

# First Example of Molybdenum Atoms in the Network of High Temperature Chevrel Phases: $\text{Mo}_y[\text{Mo}_6\text{Se}_{8-x}\text{S}_x]$

Stéphanie Belin, Roger Chevrel, and Marcel Sergent

Laboratoire de Chimie du Solide et Inorganique Moléculaire (LCSIM), UMR CNRS 6511, Université de Rennes-1, Avenue du Général Leclerc, 35042 Rennes Cedex, France

Received March 17, 1998; revised form November 15, 1998; accepted February 26, 1999

**In the literature  $\text{Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 4$ ) Chevrel phase binaries are stable compounds, synthesized by solid state reaction from stoichiometric mixture of  $\text{MoS}_2$ ,  $\text{MoSe}_2$ , and Mo powders at  $1200^\circ\text{C}$ . We report the single-crystal structure of these compounds. The structural determinations show as expected a classical Chevrel phase structure with a framework of pseudomolecular  $\text{Mo}_6\text{Se}_{8-x}\text{S}_x$  cubic units but furthermore exhibit molybdenum atoms in the channels of the host structure of these compounds, leading to the new formula  $\text{Mo}_y[\text{Mo}_6\text{Se}_{8-x}\text{S}_x]$  with  $0 \leq x \leq 5$  and  $y \sim 0.3$ . These extra molybdenum atoms stabilize the Chevrel phase host network and seem to be linking with a molybdenum atom of the  $\text{Mo}_6$  cluster, forming a kind of  $\text{Mo}_7$  cluster.** © 1999 Academic Press

## I. INTRODUCTION

The so-called Chevrel phases with formula  $M_y^+ \text{Mo}_6X_8$  ( $M$  = metal ion,  $X$  = chalcogen) have been extensively studied because of their interesting properties (superconductivity, magnetism, ionic conductivity ... (1–3)). These properties are due to the peculiar structure of these compounds, which can be considered as several subnetworks that interact weakly with each other. The structure of the  $M_y\text{Mo}_6X_8$  ternary molybdenum cluster chalcogenides can be described as a three-dimensional framework of quasi-rigid  $\text{Mo}_6X_8$  building blocks, forming quasi-orthogonal secant channels where  $M$  metal ions can take place. This situation allows small cations to be very mobile (3).

In this large family, metastable compounds exist. Chevrel *et al.* have shown that  $\alpha\text{-Mo}_6\text{S}_8$  binary cannot be prepared from the starting elements, in contrast to the case of  $\text{Mo}_6\text{Se}_8$  (4). Thus,  $\alpha\text{-Mo}_6\text{S}_8$  is a metastable binary. We recently reported the single-crystal structure determination of a new metastable binary sulfide type:  $\beta\text{-Mo}_6\text{S}_8$  (5).  $\beta\text{-Mo}_6\text{S}_8$  is only obtained by soft chemistry from heating of the  $\alpha\text{-Mo}_6\text{S}_8$  binary, and thus the  $\beta$ -type binary is stabler than the  $\alpha$ -type. In  $\beta\text{-Mo}_6\text{S}_8$  we identified molybdenum atoms in the host network, which can explain the higher stability of this

compound. We demonstrated that  $\beta\text{-Mo}_6\text{S}_8$  is really  $\text{Mo}_{-1}[\text{Mo}_6\text{S}_8]$ , a pseudoternary compound.

So, we decided to investigate the whole series of  $\text{Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 4$ ) stable compounds in order to check the occurrence of molybdenum atoms in the channels of the host.

In the system  $\text{Mo}_6\text{Se}_8\text{-Mo}_6\text{S}_8$ , at least two  $\text{Mo}_6\text{Se}_{8-x}\text{S}_x$  solid solutions exist (6–8). The first one is composed of stable “binaries” made at high temperature, so-called HT- $\text{Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 4$ ). The other one is formed by metastable compounds denoted  $\alpha\text{-Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 8$ ) obtained by soft chemistry (6–9). This last series can only come from a ternary chalcogenide compound such as  $\text{Cu}_y\text{Mo}_6X_8$  or  $\text{Ni}_y\text{Mo}_6X_8$  ( $X = \text{Se}, \text{S}$ ) from which small cations have been deintercalated by an oxidation process. For example, hydrochloric acid on  $\text{Ni}_y\text{Mo}_6X_8$  powders removes Ni cations; then  $\alpha\text{-Mo}_6X_8$  metastable binaries are obtained (4).

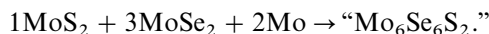
With the same stoichiometry as chalcogen atoms,  $\alpha$  and HT compounds have different crystal lattice parameters, but the same space group,  $R\bar{3}$ . Particularly the  $\alpha_R$  rhombohedral angle of HT compounds is higher than that of the  $\alpha$  corresponding binaries. This angle changes weakly as function of  $x$  in the  $\alpha$  series, while it increases greatly in the HT solid solution (2, 5).

Until now, no reason has been proposed to explain this difference, and sometimes  $\alpha$  and HT compounds have even been confused (9). A correct explanation for us is that HT- $\text{Mo}_6X_8$  are also pseudoternary compounds as  $\beta\text{-Mo}_6\text{S}_8$ . In order to confirm this assumption we report in the following the single-crystal structure results of the HT stable compounds to discover whether or not they contain extra molybdenum atoms in the channels of the host network.

## II. EXPERIMENTAL AND COMMENT

We started to synthesize HT- $\text{Mo}_6X_8$  compounds from stoichiometric mixtures of  $\text{MoS}_2$ ,  $\text{MoSe}_2$ , and Mo powders.

For instance for  $x = 2$  the reactional mixture is:



It is pressed into pellets, then sealed into silica tube, and progressively heated at  $1200^\circ\text{C}$  for 1 week. The X-ray diffraction pattern of the resulting compounds shows  $\text{Mo}_6X_8$  rhombohedral compound, but always in the presence of  $\text{MoX}_2$  impurities isotypic with  $\text{MoS}_2$  (Fig. 1). So if we want to explain the presence of  $\text{MoX}_2$  in the resulting product, in order to equilibrate the reaction, elemental Mo is necessarily in this product. But we never identified unreacted molybdenum powder in the resulting mixture. So we expect the missing molybdenum atoms to be inside the host network channels of  $\text{HT-Mo}_6X_8$  compounds.

To test this assumption, we carried out an easy experiment. We added to the starting mixture an excess of molybdenum metallic powder and then followed the previous process. The addition of extra molybdenum atoms (about  $0.30\text{Mo}/\text{Mo}_6$ ) allowed us to obtain single-phase  $\text{HT-Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $x = 2$ ) compounds without  $\text{Mo}(\text{Se,S})_2$  (Fig. 2). This new result led us to solve the crystal structure on single crystals from two mixtures of composition “ $\text{Mo}_6\text{Se}_6\text{S}_2$ ” and “ $\text{Mo}_6\text{Se}_{4.6}\text{S}_{3.4}$ .”

These single crystals of  $\text{HT-Mo}_6\text{Se}_{8-x}\text{S}_x$  are made from a “stoichiometric” mixture of  $\text{MoS}_2$ ,  $\text{MoSe}_2$ , and Mo powders pressed into pellets and placed in an alumina crucible. The crucible is then sealed into a molybdenum tube and heated around  $1550^\circ\text{C}$  for 72 h. After that, the tubes are cooled at the rate of  $100^\circ\text{C}/\text{h}$  down to  $1000^\circ\text{C}$ .

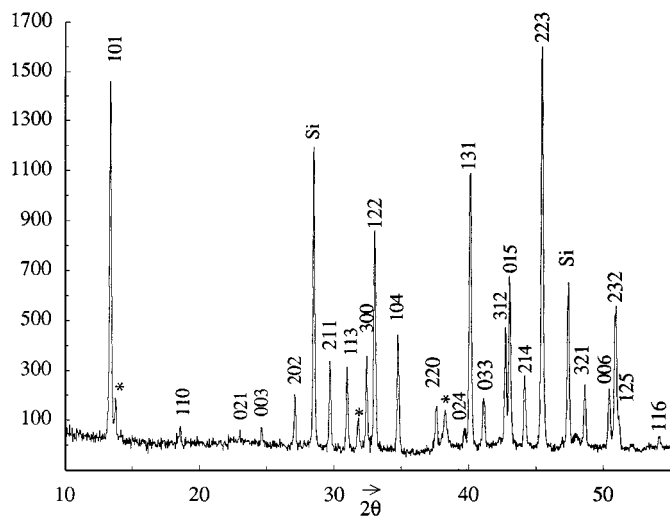


FIG. 1. X-ray diffraction pattern of  $\text{HT-Mo}_6\text{Se}_6\text{S}_2$  and occurrence of  $\text{MoX}_2$  (\*) (with silicium standard) ( $\lambda\text{CuK}\alpha 1$ ).

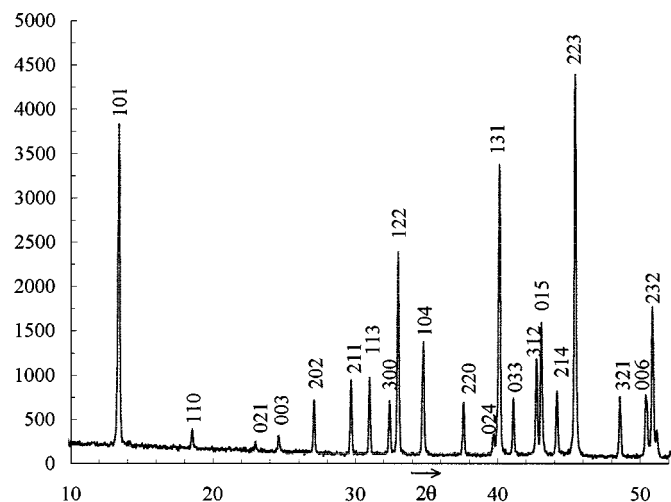


FIG. 2. X-ray diffraction pattern of  $\text{HT-Mo}_6\text{Se}_6\text{S}_2$  with  $\sim 0.3$  extra molybdenum atoms per  $\text{Mo}_6$ .

### III. RESULTS AND DISCUSSION

#### Crystal Structure Determination

We isolated small single crystals of both “compositions.” X-ray diffraction intensities were collected on a Nonius-CAD 4 four-circle diffractometer under the experimental conditions given in Table 1. All calculations are performed using the MOLEN’s program system (10) and absorption corrections were applied. We refined in a rhombohedral unit cell the atomic positions of molybdenum atoms and X chalcogen atoms constituting the  $\text{Mo}_6X_8$  cluster units as found in  $\text{Mo}_6\text{Se}_8$ , assuming that crystals contained only selenium atoms. Then, we refined the fractional occupancy of the selenium atoms: at the end of refinement we calculated the real occupancies of both the selenium and the sulfur atoms from the selenium fractional occupancy and constraint to full occupancy of the eight available chalcogen positions.

All refined parameters and results are summarized in Table 2. After refinement of all molybdenum and chalcogen atom parameters, the differential map of electronic density pointed out a significant electronic density peak on a  $6f$  position inside the channels of the network. This excess of electrons is situated in a cavity called cavity 2 centered in  $(1/2, 0, 0); (0, 1/2, 0); (0, 0, 1/2)$  inside the host. These electrons are attributed to molybdenum atoms (Fig. 3).

The most persuasive proof of the nature of these excess atoms is the release of molybdenum chloride observed when  $\text{HT-Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 4$ ) compounds are heated near  $600^\circ\text{C}$  under HCl gas flow (8). A loss of weight is noted, and the X-ray diffraction pattern shows that the resulting compounds are actually  $\alpha\text{-Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 4$ ) binaries. We

**TABLE 1**  
**Crystal Data and Experimental Parameters for Intensity Data Collection**

a. $\text{Mo}_{0.28}\text{Mo}_6\text{Se}_{4.78}\text{S}_{3.22}$		
I. Crystal data		
Formula:	$\text{Mo}_{0.28}\text{Mo}_6\text{Se}_{4.78}\text{S}_{3.22}$	M: 1083.2 g/mole
Crystal system:	rhombohedral	R-3 (no 148)
Parameters:	$a_R = 6.5807 (6) \text{ \AA}$ $a_H = 9.556 (1) \text{ \AA}$	$V_R = 283.68 (8) \text{ \AA}^3$ $V_H = 851.0 (2) \text{ \AA}^3$
Unit cell refined from reflection ( $9^\circ < \theta < 15^\circ$ )		
$\rho_{\text{cal}} = 6.34 \text{ g/cm}^3$	Z: 1	
Crystal size	$0.058 \times 0.058 \times 0.046 \text{ mm}^3$	
Linear absorption factor	$32.69 \text{ mm}^{-1}$	
II. Data collection		
Temperature: 295 K	Wavelength: MoK $\alpha$ radiation	
Diffractometer: Enraf Nonius CAD-4	Scan mode: $\omega$ -2 $\theta$	
Monochromator: graphite	Scan width: $1.20 + 0.35 \text{tg}\theta$	
$-10 < h < 10$ ; $0 < k < 10$ ; $0 < l < 10$	$\theta_{\text{max}}: 35$	
968 measured reflections		
701 independent reflections (with $I > \sigma(I)$ )	$R_{\text{int}}: 0.025$	
III. Structural determination		
Lorentz and polarization corrections		
Absorption correction: PSISCAN (11)		
Refinement on $F$		
Refined parameters: 35		
603 independent reflections with $I > 3\sigma(I)$		
Unweighted agreement factor $R = 0.030$	Weighted agreement factor $R_w = 0.041$	
$S = 0.864$		
Ponderation factor: 0.07	$\omega = 4 F_0^2 / [\sigma^2(F_0^2) + (0.07 F_0^2)^2]$	
$\Delta\rho_{\text{max}}: 1.359 \text{ e}^- \cdot \text{\AA}^3$	$\Delta\rho_{\text{min}}: -3.413 \text{ e}^- \cdot \text{\AA}^3$	
$(\Delta/\sigma)_{\text{max}} < 0.05$		
Extinction coefficient	$3.96 \times 10^{-7}$	
Atomic scattering factor from Internal Tables for X-Ray Crystallography (12)		
b. $\text{Mo}_{0.28}\text{Mo}_6\text{Se}_{4.22}\text{S}_{3.78}$		
I. Crystal data		
Formula:	$\text{Mo}_{0.28}\text{Mo}_6\text{Se}_{4.22}\text{S}_{3.78}$	M: 1056.3 g/mole
Crystal system:	rhombohedral	R-3 (no 148)
Parameters:	$a_R = 6.5660 (5) \text{ \AA}$ $a_H = 9.547 (1) \text{ \AA}$	$V_R = 281.64 (8) \text{ \AA}^3$ $V_H = 844.9 (2) \text{ \AA}^3$
Unit cell refined from 25 reflections ( $9 < \theta < 15$ )		
$\rho_{\text{cal}} = 6.23 \text{ g/cm}^3$	Z: 1	
Crystal size	$0.046 \times 0.046 \times 0.046 \text{ mm}^3$	
Linear absorption factor:	$32.93 \text{ mm}^{-1}$	
II. Data collections		
Temperature: 295 K	Wavelength: MoK $\alpha$ radiation	
Diffractometer: Enraf Nonius CAD-4	Scan mode: $\omega$ -2 $\theta$	
Monochromator: graphite	Scan width: $1.20 + 0.35 \text{tg}\theta$	
$0 < h < 10$ ; $-10 < k < 10$ ; $0 < l < 10$	$\theta_{\text{max}}: 35$	
962 measured reflections		
530 independent reflections (with $I > \sigma(I)$ )	$R_{\text{int}}: 0.072$	
III. Structure determination		
Lorentz and polarization corrections		
Absorption correction: spherical		
Refinement on $F$		
Refined parameters: 35		
446 independent reflections with $I > 3\sigma(I)$		
Unweighted agreement factor $R = 0.041$	Weighted agreement factor $R_w = 0.050$	
$S = 1.188$		
Ponderation factor: 0.05	$\omega = 4 F_0^2 / [\sigma^2(F_0^2) + (0.05 F_0^2)^2]$	
$\Delta\rho_{\text{max}}: 1.665 \text{ e}^- \cdot \text{\AA}^3$	$\Delta\rho_{\text{min}}: -0.656 \text{ e}^- \cdot \text{\AA}^3$	
$(\Delta/\sigma)_{\text{max}} < 0.02$		
Extinction coefficient:	$7.07 \times 10^{-9}$	
Atomic scattering factor from Internal Tables for X-Ray Crystallography (12)		

TABLE 2  
Positional Parameters, Isotropic Equivalent  $B^a$  and  
Their Estimated Standard Deviations

Atom	Position	x	y	z	$B$ ( $\text{\AA}^2$ )
HT-Mo <sub>0.28</sub> Mo <sub>6</sub> Se <sub>4.78</sub> S <sub>3.22</sub>					
Mo(1)	6f	0.22075(7)	0.41092(6)	0.54575(7)	1.492(7)
Se(1)	6f	0.3739(1)	0.1275(1)	0.7406(1)	1.80(1)
0.51 Se/0.49 S					
Se(2)	2c	0.2036(1)	0.2036(1)	0.2036(1)	1.872(4)
0.86 Se/0.14 S					
Mo(2)	6f	0.987(1)	0.491(1)	0.927(1)	1.1(1)
$\tau = 0.047(1)$					
HT-Mo <sub>0.28</sub> Mo <sub>6</sub> Se <sub>4.22</sub> S <sub>3.78</sub>					
Mo(1)	6f	0.2202(1)	0.4105(1)	0.5457(1)	1.83(1)
Se(1)	6f	0.3731(2)	0.1278(2)	0.7391(2)	2.28(3)
0.43 Se/0.57 S					
Se(2)	2c	0.2024(2)	0.2024(2)	0.2024(2)	2.26(1)
0.82 Se/0.18 S					
Mo(2)	6f	0.986(2)	0.492(2)	0.929(2)	0.9(2)
$\tau = 0.046(2)$					

<sup>a</sup> The isotropic equivalent displacement parameter is defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ .

have also demonstrated that  $\alpha$ -Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub> compounds are binary compounds as Mo<sub>6</sub>Se<sub>8</sub> or  $\alpha$ -Mo<sub>6</sub>S<sub>8</sub> by single crystal structure determinations (8). These  $\alpha$ -Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub> compounds constitute only host networks without cations in the channels.

The final refinements give the following formula for the HT studied compounds: Mo<sub>0.28</sub>[Mo<sub>6</sub>Se<sub>4.78</sub>S<sub>3.22</sub>] and Mo<sub>0.28</sub>[Mo<sub>6</sub>Se<sub>4.22</sub>S<sub>3.78</sub>].

### Crystal Structure Description and Discussion

From the calculated occupancies of chalcogen atoms, the HT-Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub> ( $0 \leq x \leq 4$ ) compounds exhibit an enrichment in selenium in the 2c chalcogen position on the three-fold axis (Table 2) as the corresponding mixed binaries  $\alpha$ -Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub>. This case (large anion on 2c position) seems to stabilize such compounds when they are mixed binaries, pseudobinaries such as Mo<sub>6</sub>S<sub>6</sub>Br<sub>2</sub> (13), or mixed ternaries with small cations (7, 14, 15). In contrary, in the compounds containing large cations such as La, the largest chalcogen (Se) sits preferably on a general 6f position off the three-fold axis (16). The main interatomic distances are reported in Table 3. The extra molybdenum atoms (Mo(2)) situated in cavity 2 are in distorted triangular-based pyramidal chalcogen sites (Fig. 4b). In cavity 2, two equivalent positions exist via  $\bar{1}$  inversion center located on (1/2,0,0); (0,1/2,0); (0,0,1/2). The distance between two Mo(2) positions is less

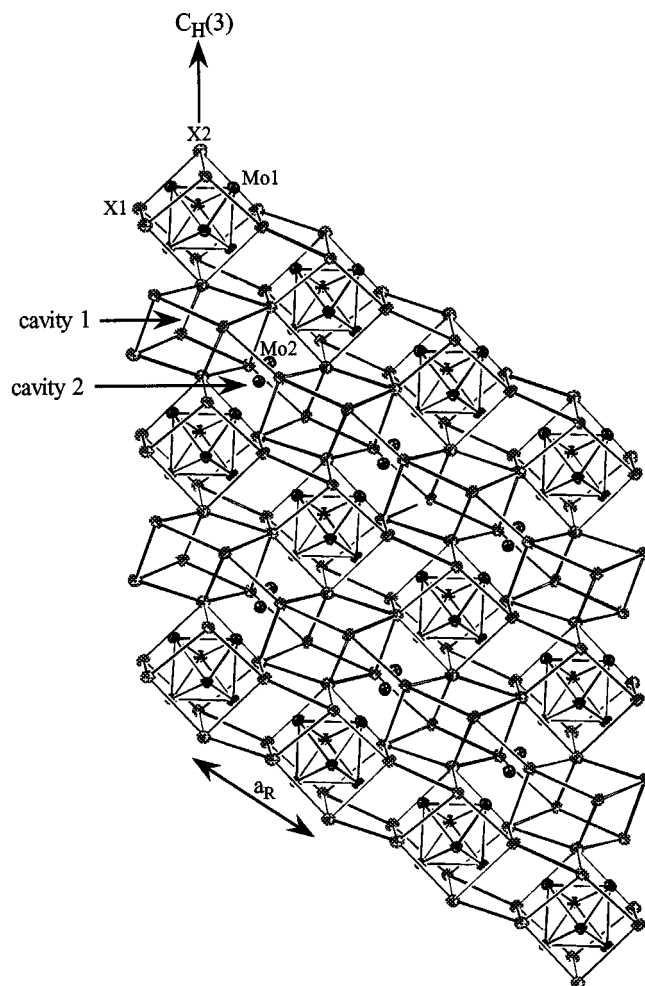


FIG. 3. Projection of the HT-Mo<sub>x</sub>Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub> ( $0 \leq x \leq 4$ ) structure on (11-20) hexagonal plane. View of the two types of cavities.

than 1.0  $\text{\AA}$ ; when a position in cavity 2 is occupied, the other one is vacant (Fig. 4a and Table 3).

In  $\beta$ -Mo<sub>6</sub>S<sub>8</sub> compound, the Mo(2) extra atoms occupy cavity 1 (6f position) in a squared planar sulfur environment. One cavity 1 over two is occupied by two Mo(2) atoms forming a fourfold bonding at 2.22  $\text{\AA}$  (5) (Fig. 5b).

In HT compounds, on the other hand, there is no bonding between Mo(2) atoms. But the shortest distance ( $\sim 2.73$   $\text{\AA}$ ) between an intercalated Mo(2) molybdenum atom and a Mo(1) molybdenum atom forming the Mo<sub>6</sub> cluster is very similar to those existing in the Mo<sub>6</sub> cluster ( $\sim 2.70$   $\text{\AA}$ ) (Table 3). So we can assume that Mo(2) atoms are single-bonded to Mo(1) atoms and form a kind of Mo<sub>7</sub> cluster (Fig. 5a). Yet the partial occupancy of cavity 2 can let us imagine more complex molybdenum clusters such as Mo<sub>8</sub> or Mo<sub>9</sub>.

Recent results on metastable  $\beta$ -type Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub> ( $0 < x < 8$ ) pseudoternaries also showed the occurrence of

**TABLE 3**  
**Interatomic Distances (Å) for HT-Mo<sub>y</sub>Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub> Compounds**

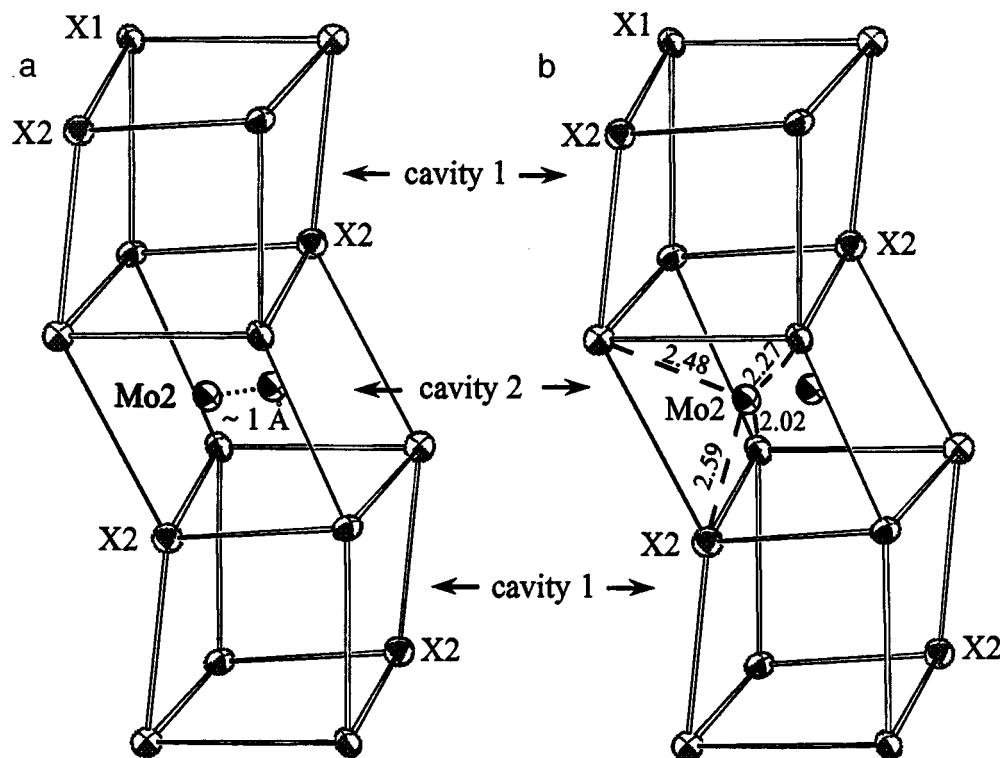
Distances	HT-Mo <sub>0.28</sub> Mo <sub>6</sub> Se <sub>4.78</sub> S <sub>3.22</sub>	HT-Mo <sub>0.28</sub> Mo <sub>6</sub> Se <sub>4.22</sub> S <sub>3.78</sub>
Mo <sub>6</sub> X <sub>8</sub> cluster unit		
Intratriangle		
(Mo(1)-Mo(1)) <sub>Δ</sub>	2.703(1)	2.704(1)
Intertriangle Mo(1) <sub>Δ</sub> -Mo(1) <sub>Δ</sub>	2.791(1)	2.788(1)
Intercluster Mo(1)-Mo(1)		
Mo(1)-X(2)	2.563(1)	2.562(1)
X(1)	2.503(1)	2.496(1)
X(1)	2.542(1)	2.530(1)
X(1)	2.588(1)	2.581(1)
Intercluster Mo(1)-X(1)	2.543(1)	2.532(1)
X(2)-X(1)	3.718(1)	3.705(1)
X(1)-X(1)	3.481(1)	3.474(1)
X <sub>8</sub> origin cubic site		
X(2)-X(1)	3.325(1)	3.321(1)
X(1)-X(1)	3.510(1)	3.500(1)
Mo(1)-Mo(2)		
Mo(2)-Mo(2)	2.73(1)	2.72(1)
Mo(2)-Mo(2)	0.97(1)	0.95(1)
Mo(2)-X(2)	2.59(1)	2.58(1)
X(1)	2.02(1)	2.03(1)
X(1)	2.27(1)	2.27(1)
X(1)	2.48(1)	2.48(1)

extra molybdenum Mo(2) atoms in the channels of the host structure (8). In the near future, those results will be compared to the ones presented here (17).

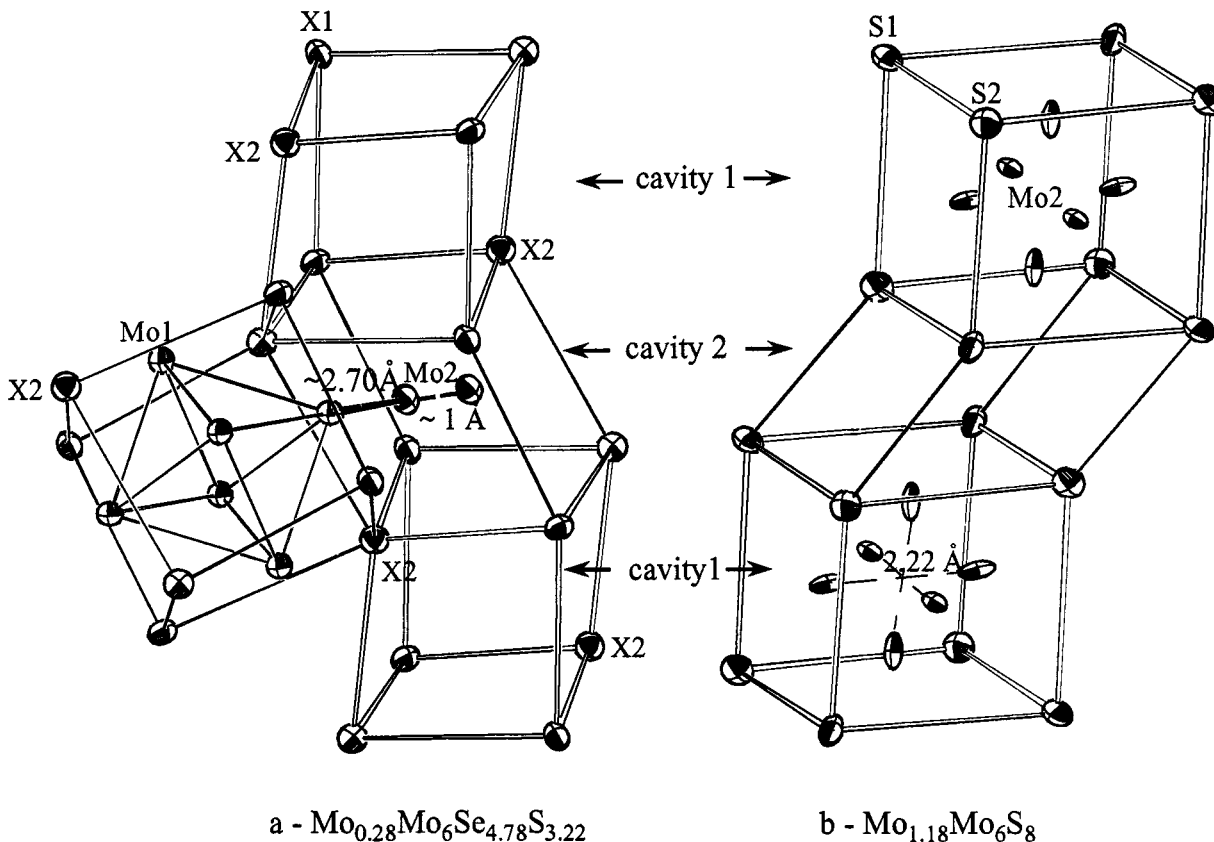
### Valence State of Mo(2)

In the Chevrel phases, there is a correlation between the valence state of the intercalated element in the host network and the Mo(1)<sub>Δ</sub>-Mo(1)<sub>Δ</sub> intratriangle distance of the Mo<sub>6</sub> cluster (Fig. 6) (18,19). Yvon has shown that the metallic element transfers its valence electrons toward the Mo<sub>6</sub> cluster. This charge transfer provokes the shortening of the Mo(1)<sub>Δ</sub>-Mo(1)<sub>Δ</sub> intratriangle distance of the Mo<sub>6</sub> cluster, which means reinforcement of the Mo-Mo bonding inside the Mo<sub>6</sub> cluster.

A model taking into consideration the difference of covalence of chalcogen (Se and S) was proposed to illustrate the variation of the distance Mo(1)<sub>Δ</sub>-Mo(1)<sub>Δ</sub> as a function of this transfer or another parameter: the valence electron concentration per molybdenum atom of the Mo<sub>6</sub> cluster called VEC (Fig. 6) (18,19). The difference of covalence between sulfur and selenium atoms involves VEC = 3.33 e<sup>-</sup>/Mo for Mo<sub>6</sub>S<sub>8</sub>, VEC = 3.50 e<sup>-</sup>/Mo for Mo<sub>6</sub>Se<sub>8</sub>, and intermediate values for α-Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub> (0 ≤ x ≤ 8) mixed binaries. Two distinct curves have been drawn for ternary molybdenum sulfides and selenides. Between these two curves are many curves for M<sub>y</sub>Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub> (0 ≤ x ≤ 8) mixed ternary compounds. From this graph we can infer different VEC for α and HT compounds having the same Se/S ratio. This VEC difference corresponds to charge



**FIG. 4.** Host network occupation of cavity 2 by Mo(2) extra molybdenum atoms in HT- Mo<sub>y</sub>Mo<sub>6</sub>Se<sub>8-x</sub>S<sub>x</sub> (0 ≤ x ≤ 4). (a) Mo(2)-Mo(2) distance ~1 Å; (b) environment of Mo(2) atoms.



**FIG. 5.** View of the two kinds of Mo(2) extra molybdenum atoms. (a) Case of HT- $\text{Mo}_y\text{Mo}_6\text{X}_8$  ( $\text{Mo}_{0.28}\text{Mo}_6\text{Se}_{4.78}\text{S}_{3.22}$ ): 2.70 Å corresponding to a single bond Mo(2)–Mo(1) with Mo(1) atoms forming the  $\text{Mo}_6$  cluster. (b) Case of  $\beta$ - $\text{Mo}_6\text{S}_8$  ( $= \text{Mo}_{1.18}\text{Mo}_6\text{S}_8$ ): 2.22 Å corresponding to a quadruple bond Mo(2)–Mo(2).

transfer coming from the Mo(2) extra molybdenum atoms toward the  $\text{Mo}_6$  cluster. Then, we calculate the charge of the Mo(2) atoms contained in the HT compounds (VEC difference divided by the quantity of Mo(2) atoms).

We have reported on the graph the  $\text{Mo}(1)_\Delta$ – $\text{Mo}(1)_\Delta$  distance found in HT ternary mixed compounds and corresponding  $\alpha$  binaries (Fig. 6). In Table 4, we collect the deduced VEC of HT and  $\alpha$  compounds, and the charge of Mo(2) atoms intercalated in HT pseudoternaries.

The Mo(2) atoms seem to be at low valence state near +2 like that of the Mo(1) atoms forming the  $\text{Mo}_6$  cluster. The low valence chemistry of molybdenum is characterized by the formation of metal–metal bonding. So the Mo(2) atoms should be linked with other metallic atoms. Indeed, the shortest Mo(2)–Mo(1) distance, around 2.70 Å, supports the hypothesis of Mo(1)–Mo(2) single bonding (Table 3, Fig. 5b). So, we probably have some  $\text{Mo}_7$  or higher nuclearity clusters in HT compounds, because of the low fractional Mo(2) occupancy ( $0.28\text{Mo}(2)/\text{Mo}_6(1)$ ).

We have shifted the old limit composition  $\text{Mo}_6\text{Se}_4\text{S}_4$  (7) by addition of extra molybdenum at richer  $\text{MoS}_2$  starting mixtures. So we stabilized a new compound close

to  $\text{Mo}_{0.50}\text{Mo}_6\text{Se}_3\text{S}_5$  composition ( $a_H = 9.51(1)$  Å;  $c_H = 10.59(1)$  Å;  $v_H = 826(1)$  Å<sup>3</sup>) (Fig. 7).

The discovery of molybdenum atoms within the network of the Chevrel phases permits determination of a more accurate composition of the HT pseudobinaries (Fig. 3) and enlarges the HT compound range.

#### IV. PHYSICAL PROPERTIES

We have studied the superconducting critical temperature ( $T_c$ ) of HT- $\text{Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 5$ ) and  $\alpha$ - $\text{Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 8$ ) compounds. We have determined the  $T_c$  onset by inductive measurements and represented the variation of  $T_c$  as a function of  $x$  for these two solid solutions (Fig. 8). Our results for  $\alpha$  compounds are in agreement with those of Chevrel and co-workers (7), Tarascon *et al.* (9), and Umarji *et al.* (20).

For the same chalcogen stoichiometry, HT pseudobinaries have lower  $T_c$  than  $\alpha$  compounds. The presence of extra molybdenum atoms seems to decrease  $T_c$ , probably because extra molybdenum atoms have 4d atomic orbitals that can

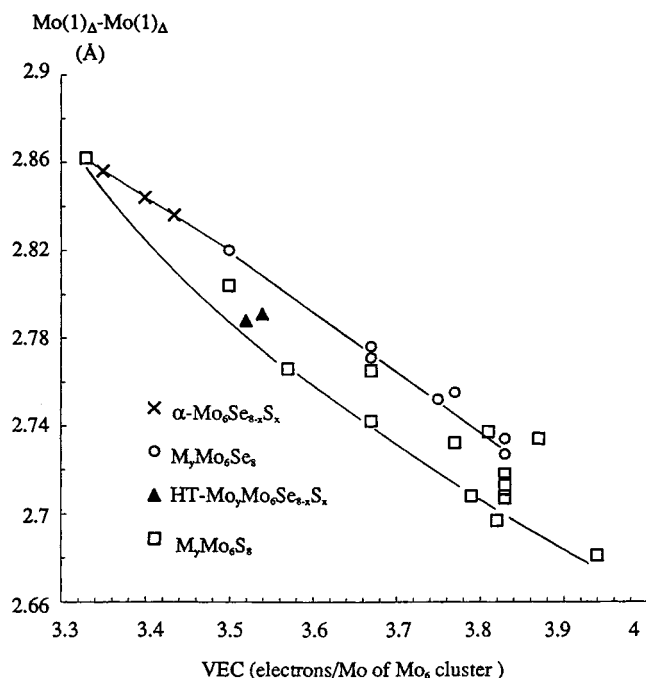


FIG. 6. Variation of  $\text{Mo}(1)_\Delta\text{-Mo}(1)_\Delta$  distance as function of VEC for  $\alpha$ , HT mixed binaries and sulfur, selenium ternaries from the model of Yvon (18, 19).

take part in the electronic band structure at the Fermi level and modify the band model compared to the one for corresponding  $\alpha$  pseudobinaries.

In HT compounds, a correlation between  $\alpha_R$  and  $T_c$  has been already reported (21).  $T_c$  is inversely proportional to  $\alpha_R$ . From our new results, the increase of  $\alpha_R$  as function of  $x$  in HT series can be now explained by the existence of extra molybdenum atoms. In fact,  $\alpha_R$  increases when the number of extra molybdenum atoms increases. For example, the richest sulfur compound  $\text{Mo}_{0.5}\text{Mo}_6\text{Se}_3\text{S}_5$  has the highest  $\alpha_R$  and actually contains the most extra molybdenum atoms, and also has the lowest  $T_c$ . In contrast,  $\text{Mo}_6\text{Se}_8$  exhibits the highest  $T_c$  and the smallest  $\alpha_R$  of the HT series, and so should have the fewest extra molybdenum atoms ( $y \sim 0$ ) in the host lattice. Really, we expected  $\text{Mo}_6\text{Se}_8$  to be a true

TABLE 4  
VEC of  $\alpha\text{-Mo}_6\text{Se}_{8-x}\text{S}_x$  and  $\text{HT-Mo}_y\text{Mo}_6\text{Se}_{8-x}\text{S}_x$  Compounds, Valence State and Charge of Mo(2) Extra Molybdenum Atoms

Composition	$\text{Se}_{4.78}\text{S}_{3.22}$ $\text{Se}_{4.22}\text{S}_{3.78}$	
	$\alpha$	
VEC electron/Mo	3.43	3.41
	3.54	3.52
Number of transferred electrons to $\text{Mo}_6$	HT 0.66	0.66
$n$ charge of Mo(2) atom	+ 2.36	+ 2.36
$n'$ charge of Mo(1) atom from $\text{Mo}_6$	$y = 0.28$	+ 2.48

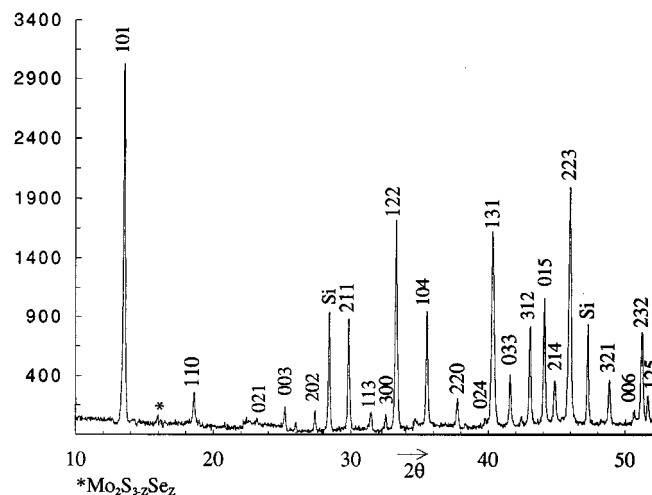


FIG. 7. X-ray diffraction pattern of a new  $\text{Mo}_{0.50}\text{Mo}_6\text{Se}_3\text{S}_5$  compound (with silicon standard) ( $\lambda\text{CuK}\alpha 1$ ).

binary because the refined unit cell parameters on single crystals give the same results for HT- $\text{Mo}_6\text{Se}_8$  and  $\alpha\text{-Mo}_6\text{Se}_8$  compounds (8).

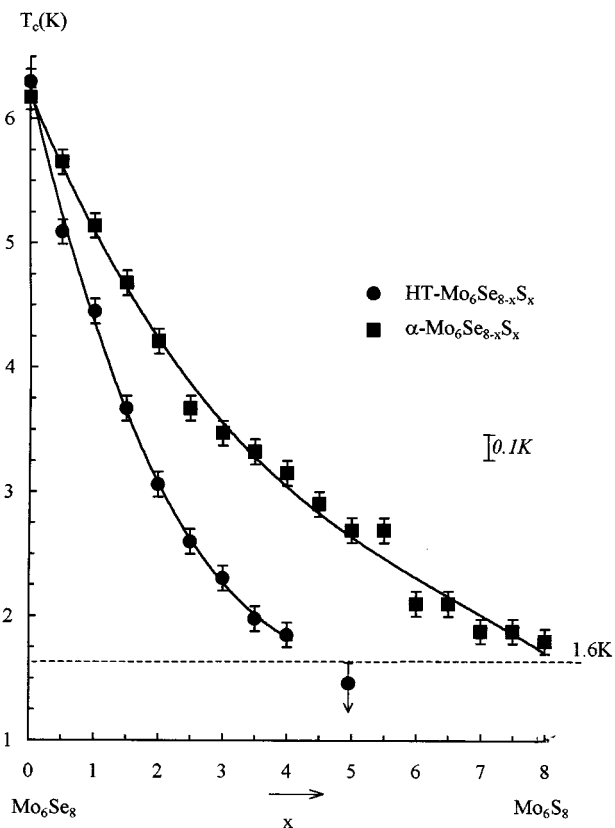


FIG. 8. Variation of  $T_c$  (onset) as a function of  $x$  amount of sulfur in  $\alpha\text{-Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 8$ ) and  $\text{HT-Mo}_y\text{Mo}_6\text{Se}_{8-x}\text{S}_x$  ( $0 \leq x \leq 5$ ) compounds.

## V. CONCLUSION

The ternary  $M_y^{n+}Mo_6X_8$  Chevrel phases are characterized by the presence of  $M^{n+}$  cations in the host network. However, some exceptions have been encountered such as  $Pd_{1.6}Mo_6S_8$  (22), where palladium atoms seem to be bonding each other in cavity 1 of the network, or  $Ni_yMo_6X_8$  (8, 23), where nickel atoms seem to form  $(Ni_2)^{2+}$  or  $(Ni_3)^{2+}$  aggregates in cavity 1 or 2. Now our interesting results show, for the first time in sulfur-selenium compounds, two kinds of molybdenum atoms: Mo(1) atoms forming the  $Mo_6$  cluster, and Mo(2) atoms intercalated into the host network.

Moreover, we have identified for the Mo(2) extra molybdenum atoms two possibilities for occupation of the host network: either they sit in cavity 1 constituting Mo(2)-Mo(2) quadruple bonds (the case of  $\beta$ - $Mo_6S_8$ ), or they occupy cavity 2 forming single bonds with Mo(1) atoms (from the  $Mo_6$  clusters) and so become a kind of  $Mo_7$  cluster.

## REFERENCES

1. B. T. Matthias, M. Marezio, E. Corenzwit, A. S. Cooper, and H. F. Barz, *Science* **175**, 1465 (1972).
2. Ø. Fischer, H. Jones, G. Bonghi, M. Sergent, and R. Chevrel, *J. Phys. C* **7**, 450 (1974).
3. R. Schöllhorn, R. M. Kümpers, and J. O. Besenhard, *Mater. Res. Bull.* **12**, 781 (1977).
4. R. Chevrel, M. Sergent, and J. Prigent, *Mater. Res. Bull.* **9**, 1487 (1974).
5. S. Belin, R. Chevrel, and M. Sergent, *Mater. Res. Bull.* **33**, 43-57 (1998).
6. R. Chevrel and M. Sergent, in "Topics of Current Physics, Vol. 32, Superconductivity in Ternary Compounds I" (Ø. Fischer and M. B. Maple, Eds.), pp. 25-86. Springer-Verlag, Berlin, 1982.
7. M. Potel, P. Gougeon, R. Chevrel, and M. Sergent, *Rev. Chim. Miner.* **21**, 509 (1984).
8. S. Belin, Thesis, University of Rennes, France, 1997.
9. J. M. Tarascon, F. J. Di Salvo, J. V. Waszczak, and G. W. Hull, *Phys. Rev. B* **31**, 1012 (1985).
10. C. K. Fair, "MOLEN. An Interactive Intelligent System for Crystal Structure Analysis," Enraf-Nonius, Delft, The Netherlands (1990).
11. N. Walker and D. Stuart, *Acta Crystallogr. Sect A* **39**, 158 (1983).
12. "International Tables for X-Ray Crystallography," Vol. IV. Kynoch Press, Birmingham, UK (distributor D. Reil, Dordrecht), 1975.
13. C. Perrin, R. Chevrel, M. Sergent and Ø. Fischer, *Mater. Res. Bull.* **14**, 1505 (1979).
14. L. S. Selwin, W. R. McKinnon, J. R. Dahn, and Y. Le Page, *Phys. Rev. B* **33**, 6405 (1986).
15. L. S. Selwin, W. R. McKinnon, and Y. Le Page, *Phys. Rev. B* **42**, 10427 (1990).
16. D. C. Johnston, J. M. Tarascon, and M. J. Sienko, *Inorg. Chem.* **22**, 3773 (1983).
17. S. Belin, R. Chevrel, and M. Sergent, submitted for publication.
18. K. Yvon, in "Current Topics in Materials Science," Vol. 3 (E. Kaldis, Ed.), pp. 53-129. North Holland, Amsterdam, 1979.
19. K. Yvon, in "Proc. VI Int. Conf. Solid Compounds of Transition Elements, Stuttgart," pp. 15-17, 1979.
20. A. M. Umarji, G. V. Subba Rao, V. Sankaranalayanan, G. Rangarajan, and R. Srinivasan, in "Proc. Ternary Superconductors" (G. K. Shenoy, B. D. Dunlap, and F. Y. Fradin, Eds.). Elsevier, North Holland (1981).
21. R. Chevrel and M. Sergent, *Mater. Res. Bull.* **10**, 1169 (1975).
22. O. Peña, M. Potel, R. Chevrel, and M. Sergent, in "Proc. VII Int. Conf. Solid Compounds of Transition Elements, Grenoble," 1982.
23. C. Prigge, W. Müller-Warmuth, E. Gocke, and R. Schöllhorn, *Solid State Ionics* **62**, 143 (1993).