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# STRUCTURE OF M07S<sub>8</sub>: A NEW BINARY SULFIDE SYNTHESIZED BY SELF MOLYBDENUM INTERCALATION

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# ABSTRACT

A new  $Mo_7S_8$  binary sulfide structure and its crystal growth are reported. It is the first example of Mo atoms in the channels of the Chevrel phases. The single crystal structure determination indicates extra molybdenum atoms located in the chalcogen site that is centered at the rhombohedral unit-cell origin. The nature and valence state of these extra atoms are discussed through chemical and physical properties. © 1998 Elsevier Science Ltd

KEYWORDS: A. chalcogenides, B. crystal growth, C. X-ray diffraction, D. crystal structure

# INTRODUCTION

The Chevrel phases  $M_xMo_6Ch_8$  (M = metal ion; Ch = S, Se, or Te) are a large class of materials exhibiting interesting properties such as superconductivity with high critical magnetic fields, coexistence of magnetic order and superconducting state, and cationic mobility [1,2]. Sulfides and selenides are mainly represented in this family, of which most compounds crystallize in the rhombohedral–hexagonal system with space group R $\overline{3}$ . Their structure is based on a tri-dimensional framework of quasi-rigid  $Mo_6Ch_8$  units with orthogonal secant tunnels between units where many vacant chalcogenide sites are located that are able to receive cations  $M^{n+}$ . The nature, size, and the amount x of cations present in these phases control their general properties.

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	Mo <sub>6</sub> Te <sub>8</sub> [1]	Mo <sub>6</sub> Se <sub>8</sub> [1]	$\alpha$ -Mo <sub>6</sub> S <sub>8</sub> [3]	$\beta$ -Mo <sub>6</sub> S <sub>8</sub> *	PbMo <sub>6</sub> S <sub>8</sub> [1]
a <sub>R</sub> (Å)	7.10	6.658	6.432	6.449	6.544
$\alpha_{\rm R}$ (°)	92.60	91.58	91.34	89.47	89.48
$a_{\rm H}$ (Å)	10.20	9.454	9.20	9.078	9.212
$c_{\rm H}$ (Å)	11.65	11.209	10.88	11.273	11.437
$V_{\rm H}$ (Å <sup>3</sup> )	1050	884	797	804	840

TABLE 1 Parameters of Binary Chevrel Phases and  $PbMo_6S_8$ 

\*This work.

This family of compounds has three binaries  $Mo_6Te_8$ ,  $Mo_6Se_8$ , and  $\alpha$ - $Mo_6S_8$  (Table 1). The latter is a metastable compound only obtained through a deintercalation method using a ternary compound such as  $Cu_2Mo_6S_8$  or  $Ni_2Mo_6S_8$  [2,3].

In 1974, Chevrel et al. [3] noted that the binary  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> is transformed into a "new sulfide," which was called  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> [2]), at about 470°C with the occurrence of MoS<sub>2</sub>. As shown in Table 1, the interesting feature of this sulfide is essentially its rhombohedral angle, which is lower than 90° and close to the one of PbMo<sub>6</sub>S<sub>8</sub>.

In this paper, we focus our interest on the  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> binary, the structure of which was unknown.

#### SYNTHESIS AND CHARACTERIZATION

Until now, the only way to synthesize  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> has been by thermal decomposition of  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> [3]. We have performed this method as follows. We have to synthesize a ternary compound that is easy to deintercalate by dilute hydrochloric acid [2,3]; we have chosen the Ni<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> Chevrel phase. This compound shows an hexagonal unit cell volume very similar to the volume of  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> and  $\beta$ -Mo<sub>6</sub>S<sub>8</sub>, allowing minimization of the crystallographic distortions related to this synthesis process. In the first stage, we prepare Ni<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> compound from a stoichiometric mixture of the starting materials, MoS<sub>2</sub>, Mo, and Ni powders, which are pressed into a pellet and placed into a degassed silica tube sealed under vacuum and heated at 800°C for 1 week. In the second stage, the microcrystalline Ni<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> powder is placed into dilute hydrochloric acid for 3 days to remove Ni<sup>2+</sup> cations from the host structure. Afterwards the powder is washed in distilled water, then in alcohol and ether, before being dried under vacuum. The third stage lies in the transformation of  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> into  $\beta$ -Mo<sub>6</sub>S<sub>8</sub>. This reaction takes place in a silica tube kept under secondary dynamic vacuum and heated at 550°C for 6 h.

The X-ray powder diffraction pattern of the  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> final compound is given in Figure 1. It is indexed in the hexagonal system as  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> (cf. Table 2 and Fig. 1) and is always obtained in the presence of MoS<sub>2</sub>. The amount of MoS<sub>2</sub> binary is minimized when the sulfur partial pressure decreases, for instance, under a dynamic vacuum or a reducing gas flow.

Of course, we have tried to synthesize  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> by other methods. These methods were based on the fact that  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> has parameters close to the ones of the large cation Chevrel phases such as PbMo<sub>6</sub>S<sub>8</sub> (Table 3) and, thus, a very similar X-ray powder diffraction pattern (Fig. 1). We have succeeded in deintercalating Chevrel phases with large cations such as SnMo<sub>6</sub>S<sub>8</sub>, PbMo<sub>6</sub>S<sub>8</sub>, or LuMo<sub>6</sub>S<sub>8</sub> [4]. Potel et al. [2] showed that InMo<sub>6</sub>S<sub>8</sub> could be



Powder diffraction pattern of  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub>,  $\beta$ -Mo<sub>6</sub>S<sub>8</sub>, and PbMo<sub>6</sub>S<sub>8</sub> (with silicium standard) ( $\lambda$  Cu K $\alpha_1$ ).

deintercalated under a flow of HCl gas because of the volatility of  $InCl_3$  chloride. In the same way, we have deintercalated Sn, Lu, and Pb from the host structure of the respective ternary compounds. Every deintercalation is successful, but the binary  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> is always obtained [4]. So far, the only way to synthesize  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> is the three-stage process previously presented.

The crystal growth was carried out in the same way. At first, we easily made single crystals of  $Ni_2Mo_6S_8$  by transport reaction from stoichiometric mixtures of the starting materials  $MoS_2$ , Mo, and Ni powders. The mixture, pressed into a pellet, was sealed with a  $MoCl_5$  transport agent in a silica tube that had been degassed. The silica tube was then placed into a horizontal furnace and heated to about 1200°C for 2 weeks with a temperature gradient of 50°C. We isolated truncated apex cubic-shaped single crystals with volumes of about 1 or 1.5 mm<sup>3</sup>.

The Ni<sup>2+</sup> cations were removed using dilute hydrochloric acid ( $\sim$ 50% vol HCl) for 2 weeks, according to the following reaction in aqueous solution:

$$Ni_2Mo_6S_8 + 4 HCl \rightarrow \alpha - Mo_6S_8 + 2 NiCl_2 + 2 H_2 \uparrow$$

After cleaning, the purity of crystals was checked on a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS). The hydrochloric acid leaching leads to traces of nickel lower than 100 ppm [3]. The single crystals have the  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> composition.

,	0.		
hkl (hex)	$d_{obs}~({\rm \AA})$	$d_{cal}$ (Å)	I/I <sub>0</sub>
101	6.4786	6.4485	76
012	4.5933	4.5809	23
110	4.5428	4.5389	18
003	3.7687	3.7578	12
021	3.7151	3.7117	7
113	2.9004	2.8945	5
211	2.8763	2.8733	29
104	2.6614	2.6530	17
122	2.6330	2.6286	68
024	2.2931	2.2905	10
220	2.2700	2.2695	17
015	2.1730	2.1673	25
131	2.1415	2.1408	45
214	2.0499	2.0449	36
312	2.0359	2.0336	22
223	1.9455	1.9427	100
006	1.8863	1.8789	14
042	1.8588	1.8558	1
125	1.8009	1.7961	5
321	1.7829	1.7809	4
116	1.7418	1.7360	2
232	1.7200	1.7178	21
107	1.5805	1.5777	8
315	1.5704	1.5674	5
051	1.5590	1.5573	6
324	1.5212	1.5192	9
226	1.4503	1.4473	12
217	1.4197	1.4159	3
511	1.4022	1.4011	10

TABLE 2 X-ray Powder Diffraction Data of Mo<sub>7</sub>S<sub>8</sub>, So-called β-Mo<sub>6</sub>S<sub>8</sub>

These crystals are then put into an  $Al_2O_3$  crucible inside a silica tube and heated at 700°C for 48 hours under secondary dynamic vacuum. Finally, small single crystals of  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> are obtained. These single crystals are very small because they arise from two successive reactions at the crystalline state, which cause some damage to the crystals (Fig. 2). The  $\alpha_R$  rhombohedral angle alters from 94°68 for Ni<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> to 91°34 for  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> and then to 89°37 for  $\beta$ -Mo<sub>6</sub>S<sub>8</sub>. These changes generate important strains, which induce the shattering of the single crystals.

# Crystal Structure Analysis and Refinement of β-Mo<sub>6</sub>S<sub>8</sub>

**Experimental determination.** A single crystal  $0.07 \times 0.047 \times 0.047$  mm<sup>3</sup> with a regular parallelepipedic shape was chosen in order to undertake the crystal structure determination. X-ray diffraction intensities were collected on a Nonius CAD-4 four circle diffractometer

			of Different	Chevrel Phase	es			
	Mo <sub>6</sub> S <sub>8</sub> [1]	AgMo <sub>6</sub> S <sub>8</sub> [1]	Pd <sub>1.6</sub> Mo <sub>6</sub> S <sub>8</sub> [5]	Cu <sub>1.8</sub> Mo <sub>6</sub> S <sub>8</sub> [1]	Mo <sub>7</sub> S <sub>8</sub>	PbMo <sub>6</sub> S <sub>8</sub> [1]	SnMo <sub>6</sub> S <sub>8</sub> [1]	InMo <sub>6</sub> S <sub>8</sub> [1]
(Mo–Mo) <sub>A</sub>								
intra $\Delta$ (Å)	2.698	2.705	2.704	2.683	2.665	2.678	2.688	2.705
$(Mo_D - Mo_\Delta)$								
inter $\Delta$ (Å)	2.862	2.804	2.795	2.752	2.742	2.726	2.737	2.725
(Mo-Mo)								
intercluster (Å)	3.084	3.154	3.169	3.237	3.164	3.267	3.232	3.258
Mo–X								
intercluster (Å)	2.425	2.459	2.472	2.494	2.536	2.559	2.550	2.529
X <sub>2c</sub> –X <sub>2c</sub> diagonals								
via Mo <sub>6</sub> (Å)	6.155	6.016	6.046	6.118	5.907	5.865	5.881	5.94
X <sub>2c</sub> -X <sub>2c</sub> diagonals								
via origin (Å)	4.724	4.814	4.695	4.132	5.366	5.572	5.482	4.74
a <sub>H</sub> (Å)	9.20	9.32	9.344	9.584	9.078	9.212	9.206	9.46
$c_{\rm H}$ (Å)	10.88	10.83	10.741	10.250	11.273	11.437	11.363	10.68
$V_{\rm H}$ (Å <sup>3</sup> )	797	815	812	815	804	840	834	828
$\alpha_{R}$ (°)	91.34	91.97	92.37	94.93	89.47	89.48	89.70	93.02
a <sub>R</sub> (Å)	6.432	6.48	6.475	6.503	6.449	6.544	6.527	6.52
VEC/Mo <sub>6</sub>	20	21	$\sim 21$	<22	22	22	22	23
$T_{c}(K)$	1.8	7.5		10.8	-	14	14	

	TABLE 3
Structural Parameters, Valence Electron	Concentration (VEC), and T <sub>c</sub> Superconducting Critical Temperature
	of Different Chaural Phagas

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FIG. 2 Photograph of the  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> "single" crystal recorded for the structural determination.

under the experimental conditions given in Table 4. All calculations were performed using the MOLEN program system [6], and a spherical absorption correction was applied.

The crystal structure of  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> is assumed to be similar to the one of  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> [2]. We have refined the atomic positions: the Mo(1) molybdenum and S(1) sulfur atoms are in 6f general positions and the S(2) sulfur atoms in 2c special positions. Under these conditions, we are not able to refine the structure completely; in fact, reliability factors are still high. The differential map of electronic density reveals a heavy peak in 6f positions located in the origin site. These sixfold peaks mean that there are atoms delocalized in this site. We attribute these electrons to molybdenum atoms. This conclusion has been confirmed by other experimental chemical features.

A good reliability factor is obtained despite the mosaic structure of the "pseudo" single crystal (Table 4 and Fig. 2). Actually, many *hkl* Bragg reflections have large FWHM (full width at half maximum), showing the poor quality of the single crystal. Many reflections have been omitted with the criterion I <  $3\sigma$ (I). The final atomic coordinates, occupancy, and thermal parameters of Mo<sub>1.18</sub>Mo<sub>6</sub>S<sub>8</sub> are summarized in Table 5

**Crystal structure description.** The crystal structure of Chevrel phases has been described in the literature as a stacking of  $Mo_6S_8$  units (Fig. 3) [1]. The distances and angles of  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> and  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> are reported in Table 6. Per unit, each Mo<sub>6</sub>S<sub>8</sub> building block is a slightly distorted cube, where the sulfur atoms sit at the corner. In  $\beta$ -Mo<sub>6</sub>S<sub>8</sub>, the six Mo(1) atoms form a distorted octahedral cluster, therefore, there are two kinds of distances: the (Mo(1)–Mo(1))<sub> $\Delta$ </sub> intracluster (or intertriangle) distances (2.665 Å) between two molybdenum atoms belonging to the same triangular plane perpendicular to the ternary axis, and the Mo(1)<sub> $\Delta$ </sub>-Mo(1)<sub> $\Delta$ </sub> intracluster distances (2.742 Å) between two Mo atoms belonging to two different triangular planes. Moreover, each Mo atom of the Mo<sub>6</sub> cluster is linked to another Mo atom belonging to a neighboring Mo cluster forming the intercluster distance (3.164 Å). The Mo atom is located slightly outside the middle of the face of the S8 pseudo-cube and is in a square-based pyramidal sulfur site.

This particular stacking of  $Mo_6S_8$  units leaves vacant three types of cavities in the sulfur atom network (Fig. 3). S8 cavities 1 and 2 are empty in the binary  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub>; they are filled

	TABLE 4	4			
Crystal Data	and Experimental Pa	arameters	for the	he Inter	isity
	Data Collection of M	Mo <sub>1.18</sub> Mo <sub>6</sub>	${}_{5}S_{8}$		

I. Crystal data Formula: $Mo_{1.18}Mo_6S_8$ Crystal system: rhombohedral Parameters: $a_R = 6.449(1)$ Å, $\alpha_R = 89.48(2)^{\circ}$ $a_H = 9.078(2)$ Å, $c_H = 11.273(4)^{\circ}$ Unit cell refined from 25 reflections (9° < $\theta$ < 20°) $\rho_{cal} = 5.855$ g/cm <sup>3</sup> Crystal size: 0.07 × 0.047 × 0.047 mm <sup>3</sup> Linear absorption factor: 91.946 mm <sup>-1</sup>	$\begin{split} M &= 945.36 \text{ g/mol} \\ \text{space group: } R\bar{3} \text{ (no. 148)} \\ V_R &= 268.2(1) \text{ Å}^3 \\ V_H &= 804.6(3) \text{ Å}^3 \\ Z &= 1 \text{ (rhombohedral)} \end{split}$
II. Data collections	
Different and the start Namine CAD 4	wavelength: Mo Kα
Monochromatori graphita	Scan mode: $\omega$ -20 Scan width: 1.20 $\pm$ 0.25 to 0
-0 < h < 0; 0 < k < 0; 0 < l < 0	Scall width. $1.20 \pm 0.55$ tg 0 $\theta = 30$
3 < n < 3, 0 < k < 3, 0 < l < 3	$0_{\rm max} = 50$
366 independent reflections (with $I > \sigma(I)$ )	$R_{} = 0.061$
	runt oroor
III. Structure determination	
Lorentz polarization and crystal corrections	
Spherical absorption correction: SAC	
Refinement on F	
246 independent reflections with $I > 3 \sigma(I)$	
Refined parameters: 33	
Unweighted agreement factor $R = 0.062$	Weighted agreement factor $R\omega = 0.068$
Ponderation factor: 0.07	$\omega = 4f_0^2 / [\sigma(F_0^2) + (0.07 F_0^2)^2]$
Validity of refinement $S = 1.105$	$(\Delta/\sigma)_{\rm max} < 0.01$
$\Delta \rho_{\rm max} = 2.29 \text{ e/A}^3$	$\Delta_{\rm rmin} = -1.305  {\rm e/A^3}$
Extinction correction: ER [7]	Extinction coefficient: $1.24 \times 10^{-7}$
Atomic scattering factor from Internal Tables for X-ray (	Crystallography [8]

in  $Cu_4Mo_6S_8$  and only site 1 is filled in  $PbMo_6S_8$  or  $SnMo_6S_8$ . Cavity 3 is not vacant because of the occurrence of the Mo–Mo intercluster weak bondings.

In  $\beta$ -Mo<sub>6</sub>S<sub>8</sub>, only site 1 is occupied by Mo(2) atoms located on a sixfold equivalent crystallographic position grouped around the inversion center (origin) with an occupancy of 0.196. The six equivalent positions of Mo(2) atoms describe a distorted octahedron (Fig. 4) with the distances "(Mo(2)–Mo(2))<sub> $\Delta$ </sub>" = 1.686 Å and "Mo(2)<sub> $\Delta$ </sub>–Mo(2)<sub> $\Delta$ </sub>" = 1.442 Å (Table 6). Mo(2) atoms are in a squared planar sulfur site. The distance from origin to sulfur atoms is different with S2 atoms (Org-S2 = 2.683 Å) and the S(1) atom (Org-S1 = 3.022 Å) in the quasi-cubic S8 origin site.

## DISCUSSION

The nature of the cations located in cavity 1 of the structure has been determined by some chemical properties of this compound. First,  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> via  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> can be obtained from

TABLE 5	
Positional, Occupancy, and Thermal Parameters	of $Mo_{1.18}Mo_6S_8$

Atom	Site	x	у	Z	$B_{eq}$ (Å <sup>2</sup> )	b <sub>11</sub>	b <sub>22</sub>	b <sub>33</sub>	b <sub>12</sub>	b <sub>13</sub>	b <sub>23</sub>
Mo(1)	6f	0.2225(3)	0.4150(3)	0.5604(3)	1.04(3)	0.0061(3)	0.0064(4)	0.0062(3)	0.0006(7)	0.0012(7)	0.0001(7)
S(1)	6f	0.1281(9)	0.7504(10)	0.3773(10)	1.4(1)	0.005(1)	0.011(1)	0.010(1)	0.000(2)	0.002(2)	0.002(2)
S(2)	2c	0.2379(9)	0.2379(9)	0.2379(9)	1.49(5)	0.009(1)	b <sub>11</sub>	b <sub>11</sub>	-0.000(2)	b <sub>12</sub>	b <sub>12</sub>
Mo(2)	6f	0.9512(15)	0.0275(15)	0.1629(16)	1.0(2)	0.004(2)	0.003(2)	0.011(2)	-0.003(3)	-0.008(3)	0.003(3)

The thermal factor is given by exp  $\{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\}$   $\tau$  (Mo(2)) = 0.196 [6].



FIG. 3

Projection of the Chevrel phase framework on (11–20) plane in a hexagonal system. View of the three types of cavities.

different ternary starting compounds such as  $Li_xMo_6S_8$ ,  $Cu_xMo_6S_8$ , or  $Ni_xMo_6S_8$ . EDS–SEM analysis displays nothing but molybdenum and sulfur. Microprobe analysis gives the  $Mo_{7.17}S_8$  formula. Moreover,  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> decomposes above 810°C into molybdenum sulfide and molybdenum, according to X-ray studies.

The DSC analysis of  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> under vacuum from room temperature to 900°C shows that the transformation  $\alpha \rightarrow \beta$  is exothermic and occurs at about 560°C because of the temperature rate (Fig. 5). We can see from the DSC curve that  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> is stable until 810°C, then it undergoes an exothermic degradation reaction.

and $\alpha$ -Mo <sub>6</sub> S <sub>8</sub>						
	$\mathrm{Mo}_{1.18}\mathrm{Mo}_6\mathrm{S}_8$	$\alpha$ -Mo <sub>6</sub> S <sub>8</sub> [3]				
Mo <sub>6</sub> S <sub>8</sub> cubic cluster unit						
Intratriangle $(Mo(1)-Mo(1))_{\Delta}$	$2 \times 2.665(3)$	$2 \times 2.698$				
Intertriangle $Mo(1)_{\Delta}$ - $Mo(1)_{\Delta}$	$2 \times 2.742(3)$	$2 \times 2.862$				
Intercluster $Mo(1)$ – $Mo(1)$	3.164(3)	3.082				
Mo(1)–S(2)	2.382(4)	2.439				
S(1)	2.423(6)	2.426				
S(1)	2.433(6)	2.460				
S(1)	2.527(7)	2.431				
Intercluster $Mo(1)$ – $S(1)$	2.536(6)	2.425				
S(2)–S(1)	$3 \times 3.497(7)$	$3 \times 3.550$				
S(1)–S(1)	$2 \times 3.384(8)$	$2 \times 3.310$				
S(1)-S(2)-S(1) angle	89°52	85°94				
S8 origin cubic site						
S(2)–S(1)	$3 \times 3.343(9)$	$3 \times 3.339$				
S(1)–S(1)	$2 \times 3.451(9)$	$2 \times 3.538$				
Org–S(2)	$2 \times 2.683$	$2 \times 2.362$				
Org-S(1)	$6 \times 3.022$	$6 \times 3.153$				
S(1)-S(2)-S(1) angle	95°85	102°37				
$(Mo(2)-Mo(2))_{\Delta}$	$2 \times 1.686(14)$					
$Mo(2)_{\Delta} - Mo(2)_{\Delta}$	$2 \times 1.442(14)$					
Mo(2)–Mo(2)	2.219(14)					
Mo(2)–S(2)	2.361(11)					
S(1)	2.412(12)					
S(1)	2.520(12)					
S(1)	2.600(12)					
Mo(1)–Mo(2)	3.237(10)					
Mo(2)	3.537(10)					
S(2)–S(1) (square-faced diagonal) in site 2	3 × 3.410(6)	3 × 3.447				
S–S chains						
S(1)-S(2)-S(1) angle	141°05	138°01				
S(1)-S(1)-S(1) angle	141°31	139°86				

TABLE 6	
Distances (Å) and Angles (°) of $Mo_{1.18}Mo_6S_8$ (	$(\beta - Mo_6 S_8)$
and a-Mo.S.	

 $\beta$ -Mo<sub>6</sub>S<sub>8</sub> sulfide is stable in aqueous hydrochloric acid, but molybdenum atoms Mo(2) located in cavity 1 can be removed from the host structure by using a flow of HCl gas heated at 600°C for 6 h; the binary  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> is then obtained anew [4].

Some cationic exchange reactions have been carried out on  $\beta$ -Mo<sub>6</sub>S<sub>8</sub>. We have intercalated Cu or Ni elements in  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> powder (with MoS<sub>2</sub> impurity) at 430°C for several days with intermediate rehomogenization [9]. The X-ray powder diffraction pattern of the mixture of phases obtained shows elemental Mo, a Cu<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> or Ni<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> phase and MoS<sub>2</sub>. Therefore, it is possible to deintercalate Mo atoms contained in  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> with smaller elements such as Cu and Ni.



Perspective view of the S8 origin cube (site 1) of some Chevrel phases.

**Formulation.** In view of these results, we claim that the atoms occurring in the channels are Mo atoms.  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> is a pseudoternary compound with two types of Mo atoms: Mo(1) atoms forming an octahedral cluster Mo<sub>6</sub> and Mo(2) atoms in site 1 of the Chevrel phase structure. The refined occupancy of Mo(2) is 0.196, meaning 1.18 Mo(2) atoms per Mo<sub>6</sub>S<sub>8</sub> formula. We think that the Mo(2) occupancy can vary slightly around this value, explaining why the c<sub>H</sub> parameter changes (11.28 Å  $\leq$  c<sub>H</sub>  $\leq$  11.32 Å) between different batches of  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> powder.

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DSC analysis on the  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> heated to 1000°C.

Therefore,  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> can be commonly called Mo<sub>7</sub>S<sub>8</sub>. Mo<sub>7</sub>S<sub>8</sub> does not arise from a phase transition of  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> but from a self-molybdenum intercalation reaction:

A part of  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> decomposes into Mo and MoS<sub>2</sub>, and, immediately, the nascent Mo atoms reduce the remaining  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> into the pseudobinary Mo<sub>7</sub>S<sub>8</sub>. It should be noted that the molar weight of Mo<sub>7</sub>S<sub>8</sub> is much heavier than that of MoS<sub>2</sub>; therefore, the weight mixture is roughly 1/4 MoS<sub>2</sub> and 3/4 Mo<sub>7</sub>S<sub>8</sub>.

To our knowledge, this is the first time that such a metal self-intercalation reaction has been observed in solid state chemistry.

**Delocalization of Mo(2) atoms.** Mo(2) atoms are located in six equivalent positions forming a distorted octahedron (Fig. 4) in site 1.

**Comparison between the "mother" and "daughter" structures.** It is very interesting to investigate the structural changes in the chalcogen network that the self-molybdenum intercalation has generated in the  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> "mother" precursor binary. One of the great differences is the S8 origin cube called site 1 in both structures. It is very compressed along the ternary axis in  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub>; the diagonal represented by the S(2)–S(2) distance is (2 × Org-S2) 4.724 Å against 5.366 Å in  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> (Table 3). This is reflected in the opening of the S(1)–S(2)–S(1) angle of the S8 origin cube. The S(1)–S(2)–S(1) angle in  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> is very



The delocalization of the cation M as a function of the  $\alpha_{\rm R}$  rhombohedral angle in M<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub>.

open, 102°37, whereas, it is 95°85 in β-Mo<sub>6</sub>S<sub>8</sub> (Table 6), which is close to 94°34 found in SnMo<sub>6</sub>S<sub>8</sub>. The S(2)–S(1) distances of the S8 origin cube are similar (3.339 Å vs. 3.343 Å), whereas, the S(1)–S(1) distances are different (3.538 Å for  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> and 3.451 Å for β-Mo<sub>6</sub>S<sub>8</sub>). We also can point out that the shortening of the S(2)–S(2) cube diagonal via the Mo<sub>6</sub> cluster is 5.907 Å in β-Mo<sub>6</sub>S<sub>8</sub> vs. 6.155 Å in  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub>.

**Comparison of Mo<sub>7</sub>S<sub>8</sub> and other ternaries.** In Figure 4, we have represented different S8 origin cubes of well known Chevrel phases showing different models of occupancy of site 1. By comparing the Org-M distances, we can easily see that Mo(2) atoms in  $Mo_7S_8$  in site 1 are more delocalized than indium atoms in  $InMo_6S_8$ , but less than Cu atoms in  $Cu_{1.8}Mo_6S_8$  or Pd atoms in  $Pd_{1.6}Mo_6S_8$ , and the pseudo cube S8 is similar to that of  $SnMo_6S_8$ .

Another interesting feature is that  $Mo_7S_8$  does not respect the model of cationic delocalization suggested by Yvon (Fig. 6) [12]. In  $Mo_7S_8$ , the rhombohedral angle is equal to 89°48. This model expects that the cation Mo(2) is localized at the origin of site 1 for such an  $\alpha_R$ rhombohedral angle, as in Pb $Mo_6S_8$  or Sn $Mo_6S_8$  compounds. Actually, the delocalization of Mo(2) is 1.109 Å from the origin of site 1. The curve predicts a rhombohedral angle larger than 94°.  $Mo_7S_8$  is not the only exception to this model: the model does not fit Pd<sub>1.6</sub> $Mo_6S_8$ either [5]. This apparent disagreement can be explained by the existence of metal–metal bonding between the atoms contained in the channels of both compounds.

**Nature of the Mo(2) atoms.** As we have already described, Mo(2) atoms are located on sixfold general positions, yielding a distorted octahedron (Fig. 4), but the occupancy on these six equivalent positions (6f) is 0.196. This means that there is more than one Mo atom per origin site, that is, there are two Mo(2) atoms in some unit cells. These two Mo(2) atoms are 2.22 Å apart on the diagonal of the octahedron. This distance is close to a multiple bond. For instance, quadruple bonds occur in the divalent molybdenum(II) complex compounds  $K_4[Mo_2Cl_8]\cdot 2H_2O$  and  $Mo_2(CH_3CO_2)_4$ ; they contain a pair of Mo atoms tightly bonded together (Mo–Mo = 2.14 Å and 2.11 Å, respectively) [10]. In these  $(Mo_2)^{4+}$  species

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FIG. 7 Environment of molydenum atoms in  $MoMo_6S_8$  and  $K_4[Mo_2Cl_8]$ .

compounds, all four electrons on each molybdenum atom are used to form a Mo–Mo quadruple bond ( $\sigma + 2\pi a + \delta$ ). The Mo atoms are in a squared planar environment of L ligands as for Mo<sub>7</sub>S<sub>8</sub> (Fig. 7). These results allow us to assume that there is fourfold bonding between two Mo(2) atoms; therefore, we can write Mo<sub>7</sub>S<sub>8</sub> as  $(Mo^{II}-Mo^{II})^{4+}_{1/2}(Mo_6S_8)^{2-}$ . The  $(Mo_2)^{4+}$  species inside the channels of the Chevrel phase structure form a kind of  $[Mo_2L_8]$  molecule like  $[Mo_2Cl_8]^{4-}$  in K<sub>4</sub>Mo<sub>2</sub>Cl<sub>8</sub>·2H<sub>2</sub>O (Fig. 7).

**Charge transfer.** Because of the divalent valence state of  $Mo^{II}(2)$  atoms, the  $Mo_6S_8$  unit in  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> has a -2 charge corresponding to a VEC (valence electron concentration) per Mo<sub>6</sub> cluster close to 22 electrons. In Chevrel phases, we have a direct relationship between VEC and (Mo<sub> $\Delta$ </sub>-Mo<sub> $\Delta$ </sub>) intracluster distances [11].

The significant Mo<sub>6</sub> cluster distances of Mo<sub>7</sub>S<sub>8</sub> and some other Chevrel phases are listed in Table 3. Mo<sub>7</sub>S<sub>8</sub> and  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> (VEC = 20 e<sup>-</sup>) present quite different Mo<sub>6</sub> clusters. The comparison of Mo<sub>6</sub> cluster distances of Mo<sub>7</sub>S<sub>8</sub> and some other ternary Chevrel phases, especially those of PbMo<sub>6</sub>S<sub>8</sub>, shows a VEC near 22 e<sup>-</sup> per cluster for Mo<sub>7</sub>S<sub>8</sub> (Table 3). This is in agreement with the quadruple bond Mo(2)–Mo(2), which presumes that the valence state of Mo(2) is +2. Chevrel phases with 22 e<sup>-</sup> per cluster often exhibit interesting superconducting properties (PbMo<sub>6</sub>S<sub>8</sub>: T<sub>c</sub> = 15 K, Bc<sub>2</sub> (0 K) = 60 tesla [12]). We have found no superconducting properties for Mo<sub>7</sub>S<sub>8</sub> compound by inductive measurements down to 1.6 K, when  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> is a superconductor (T<sub>c</sub> = 1.8 K). We have also carried out EPR and DC susceptibility (SQUID) measurements. We have not seen odd electrons (Curie-Weiss law) of the Mo(2) atoms by these methods, and Mo<sub>7</sub>S<sub>8</sub> shows a TIP (Pauli paramagnetism) about  $0.7 \times 10^{-7}$  uem CGS, which supports our hypothesis of a Mo(2)–Mo(2) quadruple bond. Such a feature can probably affect the electronic band structure of the model used for the Chevrel phases [13]. The Mo(2) dumbbells have 4d molecular orbitals that can take part in the electronic band structure at the Fermi level and, thus, prevent superconductivity.

Another assumption could be that  $Mo_7S_8$  undergoes an electronic phase transition at low temperature as in  $MMo_6S_8$  (M = Eu, Ba, Sr) compounds (VEC =  $22e^-$ ); the half-filled  $E_g$  band splits into two subbands [14].

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These probable modifications of the Fermi level can explain the loss of superconductivity in this pseudobinary compound with 22 electrons.

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