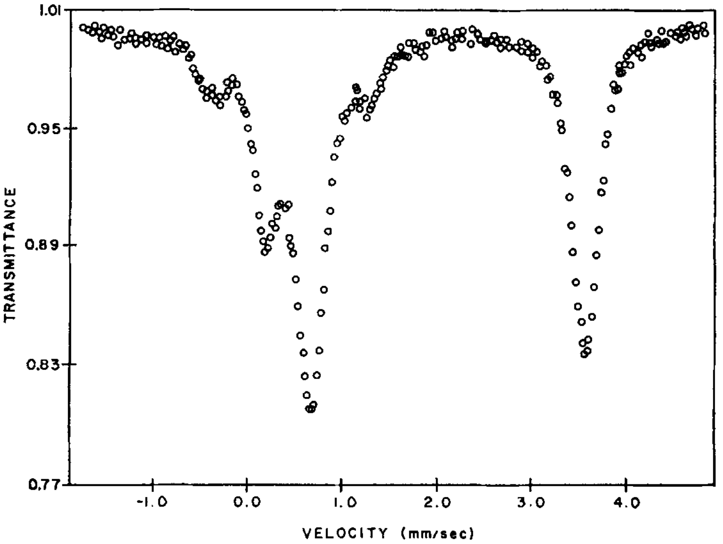

FIG. 5. Mössbauer spectrum of $FePS_3$ taken at 77°K.

for $MnPS_3$ and $FePS_3$, and for $NiPS_3$, are illustrated in Figs. 2 and 3. Honda-Owen plots (*12*) of all samples were made to determine the presence of any ferromagnetic impurity. In all cases no ferromagnetic impurity was detectable.

The Mössbauer absorption spectra at 296° and 77°K for a single crystal sample of $FePS_3$ oriented with the crystallographic c^* axis parallel to γ are illustrated in Figs. 4 and 5. The spectrum observed at 296°K is well resolved and assignable on the basis of the crystal structure, as a quadrupole split pair resulting from a noncubic (C_2) crystalline field about the iron(II) ion. The values for the quadrupole splitting, isomer shift, and intensity ratio are given in Table V. The spectrum at 77°K, which is well below the Neél point, is indicative of a magnetically ordered material. The presence of only five lines, rather than the characteristic six, is explainable on the basis of a degeneracy between transition energies. For example, an energy level diagram for $H \| V_{zz}$, $\eta = 0$, and $e^2Qq/2 > 0$ will have two equal energy transitions when $e^2Qq/2 = g_0\beta_n H$. Such an energy level scheme very nearly accounts for the eigenvalues of the observed hyperfine spectrum.

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