JOURNAL OF SOLID STATE CHEMISTRY 102, 390–399 (1993)

The Interlocked Structure of a New Thiophosphate of Transition Metal CrP_3S_{9+x} ($x \approx 0.25$)

P. FRAGNAUD, M. EVAIN,* E. PROUZET, AND R. BREC

Laboratoire de Chimie des Solides, I.M.N., CNRS UMR 110, 2 rue de la Houssinière, 44072 Nantes Cedex 03, France

Received January 23, 1992; in revised form June 26, 1992; accepted June 30, 1992

CrP_3S_{9+x} ($x \approx 0.25$) is a new phase obtained by direct synthesis at 450°C. It crystallizes in the orthorhombic *Fddd* space group with $a = 1938.22(12)$ pm, $b = 2022.30(13)$ pm, $c = 1370.54(8)$ pm, $V = 5372.0(10) \times 10^6$ pm^3, and $Z = 16$. The structure, refined to a reliability factor of $R_F = 3.4\%$, is made of three interlocked networks which are constituted by two types of helices rotating in opposite directions. The structure may be decribed as (CrS_6) octahedra and (PS_4) tetrahedra sharing edges. A partial substitution of S^{2-} anions by $(S_2)^{2-}$ pairs is observed. It seems to be important in decreasing the structure strain and in releasing the local stress. Magnetic measurements are in agreement with a semiconducting phase and a d^3 cation corresponding to the charge balance: $Cr^{3+}P_3^{5+}S_{8.75}^{2-}(S_2)_{0.25}^{2-}$. © 1993 Academic Press, Inc.

I. Introduction

The well known $M^{II}PS_3$ compounds (*1–3*) are layered thiophosphates to be found mainly with first row transition metals (M^{II} = Mn, Fe, Co, Ni, Zn). The nonstoichiometry of the vanadium derivative in the series members can be explained through the relative stability of the anionic and cationic electronic bands. Going from $ZnPS_3$ to $MnPS_3$, the transition cation sees its 3*d* molecular orbitals increase in energy. On the left of manganese the induced instability does not allow the formation of $V^{II}PS_3$. Therefore, a nonstoichiometric layered phase, $V_{0.78}PS_3$, is formed instead (*4*) in which proper stability is achieved through the occurrence of V^{III} ions that lower the electronic energy, with the charge balance $V^{II}_{0.34}V^{III}_{0.44}[\ \ ]_{0.22}PS_3$.

The phase is further stabilized by electron hopping between V^{II} and V^{III}. Of course, for the next transition element, titanium, the oxidation state still increases and it is a Ti^{IV} cation which is found. A tridimensional phase $Ti_{1/2}PS_3$ is then formed with, however, the same $(P_2S_6)^{4-}$ anionic group as in the MPS_3 compounds (*5*). One has, in the 2-D thiophosphate family, a situation similar to that of the dichalcogenide group in which the MX_2 phases move from a layered $Ti^{IV}S_2$ structure to a $Fe^{II}S_2$ pyrite one for symmetrical reasons. The case of chromium (in between vanadium and manganese) is somewhat special because of the great stability of Cr^{III} with its spherical d^3 electronic configuration. This explains why no $Cr^{II}PS_3$ phase has been obtained to date. Instead, a $Cr^{III}PS_4$ compound was found (*6*, *7*), again

* To whom correspondence should be addressed.

0022-4596/93 $5.00

with a layered structure but with P^V in inslab tetrahedral sites. It is possible to imagine metal deficient compounds of the MPS_3 type using an M^{III} cation, and $M^{III}_{2/3}[\ ]_{1/3}PX_3$ compounds were indeed obtained with M = In and X = S, Se (*8, 9*). Although the obtainment of an isostructural phase, (2-D) $Cr_{2/3}[\ ]_{1/3}PS_3$, by direct high temperature synthesis is theoretically possible, many attempts failed; a new tridimentional phase, CrP_3S_{9+x} ($x \approx 0.25$), was obtained instead. Its preparation and structure are described in this article.

II. Experimental

Synthesis and analysis. CrP_3S_{9+x} ($x \approx 0.25$) has been obtained in evacuated pyrex tubes by heating the elements in a 1 : 3 : 10 proportion with a small sulfur excess. Too high temperatures led to the formation of $CrPS_4$, a frequent byproduct, but too low ones did not yield a complete reaction of the elements. To obtain good quality single crystals and a phase as pure as possible, a moderate temperature of 450°C was chosen, the reaction time being in the 2 to 5 week range. Under these conditions, dark-brown crystals could be found not only on the tube wall, but also embedded in a homogeneous water-sensitive bulk. Most crystals were separated by letting the bulk react with water. They did not exhibit any layered habits. An electronic microprobe analysis yielded the formulation $CrP_3S_{9.3}$.

X-ray powder data. Because of the systematic presence of $CrPS_4$ as a side product, we had to carefully select small crystals of CrP_3S_{9+x} ($x \approx 0.25$) to run powder diffraction experiments. Powder pattern data were collected on an INEL diffractometer (Debye–Scherrer geometry with a curve position sensitive detector and a monochromated copper radiation, λ = 154.0598 pm). A least-squares refinement ($\delta 2\theta_{av.}$ = 0.0098°) of the F-centered orthorhombic cell parameters, found in a preliminary single crystal study, led to a = 1938.22(12) pm, b = 2022.30(13) pm, c = 1370.54(8) pm, $V = 5372.0(10) \times 10^6$ pm^3, and Z = 16. The rather peculiar $\sqrt{2}\ a/c$ ratio could be interpreted neither in terms of higher symmetry nor as a possible twinning. The indexed diffraction pattern, d_{obs}, and d_{calc}, along with observed and calculated intensities (*10*), are given in Table I.

Single-crystal studies. Weissenberg films were obtained to determine the symmetry and the cell parameters, and to sort out a crystal suitable for data recording. The symmetry appeared to be monoclinic but a Delaunay reduction (*11*) yielded an F centered orthorhombic lattice. Three sets of data (vide infra) were collected on an Enraf–Nonius CAD4 diffractometer. Hereinafter, it is the third recording we refer to, but our last refinement was identical to the two previous ones with the same agreement factors (see Table II for the recording conditions). The intensities of the reflections in the $-35 < h < 35$, $-36 < k < 36$, and $0 < l < 24$ half space were recorded. After the usual reduction (including Lorentz polarization and absorption) of the 9202 raw data, a set of 956 independent reflections with $I > 3\sigma(I)$ were kept for structure refinements.

III. Structure Refinement

All structure refinements and calculations were carried out with the MOLEN package (Enraf–Nonius 1991). A data analysis indicated an *mmm* laue symmetry with the limiting conditions on the reflections $0kl: k + l = 4n$, $h0l: h + l = 4n$ which, combined with the F cell centering, were consistent with the *Fddd* space group. Going through the MULTAN series, direct methods gave a starting set of atomic positions (Table III). An isotropic refinement (28 variables) was conducted which converged to the unweighted and weighted reliability factors $R_F = 0.209$ and $\omega R_{F^2} = 0.272$, respectively. The best agreement factors obtained after

TABLE I

INDEXED DIFFRACTION PATTERN OF CrP_3S_{9+x} ($x \approx 0.25$): I_{calc} CALCULATED FROM THE LAZY PULVERIX PROGRAM (*10*)

$d_{obs.}$ (pm)	$d_{calc.}$ (pm)	h	k	l	$I_{obs.}$	$I_{calc.}$
700.1	699.7	2	2	0	40	81
577.7	577.4	1	3	1	7	21
560.6	559.5	2	0	2	100	100
489.8	489.6	2	2	2	18	1
434.6	434.3	1	1	3	14	25
375.4	375.1	2	4	2	2	3
367.0	366.8	3	1	3	17	2
	366.8	5	1	1		3
332.4	332.6	3	5	1	4	10
326.4	326.4	3	3	3	8	2
311.7	311.6	4	4	2	4	4
307.8	307.7	2	2	4	11	9
	307.7	6	2	0		11
302.5	302.5	0	6	2	11	13
299.2	299.2	1	5	3	32	36
283.6	283.6	0	4	4	7	8
279.7	279.8	4	0	4	6	4
274.0	274.2	3	5	3	7	1
	274.2	5	5	1		6
270.8	270.7	5	3	3	3	5
269.5	269.6	4	2	4	2	2
256.5	256.6	4	6	2	1	1
251.8	251.8	1	3	5	3	2
	251.8	7	3	1		1
250.4	250.4	3	1	5	4	8
244.8	244.8	4	4	4	2	<1
242.2	242.3	8	0	0	10	5
	242.3	1	7	3		4
235.1	235.2	7	1	3	4	3
233.2	233.2	2	6	4	8	10
228.5	228.4	3	7	3	6	5
	228.4	5	7	1		1
225.4	225.4	1	5	5	6	6
222.8	222.8	8	2	2	6	4
220.3	220.3	1	9	1	3	2
214.2	214.1	3	5	5	2	3
206.6	206.6	5	7	3	7	10
203.5	203.5	2	4	6	4	1
	203.4	0	8	4		2
202.5	202.4	4	2	6	1	<1
197.8	197.8	8	0	4	7	2
	197.8	1	7	5		5
	197.8	7	7	1		4
194.0	194.0	0	10	2	2	<1
	193.9	1	1	7		1
	193.9	9	1	3		1
190.2	190.2	2	10	2	2	2
	190.1	3	7	5		1
189.1	189.1	0	6	6	4	2
	189.1	8	6	2		7
187.5	187.6	4	8	4	2	<1
186.5	186.5	6	0	6	2	1
	186.5	10	0	2		2
183.2	183.1	7	7	3	2	<1
181.4	181.4	1	11	1	5	5
175.5	175.5	1	5	7	4	1
	175.5	7	5	5		1
	175.5	9	5	3		2
171.3	171.3	0	0	8	3	2
	171.3	9	7	1		<1
166.4	166.4	2	2	8	1	1
161.5	161.5	4	0	8	5	1
	161.5	7	7	5		2
159.2	159.2	4	12	0	2	1
139.9	139.9	8	0	8	1	<1
139.1	139.2	11	5	5	2	<1
	139.1	9	11	1		1
135.7	135.7	2	0	10	2	<1
	135.7	4	14	2		1

introducing the Atomic Displacement Parameters (ADP is used instead of thermal parameter hereafter because it is more general and includes all sorts of disorders) were $R_F = 0.073$ and $\omega R_{F^2} = 0.102$ with 62 variables. Because of the low absorption coefficient (25.3 cm^{-1}) and the small crystal size ($\approx 0.2 \times 0.3 \times 0.2$ mm^3) the absorption correction did not improve these results. The refinement corresponded to the formulation CrP_3S_9 for the phase. No meaningful residue could be found on the Fourier difference map.

It appeared that two sulfur atoms (S3 and S5) had ADP values much higher (B_{eq}(S3) = 7.55×10^4 pm^2 and B_{eq}(S5) = 10.5×10^4 pm^2) than the average ($B_{eq} = 5.86 \times 10^4$ pm^2), which was itself quite high (see Table III). Because of the correlative high R value, we thought that the chosen symmetry could be wrong. Many refinement attempts with less symmetric space groups (*Fd2d*, *F2dd*,

TABLE II

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

1. Physical, crystallographic and analytical data
   Formula: CrP_3S_{9+x} ($x \approx 0.25$)
   Molecular weight: 441.53 g · mol^{-1}
   Color: dark brown
   Crystal system: orthorhombic
   Space group: *Fddd* (#70)
   Cell parameters (293 K): a = 1938.22(12) pm, b = 2022.30(13) pm, c = 1370.54(8) pm, V = 5372(1) 10^6 pm^3, Z = 16
   Density (calc): 2.18
   Absorption factor: μ(Mo $K\alpha$) = 25.27 cm^{-1}

2. Data collection
   Temperature: 293 K.
   Radiation: Mo $K\alpha$.
   Monochromator: oriented graphite (002).
   Scan mode: ω scan
   Scan angle: 1.8 + 0.35 · tan(θ).
   Recording angle: 1°–40°.
   Standard reflections: (8 0 0), ($\bar{4}$ $\bar{12}$ 0), (5 7 $\bar{3}$) (every 3600 sec)

3. Refinement conditions
   Recorded reflections in the half-space: 9202.
   Independant reflexions ($I/\sigma(I) > 3$): 956.
   Refined parameters: 80.
   Weighting scheme: $1/\sigma^2$.
   Reliability factors: $\omega R_F^2 = \sqrt{\frac{\sum \omega(F_{obs} - |F_{calc}|)^2}{\sum \omega F_{obs}^2}}$ $R_F = \frac{\sum |F_{obs} - |F_{calc}||}{\sum F_{obs}}$ $S = \sqrt{\frac{\sum \omega(F_{obs} - |F_{calc}|)^2}{N - M}}$.

4. Refinement results
   ωR_F^2: 4.4
   R_F: 3.4
   S: 1.123
   Difference Fourier intensity:
   maximum 0.414 × 10^{-6} e^-/pm^3
   minimum −0.404 × 10^{-6} e^-/pm^3

*Fdd*2, *F*222, and monoclinic ones) led to equivalent results. Because the structure is an interlocked one (vide infra), another hypothesis was the existence of a static disorder around an average position, corresponding to a slight shift from one network to another. However, differential scanning calorimetry (DSC) measurements from room temperature down to 70 K exhibited no order–disorder transition peak. In addition, a low temperature ($T \approx 100$ K) X-ray single-crystal determination did not improve the results. A crystal twinning could also have been at the origin of the unacceptable atomic displacement and reliability factors; therefore, in the hope of getting an unbiased sample, several recordings were done on different crystals (hence the three recordings mentioned above). Once again, the same structure characteristics were observed.

New structural hypotheses obviously needed to be introduced. Although the Fourier difference map did not show any

significant maximum, we emitted the idea that some sulfur anions could be partially substituted by S_2 pairs. Indeed, with such a substitution of S^{2-} anions by $(S_2)^{2-}$ pairs, the overall electroneutrality would remain unchanged. The refinement was largely improved (R_F = 0.042) with the substitution of 25% of the S5 atoms by $((S5')_2)^{2-}$ pairs.

This substitution implied a shift of the S3 position to S3′ which was to be added in the structure. This further improved the results with the reliability factors dropping to R_F = 0.034 (ωR_{F^2} = 0.044) and the formulation becoming CrP_3S_{9+x} ($x \approx 0.25$). It was checked with the Hamilton test (*12*) that the parameter increase corresponded to meaningful improvement. All other possible splittings, for instance, that of P atoms, were rejected after refinement procedures demonstrated their unsuitability. The still large but more reasonable ADP can then be understood to result from those substitutions, implying local position modifications too small to be explained when separate atomic positions are taken into account. Final atomic coordinates and ADP values are gathered in Tables IV and V[1]. Main distances and angles are listed in Table VI.

TABLE III

POSITIONAL PARAMETERS OBTAINED WITHOUT TAKING INTO ACCOUNT THE HYPOTHESIS OF SULFUR PAIRS

Atom	τ	X	Y	Z	B_{eq} (10^4 pm^2)
Cr	0.5	$\frac{1}{8}$	0.4039(4)	$\frac{1}{8}$	4.79(6)
P1	1	0.9628(4)	0.1904(4)	0.2721(6)	3.96(5)
P2	0.5	$\frac{1}{8}$	0.5490(7)	$\frac{1}{8}$	5.17(9)
S1	1	0.8633(4)	0.1770(4)	0.2454(6)	4.43(6)
S2	1	0.0218(4)	0.2180(4)	0.1531(6)	4.75(6)
S3	1	0.8637(5)	0.0069(6)	0.2608(8)	7.55(9)
S4	1	0.9970(5)	0.1123(5)	0.3426(7)	5.74(7)
S5	0.5	0.5437(7)	$\frac{1}{8}$	$\frac{1}{8}$	10.5(1)

Note. Isotropic equivalent thermal parameter defined as B_{eq} (pm^2) = $\frac{4}{3}\sum_i\sum_j \beta_{ij}a_ia_j$.

TABLE IV

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATION OF THE FINAL CrP_3S_{9+x} ($x \approx 0.25$) STRUCTURE ARRANGEMENT

Atom	τ	X	Y	Z	B_{eq} (10^4 pm^2)
Cr	0.5	$\frac{1}{8}$	0.40371(5)	$\frac{1}{8}$	4.79(2)
P1	1	0.96297(6)	0.19070(6)	0.27278(8)	3.92(2)
P2	0.5	$\frac{1}{8}$	0.54962(9)	$\frac{1}{8}$	5.16(4)
S1	1	0.86362(7)	0.17684(6)	0.24481(8)	4.43(2)
S2	1	0.02196(7)	0.21869(7)	0.15183(8)	4.69(3)
S3	0.524	0.8718(1)	0.0037(1)	0.2631(2)	4.53(5)
S3′	0.476	0.8471(2)	0.0128(2)	0.2551(2)	7.57(9)
S4	1	0.99780(8)	0.11172(7)	0.34274(9)	5.79(3)
S5	0.381	0.5449(1)	$\frac{1}{8}$	$\frac{1}{8}$	4.59(5)
S5′	0.238	0.5485(2)	0.0921(3)	0.1838(4)	4.7(1)

Note. Isotropic equivalent thermal parameter defined as B_{eq} (pm^2) = $\frac{4}{3}\sum_i\sum_j \beta_{ij}a_ia_j$.

IV. Discussion

With 208 atoms per cell, the CrP_3S_{9+x} ($x \approx 0.25$) structure cannot be described straightforwardly. To better understand the overall atomic arrangement, let us first consider the (CrP_3S_{12}) basic unit (Fig. 1a) and neglect the additional S3′ and S5′ positions. The unit is built upon one (CrS_6) octahedron sharing three edges with three (PS_4) tetrahedra. In the Evain *et al.* systematic (*13*), the connections are of the $F[b]D$ type and can be schematized as shown in Fig. 1b.

All the [CrP_3S_{12}] units of the structure are

[1] See NAPS document No. 04972 for 11 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 $.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, $1.50 for postage of any microfiche orders.

TABLE V

GENERAL DISPLACEMENT PARAMETER EXPRESSION (Us)

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Cr	0.1055(8)	0.0439(5)	0.0324(4)	0	0.0051(6)	0
P1	0.0618(7)	0.0523(6)	0.0349(5)	−0.029(6)	−0.009(5)	−0.0121(5)
P2	0.090(1)	0.0472(9)	0.0593(9)	0	0.0360(9)	0
S1	0.0694(7)	0.0616(7)	0.0373(5)	−0.0222(6)	−0.0092(5)	0.0079(5)
S2	0.0700(7)	0.0672(7)	0.0409(5)	−0.0140(6)	0.0097(5)	−0.0241(5)
S3	0.101(2)	0.039(1)	0.0320(9)	−0.002(1)	0.011(1)	0.0021(8)
S3′	0.191(4)	0.059(2)	0.038(1)	−0.032(2)	0.006(2)	0.002(1)
S4	0.0981(9)	0.0710(8)	0.0507(6)	0.0277(7)	0.0015(7)	−0.0068(6)
S5	0.041(1)	0.058(1)	0.075(1)	0	0	−0.024(1)
S5′	0.032(2)	0.081(3)	0.063(3)	−0.015(2)	0.021(2)	−0.028(2)

Note. The form of the anisotropic displacement parameter is $\exp[-2\pi^2 (h^2a^{*2} \cdot U(1,1) + k^2b^{*2} \cdot U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^* \cdot U(1,2) + 2hla^*c^* \cdot U(1,3) + 2klb^*c^* \cdot U(2,3)]$ where a^*, b^*, and c^* are reciprocal lattice constants.

TABLE VI

MAIN INTERATOMIC ANGLES (°) AND DISTANCES (pm) IN CrP_3S_{9+x} ($x \approx 0.25$)

Cr–P1	291.8(2)					
Cr–P2	294.9(3)					
Cr–S1 (×2)	242.5(2)			S1–Cr–S1	95.63(7)		
Cr–S3 (×2)	242(2)	*Cr–S3′* (×2)	242(2)	S1–Cr–S4 (×2)	82.53(5)		
Cr–S4 (×2)	244.2(2)			S1–Cr–S4 (×2)	87.62(5)		
				S1–Cr–S3 (×2)	92.9(2)	*S1–Cr–S3′* (×2)	87.1(3)
				S1–Cr–S3 (×2)	170.9(2)	*S1–Cr–S3′* (×2)	171.6(3)
				S4–Cr–S4	165.32(9)		
				S4–Cr–S3 (×2)	90.5(3)	*S4–Cr–S3′* (×2)	100.6(3)
				S4–Cr–S3 (×2)	100.9(2)	*S4–Cr–S3′* (×2)	89.6(3)
				S3–Cr–S3	78.7(5)	*S3′–Cr–S3′*	91.4(5)
P1–S1	198.4(2)			S1–P1–S2	114.60(8)		
P1–S2	209.1(2)			S1–P1–S2	110.45(8)		
P1–S2	212.3(2)			S1–P1–S4	108.10(9)		
P1–S4	198.1(2)			S2–P1–S2	94.40(7)		
				S2–P1–S4	114.51(9)		
				S2–P1–S4	114.40(8)		
P2–S3 (×2)	187.5(9)	*P2–S3′* (×2)	214(1)	S5–P2–S5	91.1(2)	*S5′–P2–S5′* (×2)	126.1(4)
P2–S5 (×2)	217.6(3)	*P2–S5′* (×2)	189.4(5)	S5–P2–S3 (×2)	115.3(3)	*S5′–P2–S3′* (×2)	113.3(4)
				S5–P2–S3 (×2)	112.3(4)	*S5′–P2–S3′* (×2)	98.0(4)
				S3–P2–S3	109.7(7)	*S3′–P2–S3′*	107.7(8)
						P2–S5′–S5′	87.8(3)
S5′–S5′	208(2)						
(S–S)min:	*S2–S2*	309.2(2)					
(S–S)max:	*S4–S5*	398.2(2)					

Note. Italic notation corresponds to the alternative structure (i.e., S5 substituted by $(S5')_2$ pairs and S3 by S3′).

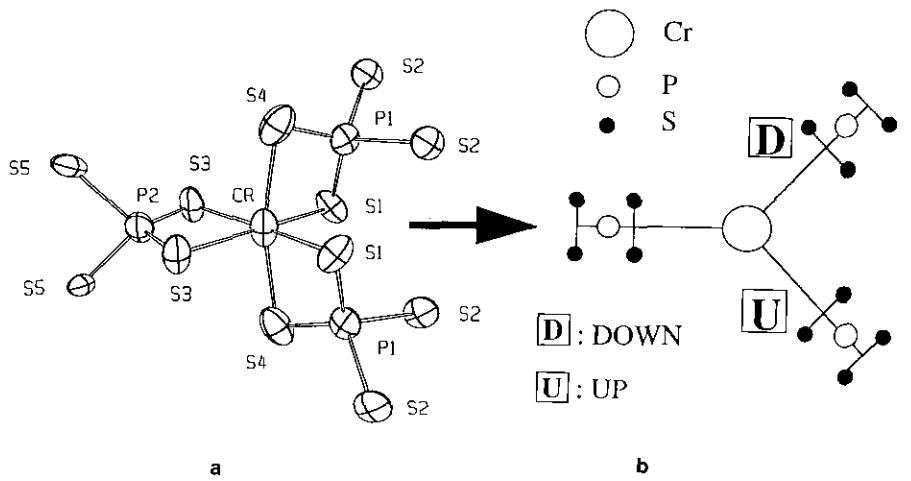

FIG. 1. (a) CrP_3S_{12} unit made of (CrS_6) octahedra sharing three opposite edges with three (PS_4) tetrahedra and (b) its schematic representation according to the M. Evain *et al.* systematics. (The labeling U and D indicates a connection above (Up) and below (Down) the figure plane.)

interconnected through the three available tetrahedron edges (*D*[*b*]*D*-type connection) to yield three networks of which one is depicted in Fig. 2 in the forementioned Evain *et al.* scheme. With the help of the U and D labels and of the elevation values, one can easily see that this network is made of inversely rotating helices that manage large tunnels. The three networks interlock in the way shown in the stereoview of Fig. 3, with only van der Waals distances in between. One should note that each network covers all the atomic positions over three adjacent unit cells along the *b* direction; that is, one needs three cells along the *b* axis to recover the same network on the same atomic positions.

If, in the octahedron, the chromium-to-sulfur distances are quite homogeneous (from 242 to 244.2 pm, with the mean value $d_{(Cr-S)} = 242.9$ pm to be compared with the $d_{(Cr-S)} = 242.5$ pm of $CrPS_4$ implying a Cr^{3+} cation), the calculated angles (from 78.7° to 95.6°) largely depart from those of a regular (CrS_6) unit. Clearly this is to be linked to the twisting introduced along the *F*[*b*]*D*[*b*]*D*[*b*]*F* links presented in the stereographic view in Fig. 4. The twisting and the correlative structural constraints, along with the large ADP of the atoms implied (in particular of S5 and S3), were the hints that led us to partially substitute the S5 atoms by $(S5')_2$ pairs and add the S3′ position to the S3 one as shown in Fig. 5. Those substitutions partially release the twisting and, consequently, the associated structural strain. The new connection between the ($P2S_4$) tetrahedra is similar to that observed in the $[(pyridine)_2H]_2^{2+}[P_2S_8]^{2-}$ compound (*14*). It is an indirect link between two *D* units. This connection, not described in the Evain *et al.* original classification, can be labeled as *D*[*b*2*,*b*2*]*D*, where the stars indicate that only one ending atom of each *b*2 link (i.e., each (S_2) pair) belongs to each *D* unit (i.e., each tetrahedron) (another example of that notation taken from the $Nb_2P_4S_{21}$ structure (*15*) would be the labeling of the links between the tetrahedra through the $(S_3)^{2-}$ group as *D*[*c*2*]*D*). The S5′–S5′ pair distance (208 pm) is in the range of that observed in various compounds. The P–S distances ranging from 187.5 to 217.6 pm in the ($P2S_4$) tetrahedra should be cautiously

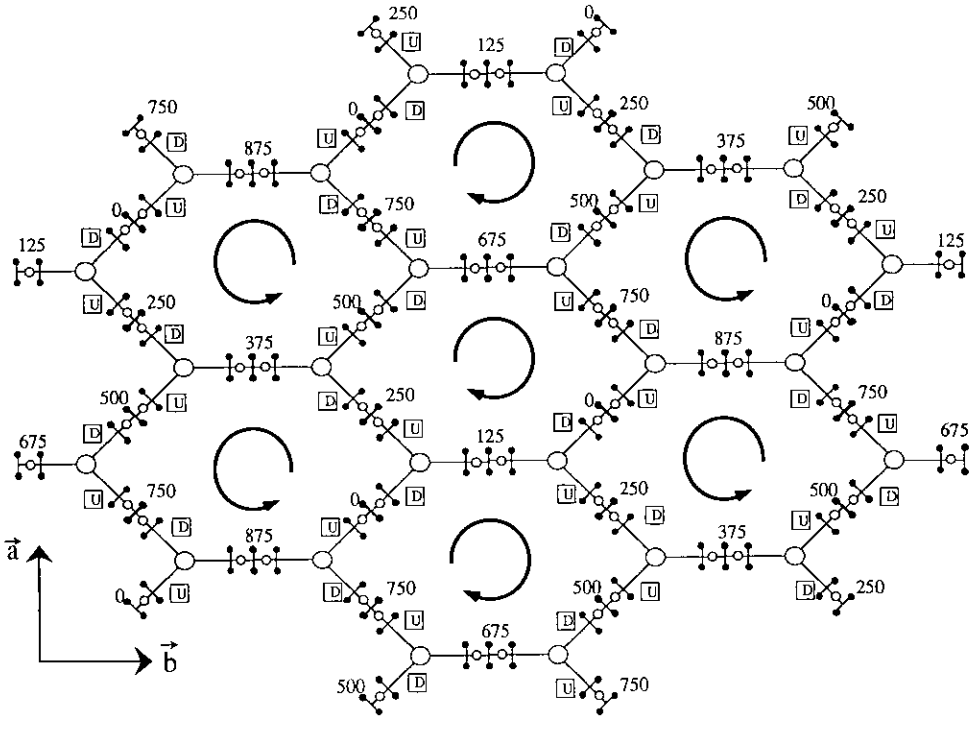

FIG. 2. One of the three interlocked network, built from the cluster of Fig. 1, constituting the CrP_3S_{9+x} ($x \approx 0.25$) structure. Numbers represent fractional heights ($\times 1000$) of the (P_2S_6) groups.

considered because of the large ADP of the atoms implied. The P2–S3 distance seems too short and the P2–S5 distance too long when compared with the distances calculated in the ($P1S_4$) unit and more generally in related compounds ($CrPS_4$, $AlPS_4$ (*16*), $BiPS_4$ (*17*), . . .). In contrast the P2–S5′ distance seems too short and the P2–S3′

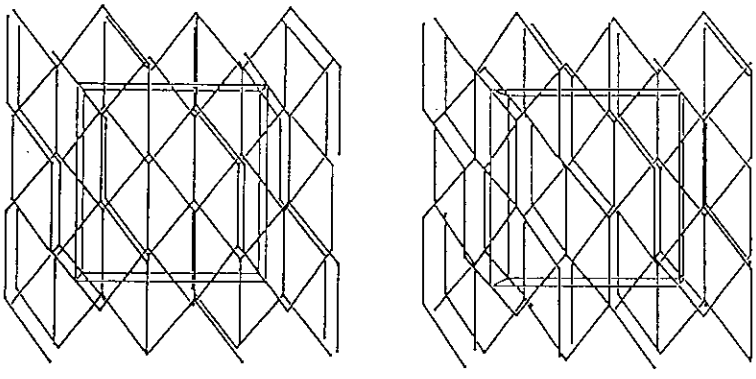

FIG. 3. Stereo view of the three interlocked networks of CrP_3S_{9+x} ($x \approx 0.25$) shown in a simplified scheme.

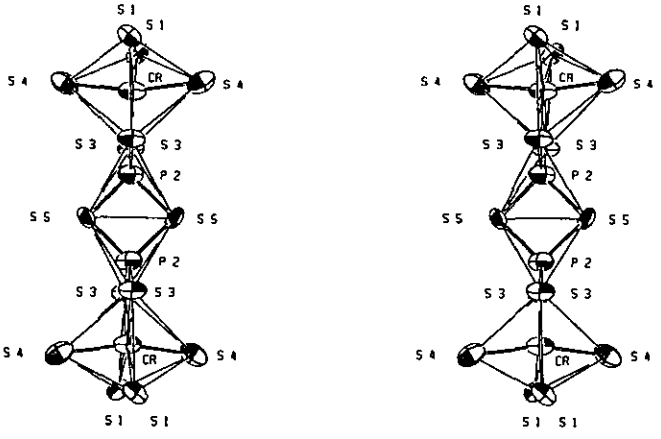

FIG. 4. Stereo view of the $(S3)_2$–P2–$(S5)_2$–P2–$(S3)_2$ group without the substitution of the two S5 sulfurs by two pairs $(S5')_2$.

distance too long. This suggests that the phosphorus P2 position should be split as was the S3 position into two different but very close positions, one, P2, closer to S5 and a little farther away from S3 than the current position and the other one, P2′, closer to S3′ and farther away from S5′. This is one of the additional splittings that we tried in the refinement calculations but that failed (vide supra). The substitution of some S5 atoms by $(S5')_2$ pairs largely perturbates the other atomic positions. The perturbation is clearly perceived on the S3 atoms, that had to be split, but it also translates in the other positions with large ADP; the closer to the substitution, the larger the ADP.

V. Magnetic Properties

Susceptibility measurements were carried out on a SQUID magnetometer in the 2–300 K temperature range. Only single

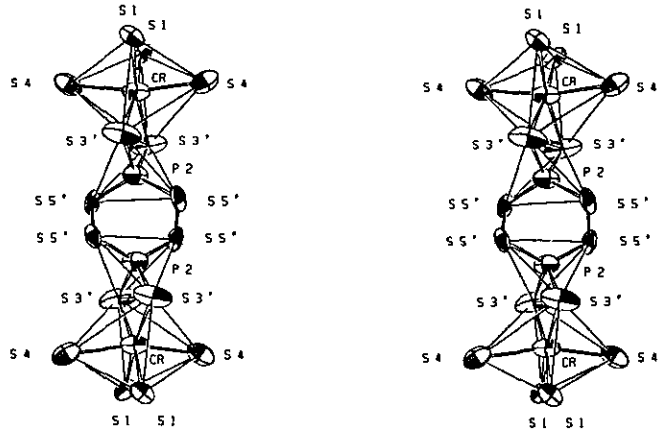

FIG. 5. Stereo view of the $(S3')_2$–P2–$((S5')_2^{2-})_2$–P2–$(S3')_2$ group with the substitution of the two S5 sulfur by two pairs $(S5')_2$ giving a (P_2S_8) group. A comparison between Figs. 4 and 5 clearly shows the strain release introduced by the sulfur substitution.

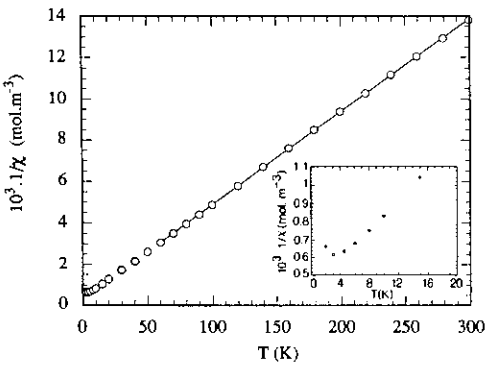

FIG. 6. Reciprocal molar magnetic susceptibility (corrected for core magnetism) vs temperature of CrP_3S_{9+x} ($x \approx 0.25$) in the 2–300 K temperature range.

crystals were studied. In Fig. 6 is reported the temperature dependence of the reciprocal molar magnetic susceptibility ($1/\chi_{mol}$) corrected for diamagnetic contribution. The Curie–Weiss law, $1/\chi_{mol} = (T - \theta_p)/C_{mol}$ (where C_{mol} and θ_p are the molar Curie constant and the Weiss constant, respectively), yielded, in the high temperature range, a Curie constant $C_{mol} = 22 \times 10^{-6}$ m^3 · K · mol^{-1} and a Bohr magneton $\mu_{obs} = 3.75\ \mu_B$. This is in good agreement with the calculated spin-only value for Cr^{III} ions ($C_{calc} = 23 \times 10^{-6}$ m^3 · K · mol^{-1}, $\mu_{calc} = 3.87\ \mu_B$). The Weiss constant is weak and negative ($\theta_p = -8$ K), that is, the magnetic interactions are weak and of the antiferromagnetic type. This is in agreement with a semiconducting phase and corresponds to the charge balance $Cr^{3+}P_3^{5+}S_{8.75}^{2-}(S_2)_{0.25}^{2-}$.

VI. Conclusion

The quest for novel $M_{2/3}^{III}[\ ]_{1/3}PX_3$ phases led to the obtainment of a new material, CrP_3S_{9+x} ($x \approx 0.25$), that presents an interlocked structure made of three independent networks. This type of structure is of a rather unusual occurrence in the solid-state inorganic compounds. Although the synthesis of a pure bulk has not been achieved yet, the atomic structure could be solved from single crystals. The high ADP values, especially for the sulfur atoms, led to the introduction of S_2^{2-} pairs in substitution of the S5 position. Qualitatively, it seems that this substitution allows a decrease in the structure strains and a release of local stresses. It would be interesting to attempt the preparation of similar compounds with M^{3+} cations stable in octahedral sulfur environments.

References

1. H. HAHN AND W. KLINGEN, *Natürwissenchaften* **52,** 494 (1965).
2. G. OUVRARD, R. BREC, AND J. ROUXEL, *Mater. Res. Bull.* **20,** 1181 (1985).
3. R. BREC, *Solid State Ionics* **22,** 3 (1986).
4. G. OUVRARD, R. FREOUR, R. BREC, AND J. ROUXEL, *Mater. Res. Bull.* **20,** 1053 (1985).
5. M. Z. JANDALI, G. EULENBERGER, AND H. HAHN, *Z. Anorg. Allg. Chem.* **470,** 39 (1980).
6. P. TOFFOLI, P. KHODADAD, AND N. RODIER, *Acta. Crystallogr. B* **33,** 285 (1977).
7. R. DIEHL, C-D. CARPENTIER, *Acta. Crystallogr. B* **33,** 1399 (1977).
8. S. SOLED AND A. WOLD, *Mater. Res. Bull.* **11,** 657 (1976).
9. A. KATTY, S. SOLED, AND A. WOLD, *Mater. Res. Bull.* **12,** 663 (1977).
10. R. YVON, W. JEITSCHKO, E. PARTHÉ, *J. Appl. Crystallogr.* **10,** 73 (1977).
11. B. DELAUNAY, *Z. Kristallogr.* **84,** 109 (1933).
12. W. C. HAMILTON, *Acta. Crystallogr.* **18,** 502 (1965).
13. M. EVAIN AND R. BREC, "Structure and bonding," Vol. 79, in press (1991).
14. P. C. MINSHALL AND G. M. SHELDRICK, *Acta. Crystallogr. B* **34,** 1378 (1978).
15. R. BREC, M. EVAIN, P. GRENOUILLEAU, AND J. ROUXEL, *Rev. Chim. Min.* **20,** 283 (1983).
16. A. WEISS AND H. SCHAFER, *Natürwissenschaften* **47,** 495 (1960).
17. H. ZIMMERMANN, C. D. CARPENTIER, AND R. NITSCHE, *Acta Crystallogr. B* **31,** 2003 (1975).