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Synthesis and Structure Determination of a New Layered Compound: $V_2P_4S_{13}$

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$V_2P_4S_{13}$ was prepared from the elements taken in stoichiometric proportions and heated in an evacuated Pyrex tube for 10 days at 450°C. The crystal symmetry is triclinic, space group $P\bar{1}$ with the parameters: $a = 9.112(1)$ Å, $b = 9.680(1)$ Å, $c = 11.620(1)$ Å, $\alpha = 72.15(1)°$, $\beta = 110.82(1)°$, $\gamma = 110.13(1)°$, $V = 879.5(1)$ Å^3, and $Z = 2$. The structure was solved from 3052 independent reflections and 173 parameters, the least-squares refinement yielding $R = 0.033$. The building units of the structure are made up of two distorted (VS_6) octahedra and four distorted (PS_4) tetrahedra sharing edges to form $(V_2P_4S_{16})$ groups. These share sulfur atoms through their four (PS_4) tetrahedra with the same neighbor groups. Infinite $(V_2P_4S_{13})$ planes parallel to (101) are thus obtained, with no bonds other than van der Waals' ones between them. Within the slabs, the layered phase presents the following average distances: $d_{V-S} = 2.471(1)$ Å, $d_{P-S} = 2.050(1)$ Å, $d_{V-V} = 3.715(2)$ Å. From the various oxydation states of the atoms, the developed formula can be written $V_2^{III}P_4^{V}S_{13}^{-II}$. The phase is semiconducting and magnetic susceptibility measurements show a Curie behavior with the occurrence of high spin d^2 vanadium. Antiferromagnetic ordering is observed below 10 K.

1. Introduction

Low-dimensional structures are encountered for most of the *M*–P–S phases (*M* being a transition metal) in relation with the strongly covalent character of the chemical bonds (*1–8*). This is indeed the case in the V–P–S system where three compounds have already been reported: (2D) VPS_3 (*3*), (2D) $P_{0.2}VS_2$ (*9, 10*), and (1D) PV_2S_{10} (*11*). The first two phases are derivatives of the $CdCl_2$ and CdI_2 structural types, respectively. Whereas thiohypodiphosphates $(P_2S_6)^{-IV}$ (anionic groups with P–P bonds) are found in VPS_3, $P_{0.2}VS_2$ contains a (PS_3) quasiflat triangular arrangement. In both compounds only S^{-II} anions are found, with vanadium cations lying, within the slabs, in octahedral sulfur environment. One-dimensional PV_2S_{10} is a more complex case with the occurrence of (PS_4) tetrahedra, the vanadium atoms being located in bicapped trigonal prisms. In contrast with both other compounds, this structure contains mono- and polyanionic sulfur species. In this V–P–S system it thus appears possible to vary not only the oxidation state of the transition metal, but also that of phosphorus and sulfur through catenation of these elements, and thus to synthesize new materials. Since the use of one- or two-dimensional oxidizing phases is of great potential interest for a secondary lithium battery operating at room temperature, the vanadium–phosphorus–sulfur system was further explored and the new layered compound $V_2P_4S_{13}$ was

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found. Its synthesis and structure determination are described below.

2. Experimental

By heating, in an evacuated and sealed Pyrex tube, stoichiometric proportions of pure elemental vanadium, phosphorus, and sulfur at 450°C for 10 days, followed by a 10-hr slow cooling, long black crystals of the phase are obtained. Their analysis by means of a microprobe (microsonde Ouest CNEXO) using a VPS_3 crystal as standard (Table I) corresponds to the formula $V_2P_4S_{13}$. Cell parameters determined on a CAD4 diffractometer indicate a triclinic cell; a Delaunay reduction did not yield higher symmetry. The triclinic parameters were least-squares refined with Guinier powder data (Guinier Nonius FR 552, $CuK\alpha_1$ = 1.54051 Å, Si as standard) (Table I) using the first 100 reflexions. Table II gathers the observed and calculated d_{hkl} interplanar distances along with the intensities calculated with the Lazy Pulverix program (*12*). Because of heavy twinning, sorting out a proper crystal for intensity data recording proved to be very hard. Only by taking advantage of the easy splitting of the samples was it possible to obtain an untwinned, very flat crystal (Table I). As with other low-dimensional compounds (*11, 13, 14*), cutting the crystal proved impossible without bending or damaging it. For that reason, and also because of the low absorption factor and the small other dimensions of the crystal, no absorption correction was made. The growth axis of the samples was found to be $[11\bar{1}]$.

TABLE I

ANALYTICAL AND CRYSTALLOGRAPHIC DATA. PARAMETERS OF THE X-RAY DATA COLLECTION AND REFINEMENT

1. Physical, crystallographic, and analytical data

Formula: $V_2P_4S_{13}$ ($V_2^{III}P_4^{V}S_{13}^{-II}$), Molecular weight: 642.61

Theoretical weight fraction concentration:
P 19.3%,, V 15.8%, S 64.9%

Microprobe analysis (average on 20 analysis points):
P 19.9%, V 15.5%, S 64.9%

Crystal symmetry: triclinic. Space group: $P\bar{1}$

Cell parameters (293 K):
a = 9.112(1)Å b = 9.680(1)Å c = 11.620(1)Å
α = 72.15(1)° β = 110.82(1) γ = 110.13(1)
V = 879.5(1)Å^3 Z = 2

Density: ρ_{calc} = 2.427

Absorption factor: $\mu(\lambda MoK\alpha)$: 28.54 cm^{-1}

Crystal size: 0.1 × 0.01 × 0.5 mm^3

2. Data collection

Temperature: 293 K. Radiation: $MoK\alpha$

Monochromator: oriented graphite (002). Scan mode: $\omega/2\theta$

Recording angle range: 3–30°. Scan angle: 1.2 + 0.347 tan θ

Values determining the scan speed:
SIGPRE 1.0, SIGMA 0.010, VPRE = 5 min^{-1}, T_{MAX} = 120 sec

Standard reflexion: $15\bar{2}$, $\bar{3}22$, $40\bar{2}$. Periodicity: 7200 sec

3. Refinement conditions

Reflections for the refinement of the cell dimensions: 25

Recorded reflections in the half-space: 10,658

Utilized reflections: 3052 with $I > 5\sigma(I)$

Refined parameters: 173

Reliability factors: $R = \Sigma|F_0| - |F_c|/\Sigma|F_0|$
$R_\omega = [\Sigma_\omega(|F_0| - |F_c|)^2/\omega F_0^2]^{1/2}$ with $\omega = 1$

4. Refinement results

$R = 0.033$, $R_\omega = 0.038$

Extinction coefficient: $E_c = 4.9 \times 10^{-8}$

Difference Fourier maximum peak intensity: 0.8(2) $e^-/Å^3$

3. Structure Refinement

Programs used belong to the SDP-PLUS package (1982 version) distributed by ENRAF-NONIUS and written by Frenz (*15*). A statistical test showed $V_2P_4S_{13}$ to be centrosymmetric. However, because of the difficulty in determining Patterson coordinates of equivalent atoms, refinement was started from three carefully chosen noncentrosymmetric atomic positions and conducted in space group P_1. A series of Fourier and Fourier difference maps helped introduce other atoms. A cell inversion

TABLE II

$V_2P_4S_{13}$ X-RAY POWDER DIFFRACTION DATA. INTENSITIES ARE THOSE CALCULATED WITH LAZY PULVERIX PROGRAM

d_{obs} (Å)	d_{calc} (Å)	*hkl*	100 I/I_0[a]
7.648	7.651	011	8.6
7.036	7.028	$\bar{1}10$	7.0
6.197	6.204	$01\bar{1}$	16.7
5.767	5.764	101	100.0
5.427	5.424	$\bar{1}12$	2.8
5.368	5.366	110	8.7
4.995	5.002	$1\bar{1}1$	6.0
4.741	4.738	$\bar{1}21$	14.8
4.682	4.685	111	4.0
4.516	4.515	$\bar{2}11$	2.6
4.251	4.251	201	2.9
4.176	4.172	$\bar{2}10$	3.0
3.884	3.884	$11\bar{2}$	7.2
3.852	3.850	$\bar{1}13$	0.6
3.824	3.826 3.823	022 $02\bar{1}$	4.5
3.700	3.701	$\bar{2}22$	2.0
3.648	3.647	$1\bar{2}1$	6.0
3.538	3.536 3.540	120 003	3.5
3.431	3.433	$\bar{1}23$	2.1
3.402	3.403 3.401	121 210	8.2
3.311	3.309	$12\bar{1}$	1.5
3.219	3.224	$\bar{1}31$	0.8
3.113	3.116	$\bar{1}32$	0.3
3.100	3.102 3.104	$02\bar{2}$ 023	1.4
3.084	3.084	$21\bar{2}$	1.1
3.056	3.056	$\bar{1}30$	6.9
3.024	3.022 3.022	$\bar{3}11$ 031	7.6
2.975	2.976	$\bar{2}32$	2.5
2.964	2.964 2.962	103 030	3.0
2.890	2.889	$\bar{3}22$	8.9
2.869	2.871	$\bar{3}21$	3.0
2.853	2.854 2.851	032 $\bar{3}01$	2.4
2.799	2.800 2.801	$\bar{1}33$ $2\bar{1}2$	7.0
2.774	2.775	$\bar{2}30$	3.4
2.760	2.762 2.762	$\bar{1}04$ $\bar{2}33$	14.1
2.714	2.712 2.714	$\bar{2}24$ $1\bar{3}1$	8.7
2.657	2.655	004	3.1
2.582	2.583	$\bar{2}04$	4.6
2.562	2.561 2.561	131 $\bar{3}32$	13.3
2.538	2.536	$\bar{3}03$	4.7
2.513	2.512	$\bar{3}31$	6.9
2.483	2.486	$31\bar{1}$	1.1
2.467	2.468	$\bar{3}33$	1.7
2.450	2.450	$22\bar{2}$	0.7
2.445	2.455	$12\bar{3}$	0.6
2.425	2.426	$\bar{1}34$	2.0
2.404	2.403 2.400	$\bar{1}41$ $31\bar{2}$	1.3
2.371	2.369	$\bar{2}42$	1.1
2.342	2.344 2.342 2.343	$1\bar{3}2$ 104 222	9.1
2.261	2.261	$\bar{1}43$	1.6
2.238	2.237 2.238	$13\bar{2}$ $\bar{4}11$	1.6
2.222	2.223 2.222 2.221	034 042 040	1.2
2.180	2.180 2.179	$\bar{4}13$ $\bar{3}42$	2.0
2.143	2.144 2.143	$2\bar{3}2$ $\bar{3}43$	0.3
2.124	2.126 2.124 2.124 2.124	$\bar{4}02$ $\bar{3}25$ $\bar{4}32$ $1\bar{4}1$	8.4
2.109	2.108	231	4.8
2.068	2.069 2.068 2.069 2.067	$\bar{1}44$ $03\bar{3}$ $\bar{4}24$ $\bar{4}31$	6.3
2.026	2.027	$2\bar{4}1$	0.2
2.015	2.016 2.014 2.014	$1\bar{3}3$ 140 $11\bar{5}$	1.6
1.9418	1.9422	$22\bar{4}$	1.3
1.9375	1.9373 1.9364	$41\bar{1}$ $14\bar{1}$	3.0
1.9136	1.9130 1.9128 1.9126 1.9139	421 044 $\bar{4}43$ 216	1.4
1.9027	1.9024 1.9020	$32\bar{3}$ $\bar{4}04$	1.6
1.8963	1.8956 1.8963	$\bar{1}26$ $\bar{2}53$	0.6
1.8599	1.8596 1.8599 1.8600 1.8591	125 $\bar{1}45$ $\bar{1}53$ $\bar{4}41$	5.4
1.8539	1.8539 1.8541	$\bar{3}26$ $\bar{4}35$	1.7
1.8451	1.8446	$\bar{3}52$	0.0
1.8318	1.8315	$23\bar{3}$	1.3
1.7749	1.7754 1.7752	$\bar{5}13$ $\bar{3}54$	0.6
1.7332	1.7335	$1\bar{5}1$	1.8

[a] Calculated intensities.

center could be found from 30 atoms and the refinement was achieved in $P\bar{1}$ to $R = 9.1\%$ with isotropic thermal factors and the whole set of atoms corresponding to the stoichiometric analytical formula $V_2P_4S_{13}$. With anisotropic thermal factors, the reliability factor then dropped to 3.3%, the Fourier difference map being then featureless (Table I).

In Tables III and IV the list of the final fractional coordinates of the 19 independent atoms of the cell can be found.[1]

4. General Structure Features

The slabs of the two-dimensional $V_2P_4S_{13}$ structure are parallel to (101) (Fig. 1). A projection in that plane and perpendicular to it are shown in Figs. 2 and 3, respectively.

The structure can be conveniently described from a constitutive ($V_2P_4S_{16}$) unit formed with two (VS_6) octahedra and four (PS_4) tetrahedra (Fig. 4). The octahedra share a sulfur–sulfur edge with each other with the tetrahedra situated on both extremities of the unit, while the two other (PS_4) groups situated above and below that unit have two S–S edges in common with the (VS_6) groups. To obtain the ($V_2P_4S_{13}$) slabs, the ($V_2P_4S_{16}$) units are bonded to one another via six apical sulfur atoms belonging to the (PS_4) tetrahedra and in the way indicated on Fig. 4. All the (PS_4) tetrahedra of the whole structure have hence one or two apex sulfur atoms in common (Fig. 2). The layer thus formed presents a thickness of approximately 3.6 Å, whereas the van der Waals' gap width is estimated to be about 3.0 Å (Fig. 3).

TABLE III

Positional Parameters and Their Estimated Standard Deviations

Atom	*X*	*Y*	*Z*	*B* (Å²)
V1	0.8960(1)	0.50639(9)	0.10937(8)	1.24(2)
V2	0.6012(2)	0.99209(9)	0.38991(8)	1.26(2)
P1	0.2227(2)	0.0653(1)	0.7521(1)	1.22(2)
P2	0.2406(2)	0.4286(1)	0.7223(1)	1.28(2)
P3	0.4982(2)	0.2580(1)	0.3914(1)	1.32(2)
P4	0.1280(2)	0.7676(1)	0.9790(1)	1.26(2)
S1	0.9001(2)	0.7654(1)	0.3530(1)	1.45(2)
S2	0.6946(1)	0.2932(1)	0.0428(1)	1.58(2)
S3	0.4625(2)	0.1345(1)	0.7835(1)	1.66(2)
S4	0.6560(1)	0.1548(1)	0.5409(1)	1.41(2)
S5	0.0854(1)	0.3646(1)	0.1139(1)	1.37(2)
S6	0.4263(3)	0.5058(1)	0.6303(1)	2.46(3)
S7	0.8687(1)	0.0876(1)	0.3559(1)	1.43(2)
S8	0.0866(2)	0.5578(1)	0.6662(1)	1.59(2)
S9	0.1441(2)	−0.0006(1)	0.9167(1)	2.19(3)
S10	0.6759(2)	0.6128(1)	0.0913(1)	1.68(2)
S11	0.7058(2)	0.7935(2)	0.5582(1)	1.74(3)
S12	0.5243(2)	0.8180(1)	0.7586(1)	1.77(3)
S13	0.8802(2)	0.2682(2)	0.8440(1)	1.65(2)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent, thermal parameter defined as $(4/3)\,[a^2 \cdot B(1,1) + b^2 \cdot B(2,2) + c^2 . B(3,3) + ab(\cos\gamma) \cdot B(1,2) + ac(\cos\beta) \cdot B(1,3) + bc(\cos\alpha) \cdot B(2,3)]$.

5. Structural Results and Discussion

Table V gathers the main interatomic angles and distances encountered in the $V_2P_4S_{13}$ structure. From these data, the occurrence of polyanionic species can be ruled out since the shortest sulfur–sulfur distance is equal to 3.182 Å (S9–S13). In the M–P–S compounds, phosphorus atoms in tetrahedral sulfur coordination have al-

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[1] Tables of observed and calculated structure factors are deposited with the National Auxiliary Publications Service. See NAPS document No. 04222 for 16 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE IV

REFINED TEMPERATURE FACTOR EXPRESSIONS (BETA'S)

Name	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
V1	0.00554(8)	0.00327(7)	0.00330(5)	0.0023(1)	0.00459(9)	−0.00123(9)
V2	0.00525(8)	0.00354(7)	0.00341(5)	0.0022(1)	0.00470(9)	−0.00113(9)
P1	0.0059(1)	0.0023(1)	0.00362(8)	0.0020(2)	0.0051(1)	−0.0007(1)
P2	0.0064(1)	0.0022(1)	0.00396(8)	0.0016(2)	0.0064(1)	−0.0007(1)
P3	0.0062(1)	0.0026(1)	0.00399(8)	0.0022(2)	0.0064(2)	0.0001(2)
P4	0.0064(1)	0.0024(1)	0.00347(8)	0.0016(2)	0.0057(2)	−0.0005(1)
S1	0.0063(1)	0.0026(1)	0.00427(8)	0.0027(2)	0.0036(2)	−0.0011(1)
S2	0.0056(1)	0.0043(1)	0.00502(8)	0.0011(2)	0.0057(2)	−0.0033(1)
S3	0.0057(1)	0.0053(1)	0.00440(8)	0.0016(2)	0.0036(2)	−0.0040(2)
S4	0.0053(1)	0.0040(1)	0.00372(8)	0.0015(2)	0.0039(2)	−0.0018(1)
S5	0.0057(1)	0.0040(1)	0.00320(8)	0.0034(2)	0.0032(2)	−0.0010(1)
S6	0.0134(1)	0.0026(1)	0.0093(1)	0.0018(2)	0.0186(2)	−0.0008(2)
S7	0.0056(1)	0.0029(1)	0.00464(8)	0.0006(2)	0.0052(2)	−0.0024(1)
S8	0.0095(1)	0.0036(1)	0.00342(8)	0.0065(2)	0.0057(2)	0.0005(1)
S9	0.0148(2)	0.0027(1)	0.00621(9)	0.0046(2)	0.0148(2)	0.0007(2)
S10	0.0066(1)	0.0053(1)	0.00431(9)	0.0051(2)	0.0034(2)	0.0024(2)
S11	0.0063(1)	0.0053(1)	0.00473(9)	0.0051(2)	0.0071(2)	0.0019(2)
S12	0.0095(1)	0.0052(1)	0.00347(8)	0.0070(2)	0.0052(2)	0.0002(2)
S13	0.0073(1)	0.0046(1)	0.00360(8)	−0.0004(2)	0.0056(2)	−0.0025(2)

Note. The form of the anisotropic thermal parameter is: $\exp[-B(1,1) \cdot H^2 + B(2,2) \cdot K^2 + B(3,3) \cdot L^2 + B(1,2) \cdot HK + B(1,3) \cdot HL + B(2,3) \cdot KL)]$.

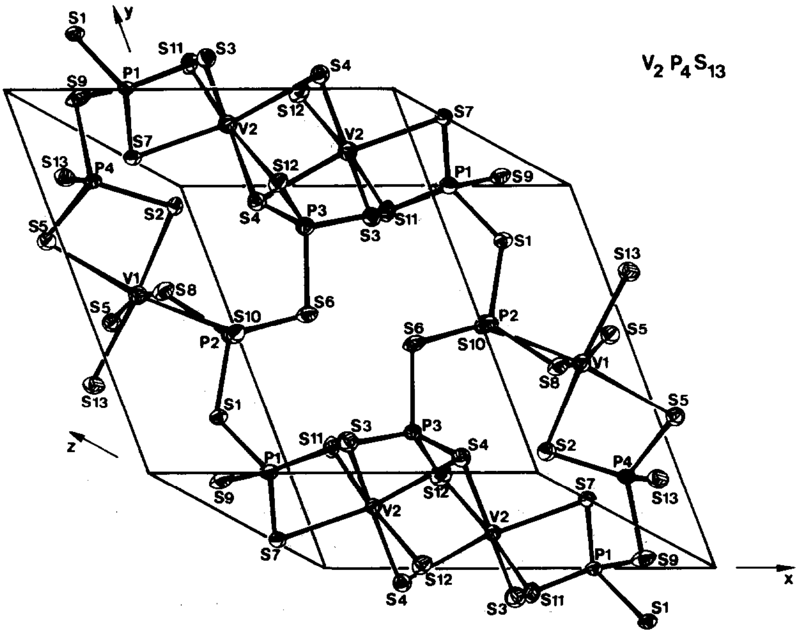

FIG. 1. Perspective view of $V_2P_4S_{13}$ structure.

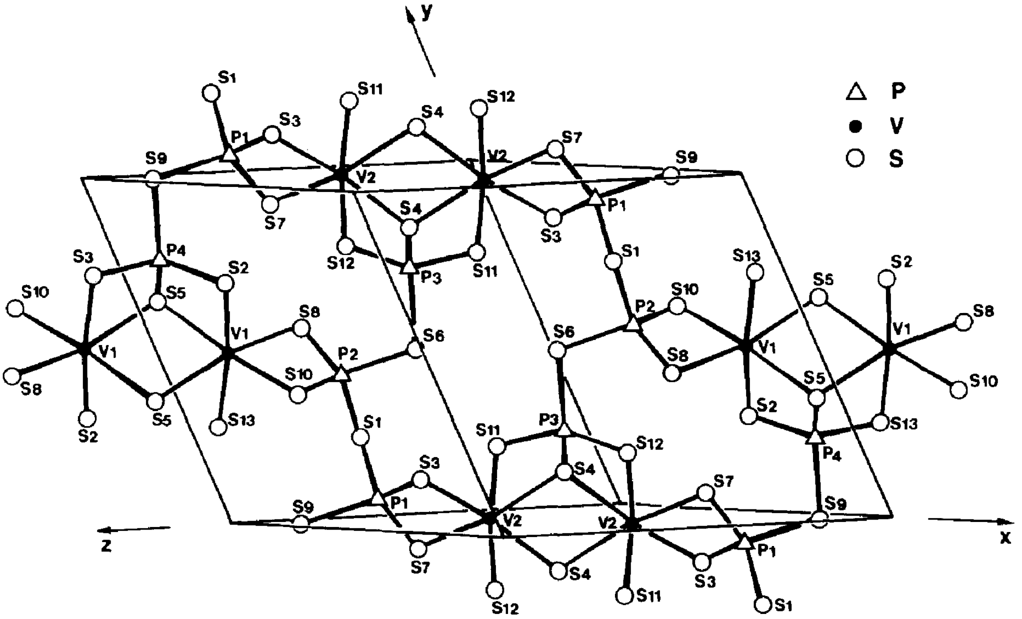

FIG. 2. Perspective drawing of $V_2P_4S_{13}$ structure perpendicularly to the slabs.

ways been found as P^V cationic species (*11, 13, 14, 16, 17*). Assuming the same behavior, the developed formula for the phase can be written $V_2^{III}P_4^{V}S_{13}^{-II}$, the charge balance being achieved with V^{III} cations. This result is in agreement with the average V^{III}–S distance of 2.471 Å intermediate between a V^{IV}–S distance of 2.459 Å (PV_2S_{10} (*11*)) or of 2.433 Å (VS_4 (*18*)) and a V^{II}–S distance of 2.49 Å calculated in VPS_3 (*19*). Moreover, using the effective S^{-II} ionic radius value of 1.84 Å, a cationic radius of 0.63 Å is found for vanadium, in very good accord with that of octahedrally coordinated V^{III} in

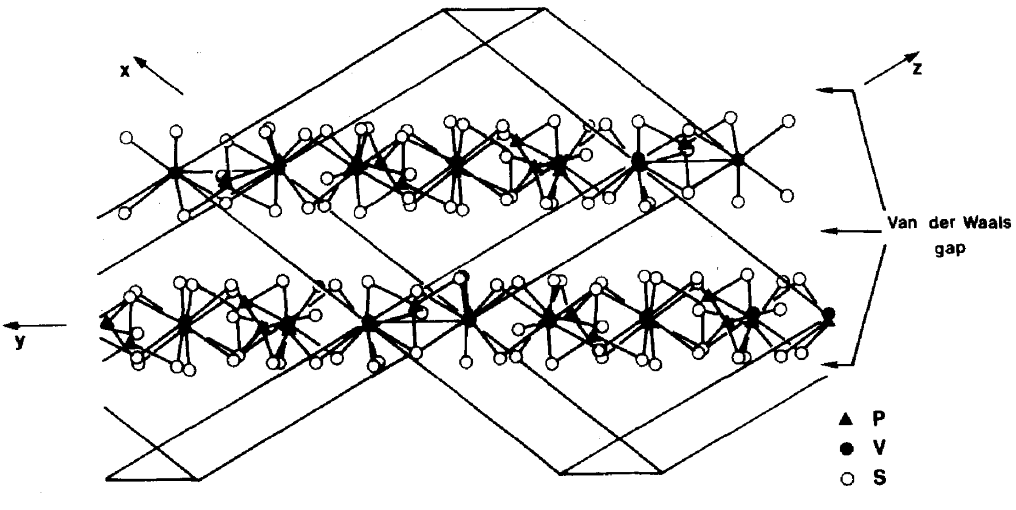

FIG. 3. Perspective drawing showing the sandwich structure of $V_2P_4S_{13}$.

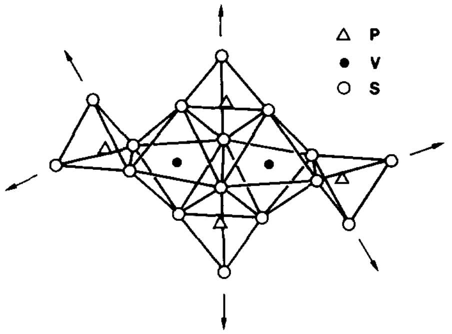

FIG. 4. ($V_2P_4S_{16}$) constitutive units encountered in $V_2P_4S_{13}$. Arrows indicate the bond directions with neighbor units.

TABLE V

(a) Main Interatomic Distances (Å) in (VS_6) and (PS_4)
(ESD between Brackets)

V1–S2 : 2.364(1)	P1–S1 : 2.120(1)	P3–S4 : 2.057(1)
V1–S5 : 2.527(1), 2.550(1)	P1–S3 : 1.982(1)	P3–S6 : 2.109(1)
V1–S8 : 2.448(1)	P1–S7 : 2.002(1)	P3–S11 : 2.001(1)
V1–S10 : 2.474(1)	P1–S9 : 2.119(1)	P3–S12 : 2.012(1)
V1–S13 : 2.468(1)		
	P2–S1 : 2.119(1)	P4–S2 : 2.015(1)
V2–S3 : 2.469(1)	P2–S6 : 2.119(1)	P4–S5 : 2.056(1)
V2–S4 : 2.518(1), 2.550(1)	P2–S8 : 2.003(1)	P4–S9 : 2.106(1)
V2–S7 : 2.421(1)	P2–S10 : 1.985(2)	P4–S13 : 2.004(1)
V2–S11 : 2.462(1)		
V2–S12 : 2.401(1)		
Average d_{V-S} = 2.471	Average d_{P-S} = 2.050	
V1–V1 : 3.721(1)	P1–P4 : 3.353(1)	
V2–V2 : 3.709(1)	V1–P2 : 2.966(1)	
	V1–P4 : 3.040(1), 3.067(1)	
P1–P2 : 3.379(1)	V2–P1 : 2.943(1)	
P2–P3 : 3.379(1)	V2–P3 : 3.034(1), 3.082(1)	

(b) Main Angles (°) in (VS_6) and (PS_4) Polyhedra
(ESD between Brackets)

S2–V1–S5 : 82.48(4), 92.58(4)	S8–V1–S10 : 82.94(4)
S2–V1–S8 : 100.59(4)	S8–V1–S13 : 81.05(4)
S2–V1–S10 : 88.58(4)	S10–V1–S13 : 95.66(4)
S5–V1–S5 : 99.33(4)	S2–V1–S13 : 172.56(4)
S5–V1–S8 : 99.33(5)	S5–V1–S10 : 171.03(4)
S5–V1–S10 : 93.16(4), 81.05(4)	S8–V1–S5 : 166.38(4)
S5–V1–S13 : 94.02(4)	
S3–V2–S7 : 83.23(4)	S12–V2–S4 : 92.86(4), 82.64(4)
S3–V2–S4 : 96.63(4)	S12–V2–S3 : 88.92(4)
S4–V2–S4 : 85.91(4)	S12–V2–S7 : 99.50(4)
S4–V2–S7 : 96.07(4)	S11–V2–S12 : 172.52(4)
S11–V2–S4 : 93.11(4), 80.66(4)	S3–V2–S4 : 171.30(5)
S11–V2–S3 : 95.50(4)	S4–V2–S7 : 167.63(4)
S11–V2–S7 : 87.03(4)	
S1–P1–S3 : 114.47(6)	S4–P3–S6 : 112.03(7)
S1–P1–S9 : 99.86(6)	S4–P3–S11 : 106.13(6)
S1–P1–S7 : 103.60(6)	S4–P3–S12 : 105.94(6)
S3–P1–S7 : 109.22(6)	S6–P3–S11 : 101.56(6)
S3–P1–S9 : 114.18(7)	S6–P3–S12 : 115.17(6)
S7–P1–S9 : 114.87(6)	S11–P3–S12 : 115.81(7)
S1–P2–S6 : 99.75(6)	S2–P4–S5 : 104.83(6)
S1–P2–S8 : 109.01(6)	S2–P4–S9 : 114.13(6)
S1–P2–S10 : 114.10(6)	S2–P4–S13 : 116.37(7)
S6–P2–S8 : 115.25(6)	S5–P4–S9 : 113.28(7)
S6–P2–S10 : 113.49(7)	S5–P4–S13 : 106.87(6)
S8–P2–S10 : 109.63(6)	S9–P4–S13 : 101.44(6)

chalcogenides (r = 0.64 Å) as published by Shannon (*20*). Interatomic angles and distances (Table V) also indicate a fairly strong distortion of the polyhedra. In that respect, a short phosphorus–sulfur distance (P1–S3 = 1.982(1) Å) is calculated. Such a small bonding length in tetrahedral (PS_4) groups had already been reported in (3D) P_2NbS_8 (*21*) (d_{P-S} = 1.981(1) Å). Nevertheless, because of other elongated bonds, the average P–S distance (d_{P-S} = 2.050 Å) fall in line with the expected mean value of more regular groups. The shortest distances between V^{III} cations are equal to 3.721(1) Å and 3.709(1) Å and correspond to the two edge-sharing (VS_6) octahedra of the $V_2P_4S_{16}$ units.

The second vanadium intraplanar neighbors are found quite away at distances $d \geq$ 5.450 Å, while the intermetallic distances of the vanadium interplanar neighbors are found at lengths $d \geq$ 6.715 Å.

Such structural features of the cationic array imply a weak direct V^{III}–V^{III} magnetic coupling and exclude any cationic orbital overlapping within the whole structure. From these observations an insulating or semiconducting behavior can be inferred for the phase, with localized magnetic moments. The resistivity measured on a single crystal along the growing axis shows indeed $V_2P_4S_{13}$ to be highly resistant ($\rho > 10^9$ Ω cm at 298 K). The molar reciprocal susceptibility variation versus temperature in the 5–298 K range is shown on Fig. 5. The curve follows a Curie law at high temperature and exhibits a magnetic ordering below 10 K. The phase behavior is characteristic of (2D) magnetic systems, with a very flat minimum of χ^{-1}. As has been demonstrated in particular with the *M*PS_3 layered family (*22, 23*) this minimum cannot be considered as the actual ordering temperature be-

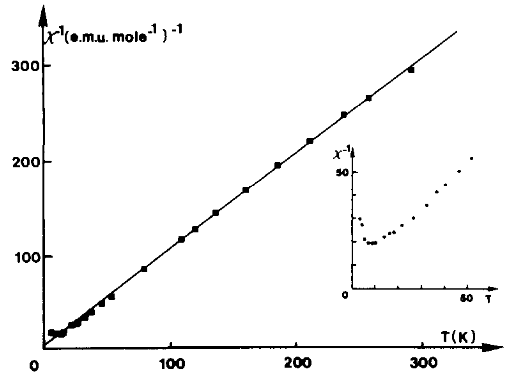

FIG. 5. Reciprocal molar magnetic susceptibility (corrected for core diamagnetism) versus temperature of $V_2P_4S_{13}$ in the range 5–295 K. (Magnetic susceptibility calculated for one vanadium mole.) Expanded low-temperature portion of $\chi^{-1} = f(T)$ on the right side.

cause of the quasibidimensional magnetic interactions encountered in such compounds. In the paramagnetic region an effective magnetic moment $\mu_{eff} = 2.82$ B.M. is observed corresponding to a calculated spin only magnetic moment of $\mu_{calc} = 2.83$ B.M. for a high-spin V^{III} cationic species. These results fit with the structural conclusions and confirm the occurrence of isolated d^2 vanadium cations; the Weiss constant ($\theta = -6$ K) indicating in addition very weak magnetic interactions.

Whereas the average isotropic equivalent thermal parameter for the anions is equal to 1.62 Å^2, that of two sulfur atoms (Table III) (S6 and S9) are found equal to 2.46 and 2.19 Å^2, respectively, in relation with the strong values of $B(1,1)$ and $B(1,3)$. To a lesser degree, such a phenomenon can be pointed out in (1D) PV_2S_{10} (*11*). In neither case it is possible, from the above structural feature considerations, to explain these observations.

Conclusion

Combination of various transition metal and phosphorus–sulfur polyhedra along with changes in the element oxydation state open the door to preparations of many new materials in M–P–S systems. This is clearly illustrated with vanadium. $V_2P_4S_{13}$ being the fourth phase discovered following VPS_3, $P_{0.2}VS_2$, and PV_2S_{10}. An attractive feature of the new phase lies in its sandwich structure, that, provided it be a good oxidizing material, makes it a potential candidate for electrochemical applications. From a chemical point of view, the occurrence of an M^{III} octahedrally coordination cation species should authorize the synthesis of a whole $M_2P_4S_{13}$ family. This is currently under way with further magnetic studies of $V_2P_4S_{13}$.

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